Potential Biological Effects of Subaqueous Disposal of Mine Tailings

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BC-MEND, ML/ARD

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Outline

- Brief history of subaqueous disposal (SAD)
  – geochemical perspective
  – hydrobiological perspective
- Objectives of present study; elements considered
- Waterborne and diet-borne metals
- How to assess metal "bioavailability"
- Recommendations

Subaqueous disposal in Canada

- Lakes (e.g., Eskay, Brucejack, Myra Falls, and Benson and Buttle Lake mines (BC); Anderson, Benson and Mandy Lakes (MB), Voisey's Bay Mine (Nfld))
- Engineered tailings ponds (e.g., Golden Giant, Samatosum, Equity Silver, Highland Valley Copper (BC), Louvicourt (QC))
- Two previous MEND reports (1993; 2009)
- Literature reviewed
  - Reports, proceedings and slide presentations provided by NRCan−CanmetMINING and BC−MEND ML/ARD
  - Journal publications

Subaqueous disposal

- Geochemical perspective – water cover
  - greatly reduces exposure to O_2
  - suppresses sulphide oxidation
  - prevents development of ARD, greatly reduces release of metals
- Exceptions observed
  - if tailings were flooded after an earlier extended period of sub-aerial exposure,
  - if tailings are partially or periodically exposed to the atmosphere due to water level changes,
  - if the SAD facility received products other than sulphidic tailings.

Subaqueous disposal

- Hydrobiological perspective
  - Lack of biological data for subaqueous disposal facilities.
  - A few exceptions found in the reviewed material:
    - Highland Valley Copper: progressive colonization of four HVC ponds + some monitoring of Cu and Mo concentrations in biota.
    - Balmer Lake: fish colonization 1978→1996→1999→2000→2005→2008.
    - Samatosum: “stream and vegetation surveys” (but no details).
  - Some data from field experiments:
    - Colonization of metal−contaminated sediments introduced into an uncontaminated habitat.

Subaqueous disposal

In summary:

- Studies to date have focused on the initial physical and geochemical performance of SAD facilities and the resulting chemistry of the surface water.
- Longer−term aspects are not as well understood.
- Major gap = biological colonization of such facilities, health of the biological communities that are established, and influence of those communities on water and sediment geochemistry.

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Objectives

- To provide updated information on potential diagenetic changes in submerged tailings and on biogeochemical interactions between submerged tailings and overlying aquatic communities
- To provide guidance regarding recommended tools and methodologies that could be used to predict and/or monitor the biological effects of submerged tailings.

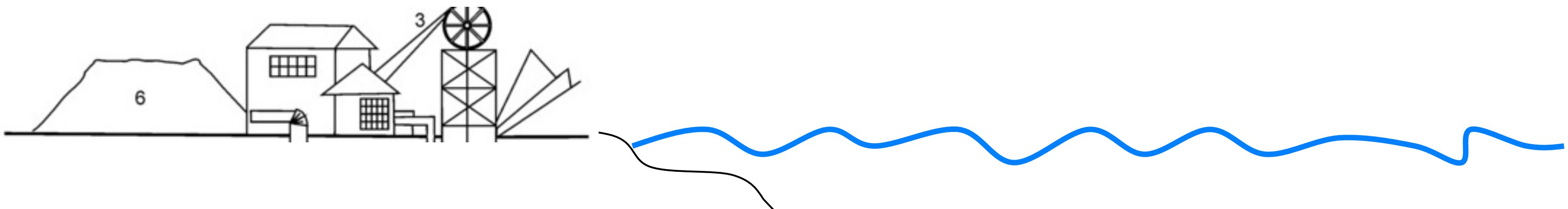
Elements considered

- (i) data-rich cationic trace elements that were covered in the previous reviews (Cd, Cu, Pb, Ni and Zn), <u>and</u>
- (ii) trace elements forming oxyanions and neutral polyhydroxy species that were not dealt with in the previous reports (As, Mo, Sb, Se).

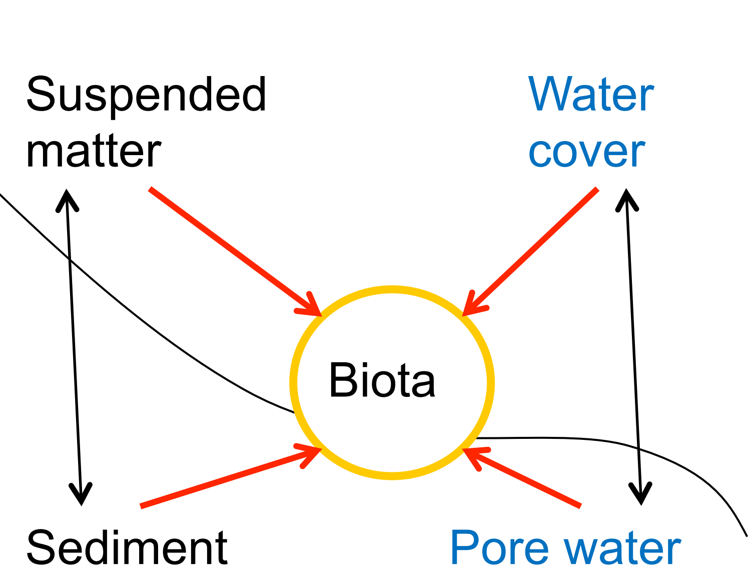
Approach

- Use studies of natural water bodies with elevated metal concentrations to help us understand the behaviour of SAD facilities.
- Consider how waterborne and diet-borne metals interact with living organisms.
- Propose how to assess metal bioavailability in sediments and in submerged tailings.

