

Modifications of Cu isotopic ratios in coastal sediments in relation to the increased use of copper based antifouling paints

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Cu is released in water by weathering processes and human activities. It is widely applied on vines and used as a biocide in antifouling paints. This study aimed to assess the potential of Cu stable isotopes to identify Cu sources in coastal sediments.

For this study, sediment cores were collected from three sites in the marina of Port Camargue on the French Mediterranean coast. This marina, the largest in Europe, was built around forty years ago and has never been dredged. Sediment samples (<63 μ m fraction), antifouling paints were analyzed for copper concentration and Cu isotope ratios. Isotopic measurements were performed using a Neptune Multi Collector ICP-MS after a double separation on anionic resin.

Copper concentrations in antifouling paints (7 different brands) ranged from 6 % w/w to 36 % w/w. Their $\delta^{65}\text{Cu}$ values varies from 0.55 to 0.97‰. Close to the boat maintenance area, Cu concentrations in sediment cores exhibited an increase from the bottom to surface with a maximum value of 1961 $\mu\text{g}\cdot\text{g}^{-1}$ at 7 centimeters depth. In parallel $\delta^{65}\text{Cu}$ values increased from 0.08‰ at the bottom of the core up to 0.52‰ around 5 cm depth (Figure 1). This evolution toward $\delta^{65}\text{Cu}$ values similar to those observed in antifouling paints in surface sediments, indicates that copper isotopes are good tracers of copper contamination by antifouling paints in a coastal marina.

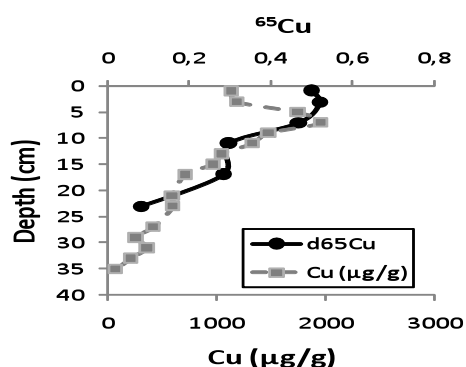


Figure 1: Depth profile of $\delta^{65}\text{Cu}$ and copper concentration in sediments from Port Camargue Marina.

Understanding the marine biogeochemical cycle of Pb in the equatorial Atlantic

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The biogeochemical cycle of Pb has been significantly perturbed by anthropogenic activity over the past 100 years, with transient changes in the relative importance of different anthropogenic Pb sources [1]. Lead isotopes are an effective tracer of anthropogenic Pb emissions, and the short residence time of Pb in ocean surface waters (~2 years, [2]) make them a useful recorder of recent Pb sources in a particular region. Furthermore, the comparatively conservative behaviour of Pb isotopes in intermediate and deep waters enables tracing advection of pollutant Pb [3].

A newly developed method, using TIMS in conjunction with a Pb double spike, has been applied to the measurement of the Pb isotopic compositions ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) and concentration of seawater depth profiles and surface seawater samples collected in the eastern equatorial Atlantic Ocean during the GA06 UK GEOTRACES cruise in 2011. The data are used to assess the current importance of anthropogenic versus natural Pb inputs to this region, and the advection of anthropogenic Pb into deep waters.

The Pb concentrations of surface waters (17-26 pmol/kg) are comparable to those determined in the early 1990's in the region [4], suggesting a stable Pb flux over the past 20 years. The Pb isotope composition of surface waters between 8° N and 3° S (1.163-1.169, $^{207}\text{Pb}/^{206}\text{Pb}$) are similar to those determined for Saharan dust [5]. In contrast, surface waters in the North Equatorial Current have higher $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (1.173-1.174), a signature which can be attributed to advection of Pb from the west, fingerprinting eastern US emissions. A deep water maximum in Pb concentration (3000 m; 46 pmol/kg) located close to the mid Atlantic ridge is interpreted to represent hydrothermal input of Pb.

[1] Wu & Boyle (1997), *GCA*, **61**, 3279-3283. [2] Bacon *et al.* (1976), *EPSL*, **32**, 277-296. [3] Alleman *et al.* (1999), *Geophys. Res. Letters*, **26**, 1477-1480. [4] Helmers & Rutgers (1993), *Journal of Geophys. Res.*, **98**, 20,261-20,274. [5] Scheuven *et al.* (2013), *Earth-Science Rev.*, **116**, 170-194.