Metals in Fertilizers:
bioavailability, methods and long-range human health and ecological risk frameworks

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US EPA-Bioavailability

- A measure of the physicochemical access that a toxicant has to the biological processes of an organism. The less the bioavailability of a toxicant, the less its toxic effect on an organism.

  (Source: Office of Water: Protocol for Developing Sediment Total Maximum Daily Load (TMDL): Glossary *Term Detail*)

- The ability of a substance to affect organisms.

  (Source: Office of Science and Technology: Contaminated Sediment: Glossary *Term Detail*)

Bioavailability is the accessibility of a chemical for biological assimilation and possible toxicity.

Bioavailability Processes

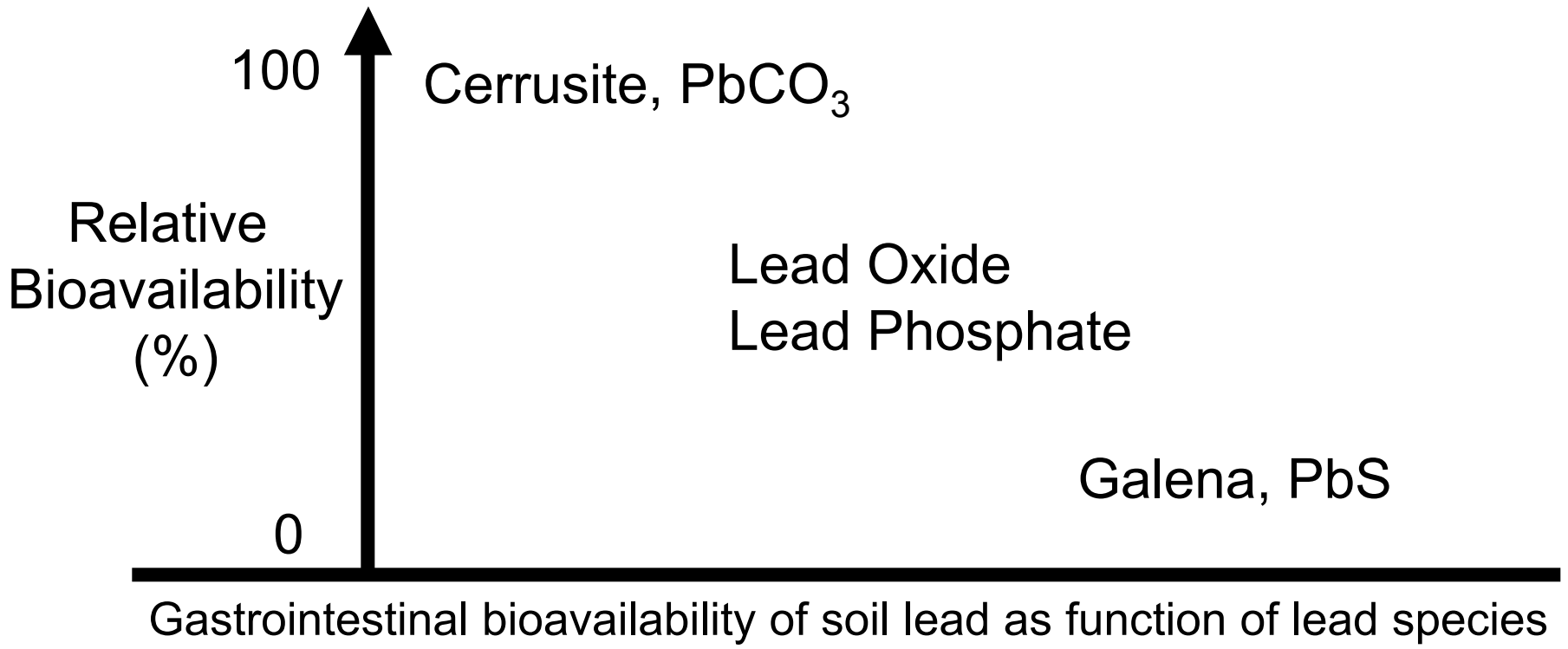
- Individual physical, chemical and biological interactions that determine the exposure to plants and animals to chemicals associated with soils.
- describes a chemicals ability to interact with the biological world
- Incorporates a number of steps not all of which are significant for all contaminants or all settings

Health ~ Risk ~ Fate
Depends on Chemical form

- Predicting environmental fate
- Effects exposure - nutrition and health or toxicity
- Describes the potential adverse effects on organisms
- "**Totals**" fail to predict the extent of bioaccumulation

