Understanding the potential for environmental impacts

speciation and toxicity of REEs

CREEN - Canadian Rare Earth Element Network

BioMET
TRIVALENCE } - Collaborative Research Initiatives

Jim McGeer
Wilfrid Laurier University
Aug 16, 2016

LAURIER
Institute *for* Water Science

Canadian REE Sector Initiatives
… an update

Ian M. London P. Eng, MBA

August 3rd, 2016

Benefits on Sector and International Collaboration

- Meeting & working with industry, academia and policy leaders in processing, downstream applications, market and technology development intelligence builds shared vision to establish Canadian REE mining and processing
- Potential to influence international standards to reflect national interests, including environment
- Participation across organizations, be it on committees, in presenting & reviewing papers and participation on other committees leverages knowledge, know-how and dollars in seeking needed solutions
- Engages new grads/post grads for future employment

Rare Earth Standards

International Organization for Standardization

Created 2015 at the initiation of Standardization Administration of China (SAC)

Scope:

Standardization in the field of rare earth ores, concentrates, metals, alloys, compounds, materials, including the reuse and recycling of waste rare earth products.

Term: three to five years

Inaugural Meeting: October 11^{th} & 12^{th}

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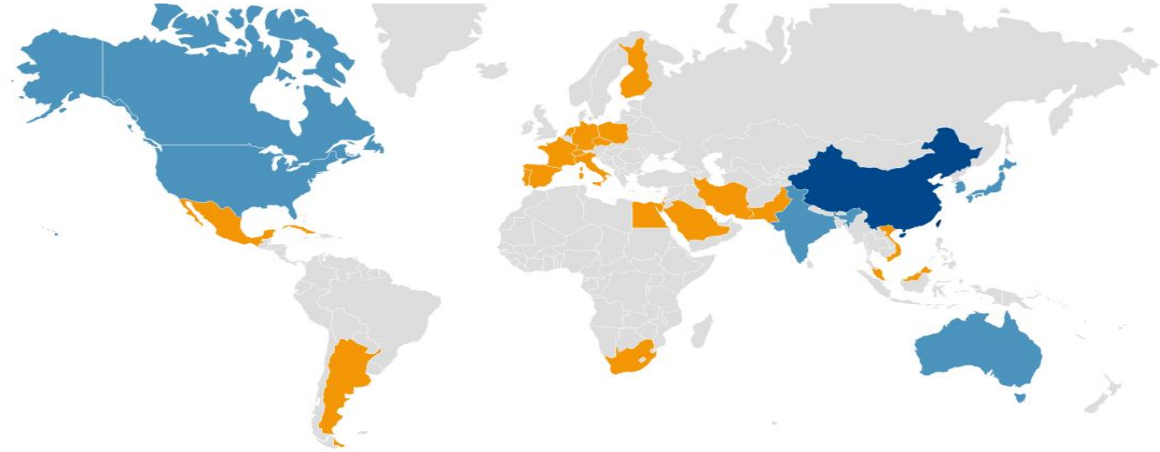
ISO TC298: Member Countries

Participating Countries
Australia (SA)
Canada (SCC)
China (SAC)
India (BIS)
Japan (JISC)
Korea, Republic of (KATS)
United States (ANSI)

Observing Countries		
Argentina (IRAM)	Israel (SII)	Portugal (IPQ)
Cuba (NC)	Italy (UNI)	Saudi Arabia (SASO)
Czech Republic (UNMZ)	Malaysia (DSM)	Singapore (SPRING SG)
Egypt (EOS)	Mexico (DGN)	South Africa (SABS)
Finland (SFS)	Netherlands (NEN)	Spain (AENOR)
France (AFNOR)	Pakistan (PSQCA)	Switzerland (SNV)
Germany (DIN)	Poland (PKN)	Viet Nam (STAMEQ)
Iran, Islamic Republic of (ISIRI)		

ISO/TC 298 - Rare earth



Canadian ISO TC298 Mirror Committee

- Canadian Mirror Committee to come to consensus on the Canadian positions relevant to REEs and submit them
- Canadian Mirror Committee members include: CREEN (chair), NRCan/CANmet (vice-chair), Avalon, Independent Consultants, Matamec, SGS,UBC, Quest. (Administrator – CSA Group)
-

Research Lecture Series

The objective of this Research Lecture Series (RLS) is to inform and educate students, researchers, policymakers and military leaders about rare-earth supply chains, the science and engineering underpinning the the supply of rare earths and the materials and systems that rely on the special properties that rare provide.

Dates and Locations

- January 19-20, 2017: Seville, Spain
- March 16-17, 2017: Munich, Germany
- April 29-30th, 2017: Montreal, Canada
- Two NATO planning/logistics centres (Brussels, Pittsburgh)
- Other institutions on request (documentation to be made available to NATO Member country institutions)

Target Audiences…

- Students, geologists, process engineers, materials scientists and engineers, policy makers, military decision makers and leaders

International Lecturer Team

- Introduction and Course Coordinator -- Gareth Hatch
- Current REE-Enabled Materials and Technologies -- Ian London, Victorino Franco
- Supply Chain Challenges -- Dudley Kingsnorth, Rod Eggert
- Geology and Resources -- Bill Mercer, Rod Eggert
- Mining and Mineral Processing -- Corby Anderson, Jane Pagu
- Primary Extractive Metallurgy -- Jane Pagu, Corby Anderson
- Components and Assemblies -- Francis Johnson
- Reuse and Recycling -- Alain Rollat, Oliver Gutfleisch
- Next Generation Materials and Applications -- Michael McHenry, Victorino Franco

- Quebec City September 11th -15th, 2016
- IMPC convenes every two years in different countries (Buenos Aires 2014; Moscow 2018); Draws world's leading mineral processing exponents to promote, network, discuss and reveal latest advances in the science; Publishes proceedings on state of the art in mineral processing.
- 56th Conference of Metallurgists, hosted by MetSoc/CIM; REE Symposium inaugurates at COM2012; In 2016 – 58 peer edited REE papers

IMPC 2016/ COM16

- Future ‘REE Symposia’ to be reframed to ‘Energy of Technology Materials’… REEs, Lithium, graphite, cobalt, indium, gallium, vanadium, scandium, etc…
  - Resources for Future Generations
    - June 2018 in Vancouver
      - in collaboration with UK’s SOSRare project
  - Extraction 2018
    - Summer August 2018 in Ottawa
      - in collaboration with TMS… tba

