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New GEOTRACES or GEOTRACES relevant scientific results

Nutrients, trace element in Western and Eastern Mediterranean Sea surface sediment: Environmental variability and anthropoghenic footprint

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ABSTRACT. During GEOTRACES MedBlack Sea cruise, our work was focused on physicochemical parameters measurements, water sampling and short core sediment sampling. Trace elements necessitate trace metal clean CTD system sampling. Analysis are assessing nutrient, trace element (Fe, Pb, Cd, Zn, Co, Mo, Cu and Ni) and trace element fractionation, carried out on sediment in eastern and western surface sediment. The X-ray diffraction is applied on the clay fraction. Results salinity section plot shows some clearly recognizable water masses. Clay minerals assemblages have distinctive sources and their dispersal reflects different agents of transport in the eastern Mediterranean Sea. Nutrients show more oligotrophic condition in eastern area. The most important sources of dissolved silicate in the Mediterranean Sea come from the continental fluvial system and from groundwater discharges. Electronic microscopy shows dominance of diatoms, which play an important role in organic matter export to the deep sea. Trace element fractionation differentiates five fractions the forth first fractions constitute bioavailable fraction that is compared to deep water (near sediment water interface). This comparison shows at first the impotence of surface sediment as potential pump of trace element to the water column and the deep influence of continental discharges on surface sediment trace element acumulation and the deep water mainly for Fe, Cu and Co.
Keywords: Bioavailability. Mediterranean Sea. Nutrients. . Surface sediment.Trace element.

INTRODUCTION

Marine biogeochemical cycling refers to the distribution of nutrients and bio-essential elements concentration that is controlled by their uptake by phytoplankton in surface waters, sinking and remineralization of organic remains in deeper waters, and subsequent redistribution by thermohaline circulation (De Baar et al. 2018). Actually, the deep waters within the Mediterranean basin may be classified as: Aegean deep water and Adriatic deep water that form the Eastern Mediterranean Deep Water (EMDW) and Tyrrhenian deep water and Gulf of Lions deep waters that form the Western Mediterranean Deep Water (WMDW) (Bergamasco and Malanotte-Rizzoli, 2010). The Mediterranean Sea is an oligotrophic sea as a consequence of general water circulation (Schroeder et al., 2010). The cycle of silicon has acquired significant importance in relation to its role in marine primary production which play an important role in organic matter export to the deep sea, required as much as phosphorus and nitrogen for their growth (Buesseler, 1998). Trace element in marine system are mainly attributed to Continental margins that receive natural and anthropogenic trace elements (TEs) from direct atmospheric deposition of aerosols on to the sea surface and from advection of riverine suspended particles and/or resuspended sediments from the continental shelf/slope (Cossa et al 2014). The transfer of trace element from marine sediment to water column is in most previous works considered as poor. Comparison of surface sediment metal

bioavailability with deep water metal concentrations permits an estimation of possible concentration growth of dissolvable bio-essential elements (Fe, Ni, Co, Cd, Cu, Zn, Pb) from sediment as dissolved bioavailable fraction.

MATERIAL AND METHODS

Samples were collected aboard the Dutch *R/V Pelagia* along the GEOTRACES-A04N section (Figure.1) spreading from the Northeast Atlantic (14.2°W, 39.7°N) to the Marmara Sea (27.5°E, 40.8°N), cruise (64PE370) and (64PE374) on 2013. All samples were collected by using the TITAN conductivity-temperature-depth (CTD), with 24 ultra-clean sampling PRISTINE bottles of 24 L each made of polyvinylidene (PVDF) and titanium (Rijkenberg et al., 2015). After deployment the TITAN system was moved to a Class 100 container for subsampling (de Baar et al., 2008). The surface core sediment Samples where sliced under N2 gas during Med Black Cruise, the profiles depth doesn't exceed 22 Cm, and they interest the first centimetres processes.

For trace element, ICPMS and ICPOES were deployed for analysis according to solution or sediment samples. Chemical fractionation was carried out Sequential extraction was according to Tessier et al. (1979); with the extraction of five fractions as cited in following steps: (I) exchangeable fraction, (II) carbonate-bound fraction, (III) reducible or Fe/Mn oxide-bound fraction, (IV) organic matter-bound fraction and/or sulfide fraction and the last one is the (V) residual fraction.

