Zinc isotopic data from the NE Pacific reveals shallow recycling

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Isotopic data for biologically-active trace metals can elcuidate their sources to seawater and their biogeochemical cycling within the oceans. Here we present new dissolved-phase Zn concentration and isotopic data for depth profiles along a transect (Line P, around 50°N) from the North American continental margin to the open ocean in the NE Pacific, with 10-25m depth resolution in the upper 100m of the water column.

Zn concentrations increase with depth, with surface or near-surface concentrations as low as 0.05 nM and concentrations at 2000m at 10-11 nM. There are two distinct differences between the new dataset and the only previous study of Zn in the NE Pacific of similar geographical scope [1]. Firstly, concentrations at 10m depth increase gradually from 0.09 nM at the marginal station to 0.65 nM at the open ocean station, a reversal of findings for samples collected in 1999, and showing a closer coupling to Si. Secondly, at some stations the shallow sub-surface (at 50-100m at the marginal station) is characterised by a distinct bulge in the concentration depth profile.

The isotopic data for the deep ocean, for Zn concentrations ≥ about 7 nM (beneath 200-600m, depending on the station), are very homogeneous, with $\delta^{66}Zn_{Lyons\text{-}JMC} = 0.52 \pm 0.10$ ‰ (2 SD, n = 15). The upper ocean is much more variable. Firstly, the immediate sub-surface (50-100m at the marginal station) is characterised by distinctly light Zn isotopic compositions, down to $\delta^{66}Zn = -0.4$ ‰. This feature persists along the transect but the depth range over which this light isotope value is found shallows oceanwards. Above the thin isotopically light layer, the surface ocean has heavier isotopic compositions at very low Zn concenttrations, by 0.5-0.8 ‰ and with the shift occuring over a depth range of 10m or less.

The three features described above – a homogeneous deep ocean, an isotopically light layer in the immediate sub-surface, and a return to variably heavy values in the photic zone – are proving to be common to Zn isotope depth profiles in the ocean in a small but building database. But they are particularly clear in the NE Pacific, perhaps partly because of a highly-stratified water column. Moreover, only here is the sub-surface isotopic feature associated with recognisable features in the concentration profile. The new isotopic data shed light on the biogeochemical cycling of Zn in the upper ocean that are not readily apparent from concentration data alone. In particular, the anomalously light isotopic compositions are most likely to be explained by the very shallow recyling of a pool of light Zn sequestered into phytoplankton cells [2] in the photic zone.

[1] Lohan et al. (2002) *Deep-Sea Res. II* **49**, 5793-5808. [2] John et al. (2007) *Limnol. Oceanogr.* **52**, 2710-2714.

Evaluating Changes in Sources and Pathways of Trace Metals Over Time Using Lake Sediment

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Abstract

Environmental regulation has reduced the loadings of metals to the environment since the advent of the Clean Air and Water Acts in the 1970's. Reducing emissions may have changed transport pathways since this legislation targeted major sources of metals which influenced the environment on a regional scale. Watershed-scale processes may now provide the significant contribution to metals loadings. Thus, our working hypothesis is that the reduction of major emission sources has allowed local influences and watershed features to affect metal transport pathways. If true then there should be differences in watershed attributes/influences (e.g., %urban, population density) changed the pathways of metals transport of these metals. In this study we examine Pb, Cu, Zn, and Ni because these metals 1) build from previous studies, 2) exhibit similar environmental behaviour but separate pathways, 3) represent various degrees of contaminant enrichment. To test this hypothesis, sediment accumulation rates of these metals at decadal intervals were compared to selected watershed attributes. Sediment cores were collected from the deepest portion of 35 inland lakes representing diverse land uses. Cores were sectioned; microwave digested, and analyzed using mass spectrometry. Sedimentation rates, ages and sediment focusing were determined via 210Pb/137Cs/stable Pb profile analysis. Similar to the previous work, the data show regional sources of the metals studied to subside upon introduction of environmental legislation in the 1970's. However, watershed-scale sources provide a more significant portion contaminant loading in nearly all lakes studied, preventing lakes from reacquisition of reference condition values. When compared to landscape attributes, these patterns provide some insights into the causes for the continued contaminant loading. Population density and percent urban provide excellent predictors for recent metals loadings. Lead also showed excellent correlation with slope percent. Unexpectedly all metals showed a change in watershed attributes influencing accumulation rates between the two decades, even though some have not had a significant atmospheric transport pathway or contaminant loading. The reasons for this are subject to further study.