Temporal Variations in the Chemical and Carbon Isotope Compositions of Marine and Terrestrial Organic Inputs in the Bay of Marennes-Oléron, France

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ABSTRACT

Composition of particulate organic matter inputs within Marennes-Oléron Bay (France) was investigated over various timescales, through multiple measurements (SPM, C:N, Chl. a, δ13C). Oceanic and terrestrial end-members show little δ13C variations over the seasonal cycle or between years. Seasonal variations in chemical and isotopic composition of riverine POM reflect the relative contribution of riverborne phytoplankton, but, except during spring bloom, POM appears to be mainly detrital. Between years, differences in rainfall regime greatly affect all the measured parameters. At the estuary mouth, seasonal variations observed within the river are blurred by sedimentation-resuspension processes linked to hydrodynamic constraints, leading to only little variations in the δ13C values. The larger variations were observed here in C:N values and were ascribed to the effect of high floods bringing more nitrogenous detritus in the lower part of the estuary. At the marine pole of the bay, POM is mainly dominated during winter by aged detritus occurring during low river flow periods, and reflects new “fresh” continental inputs during runoff events. In spring and fall, its composition appears to be primarily controlled by primary production. 14C/13C ratios of bay phytoplankton are markedly more negative than true oceanic values, probably due to differences in species composition. In Marennes-Oléron Bay, POM composition cannot be described by a simple mixing model between oceanic and terrestrial end-members, since many biological and physical processes alter their chemical and isotopic signatures. Variations between years emphasize also the need of considering meteorological events such as high floods or long drought periods.

ADDITIONAL INDEX WORDS: Estuary, river flow, seston load, detritus, phytoplankton, particulate organic carbon, particulate nitrogen, chlorophyll a.

INTRODUCTION

In coastal, and especially in estuarine areas, the organic matter pool in the water column results from the mixing of diverse sources that include natural inputs of terrestrial and riverine organic matter coming from freshwater inflow, marine phytoplankton introduced by tidal currents, autchthonous planktonic and benthic productions as well as anthropogenic inputs. Complex physical mixing of the water masses and biogeochemical processes occurring in such environments greatly affect the fate of these organic materials (Hedges et al., 1988a,b; Relexans et al., 1988; Fichet et al., 1993). This results in a large dominance of refractory materials, highly variable in their biological reactivity and difficult to characterize with regard to their origin. Therefore, deciphering the sources of organic matter requires the knowledge of both physical and biogeochemical changes and the use of multiple approaches that could give different insights.

In estuarine environments, particulate organic matter (POM) is generally expected to be a mixing of two major end-member sources: marine phytoplankton and terrestrial vascular plants originating from river runoff. The relative importance of each one can be assessed along the gradient between these sources if a marker can characterize them (Schultz and Calder, 1976; Mayer et al., 1981; Mayer et al., 1988). Several approaches have been used for this purpose, such as analysis of lignin oxydation products (Hedges et al., 1988a,b), determination of chloropigments, proteins, carbohydrates or lipids (Heral et al., 1983; Fichet et al., 1993; Navarro et al., 1993; Galois et al., in press), or calculation of C:N ratio (Pocklington and Tan, 1987; Matson and Brinson, 1990). But one of the most potentially powerful tools to trace sources, sinks and mixing processes of organic matter in coastal and estuarine environments is the stable isotope composition (Letolle and Mariotti, 1983; Simenstad and Wissmar, 1985; Rezende et al., 1990). Terrestrial organic matter is generally depleted in 13C compared to marine organic matter and carbon isotope ratios have been successfully applied to the study of the sources of organic matter in estuaries (Tan and Strain, 1983; Fry and Sherr, 1984;
Gearing et al., 1984; Lucotte, 1989). However, δ¹³C analysis alone is often not sufficient to elucidate the complex estuarine processes, especially if more than two sources are potentially important (Fry and Sherr, 1984). In such cases, combinations of several measurements can yield more valuable information on the processes occurring along an estuary, and accordingly, stable isotope analysis has been associated with measurement of lignin derivatives (Cifuentes, 1991), lipid biomarker compounds (Saliot et al., 1988), C:N ratios (Thornton and McManus, 1994), biochemical composition (Fichez et al., 1993) or several of these methods (Canuel et al., 1995).

The Bay of Marennes-Oléron (Figure 1) supports the largest area for oyster culture in France, and projects in the management of river inflow to the bay emphasized the need of a better knowledge of the relative importance of the diverse sources of organic matter in supporting its ecosystems. Freshwater inflow is only about 1/30th of the oceanic water masses entering the bay at each tidal cycle (Allen et al., 1974), but besides inorganic nutrients, freshwater brings large quantities of terrestrial and refractory detritus that may account for the main part of the suspended organic matter within the bay. Previous studies examined the hydrobiological features of the bay (Heral et al., 1983) and its planktonic primary productivity (Ravail et al., 1988), showing that inorganic nutrients originating from the Charente River support most of the phytoplanktonic production within the bay. However, planktonic primary production accounts only for a minor part of the bulk of total organic matter pool, which is largely detrital (Feuillet-Girard et al., 1988, 1994). Moreover, recent modeling studies pointed out that the phytoplankton production alone cannot account for the heavy production of cultivated mollusces (Raillard, 1991), thus requiring a close examination of other potential sources of organic matter. Although many studies have focused on the variability of total POM concentration within the whole bay, its origin and its nature have not yet been thoroughly considered.

Therefore, to elucidate the origin and fate of the organic matter supporting Marennes-Oléron Bay ecosystems, chemical and stable isotope compositions of the different sources of organic matter were investigated. This first study aimed at the characterization of the seasonal nature of the suspended organic matter entering into the Marennes-Oléron Bay from the continental and marine sources, through its chemical composition (chlorophyll a and C:N ratio) and stable carbon isotope composition. The marine and riverine sources of POM were first investigated in order to estimate their variability over an annual cycle, but since large changes in chemical and isotopic composition can occur within the time scale of mixing along the estuary before reaching the bay (Bennet et al., 1987; Lucotte, 1989; Fichez et al., 1993; Thornton and McManus, 1994), we also studied the composition of the POM that actually enters the bay through POM analysis at the mouth of the estuary at different periods of the year and during successive tidal cycles.

