Multiple oxidation state trace elements in suboxic waters off Peru: in situ redox processes and advective/diffusive horizontal transport

JAMES W. MOFFETT[1*], GREGORY A. CUTTER[2], MARIA C. NIELSDOTTIR[2], AND VIRGINIE SANIAL[4]

[1]University of Southern California, Los Angeles CA 90089, USA (correspondence: jmoffett@usc.edu).
[2] Old Dominion University, Norfolk, Virginia 23529, USA (gcutter@odu.edu)
[2] Old Dominion University, Norfolk, Virginia 23529, USA (maria.nielsdottir@gmail.com)
[4] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA(vsanial@whoi.edu)

Secondary nitrite maxima are a persistent feature of upper oxygen minimum zones (OMZs) and are 'hot spots' for denitrification and microbial activity in general. They are often associated with accumulation of reduced forms of trace elements. It is difficult to determine the relative contribution of in situ processes and lateral transport from boundaries to these features. Combinations of such processes could lead to the co-occurrence of redox species that are not in thermodynamic equilibrium. On the the US GEOTRACES GP16 transect in 2013, the cycling of nitrate/nitrite, iodate/iodide, Fe(II)/Fe(III), As(III)/As(V), and hydrogen sulfide was examined in the Peruvian OMZ. Nitrite, Fe(II), and iodide were observed from the shelf to 95^{o} W, while reduced forms of sulfur, and surprisingly, arsenic, were absent. Maxima in nitrite, Fe(II) and iodide were coincident, indicating the utilization of Fe(III), iodate and nitrate as terminal electron acceptors was possible. For iron, this finding was unexpected with regards to thermodynamics. However, closer inspection combined with advective/diffusive modeling of water column data and ^{228}Ra-based flux calculations, showed that benthic redox processes, coupled with westward isopycnal transport, influence the chemical composition and redox speciation within the upper OMZ well offshore. This horizontal transport contributes to the coexistence of Fe(II) with nitrate, which is at odds with equilibrium calculations. It was also unequivocally important in the pronounced maxima in 'excess' iodide in the secondary nitrite maximum.