Waterborne metals

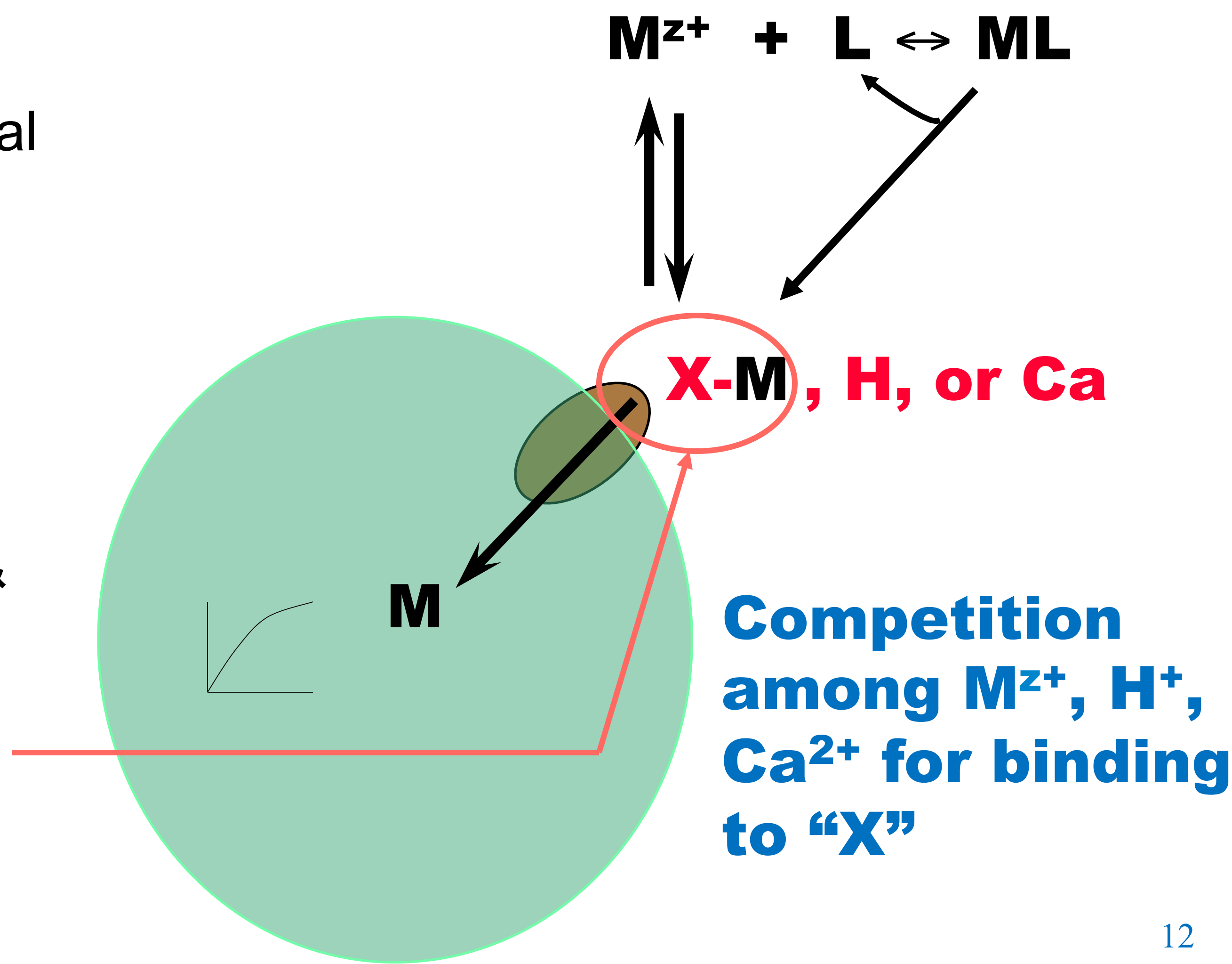


- Water column and pore water, i.e., dissolved metals.
- Clear consensus that best predictor of "bioavailability" of dissolved metals = free metal ion concentration (M^{z+})
- Biotic Ligand Model (BLM)



Chemist's view of BLM

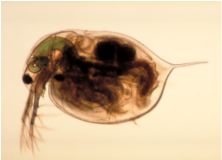
- Cell membrane = primary site of metal interaction
- Formation surface complex, {M-X-membrane}
- Rapid equilibrium between solution & biological surface
- Response α {M-X-membrane}



BLM

- BLMs include
  - *speciation module*, which calculates the free metal ion concentration in solution
  - *biological interaction module*, which takes into account the binding of M^{z+} & other cations to the so−called 'biotic ligand'
- BLMs are available for a suite of metals (Ag, Cd, Co, Cu, Ni, Pb, Zn) and for algae, invertebrates, fish.
- Required input data = water chemistry, including pH, cations, anions and dissolved organic carbon.

Diet-borne metals



- Dietary metals less studied than dissolved metals; role well recognized for Hg and Se; less so for other metals.

$$\frac{d[M]_{organism}}{dt} = k_u [M^{z+}] + (AE \times IR \times [M]_{food}) - k_e [M]_{organism} - k_g [M]_{organism}$$

uptake from water | uptake from food | excretion | growth dilution

- Models take into account assimilation efficiency; roles of gut chemistry, of metal partitioning in the ingested food; TAM.
- But still limited to accumulation rather than toxicity.

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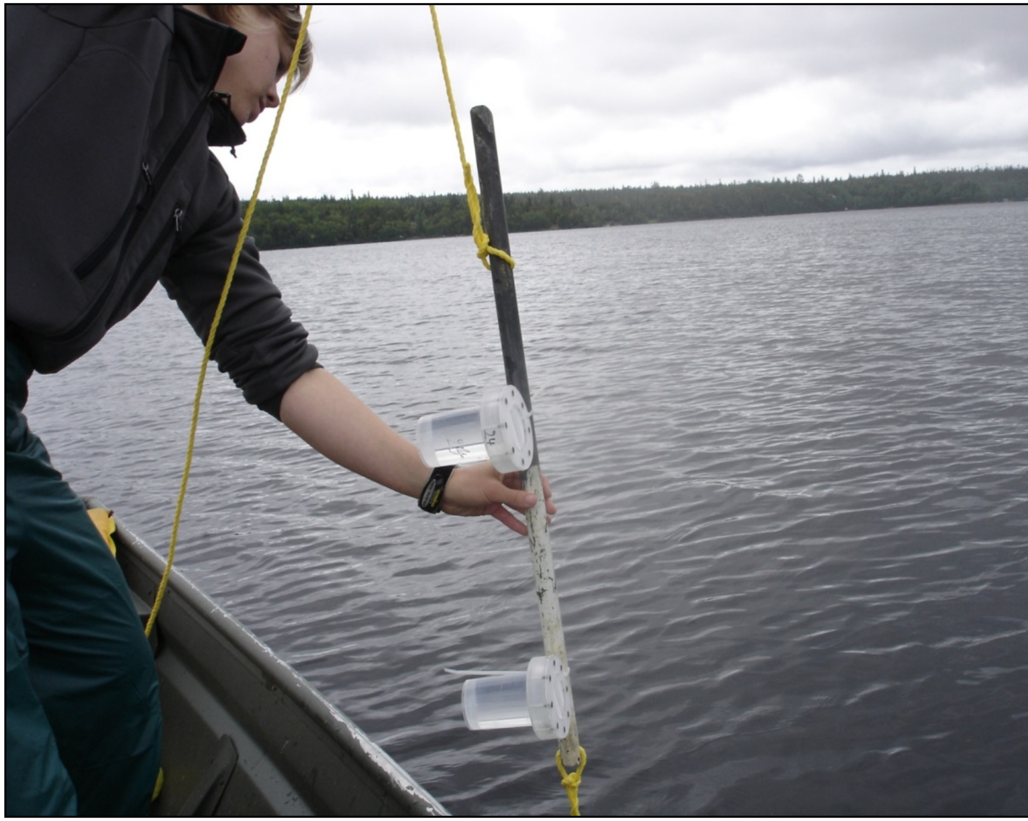
- Recommendations