MATERIAL AND METHODS

Study Area

The Bay of Marennes-Oléron is a very shallow estuarine bay (average depth 4 m) situated centrally on the Atlantic coast of France (Figure 1). Its extends north to Ile Madame, south to Pertuis de Maumusson, and it is well protected by Ile d'Oléron to the west. It is a well mixed estuary, with a maximum tidal range of 6 m and strong currents generally leading to high turbidity (Ravail-LeGrand, 1993). Marine water masses enter mainly by the north entrance (Pertuis d'Antioche) and move south, with a mean residence time of 5 to 11 days. Freshwater flows into the bay mainly from the Charente River (minimum flow of 5 m³.s⁻¹ during summer, maximum up to 500 m³.s⁻¹ during normal winter months). The Charente River catchment extends over 10,000 km² of agricultural and forested land. During periods of high discharge, some inputs from the Gironde River, one of the most important rivers on the Atlantic coast, that discharges 40 km south of the bay, enter by the north entrance after having turned around the Ile d'Oléron, and in a lesser extent with high tide through the Pertuis de Maumusson (Dechambeau et al., 1977). The bay includes extended and bare intertidal mudflats (more than 55% of the total area at the lowest tide) and is surrounded by wide areas of salt marshes, that are entirely managed and are used for oyster rearing. Therefore, these salt marshes, which are free of C4 plants, do not bring significant amounts of particulate detritus to the organic matter pool within the bay, as Spartina marshes do in many other coastal areas (Pomeroy et al., 1981).

Sampling and Analytical Procedures

We first investigated the characteristics and the seasonal variability of the main inputs of organic matter. For the freshwater end-member, samples were taken at St. Savinien, 50 km upstream from the estuary mouth, where a dam prevents any influence of tide (Figure 1). Fort Boyard in the middle of the Pertuis d'Antioche was considered in this study as the marine pole for the oceanic inputs and sampling was carried out just north of Fort Boyard, in the main channel. Taking account of the possibility of mixing of true marine water with Gironde River water during high-discharge periods, additional samples, representative of the true oceanic POM were collected at about 100 km off-shore. However, that
first study was done during a drought period and no high flood from the Gironde river occurred. In order to characterize the two end-member sources, sampling was carried out every month from September 1990 to September 1991 at St. Savinin and Fort Boyard. At this latter, to prevent any contamination by resuspended sediment and detritus, sampling was always done at high tide and after a few days of calm weather. Samples taken at St. Savinin during October 90 and September 91 have been discarded because riverworks upstream from that site gave an abnormally high turbidity at the time of sampling during those periods.

The seasonal nature of the POC actually brought by the Charente River to the bay was followed at one station right at the mouth of the estuary (La Mouciere buoy) by sampling at high tide ± 1 hr at diverse periods from May 1992 to January 1993. Since 1990 and 1991 were very dry years, and 1992 was wetter with high discharge periods during December, we repeated also the samplings at St. Savinin during the same period in order to check any effects of the change in the rainfall regime on the riverine composition.

Tidal variability at the estuary mouth was investigated during a preliminary investigation in May and June 1990, by sampling at low tide and at the next high tide during several tidal cycles. Samples of terrestrial vegetation (tree leaves and pasture grass) were also taken at different occasions during these sampling periods around St. Savinin. Data on river flow were obtained from the Service Regional d’Aménagement des Eaux, the local public water agency. Oceanic samples were obtained by filtration on GF/F filters as whole POM, or after previous removal of zooplankton on a 40 µm screen to get only phytoplankton.

At each station 201 l of water were pumped from about 50 cm under the water surface in the river and 1.5 m in the sea. For the measurement of the isotope ratio of dissolved inorganic carbon (DIC), water was taken using a small sampling bottle and transferred, avoiding any contact with air, to a HgCl2-poisoned BOD bottle. Particulate organic matter for pigment, elemental and isotopic analyses was obtained from the water by filtration on precombusted Whatman GF/F glass fiber filters that were kept frozen until analysis. Duplicate samples were collected and measured for all the analyses, except for isotope determinations.

Chlorophyll a was measured by spectrometry according to Holm-Hansen and Riemann (1978), after methanol extraction. Samples for the determination of particulate organic carbon (POC) and particulate nitrogen (PN) were acidified by HCl fumes during 2 hr to remove carbonates, and measurements were made with a Carlo Erba 1500 analyzer. Samples for 14C analysis were also acidified by HCl fumes and rinsed with distilled water to remove chlorides. They were then freeze-dried and combusted at 900°C using CuO as an oxidant in evacuated quartz tubes (Stump and Frazer, 1973). The CO2 was purified using a cryogenic distillation method similar to that described by Boutton (1991a) and its carbon isotope ratio measured with a Sigma 200 (CIS Sciences) double inlet, triple collector isotope ratio mass spectrometer. Preparation of samples for analysis of DIC δ13C was performed by cryogenically collecting and purifying the CO2 under reduced pressure from about 80 ml acidified sample.

Table 1. Carbon isotopic composition of the terrestrial and oceanic primary sources.