Speciation- all species (of lead) are NOT equally hazardous

(Weis & La Velle, 1991, Weis, 1994, Swine model)



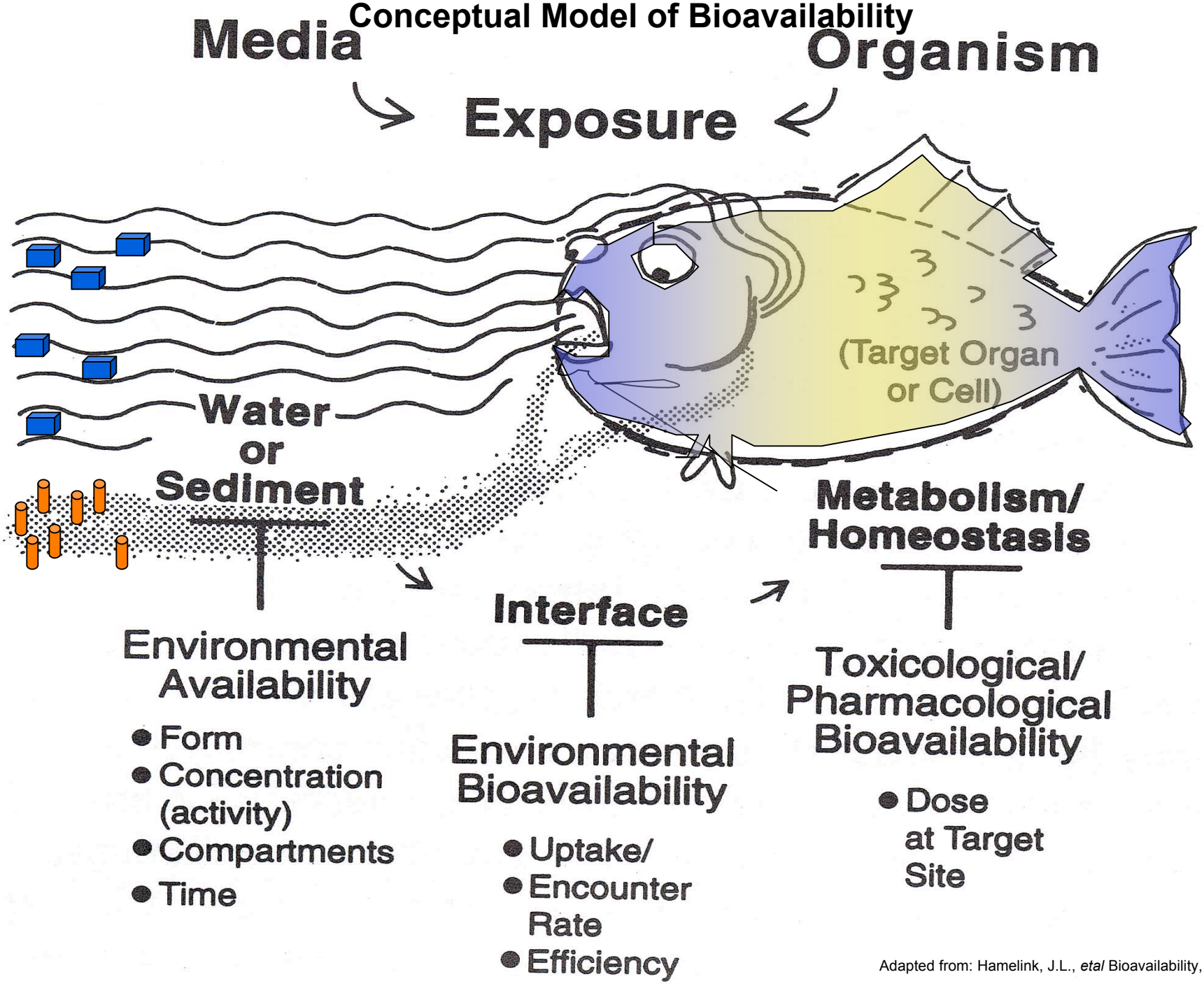
Bioavailability

is not an intrinsic property of compound (contaminant), rather bioavailability reflects the response of a biological system to many integrated processes

Factors Affecting Bioavailability

- Inorganic Contaminants
  - **Water chemistry**
    - pH
    - Dissolved ligands
      - Carboxylic / phenolic
      - Hardness (Ca, Mg),
    - Free metal conc
- Organic Contaminants
  - Water chemistry
    - Structure-activity relationships
    - Partition coefficient
    - pH
  - Solid Phases
    - Partition coefficient
  - **Solid phases**
    - Aerosols
      - Chemical form
      - Size of particulates
    - Food
      - Size of particle
      - Diet
    - Sediments
      - Ability to partition into water
      - Ingestion of solids by benthic species

