METAL POLLUTION FINGERPRINTS IN SEDIMENTS OF DEEP WESTERN MEDITERRANEAN SEA

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Abstract

A survey in the deep Western Mediterranean Sea sediments (depth 2,850 m) revealed relatively enhanced concentrations of Cd, Pb and Zn at the surface (2 cm) in comparison to deeper layers. Lead isotope analysis indicated that this surface enhancement is not caused by an in-situ diagenetic migration of natural metals towards the surface but to an anthropogenic input associated to land-based pollution in the Western Mediterranean Region.

Keywords : Western Mediterranean, Deep Sea Sediments, Metals, Pollution.

Anthropogenic influence on the metal content of near-shore sediments is detectable in large parts of the Western Mediterranean littoral zone. However, anthropogenic impact on deep Mediterranean sediments is not well documented, although it is recognized that atmospheric pathway and lateral transport from continental margins are important modes of metal transport from land to the sea [1-3]. Increased metal concentrations have already been found in surface layers of western deep Mediterranean sediments [4], but it is not always clear whether they reflect pollution processes or diagenetic up-wards movement of naturally occurring metals. In the present study, using metal analysis combined with lead isotope analysis on dated sediment cores, it was attempted to investigate evidences for metal contamination in deep Mediterranean sediments. Isotopic lead signature allows discriminating the origin of lead (anthropogenic vs natural) independently of any variations in their contents. This work was part of the European project ADIOS, aiming to study the impact of atmospheric deposition in the open Mediterranean Sea.

A sediment core of 37 cm depth was collected in the Western Mediterranean Sea (station WB, 39° 29.51' N and 06° 10.88' E). For dating purposes, ²¹⁰Pb activities were measured by alpha spectrometry of its granddaughter ²¹⁰Po. Total metal concentrations were determined by AAS and GFAAS, after decomposition in a mixture of aqua regia and HF. Samples for lead isotopes analyses were oxidized using HNO3, HF, HCl and purified through AG1X8 resins in clean dust laboratory. Isotopic ratios were determined by thermo-ionisation mass spectrometry (FIN MAT 262). The core WB shows a regular profile of excess ²¹⁰Pb decreasing exponentially with depth, but restricted to the first three centimetres. Using a CFCS model, maximum sedimentation rate was estimated to be 0.0227 cm y^{-1} or 0.0225 g cm⁻² y^{-1} . These rates are high compared to those obtained from ¹⁴C in the same area and the ²¹⁰Pb distribution is probably entirely due to mixing. Assuming negligible sedimentation rates (S=0 cm/yr) the maximum mixing rate is 0.016 cm²/y, which is probably representative of the mean sedimentation-bioturbation processes occurring in this abyssal plain. Increased concentrations of Cd, Pb (and to a lesser extend Zn) were recorded in the upper 2 cms of the core (maximum values 0.165 mg/kg, 38.4 mg/kg and 82.6 mg/kg, respectively), while metal concentrations were relatively stable in deeper layers (Cd 0.067-0.107 mg/kg, Pb 14.1-24.8 mg/kg, 50.5-74.7 mg/kg). Copper concentrations did not show any increase in the surficial sediments. According to the ²¹⁰Pb profile, the upper 2 cms represent the more recent (and important) anthropogenic influence related to industrial development and increased leaded gasoline utilization in Western Europe after 1950. The profile of ²⁰⁶Pb/²⁰⁷Pb ratio in the core is plotted in Figure 1. In the Mediterranean Sea 206 Pb/207 Pb ratios higher than 1.195 generally reflect natural lead, whereas lower ratio is typical of anthropogenic origin from gasoline and industry emissions [5-6]. Our isotope ratio profiles show a decrease from an anthropogenic value in surface layers to natural values at 6 cm depth, i.e. deeper than the ²¹⁰Pb. However, we observed a sudden shift in the isotopic ratio between 3 and 4 cm depth. This shift occurs just below the surface layer where excess ²¹⁰Pb is observed and is not due to local mixing processes (ingestion of subsurface sediment at 2 cm and rejection at 3,5 cm) since no ²¹⁰Pb excess was observed at this depth. This shift could be explained by turbidite type dynamics in the area. It was concluded that the enhancement of metal concentrations in the upper sediment layers of deep Western Mediterranean sediments are caused by recent anthropogenic contamination due to increasing land-based human activities (industry and traffic).

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Fig. 1. Profile of $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ in core WB from the Western Mediterranean.

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