<table>
<thead>
<tr>
<th>Terrestrial Plants</th>
<th>Off-shore Oceanic POM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Date</td>
</tr>
<tr>
<td>Oak dead leaves</td>
<td>02/91</td>
</tr>
<tr>
<td>fresh leaves</td>
<td>02/91</td>
</tr>
<tr>
<td>05/91</td>
<td>25.8%</td>
</tr>
<tr>
<td>11/91</td>
<td>25.5%</td>
</tr>
<tr>
<td>02/93</td>
<td>27.0%</td>
</tr>
<tr>
<td>05/93</td>
<td>27.7%</td>
</tr>
<tr>
<td>10/93</td>
<td>28.0%</td>
</tr>
<tr>
<td>Elm fresh leaves</td>
<td>02/93</td>
</tr>
<tr>
<td>05/93</td>
<td>27.3%</td>
</tr>
<tr>
<td>Hornbeam leaves</td>
<td>02/93</td>
</tr>
<tr>
<td>Pasture grass</td>
<td>02/93</td>
</tr>
<tr>
<td>05/93</td>
<td>30.0%</td>
</tr>
</tbody>
</table>

Results and Discussion

Carbon Isotope Composition of Oceanic and Terrestrial Primary Sources

Table 1 summarizes the analytical results of off-shore whole POM, for POM after removal of zooplankton, that can be taken as representative of true oceanic phytoplankton, and for the different samples of terrestrial primary producers. The isotopic composition of these primary sources varied only slightly during the year and between years. The oceanic POM δ13C, ranging from −19.1‰ to −21.5‰, are typical of phytoplankton in temperate seas (Fontugne and Duplessy, 1981; Gearing et al., 1984) and are close to values found in the same area by Fontugne and Jouanneau (1987).

Terrestrial vegetation is generally much more depleted and is usually considered to have rather stable δ13C values due to the small variations, generally <1‰, of its inorganic supply (Mook et al., 1983; Mook, 1986). In temperate areas, most of the plants, and all forest ones, use the C3 photosynthesis pathway leading to a mean δ13C organic matter of −27‰ (Boutton, 1991b). Our data for tree leaves (mean −27.3‰) are around that value, while the ones for grass from meadows are more negative (mean −31‰), similar to the values found for C3 grass in East Africa by Tieszen and Boutton (1989).

The difference between carbon isotope ratios of organic matter from oceanic and terrestrial primary producers therefore appears large enough relative to the variability of these two end-members to clearly assess their contribution to the estuarine pool.

Particulate Inputs into the Bay

The main inputs of organic matter in the Marennes-Oleron Bay come from the oceanic waters bodies passing by the entrances of the bay (mainly by the Pertuis d’Antioche), and
from the Charente river, that we have considered here as the marine and freshwater poles respectively. Freshwater inputs are always highly variable, due to the fluctuations in the river flow that is often <5 m³.s⁻¹ during summer months and rises above 300 m³.s⁻¹ for weeks during winter. During the 1990-1991 study, freshwater flow did not exhibit such large variations (Figure 2): summer values were <3 m³.s⁻¹, but in winter only a few days presented a high flow (mean 164 m³.s⁻¹ in January). Indeed, this sampling period took place by the end of a 3 year drought, without any high river flood, thus, excluding the possibility of input from the Gironde river. However, even if the flow of the Charente River was rather low for winter months, it affected in some extend the hydrology at the Fort Boyard site, as shown by the slightly lowered salinities around 31 g.l⁻¹ measured in January and February (Table 2).

River flow began to increase in November, but it was not sufficient to place bottom sediment in suspension in the river, as indicated by the decrease in the SPM at St. Savinien (Figure 2 and Table 2). More heavy rainfall in January led to higher flows and to a sharp increase in the seston load, which stayed high until May. At Fort Boyard the SPM peak occurred in January when Charente River flow was maximal (Figure 2 and Table 2) and could be due to scouring of the sediment accumulated in the lower part of the estuary, as observed by Uncles and Stephens (1993) in the Tamar estuary. However, since the seston load of the river was decreasing till December, the SPM increase at Fort Boyard in November and December is more likely linked to resuspension of sediment in the whole bay, when the degradation of meteorological conditions induced stronger wind currents and waves. As also noticed by Canuel et al. (1995) in San Francisco Bay, wind can have a strong effect on the turbidity by enhancing the action of tidal currents, especially in very shallow estuaries.

Variations in POM Composition at the Freshwater Pole

Freshwater POM originates from riverborne plankton and from detritus of terrestrial plants brought into the river by rainfall. These two sources are quite different with regard to their biological reactivity and their relative contribution to the total pool of organic matter over an annual cycle was assigned on the basis of the chemical and isotopic measurements made during the first sampling period.

Seasonal Variations in Chemical Composition of POM in the River

Organic matter content, as POC and PN, was always relatively high at St. Savinien (Table 2), and it followed SPM variations (Figure 2). POC concentration ranged from 1.4 mg.l⁻¹ in December just before the highest flow, to 3.7 mg.l⁻¹ in April. PN content was also lowest in December (0.09 mg.l⁻¹), but peaked slightly later, in May (0.5 mg.l⁻¹). Very low chlorophyll a values (0.3 to 0.7 µg.l⁻¹) were measured during the period of discharge (Figure 2, Table 2), and the development of phytoplankton blooms occurred always for low river flow. Chlorophyll a showed the highest value (19.1 µg.l⁻¹) in April when the spring phytoplankton bloom oc-

Table 2. Salinity, SPM, POM chemical and isotopic compositions, and ¹³C composition of DIC at the marine (Fort Boyard) and freshwater (St. Savinien) poles from September 1990 to September 1991.

