TRACE ELEMENTS, HEAVY METALS AND PB ISOTOPIC RATIOS IN MARINE SEDIMENTS OF THE SOUTH MEDITERRANEAN SEA (MOROCCO).

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Abstract.

A sediment core collected in the South Mediterranean Sea was analyzed for trace metals and selected radionuclides. The resulting data was evaluated and the interpretation reported herein. High-resolution (5 to 10 mm) sediment core sections were analyzed for ^{210}Pb, ^{137}Cs, ^{239,240}Pu geochronology. Using a CRS model, ^{210}Pb gives a sediment accumulation rate (AR) of 0.11 g cm^2 y^{-1} and a sedimentation rate (SR) of 0.112 cm y^{-1}. These values are in good agreement with those calculated using ^{137}Cs and ^{239,240}Pu (0.149 g cm^2 y^{-1}) as well as comparable values measured in the Mediterranean Sea under similar hydrological conditions. Heavy metals can be separated into two groups: one that demonstrated an enhancement from a geogenic background (e.g. Pb, Mn, U, Cu, Co, Sb, Zn and As), the second group (Ni, Cd, Cr, Tl, Fe, Mo and V) shows no clear changes along the sediment core. At the beginning of the century, Pb input flux was in the range of 1mg cm^2 y^{-1}, increased to 3 μg cm^2 y^{-1}later on in the 1900's, and thereafter was rather constant until 1960, increasing to 3.5 μg cm^2 y^{-1} until mid 80's and then increased again towards 1997. The isotopic ratio follows the same trends as the lead flux with one exception at around 1960. Apparently a more radiogenic (natural) source of Pb entered the system. However towards recent years the flux of Pb may be attributed to an urban source (Moroccan alkyl lead additive type) rather than a radiogenic one.

Introduction

Assessment of Pb and heavy metals in general anthropogenic or geogenic have been the subject of several environmental studies in the last decade, especially in the northern hemisphere and the northern countries of the Mediterranean sea (1.2.3.4). Industrial manufacturing has produced these metals in the past in substantial quantities. Recently, due to improvement in emission control, their input has globally decreased since 1975 (5). However, the historical inputs of these metals are still a primary problem for fragile ecosystems and coastal areas, particularly in economically-challenge countries.

As part of a regional program RAF7004, we have attempted to combine the use of Pb isotopes with metal concentrations to describe the historical (^{210}Pb, ^{137}Cs, ^{239,240}Pu chronologies) concentration of heavy metals in the South Mediterranean Sea. The findings from a sediment core collected off the Moroccan Coast are reported herein.

Material and Methods

In 1999 a sediment core was collected using a Ocean Instrument Box Corer of 50x50x80 cm. The sediment was sampled off the Moroccan Mediterranean shelf at 900-m water depth. ^{137}Cs was measured in the whole sediment sample using a HpGe detector. ^{239,240}Pu was measured by alpha spectroscopy using ^{242}Pu as a chemical yield determinant. ^{210}Pb analysis was done by measuring its granddaughter ^{210}Po (considered in secular equilibrium with ^{210}Pb) by alpha spectrometry. ^{209}Po was used as a chemical yield determinant. Supported ^{210}Pb was estimated by directly measuring ^{226}Ra (gamma spectrometry) on some sections throughout the core. Heavy metals and Pb isotopic composition were determined by ICPMS following a complete digestion of a 150-mg sediment aliquot. Samples were prepared in batches of 8 to 10, which included up to 4 samples in duplicate, a reagent blank, and a representative standard reference material; SD-2/TM.

Result and Discussion.

The excess concentration of Co, Cu, As, Sb, Zn, Mn, U and Pb increased towards the surface. In contrast Cr, Cd, V, NI, Tl, Fe and Mo, in this particular core, did not show a trend, rather their excess concentration was scattered. On the other hand, Cd, Ni, V, and Cr showed some subsurface maxima at around 20 cm. In the case of Ni there is apparently a second peak at five cm. To date we do not have a good hypothesis to explain this. The CRS was used to reconstruct the depositional history of the sediment core. The average sediment accumulation rate calculated in this fashion was 0.11 g cm^{-2} y^{-1} (0.124 cm y^{-1}) which is not different than the values obtained using the activity profiles of ^{239,240}Pu and ^{137}Cs. The latter gives an accumulation rate of 0.13 g cm^{-2} y^{-1} (0.149 cm y^{-1}).

The excess flux of Pb and the ^{208}Pb/^{207}Pb isotopic ratio vs time is shown in Figure 1. In pre-anthropogenic time (1800) a less radiogenic isotopic signature (coal burning, Eurasian aerosol) follows the increment of Pb flux. Until the 1950s the isotopic signature nicely mirrors the changes in the flux of lead. Between 1970-1984 the ratio was rather constant decreasing towards mid 90s and this may be the result of worldwide practices in the use of unleaded products. However, the increase during the last few years is also followed by a less radiogenic signature and perhaps is the result of a more anthropogenic lead input to the study area.

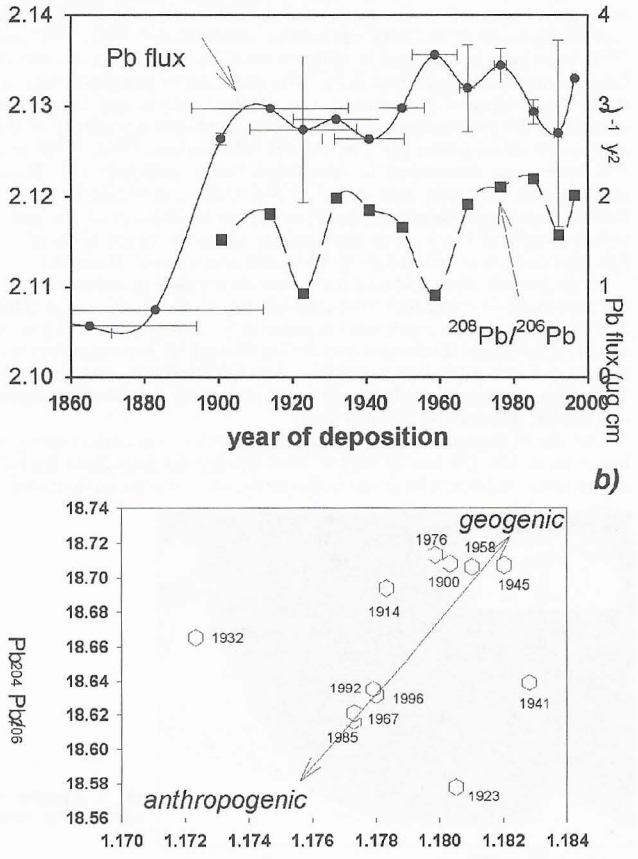

Figure 1. Isotope core profile a) the 208Pb/206Pb ratio plotted versus time of deposition. Also superimposed is the excess Pb fluxes vs. time of deposition. b) 206Pb/204Pb versus 206Pb/207Pb ratios. In the early 1900s, the input of Pb may have resulted from atmospheric deposition. However, in recent years, the 206Pb/207Pb ratio is within the range of the Moroccan Alkyl additive (1.16-1.18). Non-atmospherical input can also be responsible for the input of Pb in 1976.

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