Enhanced Mobility of Arsenic and Molybdenum in a Tailings Pond in Response to Nitrate Depletion

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Metal Leaching Mechanism

Depletion of nitrate in water cover

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Alternation to redox conditions in tailings porewater

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Decrease in diffusive path length for dissolved As+Mo

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Increased flux to water cover

Study Site: Equity Mine, B.C.

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- Equity Mine was operated by Placer Dome Inc. between 1980 and 1994, producing ore from three open pits and underground workings.
- Site is currently under care and maintenance by Goldcorp Inc. who acquired the site in 2006.
- Primary closure activities are associated with the collection and treatment of acid rock drainage (ARD).
- During mine operations, potentially acid generating mill tailings were discharged subaqueously to the Equity Silver Tailings Pond (ESTP).
- The ESTP also received sludge from the historic lime-treatment plant, as well as untreated acid rock drainage (ARD).

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Study Site: Equity Silver Tailings Pond

- Area = 120 ha
- Local catchment = 15 ha
- Water volume ≅ 5 Mm^3
- Mean water depth ≅ 4.5 m
- Residence time ≅ 5 yrs

- Materials in the ESTP represent a combination of relatively unaltered (sulfide) tailings and secondary phases (*e.g.*, gypsum, Mg-Al-Fe hydroxysulfate, Fe oxides) associated with:
  - Input of ARD neutralization sludge
  - Input of untreated ARD

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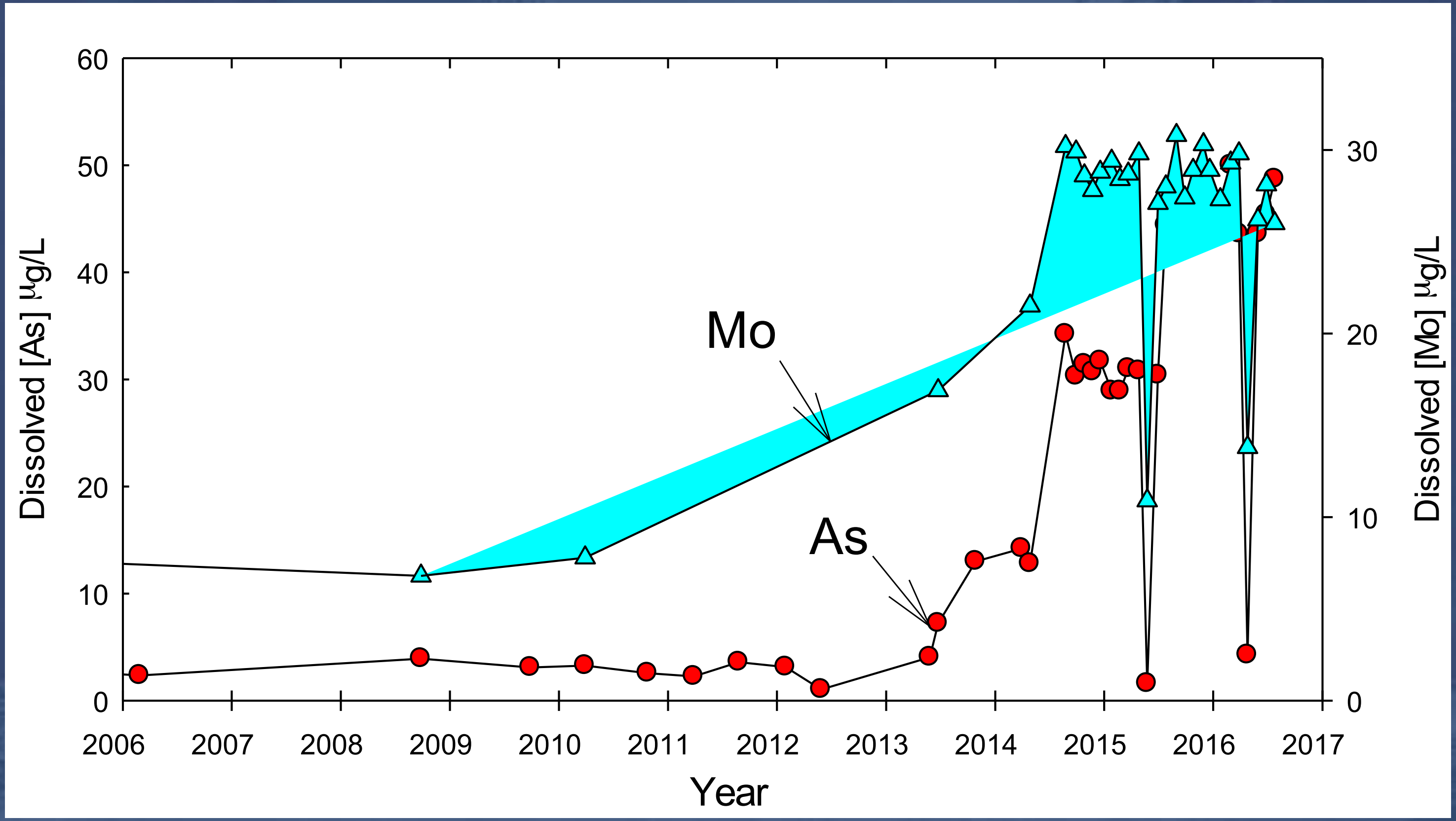
Problem Definition – Arsenic & Molybdenum

