## DISSOLVED ORGANIC MATTER AND NUTRIENT ENRICHMENT IN THE ESTUARINE MIXING ZONE OF THE PO RIVER DELTA (ITALY)

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# Abstract

Dissolved organic matter (DOM) was investigated in the estuarine mixing area of the Po River-Adriatic Sea. The linear decreasing trend which was observed with salinity underscored the role of riverine input as a major source of humic-type DOM. However, laboratory experiments undertaken on field samples to evaluate the contribution of phytoplankton to the DOM showed an increased extracellular production following nutrient enrichments. These results suggest that the Po River input can be regarded not only as a direct source of terrigenous DOM, but also as a trophic source enhancing the potential of autochthonous DOM production in North Adriatic waters.

Key-words: Dissolved Organic Matter, Extracellular Organic Matter, estuarine waters

#### Introduction

Dissolved organic matter (DOM) in the ocean is the largest pool of organic carbon in aquatic environments, and as such represents a major reservoir of reactive carbon in the global carbon cycle. While riverine inputs of terrestrial humic substances provide DOM enrichments in estuarine and coastal zones, they still can be regarded as localized sources, representing a probably insignificant contribution to the marine DOM on a global scale. By contrast, biological production, which can significantly contribute to the in situ DOM formation, is rarely documented or quantified (1).

Fluorescence spectroscopy has been suggested as an useful approach to investigate the behavior of DOM in marine and estuarine waters (2). The same technique has been recently proposed to evaluate the phytoplankton production of extracellular organic matter (EOM) in laboratory experiments (3,4). In the present investigation DOM was studied in the estuarine system of the River Po using fluorescence spectroscopy. Since relationships linking the nutrient loads carried by the Po River

with the amounts of organic matter involved in the mucilage formation are still unclear (5), field and laboratory investigations have been coupled in this study to evaluate interactions between trophic potential and phytoplankton EOM production.

### **Methods and Materials**

Surface water samples were collected from eight stations in the estuarine mixing zone (riverine St.0 and marine St. 1 to 7) with a salinity range of 0.2-35 psu. DOM was analyzed by synchronous fluorescence spec-troscopy in unconcentrated filtered samples using a Spex FluoroMax spectrofluorimeter (4). Fluorescence intensity maxima were recorded in the excitation wavelength band of 340-350 nm with 25 nm  $\Delta\lambda$ . Dissolved phosphorus (DP) and total dissolved nitrogen (TDN) were analyzed to characterize the nutrient content using a Tracs 800 autoanalyzer. Chlorophyll a was measured in situ at marine stations using a Sea Tech fluorimeter connected with a multiparameter Idronaut probe.

Laboratory experiments were undertaken to monitor the EOM production in the samples from marine stations (St. 1-7; 10.1-35 salinity range). The unfiltered samples containing the natural phytoplankton were incubated without any further enrichment and subsamples were taken for the fluorimetric characterization of the extracellular medium according to previously described procedures (4).

## **Results and Discussion**

The analyzed concentrations are plotted in Fig. 1 as a function of salinity. As previously found in most estuarine waters (2,4), the fluorescence intensity in the humic-like band was found to decrease linearly with salinity (r2=0.97), thus behaving as a good tracer of the terrestrial DOM in marine waters. Linear relationships were also found between salinity and dissolved P, N and Chl a ( $r^2=0.98, 0.99, 0.94$ , respectively). While it seems clear that the trophic potential of Po River input can control the productivity of the marine system, no evidence can be provided by these results for any increased production of organic matter of autochthonous origin.

In laboratory experiments undertaken on natural phytoplankton, fluorescence intensity was observed to linearly increase over time in all the incubated samples. The production rate of EOM was higher in the lower salinity samples (3.1, 2.6 FU/day, St. 1 and 2 respectively), while lower values (in the 0.9-1.4 FU/day range) were measured in the higher salinity samples (St.3-7, sal>25 psu) which were characterized by significantly lower nutrient levels (Fig.1).

To confirm the relationship found between trophic level and EOM production, a further experimental evaluation was made during the incubation (day 19) by enriching one (St.6, 33 psu) from the last group of samples with algal culture medium (CM).

In Fig.2, where some of the incubated samples (St.3, 5, 6, 7) are compared, a significant change in the EOM production rate can be observed in sample 6 after the CM enrichment. According to the highest nutrient level, the measured new rate (6 FU/day) was largely exceeding all the others.



Fig. 1 - DOM and nutrients as a function of salinity



Fig. 2 - EOM production over time in untreated and nutrient enriched (+CM) samples

Our results suggest that the Po River input, as a nutrient source, can largely affect the potential of autochthonous DOM production in North Adriatic waters. Since in estuarine waters the concentrations of both terrigenous DOM and parameters stimulating algal growth and EOM enrichment are generally following the same dilution trend, coupling laboratory experiments with field-based investigations can be an useful approach to study the potential contribution of phytoplancton to the DOM pool.

References

1. Chen FR, Bada JL ,1992. The fluorescence of dissolved organic matter in seawater. *Mar. Chem.* 37: 191-221

2. De Souza Sierra MM, Donard OX, Lamotte M, 1997. Spectral identification and behavior of dissolved organic fluorescent material during estuarine mixing processes. Mar. Chem., 58: 51-58.

3. Mingazzini M, Colombo S, Ferrari GM, 1995. Application of

spectrofluorimetric techniques to the study of mucilages in the Adriatic Sea:

 preliminary results. Sci. *Total Environ.* 165: 133-144.
Mingazzini M, 2000. Synchronous fluorescence spectra as chemical tracers to monitor the organic matter dissolved in North Adriatic waters. In: Mediterranean Ecosystems: Structures and Processes. (Faranda F.M.,

 Guglielmo L., Spezie G. Eds.) Ch.16: 115-122, Springer Verlag.
Rinaldi A, Vollenweider RA, Montanari G, Ferrari CR, Ghetti A, 1995. Mucilages in Italian seas: the Adriatic and Tyrrhenian Seas, 1988-91. Sci. Total Envir. 165: 165-183.