Conceptual Model of Bioavailability



Adapted from: Hamelink, J.L., *etal* Bioavailability, 1994

Tools to Estimate Bioavailability

- Equilibrium Partitioning
- Bioassays
- Field measurements of body residue
- "Biomimetric Approaches" –physical chemical measurements that will measure the expected bioavailable fraction
  - **_In-situ_ passive sampling devices**

Passive Sampling Devices:

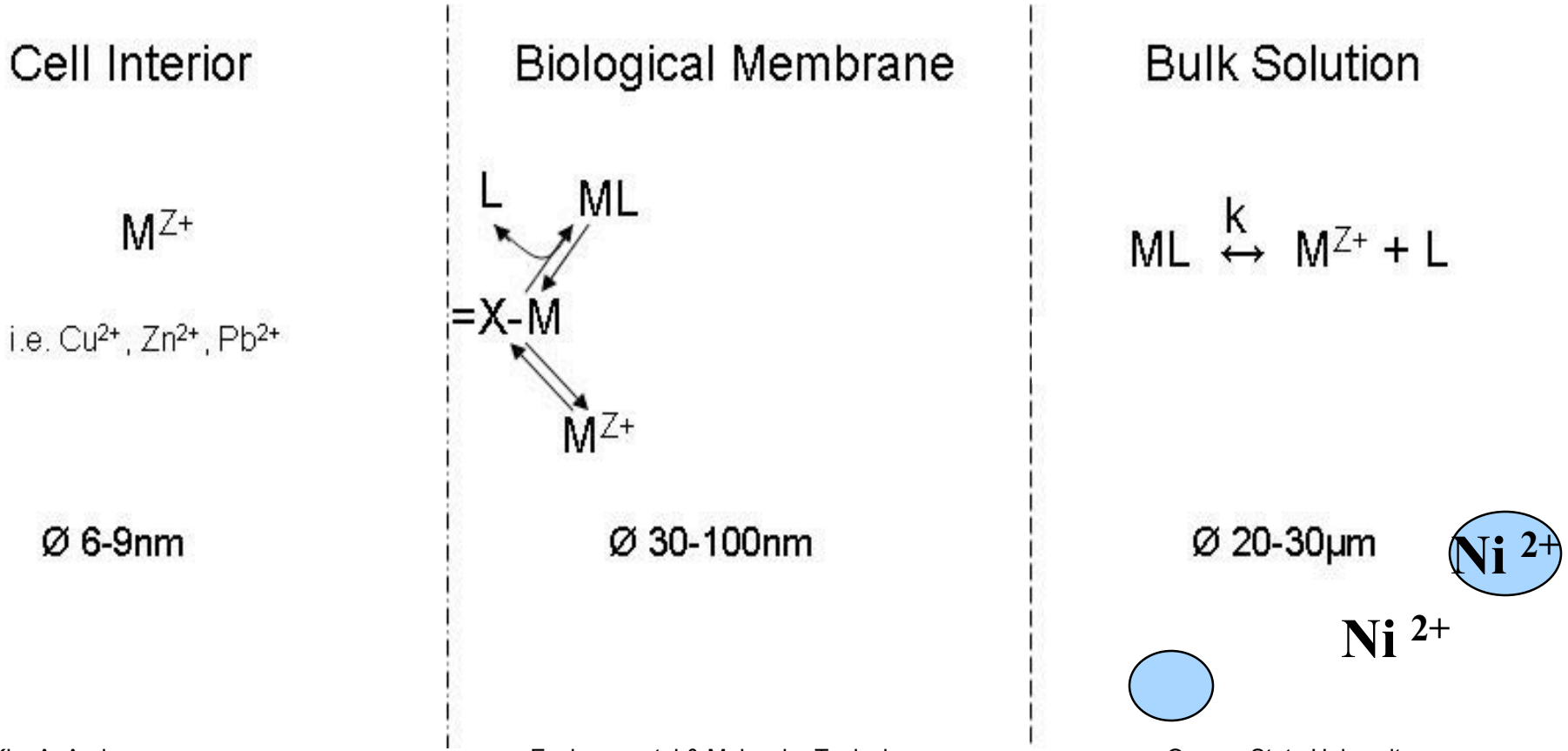
- **pros:**
  - some comparative data
  - iterative (captures episodic events)
  - composite without mechanical equipment
  - analytically easy
  - no seasonal issues with PSD
  - very low detection limits possible with relative analytical ease

