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Weight of evidence approach to assess fate and effect of metals in sediments

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Overview

Standard laboratory toxicity tests are often conducted in isolation of techniques that can quantify or help to understand exposure. At CanmetMINING our focus has been to incorporate multiple techniques to help gain a better understanding of metal fate and effects in sediments. The use of mini-peepers and DGTs has been employed alongside toxicity tests using the benthic invertebrate *Chironomus dilutus* and the freshwater fish *Pimephales promelas*. This allowed a comparative assessment of both pore-water and overlying water metal concentrations with toxicity data and tissue concentrations in the organisms tested. In addition, techniques to understand the biological and physical influences affecting metal fate in sediments were also incorporated. For example, sequential extractions to determine the operational speciation of metals, microbiology to understand the drivers behind metal releases from the sediments and mineralogy to assess the properties of the different phases in which the metals reside. The use of multiple techniques has improved our understanding of metal fate and effects within sediments.

Techniques

Toxicity Tests

Prior to exposure sediments are homogenized and sorted for removal of macro-organisms and debris. Invertebrate and fish exposures are conducted.

Chironomus dilutus: 10 d exposure to assess larval survival and growth (Figure 1a). Environment Canada method (EPS1/RM/32).
Fathead minnow*:* 21 d exposure in overlying water to assess embryo and larval survival and growth. Method adapted from Colavechia *et al* (2004) using imhoff settling cones (figure 1b)

The test beakers/cones are placed in the dark at room temperature for a minimum of 10 days to allow for equilibrium to occur. All tests are conducted within two weeks of receiving sediment samples.

After exposure, organisms are dried (60°C) and re-weighed to establish a dry weight (mg), then digested (HNO_3, H_2O_2) for analysis of tissue metal concentrations.

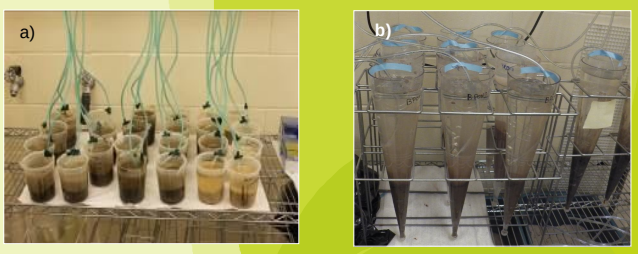

Fig 1. Lab testing set-up for a) C. dilutus and b) fathead minnow sediment toxicity testing.

Microbiology

Several groups of anaerobic microorganisms were enumerated from river sediment samples, including:

1) Ferric iron-reducing bacteria – important role in the mobility of metals through Fe(III) to Fe(II) reduction

2) Sulfate-reducing bacteria – important role in metal deposition through conversion of sulfate to sulfide and the precipitation of metal sulfide minerals

Microbes are enumerated following a standard 3-tube most probable number (MPN) assay. Enumeration is conducted on both bulk sediments and cores (Fig 2) to establish microbial profiles at various depths.

Fig 2. Core sample used for enumeration of microbes at various depths in the sediment profile

Chemistry

Two *in situ* devices, a diffusive gradient in thin films (DGT) and a dialysis mini-peeper, are used to measure the dissolved concentrations of metals in sediment (Fig 3).

DGT probe and mini peepers are placed in sediments and left undisturbed for 10-d in test units to attain equilibrium with the surrounding medium. On day 10, samples in peeper cells and DGT probe are collected and analyzed using ICP-MS to determine the dissolved metal concentrations and, if required, speciation.

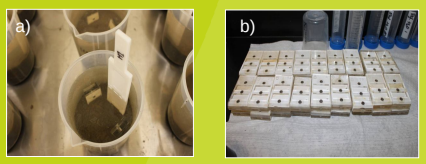

Fig 3. a) Mini-peeper and DGT installed in test beakers and (b) collected for processing after exposure

Sequential extractions

Determine the distribution of metals in sediments by operationally separating three phase fractions: Exchangeable elements and associated with carbonates; associated with iron and manganese oxides and associated with organics and sulfides (Table 1).

Table 1. The fraction, operational speciation and environmental relevance assessed through sequential extraction

Fraction	Solid phase or '*operational speciation*'	Environmental Relevance
Water-soluble	Weakly adsorbed ions	Highly labile and potentially bioavailable
Exchangeable	Bound to carbonates	Released readily into the environment (ion-exchange process)
Reducible	Bound to hydrous oxides of Fe and Mn	Oxic environment: metals less mobile Anoxic environment: metals more mobile
Oxidizable	Bound to organic material	Metals remain in solid phase. But may be mobilized by decomposition process
Residual	Bound to silicate and mineral phases	Non-leachable & non-bioavailable fraction

Mineralogy

Assess properties of the phases in which metals reside: 1) Crystallographic (e.g. amorphous vs. crystalline), 2) Compositional (e.g. metal concentration), 3) Textural (e.g. liberation) and 4) Morphological (e.g. crystallite size, surface area)

Techniques employed:
X-ray diffraction (XRD): allows the identification of the crystalline phases present in the solid fraction.
Electron Probe X-ray Microanalysis (EPMA): Obtain textural information and determine the chemical composition of relevant minerals.
Field-emission scanning electron microscopy (FE-SEM): obtain nanometer-scale spatial resolution during the characterization of fine features.

Case study: Mobilization of Arsenic

Objective:

River assessment conducted to assess metal bioavailability and mobility in sediments.

Method:

Incorporated multiple techniques:
1) Toxicity using *C. dilutus* (10-day growth test) and fathead minnow (21 d embryo-larval test)
2) Concentrations of metals in tissue, pore- and overlying water (using peepers and DGTs) and total sediments
3) Sequential extractions to establish primary phase
4) Dissolved organic matter in pore-water and particle size analysis
5) Microbiology to assess populations influencing metal mobility
6) Mineralogy of core samples

Results:

- No toxicity observed in 10-day test, however, elevated concentrations of some metals in tissues, e.g. As.
- Correlation observed between As in tissue and pore-water (Fig 4a) and DOC and pore-water (Fig 4b).
- Sequential extractions identified As primarily in reducible fraction (70-80%), remainder in carbonate/exchangable fraction
- Trend observed between particle size and reducible fraction of As in sediments. As particle size decreased reducible fraction increased
- Microbial analysis observed elevated MPN for Fe-reducing bacteria. Correlation with FeRB's and As in pore-water (Fig 4c).

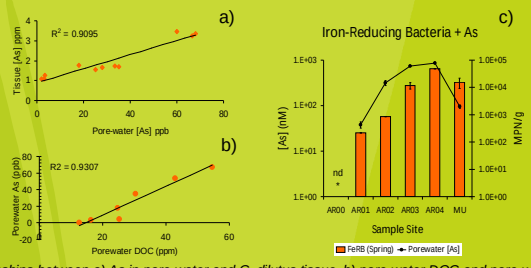

Fig 4. Relationships between a) As in pore-water and C. dilutus tissue, b) pore-water DOC and pore-water As and c) pore-water As and FeRB

Hypothesis for elevated As:

- Elevated organic matter (DOC) in pore-water stimulates growth of FeRB.
- FeRB mobilize adsorbed As from iron oxide phases which leads to elevated As in pore-water.
- Elevated As in pore-water led to elevation in tissue concentrations.

Conclusions

- Understanding the processes (chemical, biological and physical) involved in metal mobility and assessing their influence on bioavailability is beneficial for sediment risk assessment.

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