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Leaf litter degradation in highly turbid transitional waters: preliminary results from litter-bag experiments in the Gironde Estuary

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The rates of decomposition of oak (\textit{Quercus robur}) leaves have been examined using litter bags in a very high turbidity macrotidal estuary, the Gironde Estuary (S.W. France). The first experiments show a marked decrease in the decomposition rate of oak leaves at the water-sediment interface (mud-contact: anoxic conditions, reduced physical fragmentation) in comparison to the water column. The results point out the impact of hydrodynamic conditions on leaf litter degradation in such fluvio-estuarine systems. Regarding the aquatic-terrestrial linkage, our observations suggest direct changes in leaf decomposition kinetics and then, a potential delay on the recycling and transport processes of coarse particulate organic matter, especially in a context of modification of the natural water flow, due to global and land use changes.

1. Introduction
In European macrotidal estuaries, the tidal influence induces long residence times for water and suspended matter and causes the formation of a turbidity maximum zone (TMZ), where low light availability strongly limits photosynthesis (Cole, Caraco, & Peierls, 1992; Irigoien & Castel, 1997), while bacterial activity is very high (Heip et al., 1995). Consequently, TMZ is a heterotrophic system where respiration dominates over production (Goosen, Kromkamp, Peene, van Rijswijk, & van Breugel, 1999). Furthermore, residence times in macrotidal estuaries are long enough to allow the labile fraction of the organic matter to be mineralized at a seasonal scale. The organic matter amount in the TMZ and its biodegradability are major ecological factors controlling the oxygenation level of waters and estuarine aquatic life (Etcheber et al., 2007). From a sedimentological perspective, present-day estuaries are ephemeral environments acting as highly effective traps of sediments issued from the watershed (Biggs, Howell, & Kennedy, 1984; Meade, 1972; Nichols & Biggs, 1985). Tidally-induced repetitive cycles of deposition and resuspension of estuarine particles are essential for the transformation and degradation of riverine carbon inputs, modifying their characteristics during the transfer from the river to the sea (Middelburg & Herman, 2007), and in sustaining the heterotrophic status of estuaries (Heip et al., 1995; Middelburg & Herman, 2007). In addition, the modifications of the natural water flows, due to changes in climate and local land use, disrupt the patterns of material transport and dynamics, availability of resources, and composition of biological communities, thus altering the ecosystem services (Naiman, Latterell, Pettit, & Olden, 2008).

The Gironde Estuary is the largest estuary of the European Atlantic coast, with a well-developed TMZ. Different pools of particulate organic matter (POM) entering the Gironde Estuary have already been quantified (Veyssy, Etcheber, Lin, Buat-Menard, & Maneux, 1998). The major particulate organic carbon (POC) sources originate from allochthonous organic matter (50% soil and 40% litter) and only 10% are autochthonous (phytoplankton). The contribution of coarse particulate matter (CPM) and its associated fraction, coarse particulate organic carbon, to the mass and carbon budgets was estimated to be minor in the TMZ in comparison to fine particulate material (Fuentes-Cid et al., in press). However, little is known about the transit time and transformation of this specific organic matter in the estuarine system.

The purposes of this work are to improve our knowledge about rates of litter degradation in the TMZ of a macrotidal estuary and to discuss the contribution of this process to the recycling of coarse POM in this environment. We have applied the litter-bag technique, a common measure of functional integrity in streams (Death, Dewson, & James, 2009; Gessner & Chauvet, 2002; Sandin & Solimini, 2009), because decomposition rates are supposed to reflect changes in the environment (Graça, 1993). However, there are only a few studies that have been carried out using this method in transitional aquatic ecosystems (Lopes, Martins, Ricardo, & Rodrigues, 2011; Quintino et al., 2009; Sangiorgio et al., 2008). Here, we describe the first results of an in situ
degradation experiment in a highly turbid estuarine system.

2. Material and methods

2.1. Study area

The study was conducted in the Gironde fluvio-estuarine system (Figure 1), located in southwestern France. It is the marine-influenced part (635 km$^2$ of area) of the hydrological system that drains the Aquitaine Basin (catchment area of 71,000 km$^2$) through the Garonne and the Dordogne Rivers (65 and 35% of the fresh water inputs, respectively). Water residence time is estimated to be 20–86 days, compared to 1 and 2 years for suspended particles (Jouanneau & Latouche, 1981).

