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REMEDIATION TECHNOLOGIES SYMPOSIUM 2025

Session: PTAC Panel, Wednesday October 15th, 1:00pm to 2:50pm

DEVELOPMENT OF SUPPORTING INFORMATION FOR A CHLORIDE WATER QUALITY GUIDELINE HARDNESS AND CONSIDERATION FOR CATION TOXICITY

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Acknowledgements

- PETROLEUM TECHNOLOGY ALLIANCE CANADA (PTAC)
  - ALBERTA UPSTREAM PETROLEUM RESEARCH FUND (AUPRF)

    Project Champion: Linda Eastcott (Imperial Oil Ltd)

- TOXICITY TESTING LABS
  - Wisconsin State Laboratory of Hygiene
  - Warnell School of Forestry and Natural Resources
  - Nautilus Environmental

- EQUILIBRIUM SCIENTIFIC STAFF
  - Vicky Winter
  - Anthony Knafla

- ADDITIONAL SCIENTIST CONTRIBUTIONS
  - Ian McIvor

Brief Background

- Natural Sources of Chloride for Terrestrial Environments
  - Ancient marine evaporite, weathered geological material, sea spray

- Anthropogenic sources
  - Municipal – Road salts for motorist safety, salt storage yards
  - Agricultural – irrigation drainage, salt blocks, feedlots, manure
  - Industrial – Oil and gas activities (produced water)
  - Residential – water softener discharge, septic fields

- National Guideline Available
  - CCME (2011)
  - Acute guideline – 640 mg/L chloride
  - Chronic guideline – 120 mg/L chloride

  - Prior chronic guideline was 230 mg/L chloride (US EPA)
  - Can drive remediation – need to ensure guideline derivation and supporting dataset is strong, and critical Toxicity Modifying Factors are incorporated