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Natural Resources Canada / Ressources naturelles Canada

Canada

REE R&D Initiative

- April 2015, Federal Budget included $23 million over 5 years for REE/Chromite R&D Initiative… to be Industry-led and NRCan delivered; Approx 2/3 of budget to focus on REE priority issues as identified by Industry Steering Committee; FY 2016-2017 REE budget $2.6 million
- Approx 1/3 of annual REE expenditures to be contracted with academia & industry experts

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Year 1 Achievements and Reports

- Resources, Mineralogical Characteristics & associated metallurgical data for advanced Canada REE projects (2016) – SGS
- LitRev… Naturally Occurring Radioactive Materials (NORM) & Their Implications for Developing Canada REE Industry (2016) – Golder Associates Ltd.
- LitRev… Secondary Sources of Rare Earth Elements (2016) – Golder
- LitRev… Potential Ecotoxicological Effects Arising from Rare Earth Element (REE) Processing (2016) – Golder
- Review of the Leaching & Separation Challenges for Canadian REE Projects (2016) – Expert Panel
- Summary Report of A Review of the Leaching and Separation Challenges for Canadian REE Projects (2016) - NRCan
- LitRev & Gaps Analysis… REE Metallurgical Extraction Methods (2016) – SGS Canada
- Review of Separation Technologies for REE, Techno Economic Analysis and Gaps (2016) – Laval University
- Global REE Industry: A review of market, production, processing & associated environmental issues (2016) – NRC
- LitRev… Concentration of REE through Flotation Processes (2016) – Laval University
- Study of Coarse Ore Pre-Concentration & Potential Applicability to Canadian REE Deposits (2016) – J.R. Goode
- Rare Earth Elements: 2015-20 Demand/Supply Forecast (2016) - NRCan
- Mines to Markets: Natural Resources Canada REE Technical Workshop Summary Report (2015) – NRCan
- REE Characterization: Linking mineralogical variation to leaching and flotation performance (2016) - NRCan
- Solid-Phase Separation of Lanthanides and Actinides (2016) - NRCan
- Accelerated Leaching and Recovery Process for Actinides-Free REE Separation (2016) - NRCan
- Direct Oxalate Precipitation for REE Recovery from Low-Grade REE Pregnant Solution (2016) - NRCan
- REE recovery from secondary sources (2016) - NRCan

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Year 2 Deliverables

Mineralogy/Characterization
Determine mineral assemblages amendable to ore sorting
Linking mineralogy to flotation and leaching response
Physical Processing
Bench-scale ore sorting tests
TEA of ore sorting and dense media separation
Process mineralogy
Flotation reagents
Restrictions on shipment of concentrate
Surface chemistry linked to flotation reagents
Flowsheet development to increase concentrate grade
Leaching and Separation
Impurity control (SO_4/Cl) – Fe, Al, Si, Th
Acid baking. Methodologies and equipment selection
REE recovery oxalate, SX, double sulphate salt
REE recovery options from partial purified leach solutions
Bulk solvent extraction for REE recovery
Early removal of Ce, La and Y
Acid regeneration
Leaching database
REE separation processes
Environment
REE recovery from uranium processing and tailings
REE recovery from other secondary sources
Accelerated leaching optimization using surface modeling
Actinides & lanthanides recovery in continuous mode
Rare earth separation by electrolytic reduction
Solid-phase separation of rare earth elements
Ecotoxicity of REE processing reagents and contaminants
Environmental guidelines for REE mines and NORM management

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Speciation and Toxicity of REEs

CREEN - Canadian Rare Earth Element Network

BioMET
TRIVALENCE } - Collaborative Research Projects

BioMET

2012 - 2015

Bioavailability, toxicity, mobility and modeling of data poor metals

Université de Montréal

Kevin Wilkinson
Marc Amyot

INRS Université d'avant-garde

Claude Fortin
Peter Campbell

Wilfrid Laurier University

Scott Smith
Jim McGeer

TRIVALENCE

2015 – 2018

Tools for Risk Identification and Validation of Effects of Elements in Northern Canadian Ecosystems.

Partners

- **Environment Canada**
- MOECC
- NRCan
- CEAEQ
- IZA
- Avalon
- CREEN

Objectives / Deliverables

- Science-based understanding and diagnostic tools for assessing the potential impacts of REEs.
  - *physical, geochemical and biological interactions* underpinning metal fate and impacts in the environment;

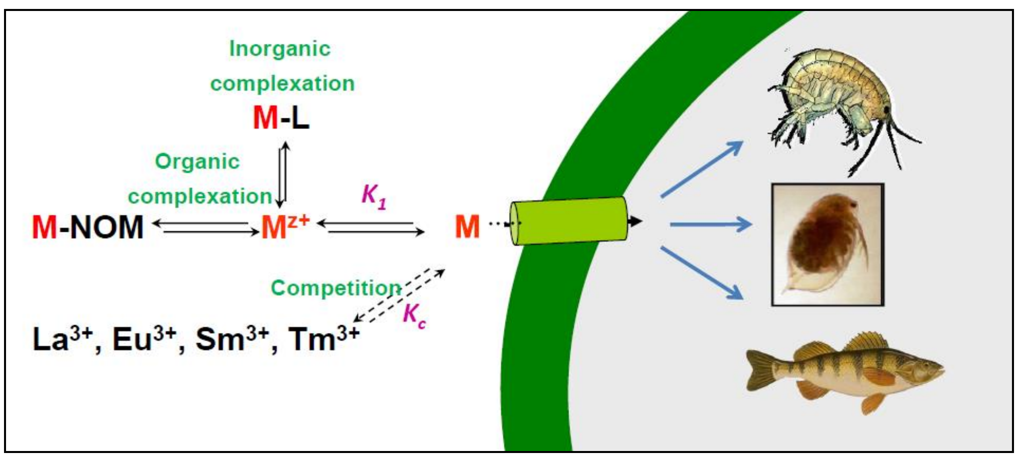
- Build the capacity of regulatory agencies in ecological risk assessment (ERA).

