# Resolvong inconsistent sedimentary carbon mass balances: Implications for ancient C and S cycles

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Inventory and isotope mass balance estimates of the organic carbon/∑carbon ratio ($X_{org}$)of the upper crust (dominated by sediments) appear to differ systematically. Inventory-based estimates yield $X_{org} \approx 0.10$ to 0.17, while $\delta^{13}C$ mass balance estimates are 0.19 to 0.34. The $\delta^{13}C$ mass balance approach typically assumes a steady state form $\delta_{in} = f_{org}^{bur}\delta_{org} + f_{carb}^{bur}\delta_{carb}$, where $f_{org}^{bur}$ is the burial fraction of organic carbon. Over long times the time integrated value of $f_{org}^{bur}$ should approach the value of $X_{org}$, and $\delta_{in}$ should approach the mean $\delta^{13}C$ value of the upper crust. If the inventory-based estimates of $X_{org}$ are approximately correct, the isotope mass balance approach as conventionally applied cannot be. Two modifications to the $\delta^{13}C$ mass balance can reconcile the discrepancy. First, increasing data indicates that even in the modern environment with $pO_2 = 0.21$, the oxidation of old carbon is incomplete [1]. Second, a substantial fraction of carbon is returned to the ocean-atmosphere system as isotopically depleted $CH_4$ [2]. At low $pO_2$ though to be characteristic of the Precambrian, the oxidative weathering efficiency of kerogen was lower, implying a larger fraction of C recycling via methanogenesis. In that case the revised steady state isotopic mass balance implies both lower absolute and fractional burial rates of sedimentary organic carbon than for Phanerozoic conditions. The generation and oxidation of $CH_4$ was a dominant term in the organic carbon mass balance at low $pO_2$. Model results show that large $CH_4$ fluxes result in low steady state marine $SO_4$ levels via AOM, consistent with inferences from $\delta^{34}S$ studies of Proterozoic sediments [3].

[1] Blair & Aller (2012) *Ann Rev Mar Sci* **4**, 401-423. [2] Etiope *et al*.. (2011) *Planet. Space Sci*. **59,** 182-195. [3] Li *et al*.. (2010) *Science* 328:80-83.

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# Pb-Zn-Cd-Hg multi isotopic characterization of the Loire River Basin, France

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The Loire River in Central France is approximately 1010 km long and drains an area of 117 800 km$^2$. Upstream, the Loire river flows following a south to north direction from the Massif Central down to the city of Orléans, 650 km from its source. The Loire River is one of the main European riverine inputs to the Atlantic Ocean. Over time, its basin has been exposed to numerous sources of anthropogenic metal pollutions, such as metal mining, food industry, agriculture and domestic inputs. The Loire River basin is thus an excellent study site to develop new isotope systematics for tracking anthropogenic sources of metal pollutions.

We have chosen to analyze the isotope composition of cadmium (Cd), zinc (Zn), mercury (Hg) and lead (Pb). These heavy metals have been chosen for their toxicity, even at low levels, to humans. The main goal of this study is to characterize 1) the sources and behavior of these heavy metals in the aquatic environment, and 2) their spatial distribution using a multi-isotope approach. Sources responsible for the release of Pb-Zn-Cd-Hg in the Loire basin were sampled and analysed for their concentrations and corresponding isotope compositions. We also analyzed river waters and suspended solids samples, known to play an important role in the transport of heavy metals through river systems. Biota samples (mussels, oysters), as natural accumulators of metal pollutants, were also analyzed.

All trace elements were analysed in the BRGM laboratories using a Q-ICPMS. Pb-Zn-Cd isotope compositions were measured using a Neptune MC-ICPMS at the BRGM. Hg isotope compositions were measured at the U. of Illinois using a Nu Plasma MC-ICPMS. To analyse Zn and Cd, we carried out a two-steps analytical development: 1) a chromatographic separation, followed by 2) analysis on the MC-ICPMS.

The results showed that, on their own, each of these isotope systematics reveals important information about the geogenic or anthropogenic origin of these metals. Considered together, they are however providing a more integrated understanding of the overall budgets of these pollutants at the scale of the Loire River Basin.

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