How to assess metal ‘bioavailability’

- Geochemical approach
  - measure or calculate the free metal ion concentration in overlying water and submerged tailings
  - apply BLM
- Biomonitoring approach
  - passive or active biomonitoring

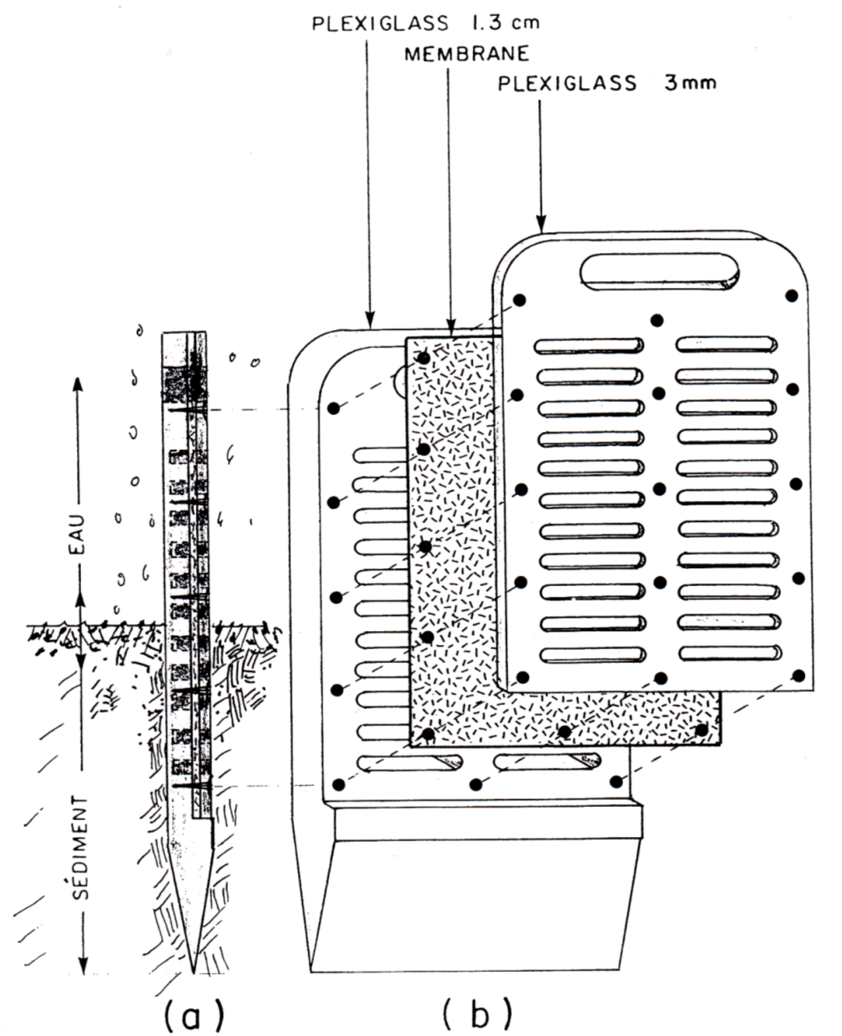
Geochemical approach - water

- Collect water samples (dissolved metals)
- Water column (*in situ* diffusion)
- Analytes = metals, major cations and anions, pH, DOC

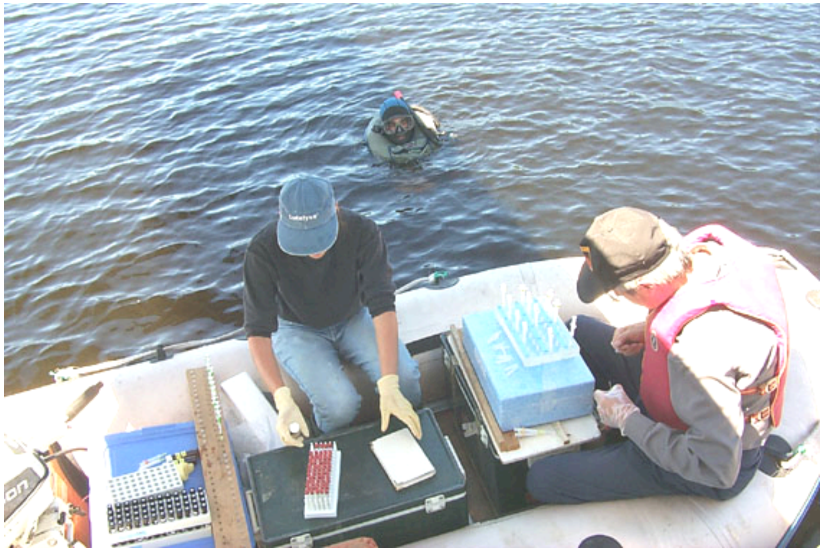


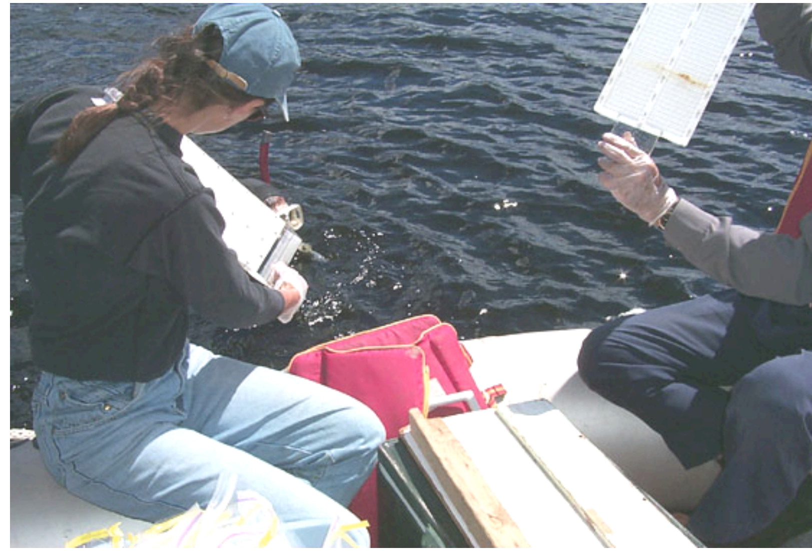
Geochemical approach - water

- Collect water samples (dissolved metals)
- Water column (*in situ* diffusion)
- Tailings-water interface (peepers)
- Analytes = metals, major cations and anions, pH, DOC, O_2; $\Sigma S(-II)$; $\Sigma S(0)$; thiosalts; process chemicals & their degradation products