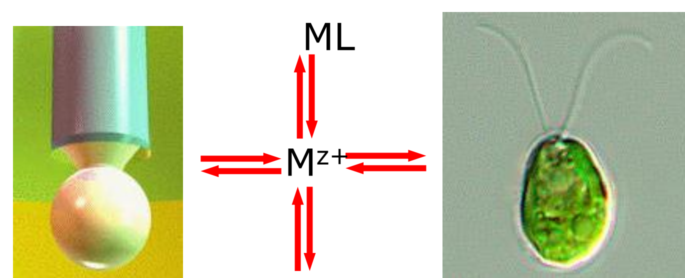
La, Ce, Sm, Eu, Dy, Tm, Yb, Ru, Rh, Pd, Pt, Nb, Ga, In and Cr

Kevin Wilkinson

- Molecular environmental chemistry:
    - biological and environmental processes at a molecular
    - bioaccumulation by microorganisms (algae).

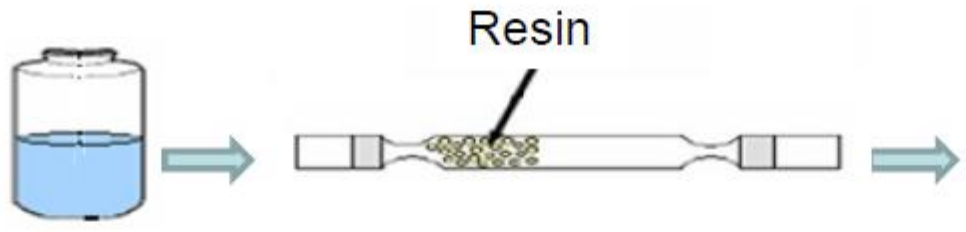
- Speciation by ultrafiltration + SP-ICP-MS
- Development of whole cell biosensors.
    - bioengineering with metal regulated reporter genes.





Claude Fortin
Peter Campbell

- Geochemistry and toxicology in aquatic media
- Dynamics of uptake and distribution (algae)
  - Uptake kinetics
  - Subcellular distribution in relation to effects.
- Fate and transport in the environment
- Methods for speciation



Scott Smith

- Molecular forms of metal in relation to potential for biological impact.
  - Interactions at biological surfaces
- Natural organic matter attenuation of metal toxicity
- Analytical methods for metal speciation in aquatic systems.

Speciation and toxicity studies with REES

Cerium, Dysprosium, Thulium & Samarium:

Geochemistry ←→ Bioavailability & Toxicity

Site Specific Estimates of Risk to Aquatic Ecosystems

Environmental concerns for REEs

- Potential for environmental impacts?
  - Currently no water quality criteria/guidelines
  - Few toxicity studies
  - Poor understanding of environmental risks
    - uncertainty

http://www.canadian-german-mining.com/files/canada_materials.png

What we know from metals toxicology

Toxicity values for metal:

- vary by orders of magnitude
- variation is related to underlying aquatic chemistry
  - e.g. Cu, Ag, Fe, Zn, As, Cd, Pb, Co, Mo, Pd, Ni

Influence of water hardness (Ca^{2+}) on toxicity

- Well established
- US EPA water quality criteria, Canadian guidelines

Toxicity is related to

- the chemical forms (speciation)
- how forms interact with biological pathways.
- understanding the mechanisms of toxicity

Interaction of geochemistry & biology

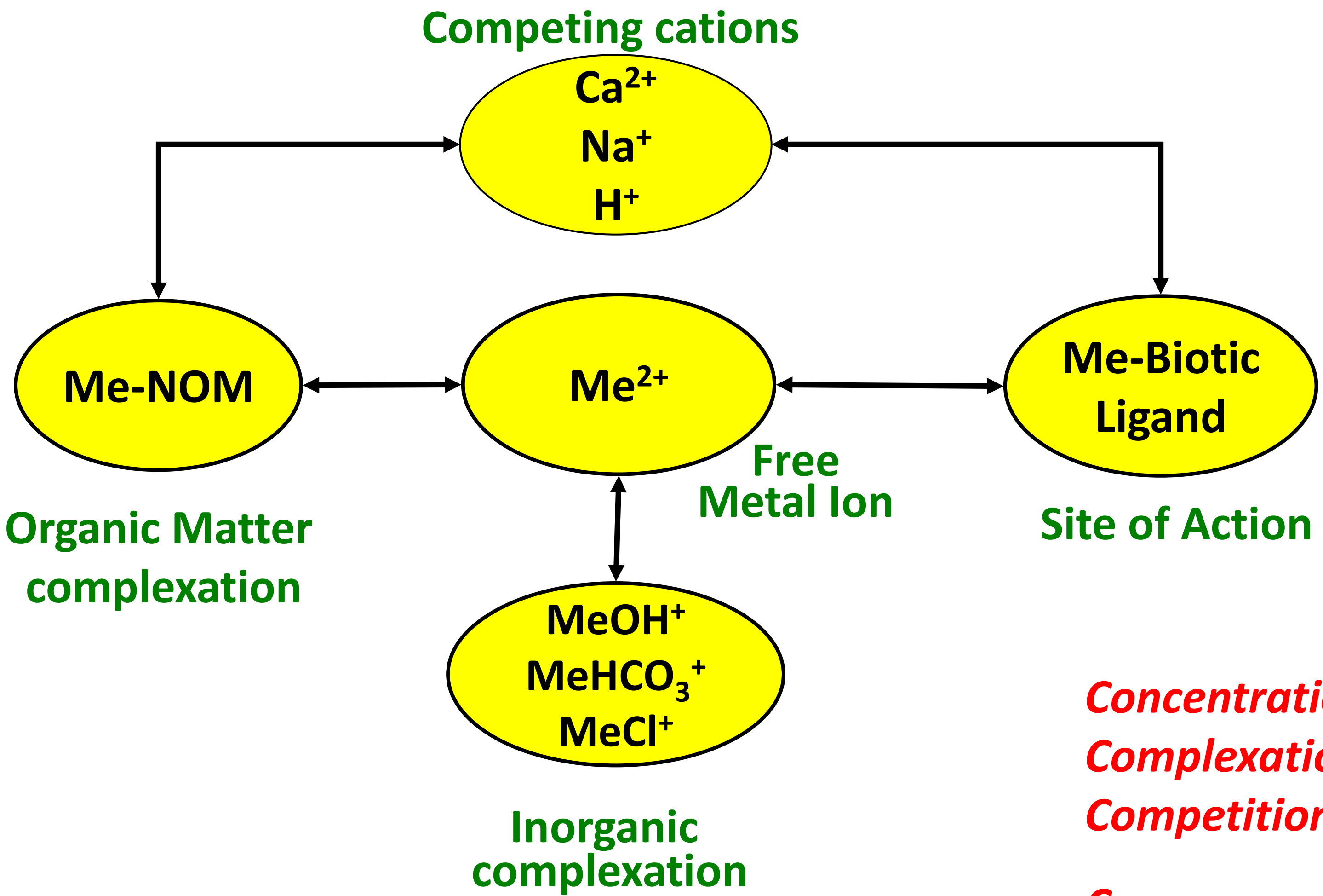
Understanding mechanisms of toxicity

Establish site specific approaches that estimate risk based on water chemistry.

