Can hydrogen sulfide in oxygen-deficient zones affect metal cyling?

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Five years ago Janssen et al. [1,2] hypothesized that apparent deficits of cadmium and zinc in oxygen-deficient zones of the North Pacific Ocean could be explained by the precipitation of CdS and ZnS within anoxic microzones of suspended particles. Shipboard analytical methods with picomolar detection limits for dissolved and particulate hydrogen sulfide allowed an examination of their hypothesis during the 2018 US GEOTRACES GP15 Pacific Meridional Transect from 56°N to 20°S. The sampling was focused in the upper ODZ where Janssen et al. found the greatest Cd and Zn deficits.

Dissolved samples were collected using the US GEOTRACES clean carousel with 12L GO FLO bottles, filtered through 0.2 µm Supor capsules, and placed in hermetically-sealed cubitainers for filling and dispensing without exposure to the atmosphere. Samples for particulate acid-volatile sulfide (pAVS; CdS and ZnS quantitatively release H_2S when acidificd) were collected on 0.8 µm Supor filters using modified McLane in situ pumps. Within 12 hours water samples were were analyzed using an acidification, cryogenic trapping and GC/flame photometric method of Radford-Knoery and Cutter [3]; this quantifies dissolved sulfide as free ions and metal-sulfide complexes (TDS) with a 0.2 pmol S/L detection limit. The pump filters were subjected to a similar analysis for pAVS with a detection limit of 0.1 pmol S/L

At 22 stations between 56°- 5°N from the surface to the top of ODZ, TDS averaged 34.6 pmol/L and decreased with depth. Within the upper 200 m of the ODZ, TDS averaged 41.1 pmol/L. In contrast, pAVS was highest in the upper 100 m of the water column and averaged 1.4 pmol/L. In the ODZ it only averaged 0.4 pmol/L. Stoichiometrically, these picomolar values of pAVS in the ODZ are too low to match the 100-250 pmol Cd/L deficits observed by Jenssen et al. The TDS vertical profiles also do not indicate enhanced H_2S concentrations in the ODZ.

[1] Janssen, D.J., et al. 2014., Proc. Natl. Acad. Sci. U.S.A,, 111: 6888-6893. [2] Janssen, D.J. and Cullen, J.T., 2015. Mar. Chem., 177: 124-133. [3] Radford-Knoery, J. and G.A. Cutter. 1993.Anal. Chem., 65: 976-982.