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Non-conservative behavior of Cd in estuarine systems – new constraints from combined Cd concentration and isotope analyses

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Cadmium (Cd) is a micronutrient with an important role in marine biological productivity. In the open ocean, the distribution of dissolved Cd is correlated with that of phosphate, with low concentrations in surface waters due to biological utilization and higher abundances at depth from remineralization of organic material [1]. Previous studies have furthermore shown that biological uptake of isotopically light Cd generates significant Cd isotope variability in surface seawater (typically $\varepsilon^{114/110}$Cd $\approx$ +5 to +40), whilst the deep ocean is characterized by a relatively constant Cd isotope composition of $\varepsilon^{114/110}$Cd $\approx$ +3 [2,3] ($\varepsilon^{114/110}$Cd is the deviation of the ^{114}Cd/^{110}Cd ratio of a sample from the NIST 3108 Cd isotope standard in parts per 10,000).

Riverine fluxes are an important source of marine Cd but the behavior of Cd in estuaries is only poorly constrained. To further investigate the cycling of Cd in estuarine systems, we determined the Cd concentrations and isotope compositions of 19 water samples that were collected during the ISSS-08 (International Siberian Shelf Study) cruise along the Arctic Siberian Shelf, with emphasis on the Laptev and East Siberian Seas of the Arctic Ocean. This is the first study to investigate the cycling of Cd in such environments with the aid of combined Cd isotope and concentrations measurements.

The majority of the samples define a linear correlation in a diagram of [Cd] vs. salinity (with S $\approx$ 3 to 32) and a curvilinear trend for the $\varepsilon^{114/110}$Cd vs. [Cd] data. These observations are in accord with conservative behavior of Cd during mixing of riverine water and seawater. In addition, they suggest that the seawater endmember is characterized by [Cd] $\approx$ 0.2 nM, in accord with previous work [4,5,6], and $\varepsilon^{114/110}$Cd $\approx$ +5. These characteristics resemble Cd-rich surface waters from other locations, where biological uptake of Cd is incomplete. For the riverine endmember, the data suggest [Cd] $\leq$ 0.04 nM, in general agreement with previous analyses [5,6]. The isotope composition of $\varepsilon^{114/110}$Cd $\leq$ +2 is similar to or slightly more positive than the upper continental crust, which is inferred to be characterized by $\varepsilon^{114/110}$Cd $\approx$ 0 [7]. This indicates that Cd isotope fractionation during weathering and release of Cd from crustal materials is limited.

Six of the 19 samples, however, show clear deviations from the conservative mixing trend defined by the majority. One sample from the Ob Estuary (S $\approx$ 8) features a highly negative $\varepsilon^{114/110}$Cd value of about -7±1. This signature might reflect Cd pollution, as anthropogenic emissions of Cd to the atmosphere are commonly characterized by light Cd isotope compositions with $\varepsilon^{114/110}$Cd < 0 [8,9]. The remaining five samples, and in particular three from the vicinity of the Indigirka Estuary, display positive deviations from the conservative [Cd] vs. S mixing trend. The Cd isotope data support the interpretation that this deviation reflects release of Cd from particles and suggest that the desorbed Cd is characterized by an isotope composition similar to that of dissolved riverine Cd, with $\varepsilon^{114/110}$Cd $\leq$ +2.

Taken together, these results underline the important role that trace metal stable isotope analyses can play in investigations of marine biogeochemical element cycles. For Cd, the isotopic data (i) confirm the reactive behavior of Cd in estuarine systems, where Cd is released from suspended particles and (ii) may be of value for fingerprinting anthropogenic Cd additions.

References:

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