Peeper recovery and sampling





Geochemical approach - sediment

- Collect cores of submerged tailings
- Preserve cold or frozen, not dried.
- Section under nitrogen
- Use partial extractions
- Analytes: organic carbon; SEM, AVS; amorphous iron oxyhydroxides + associated metals, including Fe, Mn

Photo courtesy of Sam Alpay, NRCan

Geochemical approach – pore water

- Use pore water to assess bioavailability of metals in sediments/tailings
  - collect water and measure $[M^{z+}]$

    or

  - calculate $[M^{z+}]$
- Key point: distinction between oxic and anoxic regimes
  - oxic: sorptive equilibria (e.g., amorphous iron oxyhydroxides)
  - anoxic: sulphide precipitation (SEM-AVS)

Equilibrium calculations

- Competitive adsorption (cf. Farley *et al*. 2011)

$$M^{z+} + HO\text{-}S_n^{\sim} = M\text{-}O\text{-}S_n^{▓} + H^+ \qquad K_A(n)$$

$$K_A(n) = \frac{[M\text{-}O\text{-}S_n^{▓}][H^+]}{[M^{z+}] \times [HO\text{-}S_n^{▓}]}$$

- Mathematically similar to a mixture of ligands in solution
- Necessary input data: $K_A(n)$ values, plus $[HO\text{-}S_n]$ or [adsorbents] + capacity of each adsorbent

Manipulation of equilibrium equations

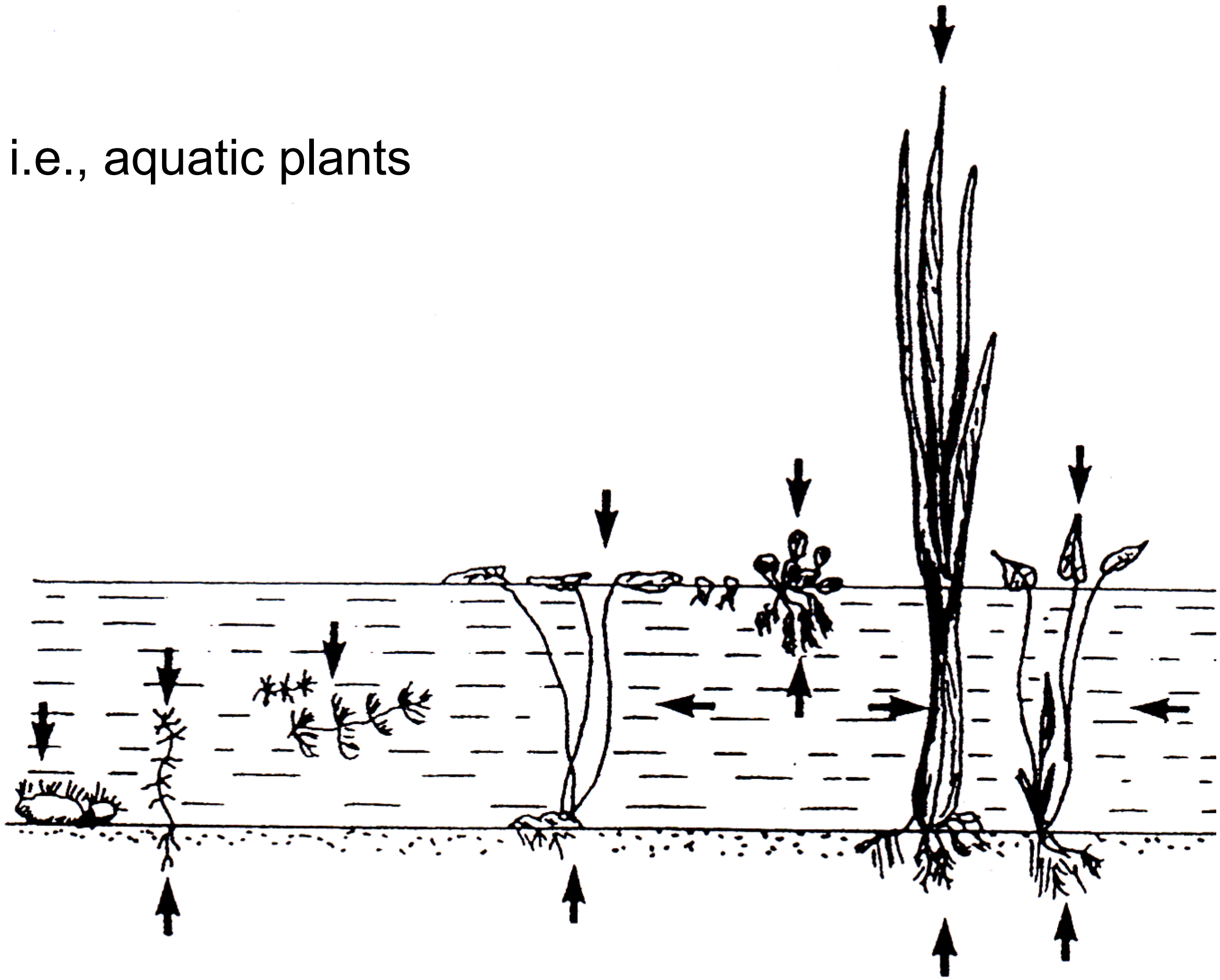
$$K_A(n) = \frac{[\text{M-O-S}_n \equiv][H^+]}{[M^{z+}] \bullet [\text{H-O-S}_n \equiv]}$$

$$[M^{z+}] = \frac{[\text{M-O-S}_n \equiv][H^+]}{K_A(n) \bullet [\text{H-O-S}_n \equiv]}$$

$$[M^{z+}] = \frac{[\text{M-O-S}_n \equiv]}{[\text{H-O-S}_n \equiv]} \times \frac{[H^+]}{K_A(n)}$$