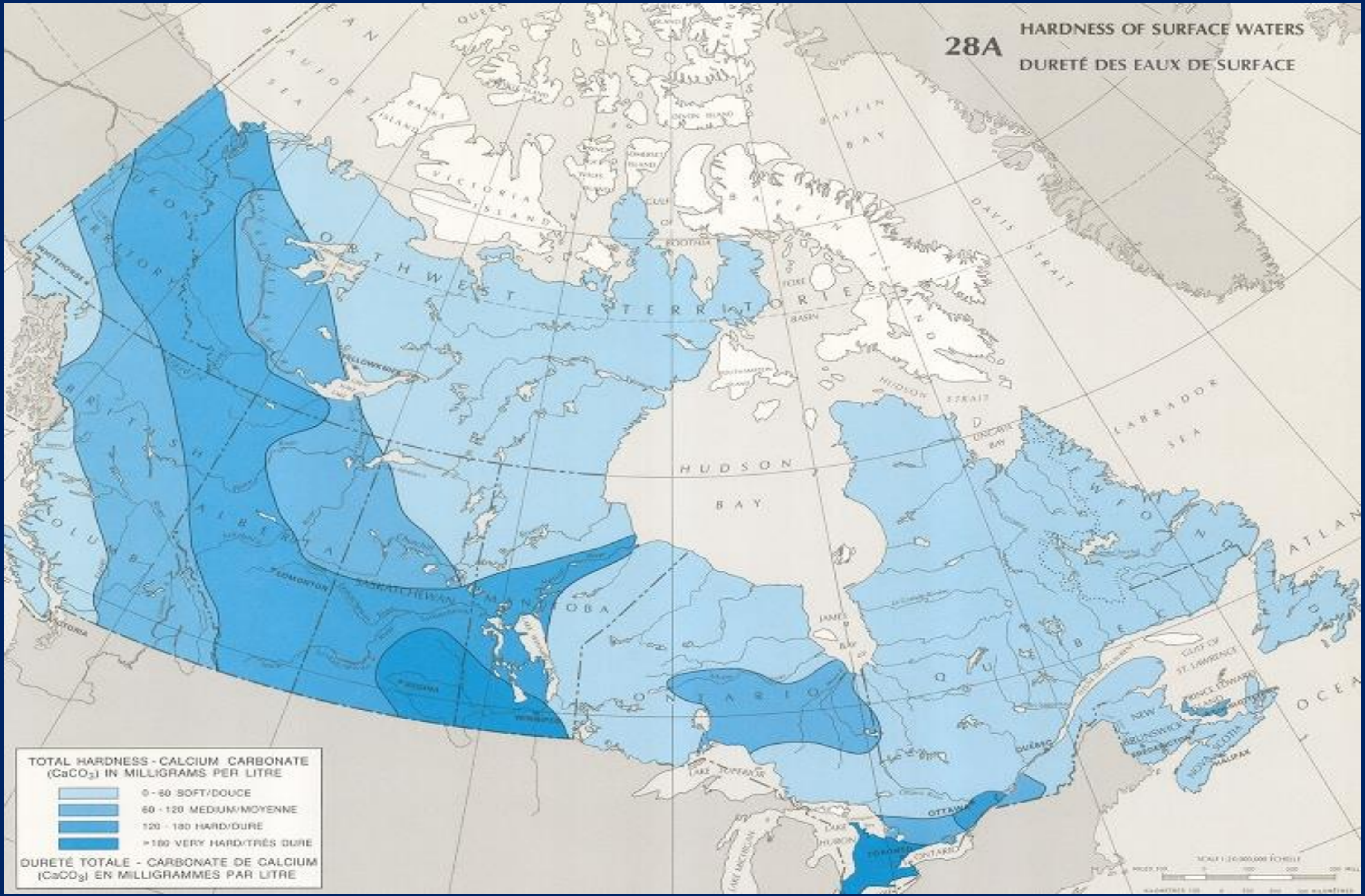
Toxicity Modifying Factor – Hardness

- **What is a Toxicity Modifying Factor (TMF)?**
  - *'An element that changes the toxicity of a substance by directly altering the substance or changing an organism's response to the substance'*
  - Example #1: Grapefruit and medications for blood pressure, cholesterol, depression – furanocoumarins in grapefruit don't interact directly with the medicines, but binds to small intestine enzyme (CYP3A4) that normally metabolizes xenobiotics reducing amount absorbed into the blood – result is you get higher dose levels
  - Example #2: manganese dioxide – can oxidize Cr (III) to Cr (VI), with the latter being a more bioaccessible and toxic version

  - CCME and Hardness
  - in 2011, CCME indicated adjusting for water hardness may be appropriate, but some data were equivocal and more study needed
  - Insufficient database for chloride and hardness TMF – CCME will re-visit the chloride guidelines when sufficient studies are available
    - Jurisdictions have the option of deriving site-specific hardness adjusted water quality criteria if they so choose

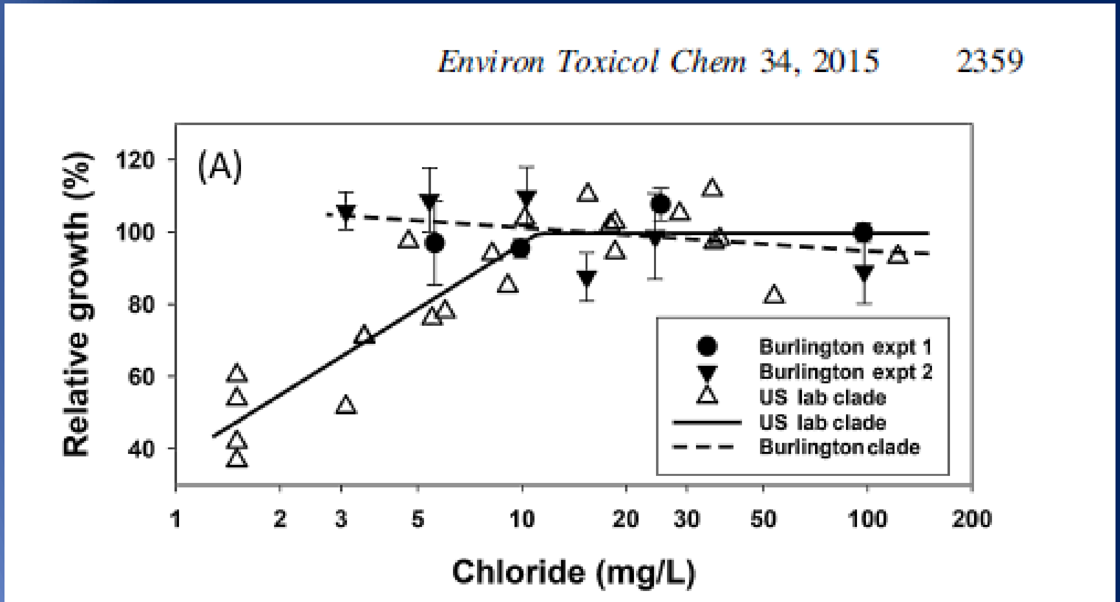
Why is Hardness Important across Canada?

