Pb, Cd and Zn isotopes as source tracers in Pacific/Atlantic bivalves

ALYSSA E. SHIEL*, DOMINIQUE WEIS
AND KRISTIN J. ORIANS

PCIGR, Earth and Ocean Sciences, University of British Columbia, Vancouver, Canada
(*correspondence: ashiel@eos.ubc.ca)

Lead, Cd and Zn isotopic compositions (MC-ICP-MS) and elemental concentrations (HR-ICP-MS) are used to distinguish between natural and anthropogenic sources of these metals in bivalves collected from western Canada (B.C.) and France.

Although B.C. oyster tissues have relatively low Pb contents, their Pb isotopic compositions reflect mixing of natural Pb (high $^{206}Pb/^{207}Pb$) with modern anthropogenic Pb emission sources (variable $^{206}Pb/^{207}Pb$). These emission sources include unleaded automotive gasoline (high $^{206}Pb/^{207}Pb$), diesel fuel (e.g. trucks, ferries, cargo and container ships; variable $^{206}Pb/^{207}Pb$) and leaded aviation gasoline or smelting of Pb ores in Trail, B.C. (low $^{206}Pb/^{207}Pb$ source). B.C. oyster tissues and gut contents (diet) have $\delta^{114/110}Cd$ values (-0.69 to -0.09‰) significantly lighter than those of North Pacific seawater suggesting preferential phytoplankton uptake of light Cd isotopes. The relatively light Cd isotopic compositions of the oysters from the B.C. mainland, as compared to those from the west side of Vancouver Island, are attributed to the larger contribution of anthropogenic Cd emissions. In a $\delta^{114/110}Cd$ vs. $^{206}Pb/^{207}Pb$ diagram, B.C. oysters form a positive trend. Natural Zn concentrations are much higher than those of Cd in bivalve tissues; therefore any anthropogenic contribution will need to be correspondingly large to be recorded in the Zn isotopic signature. So it is not surprising that $\delta^{66/64}Zn$ values of B.C. oysters (0.28 to 0.36‰) are within error of those of North Pacific seawater.

French bivalves exhibit $^{206}Pb/^{207}Pb$ ratios resulting from the mixing of natural Pb with industrial Pb emissions. Samples collected ~20 yrs apart, in the polluted Marennes and Gironde estuaries, exhibit large decreases in Pb concentration and increases in $^{206}Pb/^{207}Pb$ toward pre-industrial Atlantic sediment values. French bivalves form a trend, from relatively light Cd and heavy Zn isotopic compositions (smelter polluted sites) to relatively heavy Cd and light Zn isotopic compositions (relatively pristine areas), reflecting the large variability of anthropogenic inputs and environmental health among French sites.

These results demonstrate the ability of Cd and Zn isotopes to monitor spatial and temporal trends in environmental contamination and the usefulness of coupling them with Pb isotopes.

Colloidal iron in rivers and estuaries

A.M. SHILLER

Dept. Marine Sci., Univ. Southern Mississippi, Stennis Space Center, MS 39529 (alan.shiller@usm.edu)

Iron is transported in most rivers predominantly in two physical-chemical forms: a) organic complexes and b) crystalline or poorly-ordered suspended phases frequently dominated by iron oxides. Both of these forms are usually classified as ‘colloidal’, though they have very different properties with respect to transport, bioavailability, and sorption. Evidence from flow field flow fractionation suggests that organic-Fe complexes are predominantly in the 0.5 - 4 nm size range (corresponding to <10 kDa) while the iron oxides are larger than this. TEM evidence furthermore suggests that fluvial Fe oxides are composed of aggregates of ~5 nm precipitates. Using 20 nm filtration we make an approximate operational separation between the two types of materials which might be termed macromolecular complexed iron and suspended colloidal iron.

Possible sources of suspended colloidal iron include ferric oxides precipitated from the oxidation of ferrous iron derived from reducing environments, alumino-silicates derived from physical weathering, other products of chemical weathering, and flushing of soils. We observe most commonly that increasing concentrations of colloidal suspended iron follow indicators of reducing sources (e.g. higher dissolved Mn and a Ce anomaly close to one), suggesting that this material is dominated by freshly precipitated iron oxides. Only in glacial watersheds do we find colloidal suspended iron instead correlating with colloidal suspended Si and Al, and hence, likely to be associated with alumino-silicates. We also observe that colloidal suspended iron correlates well with the UV absorbance associated with this size range (20 - 450 nm). In estuarine environments, this material rapidly flocculates out.

The behavior of macromolecular complexed Fe can be generally reproduced by a simple model balancing organic complexation versus FeOOH solubility control, both of which are pH-dependent. Such a model explains the observed non-linearity of the ‘dissolved’ Fe-DOC relationship. It also leads to simple predictions of apparent binding strength changes based on pH-DOC-Fe relationships. In estuaries, there is some evidence of removal of this fraction, though the removal is less extensive than that of the larger suspended colloidal iron.