EXPERIMENTS MEASURING COPPER BIOAVAILABILITY IN OXIC AND SPIKED SEDIMENTS

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Abstract

Metal partitioning and bioavailability in sediments has been primarily linked to sulfides and organic carbon, yet metals can also sorb to Fe oxides in aerobic sediments. Our research aims to improve metal bioavailability models for stream ecosystems by incorporating an oxic partitioning component. Two reference sediments, with differing binding capacities, were spiked with five concentrations each of Cu and aged under flow-through conditions in the lab while concurrently exposing *Hyalella azteca* to those sediments to measure changes in toxicity as the sediment ages. Frequent temporal sampling produced a fine scale understanding of geochemical and toxicological dynamics in the sediment, and ultimately determined the length of time necessary for lab-spiked sediments to reach a steady-state in an oxic environment. Metal release from spiked sediments rapidly decreased through time when exposed to flowing waters. As predicted, toxicity declined during the equilibration as Cu was absorbed to Fe oxides in sediments and made less available for uptake by *H. azteca*. Comparison of flume-aged sediments to freshly-spiked sediments at the same Cu concentrations (28 day *H. azteca* growth assay) revealed lower EC20s in the freshly-spiked sediments. The flume aged sediments may be used as surrogates for field contaminated stream sediments, allowing for more accurate predictions of effects under natural conditions.

Objectives

Objective 1 - Explore the role of Fe and Mn oxides in metal binding and bioavailability by following spiked sediments through time. We expect sediments to become less toxic through time as biogenic Fe and Mn oxides develop and sorb metals.

Objective 2 - Develop a spiking correction value for converting effects criteria (e.g., EC20) from bioassays with spiked sediments to values expected from bioassays with field-aged contaminated sediments.

Experimental Design & Methods

OBJECTIVE 1: Flow-through aging of spiked sediments

- Two reference sediments differing in binding capacity (Table 1) were amended with Cu to span a range from non-toxic to highly toxic (4 spike + reference per sediment).
- Equilibrated for 2 weeks under anoxic conditions and neutral pH.
- Sediments were placed in plastic cups (15 per treatment) within a flow-through artificial stream and sampled through time (Fig. 1)

Table 1. Initial geochemistry of the two experimentally manipulated sediments

Sediment	AVS (umol/g)	Organic matter (%)	Total Fe (g/kg dw)	Nominal Cu (mg/kg dw)
Dow	1.3	3	0.5	0, 60, 140, 340, 800
Ocoee	7	7	36	0, 160, 380, 900, 2100

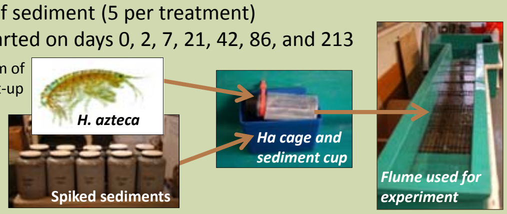
Temporal geochemical sampling: one cup per treatment was destructively sampled on days 0, 1, 2, 4, 7, 14, 21, 42, 86, and 213

- DO vertical penetration using microelectrodes
- AVS, SEM metals (Cu, Fe, Mn), total metals, organic C, and pH measured in surface (1 cm) and deep sediments
- Fe oxides and associated Cu measured with ascorbate and dithionite extractions in surface and deep sediments
- Cu flux from sediment to surface water measured with DGTs
- Dissolved porewater metal and dissolved organic C with peepers

Acute toxicity tests: *Hyalella azteca* 7-day growth test in cages placed on surface of sediment (5 per treatment)

- Tests started on days 0, 2, 7, 21, 42, 86, and 213

Figure 1. Diagram of experimental set-up in laboratory



*****Once the flume-aged sediments reached equilibrium…**

OBJECTIVE 2: Static renewal toxicity testing

Follow methods of Roman et al. (2007) for EU Cu risk assessment to allow for comparisons. Performed a 28-day *H. azteca* toxicity test using the 213 day flume-aged amended sediments and freshly spiked sediments of same origin and Cu concentrations.