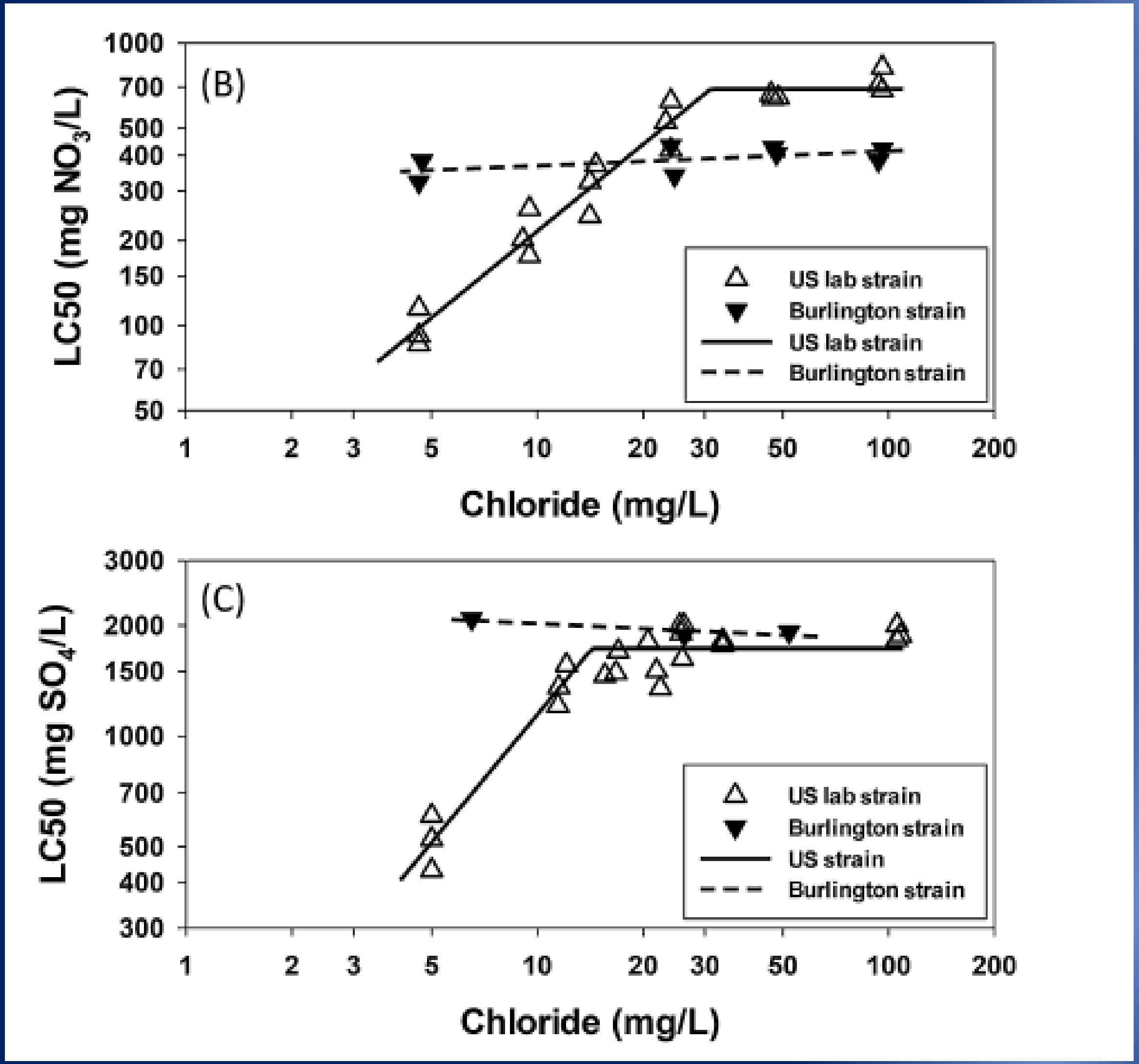
- Variable water hardness in Canada (NRCAN, 1978)
  - If chloride toxicity varies with hardness, then guidelines across Canada should vary
  - Important issue of national importance



Low Level Chloride and other TMFs

- Chloride interacts with some aquatic biota at very low levels (Soucek et al., 2015; Hyalella Azteca) – poor growth at < 10 mg/L chloride (likely due to cations)
- Low level chloride also affects nitrate and sulphate toxicity (TMF examples)





Key Data Gaps

- Key gaps for sensitive species & sodium/calcium chloride toxicity at varying hardness levels
- Questions related to cation, associated with chloride ion, toxicity

