NICKEL PHASE PARTITIONING, FLUX AND TOXICITY IN FIELD-DEPLOYED SEDIMENTS

G. Allen Burton[1], David M. Costello[1], Chad R. Hammerschmidt[2], Emily C. Rogevich Garman[3], and Christian E. Schlekat[3]
[1] University of Michigan, [2] Wright State University, [3] NiPERA

Summary

Ni speciation, bioavailability, and toxicity is modified by sediment geochemistry and empirical surveys and laboratory assays have highlighted the importance of acid-volatile sulfides (AVS) and organic carbon (OC) for altering Ni bioavailability. In this study, we amended 5 geochemically distinct lotic sediments with a range of Ni concentrations and monitored geochemistry, flux (by DGT), and toxicity under field conditions. After 4 weeks, colonizing macroinvertebrates exhibited a negative response to sediment Ni, and SEM-AVS models of bioavailability differentiated toxic and non-toxic sediments. After 8 weeks, relationships between macroinvertebrates and Ni deteriorated as sediments previously identified as toxic exhibited no toxicity. Our data suggested that Ni binding to Fe oxides may be responsible for the decline in toxicity. DGTs placed in the sediment indicated that Ni flux and speciation changed through time as partitioning shifted from NiS to Ni sorbed to Fe oxides. Although DGTs did provide a greater understanding of Ni phase partitioning, DGT-measured Ni was not better than SEM-AVS or total Ni at predicting macroinvertebrate response, which suggested that DGTs cannot replace SEM-AVS models for measuring bioavailability. Our results suggest that Ni speciation in lotic sediments may be more complex than what is accounted for in SEM-AVS models and additional research on Fe oxide sorption is needed to improve bioavailability models.

Objectives

- Determine if SEM-AVS bioavailability models can predict freshwater invertebrate response to Ni-contaminated sediments
- Follow Ni speciation through time to see whether Ni partitioning changes as spiked sediments age
- Assess whether DGT-measured labile Ni accurately predicts Ni bioavailability and invertebrate toxicity

Methods

- Five geochemically diverse sediments were amended with Ni and placed in lotic ecosystems for 8 weeks (Table 1)
- Surface (top 1 cm) and deep sediment, were sampled at day 0, week 4, and week 8 for sediment geochemistry
- Sediment DGT probes were deployed for 24 h in sediments at the same time as geochemical sampling
- Colonizing macroinvertebrates were recovered from the sediment at 4 weeks, identified to family, and enumerated

Table 1. Geochemistry of sediments used in experiment at day 0

Sediment	AVS (µmol/g dw)	OC (%)	Total Ni (mg/kg dw) Ref.	Low	Medium	High
Spring	1	0.47	2.7	32	157	468
Dow	0.4	1.1	1.8	133	323	1382
St. Joseph	2.5	1.3	2.7	391	649	1170
Raisin	0.8	0.69	4.0	151	328	1143
Mill	29.8	4.9	18	1282	3105	4978

Results

Invertebrate Diversity & Richness

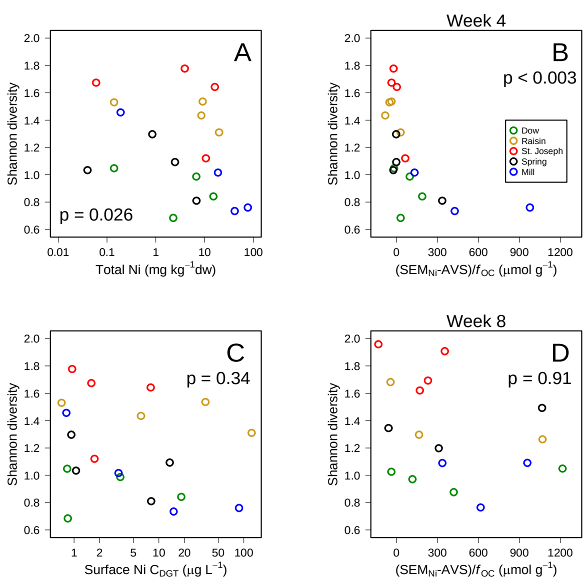

Figure 1. At day 28, invertebrate responses were best predicted by SEM-AVS models of bioavailability (B). Total Ni (A) and DGT-measured Ni (C) both overestimated bioavailability for some sediments. At day 56, invertebrates showed little response to sediment Ni (D) though sediments exceeded non-toxic thresholds.

Nickel Partitioning

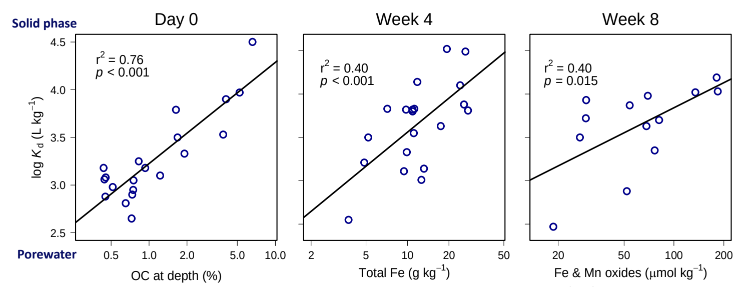

Figure 2. Ni partitioning between porewater and solid phases (K_d) was related to sediment geochemistry. At deployment, a greater fraction of Ni partitioned to the porewater in sediments with low OC (A). At week 4 and 8, controls on partitioning shifted to Fe and Mn fractions with a greater fraction of Ni partitioning to porewater in Fe poor sediments (B & C).

Table 2. Sediment geochemistry parameters predicting five benthic invertebrate indices from forward stepping multiple linear regression. Ranking (1° to 3°)

Benthic index	1° variable	2° variable	3° variable
Richness	SEM_{Ni}/AVS (deep) [-]	SEM_{Mn} (surface) [+]	K_d
Abundance	SEM_{Ni} (deep) [-]	SEM_{Ni}/AVS (surface) [+]	
Diversity	SEM_{Ni}-AVS/fOC (surface) [-]	AVS (deep) [+]	
EPT	SEM_{Ni} (deep) [-]	AVS (deep) [-]	
Chironomids	FeO_X+MnO_X (surface) [-]		
Gammarus	SEM_{Ni} (deep) [-]	SEM_{Mn} (surface)	

Conclusions

- Ni partitioning and toxicity changed through time, which revealed that Fe and Mn oxides may be more important than recognized for reducing the fraction of bioavailable Ni.
- Measuring AVS improves predictions of invertebrate toxic response, yet AVS is not the major ligand in oxic surface sediments.
- DGT-measured labile Ni is not superior to SEM-AVS bioavailability models for predicting freshwater invertebrate response.

Citations

Costello, Burton, Hammerschmidt, Rogevich, and Schlekat. 2011. Nickel phase partitioning and toxicity in field-deployed sediment. *Environmental Science & Technology* 45:5798-5805.

Costello, Burton, Hammerschmidt, and Taulbee. 2012. Evaluating the performance of diffusive gradients in thin films for predicting Ni sediment toxicity. *Environmental Science & Technology* 46:10239-10246.

Acknowledgements

We thank K. Taulbee, A. Honick, K. Custer, J. Besser, W. Brumbaugh C. Ingersoll, and A. Harrison. Funding was provided by NiPERA.