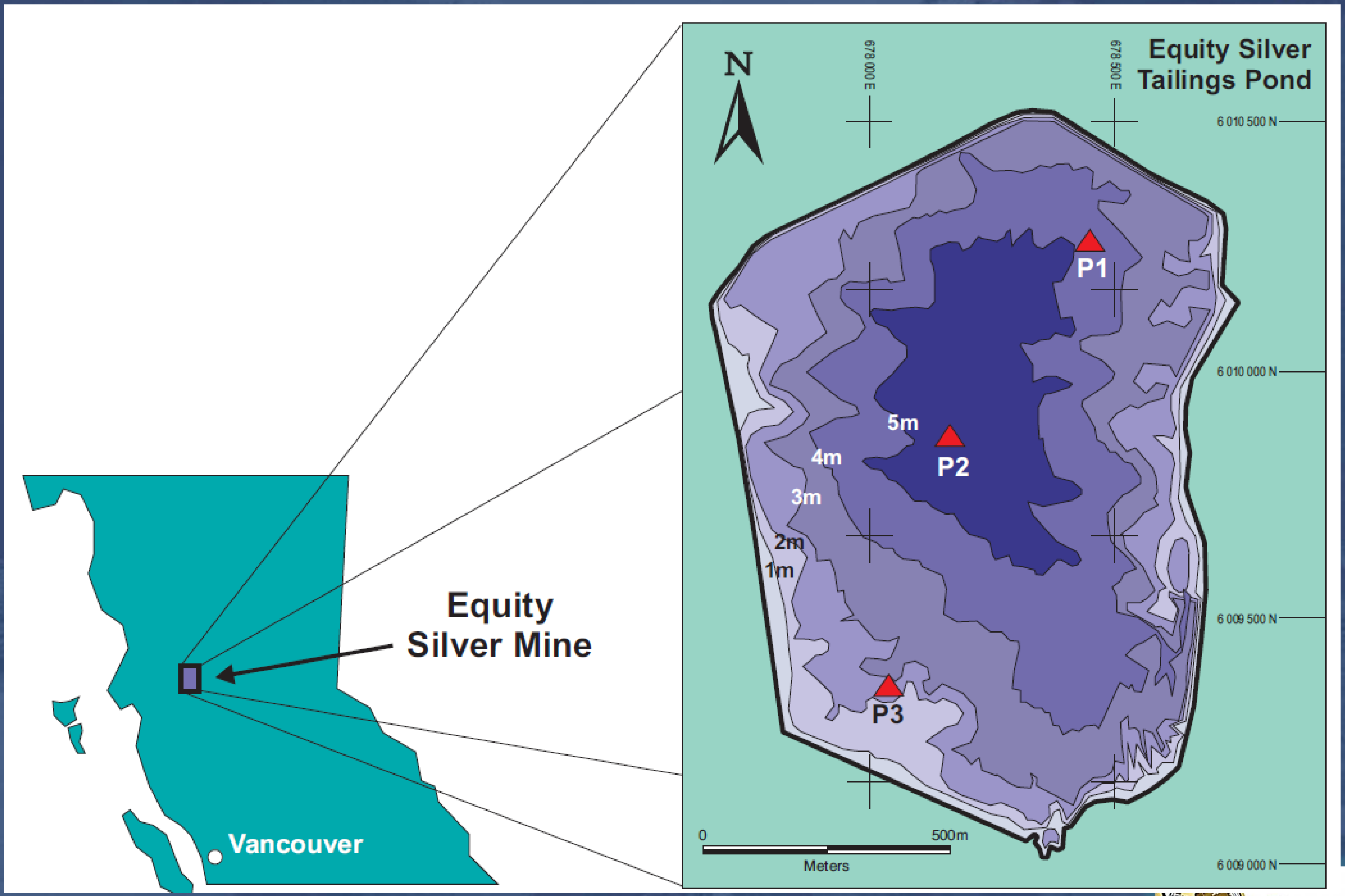


- Dissolved As and Mo concentrations in the water column show pronounced increases beginning in 2013.

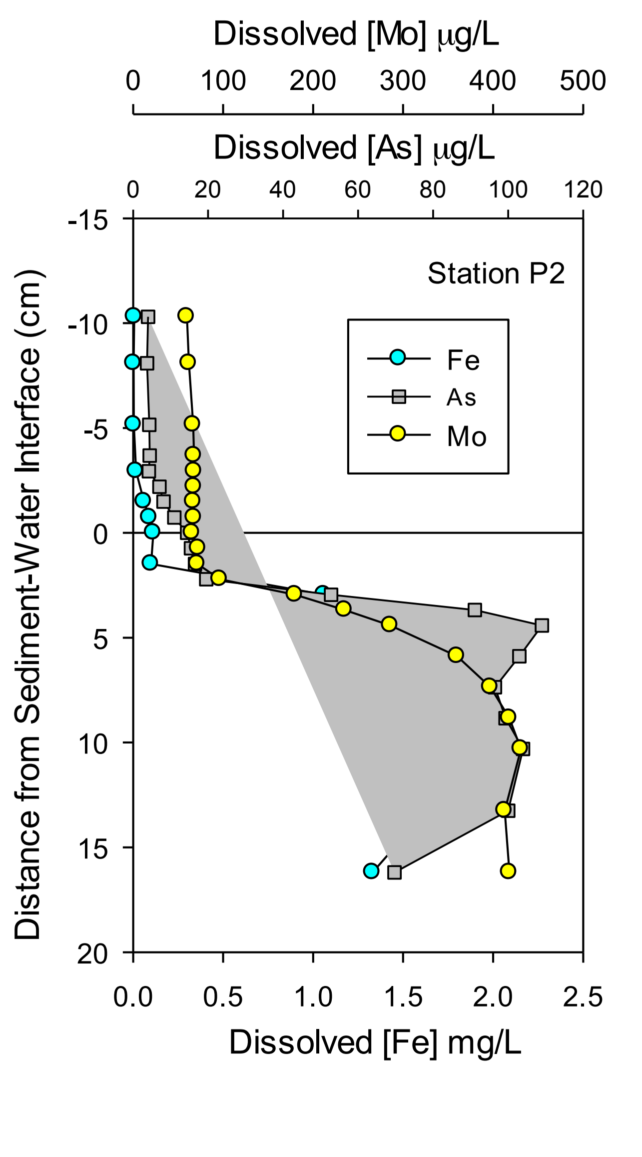
Potential Causes for As+Mo Increases

1. Water balance: Long-term changes in the amount of freshwater input to the ESTP.
2. Acid rock drainage and metal leaching associated with the oxidation of subaerially-exposed dam materials.
3. Desorption: The desorption of As+Mo from pond substrates can be influenced by changes in water composition (*e.g.*, pH, alkalinity)
4. Benthic redox conditions: As+Mo mobility is sensitive to changes in redox conditions in the submerged tailings materials.

Equity Mine
1999 Study of Equity Silver Tailings Pond



Redox Controls Governing As+Mo Mobility (1999 data)



- High resolution profiles across tailings-water interface show congruent increases of dissolved Fe, Mn, As and Mo in porewater.
- Remobilization occurring via reductive dissolution of Fe/Mn-oxides.
- In 1999: Remobilization occurred 3-5 cm below benthic boundary.

