Chemical Geology 336 (2013) 62–71

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Tracing anthropogenic Hg and Pb input using stable Hg and Pb isotope ratios in sediments of the central Portuguese Margin

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ARTICLE INFO

Article history:
Accepted 23 February 2012
Available online 1 March 2012

Keywords:
Portuguese Margin
Marine sediments
Total Hg and Pb concentrations
Stable Hg isotopes
Stable Pb isotopes

ABSTRACT

Three short marine sediment cores from the Cascais Submarine Canyon (CSC; cores 252-32 and 252-35) and the Estremadura Spur (core 252-16) on the central Portuguese Margin were analysed for Hg, Pb, Al, and Mn concentrations, and both Pb and Hg stable isotope compositions, in order to reconstruct trends in Hg and Pb sources and accumulation. Sediment ages were determined based on ^{210}Pb measurements. The studied cores reveal increasing Hg and Pb concentration, independent of grain-size variations, since the middle of the 19th century towards the Present. Concomitantly, a decreasing trend of $^{206}Pb/^{207}Pb$ to less radiogenic values towards the surface was found, indicating increasing anthropogenic inputs. The lowest values of $\delta^{202}Hg$ were generally observed in the older sediments characterized by low Hg and Pb concentrations, suggesting a low input of anthropogenic metals. Odd mass number (^{199}Hg and ^{201}Hg) Hg isotopes in sediment samples from core 252-16 were characterized by positive mass independent fractionation (MIF), while recent sediments from cores 252-32 and 252-35 did not reveal significant MIF, probably reflecting both the proximity to the source of anthropogenic Hg contamination (Tagus Estuary) and the importance of the CSC as a particle carrier. The multi-tracer approach, based on both stable Hg and Pb isotopic signatures, confirms anthropogenic Hg and Pb enrichment in recent marine sediments and also allows us to distinguish between areas dominated by detrital (e.g. CSC) versus hemipelagic (Estremadura Spur) sedimentation.

1. Introduction

Toxic heavy metals (e.g. Hg, Pb) are released into the environment by both natural processes and anthropogenic activities (Selin, 2009), and are transported through (and stored in) environmental reservoirs, including the atmosphere, water, soils and sediments. Humans in their activities have been using Hg and Pb for thousands of years in various applications (e.g. manufacturing of materials, health applications, fossil fuel burning and mining; Patterson, 1972; Nriagu, 1993). Although anthropogenic impacts started during Greek and Roman times, the Industrial Revolution corresponds to the historical period where large increments in the use of heavy metals resulted in significant release into the environment (Nriagu, 1996). Due to their toxicity these metals represent a serious threat to human health (Jarup, 2003), especially when bioaccumulated in the tissues of organisms and biomagnified through the food web (Harada, 1995). Technological improvements in the treatment of industrial and domestic effluents together with the decreasing use of Hg in industry (e.g. chlor-alkali production using Hg cells) and the worldwide reduction in use of alkyl-leaded gasoline since the late twentieth century, have led to a reduction of anthropogenic emissions (Nriagu, 1996; Pacyna et al., 2001). In order to implement remediation strategies for contaminated sites and policies for regulating contaminant emissions it is necessary to increase the level of knowledge regarding contamination effects of toxic metals and their preservation in the environment, including distinction between natural and anthropogenic contributions.

Stable Pb isotopic ratios have been used for decades for investigating biogeochemical cycling of trace metals and for tracing natural and anthropogenic sources of Pb in the environment (Gobeil et al., 1995; Ferrand et al., 1999; Ritson et al., 1999; Weiss et al., 2008). Lead has

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0009-2541/$ – see front matter
doi:10.1016/j.chemgeo.2012.02.018