Endpoints:

- Sediment (start & end): total Cu, AVS/SEM-Cu, organic content
- Overlying water (throughout): dissolved Cu, pH, DO, hardness
- *H. azteca:* relative growth rates

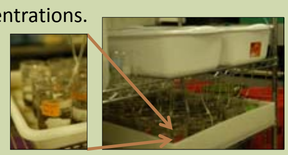
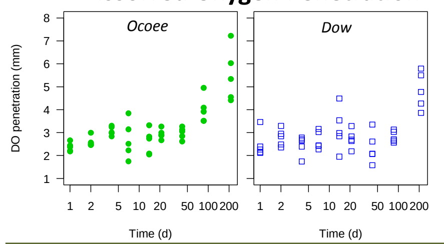


Figure 2. Static renewal system (left) and individual test beaker

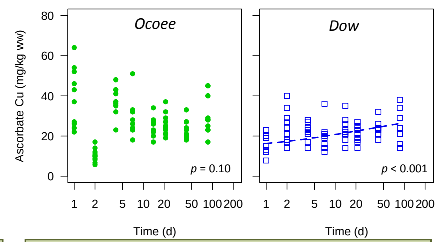
Results: Objective 1

Dissolved Oxygen Penetration



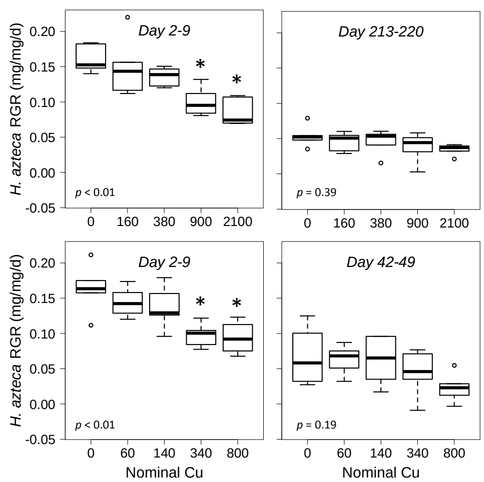
Dissolved oxygen penetration in the sediment increased through time. DO penetration increased more rapidly and to a greater depth in Ocoee.

Cu bound to Fe oxides



Cu in the ascorbate extraction (i.e., bound to amorphous Fe oxides) increased through time in Dow but was stable in Ocoee.

H. Azteca Toxicity

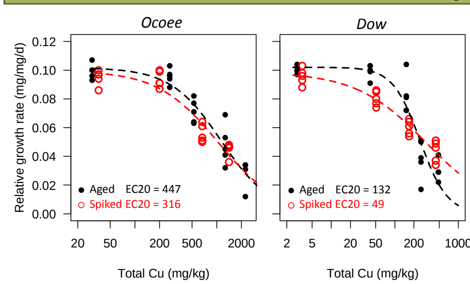


Relative growth rates (n = 5) of *H. azteca* exposed to Cu-spiked Ocoee (TOP) and Dow (BOTTOM) sediments at the initial sampling period and the first date when all treatments were no different than controls.

H. azteca sensitivity to sediment Cu changed through time in both sediments.

Dow sediments with high Cu became less toxic much sooner than Ocoee sediments (42 v. 213 d).

Results: Objective 2



Relative growth rates of *H. azteca* from 28-d static renewal bioassay.

For both Ocoee and Dow sediments, freshly-spiked sediments were more toxic than flume-aged sediments.

Using spiked sediments in these assays under-estimated EC20 by ~30-60%.

Conclusions

- Under flow-through conditions, spiked sediments change both in geochemistry and toxicity through time (weeks to months for some changes), suggesting that short-term experiments using spiked sediments may miss important dynamics expected in the field.
- Fe oxides may be important for reducing Cu toxicity, but more information is needed about the mechanisms of formation, crystal structure, and sorption capacity of Fe oxides.
- Standard bioassays with flume-aged sediment yielded effects criteria that were higher than those observed from paired freshly-spiked sediment bioassays. This suggests that criteria derived from spiked-sediment assays may be conservative with respect to field conditions.

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