

# CHARACTERISATION OF NATURAL ORGANIC MATTER IN DEPTH PROFILE OF THE MEDITERRANEAN SEA BY 3D-FLUORESCENCE FOLLOWED BY PARAFAC TREATMENT

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## Abstract

The experiments made for the projet DYCOMED permit a better understanding of the natural organic matter (NOM) variation in seawater from surface to 2200m depth profile. Besides the dissolved organic carbone (DOC) concentration, the NOM fluorescence gives an additional explication in sight of this particular ecosystem. The fluorescence data have been analyzed by the mathematic method PARAFAC. Four fluorescent NOM components have been found and have been compared.

**Keywords:** *Organic Matter, Analytical Methods, Deep Sea Processes, Deep Waters*

## Introduction

As a semi-enclosed sea which presents a particular aquatic ecosystem, the Mediterranean Sea is a special reservoir of dissolved organic matter (DOM). Following the study of B. Avril (2002)<sup>1</sup>, a periodic series of samplings have been performed during one year (2008) in the central Ligurian Sea (DYFAMED site, 43°25'N, 07°52'E, NW Mediterranean Sea). The samplings have been made at 12 depths every month from 0 to 2200m-depth. Unfiltered samples have been collected in precombusted glass bottles (particulate organic matter represents less than 2%) and conserved with sodium azide (NaN<sub>3</sub>, 1M) to prevent any biological development.

## Methodology

DOC measurements were made by High Temperature Catalytic Oxidation Technique (Shimadzu TOC-V). The Excitation and Emission Matrix (EEM) spectra were obtained by spectrofluorimetry (HITACHI 4500) at excitation wavelengths from 250 to 500nm and emission wavelengths from 200 to 550nm, both wavelength slits for 5nm, scan speed is 2400nm/min. Analysis of fluorescent dissolved organic matter (FDOM) in the depth profile has been done with the help of parallel factors analysis (PARAFAC) software. It is a powerful statistical technique to treat the 3D-fluorescence spectra leading to the decomposition by a number of independent fluorescent compounds. In order to treat the Inner Filter Effect (IFE), 119 EEM of diluted samples have been made besides of 119 EEM spectra of original samples<sup>2,3,4</sup>.

## Results and Discussion

Two data treatments have been taken for this project according to the presence of FDOM components in the different depths. Treatment of all sample spectrums from the depth 0 to 2200m-depth gives 4 fluorescent components (Fig.1) that represent the fluorescence maxima of previously identified moieties : [Tyr] maximal excitation wavelength and emission wavelength 265nm/305nm (tyrosine-like) ; [Trp] maximal  $\lambda_{EX}/\lambda_{EM}$  =280nm/340nm (Peak T, tryptophan-like group); [M] maximal  $\lambda_{EX}/\lambda_{EM}$ =295nm/410nm (Peak M, marine humic-like substance) and a double maximum component [CA] with maximal  $\lambda_{EX}/\lambda_{EM}$ =335nm/445nm (Peak C, visible humic-like group) and  $\lambda_{EX}/\lambda_{EM}$  = 250nm/445nm (Peak A, UV humic-like substance).

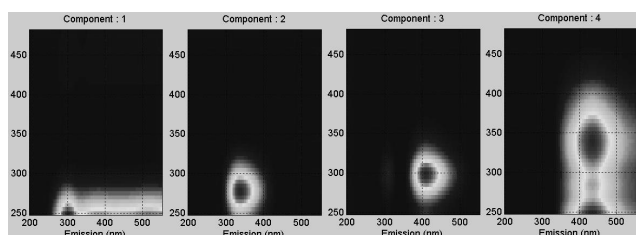


Fig. 1. 4 Components: Component 1, Tyrosine-like fluorophore; Component 2, Peak T-Tryptophane-like fluorophore; Component 3, Peak M-Known as marine humic-like substances fluorophore; Component 4, Peak C and A-coupled humic-like substances fluorophore.

Fluorescence contribution of each component at different logarithmic depths (Fig. 2a) shows that the most concentrated fluorophores zone is deeper than 100m throughout the year, which is different from the results of DOC concentration of which the most concentrated zone is on the seasurface<sup>1</sup>. It makes clearer the difference between living organism molecules and NOM

because of the probable existence of some less or no-fluorescent substance (huge moleculars or longer chained protein, etc.) in the surface waters and more fluorescent substances like NOM in the deeper sea. This might be owed to 3 reasons: the better recycling of NOM by living organisms thanks to the sun rays at the water surface than deep sea; the deposition of no-bioactive NOM towards deeper seawaters; the influence of photo bleaching on chromophoric compounds to the presence of FNOM. The fluorescence contribution of protein substances (Tyr and Trp) is important (+ and O, Fig.2a), this could be due to unfiltered sampling protocol. Humic-like substances are generally less fluorescent comparing to other compounds, particularly the M compound. An important peak contribution of marine humic-like substance has appeared in May at the depth from 100m to 2200m, although the other fluorophores kept their values reasonable. Moreover, the intensity maxima was associated to the mesopelagic layer (100–400m), while an increase of protein substances in the deep sea occurred at 400 m followed by a sharp decrease at 600 m in July, August and September. This is probably due to the thermal stratification of water column. In the intensity comparison among minima, averages and maxima (Fig.2b), we have observed the averages close to the minimal data, which signifies generally the low NOM concentration throughout the year, besides of period of mesotrophy (spring bloom). In the deep sea, there is normally less NOM concentration because of lysis and low carbon production. But occasionally, an increase of FNOM is observed for a reason not yet explained, estimated could be brought by deep current (the third compound in Fig.2b). This project will be continued for several years. It permits us to study the variation of an ecosystem in a 2200m depth oceanic water column.

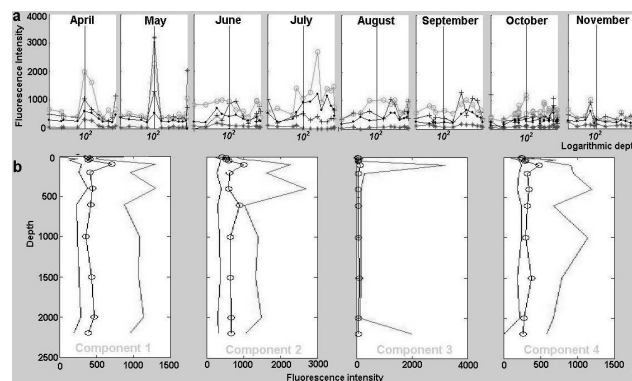


Fig. 2. Comparison of 4 components in depth profile. a): 4 components in each illustration with sea depths at Axis X and fluorescence intensity at Axis Y, totally 8 months from April to November. b): Fluorescence Minimal, Average and Maximal intensity in each illustration standing for each component.

## References

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