<table>
<thead>
<tr>
<th>Months</th>
<th>Salinity</th>
<th>SPM mg.l⁻¹</th>
<th>PN µg.l⁻¹</th>
<th>POC µg.l⁻¹</th>
<th>Chl. a</th>
<th>¹³C POM</th>
<th>¹³C DIC</th>
<th>SPM mg.l⁻¹</th>
<th>PN µg.l⁻¹</th>
<th>POC µg.l⁻¹</th>
<th>Chl. a</th>
<th>¹³C POM</th>
<th>¹³C DIC</th>
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<td>35.0</td>
<td>3.0</td>
<td>64</td>
<td>621</td>
<td>4.7</td>
<td>-23.8</td>
<td>-</td>
<td>27.6</td>
<td>314</td>
<td>3,550</td>
<td>11.0</td>
<td>-31.3</td>
<td>-8.9</td>
</tr>
<tr>
<td>10/90</td>
<td>35.0</td>
<td>5.5</td>
<td>33</td>
<td>748</td>
<td>5.2</td>
<td>-</td>
<td>0.0</td>
<td>21.3</td>
<td>214</td>
<td>2,179</td>
<td>1.4</td>
<td>-25.5</td>
<td>-12.5</td>
</tr>
<tr>
<td>11/90</td>
<td>33.7</td>
<td>13.6</td>
<td>50</td>
<td>1,389</td>
<td>4.0</td>
<td>-26.5</td>
<td>-</td>
<td>21.3</td>
<td>214</td>
<td>2,179</td>
<td>1.4</td>
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<td>21.1</td>
<td>79</td>
<td>2,046</td>
<td>4.3</td>
<td>-</td>
<td>0.0</td>
<td>10.6</td>
<td>91</td>
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<td>01/91</td>
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<td>79</td>
<td>1,328</td>
<td>1.9</td>
<td>-27.1</td>
<td>-4.5</td>
<td>38.2</td>
<td>152</td>
<td>2,441</td>
<td>0.4</td>
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<td>-</td>
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<td>11.3</td>
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<td>-</td>
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<td>36</td>
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<td>8.0</td>
<td>-</td>
<td>-</td>
<td>34.2</td>
<td>420</td>
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<td>2.6</td>
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<td>-</td>
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<td>2.2</td>
<td>54</td>
<td>434</td>
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<td>18.8</td>
<td>280</td>
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<td>-</td>
<td>-8.4</td>
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<tr>
<td>07/91</td>
<td>34.5</td>
<td>5.3</td>
<td>123</td>
<td>697</td>
<td>11.7</td>
<td>-29.6</td>
<td>+0.2</td>
<td>21.8</td>
<td>529</td>
<td>2,041</td>
<td>11.9</td>
<td>-28.3</td>
<td>-10.9</td>
</tr>
<tr>
<td>08/91</td>
<td>33.4</td>
<td>4.6</td>
<td>65</td>
<td>614</td>
<td>7.3</td>
<td>-</td>
<td>-</td>
<td>21.8</td>
<td>529</td>
<td>2,041</td>
<td>11.9</td>
<td>-28.3</td>
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<td>-10.9</td>
</tr>
</tbody>
</table>

(= not available data; * = discarded samples, see text)
curred in the river, and a secondary peak of 11.9–11.0 μg l⁻¹ in August–September (Table 2, Figure 3A). These two peaks corresponded to different microalgal assemblages, dominated by diatoms during spring bloom and by green flagellates during summer, as shown by fatty acid composition of POM (GALOIS et al., in press). The inverse relationship observed between river discharge and POM pigment content confirms the effect of discharge on phytoplanktonic populations in rivers, as pointed out by De BECKER (1986) and RELEXANS et al. (1988).

C:Chl. a ratio varied at the opposite of chlorophyll a values (Figure 3A), reaching extremely high values in winter (>6,000) and the lower values during plankton blooms (193 in April and 171 in August). C:Chl. a ratio has often been used as an indicator of the importance of the detrital part within the organic seston. ZEITZSCHL (1970) estimated that values of 100 or less are typical of the dominance of living phytoplankton within the organic matter pool, while CIFUENTES et al. (1988) considered as detrital the organic matter with a C:Chl. a ratio > 200. Our data indicate that C:Chl. a was within the typical range for live phytoplankton only during short periods (April and August), using criteria from CIFUENTES et al. (1988). Therefore, riverine POM was almost exclusively detrital during winter months, and also largely dominated by detrital organic matter during the rest of the year, except in April and August. Similar trends were also observed in the St. Lawrence River by POCKLINGTON and TAN (1987), but in the Loire River, living algal organic matter was shown to be largely dominant during summer (RELEXANS et al., 1988), due to the eutrophication of the river.

C:N ratio has also been used as an indicator of the relative proportion of detrital material in the POM (POULET et al., 1986). Terrigenous organic matter usually has a C:N ratio > 12 (BORDOVSKY, 1965; THORNTON and McMANUS, 1994) while riverine phytoplankton exhibit a much lower ratio, typically around 6 (KILHAM, 1986, 1990; REYNOLDS, 1984). At St. Savinien, C:N ratio ranged from 18.7 in January to 6.2 in May (Figure 3B). Such large ranges of C:N ratios were also noticed in the upper part of the Delaware estuary (CIFUENTES et al., 1988) and in the Amazon River (HEDGES et al., 1994) and were ascribed to the changes of POM composition in different particle classes (i.e., large terrestrial detritus or microalgal cells). In the Charente River, the high C:N ratios noticed during winter were clearly due to high inputs of terrestrial detritus to the river. In spring and summer, a larger part of the organic matter comes from phytoplankton, giving lower C:N ratios when POM pigment content was higher (Figure 3). However, some disparities relative to that inverse relation are shown by the gap between the chlorophyll a peak in April (Figure 3A) and the C:N minima in May (Figure 3B), and by the occurrence of a high C:N ratio in September. In fact, even if phytoplanktonic production was high in April, a large part of the POM organic matter was still coming from terrestrial detritus, as indicated by the highest value of POC recorded during that month (Table 2). The same figure seems to have also prevailed in September, at a lesser extent.

### Carbon Isotopic Composition of River POM

Stable carbon isotope composition of POM exhibits rather large seasonal variations at St. Savinien (Figure 3B). POM was very depleted in ¹³C in September (δ¹³C = −31.3‰) and May (−30.5‰) and less depleted during winter months (δ¹³C = −25.5‰ in November). These changes reflect the weighted ¹³C/¹²C of different mixtures of detritus from terrestrial plants and of riverine phytoplankton.