This macrotidal estuary is characterized by a TMZ that presents suspended sediment concentrations >1 g L$^{-1}$ in surface waters (Sottolichio et al., 2011). This TMZ moves along the estuary depending on fluvial discharges and tidal regime. During the period of low discharge (May–November), the TMZ moves up estuary, oscillating between PK30 and PK-20 (Figure 2); on the contrary, during high-fluvial discharge (December–May), the TMZ moves down-estuary (between stations PK30 and PK70) (Allen, Sauzay, Castaing, & Jouanneau, 1977; Saari et al., 2010). There is a clear relationship between low-fluvial discharge periods and the presence of the TMZ in the fluvial sections of the Gironde Estuary. This context is usually encountered in autumn, i.e. corresponding to and the peak of litterfall and riparian vegetation inputs. During the past 30 years, the year-averaged river flow of the cumulated Garonne + Dordogne system decreased significantly, from 1030 m$^3$ s$^{-1}$ in early 80s to 740 m$^3$ s$^{-1}$ in late 2000: this fact causes a salinization of the system (David et al., 2005) and promotes the presence of TMZ in the estuarine fluvial sections (Sottolichio et al., 2011).

Moreover, the Gironde is a typical macrotidal estuary, where fine sediment dynamics and TMZ are submitted to the variability of tidal currents, following semidiurnal and fortnightly tidal cycles. At semidiurnal tidal scale, suspended particulate matter (SPM) concentration varies under the effect of following erosion/deposition fluxes, which are governed by ebb/flood currents alternating with water slack periods (Grabemann, Uncles, Krause, & Stephens, 1997). At decreasing tidal ranges, decreasing velocities promote higher TMZ particles deposition flux, leading to the formation of fluid mud layers on the bottom (Allen, Salomon, Bassoulet, Du Penhoat, & Grandpré, 1980; Parker, Marshall, & Parfitt, 1994). These highly concentrated benthic layers may reach a thickness of up to 2 m, with average SPM concentrations exceeding 100 g L$^{-1}$ and turn anoxic after several hours (Abril et al., 1999; Maurice, 1994; Sylvester & Ware, 1976). In the Gironde Estuary, it has been proved that particles alternating between the TMZ and fluid muds are subject to oxic–anoxic oscillations (Abril et al., 2000). These recurrent
changes in environmental conditions may induce re-partitioning of organic matter between particulate and dissolved phases with major consequences for the composition and degradability of organic matter (Hedges & Keil, 1999; Keil, Mayer, Quay, Richey, & Hedges, 1997; Komada & Reimers, 2001). Then riverine organic matter is likely to be extensively modified in tidal estuaries before its transfer to coastal waters.

2.2. Experimental conditions

Since 2005, an automated continuous monitoring network, so called MAGEST (MArel Gironde ESTuary), provides real-time measurement of the water quality of the Gironde at four stations, including Bordeaux (Etcheber et al., 2011) (Figure 1). Every 10 min, temperature, salinity, turbidity, and dissolved oxygen concentration in waters pumped 1 m below the surface are determined. The turbidity sensor measures values between 0 and 9999 NTU, with a precision of 10% on the value; 9999 NTU correspond to about 12 g L\(^{-1}\). The architecture and the details of these automated stations are described in (Etcheber et al., 2011).

2.3. Litter-bag experiments

2.3.1. Sampling of leaf litter

Freshly fallen leaves of oak (Quercus robur) were collected from the floodplain of the Dordogne River. These leaves were dried at room temperature for two weeks and stored in carton boxes. For the experiments, leaves were weighted into portions of 3.00 ± 0.05 g and enclosed in nylon bags (18 × 15 cm) with a mesh size of 1 mm.

2.3.2. Mass loss experiments

To study the impact of high turbidity on leaf decomposition, we deployed two sets of litterbags from 4 November 2011 to 30 May 2012 at the Bordeaux station. This site is localized in the fluvial section of the Gironde, where TMZ is present in summer and autumn (Lanoux et al., 2013), in close links with the watershed. It is instrumented with a real-time measurement system of water quality (see above). To evaluate the effects of high turbidity on the leaf decomposition rate, 30 litter bags were anchored to three bars (3 m) and immersed in the water column. A second set of 30 litter bags were anchored to two structures placed at the sediment surface, at the same location. Five additional bags were used the first day to determine the residual leaf content in water.

After 6, 14, 28, 34, 61, and 110 days of immersion in water, and 29, 78, 118, 149, and 176 days at the water-mud interface, five bags were retrieved from both conditions and returned to the laboratory in a zip plastic bag.

In the laboratory, leaves were removed from the litter bags and individually rinsed with water to remove adhering sediments. Afterwards, they were dried at 60 °C for at least 24 h and weighed to the nearest 0.01 g.