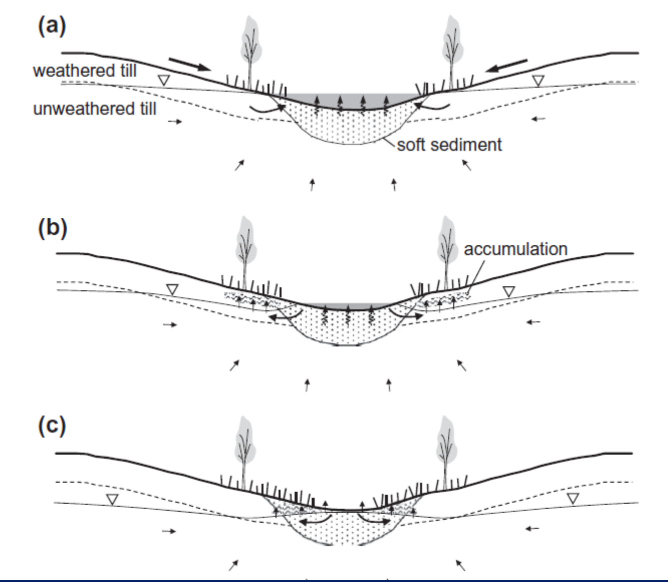
- PTAC Commissioned Studies
  - *Anodonta subangulata* (freshwater mussel)
  - *Lampsilis fasciola* (wavy-rayed lampmussel)
  - Lampsilis siliquoidea (freshwater mussel)
  - *Pimephales promelas* (fathead minnow)
  - *Ceriodaphnia dubia* (water flea)
  - *Raphidocelis (Pseudokirchenella) subcapitata* (microalgae)
  - *Centroptilum (Neocloeon) triangulifer* (mayfly)
  - *Lithobates pipiens* (Northern leopard frog)

- One sensitive species not tested – Endangered
  - *Epioblasma torulosa rangiana* (Northern Riffleshell)

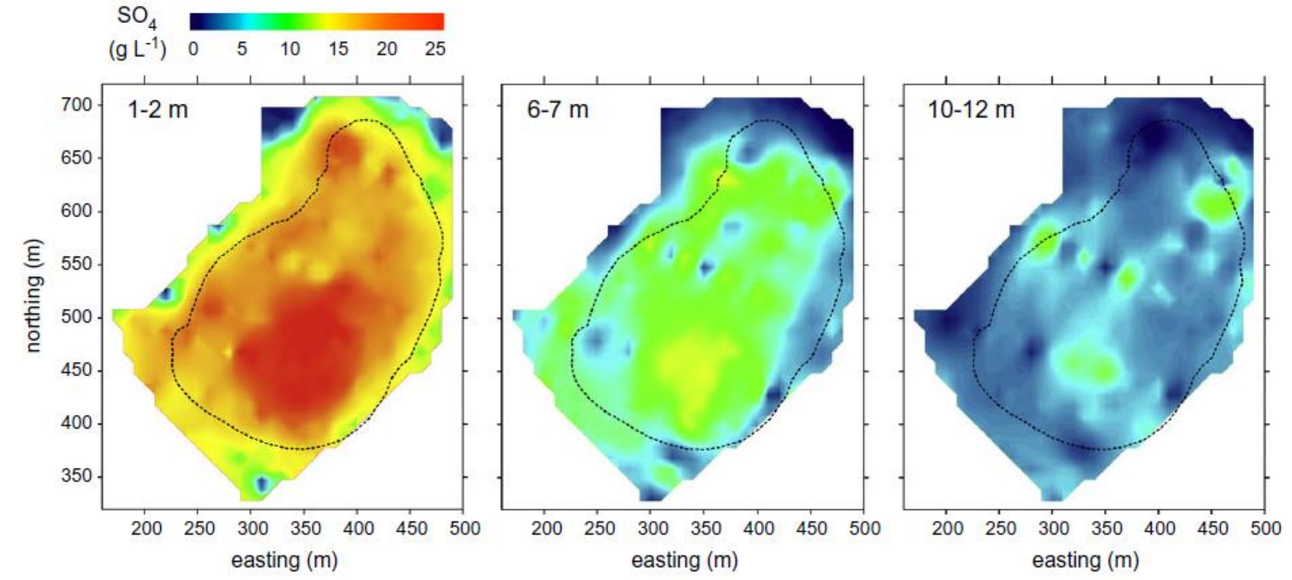
Another Current Interest Area of relevance to WCSB

- Variability within WCSB for wetlands in terms of **background salinity**
  - due to permanence, climate, aspect, parent geology, recharge/discharge, groundwater
  - Species biodiversity is highly affected by background conditions
  - TDS ranges naturally from <100 to 35,000 mg/L; LaBaugh *et al.*, 2018)