Free ion activity model (FIAM) & Biotic Ligand Model (BLM)

Biotic Ligand Approach to Metal Toxicity.

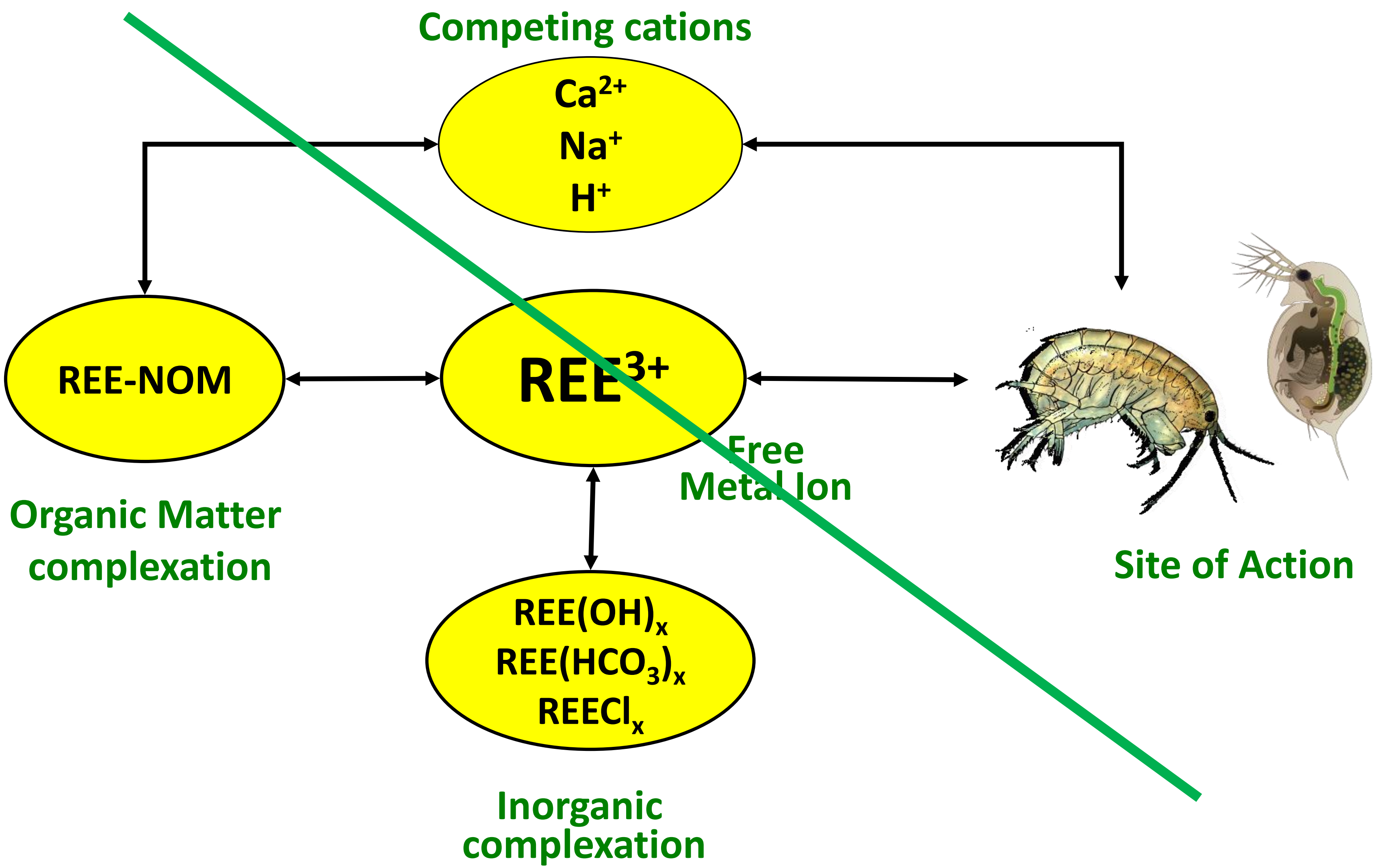
- simultaneously account for toxicity modifying factors.
- geochemical equilibrium
- Di Toro et al 2001



Concentration
Complexation
Competition

Consequences

Biotic Ligand Approach to REE Toxicity.