DISCUSSION/RESULTS

The sediment water interface biogeochemical processes have resulted in a number of environmental issues including the enrichment with nutrient and chemicals and affect their bioavailability. Most of marine deposits originate from land-based sources which are primarily continental alteration products, industrial, agricultural and urban.

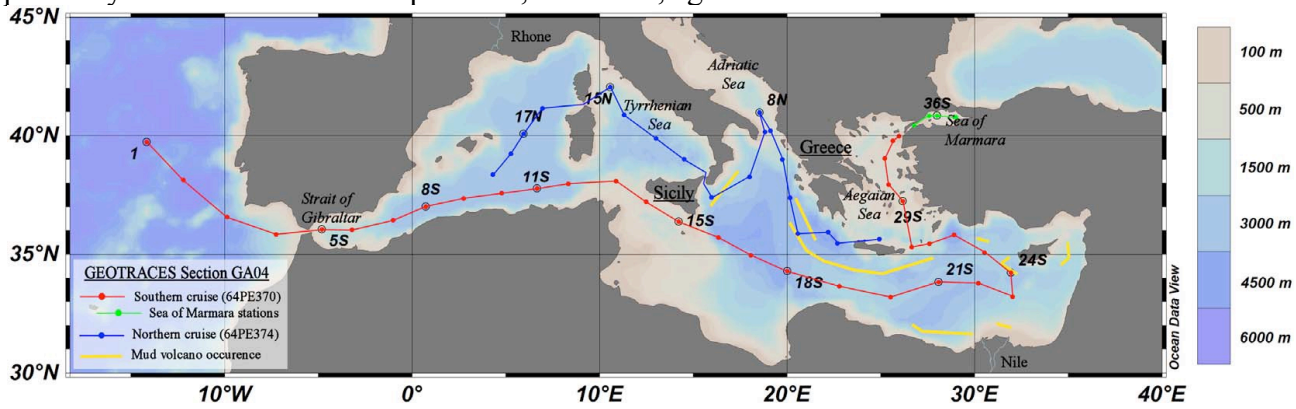

Figure 1: sampling sites in Mediterranean Sea

Mineralogy of surface sediment shows 34% of carbonates and around 60% of phllosilicates. On the basis of the abundances and the distributional patterns of the different clay minerals assemblages are distinguished. Clay's assemblages have distinctive sources and their dispersal reflects different agents of transport in the eastern Mediterranean Sea. In deep first centimetres layers there is Gradual disparition of smectite indicating Diagenetic processes. These assemblages have distinctive sources and their dispersal reflects different agents of transport in the eastern Mediterranean Sea. A Nile assemblage with smectite (> 15%) and 15–25% kaolinite is found on the eastern Nile cone and within the eastern Levantine Basin.

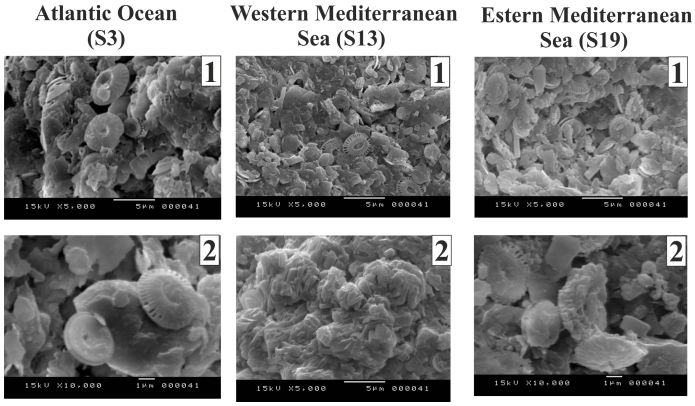

Figure 2 electronic microscopy of surface sediment from sites S3, S13, S19

A Sicilian assemblage with 30–50% kaolinite and 15–20% Smectite in the western most part of the Ionian Basin south of Sicily, has mainly resulted from the dispersal by easterly moving surface waters from the western Mediterranean Sea. On the other hand, silicates are abundant in surface sediment as we can observe in electronic microscopy (Figure. 2) diatoms are the most abundant taxonomic groups of phytoplankton that figure in surface sediment matrix, which play an important role in organic matter export from water column to the deep sea, require silicon as much as nitrogen and phosphorus for their development (Buesseler, 1998).