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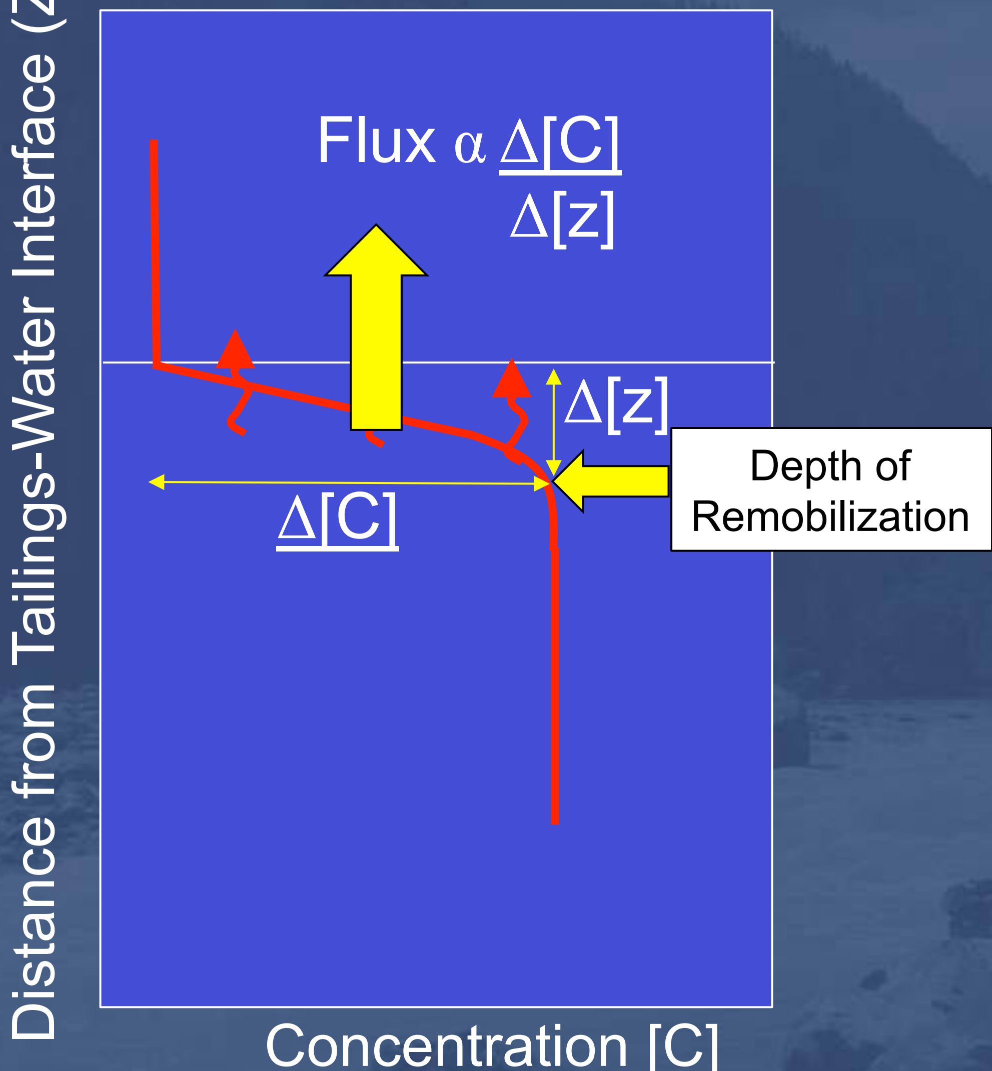
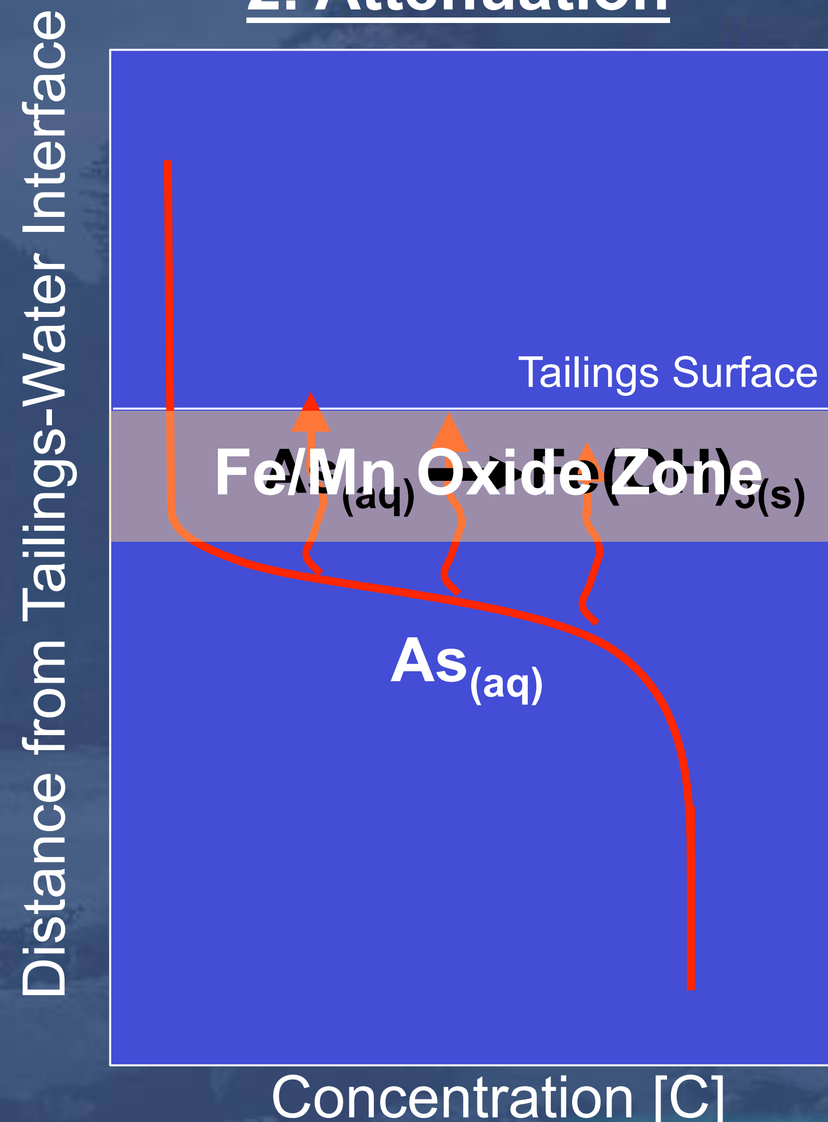
Importance of Depth of Remobilization

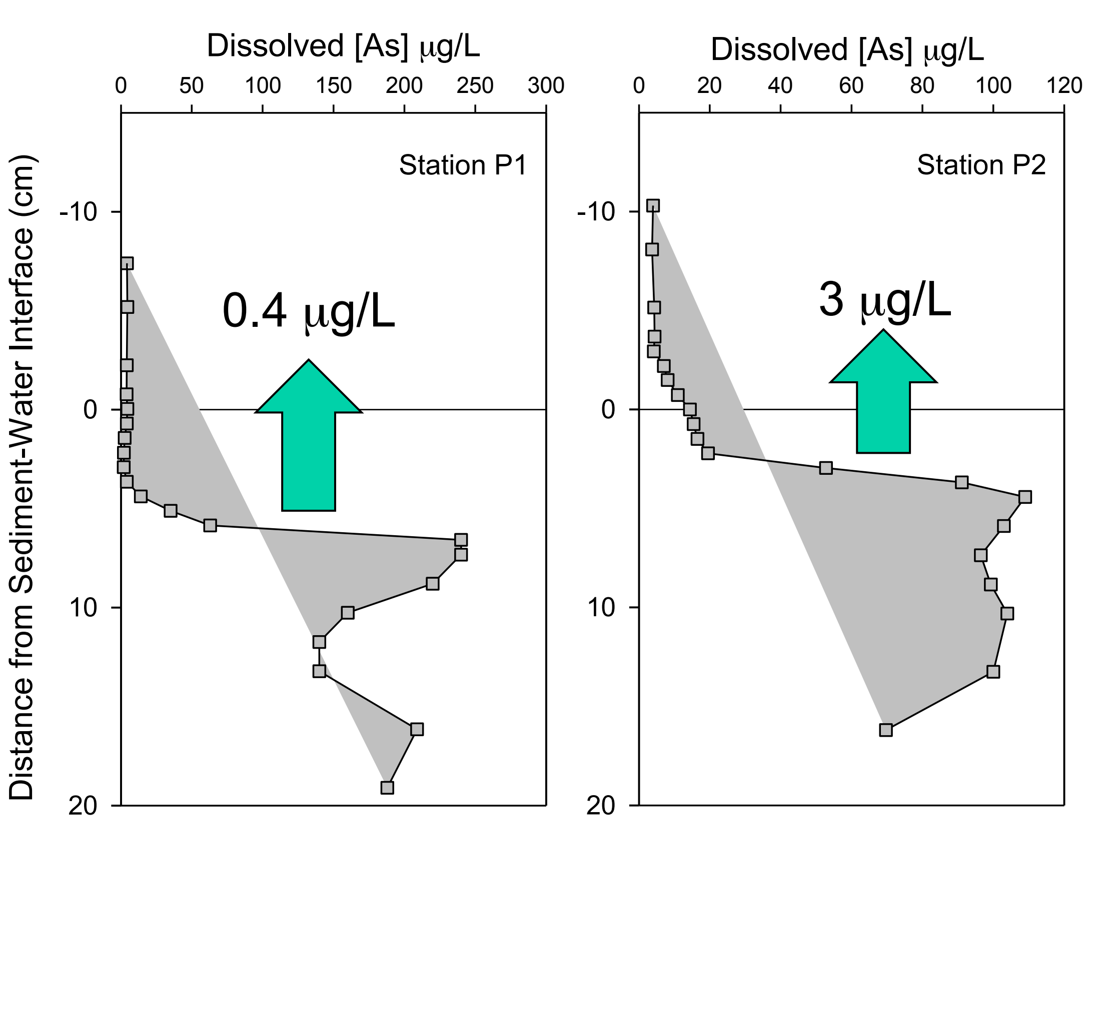
1. Diffusion



2. Attenuation



1999 Arsenic Fluxes to Water Cover



- Flux calculations for the 1999 profiles yield contributions of 0.4 and 3 μg/L to the water column.
- Predictions were within the range of observed values at that time (3-4 μg/L).
- Overall: minimal effect to water cover WQ in 1999.