Water balance, sulphate flow



Estimated pore water sulphate beneath wetland based on ERI



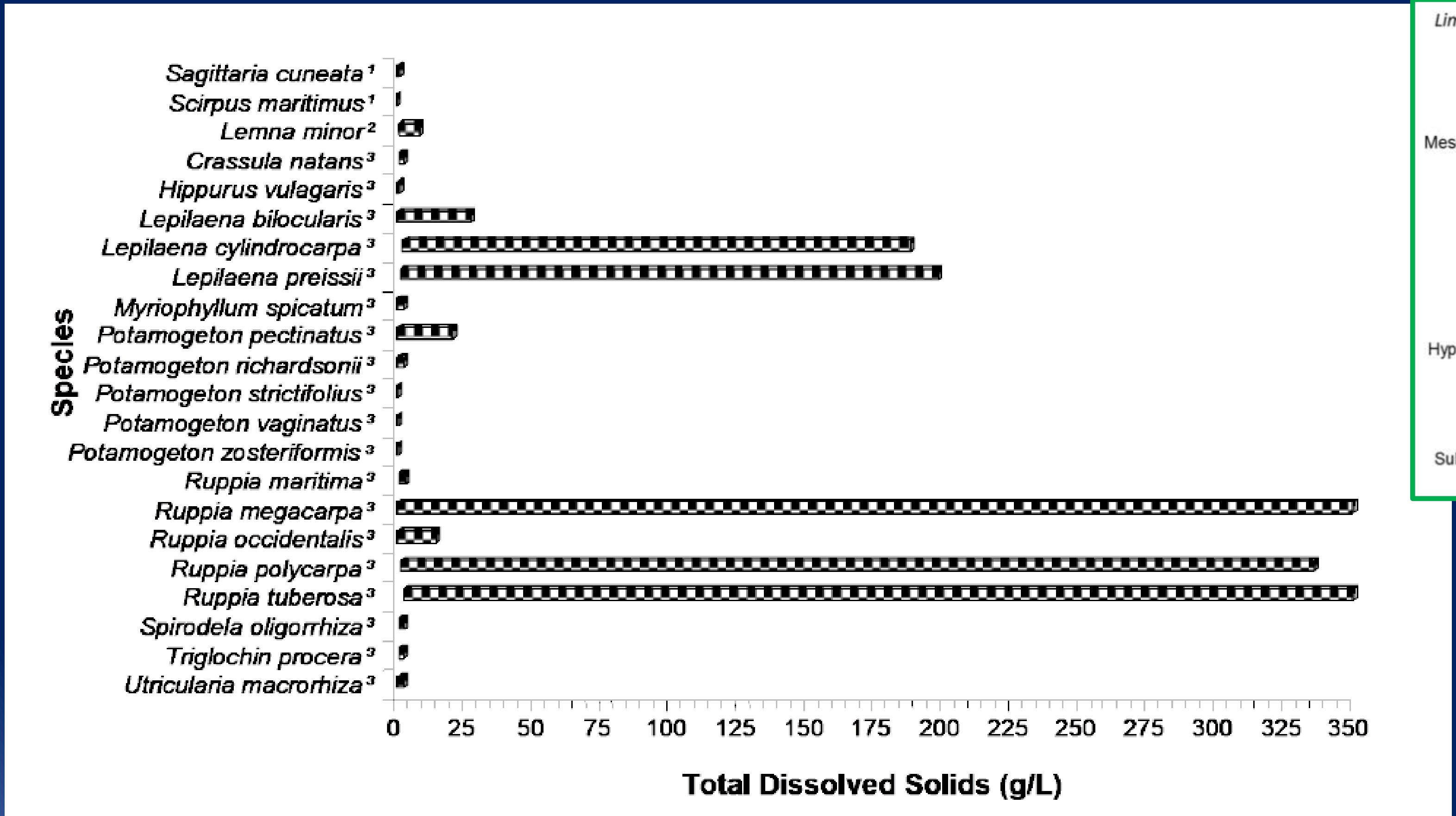
Heagle et al, 2013

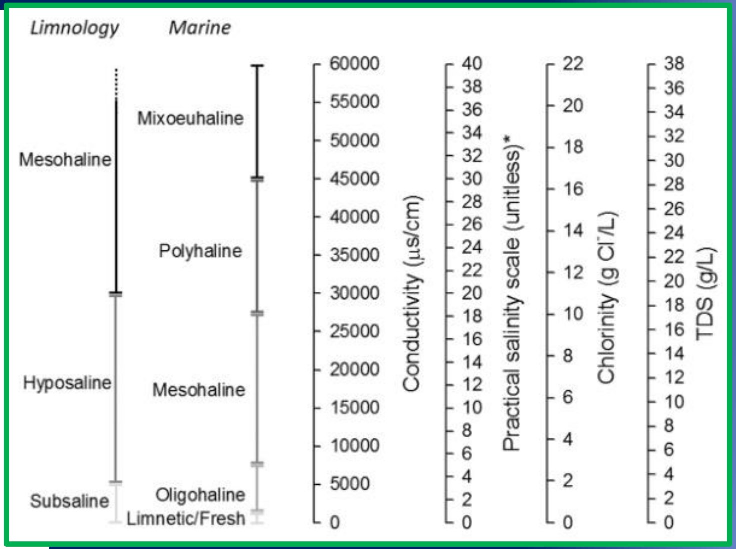
Low Background Salinity Environment

High Background Salinity Environment

Background Species Diversity & Salinity Tolerance

- **Macrophyte** (Plant) salinity tolerance & adaptation for Alberta species
  - Limnetic to Mixoeuhaline (Huerbert et al., 2015)
    - Tolerance ranges from <5,000 mg/L to > 350,000 mg/L
  - 120 mg/L chloride still applies to wetlands with > 100,000 mg/L TDS
