

Concentration and speciation of W and Mo in estuarine surface and underlying porewaters

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The recognition of tungsten (W) as a possible human health hazard has stimulated increased scrutiny of this transition metal, along with its chemical analog, molybdenum (Mo), in the environment. We focus here on W and Mo in surface waters and porewaters from an estuary/salt marsh in southeast Louisiana. Dissolved concentrations of Mo in the surface waters increased linearly with increasing salinity demonstrating conservative mixing of fresh water with marine water. Tungsten does not exhibit conservative mixing behavior as a function of salinity in the estuary. Instead, a mid-salinity maximum for W is observed at ~ 11‰, which subsequently decreases with both increasing and decreasing salinity. The reactive behavior of W in this estuary indicates a mid-salinity source of W that is then either scavenged or diluted with sea water.

Although W and Mo demonstrate distinct behavior in the surface estuary, their concentrations are strongly correlated in the porewaters ($r = 0.86$, $p \leq 0.0001$). Compared to overlying fresh surface waters, interstitial W and Mo concentrations are enriched 130- and 3-fold, respectively. The elevated porewater concentrations of W and Mo are likely due to dissolution of Fe/Mn oxides/oxyhydroxides and subsequent release of sorbed W and Mo. For porewaters underlying brackish surface waters (i.e., $7‰ \leq S \leq 22‰$), bacterially mediated sulfate reduction produces dissolved sulfide that ranges from 200 to 2264 $\mu\text{mol/kg}$. The W and Mo concentrations in these highly sulfidic porewaters are, on average, 15- and 19-fold lower, respectively, than in porewaters from sediments underlying fresh surface waters. Speciation modeling predicts thioanion species of W and Mo dominate in the highly sulfidic porewaters [1, 2]. Tetrathiomolybdate is known to adsorb to precipitating pyrite [3], which may explain the lower Mo concentrations. We hypothesize that scavenging of thiotungstate anions may explain the low W concentrations in the sulfidic porewaters.

[1] Erickson and Helz (2000) *Geochim. Cosmochim. Acta* **64**, 1149-1158 [2] Mohajerin *et al* *Geochim. Cosmochim. Acta* under review. [3] Bostick *et al* (2003) *Environ. Sci. Technol.* **37**, 285-291