The mean δ¹³C of vascular plants, that brings the bulk of terrigenous organic matter within rivers, is around −27‰ in temperate areas (TIEZHEN and BOUTON, 1989) and was found to be −27.3‰ from our data (Table 1). However, during winter months, when POM is mainly terrestrial detritus, its δ¹³C is around −25.6‰, slightly enriched (by 1.2 to 1.4‰) relative to the mean isotope composition of the terrestrial plants. Evidence of abnormally enriched POM in the upper reaches of estuaries have sometimes been ascribed to transport, related to tidal currents at the benthic boundary layer, of heavy marine organic matter (MOOK and TAN, 1991; FICHEZ et al., 1993). However, this is not the case here, since sampling at St. Savinien was made upstream a dam. The enrichment could therefore come from an undetermined enriched source, like freshwater macrophytes (FRANCE, 1995) or could be due to some discrimination among fractions of leaf litter during leaching on the soil, a larger part of δ¹³C-en-
riched components being carried to the river by rainfall. This latter hypothesis is supported by the results of Hedges et al. (1994) on the Amazon River, who measured marked differences in the chemical composition of vascular plant detritus relative to fresh material and in the δ13C composition of different size classes of river detritus.

The isotopic composition of phytoplankton cannot be measured directly since there is no means to physically separate microalgal cells from the fine detritus as to get pure phytoplankton. Its carbon isotope composition can however be indirectly estimated from the measurements of the DIC δ13C, assuming that a constant fractionation factor exists between plankton and DIC (Tan and Edmond, 1993). The carbon isotopic composition of DIC is controlled by complex fractionation processes among solid, dissolved and gaseous phases (for a review, see Tan, 1989). In most rivers, it depends mainly on the type of groundwater (i.e. carbonate or silicate type) and on the importance of the vegetation in the drainage basin. In the Charente river, DIC δ13C varied between −8.4‰ and −13.1‰ during the 1990–1991 sampling period (mean −10.5‰, Table 2), well in the range of many other studies (Sackett and Moore, 1966; Strain and Tan, 1979; Tan and Edmond, 1993). We calculated the phytoplankton δ13C from these values, using the mean carbon isotopic fractionation factor between DIC and phytoplankton determined by Tan and Strain (1983) to be 22.3‰ for a riverine environment. The expected range for phytoplankton δ13C was therefore −36.4 to −30.7‰ in the Charente River.

δ13C of POM reflects the relative importance of terrestrial detritus and phytoplankton in the organic matter pool. Its high values from November to January confirm that POM comprise almost exclusively terrestrial detritus in winter. δ13C were within the phytoplankton range only in May and September. In May, the low C:N values and low δ13C indicate that POM was largely dominated by living or undegraded microalgal organic matter. In September, the C:N ratio was much higher than the typical value for living cells (>13, Figure 3B), but δ13C was the lowest measured (−31.3‰), well in the phytoplankton range. These results could be explained by the presence of a large fraction of decaying phytoplankton within the organic matter pool. Living microalgae are N-rich but they lose their nitrogen very quickly during degradation, thus leading to higher C:N ratios (Pennock, 1987; Cifuentes, 1991). This phenomenon would be more pronounced by the end of summer, after a long period of high production, and when temperature is still high, as in our case.

Variations in POM Composition at the Marine Pole

Seasonal Variations in Chemical Composition of Marine POM

At Fort Boyard, the marine pole for oceanic inputs into the Marennes-Oléron Bay, particulate organic matter showed much lower, but also more variable POC and PN contents. POC closely followed seston load and exhibited high values from November to January (up to 2 mg.l−1), contrasting with low ones during the rest of the year (Table 2). PN was always low, except in August (123 μg.l−1), when the main phytoplankton bloom occurred. Chlorophyll concentration was lowest in winter (Figure 4A), when short day duration, low temperature and high turbidity in the water prevented the development of phytoplankton populations. In 1991, the highest planktonic production occurred in August (Figure 4A), but several chlorophyll a peaks during the year attested to the development of multiple plankton blooms, ascribed to the succession of diatoms (spring) and flagellates (summer and fall) populations (Galois et al., in press). This is an usual feature in Marennes-Oléron Bay, although the main bloom generally occurs in May and the second main one in September (Herel et al., 1983). The relatively low production during spring months in 1991 might be due to the previous drought that led to weak winter and spring inputs of nutrient-rich freshwater. Such a situation was also noticed in North Carolina estuaries by Matson and Brinson (1990). C:Chl a ratio varied as the POC content in the seston and the river discharge (Table 2 and Figure 4A); it began to increase in November and peaked at 700 in January, then decreased after March to values between <100 typical of living phytoplankton (Zeitzschel, 1970).

C:N ratio varied roughly as C:Chl a, exhibiting high values in winter and low ones, typical of living phytoplankton, in summer (6.6 in August). However C:N ratio increased more sharply that C:Chl a in fall 1990 and reached the highest
value (34.1) in December (Figure 4B). It must be noticed that the C:N ratios measured in October to March are far higher than the C:N within the Charente river at any time during the same period (Figures 3B and 4B). These results could reflect the difference in the degradation state of the detritus within these two environments. In the river, the higher C:N values could be due to a higher bacteria colonization of the relatively more “fresh” detritus. C:N ratio of poorly nitrogenous terrestrial detritus generally decreases during microbial decay as N-rich bacterial biomass is added to the detrital pool (Harrison and Mann, 1975a,b) or incorporated within complex biochemical compounds (Rick, 1982; Wilson et al., 1986). Indeed, inorganic nitrogen is rapidly taken up by bacteria during plant decomposition and often results in a C:N ratio increase of the detrital complex (Benner et al., 1988; Benner et al., 1991). In the bay, high C:N values indicated the presence of aged and very degraded terrestrial detritus, that have lost the larger part of their nitrogen while keeping their more refractory components such as lignin, that contains about 50% more carbon than cellulose (Benner et al., 1987). The dramatic C:N decrease occurring in January in the bay (Figure 4B) could therefore be ascribed to a larger input of less degraded terrestrial detritus, with a lower C:N ratio (and more highly colonized by bacteria), brought within the Bay by the high river flow occurring at that time, and extending as far as Fort Boyard (Figure 3B). This was further attested by the high content of POM in bacterial fatty acids noticed at the same time by Galois et al. (in press).