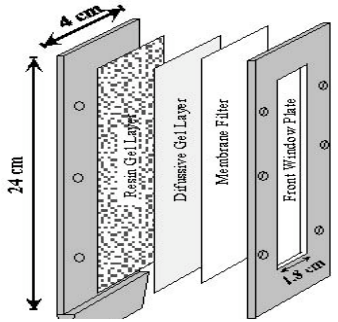
- **cons**:
  - not all species correlate directly with PSD
  - not as much comparative data as grabs
  - concentration must be calculated

- **issues:**
  - mimics biological
  - not as many negatives as organisms with more positives than grabs
  - *in-situ* extraction of contaminants that are most biologically relevant

Dissolved (Free-ion activities) of metals determine the biological effect and toxicity = Bioavailable

Ni^{2+} + Ligand (e.g. Organic matter, anion) -----> NiL





Schematic of DGT mimic of metal availability for biological accumulation

DGT -bound

Membrane

Bulk Soil Solution

Concentration

Chelex resin

Diffusive gel

DBL

Solution

C

Ni2+
Cd2+
Pb2+

Ni 2+

Δg

δ

Distance

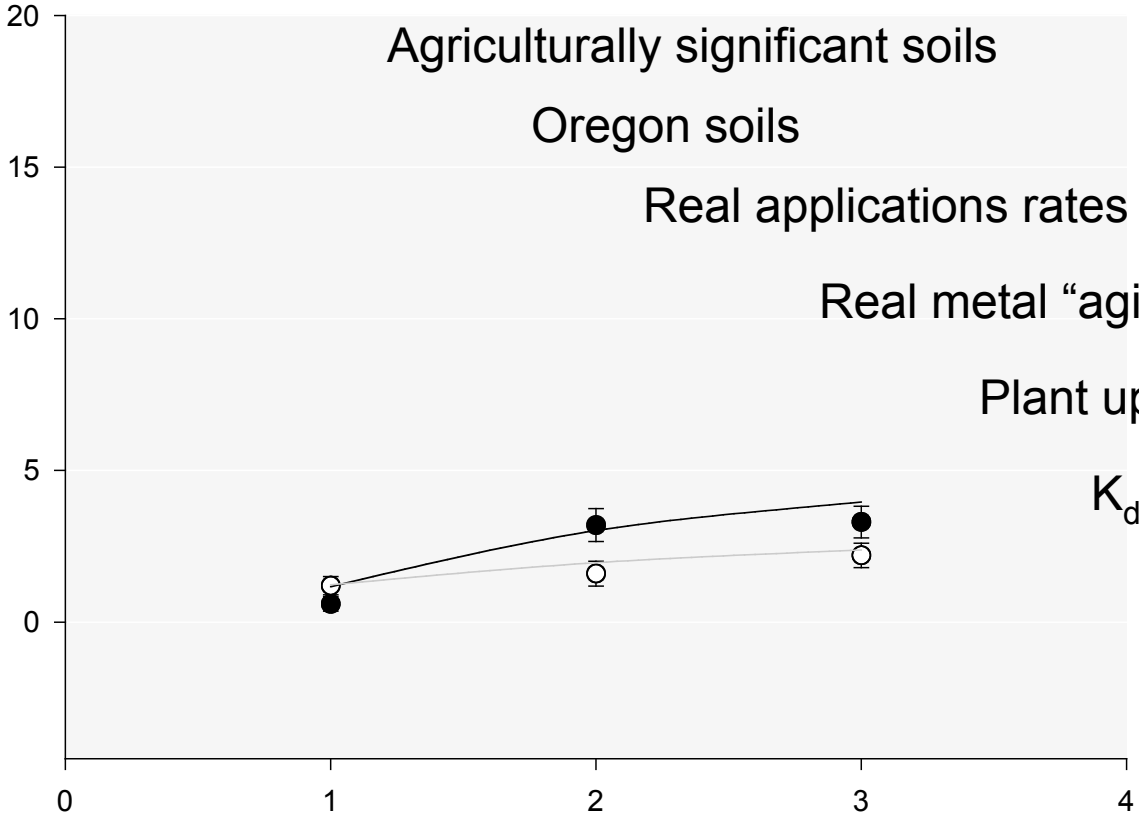
Goal of Bioavailability Analysis

- To reduce uncertainty in exposure estimates
- Thus improve the accuracy of risk assessment

Risk Prediction Framework

Conceptualized Lead Risk Assessment
Requires estimates of soil metal concentration,
similar fashion K_d (soil-to-water concentration ratio)
for each metal accumulated over time (site specific..)

