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Studies of the DOM aqueous extracts from coastal marine sediments

F. Sakellariadou

Lab. of Oceanography and Marine Geochemistry, Dept of Maritime Studies, University of Piraeus, 80 Karaoli and Dimitriou st, Piraeus 18532, Greece, email: fsakelar@unipi.gr

Dissolved organic matter (DOM) represents a major exchangeable organic pool playing an outstanding role in the ocean carbon cycle. It has a complex chemical structure made up of a wide range of organic molecules. The composition of DOM depends on the sources proximity and the exposure to any sort of degradation mechanism. The coloured (or chromophoric) dissolved organic matter (CDOM), representing the optically active fraction of DOM, consists of aromatic rings able to absorb light in the visible and UV regions (Kirk, 1994) and fluorophoric molecules that emit light. The main fluorophoric moieties of CDOM are humic material with a blue fluorescence and protein material with an ultraviolet (UV) fluorescence (Mopper and Schultz, 1993).

Dissolved organic matter interacts with pollutants either by enhancing their bioavailability or by influencing their transportation to the soluble phase. In addition, DOM affects the remineralisation of carbon and its preservation in marine sediments. Referring to its origin, it can be terrestrial, freshwater or marine one.

Fluorescence spectroscopy is a technique widely applied for the identification and characterization of organic matter, being fast, simple, non-destructive and sensitive. In addition, the fluorescence analysis for the physico-chemical characterization of organic matter requires a small amount of aqueous sample at a low concentration, in comparison with the large sample volumes needed for conventional techniques.

At the present study coastal sediment samples were collected from Messiniakos gulf in the south western Peloponnese in South Greece. Messiniakos gulf has a seabed dominated by very abrupt inclinations reaching depths of more than 1000m. All samples, according to their grain size, are classified as fine clayey silt. Dissolved organic matter was extracted under gentle extraction conditions (4 mM CaCl2 solution). The various classes of organic components present at the DOM aqueous extracts were characterised by fluorescence spectroscopy technique as DOM fluorescence is a property furnishing valuable information for its composition and biogeochemical cycling.

Fluorescence spectra were recorded using a Perkin-Elmer LS 55 luminescence spectrophotometer equipped with the WinLab 4.00.02 software for data processing. Conventional mono-dimensional emission, excitation and synchronous-scan excitation spectra were recorded. Mono dimensional emission spectra were recorded over the range 380–600 nm at a constant excitation wavelength of 360 nm. Excitation spectra were recorded over the range 300–500 nm at a fixed emission wavelength of 520 nm. Synchronous-scan excitation spectra were measured by scanning simultaneously both the excitation and the emission wavelengths (from 300 to 550 nm), while maintaining a constant, optimised wavelength difference $\Delta\lambda$ (λem – λexc) = 18 nm. (Senesi et al., 1991).

Total Luminescence Spectra (3D fluorescence spectra) were obtained in the form of excitation/emission matrix spectra (or contour maps) by scanning the wavelength emission over the range 300 to 600 nm, while the excitation wavelength was increased sequentially by 5-nm steps from 250 to 500 nm. In comparison with the limited provided information from the conventional fluorescence spectroscopy, EEM analysis seems to be sufficiently sensitive to distinguish between the various types of marine gelbstoff as well as to help estimating the contribution of each of them.

Humification indices according to Ohno (2002) and Zsolnay (1999) were calculated. The Humification index (HIX) according to Ohno is calculated by dividing the emission intensity in the 435 to 480 nm region by the emission intensity in the 300 to 345 nm region; HIX quantifies the red shift of the emission spectra toward longer wavelengths with increasing humification. The HI index according to Zsolnay is defined as the area in the upper quarter (Σ435-480nm) of the usable emission peak divided by the area in the lower usable quarter (Σ300-445nm).

All fluorescence spectra were thoroughly evaluated for the classification of chromophoric units present. Variations were observed according to the sampling site and more precisely its proximity to the coastline and the corresponding water column's depth; the oceanographic characteristics allowing or obstructing sea water circulation; as well as the proximity of each sample to the seabed, in other words the characterization of each sediment sample as surface of subsurface one.