    - Some species are capable of colonizing sea water levels, such as distant relatives of coastal saltwater species



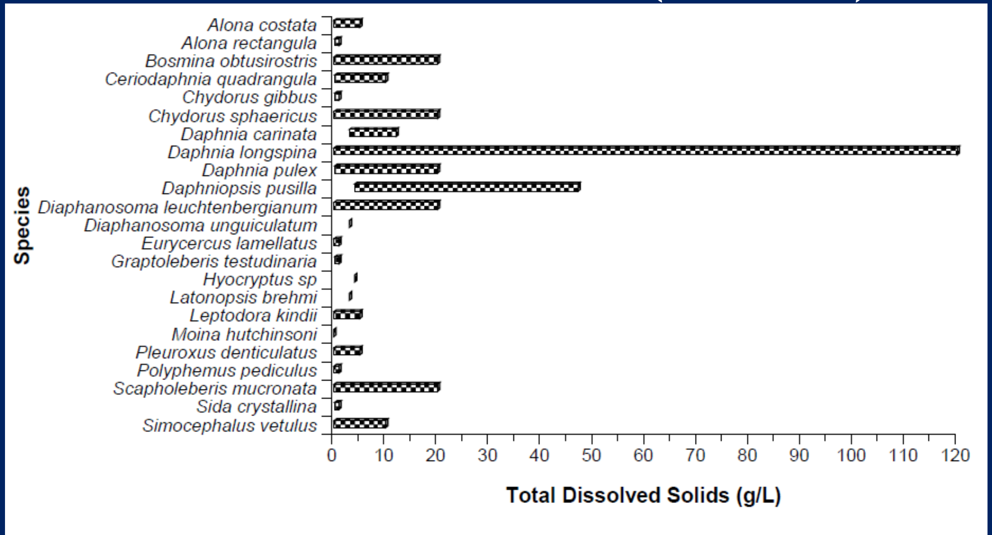


Notes: Range for emergent[1], floating[2], and submergent[3] aquatic macrophytes – Various literature sources

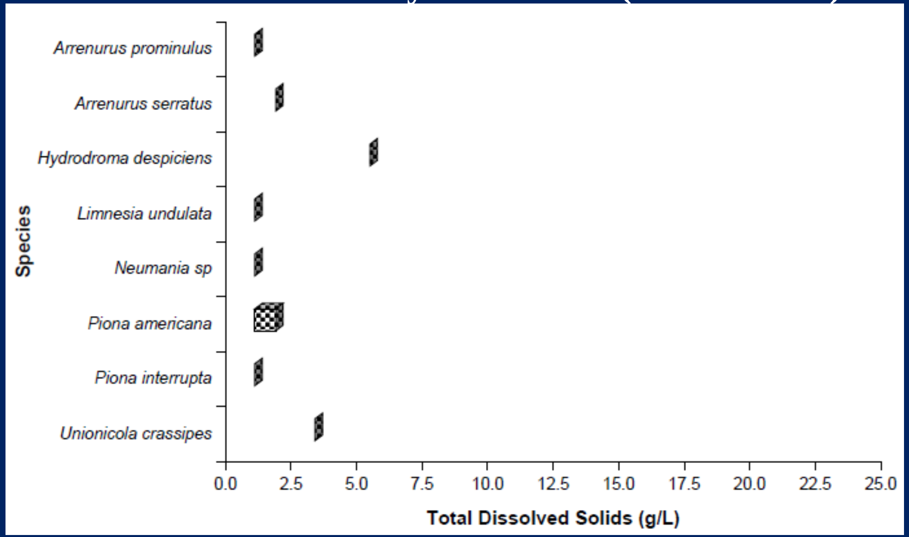
Background Species Diversity

- **Invertebrate** salinity tolerance & adaptation for Alberta species
  - Tolerance ranges from <1,000 to 120,000 mg/L for various species encountered in Alberta wetlands; Some distant saltwater relatives
  - Raises question of relevance of 120 mg/L chloride guideline in high background salinity environments