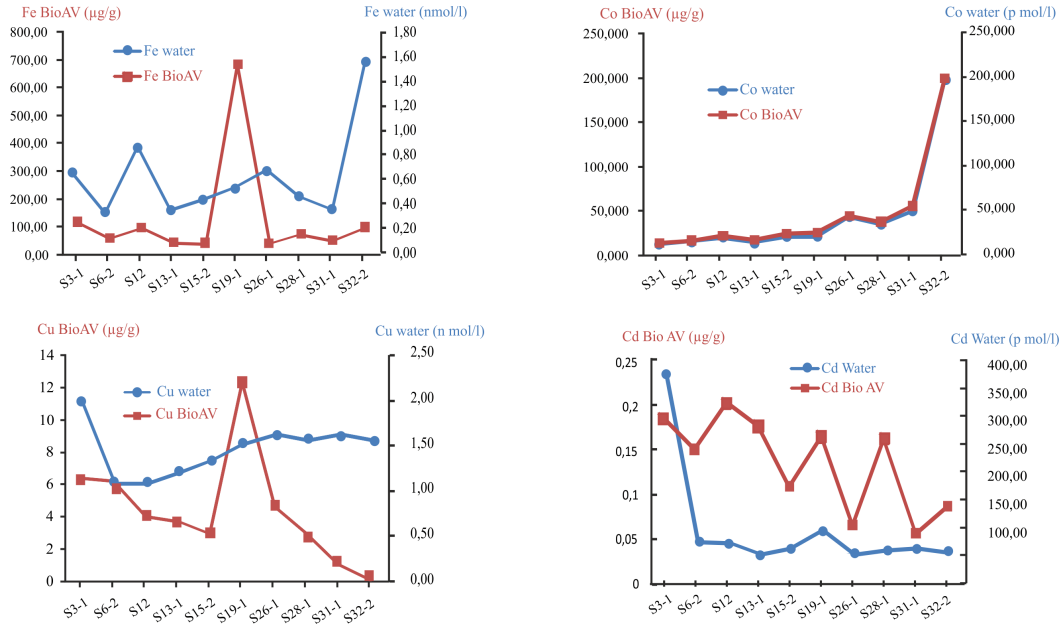

Figure 3: trace element in deep water and surface sediment bioavailable fraction in Mediterranean sea

Distributions of trace element in southern Mediterranean sea Cu, Ni, Pb, Zn, Pb, Co, Mo and Fe in deep water close to sediment water interface compared to bioavailable fraction (Phase I, II, III, IV) from surface sediment, shows a large similarity of distribution with clear footprint of local patches were found where high bioavailable trace element such as Fe and Cu in front of Nile canyon are well developed (Figure. 3).

The surface morphology confirms their terrigenous origin in association with clay minerals, whereas Cd is more associated with organic matter (OM). All these trace element are anthropogenically enriched from dust input and from submarine canyons sediments (Cossa et al., 2014). Anthropognic influence remains clearly discernible. Dissolved Co concentrations

decreased close to sediment water interface, the bioavailable Co fraction (Co BioAV) typically follows deep water one, which we attribute to sediment resuspension (Figure 3) that increase Co exchange, and can be used by organisms as important element for in phytoplankton growth, productivity, and diversity. Recent works of Dulaquais et al (2017), on cobalt origin using the same sediment and water samples shows that the particulate Co reaching the sediment is mainly authigenic but still contains a substantial biogenic fraction, in agreement with our hypothesis of large exchange between bioavailable Co fraction and dissolved Co.

Relative elevated concentrations of dissolved trace elements were observed in some Mediterranean deep waters with sediment resuspension during episodes of deep water formation as the most likely source of the additional dissolved trace element from bioavailable fraction of trace element (Figure 3). Intense sediment resuspension has been extensively documented during times of dense shelf water cascading down through submarine canyons carved on continental shelves at multiple locations in the Mediterranean Sea (e.g. Puig et al., 2014).

CONCLUSION

In Mediterranean Sea a large exchanges between deep water trace element concentrations, close to sediment water interface and surface sediment bioavailable fraction. The presence of distinct patches in deep waters with elevated trace elements concentrations can only be explained by a combination of physical processes and sources at specific locations and depths as in front of Nile canyon.

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