FINAL DRAFT:
SUMMARY OF MAJOR ERA FINDINGS FROM MITE-RN
(as of April 2002)

Sources

Measurement of background concentrations of metals to assess natural versus anthropogenic influences on metal budgets.

- Methods developed to differentiate natural from anthropogenic sources, e.g.:
  - A multi-faceted approach from experimental field design (size-fractionated concentrations, profiles, wind analysis) coupled with techniques such as statistical analysis on elemental concentrations, can help to identify sources of metals at receptor sites
  - smelter particle morphology (modern and historical) promising for differentiation, especially when coupled with actual particle chemical composition
  - atmospheric particulate matter from a Cu smelter has distinct chemical characteristics – fingerprinting possible (e.g., differences in both lead isotope ratio - $^{206}Pb/^{207}Pb$ – and copper and lead chemical speciation)
  - Hg species in atmospheric samples can be separated and analyzed
  - metal-specific differences in metals in lake sediments occur with distance from a source
  - ^{210}Pb and ^{137}Cs chronologies are generally consistent, except possibly close to a major source

- Hg [only?] enrichment in surficial sediments of remote lakes related not just to atmospheric deposition, but also to diagenesis and affected by local perturbations (e.g., watershed sources from historic deposition, forest fires, beaver activity, [removal of dams?])

- Sulfate reduction may be a sink for metals in lakes near the sediment-water interface

Processes - Terrestrial

- In northern forest ecosystems, tree and shrub species dominating plant community biomass control trace metal dynamics

- Plant metal burdens greater than current atmospheric inputs

- Laboratory soil solution extraction method developed that produces results comparable to the field

- Root cycling, including rhizosphere, more important than foliar for soil metals

- Decomposing litter a sink for metals (metal-specific differences, primarily atmospheric inputs) but poor general predictor of metal returns to soil

- Lability of metals in soils influenced by source(s) (e.g., atmosphere, foliage, roots)

- A new protocol to estimate the total metal content in woody vegetation

- Metal concentrations in standing wood at contaminated sites increased by 10-fold compared to a reference site

Processes - Aquatic

- Dietary exposures can be predominant, and seasonal differences can occur (consider food chains)

- Food chain characteristics (components, lengths) influence metal bioaccumulation and effects

- Animalss feed selectively: measurements of metals in prey based on well defined taxonomic units are required for assessing relationships of metals in predators

- Species of the same genus can differ in metals accumulation

- Pharmacokinetics differ between water and dietary exposures (affecting BLM)

- Due to dietary uptake, results of water only bioassays can be misleading

- Behaviour (e.g., burrowing, irrigation) influences exposure, affecting bioaccumulation and toxicity

- Metal mobilization changes seasonally as sediment chemical environment (e.g., redox) conditions change

- Freshwater lakes can change from sinks to sources of metals depending on the chemical environment (e.g., oxic status)

- Possible wide-spread phenomenon: historical decreases in Cd^{2+} and H^{+} concentrations in acidic lakes but increased biota Cd concentrations (Cd and H ions compete for biological uptake sites) – emphasizes importance of biomonitors for ERA

- Cd concentrations can decline along food chains (biodilution); Hg does not always biomagnify

- Generalized speciation / fate model (TRANSPEC) has been developed applicable to most metals, most freshwaters (estimates of bioavailable fractions in waters and sediments)

- Methodology developed for determination of very low free metal ion concentrations – characterization and speciation

- ERA investigations need to consider natural horizontal and vertical sediment heterogeneity

- Revisions to computer thermodynamic models (e.g., HYDRQAL, WHAM) allow calculation of metal speciation in the presence of reduced sulfur species (RSS)

- Metal-RSS complexes not only dominate the speciation of many metals in anoxic waters (e.g., sediment interstitial waters, hypolimnetic waters), but can also be present in oxic surface waters. Methods for determining RSS and metal-RSS complexes have been developed (ERA must consider RSS re metal speciation in surface waters, especially where a continuous supply of metal-sulfide complexes exists)

- Zn-sulfide complexes are relatively stable in oxic waters and may account for a significant portion of dissolved zinc measured in surface waters.