For water-column and water-mud-contact experiments, decomposition rates (k, day\(^{-1}\)) were determined by fitting the percentage of leaf dry mass remaining to the exponential model (1):

\[
M_t = M_0 e^{-kt}
\]

where \(M_t\) is the leaf dry mass remaining at time \(t\) (in days), \(M_0\) the leaf dry mass at the initial time, and \(k\) the breakdown rate (Petersen & Cummins, 1974).

Half-life \((t_{1/2})\), defined as the time required for the leaf dry mass to fall to half its value as measured at the beginning of the experiment \((M_0)\) is calculated according to:

\[
t_{1/2} = \frac{\ln (2)}{k}
\]
3. Results

3.1. Hydrological context

During the litter-bag experiment, mean-daily water temperatures recorded by the automated station were comprised between 10 and 20 °C, except for a short cold period at mid-February, when temperature decreased close to 0 °C (Figure 2(A)). Daily-averaged salinity reveals a low marine intrusion, with values always lower to 0.4. Turbidity is the parameter that presented the highest variability, with values ranging from 51 NTU in January to 4217 NTU (about 5 g L\(^{-1}\)) in April (Figure 2(B)). It has to be noted that salinity and turbidity peaks occurred at the same time, suggesting an upward shift of salinity front and TMZ due to a decrease in the river discharge.

Figure 2(C) and (D) shows an example of raw data recorded at the time step of 10 min. The semidiurnal tidal cycle can be inferred from changes on salinity, with maximum values (close to 0.5) occurring at high tide and minimum (0.1) at low tide, while temperature remained in the range comprised between 12 and 14 °C. Turbidity values follow the typical pattern resulting from bottom erosion and deposition processes, with significant peaks during flood and ebb phases. In the example shown here, ebb increase is much higher than flood (peak of 8000 NTU vs. less than 2000 NTU, respectively) because of the contribution of lateral advection from the tidal flat. At high and low tides, turbidity decays to minimum values due to deposition at slack waters.

3.2. Litter decomposition

Leaf mass loss at the water-mud interface was clearly delayed, especially during the first four months, when compared to suspended conditions (Table 1, Figure 3). Accordingly, half-life was longer when decomposition occurred at the water-mud interface (256 days) than in the water column (91 days). Beside the few published breakdown rates for oak leaves concerning fluvial environments, decomposition rate obtained in the estuarine water column falls in the range of these values (Table 1); whereas, \( k \) obtained in mud contact environment is lower compared with these ones.

4. Discussion

Breakdown rate of submerged leaves is known to strongly depend on the characteristics of the aquatic environment (Chergui & Pattee, 1990; Rounick & Winterbourn, 1983), in addition to other factors as leaf species (Webster & Benfield, 1986) or season (Chergui & Pattee, 1990; Reice, 1974). In aquatic ecosystems, three stages are recognized (leaching, conditioning, and fragmentation) for controlling the decomposition of organic matter (Petersen & Cummins, 1974; Webster & Benfield, 1986) and for being related to many biotic (microfungi and invertebrates activities, etc.) and abiotic factors (hydrodynamics, temperature, salinity, pH, nutrients, etc.) (Abelho, 2001).

The extent of organic matter burial in large rivers and estuarine ecosystems is poorly known. So far, most studies on differences in breakdown rates between buried litter

<table>
<thead>
<tr>
<th>Stream order</th>
<th>Location</th>
<th>Duration (day)</th>
<th>( k ) (day(^{-1}))</th>
<th>( t_{1/2} ) (day)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Southwest France</td>
<td>Estuary</td>
<td>110</td>
<td>0.0076</td>
<td>91 This study (water column)</td>
</tr>
<tr>
<td>7</td>
<td>Southwest France</td>
<td>Estuary</td>
<td>176</td>
<td>0.0027</td>
<td>256 This study (mud contact)</td>
</tr>
<tr>
<td>1</td>
<td>North Spain</td>
<td>River</td>
<td>155</td>
<td>0.0037–0.0051</td>
<td>136–190 Molinero, Pozo, and Gonzalez (1996)</td>
</tr>
<tr>
<td>2</td>
<td>North Portugal</td>
<td>River</td>
<td>61</td>
<td>0.0084</td>
<td>83 Sampaio, Cortes, and Leão (2001)</td>
</tr>
<tr>
<td>3</td>
<td>Central Portugal</td>
<td>River</td>
<td>63</td>
<td>0.0058–0.0273</td>
<td>25–120 Castela et al. (2008)</td>
</tr>
</tbody>
</table>