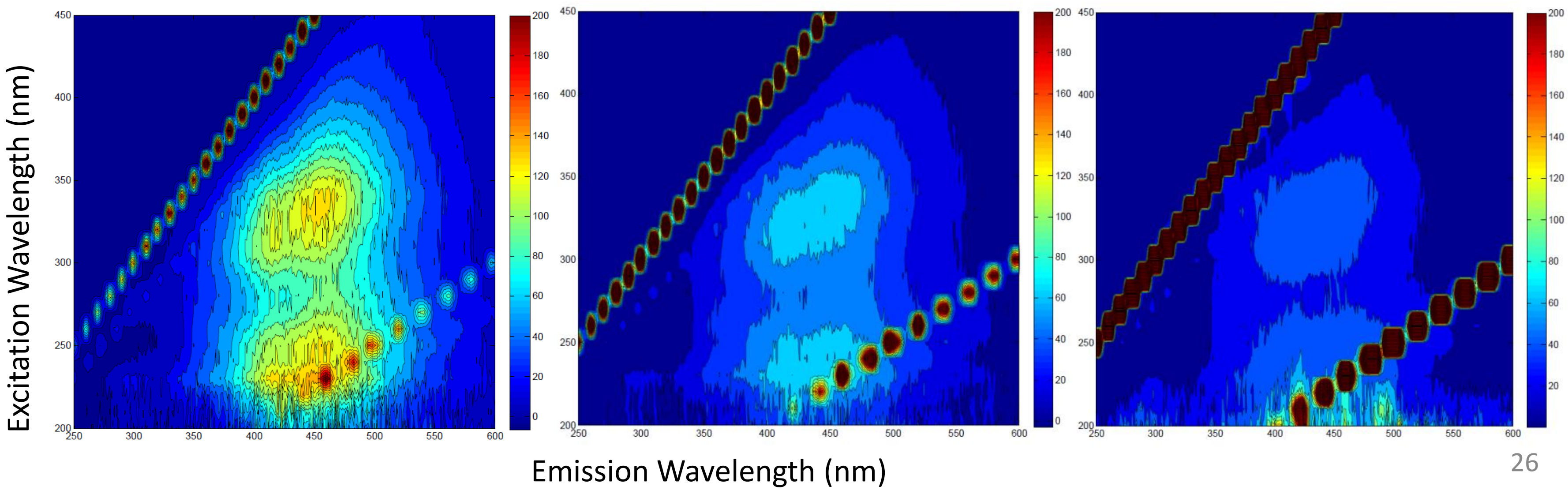


Speciation Studies

Smith lab

- No well-established technique to measure Lanthanide speciation
- Method development
  - fluorescence quenching (FQ)
    - applied to Sm and Dy
  - ion selective electrode (ISE)
    - Sm

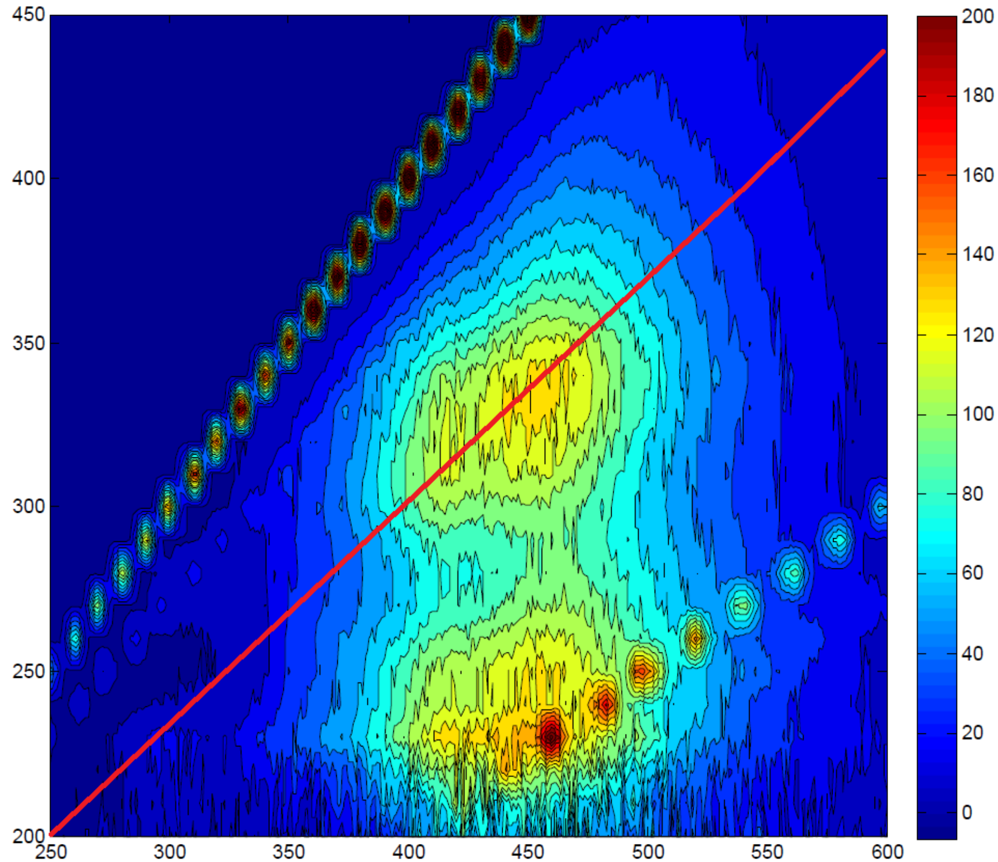
- Fluorescence Quenching example
  - Using 3 different sources of dissolved organic matter (DOM)



Experimental Design

- REE concentrations
  - from 0 µM to 100 µM
- DOC concentration
  - 10 ppm (3 sources)
- pH of 7.3±0.05
  - $NaHCO_3$ buffered
- IS 0.011M
  - Na_2SO_4 and $NaHCO_3$

- Variable angle synchronous scan (red)
  - Flow-through cuvette



Data Analysis

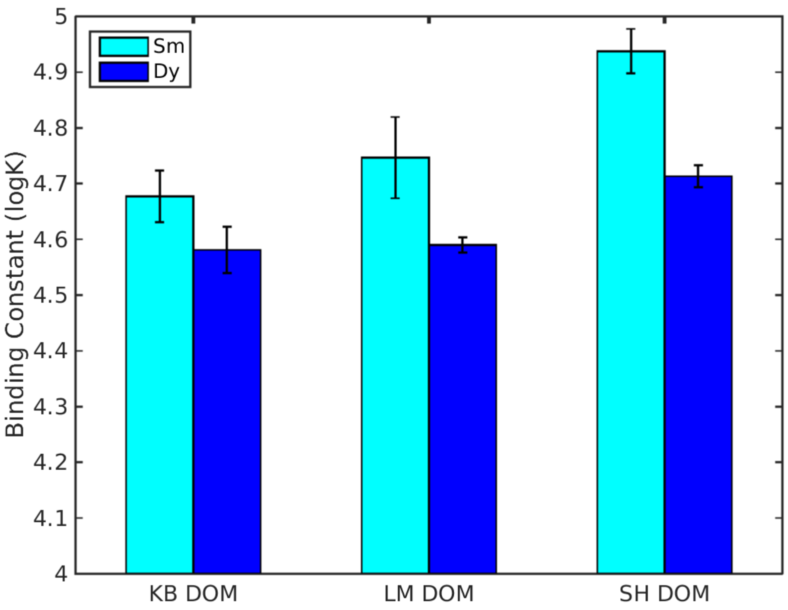
- SIMPLISMA (SIMPLe-to-use Interactive Self-modeling Mixture Analysis)
  - MATLAB code through file exchange
  - Used for spectral analysis
- Ryan-Weber model
  - To calculate binding constants and capacity
  - Assumed 1:1 binding