TDS Tolerance for Cladocerans (Water Fleas)



TDS Tolerance for Hydracarinids (Water Mites)



D. longspina

A. costata

Arrenurus

Back to Hardness TMF and Chloride Guideline Support Work
Research Methods

Update Chloride Toxicology Databases since 2011

Scour Literature for Multi Ion-Interactions and update Database

Develop a Hardness Adjustment to Chloride Guideline

Chloride-Hardness Water Quality Guideline

Scour Literature for Hardness Relationships and Chloride Toxicity

Develop an Updated SSD based on Updated Dataset following CCME Methods

Identify Data Gaps and Commission Toxicity Studies

SSD Database Development

- Citation search resources
  - Existing reviews, USEPA ECOTOX Database, ISI Web of Knowledge
- Minimum data quality requirement (CCME, 2007)
  - Primary, Secondary, Unacceptable
- Experimental Variables
  - Effect [conc], other ion [conc], exposure durations, hardness, endpoint, taxonomic details, O_2, temp, pH, life stage, etc.
- Summary of dataset collection
  - >210 studies
  - 2082 entries: Unacceptable: 16%;
    NaCl: 37%; KCl: 12% ; $CaCl_2$: 4%;
    $MgCl_2$: 1%; multiple ions: 30%

Water Hardness Influence on Guidelines

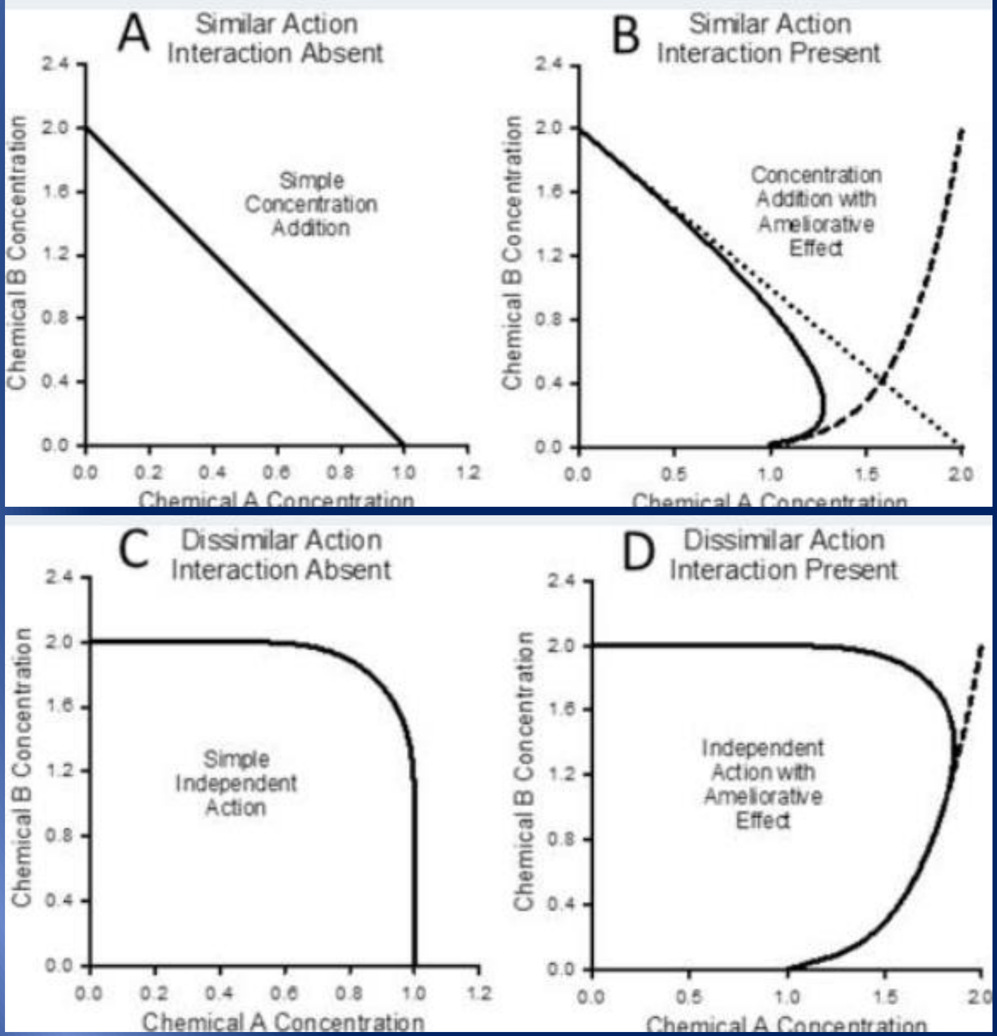
- Literature data indicates hardness may modify chloride toxicity
  - Possible mechanisms:
    - Competition for binding sites (Paquin et al 2002)
    - Ion pairing (Davies & Hall 2007)
    - Ca^{2+} impact on membrane permeability (Penttinen et al 1998)
    - Electrochemical gradient changes

