

Temporal variations in the stable isotopic composition of Hg in sediments of the Central Portuguese Margin

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Three short marine sediment cores from the Cascais canyon (PE252-32 at 38.36307N; 9.50690W; 2100 m water depth; and PE252-35 at 38.49345N; 9.47880W; 445 m water depth) and the Estremadura Spur (PE252-16 –at 39.17670N; 10.66612W; 2084 m water depth) on the Portuguese Margin, collected during cruise *Canyons 2006* onboard the RV Pelagia, were analysed for Hg, Pb, Al, and Pb (²⁰⁶Pb/²⁰⁷Pb) and Hg ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, $\Delta^{201}\text{Hg}$) isotope stable ratios in order to reconstruct Hg and Pb metal contamination. Geochronology is based on ²¹⁰Pb. The studied cores reveal increasing Hg and Pb, independent of grain-size variations, since the middle of the nineteenth century towards the Present-day. At the same time we have observed a decreasing trend of ²⁰⁶Pb/²⁰⁷Pb to less radiogenic values towards the surface, indicating anthropogenic contamination with different intensities. Down-core $\delta^{202}\text{Hg}$ values do not show a clear pattern implying either multiple sources, or varying amounts of microbial Hg reduction and loss, or a combination of both. The lowest values of $\delta^{202}\text{Hg}$ are shown in general in the older sediments encompassed by low Hg and Pb contents, suggesting a low input of the anthropogenic component. Core PE252-16 (located in an area of predominant hemipelagic sedimentation) has an average $\delta^{202}\text{Hg}$ of $-0.69\text{‰}\pm 0.24\text{‰}$ in sediments older than AD 1800, similar to values obtained by Gehrke et al. (2009) for Mediterranean sapropel samples. In this core, both odd isotopes deviate from the theoretical mass-dependent fractionation line ($\Delta^{199}\text{Hg}$, $\Delta^{201}\text{Hg}$), showing that sediments

were subject to mass-independent fractionation (MIF) with $\Delta^{199}\text{Hg} = +0.09\text{‰} \pm 0.04\text{‰}$ and $\Delta^{201}\text{Hg} = +0.04\text{‰} \pm 0.04\text{‰}$. These slightly positive values indicate that the cause of MIF could be photochemical reduction of Hg^{2+} . The 2 cores from the Cascais Canyon located closer to the Tagus estuary (an area highly influenced by Hg contamination derived from pyrite roasting and chloralkali plants) do not reveal significant MIF, which is consistent with the addition of direct emissions from anthropogenic Hg sources. This trend has also been observed by Estrade et al. (2010) in lichens where anthropogenic Hg is added near an industrial point source. In synthesis, the integration of stable Hg and Pb isotopic ratios, ^{210}Pb chronology, and Hg and Pb concentrations, were useful in reconstructing the Hg and Pb contamination history in sediments of the Central Portuguese Margin.