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ORGANIC MATTER DYNAMICS IN A HUMAN-IMPACTED ESTUARY: INSIGHTS FROM BIOMARKERS AND EXCITATION-EMISSION MATRIX FLUORESCENCE

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Estuaries are key zones from economic and ecological points of view. They are highly dynamic and productive ecosystems that link the continents to oceans. Estuaries are crucial in the production, transformation and transfer of Organic Matter (OM), which is the largest reactive reservoir of C-based compounds on earth. Dissolved Organic Matter (DOM; <0.7 µm) and Particulate Organic Matter (POM; >0.7 µm) are two fractions of OM that can influence the water quality (*via* controlling transport and bioavailability of pollutants) and trophic network. Hence, investigating the fate of DOM and POM in estuaries is a major environmental concern. However, tracing the dynamics of estuarine OM remains challenging as it has complex chemical composition, distinct sources, and is subjected to numerous transformation processes. Furthermore, DOM and POM were usually studied separately in estuaries due to the limitations of the analytical techniques and the complexity of the estuarine sample. The simultaneous study of both of these carbon pools in estuaries is still rare despite the fact that each carbon pool has its own dynamics and properties.

For a complete assessment of OM dynamics and better understanding of estuarine biogeochemical functioning, we concomitantly investigated dynamics of DOM and POM in a human-impacted estuary using multi-disciplinary approaches. Water samples were collected from 24 monitoring campaigns (2015-2022) along the Seine Estuary (NW France) covering its freshwater, brackish and seawater parts in high-flow (>700 m^3/s) and low-flow (<250 m^3/s) seasons. These samples were immediately filtered (GF/F 0.7 µm) to separate POM and DOM. Excitation-Emission Matrix (EEM) fluorescence was used for DOM characterization, whereas bulk ($\delta^{13}C_{org}$, total nitrogen contents, and $\delta^{15}N$) and molecular (such as Glycerol Dialkyl Glycerol Tetraethers, GDGTs) tools were used for POM characterization.

In this study, EEM fluorescence spectra were decomposed by PARAllel FACtor analysis (PARAFAC) into six fluorescent components (C1-C6; Fig.1a). These fluorescent components represent groups of similar fluorophores and were linked to distinct sources (i.e. terrestrial and biogenic) of DOM or transformation processes (e.g. photodegradation). Our results showed significant seasonal variations of both DOM and POM characteristics in the Seine Estuary (Fig. 1). During the high-flow season, inputs of terrestrial DOM (C1 and C2) and POM (reflected by Branched and Isoprenoid Tetraether index, BIT) were much higher compared with those in the low-flow season, implying more efficient transport of terrestrial OM under high discharge conditions. Biogenic DOM (C3 and C5), on the other hand, were more abundant in the low-flow season (Fig. 1a). This can be associated with higher phytoplankton productivity and biological activity during the low-flow season, which is facilitated by increased nitrogen loadings and ^{15}N-enriched nitrate uptake at low discharges (Fig. 1b).

In the low-flow season, a linear decrease in the POM of terrestrial origin was observed from upstream to downstream, as reflected by the bulk and molecular tracers (BIT and $\delta^{13}C_{org}$) (Fig. 1b), indicating the mixing of riverine and marine water masses along the estuary. Such a simple dilution effect was not observed in the high-flow season due to the effective transfer of riverine water masses. Moreover, terrestrial DOM (C1 and C2) did not undergo simple dilution from the upstream to the downstream part of the Seine Estuary (Fig. 1a), which reflects the processing of terrestrial DOM along the estuary. Last, four functional zones of the Seine Estuary can be divided based on different properties of the DOM and POM (Fig. 1): an anthropogenic zone (KP<260 km) with the effects of urbanization in the upstream estuary characterized by high levels of human-impacted DOM with biological origin; a high productivity zone (260 km<KP<310 km) characterized by higher TN and $\delta^{15}N$ as well as processed DOM associated with enhanced phytoplankton productivity and biological activity in the low-flow season; a mixing zone (310 km<KP<340 km) characterized by sharply decrease of terrestrial POM under low and high flow conditions; a coastal zone (KP>340 km) with high marine influence characterized by decreased terrestrial POM and increased biogenic DOM.