Type «A» organisms

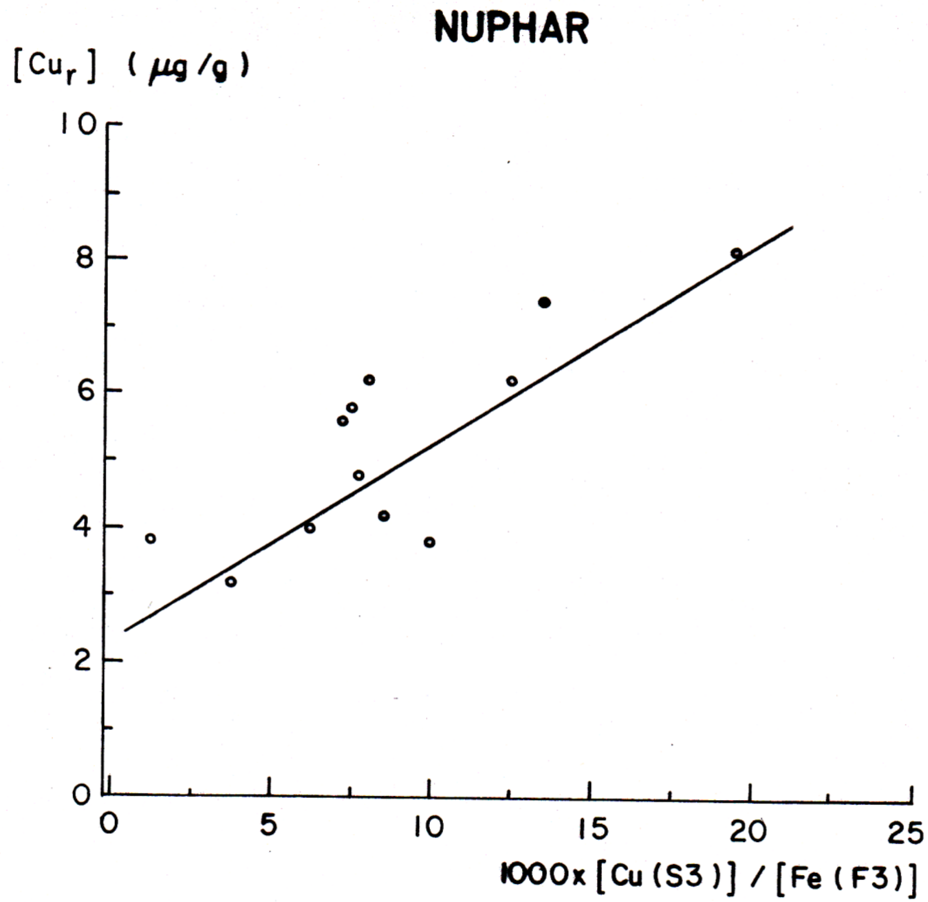
i.e., aquatic plants



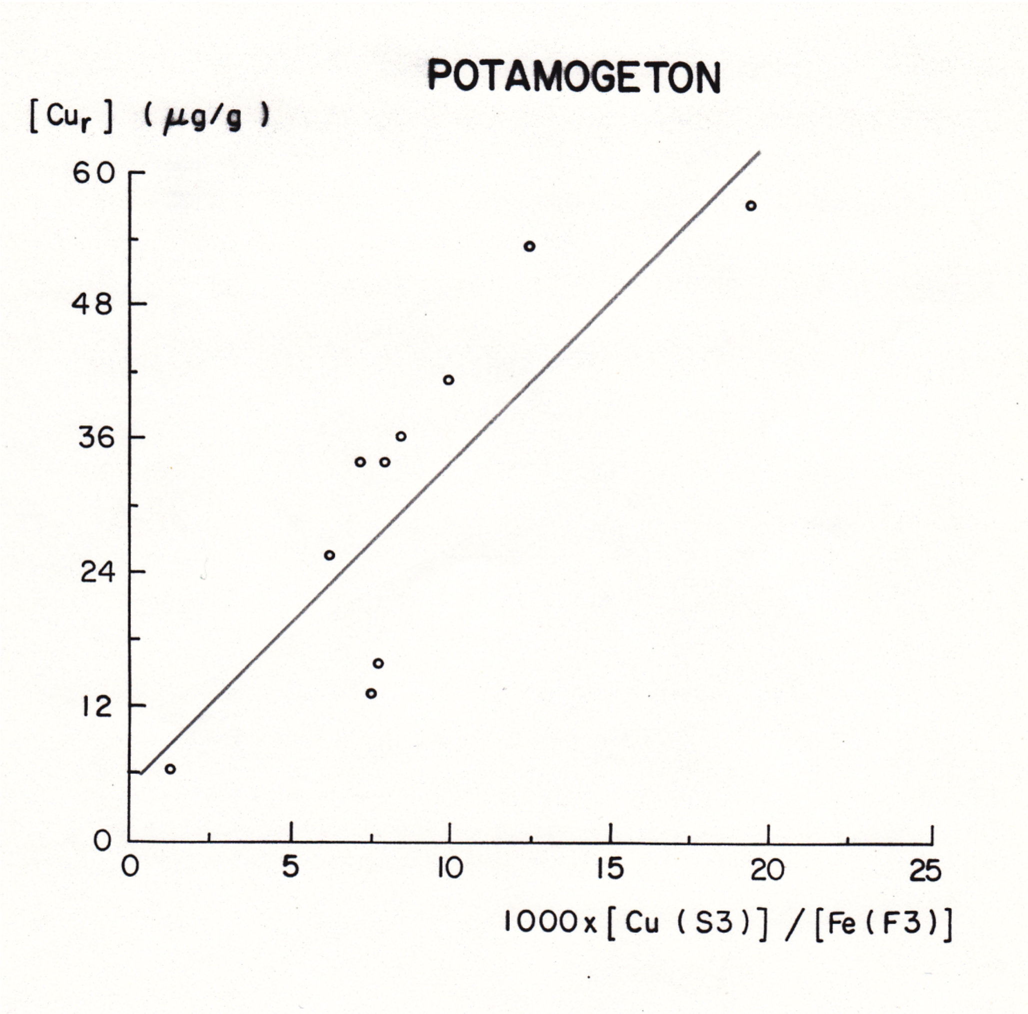
[M

Test - rooted aquatic plants

Nuphar variegatum

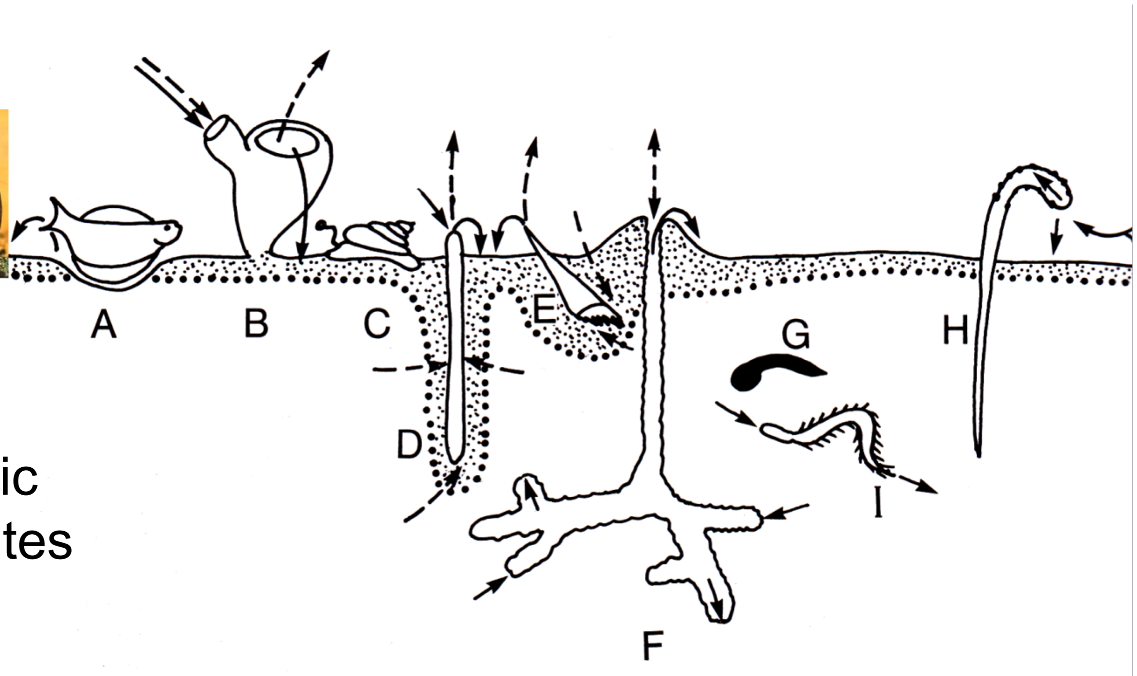


Test - rooted aquatic plants



Type «B» organisms

Pyganodon grandis, the giant floater, in living position and associated with cyprinid fishes. Photo by Alan M. Cvancara.



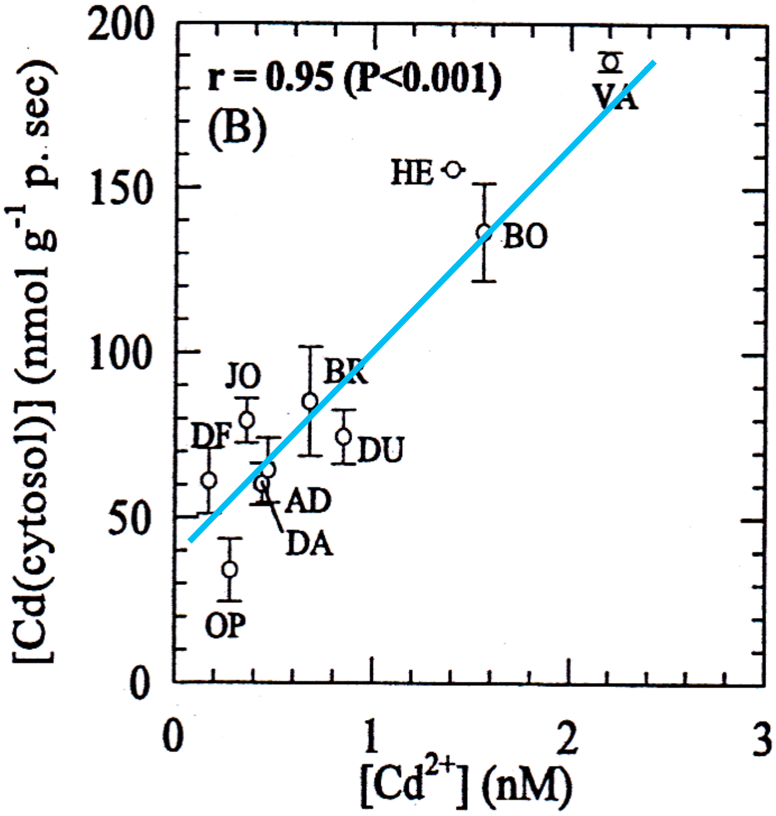
i.e., benthic invertebrates

Test - benthic bivalve

Pyganodon grandis