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How Can we Increase the Rate of As+Mo Release from Submerged Tailings?

Promote shallowing of the depth of remobilization (Fe-III redox boundary)

1. Increase benthic oxygen demand

2. Decrease the availability of electron acceptors (e.g., nitrate)

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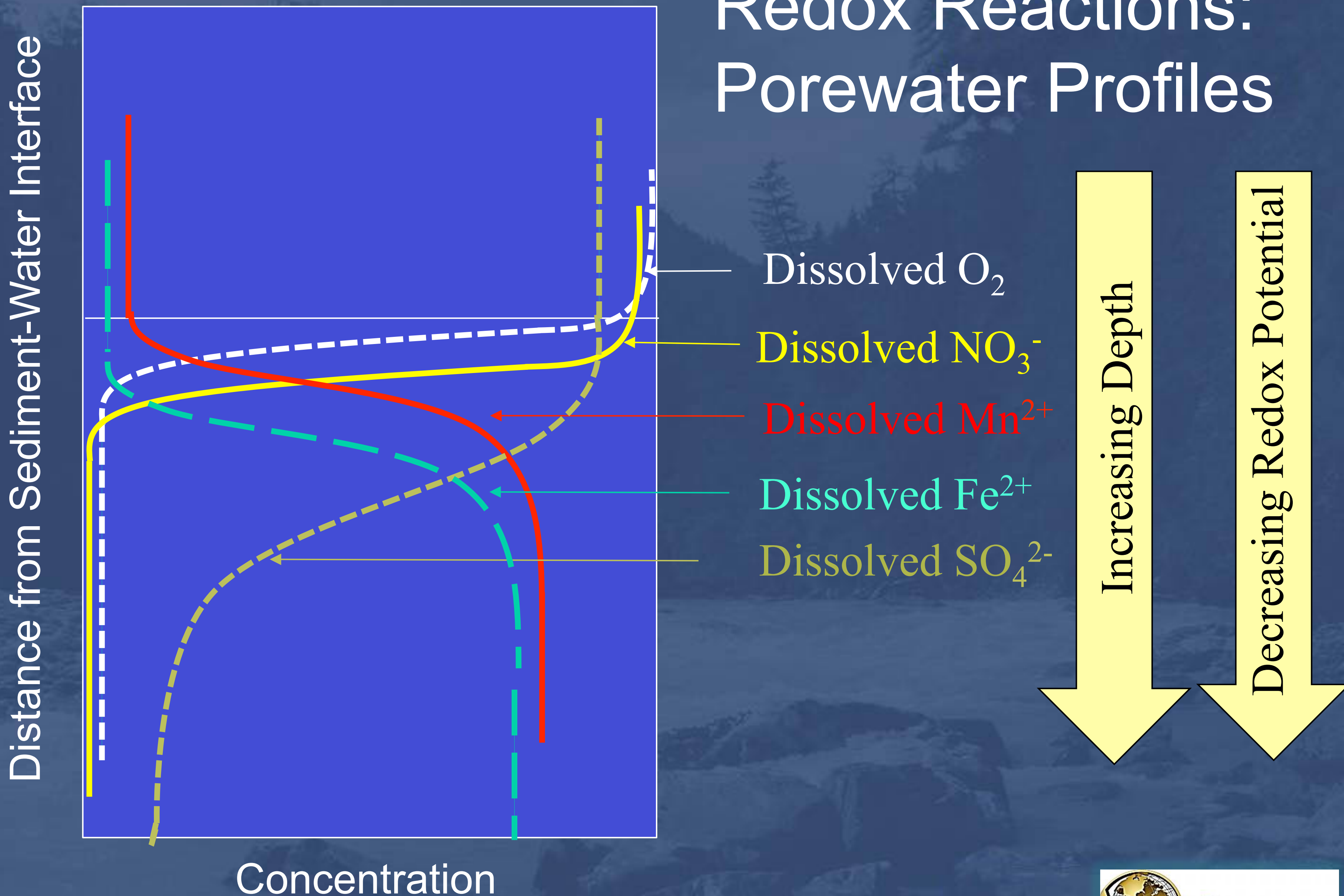
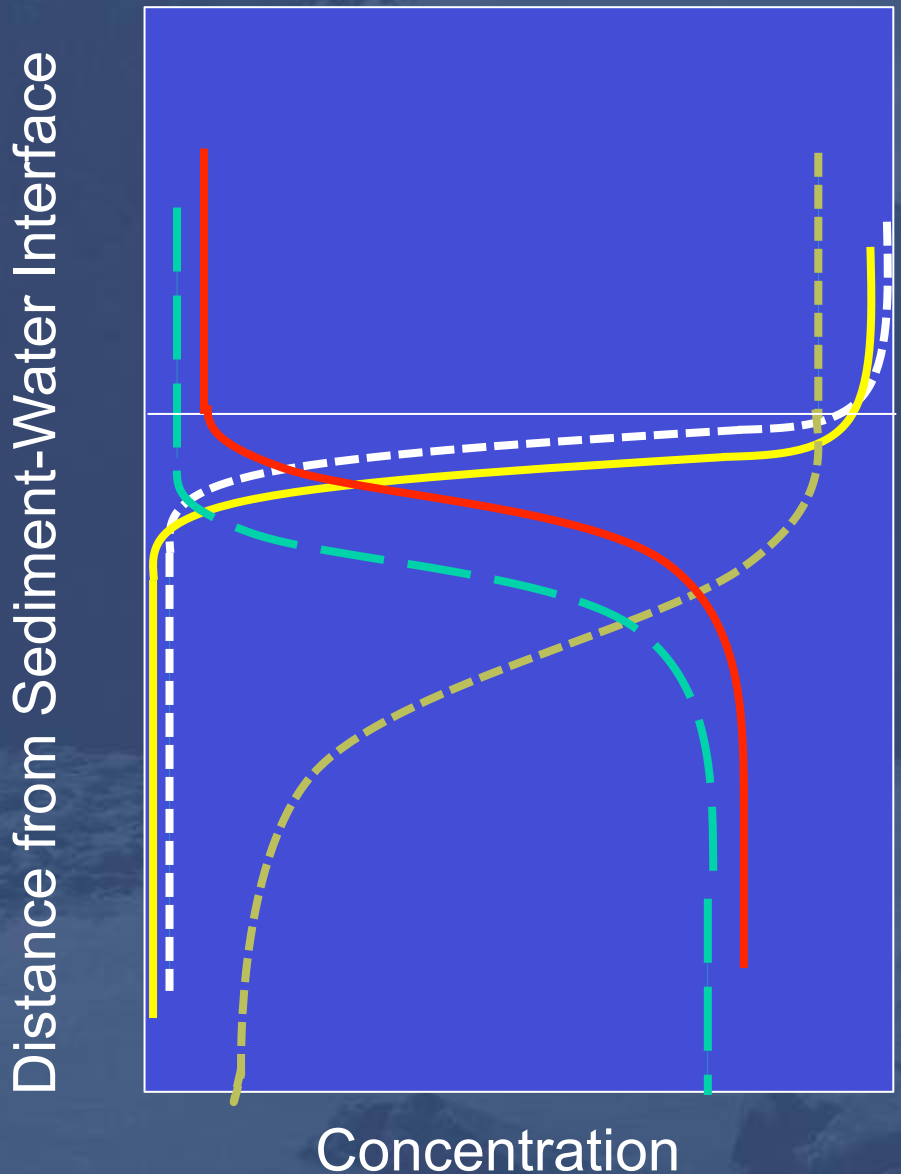
Oxygen Demand in Submerged Tailings

- Benthic oxygen demand is defined by the rate of oxidation of organic compounds.
- In the ESTP, organic matter can be in the form of:
  - Organic-based mill reagents
  - Organic matter produce in situ through algal production
- Organic matter oxidation drives redox reactions.