Note: Comparison with equivalent work in the southwest Europa.
and litter exposed to sediment surface have been conducted in headwater streams (Cornut, Elger, Greugny, Bonnet, & Chauvet, 2012; Cornut, Elger, Lambrigot, Marmonier, & Chauvet, 2010; Herbst, 1980; Metzler & Smock, 1990; Naamane, Chergui, & Pattee, 1999; Smith & Lake, 1993). In streams, the amount of buried leaf material depends on the timing and the quantity of leaf litter input, the degree of sediment movement (which is directly related to the geomorphological characteristics of the stream bed), and discharge levels (Pattee & Chergui, 1999). Previous works (Herbst, 1980; Smock, 1990) have reported that approximately 25–46% of leaf material entering channels become buried within stream sediments.

Breakdown rates of buried leaves are mainly linked to the physical abrasion and fragmentation phase together with two driving abiotic factors (oxygen concentration and the surface exposed to biological activity): (i) physical abrasion, which enhances decomposition, is both related to the water current velocity and the size fraction of the suspended substratum; (ii) the level of dissolved oxygen may limit the activity of microbial decomposers; and (iii) finally, the mass of deposited sediment provokes compaction of the leaves thereby reducing the surface exposed to micro-organisms and invertebrates.

In addition, the breakdown of buried organic matter is supposed to be largely influenced by the activity of benthic organisms temporarily residing within the interstitial environment (Mayack, Thorp, & Cothran, 1989; Smith & Lake, 1993). However, in the Gironde Estuary, the implication of benthic macrofauna is probably minor. Monthly, over 30 years, ecological surveys in the Gironde Estuary show that species richness of benthic macrofauna is very low in the TMZ, as typical for meso- and oligohaline areas in estuaries (Quintin et al., 2011). Hence, we consider physical abrasion, fragmentation phase, and oxygen concentration (abiotic factor directly related with microbial activity) to be the main driving responsible for the decomposition of suspended or surface placed-litter in the Gironde Estuary.

As the fluvial-tidal transition zone can be considered as a separate sedimentary environment (Van den Berg, Boersma, & Van Gelder, 2007), the breakdown rate of leaf litter that enters in the system is deeply marked by tidal, hydrological, and seasonal trends, as a result of suspended matter dynamics. At the scale of the semidiurnal tidal cycle, leaf litter experiences resuspension/deposition cycles, and advection processes. During ebb or flood phase, as long as tidal currents are higher than the erosion threshold, leaf litter is expected to be in suspension in the water column and thus more exposed to physical abrasion due to ambient turbulence. It has to be noted that current velocity is extremely high in the Gironde Estuary (typical values of 2 m s$^{-1}$ at the surface, Allen et al., 1980), therefore abrasion is postulated to be a categorically determinant factor favoring degradation. When slack water approaches, leaves can settle and thus be temporarily protected from abrasion and placed in a context of a very reduced biotic activity (anoxic conditions). Because of spring-neap tidal cycles, there is a significant variability of the intensity of these mechanisms. For increasing tidal ranges and springs, maximum velocities increase up to 2 m s$^{-1}$ above the bottom and exceed more often resuspension threshold (Castaing & Allen, 1981). Therefore, time in suspension is higher during spring tides and conditions for degradation, especially physical ones, are favored. During neap tides, the opposite happens, deposition time increases and conditions for protection predominate, inhibiting degradation processes.

5. Conclusion

This first litter-bag in situ experiment on oak leaves showed that in the Gironde Estuary, a highly turbid environment, decay rates of leaf litter decreased under mud-contact conditions in comparison with water-column ones. The former conditions most probably create an excellent refuge to impede the effects of mechanical abrasion and fragmentation, which was not compensated by the activity of invertebrate decomposers due to their minor importance in the central and upstream Gironde Estuary.

Leaf litter degradation process in the Gironde Estuary must be defined directly in correspondence with the TMZ dynamics, which is strongly influenced by tidal cycles and the intensity of freshwater discharge. In a context of future hydro-climatological changes (droughts, increase of water usage by human activity, etc.), one could expect an increased presence of TMZ in the fluvial sections of the Gironde, which is consistent with the present-day record of SPM. Leaf litter issued from the watershed will be more rapidly in contact with TMZ, in the up estuary. Our results suggest that recycling of this CPM process and its transport will be delayed. If confirmed, the resulting increase of coarse POM, which is available to be remobilized and exported during the rainy season, can be traduced as a risk of disturbances for industrial activities that require high volumes of filtered estuarine waters.

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