DOC AND FDOM DISTRIBUTION IN THE MEDITERRANEAN SEA: RESULTS FROM THE MEDBLACK GEOTRACES CRUISE

L. Mercadante¹, D. Hansell², M. Gonnelli¹, E. Pitta³, M. Rijkenberg⁴, S. Vestri¹, C. Zeri³ and C. Santinelli^{1*}

¹ Biophysics institute, CNR, Pisa, Italy - chiara.santinelli@pi.ibf.cnr.it

² Rosenstiel School of Marine and Atmospheric Science, University of Miami, USA.

³ Institute of Oceanography, Hearine Research, Anavllenic Centre for Myssos 19013, Greece

⁴ NIOZ Royal Netherlands Institute for Sea Research, Department of Ocean Systems (OCS), and Utrecht University, P.O. Box

59, 1790 AB Den Burg, Texel, the Netherlands

Abstract

Vertical distributions of Dissolved Organic Carbon (DOC) and Fluorescent Dissolved Organic Matter (FDOM) were studied in the framework of the international cruise "MedBlack Geotraces". DOC vertical distributions were similar to those reported for the open ocean. Fluorescence analysis together with Parallel Factorial Analysis (PARAFAC) highlighted the occurrence of humic-like, protein-like and PAH-like compounds in the open Mediterranean Sea.

Keywords: Organic matter, Deep waters, Global change, Geochemical cycles, Mediterranean Sea

Dissolved Organic Matter (DOM) represents the largest reservoir of organic carbon on the Earth and the main source of energy for heterotrophic prokaryotes [1]. A fraction of DOM is Fluorescent (FDOM) and is therefore able to absorb light in the visible and UV wavelengths and to emit fluorescence. This fraction affects the penetration of light through the water column, limiting the quantity of light available for photosynthesis but also reducing the amount of harmful UV rays. Despite its importance, there is still little information about FDOM for the Mediterranean Sea (Med Sea); existing data are mostly limited to coastal areas. The main goals of this work are: (1) to present the first FDOM data for a large area of the Med Sea, (2) to study Dissolved Organic Carbon (DOC) distribution on a basin scale and (3) to evaluate DOC variability on the short temporal scale. In the framework of the international cruise "MedBlack Geotraces", held between April and August 2013, 880 samples were collected in the Med Sea (Fig. 1).



Fig. 1. Study area and sampling station.

Dissolved Organic Carbon concentrations and fluorescence Excitation Emission Matrices (EEMs) were measured in order to gain quantitative and qualitative information on DOM. DOC showed the highest values (60-80 μ M) in the surface layer (0-150 m), with local maxima in the areas affected by mesoscale activity and a gradual decrease to values of 38-40 μ M below 1000 m. A slight increase was observed close to the bottom (41-43 μ M) (Fig. 2). Even if these values and distributions are in agreement with previous studies [2-3] and with oceanic observations [1, 4], DOC concentrations in the deep waters (>2000 m) of the western Med Sea were lower than observed in 2008, when values up to 50 μ M were measured [3]. This difference could be attributed to warmer winters and consequently to a reduced deep water formation rate in recent years.

The application of PARAFAC to the EEMs allowed for the validation of a 6component model. The components were identified by comparison with the literature [5-8] and similarity with spectra of commercial substances. Three components (C1, C3, C4) were identified as humic-like substances, of both marine and terrestrial origin; 2 components (C2, C5) were identified as proteinlike; while the last (C6) was identified as PAH-like, due to its spectroscopic characteristics similar to fluorene [7]. Humic-like components showed a minimum in the surface layer, probably due to the photobleaching, and higher values below 150 m. Protein-like components showed an opposite distribution with a maximum in the surface layer and a decrease up to 200 m, without any particular trend down the column water. FDOM distributions are similar to those reported for open ocean areas [5], even if fluorescence intensity is higher than that reported for both humic-like and protein-like components for the Atlantic and Pacific Oceans [6].

The similarities between DOC and FDOM dynamics in the Med Sea and in the open ocean confirm that the Med Sea can be a natural laboratory to study how climate change can affect the global DOM cycle.



Fig. 2. DOC vertical distribution along the West-East section reported in Fig. 1

References

1 - Carlson C. A. and Hansell D. A. 2015. DOM sources, sinks, reactivity and budgets. *In:* Hansell, DA and Carlson, CA, (eds.), Biogeochemistry of marine dissolved organic matter 2nd ed., Elsevier, pp 66-109.

2 - Santinelli C., Nannicini L.and Seritti A. 2010. DOC dynamics in the meso and bathypelagic layers of the Mediterranean Sea. *Deep Sea Research Part II: Topical Studies in Oceanography*, 57 (16): 1446-1459.

3 - Santinelli C. 2015. DOC in the Mediterranean Sea. *In:* Hansell, DA and Carlson, CA, (eds.), Biogeochemistry of marine dissolved organic matter 2nd ed., Elsevier, pp 579-608.

4 - Hansell D. A. 2013. Recalcitrant dissolved organic carbon fractions. *Marine Science*, 5: 421-445

5 - Stedmon C. and Nelson N. B. 2015. The optical properties of DOM in the ocean. *In:* Hansell, DA and Carlson, CA, (eds.), Biogeochemistry of marine dissolved organic matter 2nd ed., Elsevier, pp 481-502.

6 - Jorgensen L., Stedmon C. A., Kragh T., Markager S., Middelboe M., and Sondergaard, M. 2011. Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter. *Marine Chemistry*, 126(1): 39-148.

7 - Ferretto N., Tedetti M., Guigue C., Mounier S., Redon R. and Goutx M. 2014. Identification and quantification of known polycyclic aromatic hydrocarbons and pesticides in complex mixtures using fluorescence excitation–emission matrices and parallel factor analysis. *Chemosphere*, 107: 344-353.