Redox Reactions: Porewater Profiles



Diagenetic Rubber Band



- Sequence from O_2 reduction to SO_4 reduction in porewaters can vary from a few millimetres to a several decimetres.
- High oxidation demand = reactions are compressed.
- Low oxidation demand = reactions are expanded.

Oxidation Demand in the Equity Silver Tailings Pond

- Phosphorus represents a limiting nutrient for algal growth.
- No evidence of increasing phosphorus concentrations in ESTP.
- Hence, we can rule out changes in oxygen demand as a cause for the increase in As mobility.

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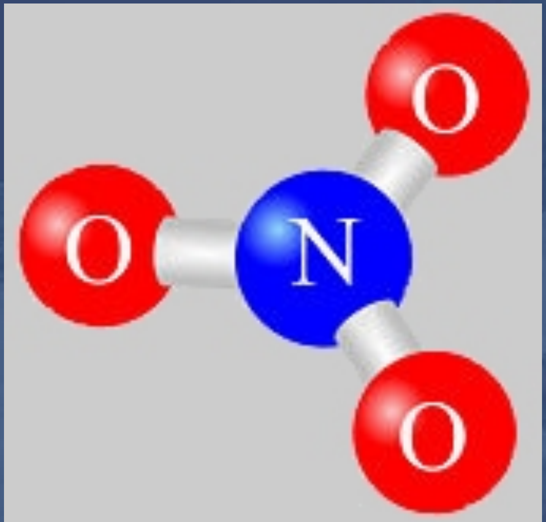
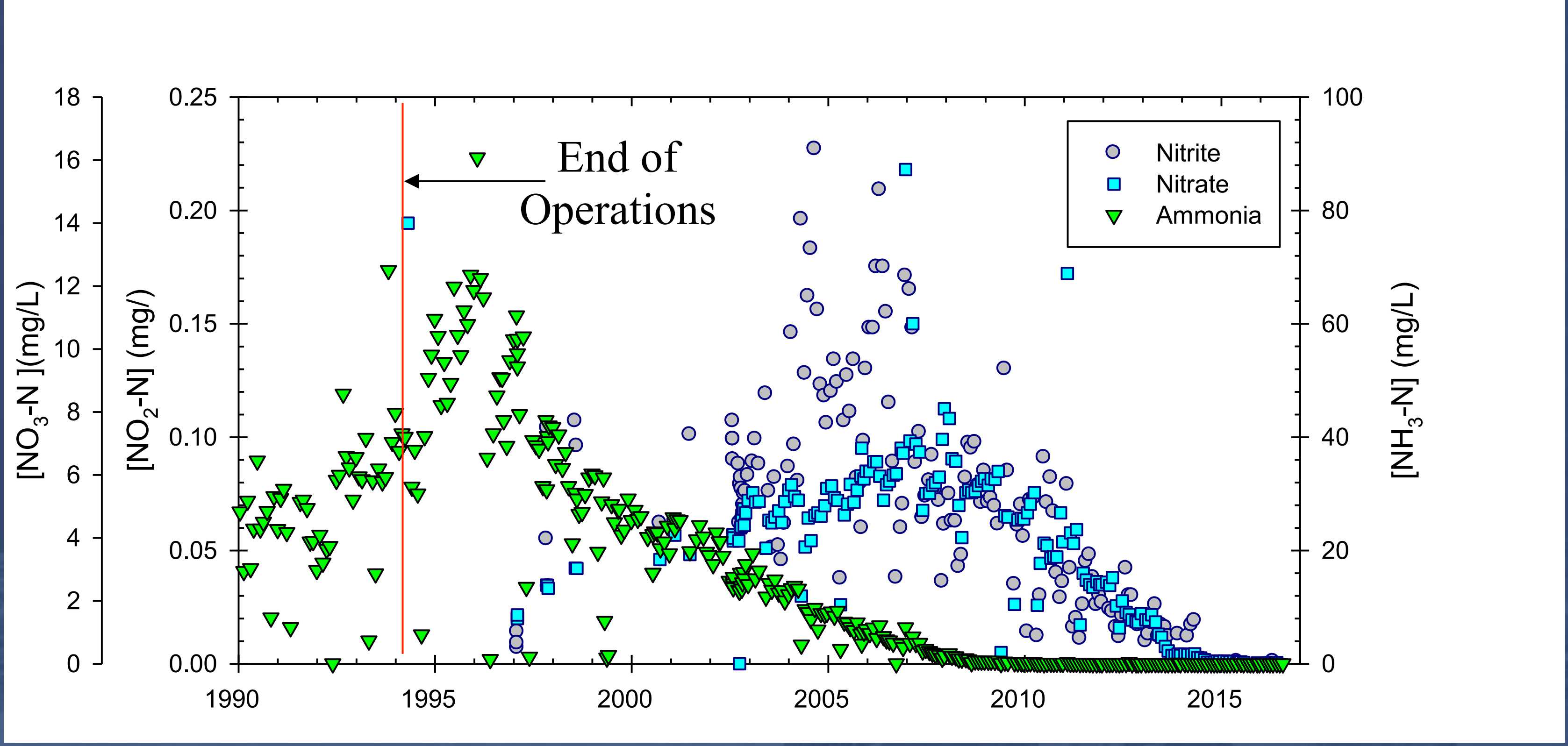
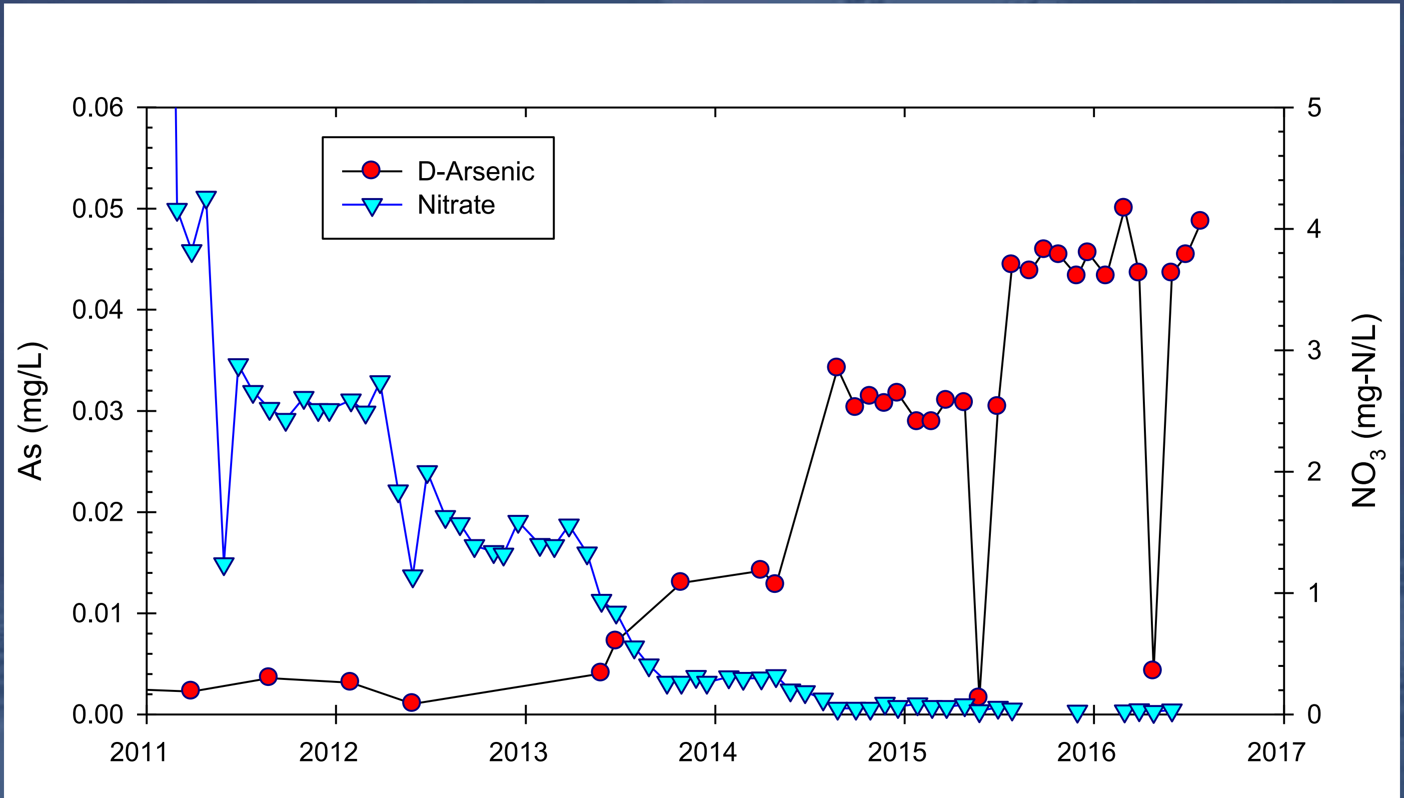
Finally, to oxidant availability and nitrate…….