$$K = \frac{[ML]}{[M][L]}$$

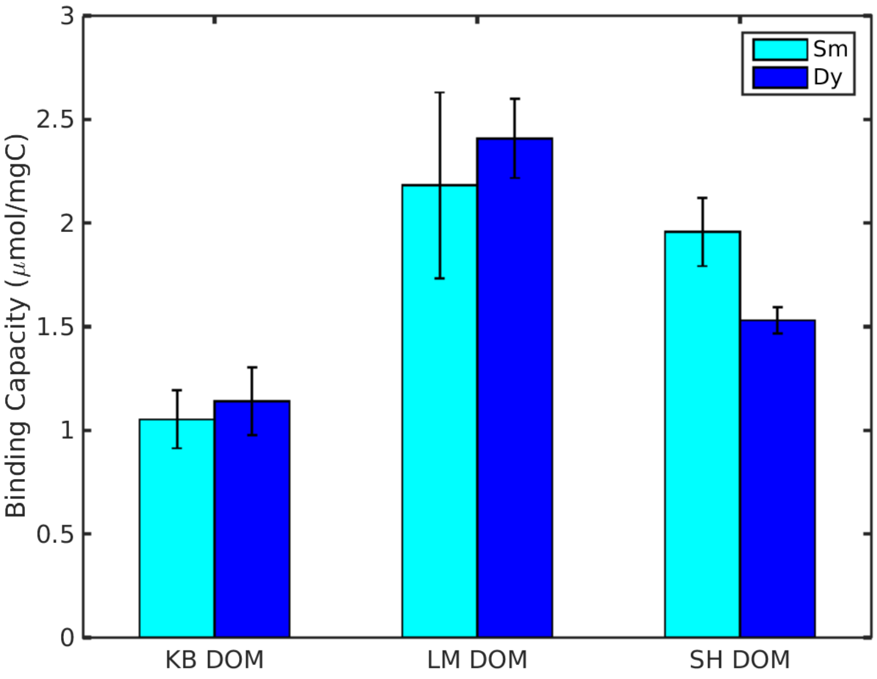
Source: Ryan and Weber (1982) *Anal. Chem.* and Windig and Guilment (1991) *Anal. Chem.*

Results: DOM binding characteristics

Binding Constants



Binding Capacities

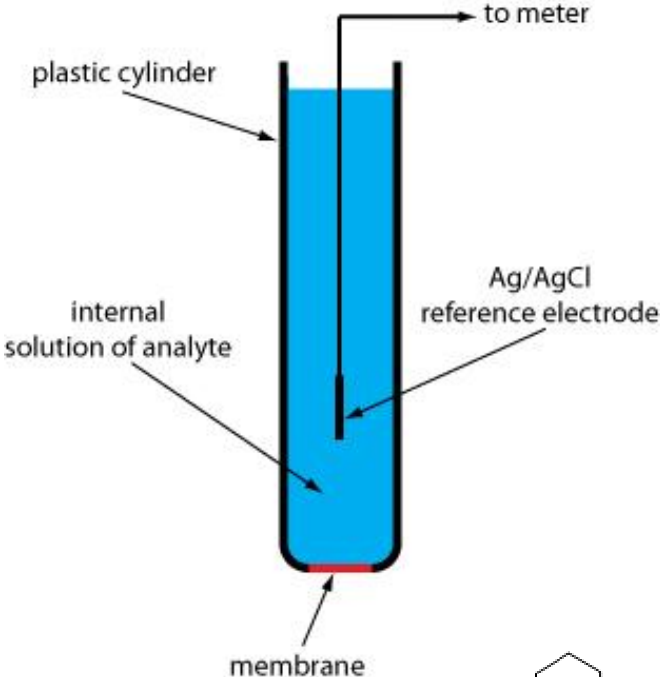


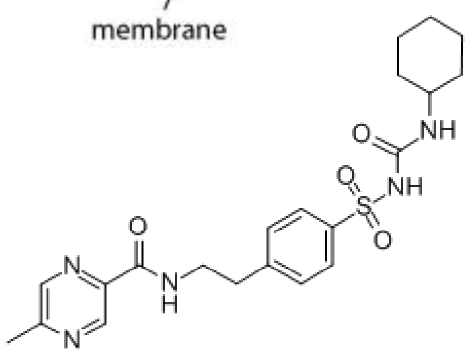
Summary

- Spectral resolution:
  - Identified 2 main components
  - Only one of them exhibiting quenching
- Binding constants:
  - Similar between all samples (4.58-4.94)
  - Comparable to previous research (Sm 4.21-4.28 to FA)
  - Sm exhibiting slightly stronger binding than Dy
- Binding capacity:
  - DOM sources differ

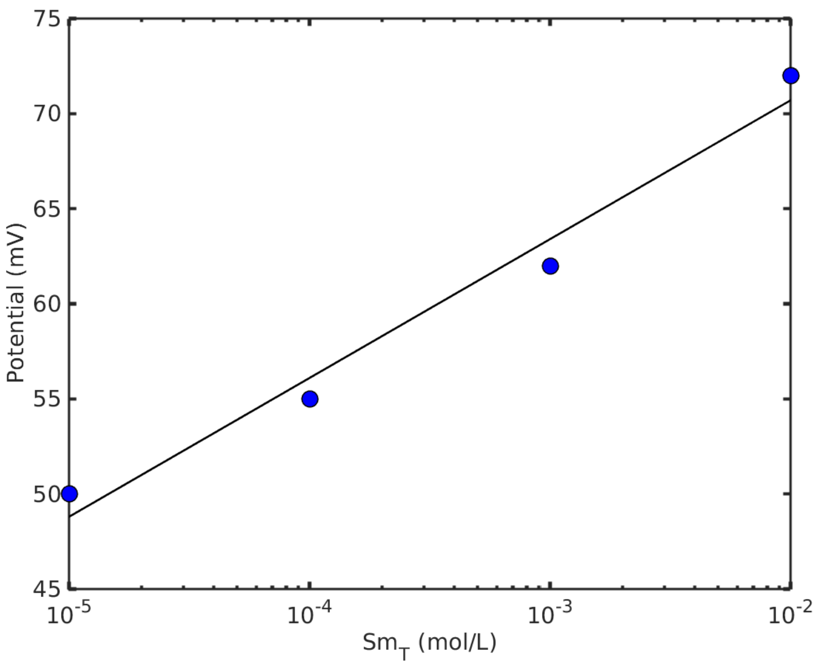
Reference: Gu et al. (2001) *Talanta*

ISE for Sm





Glipizide



Speciation so far

- ISE was generally a more comprehensive method
    - Does not rely on fluorescence of ligands

- But for Sm
    - intrinsic issues associated with cation competition
    - analysis was not possible in solutions with high salts conc.

