



Geochemical study of the mobile metal/metalloid fraction and the fluorescent properties of the aqueous extracts of dissolved organic matter present in marine sediments from the Messiniakos gulf at the southern part of Greece



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ABSTRACT

Sediment samples from the Messiniakos gulf, at the southern part of Greece, were studied for the metals/metalloid content in the non-residual fraction and the fluorescent properties of the aqueous extracts of dissolved organic matter as both groups of metals/metalloid and dissolved organic matter are highly important from an environmental aspect. Applying the useful tool of Kriging method, prediction surfaces for each non-residual metal/metalloid were produced. Hierarchical cluster analysis and factor analysis with varimax rotation were performed on the data for the non-residual metal/metalloid content in sediments. The aqueous extracts of dissolved organic matter were characterized by fluorescence spectroscopy recording mono dimensional emission, excitation, synchronous-scan excitation and total luminescence spectra for the classification of chromophoric units present.

In general, it was found that sediments from the central part of the gulf correspond to mobile metal fraction enrichment while those from the western gulf had lower values. Fluorescence studies in the DOM extracted from sediments revealed the presence of autochthonous organic matter with a low degree of aromatic polycondensation and a low level of conjugated chromophores. Fluorescence intensity and humification decrease in buried sediments. Samples with more humified structures were also the ones having more intense peaks.

Spatial and vertical distributions of temperature, salinity and chlorophyll content in the water column were also studied.

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1. Introduction

Messiniakos gulf is located in the south west Peloponnese at the southern part of Greece. The geology around the gulf consists of geotectonic units and post Alpine deposits made up of: marine deposits northwards of Koroni; the Pindos Unit, that comprises pelagic sediments and flysch, at the west coasts; Holocene deposits at the north coasts; marine deposits and the Gavrovo–Tripolis Unit, that contains neritic carbonates and flysch, at the east coasts till Kardamyli; marine deposits and the Mani Unit, which consists of crystalline carbonates to marbles and metaflysch, south-eastwards of Kardamyli (Fountoulis et al., 2014). Messiniakos is a deep gulf characterized as a fault-controlled, steep submarine valley that continues down-slope as a canyon that out flows into

the deep basins of the Hellenic Trench (SoHelME, 2005). Its morphology is rather simple involving one asymmetric structure with north, northwest-south, southeast direction and a considerable tilt toward the northeast. The gulf is regarded as the direct continuation of the continental slope from the trench to the island arc (Papanikolaou et al., 1988). Its bathymetry corresponds to abrupt inclinations and intense landslips causing sediment transport (Pavlikis et al., 1989). Pamissos and Nedonas are the two main rivers flowing into the northern part of the gulf and supplying the marine area with terrigenous material.

The present study focuses on an environmental consideration of the Messiniakos gulf. In particular, the non-residual metal/metalloid content and the aqueous extracts of dissolved organic matter (DOM) present in a selection of representative sediment samples were studied. The selection of these two categories of constituents is supported by their significance in the ecological consideration. The choice to deal with sea bottom sediments was based on their important role as natural ultimate sink of pollutants

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Table 1

Surface and subsurface sediment samples, corresponding sea water depth and coordinates.

Sample I.D.	Sea water depth (m)	North	East
1, 2	330	36.68°	22.37°
3, 4	208	36.83°	22.26°
5, 6	517	36.81°	22.05°
8, 9	191	36.86°	21.98°
10, 11	241	36.91°	22.12°
12, 13	573	36.93°	22.02°
14, 15	47.5	36.96°	21.93°
16, 17	33	36.95°	22.14°
18, 19	65	37.00°	22.00°
20, 21	20	37.01°	22.04°

entering into the marine environment. Additionally, the physical parameters of temperature and salinity as well as the chlorophyll content, due to its potential to act as an indicator of phytoplankton abundance, were studied at the at sea surface and the bottom of the water column for each sediment sample location.

Especially, trace metals enter the gulf via weathering of soil and rocks as well as a wide range of anthropogenic activities. Metals are associated with sediment components in various ways (Tessier et al., 1979) while environmental changes may lead to metal release from solid to liquid phase (Eggleton and Thomas, 2004; Calmano et al., 1993). The residual metal fraction contains most of the metals hosted in the lattice structure of silicate minerals, clays and other resistant minerals. These metals are not expected to be released rapidly in the secondary environment under the conditions normally encountered in nature. The non-residual metal fraction contains the metals associated with the exchangeable, carbonate hosted, reducible plus organic and sulfide bound geochemical phase. The non-residual metal fraction is more important than the residual one, from an environmental point of view, as it participates in most aqueous transport mechanism of pollution being therefore a good indicator of the metal biological availability. The current geochemical study includes the application of Kriging which is a geostatistical model based on autocorrelation, that is the statistical relationships among the measured points. In that way, the formation of prediction surfaces for the non-residual metal/metalloid content was accomplished.

