

# LIPID BIOMARKERS AND BULK ORGANIC PARAMETERS IN NORTHEASTERN MEDITERRANEAN SEDIMENTS

Alexandra Gogou<sup>1\*</sup>, Ioanna Bouloubassi<sup>1</sup>, Roselyne Buscail<sup>2</sup>

<sup>1</sup>. LPCM, Université P. et M. Curie, Case 134, Paris, France.

<sup>2</sup>. CEFREM, Université de Perpignan, France.

## Abstract

This study focuses on two marine sites of the Eastern Mediterranean (north and south Aegean Sea) and aims at assessing the various sources and the diagenetic state of organic matter in recent sediments using the biomarker approach. Mean organic carbon (OC) values in the surface sediments were two-fold higher in the north compared to the south Aegean (0.9% and 0.5%, respectively). The abundance of the various biomarker classes of terrestrial origin (long chain n-alkanes, n-alkanol and fatty acids) was significantly higher in the north site, reflecting the importance of riverine discharges in fueling this area with terrestrially-derived material. Concomitantly, the supply of nutrients leads to a higher productivity in the north compared to the south Aegean Sea, which is reflected by the relative abundance of various marine biomarkers (short chain alcohols and fatty acids, alkenones, sterols, diols and keto-ols). Dispersal pathways of organic matter and the various types of primary producers in the overlying waters were also investigated.

## Introduction

The Mediterranean Sea is considered as a unique setting for the investigation of fundamental topics in the biogeochemical cycling of organic matter (OM). While a large body of studies has been carried out in the Western Mediterranean (1,2), there are only scarce data for the Eastern sub-basin (3).

This study is focused on the north and south Aegean Sea and aims at assessing the organic matter sources and highlighting alteration processes during its transport and burial in recent sediments. Biomarker compounds within several lipid classes (hydrocarbons, alcohols, long-chain alkenones, sterols, diols and keto-ols, and fatty acids) have been used in order to address these questions.

The selected marine sites have contrasting hydrological features. The north Aegean Sea receives considerable freshwater inputs from river discharge as well as inflow from the Black Sea, resulting in higher productivity compared to the south Aegean (Cretan Sea). The latter is considered as one of the most oligotrophic regions of the world ocean(4).

## Methods and Materials

The analytical methodology comprises the freeze-drying of sediment samples, extraction with organic solvents for the isolation of the total extractable organic matter (TEOM), column chromatography for the separation of the various lipid classes, gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) for the qualitative and quantitative analysis of individual lipid components.

## Results and Discussion

Mean organic carbon and total nitrogen values are two-fold higher in the north compared to the south Aegean (0.9% and 0.12% in the north Aegean and 0.5% and 0.08% in the south Aegean Sea, respectively).

The n-alkane concentrations varied from 1.46 to 5.21 mg/g of dry sediment in the north and from 2.23 to 3.22 mg/g in the south Aegean Sea. The predominance in most cases of the high molecular weight homologues (>C<sub>23</sub>), showing an important odd/even preference as indicated by the values of the CPI ratio in the range C<sub>23</sub>-C<sub>36</sub> (from 3.31 to 4.23), reveals an allochthonous contribution from terrestrial plant waxes.

In the north Aegean sediments, the total concentrations of homologues with more than 23 carbon atoms ranged from 573 to 2257 ng/g, reaching the maximum value at the sampling site N2 (960 m water column depth) located in the Thermaikos Plateau, and the minimum at N4 (87 m water column depth), located in the upper continental shelf of Lesbos Island. The higher concentrations found in the deeper sampling stations of the North Aegean can be partially attributed to different sedimentological characteristics of shallow and deep stations.

In the Cretan Sea sediments, long chain homologues (>C<sub>23</sub>) ranged from 977 to 1401 ng/g, showing a uniform spatial distribution with slightly lower concentrations in the deeper sampling site (S1). The absence of major differences in the spatial distribution of terrestrially-derived homologues in the open Cretan Sea can be explained by: i) the absence of riverine inputs and ii) the homogeneous sedimentological characteristics of the different sampling sites.

The homologues of n-alkanes with less than 20 carbons (C<sub>15</sub>-C<sub>20</sub>) were found in relatively high abundance in both the north and the south sampling sites (from 572 to 2266 ng/g), and showed in most stations a slight even to odd predominance. The low CPI values calculated

for all samples (from 0.58 to 0.79) indicate an important contribution of alkanes with bacterial and/or petrogenic origin. Petroleum inputs are further confirmed by the presence of an unresolved compound mixture (UCM), which appears as a hump in the aliphatic fraction as well as a series of hopanes and steranes.

Identifying biomarkers derived from marine sources permits determining the various types of algal species contributing to the overall surface water production. Contribution from coccolithophorids and diatoms, the main primary producer species in the overlying waters, was higher in sediments of the north Aegean as indicated by the spatial distribution patterns of alkenones and C<sub>28</sub> desmethyl-sterols. The occurrence and distribution of other algal biomarkers, such as dinosterol and long-chain alkyl diols and keto-ols, reflect the same spatial trends, for the contribution from dinoflagellates and other nanoplankton species. Early diagenetic alterations of marine OM through heterotrophic processes, occurring during its transport and burial, are also investigated by means of diagnostic zooplanktonic and microbial biomarkers.

The whole data set is discussed in relation to environmental conditions prevailing in the study area. This allows gaining a better understanding of the biogeochemical functioning of the Aegean Sea, an area that has received increasing attention during recent years due to significant changes in its hydrological regime. The latter is most likely driven by climatic change (5), resulting in a possible impact on the entire Mediterranean Sea.

## References

1. Bouloubassi I., Lipiatou E., Saliot A., Tolosa I., Bayona J.M., Albaiges J., 1997. Carbon sources and cycle in the Western Mediterranean: II. The use of molecular markers to determine the origin of organic matter. *Deep Sea Res.* 44: 781-799.
2. Buscail R., Pocklington R., Daumas R., Guidi L., 1990. Fluxes and budget of organic matter in the benthic boundary layer over the North Western Mediterranean margin. *Continental Shelf Research* 10: 1089-1122.
3. Gogou A., Bouloubassi I., Stephanou E., 2000. Marine organic geochemistry of the Eastern Mediterranean: 1. Aliphatic and polyaromatic hydrocarbons in Cretan Sea surficial sediments. *Marine Chemistry* 68: 265-282.
4. Psarra S., Tselepidis A., Ignatiades L., 2000. Primary productivity in the oligotrophic Cretan Sea (NE Mediterranean): seasonal and interannual variability. *Progress in Oceanography* 46: 187-204.
5. Roether W., Manca B.B., Klein B., Bregant D., Georgopoulos D., Beitzel V., Kovacevic V., Luchetta A., 1996. Recent changes in Eastern Mediterranean deep waters. *Science* 271: 333-335.