Overall, DOM and POM are largely decoupled in the Seine Estuary, emphasizing the need of characterizing these carbon pools simultaneously. Our results showed that lipid biomarkers, bulk geochemical analyses and EEMs are powerful and complementary tools for OM monitoring in the Seine Estuary. The multi-disciplinary approaches presented in this study can be applied in other urbanized estuaries, which is important for sustainable estuary management.

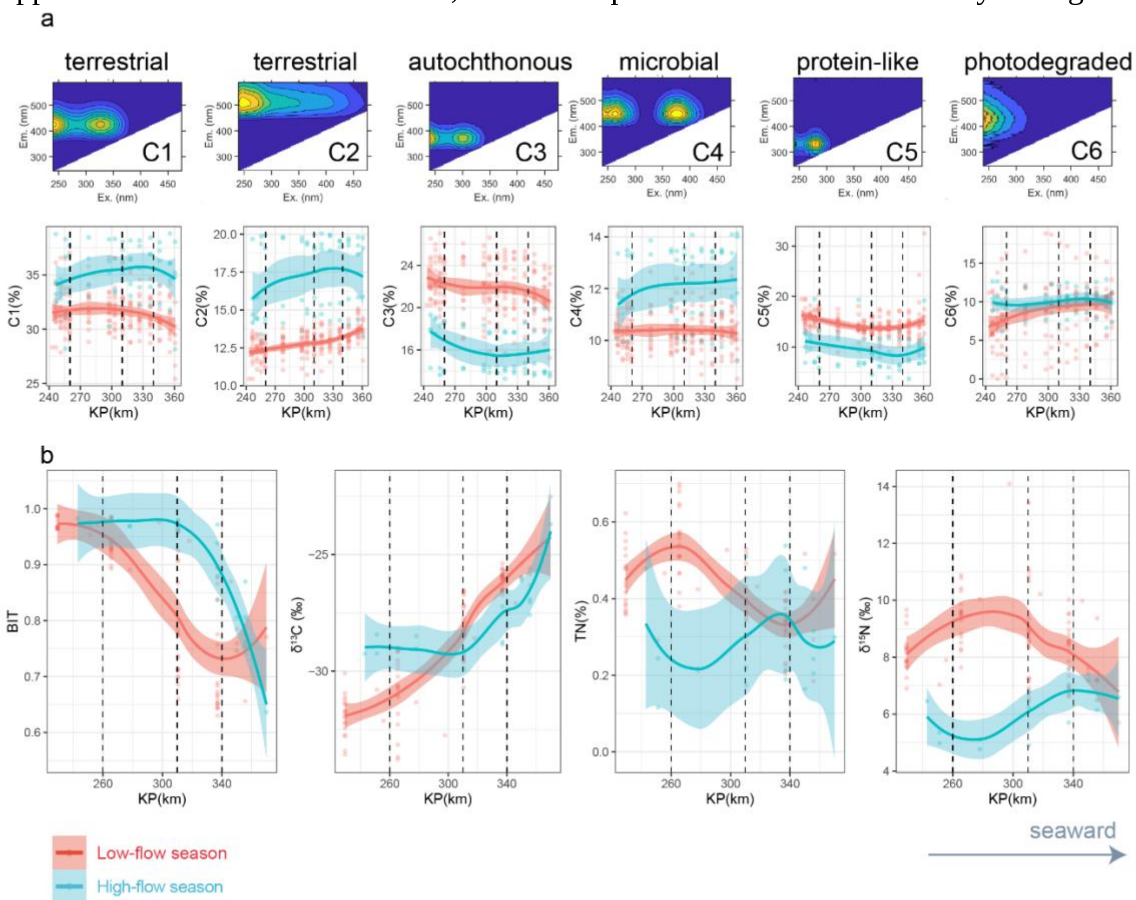

Figure 1 *(a) Contour plots and spatio-temporal variations of the PARAFAC components (C1-C6) for the surface water samples (n=249) collected in the Seine Estuary from 2019 to 2022. (b) Spatio-temporal variations of the bulk and molecular proxies (BIT, $\delta^{13}C_{org}$, TN, and $\delta^{15}N$) for the POM samples collected in the Seine Estuary from 2015 to 2021 (n=107). The trends were based on locally estimated scatterplot smoothing (LOESS) method with 95% confidence intervals. KP represents the distance in kilometers from the city of Paris.*