Moreover, DOM corresponds to the most active and mobile form of soil organic matter and the major soluble component of natural aquatic systems. It plays an important role in the environmental fate of numerous contaminants in a variety of ecological functions. It interacts with a wide range of trace metals and organic pollutants enhancing their bioavailability, causing increased pollutant's toxicity and allowing to the relatively insoluble ones to be incorporated into biology systems (Akkanen et al., 2004; Hirose, 2007; Piccolo, 1994). It is a rather complex and heterogeneous variety of high to low molecular weight components with diverse solubilities, reactivities and optical properties. In marine sediments DOM can be allochthonous with a terrigenous origin transported from the adjacent coastal area and/or autochthonous produced in situ and having a marine origin. Also, part of it can be associated with human activities, introduced to the marine environment through direct point discharge, diffuse leaching and aerial dispersion. The composition of DOM depends on the sources proximity and the exposure to any sort of degradation mechanism. The colored (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, 2011) and fluorophoric molecules that emit light. Organic matter fluorescence takes place when an excited electron in an atom or molecule returns to its ground state by losing energy as light; humic material have blue fluorescence while protein material has an ultraviolet (UV) fluorescence (Mopper and Schultz, 1993). In this study, the

various classes of organic components present at the DOM aqueous extracts were characterized by fluorescence spectroscopy which is a technique widely applied for the identification and characterization of organic matter, as it is fast, simple, non-destructive and sensitive to low concentrations. Mono dimensional emission spectra, excitation spectra, synchronous-scan excitation and total luminescence spectra were obtained. The difference between conventional fluorescence spectroscopy and the 3D one is that the former measures fluorescence at a single set of excitation and emission wavelengths while the latter producing excitation/emission matrix spectra furnishes more detailed information. All fluorescence spectra were evaluated in detail.

2. Materials and methods

Sediment samples were collected from various sampling sites (Fig. 1) of the Messiniakos gulf during an oceanographic cruise with the R/V Aigaeo using a stainless steel box corer. This device could contain a sediment block as large as 40 × 40 × 50 cm with negligible disturbance (US Environmental Protection Agency, 2003). From each sampling site one surface (0–5 cm depth) and one subsurface (20–25 cm depth) sample were collected (Table 1). All samples were carefully taken away from the sampling device walls to avoid possible sediment contamination by the box corer material. All sediments were treated by hand for the removal of unrepresentative material (e.g., stones or vegetative material) and then homogenized. Particle-size analysis by sieving classified sediment material as very fine silt/clay.

2.1. Temperature, salinity, chlorophyll

Values for temperature (T), salinity (S) and chlorophyll content at the sea surface and the bottom of the water column, for each sediment sample location and corresponding to sediment sampling time (mid October), were obtained from MyOcean Data Access Portal (MyOcean Data Access Portal, 2015). MyOcean Data Access Portal offers online catalog of products provided by the EU Copernicus Marine Service. They refer to the Global Ocean or specific marine areas (i.e. Mediterranean Sea), a wide range of oceanographic parameters and a variety of time span with a vertical coverage. Data is produced by satellites observations, in situ observations and models.

In the present paper, temperature and salinity values were supplied by the “Global observed ocean physics temperature salinity and currents reprocessing” product while chlorophyll by the “Mediterranean sea biogeochemistry reanalysis” one. The former includes combined products from satellite observations and in-situ, on a 1/4 degree regular grid, measurements over the time period 1993–2012. The latter refers to a reanalysis of Mediterranean Sea biogeochemistry at 1/16 degree along a time period of 16 years (1993–2012), using the OPATM-BFM biogeochemical model and a data assimilation of surface chlorophyll concentration.

2.2. Metal content

All surface sediment samples were digested with nitric acid using microwave heating with a suitable laboratory microwave unit, following the EPA 3051A method (EPA Method 3051A, 2007) which prepares samples for a variety of metal analyses. More specifically, 0.500 g of each sample was weighted into a Teflon digestion tube and 9 ± 0.1 mL of concentrated nitric acid and 3 ± 0.1 mL of concentrated hydrochloric acid were added. The tubes were sealed and placed into the microwave system (Multiwave 3000, Sample Preparation System, Anton Paar, Perkin Elmer). In order to achieve uniform radiation distribution a 16-position rotor

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