- Comparison commonly used geochemical speciation model
    - Windemere Humic Aqueous Model (WHAM)
    - WHAM dramatically overestimates of DOM binding at low concentrations.

Toxicity Studies

Objectives & Design

1. Acute toxicity studies:

- Ce, Sm, Dy and Tm

  Hyalella azteca
  - 96 h, following EPS 1/RM/33 (2013)

  Daphnia pulex
  - 48 h, following EPS 1/RM/11 (1996)

- Toxicity modifying factors

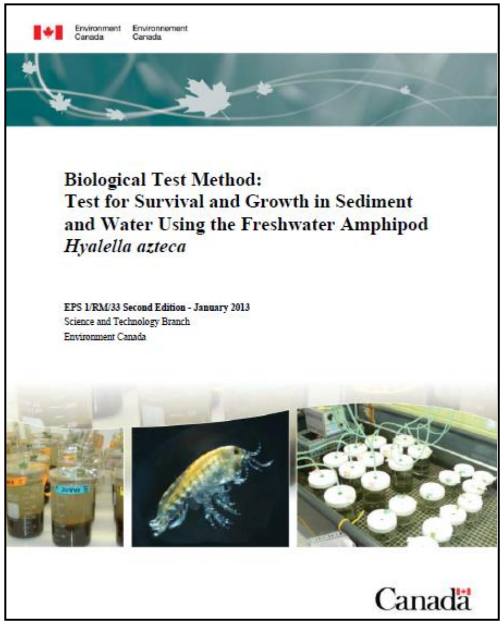
  cationic competition
  - Ca^{2+}, Na^{+} and Mg^{2+}

  complexation
  - DOC quantity
  - DOM quality

  Do BLM principles apply?