Carbon Isotopic Composition of POM at Fort-Boyard

POM δ13C varied largely during the year, with very low values (around −27‰) during winter and higher values (−23.3‰) in summer (Table 2, Figure 4B), and followed almost exactly (with an inverse sign) C:N ratio variation, except that it did not show the January change (Figure 4B). These results confirm that POM in winter was exclusively detritus derived from terrestrial vegetation since its δ13C ratio (around −27‰ during winter months) was typical of this type of organic matter (Table 2 and Figure 4B). It must be noticed that the δ13C values were more negative than in the Charente River during the winter months, confirming that POM is more degraded in the bay. Indeed, the depletion in 13C generally observed in decaying vascular plants is mainly due to their enrichment in lignin that has a δ13C 2 to 6‰ more negative than the whole plant (Benner et al., 1987).

The negative DIC δ13C measured in winter (−4.5‰ in January) indicate also higher heterotrophic activity. In off-shore waters, variations in the isotopic ratio of inorganic carbon is generally linked to photosynthesis/degradation processes, primary production resulting in DIC δ13C > 0 and decomposition leading to negative values (Tan, 1989). At Fort-Boyard in January, mixing of oceanic waters with a DIC δ13C around 0‰ (Tan, 1989) with Charente waters (around −10‰, Table 2) in the proportion attested by the slight decrease in salinity, would have led only to a 1.5‰ depletion. Therefore, the more negative values at that time seem to indicate a strong increase of organic matter decomposition processes, that could be associated with the input of detritus undergoing bacterial degradation.

During spring and fall, low C:N and C:Chl. a ratios indicate that POM consisted mainly in live phytoplankton. But they were associated with δ13C values between −23.8 and −23.3‰, markedly more negative than true oceanic phytoplankton δ13C that usually range between −19 and −21‰ in temperate seas (Fontugne and Duplessy, 1981; Gearing et al., 1984), and was measured around −20‰ in this study (Table 1). During the blooms, DIC δ13C was close to 0‰ or even positive at Fort Boyard (Table 2), and the difference between DIC and POM δ13C is close to the value of 24.3‰ measured by Tan and Strain (1983) in the St. Lawrence Gulf. Many factors, often not independent, have been invoked to explain observed variations in plankton δ13C: surface water temperature and latitude (Sackett et al., 1965; Fontugne and Duplessy, 1978; Rau et al., 1982), concentration of DIC (Rau et al., 1992; Kopczynska et al., 1995), irradiance (Thomson and Calvert, 1994), biochemical composition (Wong and Sackett, 1978), aging (Descolas-Gros and Fontugne, 1990), growth rate and productivity (Fry and Wainright, 1991). Species composition has also often been considered since many laboratory studies have already demonstrated a large range in C isotopic fractionation between different phytoplankton species (Wong and Sackett, 1978; Descolas-Gros and Fontugne, 1985, 1990; Falkowski, 1991). Furthermore, several recent field studies clearly highlighted the relation between species composition and plankton δ13C (Wainright and Fry, 1994; Kopczynska et al., 1995). In Marennes-Oléron Bay, phytoplankton generally comprise more flagellates than in the open ocean and if spring blooms are mainly composed of diatoms, flagellates dominate in summer and fall (Heral et al., 1977). We have no data on species composition of plankton for 1990–1991, but in April, a high content of POM in some fatty acids (16:1ω7, 16:4ω1, 20:5ω3) indicated the dominance of diatoms, while phytoplankton was mainly flagellates as shown by the importance of some other fatty acids (16:4ω3, 18:4ω3, 18:5ω3, 22:6ω3) during August and September 1991 (Galois et al., in press). Such a change in phytoplankter populations seems to be an usual figure in estuarine and coastal waters (Pennock and Sharp, 1986). Since flagellates have been found more depleted in 13C than diatoms in laboratory cultures (Wong and Sackett, 1978; Falkowski, 1991; Freeman and Hayes, 1992), low δ13C of POM were sometimes ascribed to blooms of flagellates (Cifuentes et al., 1988) that Gearing et al. (1984) found to be about 2‰ more negative than diatoms. We have no isotope data in April when diatoms dominated, but the low POM δ13C noticed from July to September relative to open ocean phytoplankton could also be explained by this depleted composition of flagellates.

Tidal and Seasonal Variations of POM Composition at the Estuary Mouth

Tidal effect on composition of POM actually input within the bay was investigated at the mouth of the estuary (La Mouclière buoy) by sampling at consecutive high and low tides. Some of the measured parameters (salinity, SPM, PN
and POC) exhibited large differences between high and low tide (Table 3). SPM showed the strongest variability between low tides, with a direct relation to tidal coefficient. Mean SPM increased more than 20 times between high and low tide, while PC and POC increased only 4 times (Table 3). However, the differences between high and low tides were much less marked in C:Chl. a, C:N ratio (+2 at low tide) and carbon isotope composition (−0.9%). This indicates that, although these samplings were done during spring bloom (in the Charente river and in the Bay), POM was mainly detrital, and was comprised of tidally current-resuspended sediment and organic matter, especially at low tide.