Evolution of Nitrogen Species in ESTP

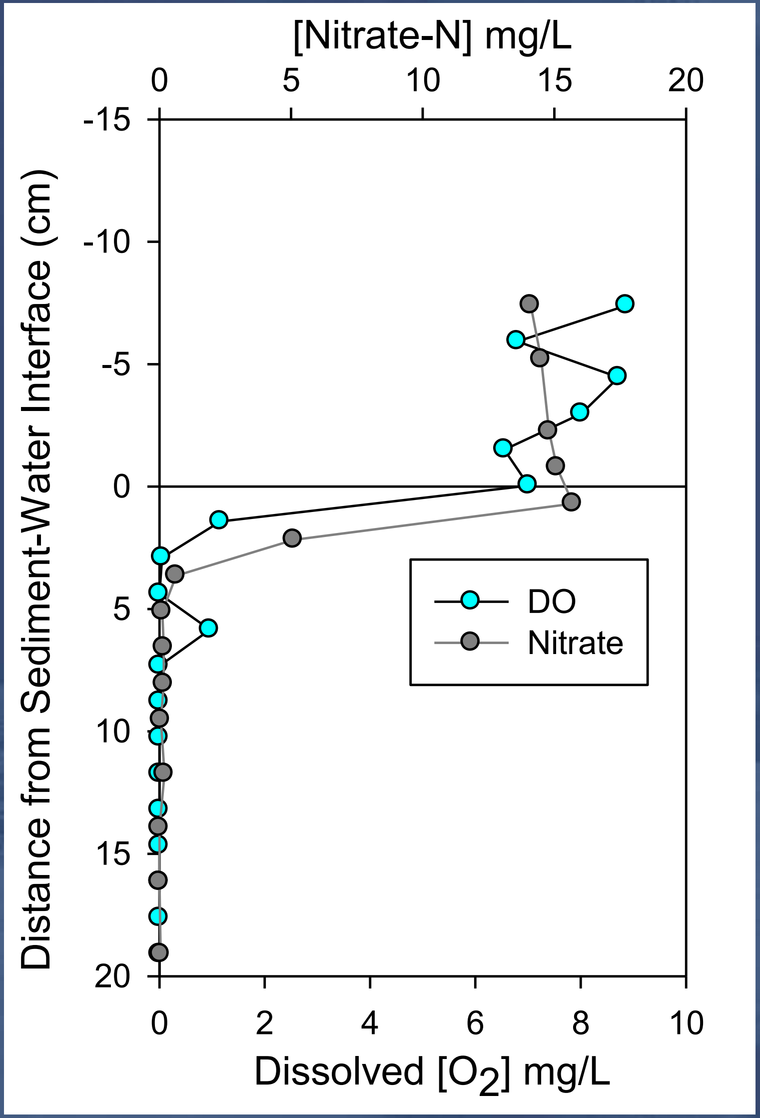


Nitrate Depletion in Water Cover linked to Increase in As+Mo mobility



- Nitrate depletion occurs as a result of dilution, biological uptake and denitrification in shallow porewaters.

Role of Denitrification



- In 1999, denitrification was a dominant redox pathway in near surface porewaters.
- Denitrification was occurring between 3 and 5 cm below benthic boundary.
- This served to maintain the depth of Fe(III) reduction below a depth of 5 cm.