Cross section of soil types



Agriculturally significant soils

Oregon soils

Real applications rates

Real metal “aging” processes

Plant uptake multi-crop

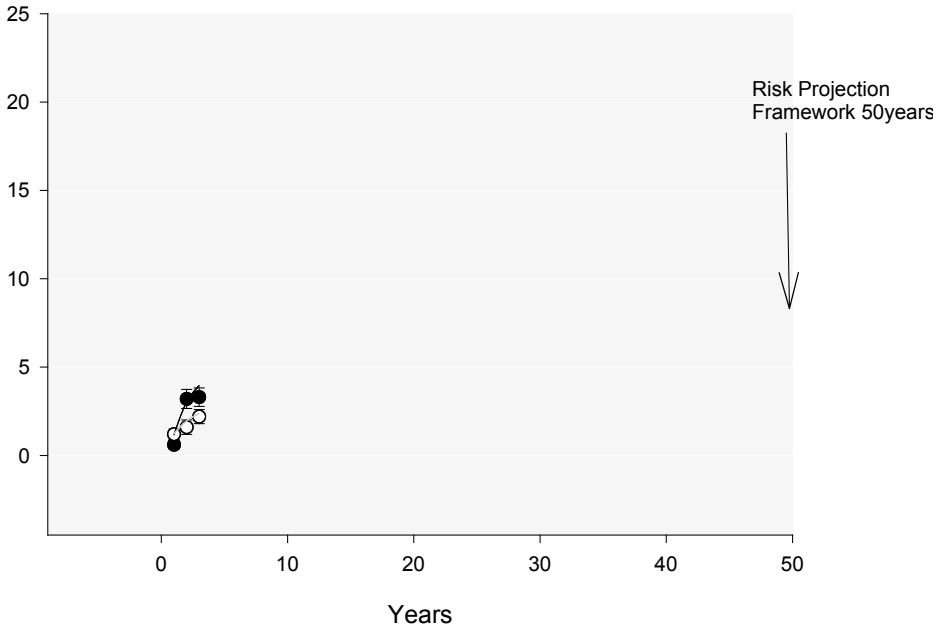
K_d and pore waters

Dose response

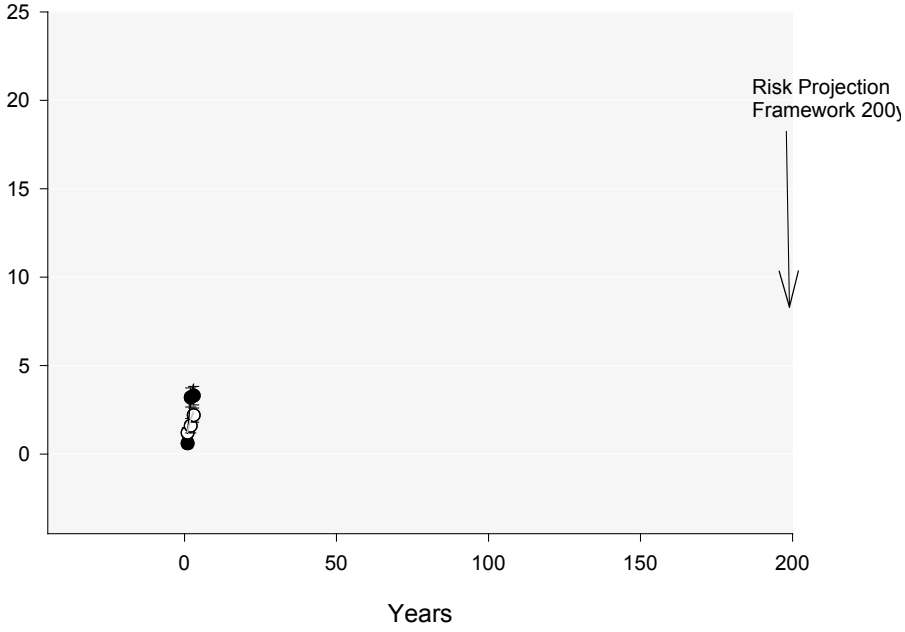
Bioavailable

Risk Prediction Framework

Risk Assessment
Requires estimates of soil metal concentration after 50 years



Lead Risk Assessment
Requires estimates of soil metal concentration after 200 years



Move forward, in the hope of what can be accomplished, and do not be held back by what can not be done.

Wherever there is forward movement, there is bound to be turbulence.