The narrow range of δ13C at the mouth of the estuary was also noticed during the seasonal survey at the mouth of the estuary in 1992–1993 (Table 4) when they varied from −24.0‰ (May) to −22.6‰ (January). POM at the estuary mouth is expected to be a mixture of riverine POM (−32.8 to −26.9‰, Table 4) and marine, or more likely autochthonous plankton (−23.5‰, see above). However, the latter should have a very negative value when considering the low DIC δ13C (−8.6 to −2.9‰) measured at that site around the year. Therefore a mixture of these two sources, even considering true marine plankton as the second member, could not account for the relatively enriched POM. Many processes have been invoked to explain the various distributions of POM 14C/13C ratios found in estuaries. While in some estuaries a progressive increase of POM δ13C from the upper reaches to the marine pole is described (Fontugne and Jouanneau, 1981; Matson and Brinson, 1990), unexpected enriched POM 14C/13C ratios have also been measured in various part of estuaries. Tidal currents transporting upstream enriched organic matter derived from the marine end-member were related to high δ13C observed in the tidal freshwater reach in the Great Ouse estuary (Fichez et al., 1993), or at the limit of the saltwater intrusion in the Tay estuary (Thornton and McManus, 1994). Tan and Strain (1983) noticed also enriched POM in the lower St Lawrence estuary, that might have been due to the high productivity or a change in species composition within the plankton. At the mouth of the Charente estuary, the phytoplankton productivity is always very low, probably because of the strong turbidity (Ravaillegrand, 1993) and, even if a different and 14C-enriched phytoplankton population was present here, its weak abundance could not account for the observed high δ13C of POM. Another explanation may lie in the presence of another source of organic matter in that area, which might be the microphytobenthos put in suspension in the water column by waves and tidal currents. Indeed, the mouth of the estuary is lined by extensive mudflats that support year-round a very high production of benthiic diatoms with a δ13C around −15‰ (Riera and Richard, 1996). The relatively high and stable pigment concentration in POM at the mouth of the estuary further supports this hypothesis.

Although the δ13C measured at the mouth of the estuary in spring 1990 and in 1992–1993 were very similar, the other parameters were for some very different. SPM sampled at high tide during the 1992–93 seasonal survey exhibited much stronger values (Tables 4 and 3), even only considering spring values (159 mg l−1), than during the tidal survey (19 mg l−1). POC and Chl. a presented close values during these two sampling periods, but POC was increased by 2.5 times in spring 1993, giving a C:N ratio around 6.8 in May, typical of living or freshly dead organisms (Cifuentes et al., 1988), while C:Chl. a ratio indicated that a large proportion of this material was non-algal. The striking differences between years in C:N ratios may be essentially related to the meteorological conditions during these years: a severe drought lasted from 1989 to 1991 while 1992 and 1993 were normal years in regard to rainfalls, with high floods during winter months, and rainy springs. Increased runoff led to larger terrestrial carbon inputs within the river, as particulate or DIC, as shown for this latter by the more negative DIC δ13C values in 1992–93 (−17.5 to −13‰, Table 4) than in 1990–91 (−12.5 to −8.4‰, Table 2). As a result, riverine POM was also slightly more depleted. Particulate concentration in the river was found lower in 1992–93 than during drought, but since river flow steadily increased also, POM absolute amounts flushed to the sea were much more important. In the river and all along the estuary, SPM and POM concentrations were very low after winter high floods in 1992 and 1993 (Riera, 1995), showing

### Table 3. Salinity, chemical and δ13C composition of POM during 5 high tides and the following low tides at La Moulière buoy (mean ± s.e.).

<table>
<thead>
<tr>
<th>Date</th>
<th>Salinity</th>
<th>SPM mg l−1</th>
<th>PN µg l−1</th>
<th>POC µg l−1</th>
<th>Chl. a µg l−1</th>
<th>δ13C in POM</th>
<th>δ13C in DIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/02</td>
<td>159</td>
<td>264</td>
<td>1,798</td>
<td>5.5</td>
<td>−24.0</td>
<td>−5.2</td>
<td>−32.8</td>
</tr>
<tr>
<td>08/02</td>
<td>358</td>
<td>676</td>
<td>5,964</td>
<td>6.8</td>
<td>−23.2</td>
<td>−2.9</td>
<td>−29.8</td>
</tr>
<tr>
<td>10/02</td>
<td>747</td>
<td>1,103</td>
<td>7,543</td>
<td>6.9</td>
<td>−23.2</td>
<td>−8.6</td>
<td>−27.4</td>
</tr>
<tr>
<td>01/03</td>
<td>292</td>
<td>732</td>
<td>5,373</td>
<td>1.6</td>
<td>−22.6</td>
<td>−5.2</td>
<td>−26.9</td>
</tr>
</tbody>
</table>

### Table 4. SPM, POM chemical and isotopic compositions, and δ13C composition of DIC at the estuarine (La Moulière buoy) and freshwater (St. Savinien) sites (—: not available data).

<table>
<thead>
<tr>
<th>Date</th>
<th>SPM mg l−1</th>
<th>PN µg l−1</th>
<th>POC µg l−1</th>
<th>Chl. a µg l−1</th>
<th>δ13C in POM</th>
<th>δ13C in DIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/02</td>
<td>135</td>
<td>400</td>
<td>2,675</td>
<td>43.6</td>
<td>−32.8</td>
<td>—</td>
</tr>
<tr>
<td>08/02</td>
<td>21</td>
<td>171</td>
<td>1,246</td>
<td>8.1</td>
<td>29.8</td>
<td>−13.0</td>
</tr>
<tr>
<td>10/02</td>
<td>33</td>
<td>101</td>
<td>1,081</td>
<td>1.6</td>
<td>27.4</td>
<td>−17.5</td>
</tr>
<tr>
<td>01/03</td>
<td>8</td>
<td>79</td>
<td>768</td>
<td>0.8</td>
<td>26.9</td>
<td>−13.7</td>
</tr>
</tbody>
</table>

that a large part of the riverine and estuarine sediment was expelled outside the estuary by these high floods. This sediment was associated with aged and refractory detrital organic matter and the lower C:N ratios measured later at St. Savinien and at the mouth of the estuary might reflect the replacement of that old detritus by fresh one. This less degraded detritus could be either sedimented phytoplankton (riverine at St. Savinien, estuarine at the mouth of the estuary), or "fresh" terrestrial detritus highly colonized by bacteria, or both.

