# ORGANIC MATTER DYNAMICS ALONG THE ARNO RIVER (ITALY) AND ITS ESTUARY

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## Abstract

Organic matter concentration and the optical properties of its chromophoric fraction (CDOM) were measured along the Arno River and in its estuary, in September 2015. Organic matter concentration strongly increased along the river, while in the estuary it was mainly affected by conservative mixing.

*Keywords: River input, Tyrrhenian Sea, Organic matter, Estuaries*

Over the last years, the interest in organic matter (OM) dynamics in rivers and estuaries has grown, due to the potential role of these areas as a source of $CO_2$ to the atmosphere and to the impact of climate change on river floods. The Arno River is the largest river in Tuscany, it is characterized by a highly variable water discharge and it is impacted by many different anthropic activities [1]. It is also an important source of C to the Med Sea, due to its high dissolved organic carbon (DOC) concentration [2-4]. The main goals of this work were: to elucidate the main sources/origin (natural, industrial, agriculture, anthropic) of OM along the Arno River, and to investigate the main processes removing DOC in the estuary. In September 2015, in the framework of the Envimed-Comecom Project, samples were collected along the Arno River and in its major tributaries. In the estuary, samples were collected in the surface layer, across the salinity gradient, and in the bottom layer, across the deoxygenation gradient. The application of PARAFAC to the Excitation-Emission matrixes resulted in the validation of a 5-component model, identified as: humic-like (C1, C4), fulvic-like (C2), protein-like (C3) and PAH-like (C5) compounds. Flow cytometry was used to enumerate free-living heterotrophic prokaryotes and to evaluate ultraphytoplankton abundance and structure. DOC and POC concentration, as well as absorption, humic-like fluorescence and heterotrophic prokaryotes abundance (HPA), increased from the spring to the estuary ($\Delta$DOC= 405 µM; $\Delta$POC= 286 µM; $\Delta$HPA = $3.3\times10^6$ cells/ml) (Fig. 1).

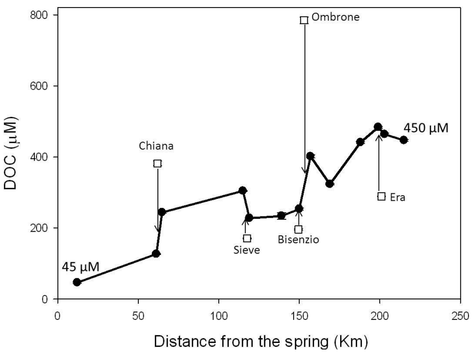


Fig. 1. DOC concentration along the Arno River (black circles) and in its major tributaries (empty squares).

Protein-like and PAH-like fluorescence started to increase after Florence. CDOM fluorescence, normalized on DOC concentration, indicated that the increase in humic-like compounds was mainly related to the increase in DOC, while protein-like and PAH-like fluorescence increased not linearly with DOC. Along the river, the percentages of DOC and POC were highly variable (~25-75%). The major tributaries had highly variable DOC and POC concentrations (DOC = 171 - 786 µM, POC = 96 - 455 µM). Chiana and Ombrone showed the highest DOC values (368 and 786 µM, respectively; Fig. 1) and CDOM absorption and fluorescence, but the lowest HPA. In the estuary, POC, DOC and CDOM were mainly affected by conservative mixing, as confirmed by their good linear relationship with salinity. At intermediate salinity, DOC values were slightly lower than those predicted by the relationship ($\Delta$DOC=17-18 µM), suggesting the occurrence of removal processes. In order to assess if the removal can be due to biological activity, two mineralization experiments were carried out in March and September 2015 by adding the microbial community of the estuary (S=12), to the water collected at a S=12 and filtered at 0.2 µm. The bottles were incubated in the dark and at in situ temperature for 2 months. In both experiments, DOC showed an exponential decrease with time. The largest decrease was observed in the first 48 h, together with a marked increase in HPA (Fig. 2).

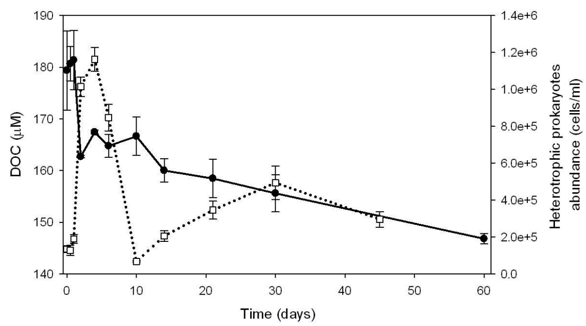


Fig. 2. DOC concentration (black circles) and heterotrophic prokaryotes abundance (empty squares) during the March 2015 experiment. Error bars refer to standard deviation between three replicates.

DOC removal rates ranged between 15 and 24 µM/month. In the bottom layer, a very thick salt intrusion was observed up to 12 Km inside the river, where a hypoxic zone was observed below 0.5 m. Following the deoxygenation gradient DOC concentration and HPA increased linearly. These data suggest that DOM accumulates under hypoxic conditions despite HPA is ≈ 3-fold higher than in marine surface waters.

## References

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