Pyganodon grandis, the giant floater, in living position and associated with cyprinid fishes. Photo by Alan M. Cvancara.

Cd bioaccumulation



$[Cd^{2+}]$ calculated
on the basis of

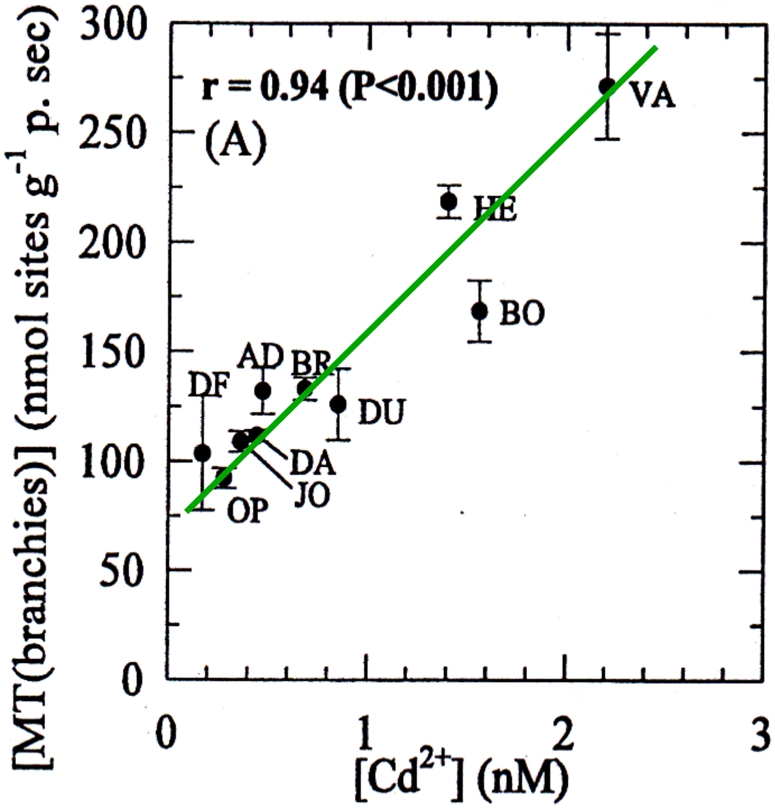
$$[Cd^{2+}] = \frac{[Cd\text{-}O\text{-}S_n \equiv]}{[H\text{-}O\text{-}S_n \equiv]} \times \frac{[H^+]}{K_A(n)}$$

Test - benthic bivalve

Pyganodon grandis

Pyganodon grandis, the giant floater, in living position and associated with cyprinid fishes. Photo by Alan M. Cvancara.