CONCLUSIONS

The present study, aimed at describing variations of chemical and isotopic compositions of organic matter sources in Marennes-Oléron Bay, enabled us to develop new insights into the dynamics of the diverse inputs and processes occurring at the marine and freshwater poles. While oceanic and terrestrial primary sources present little variation, the large fluctuations in the actual inputs within the bay can be associated with the succession of phytoplankton blooms and runoff events.

In the river, POM composition varies seasonally and is largely affected by the meteorological conditions in the short (i.e., rainfalls) or longer term (drought). However, at the estuary mouth, the composition of the organic matter input to the bay is not directly related to the POM composition at the upper reaches of the river and reflects mainly the sedimentation-resuspension processes linked to physical events (i.e., tidal and wind currents and river flow). During drought periods and winter months, when no high flood flushes the sedimented organic matter out the estuary, POM at the marine pole consists almost exclusively in aged and highly refractory terrestrial detritus. High floods lead to a change in the C:N ratio probably associated to more "fresh" terrestrial detritus supporting a higher bacterial biomass. In spring and fall, POM composition at the marine pole relies on primary production. However, phytoplankton δ13C does not match oceanic values, confirming previous conclusions of different assemblages of primary producer populations, obtained through lipid biomarkers (Galois et al., in press). In Marennes-Oléron Bay, POM carbon isotopic composition does not reflect a simple mixing between two pure (oceanic and terrestrial) end-members. This study gives evidence that elucidating the origin and fate of the organic matter sources is greatly helped by the use of multiple tracers, especially where more than two sources are present, by giving clues of the organic matter transformations. Temporal variations investigated at different time scales also stress the importance of considering both the processes that may change organic matter composition and the global meteorological conditions prevailing sometimes over long periods.

ACKNOWLEDGEMENTS

We appreciate the technical assistance with chemical analysis provided by L. Jouassard. Comments from two anonymous reviewers greatly helped to improve the manuscript.

LITERATURE CITED


La composition des apports marins et terrestres en matière organique particulaire dans la baie de Marennes-Oléron (France) a été étudiée sur différentes échelles de temps, en mesurant plusieurs paramètres (MRS, C, N, H, δ13C) à l’entrée marine de la baie, dans la Charente et à son embouchure. Les δ13C des sources primaires océaniques et terrestres présentent peu de variations saisonnières ou inter-annuelles. La composition chimique et isotopique de la MOP de la rivière reflète les variations saisonnières de la contribution du phytoplancton d’eau douce, mais apparaît principalement déterminée pendant la plus grande partie de l’année. Tous les paramètres mesurés sont grandement influencés par le régime pluviométrique. À l’embouchure, les variations saisonnières de la MOP de la rivière sont marquées par les processus de sedimentation-re suspension liés aux facteurs physiques, conduisant à des fortes variations des δ13C. Les plus fortes variations observées sur ce site sont celles des rapports C/N, qui peuvent être attribuées aux effets des crues entraînant l’apport de détritus plus riches en azote dans la partie oual de l’estuaire. À Fort Boyard, où se situe l’entrée des eaux marines dans la baie, la MOP est en hiver principalement dominée par le matériel détritique terrestre agissant pendant les périodes de faible débit de la rivière, mais reflète l’apport de détritus terrigènes “frais” des que ce débit s’accroît. Au printemps et à l’automne, la composition de la MOP dépend de la production primaire et les valeurs plus negatives des δ13C du phytoplancton de la baie par rapport aux valeurs océaniques sont sans doute liées aux variations de composition spécifique. Dans la baie de Marennes-Oléron, la composition de la MOP ne peut être décrite comme un simple mélange entre sources océanique et terrestre, car de nombreux processusbiologiques agissent, modifiant les signatures chimiques et isotopiques. Les variations inter-annuelles du δ13C mettent en évidence la nécessité de prendre en compte les événements météorologiques, comme les crues et les sécheresses prolongées.

Titre de la page: Chemical and Isotopic Composition of POM

Résumé du texte: La composition des apports marins et terrestres en matière organique particulaire dans la baie de Marennes-Oléron (France) a été étudiée sur différentes échelles de temps, en mesurant plusieurs paramètres (MRS, C, N, H, δ13C) à l’entrée marine de la baie, dans la Charente et à son embouchure. Les δ13C des sources primaires océaniques et terrestres présentent peu de variations saisonnières ou inter-annuelles. La composition chimique et isotopique de la MOP de la rivière reflète les variations saisonnières de la contribution du phytoplancton d’eau douce, mais apparaît principalement déterminée pendant la plus grande partie de l’année. Tous les paramètres mesurés sont grandement influencés par le régime pluviométrique. À l’embouchure, les variations saisonnières de la MOP de la rivière sont marquées par les processus de sedimentation-re suspension liés aux facteurs physiques, conduisant à des fortes variations des δ13C. Les plus fortes variations observées sur ce site sont celles des rapports C/N, qui peuvent être attribuées aux effets des crues entraînant l’apport de détritus plus riches en azote dans la partie oual de l’estuaire. À Fort Boyard, où se situe l’entrée des eaux marines dans la baie, la MOP est en hiver principalement dominée par le matériel détritique terrestre agissant pendant les périodes de faible débit de la rivière, mais reflète l’apport de détritus terrigènes “frais” des que ce débit s’accroît. Au printemps et à l’automne, la composition de la MOP dépend de la production primaire et les valeurs plus negatives des δ13C du phytoplancton de la baie par rapport aux valeurs océaniques sont sans doute liées aux variations de composition spécifique. Dans la baie de Marennes-Oléron, la composition de la MOP ne peut être décrite comme un simple mélange entre sources océanique et terrestre, car de nombreux processus biologiques agissent, modifiant les signatures chimiques et isotopiques. Les variations inter-annuelles du δ13C mettent en évidence la nécessité de prendre en compte les événements météorologiques, comme les crues et les sécheresses prolongées.