Denitrification = “Microbial” or “thermodynamic” diffusion barrier to As release

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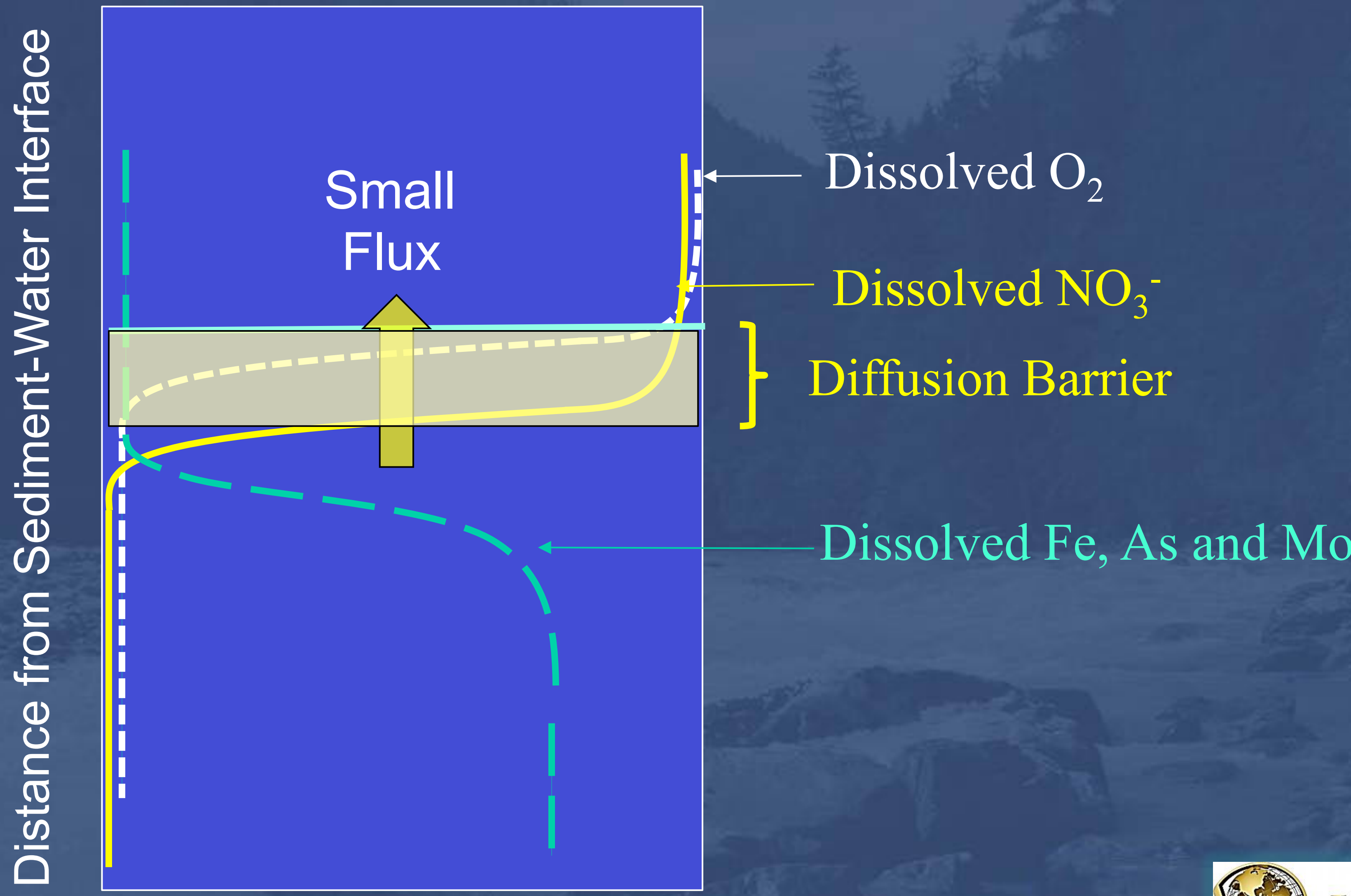
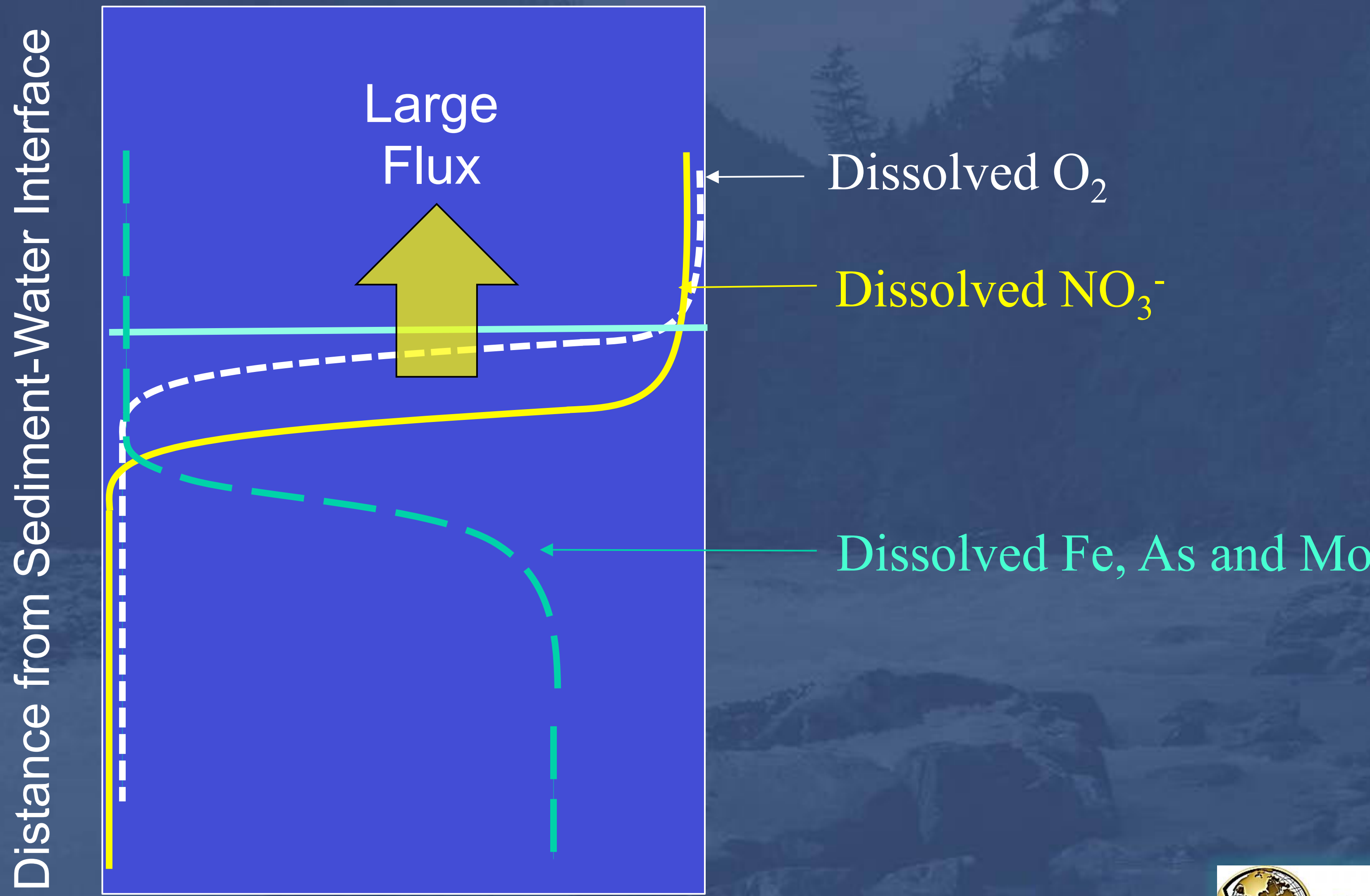
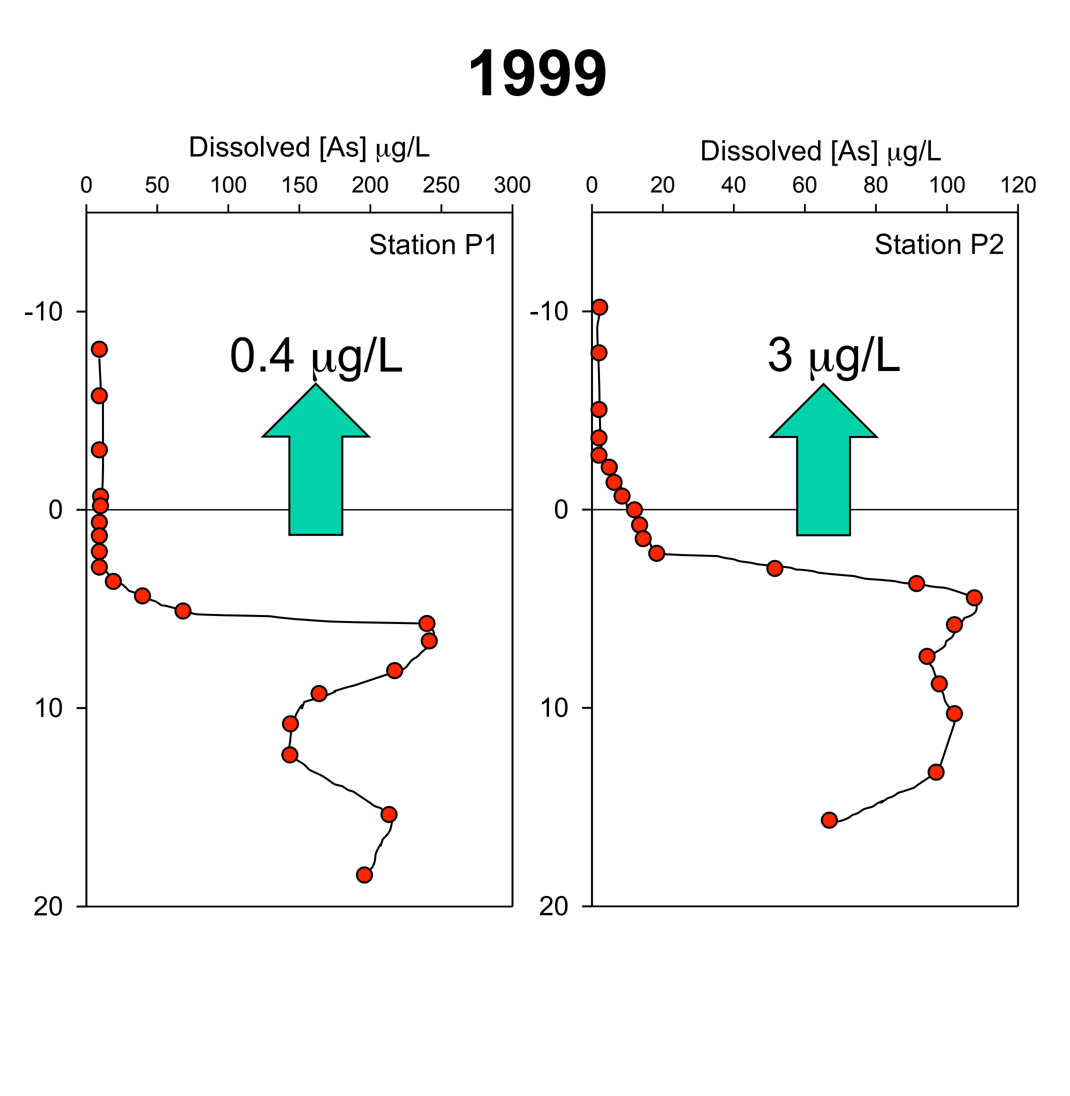
Conceptual Model for As+Mo Release: Abundant Nitrate in Water Cover



