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## The record of human impact in the sedimentary record at *Portus*, the harbor of ancient Rome

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The present study focuses on the analysis of palaeo-pollutions and the sedimentary environments in which they were trapped in the Roman *Portus* harbor. *Portus* received heavy-metals pollution both from local foundries, fulling, and tanning and from distal upstream development in Rome. Rome wastewaters, which accounted for up to 3 percent of the total Tiber discharge, were forwarded to *Portus* through a network of canals (*Canale Romano* and *Canale Trasverso*) connecting the river to the sea. In this manner, harbor basins accumulated both allochthonous and autochthonous heavy metals.

We determined major and trace element concentrations as well as Pb isotope compositions in a high-resolution set of samples from sediment cores recovered in the *Portus* area. Principal component analysis of elements that are less prone to the influence of human activities, such as Ca, Mg, Mn, Zr, K, Al, Ti, Na, Sr, and Mn, was used in conjunction with metallic elements to break down the sedimentary load into local and regional components.

The record of Pb concentrations and isotopic compositions reveals an overall general trend on which other signatures are superimposed. The geochemical background of the Tiber catchment (24.7-26.2 ppm Pb and  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.198$ ) represents geologically young (model age  $T_m < 50$  Ma) Pb derived from natural runoff over young sediments and volcanics in the Latium. From the 1<sup>st</sup> century AD to the end of the roman period, the harbor regime evolved from a dominant fluvial (enriched in Al, Ti, Mg, K, and Zr) to a more marine influence (high Ca/Mg, Na/Al, Sr, and  $\text{CaCO}_3$ ) in the upper part of the harbor unit. “Imperial” Pb (90.5-35.4 ppm Pb and  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.187$ -1.192) requiring the prevalence of Hercynian ( $T_m > 200$  Ma) Pb, probably imported from central or northern Europe, gets progressively diluted with time. The transition from the roman to the medieval period is characterized by a closed environment (high Ca/Mg, Na/Al, Sr, and  $\text{CaCO}_3$ ) with a spike of unradiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  ( $\sim 1.184$ ). Either an alluvial plug formed, which blocked fresh water entry into the harbor from the *Canale Trasverso*, or the harbor burned, causing melting of the ancient waterworks. Finally, the upper part of the sediment cores consists of overflow deposits enriched in Al, Ti, K, Mg, and Mn associated with the return of the pre-anthropogenic geological background (18.9-28.2 ppm Pb and  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.196$ -1.201). In this post-roman sedimentary unit pollution signatures shift to a mix of heavy metals dominated by Co, Cr, Ni, and Zn, whereas during the roman period elements such as Pb, As, Fe, Cu, and Sn were predominant.

## The fractionation of Lithium isotopes during continental weathering: clues from the Amazon and Mackenzie rivers

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Numerous studies on river systems have shown that Lithium isotopes are fractionated during chemical weathering as  $^6\text{Li}$  is preferentially retained in solid secondary phases whereas dissolved fractions are enriched in  $^7\text{Li}$ . In this study we investigate the Li isotope composition of Suspended Particulate Matter (SPM) and bedload transported in two of the largest world river systems having drastically differing climate conditions: Amazon and Mackenzie rivers. In order to separate the effects of hydrodynamic sorting and chemical weathering, Li isotope were measured along river depth profiles to capture all the SPM grain size variability.

We find that Li content and isotope composition display a strong variability in relation with grain size within a single water column in both Amazon and Mackenzie Rivers. Li content in SPM increases by a factor up to 3 from coarse (river bed) to fine (channel surface) particles, ranging from 30 to 90 ppm. All bedloads and SPM samples have Li/Al molar ratios higher than that of the mean Upper Continental Crust (UCC), despite the fact that 10 to 20% of total Li in both rivers is transported in the dissolved load.

River sediments Li isotopic composition ( $\delta^7\text{Li}$ ) ranges between -3.5 to 5‰ and displays an inverse relationship with grain size.  $\delta^7\text{Li}$  is also well correlated ( $R^2 > 0.9$ ) to the weathering index Na/Al, further illustrating the fact that weathering products are isotopically fractionated toward low light  $\delta^7\text{Li}$  values. Amazon river-sediments  $\delta^7\text{Li}$  values are more than 1‰ lower than those of the Mackenzie for a given Na/Al value. We interpret these relationships between Li content,  $\delta^7\text{Li}$ , Na/Al and grain size as a binary mixing between a coarse-grained, relatively Li-poor, high  $\delta^7\text{Li}$  component ( $\delta^7\text{Li} \sim 5\%$ ) and a fine end-member having low  $\delta^7\text{Li}$  and high Li concentrations. The low  $\delta^7\text{Li}$  value of the fine component could be the result of either present day light-Li co-precipitation/adsorption into secondary minerals or of the recycling of fine-grained silicate sedimentary rocks or a combination of both processes. These results have important implications for establishing global mass budgets of erosion and for using lithium concentrations and isotopes as a tracer of sedimentary recycling.