ORIGIN AND DYNAMICS OF ORGANIC MATTER IN THE SEINE ESTUARY (FRANCE): INSIGHTS FROM BULK AND MOLECULAR CHARACTERISATIONS

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Estuaries are key ecosystems from ecological and economical points of view, making their protection a real societal concern. This is especially true for the Seine Estuary (France), as its watershed contains one of the biggest megalopolis in Europe (Paris area, 12 million inhabitants) and covers 14 % of the French territory and 40 % of the national economic activity. The quality and amount of organic matter (OM) exert a key role on water quality and biogeochemical processes in estuaries. It is thus essential to investigate the nature and characteristics of OM in these ecosystems, which condition the transfer of both natural and anthropogenic substances from continents to oceans. Nevertheless, to date, the elucidation of the OM dynamics in estuaries remains a huge challenge due to (i) the heterogeneous and complex nature of this material, constituted of a large variety of compounds of different size and physico-chemical properties and (ii) the high variability of environmental (e.g. light, salinity) and physical (river discharge, tidal currents, resuspension, …) processes in estuaries. Aquatic OM consists of particulate (POM) and dissolved (DOM) organic matter, which are commonly separated by filtration. The low concentration of DOM in estuaries (few mg/L) coupled to the high salinities observed in marine environments (ca. 35 g/L) makes the characterisation of the estuarine DOM especially challenging.

The aim of this study was to constrain the sources and fate of the OM in the Seine Estuary and to investigate its spatiotemporal variability. To this end, 5 sampling campaigns were performed in the estuary under contrasting environmental conditions between January 2015 and April 2016. Water samples (ca. 100 L) and sediment cores (10 cm) were collected in the different parts of the estuary: (i) upstream, (ii) maximum turbidity zone (i.e. mixing of riverine freshwater and marine saline waters) and (iii) downstream. Water samples were filtered through glass fiber filters (0.7 µm) to separate DOM and POM. Filtered water samples were then concentrated and desalted by reverse osmosis coupled to electrodialysis, as previously described (Koprivnjak et al. 2009). This innovative method allows the isolation of representative DOM samples (i.e. without altering the quality of the OM as controlled through 3D fluorescence spectroscopy and with limited losses), in contrast with techniques classically used for DOM isolation (Green et al., 2014). The dynamics of the OM along the Seine Estuary was investigated by comparing the bulk and molecular characteristics of the OM in the different compartments (DOM, POM and sediment). Such characterization was performed by combining (i) elemental and isotopic analyses (elemental analysis-isotope ratio mass spectrometry; ^{14}C dating), (ii) optical characterisation of DOM (3D fluorescence; UV spectroscopy) and (iii) state-of-the-art molecular analyses (^{13}C solid state NMR; pyrolysis coupled with GC-MS and ultrahigh resolution mass spectrometry (FT-ICR-MS)).

Principal component analysis (PCA) was performed on bulk and molecular data from the Seine Estuary samples and showed that DOM composition significantly differs from that of sediment OM and POM (Fig. 1). DOM exhibits higher C/N ratio, is enriched in alkoxyl C and depleted

in aromatic C compared to POM and sedimentary OM, which is consistent with the more hydrophilic nature of DOM. In addition, ^{14}C dating reveals the recent age of DOM and POM (> 1950 AD), in contrast with sedimentary OM, whose age (up to 1000 yrs BP) strongly depends on the sampling season and related hydroclimatic conditions.
The third axis of the PCA shows that the OM characteristics vary along the estuary (Fig. 1). The mixing of riverine and marine water masses seems to be the main factor controlling the OM composition in the estuary, as revealed (i) by the linear increase in $\delta^{13}C$ of POM from upstream to downstream but also (ii) the concurrent decrease in the molecular diversity of DOM inferred from FT-ICR-MS analyses (ca. 5000 molecules detected upstream vs. 2700 downstream). Moreover, the non-linear dilution of the chromophoric DOM along the estuary based on UV and fluorescence analyses confirmed the mixing of marine and freshwater end-members, but also highlighted other sources or transformation processes of DOM and thus its highly dynamic character. Both isotopic and molecular analyses point to a predominant autochthonous origin of the OM in the Seine Estuary, even though terrestrial-derived compounds (e.g. lignin) were also detected in all samples. Seasonal variations in OM composition were, to a lesser extent, also highlighted, spectroscopic analyses revealing that the mean molecular weight and the aromaticity of DOM are higher in winter than in summer season.

In conclusion, chemical and statistical analyses show that the OM pool (DOM vs. POM and sedimentary OM) and the OM origin (marine vs. fresh waters) are the main factors controlling the OM composition in the Seine Estuary, the seasonal variations being less pronounced. This work emphasizes the necessity to combine complementary bulk and molecular techniques to better understand the complex estuarine OM dynamics.

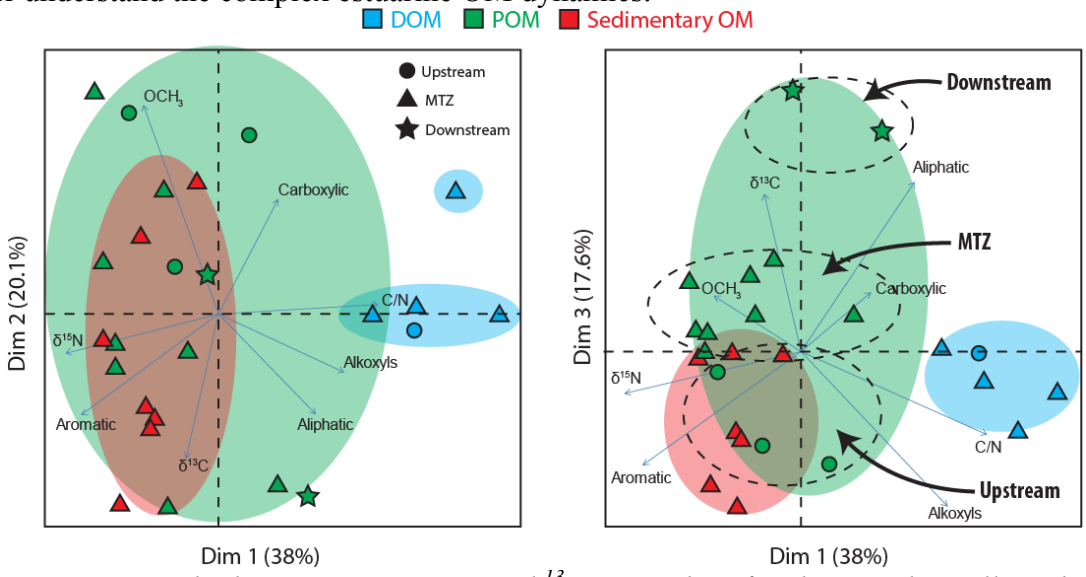

***Figure 1**: PCA with elementary, isotopic and ^{13}C NMR data for the samples collected along the Seine Estuary. MTZ = maximum turbidity zone.*

References

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