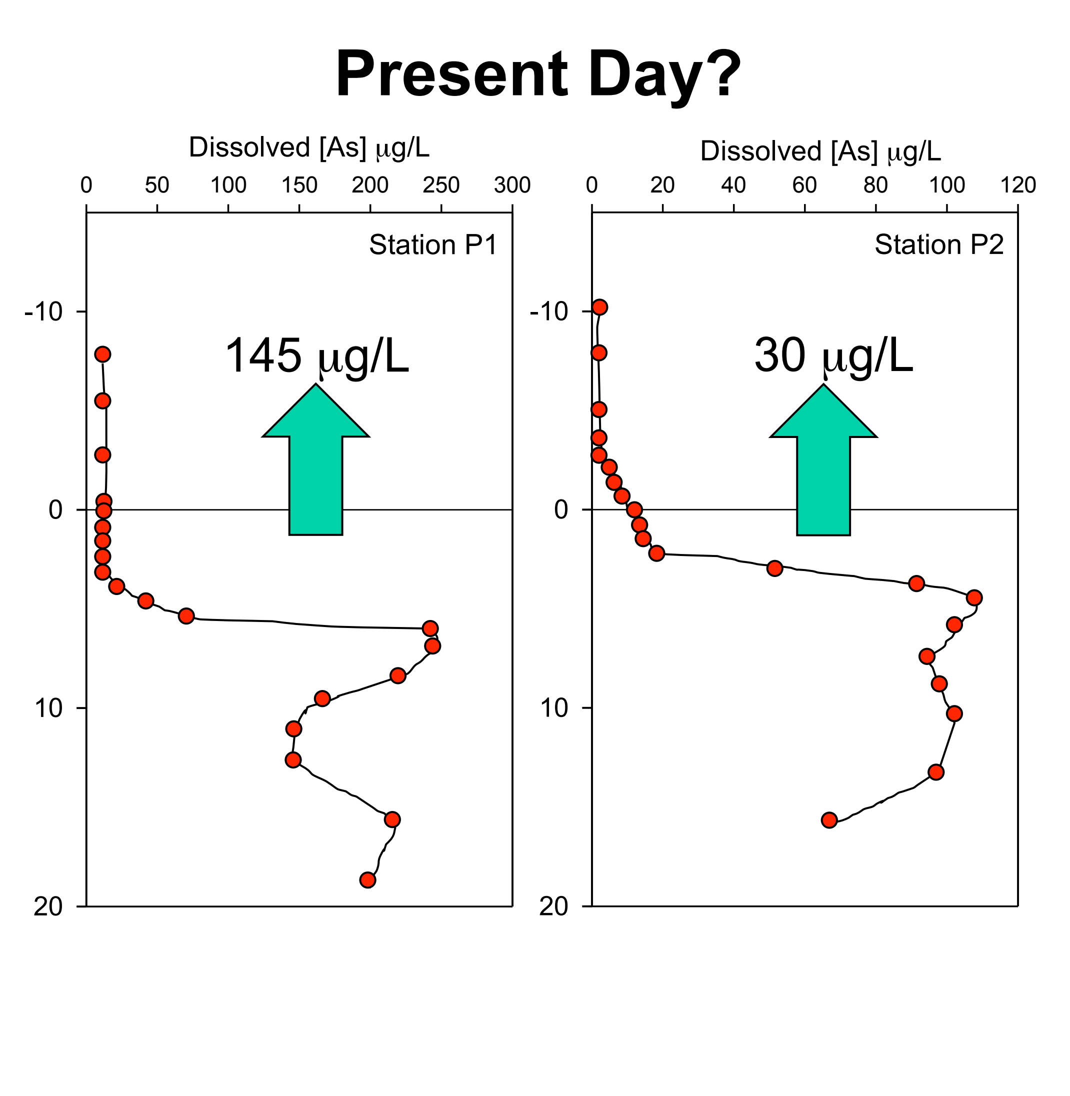
Conceptual Model for Arsenic Release: Nitrate Depleted in Water Cover



Flux Calculations



Arsenic Flux Calculations



- Allowing a shallower depth of remobilization, modified fluxes yield contributions of 145 and 30 µg/L to the water column.
- Predictions are within the range of observed values in 2016 (~50 µg/L).
- Data suggest, in theory, diffusive transport can account for current As inventory in water cover.

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Summary

- In mine settings, nitrate can serve as a dominant electron acceptor in submerged mine wastes.
- When nitrate is abundant, denitrification in near-surface porewater can act as a diffusion barrier, limiting the release of elements associated with Fe/Mn-oxide reductive dissolution.
- Upon nitrate depletion (<1 mg/L), Fe/Mn-reduction pathways can move closer to the benthic boundary, potentially leading to increased loadings to water cover.
- Pre-requisites:
  - Shallow water cover
  - Redox-sensitive solid phases
- Understanding cyanide/nitrogen cycles is key
- <u>**Diffusion-driven transport processes can be important**</u>

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Thank You!

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