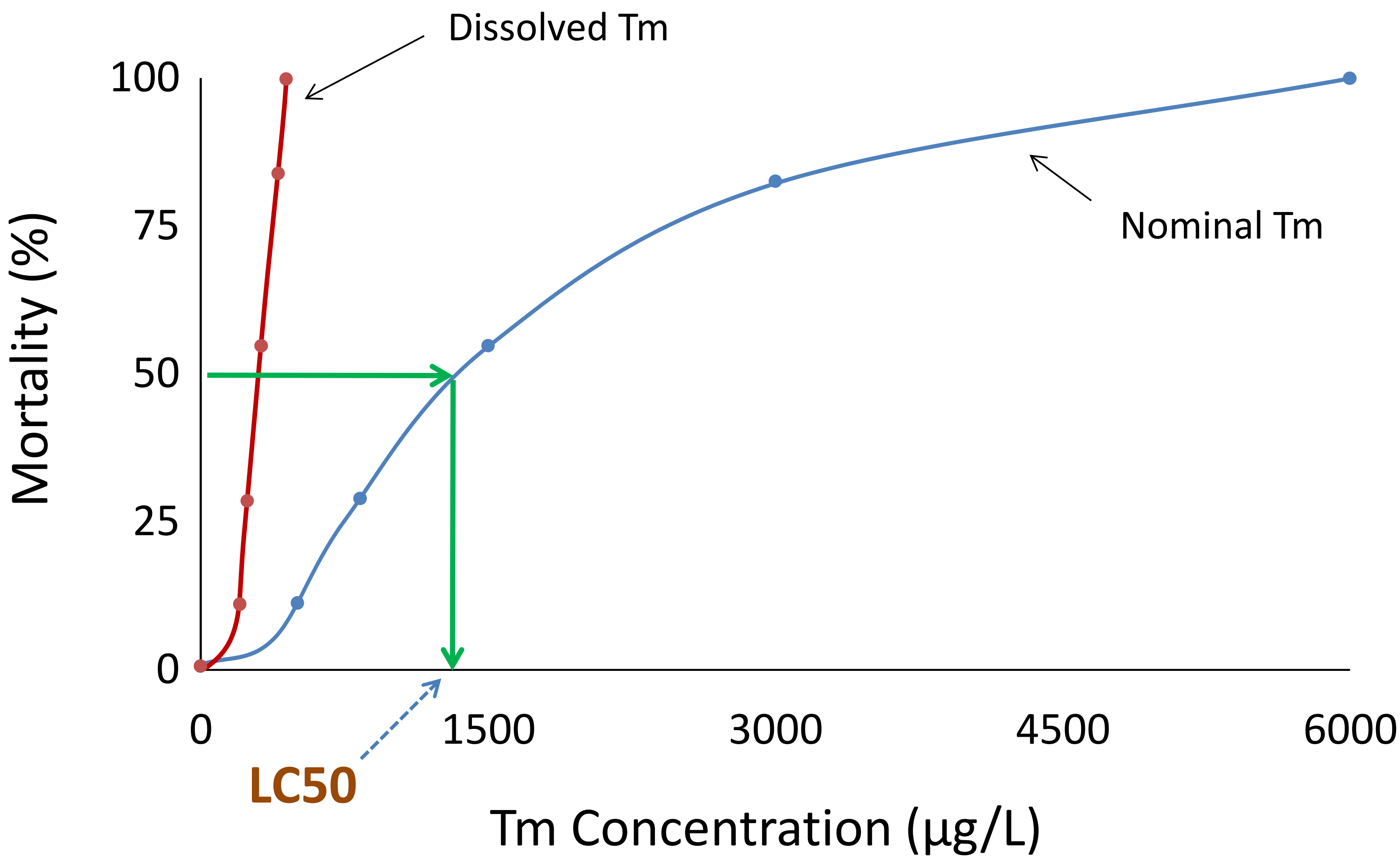
- Modelling

  geochemistry – effect linkages

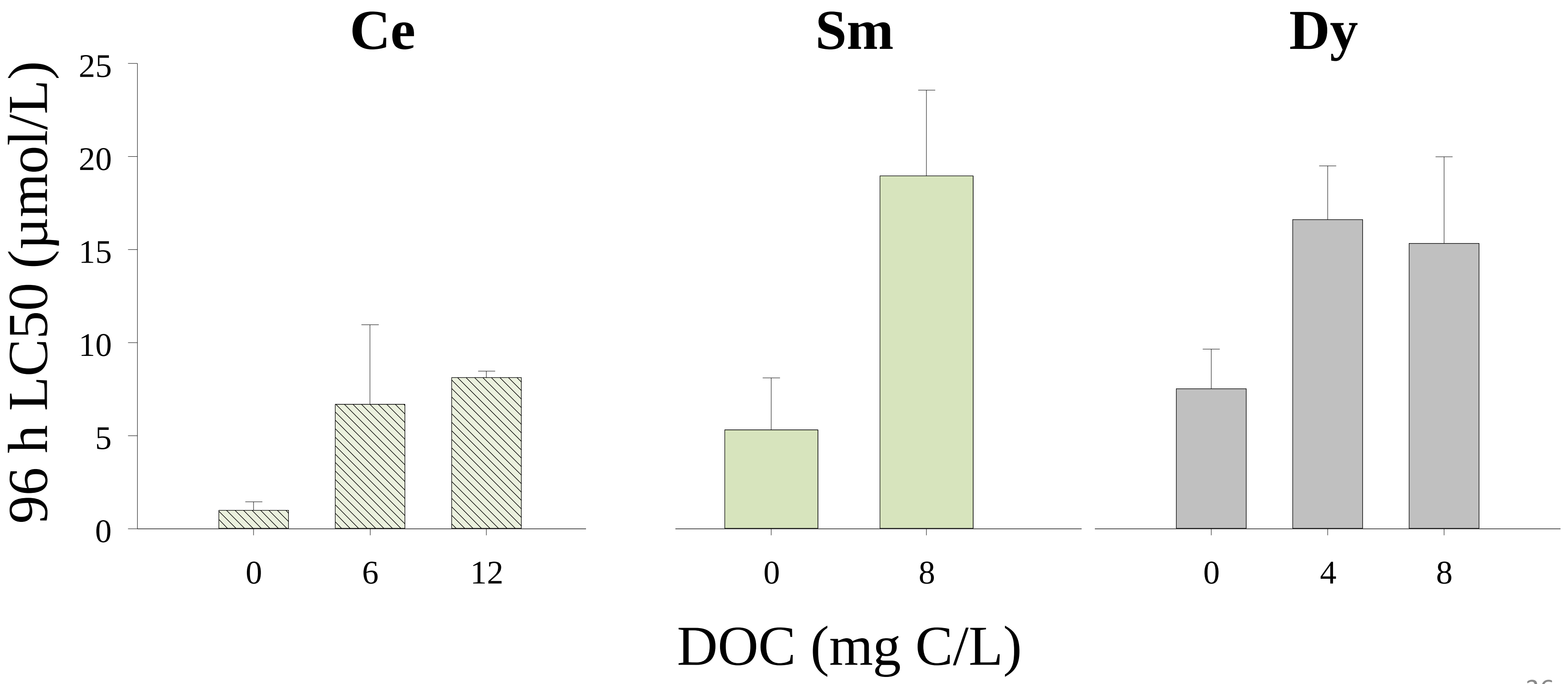


2. Targeted chronic toxicity studies:

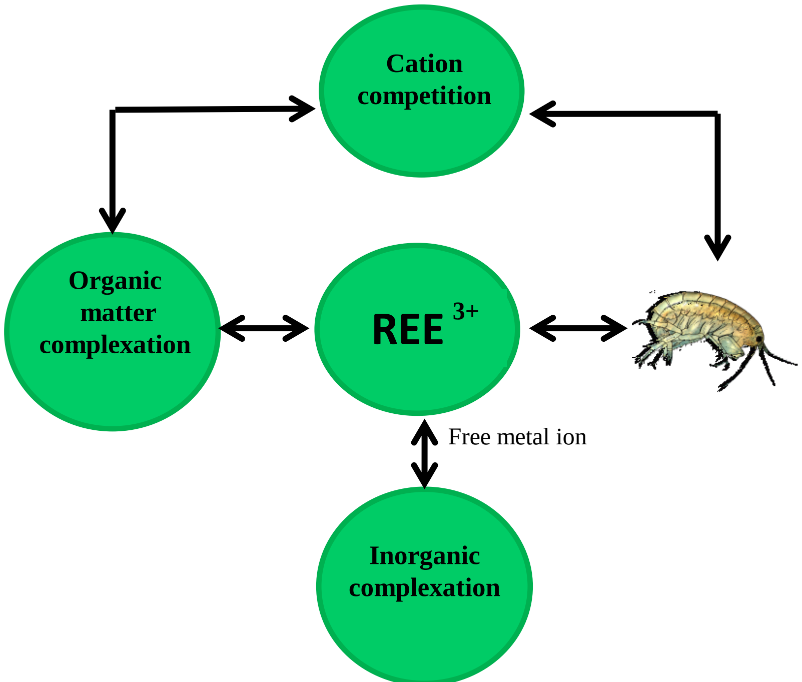
Exposure – response curves for Tm toxicity to *Hyalella azteca*

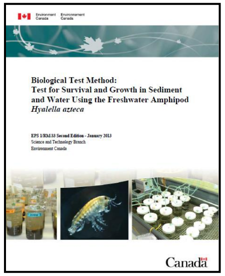


Effect of DOM on REE toxicity to *Hyalella azteca*



Acute toxicity studies with Ce, Dy, Sm & Tm





Environment Canada Environnement Canada

Biological Test Method:
Test for Survival and Growth in Sediment and Water Using the Freshwater Amphipod *Hyalella azteca*

EPS 1/RM/33 Second Edition - January 2013
Science and Technology Branch
Environment Canada

Canada

Potential toxicity modifiers

	Ce	Dy	Sm	Tm
Na^{+}	✓	✓	x	x
Ca^{2+}	✓	✓	✓	x
H^{+}		✓		
Mg^{2+}	x	x	x	x ✓
DOC	✓	✓	✓	✓

Conclusions & ongoing activities

- REEs differ in their toxicology
- Water chemistry matters
  - Understanding speciation essential
    - measured & modelled

- Exposure – response relationships
  - characterization of exposure
    - Speciation methods
    - Natural waters

  - characterizing responses
    - Expanding species database
    - Chronic studies

  - Linkages

- Mechanisms of uptake and bioaccumulation
- Prediction model development and validation

Acknowledgments

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Veritas Omnia Vincit

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CRSNG

Ontario

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Environnement Canada

CREEN
Canadian Rare Earth Elements Network

VALE

Glencore

Centre d'expertise en analyse environnementale
Québec

National Resources Canada
Ressources naturelles Canada

INNOVATION.CA
Canada Foundation for Innovation
Fondation canadienne pour l'innovation

Northwest Territories

Avalon

Zinc ...essential for life
international zinc association