Metallothionein



$[Cd^{2+}]$ calculated
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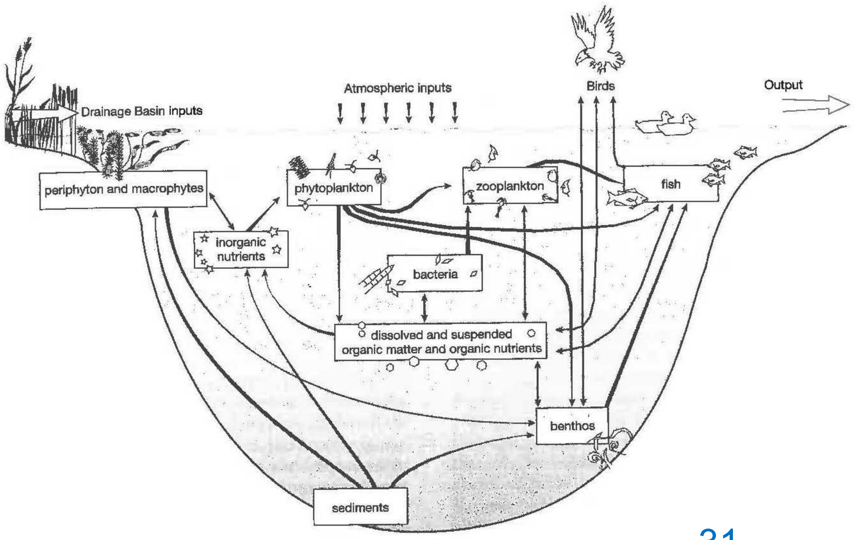
$$[Cd^{2+}] = \frac{[Cd\text{-}O\text{-}S_n \equiv]}{[H\text{-}O\text{-}S_n \equiv]} \times \frac{[H^+]}{K_A(n)}$$

How to assess metal ‘bioavailability’

- Geochemical approach
  - measure or calculate the free metal ion concentration in overlying water and submerged tailings
  - apply BLM
- Biomonitoring approach

Biomonitoring approach

- Biomonitoring approach
  - passive biomonitoring (compare indigenous fauna and flora with reference specimens)
  - active biomonitoring (introduce ‘naïve’ plants and animals into SAD facility and monitor their ‘performance’)
  - possible biomonitors?



Examples of biomonitors

Type	Common name	Metals
Benthic invertebrates	Floater mussel	Cd, Cu, Ni, Pb, Zn
	Snail	Cu, Ni, Pb
	Phantom midge larva	Cd, Ni, Se
	Mayfly larva	Cd, Hg
	Amphipod	As, Cu, Ni, Sb, Se, …
Benthic feeding fish	Yellow perch	Cd, Cu, Ni
	White sucker	Cd, Cu, Hg, Se
Rooted aquatic plants	Water lily	Cu, Zn
	American eel grass	Cd, Cu, Ni, Pb, Zn
Periphyton	Biofilm	Cd, Cu, Mn, Ni, Pb, Zn

Recommendations (1)

- Coordinated geochemical and biological measurements; phased approach
- Standardized methodologies (cf. AETE = Aquatic Effects Technology Evaluation, www.mend-nedem.org)
- Field trials for methods recommended for use in SAD facilities
- Focus on approaches that will yield estimates of [M^{z+}]
- In the tailings, focus on upper strata (contact zone with benthic fauna and flora)
- Measure pore−water composition at different depths (fluxes across interface; biogeochemical processes governing contaminant mobility)

Recommendations (2)

- Within tailings, measure solid phases exerting geochemical controls on pore−water metal/oxyanion concentrations, and pH.
- Biomonitoring focus on plants and animals (i) in direct contact with the bottom sediments/tailings and (ii) for which there are already some biomonitoring data (in Canada)
- When feasible (e.g., in multicellular biomonitor organisms), focus on specific organs or tissues (e.g., liver, gills, gonads; roots, stems, leaves) rather than on the whole biomonitor organism

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MEND Report 2.19.1

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END

Ideas to retain (1)

How to address the question of metal bioavailability in sediments / tailings…

Step	Comments / Rationale
1. Concentrate on upper sediment stratum	The effective contact zone between aquatic biota and deposited tailings
2. In the case of metal exposure via the dissolved phase, consider possible controls on metal concentrations in the interstitial (pore) water	Two possible approaches: (i) control by sorption reactions on Fe, Mn-oxyhydroxides, or on sedimentary organic matter; (ii) control by substitution reactions with amorphous sulphides
3. Depending on which approach proves more appropriate for contaminated sediments in their natural setting, estimate $[M]_i$ based on the geochemistry of the surficial sediments after diagenesis	In the real world, the distinction between oxic and anoxic sediments is often blurred; most aerobic benthic organisms survive in sediments that are underlain or even surrounded by completely anaerobic sediments
4. Consider the bioavailability of these dissolved metals (in the pore water; in the overlying water, assuming vertical transfer), using the BLM	BLM should apply to organisms that do not assimilate particulate metals (e.g., rooted aquatic plants) and to organisms that do ingest particles but for which the dissolved phase remains the primary vector for metal uptake (e.g., bivalves)

Ideas to retain (2)

How to address the question of metal bioavailability in sediments / tailings…

Step	Comments / Rationale
6. Having dealt with dissolved metals (geochemical controls, bioavailability) now consider those metals that remain in particulate form. Review results of laboratory feeding experiments designed to determine the assimilation efficiencies of metals present in different forms in the ingested particles.	Apples to organisms for which particles constitute the primary vector of metal uptake. Key factors include particle size ingested, digestion chemistry in the gut (pH, pE, residence time).
7. To complement the "reductionist" approach outlined in steps 1 to 6, consider a holistic (eco-toxicological) approach.	What can indigenous biota tell us about the bioavailability of metals in submerged tailings? (metal burdens; biochemical indicators of metal exposure).