- The distribution of sulfide (and hence of many metals) in sediment can be extremely heterogeneous both laterally and vertically; bulk sediment / porewater chemistry / bioassay may be inappropriate for ERA (sulfide concentrations and metal speciation changed by manipulations)

Impacts – Aquatic

- Chronic toxicity can be predicted from body burdens for a “laboratory white amphipod” for 10 metals / metalloids

- Organism-specific critical body concentrations (CBCs) provide useful screening-level predictors that are better than metal concentrations in water or sediment

- Mechanisms being elucidated for metals uptake by trout and yellow perch; the mechanisms appear common but sensitivities differ

- Metals uptake and elimination by fish affected by nutritional status (ERAs must consider feeding regimes and growth rates); may not be true for all invertebrates (e.g., *Hyalella*)

- Food chains can change in metal contaminated waters (e.g., dietary Ca protects against Cd uptake; dietary Na reduces Cu uptake) – ERAs must consider such possibilities

- Simplified food webs (e.g., from metal pollution) reduce efficiency of energy transfer (e.g., reduced growth of predators)

- Many implications to acute and chronic BLM development for both fish and invertebrates (e.g., dietary uptake, water chemistry, tissue burdens, species differences)

- A single BLM may not work for ERA (e.g., differential sensitivity – rainbow trout and yellow perch) but can probably be adjusted for multiple species by relatively simple procedures (e.g., adjustment of the LA50 parameter) as mechanisms of toxicity appear to be the same between species.

- Tissue specific bioaccumulation in fish not useful in ERA unless trophic status is known, because of the confounding effects of food ration and growth rate

- Metals can influence quantity and quality of fish forage food resources directly and indirectly (selective feeding) -ERAs must consider both bioenergetics and protection of key prey species

- Metal additivity may be worst case; less than additivity also possible

- Classic metallothionein spillover model may not apply to chronic exposures

- Inorganic Hg from typical geological sources (e.g., HgS - cinnabar) may be poor substrate for methylation, based on observed low bioconcentration / biomagnification of methylmercury in such environments

- In loons, neutrophil phagocytosis (one measure of immune function) is not negatively affected by environmentally relevant range of blood-Hg concentrations

- Improved estimates of Hg toxicity thresholds for diets and tissues of wild avian species

- Assumption that all Hg in fish-eating wildlife tissue (e.g. - liver, kidney, brain) is methylated and toxic may be incorrect due to demethylation and production of Se-Hg complexes that are less toxic than methylmercury.

Impacts - Terrestrial

- Applicability of Environment Canada's terrestrial toxicity methods determined for forest soils (only minor modifications necessary)

- Toxicity determined for contaminated forest soils (plant, earthworm and springtail)

ANTICIPATED HERA 2003 PAPERS

{Volunteer lead authors noted in green. Manuscripts (minimum 2-3,000 words) in format for the peer reviewed, international journal Human and Ecological Risk Assessment (www.aehs.com; journals; HERA; Instructions to Authors) to be provided to Peter M. Chapman via e-mail no later than December 1, 2002. After peer review, mss will be published in the June 2003 issue of HERA as a series of Commentary articles; Peter M. Chapman will provide a Perspective article that updates his previous white paper on ERA for metals. Note that additional or different titles and volunteer lead authors welcome – contact Peter M. Chapman. Note that titles and subject of any additional paper(s) must be similarly broad-scale. And finally, note that it is expected that each paper will involve multiple authors, ideally not only within research groups and disciplines, but also across these.}

1. "Differentiating Natural and Anthropogenic Sources of Metals to the Environment" Grant Edwards et al.

2. "Deposition and Mobilization of Metals in Freshwater Lakes" Richard Carignan et al. + Feiyue Wang

3. "Metals in Northern Forest Ecosystems" Bev Hale et al.

4. "Dietary Exposures to Metals in Freshwater Environments" Laurie Chan and Tony Scheuhammer (fish eating birds and humans); Landis Hare et al. (invertebrates and fish)

5. "Predicting Metals Effects in Aquatic Biota" George Dixon et al.

6. "Differentiating Between Direct (Physiological) And Food-Chain Mediated (Bioenergetic) Effects In Metal-Impacted Lakes" Peter Campbell, Alice Hontela et al.

7. "Factors Affecting a Freshwater Chronic BLM" Chris Wood et al.