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Shelf supply of isotopically light particulate Cd to Peruvian coastal waters

RUIFANG C. XIE[1], MATTHIAS SIEBER[2,3], INSA RAPP[4], YISEN ZHONG[1], TIM M. CONWAY[2], MARK J. HOPWOOD[4,5], MARTHA GLEDHILL[4] AND ERIC P. ACHTERBERG[4]

[1]Shanghai Jiao Tong University
[2]University of South Florida
[3]ETH Zürich
[4]GEOMAR Helmholtz Centre for Ocean Research Kiel
[5]Southern University of Science and Technology

A decoupling between Cd and PO_4 towards lower Cd concentrations within the Atlantic and Pacific oxygen minimum zones has been reported. This decoupling has been explained by processes that include but are not limited to authigenic Cd sulfide (CdS) precipitation within protected micro-environment of decaying organic matter[1], water mass mixing[2], and varying cellular Cd:P ratios in marine phytoplankton[3,4]. Cadmium in the particulate phase within OMZ waters are isotopically lighter than in the dissolved phase, yet how Cd and Cd isotopes partition between the dissolved and particulate phases remains underexplored.

Here, we present dissolved and particulate Cd concentrations and Cd isotope compositions from the Peruvian coastal zone. Our data show that water column profiles of both Cd concentrations and Cd isotope ratios ($d^{114}Cd$) of the dissolved phase are similar to those in the open ocean. Conversely, particulate Cd concentrations decrease exponentially with depth. Fitting these data with a Martin curve suggests that Cd is remineralized faster ($b = -0.93$ to -0.86) than particulate organic carbon ($b = -0.79$)[5]. We observed a sharp decrease in particulate $d^{114}Cd$ by ~1‰ when dissolved oxygen concentrations dropped below detection limit of 2 uM at both shelf and offshore stations. Correspondingly, particulate Fe/Al ratios were enhanced just below the oxic-anoxic interface, which could be attributed to oxidation of Fe(II) that was reductively released from shelf sediment and transported offshore. Similar shifts toward more negative particulate $d^{114}Cd$ have been previously reported in the Oyashio Extension[6] and Line P[7] in the upper oxycline and at roughly the same neutral density range. We propose that these light particulate Cd isotopic signatures in our study and others are supplied from the shelf, likely in the form of CdS. Our hypothesis is further supported by a Lagrangian particle tracking model that confirms cross-shelf particle transport within these systems.

[1] Janssen et al. (2014) PNAS 111(19):6888-6893; [2] Middage et al. (2018) EPSL 492:79-88; [3] Liu et al. (2023) GBC 36, e2022GB007466; [4] de Souza (2023) GCA 322:274-296; [5] Bam et al. (2023) Mar. Chem. 257:104325; [6] Yang et al. (2018) GCA 233:66-80; [7] Janssen et al. (2019) EPSL 515:67-78