Selection criteria - biomonitors

Criterion	Explanation
associated with sediments	(none needed!)
limited home range (sedentary)	bioaccumulated metal related to a specific location
widespread (cosmopolitan)	ease of comparison of the biomonitor species among different sites
abundant (not threatened species)	sample collection will not affect species abundance
metal-tolerant	biomonitor species must be present in metal-rich environments or survive when introduced there

Selection criteria - biomonitors

Criterion	Explanation
tolerant of manipulation	when absent from a contaminated site, can be transplanted into and maintained (caged) there
net metal accumulator	will yield a wide usable range of metal concentrations across different sites
known biology, known biodynamic constants	useful for calculating the length of time necessary to reach steady-state (active biomonitoring)
ease of collection and identification	reduces the need for taxonomic expertise
organism size	need sufficient tissue for multiple analyses

Examples of biomonitors

Type	Species	Metals
Benthic invertebrates	*Pyganodon grandis*	Cd, Cu, Ni, Pb, Zn
	Physa gyrina	Cu, Ni, Pb
	Chaoborus sp.	Cd, Ni, Se
	Hexagenia limbata	Cd, Hg
	Hyalella sp.	As, Cu, Ni, Sb, Se, …
Benthic feeding fish	*Perca flavescens*	Cd, Cu, Ni
	Catostomus commersonni	Cd, Cu, Hg, Se
Rooted aquatic plants	*Nuphar variegatum*	Cu, Zn
	Vallinsneria americana	Cd, Cu, Ni, Pb, Zn
Periphyton	-	Cd, Cu, Mn, Ni, Pb, Zn

Subaqueous disposal

Flooded impoundment ≠ Natural water body

- age; presence of engineered structures (dams; runoff diversions)
- water balance; hydrology
- limited inputs of plant nutrients from catchment
- depth of water cover
- sediment mineralogy; physical composition, cohesion, porosity; presence of mine wastes other than tailings; lack
- initial pore and surface water chemistry (e.g., presence of process chemicals)

Primary goal is sustaining safe management of mined materials; reclamation to productive landscape is an important but secondary objective…

Subaqueous disposal

- Hydrobiological perspective
  - Creation of small reservoirs a possible analogy to SAD
    - Colonizing species arrive in runoff from the catchment, in litter-fall from riparian terrestrial vegetation, as airborne seeds and particulates, or in excrement from birds and terrestrial animals.
    - Initial benthic colonization of newly flooded terrestrial soils normally occurs rapidly.
    - Invertebrate distribution & abundance vary according to particle size and organic matter concentration.
    - Aquatic plants strongly influenced by water transparency, underwater slope and by exposure to waves.

Subaqueous disposal

- Geochemical perspective – water cover
  - greatly reduces exposure to O_2
  - suppresses sulphide oxidation
  - prevents development of ARD, greatly reduces release of metals
- Exceptions observed
  - if tailings are partially or periodically exposed to the atmosphere due to water level changes,
  - if tailings were flooded after an earlier extended period of sub-aerial exposure

Subaqueous disposal

- Hydrobiological perspective
  - In an SAD facility
    - Elevated concentrations of metals and oxyanions present in submerged tailings might potentially affect the rate of colonization and influence which taxa succeed in occupying the habitat.
    - The physical properties of the tailings (e.g., granulometry, cohesion, presence of hardpan or cemented layers), a scarcity of certain key components (e.g., inorganic nutrients; natural organic matter) or other factors (e.g., pH) might also impede colonization and limit the development of the aquatic community.

Subaqueous disposal

- Exceptions observed (2)
  - dissolution of precipitates from acidic drainage discharged into impoundment & subsequently neutralized (Equity Silver, BC) — Cu Zn
  - post-closure dissolution of treatment sludges deposited in the impoundment during mine operation (East Lake, ON) — Cu
  - alterations to redox conditions at the tailings-water interface and dissolution of Fe-oxyhydroxides (Balmer Lake, ON) — As
  - remineralization of sedimented plankton (Balmer Lake, ON). — Zn

(see Price & Aziz 2012; Martin et al. 2001, 2003)

- i.e., exceptions (2) not due to sulphide oxidation

Geochemical approach - water

- Collect water samples (dissolved metals)
- Water column (*in situ* diffusion)
- Tailings-water interface (peepers)
- Analytes = metals, major cations and anions, pH, DOC, O_2; $\Sigma S(-II)$; $\Sigma S(0)$; thiosalts; process chemicals & their degradation products

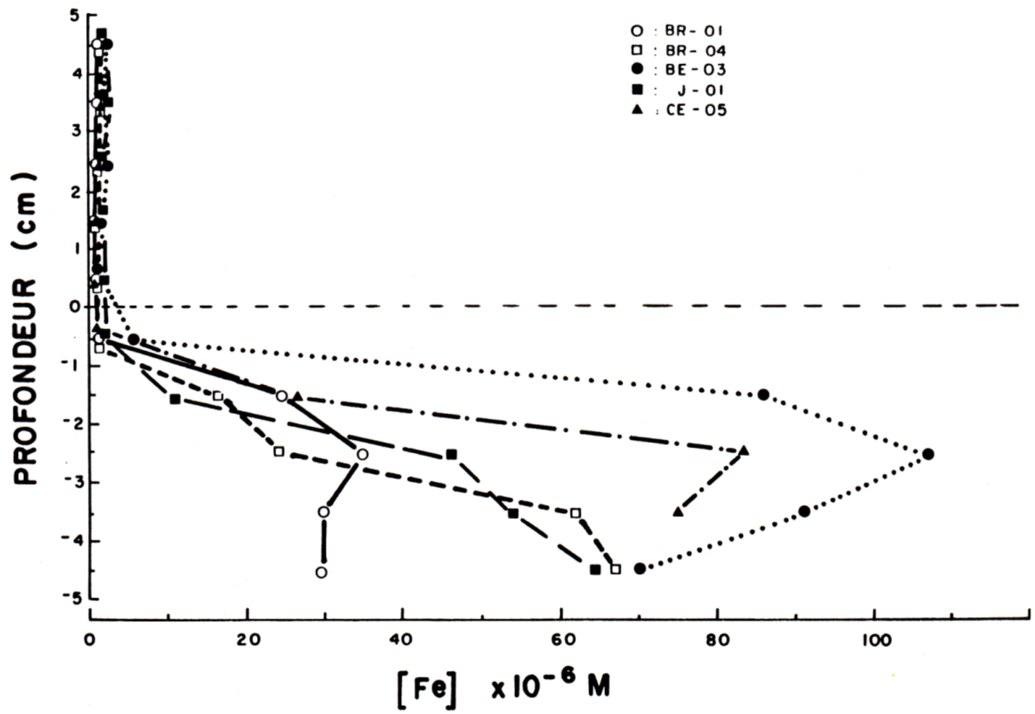

FIGURE 4.13 Profils de concentration de fer dans l'eau interstitielle et surnageante aux stations BR-01, BR-04, BE-03, J-01 et CE-05.