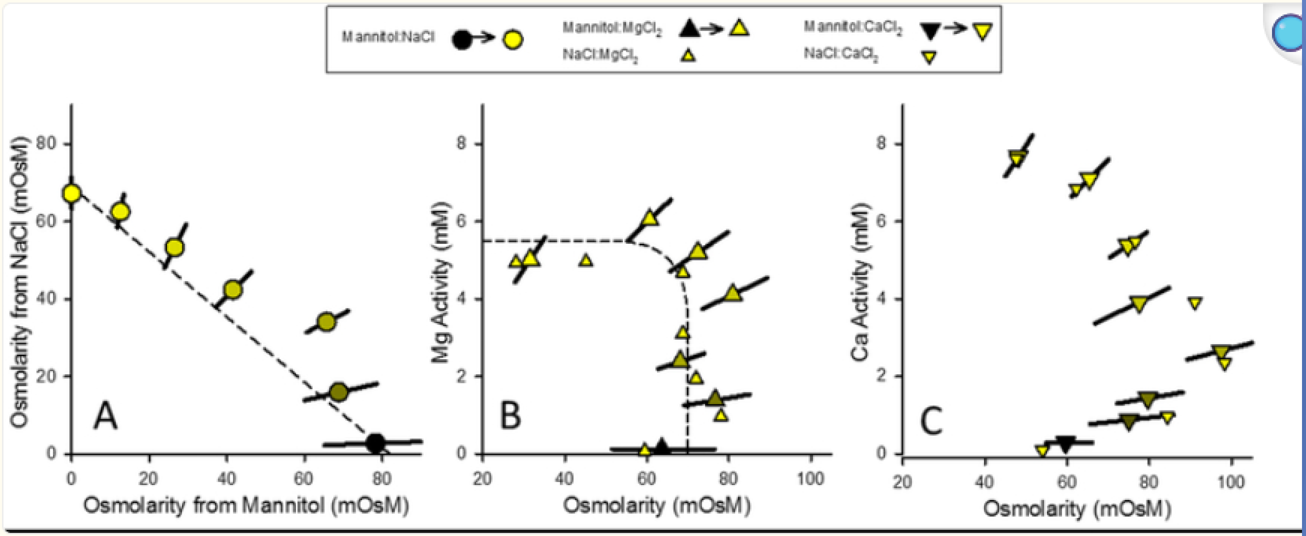
- Regulatory guidelines have considered hardness (Cd, Zn)
- Iowa (IDNR 2009)
  - Guideline corrected for TMFs (water hardness)
  - Chronic guideline: 250 –624 mg/L over hardness from 50–800 mg/L
  - Governments of Australia and New Zealand consider water softness an important factor in sodium chloride toxicity (ANZECC, 2000)

- Elphick (2011) published a means of evaluating reduced chloride toxicity due to increasing hardness

TMF and Multi-Ion Exposures

- Interactions are complex – simple additive, ameliorative (hardness), simple independent action, independent with amelioration
- Erickson et al., 2018 https://pmc.ncbi.nlm.nih.gov/articles/PMC6157913/
- Identifying mode of toxic action is important





Open in a new ta

Isobolograms for 48-h LC50s from binary mixture experiments of mannitol with NaCl, $MgCl_2$, and $CaCl_2$ on basis of exposure metrics of osmolarity, Mg activity, and Ca activity. Small triangles provide LC50s for NaCl×$MgCl_2$and NaCl×$CaCl_2$ experiments for comparison to relationships with mannitol. Dashed lines denote approximate isoboles for simple concentration addition (panel A) and simple independent action (panel B). Gradation from black to yellow indicates gradation of mixtures from mannitol to pure Cl salt.

Chronic Chloride Guideline Derivation

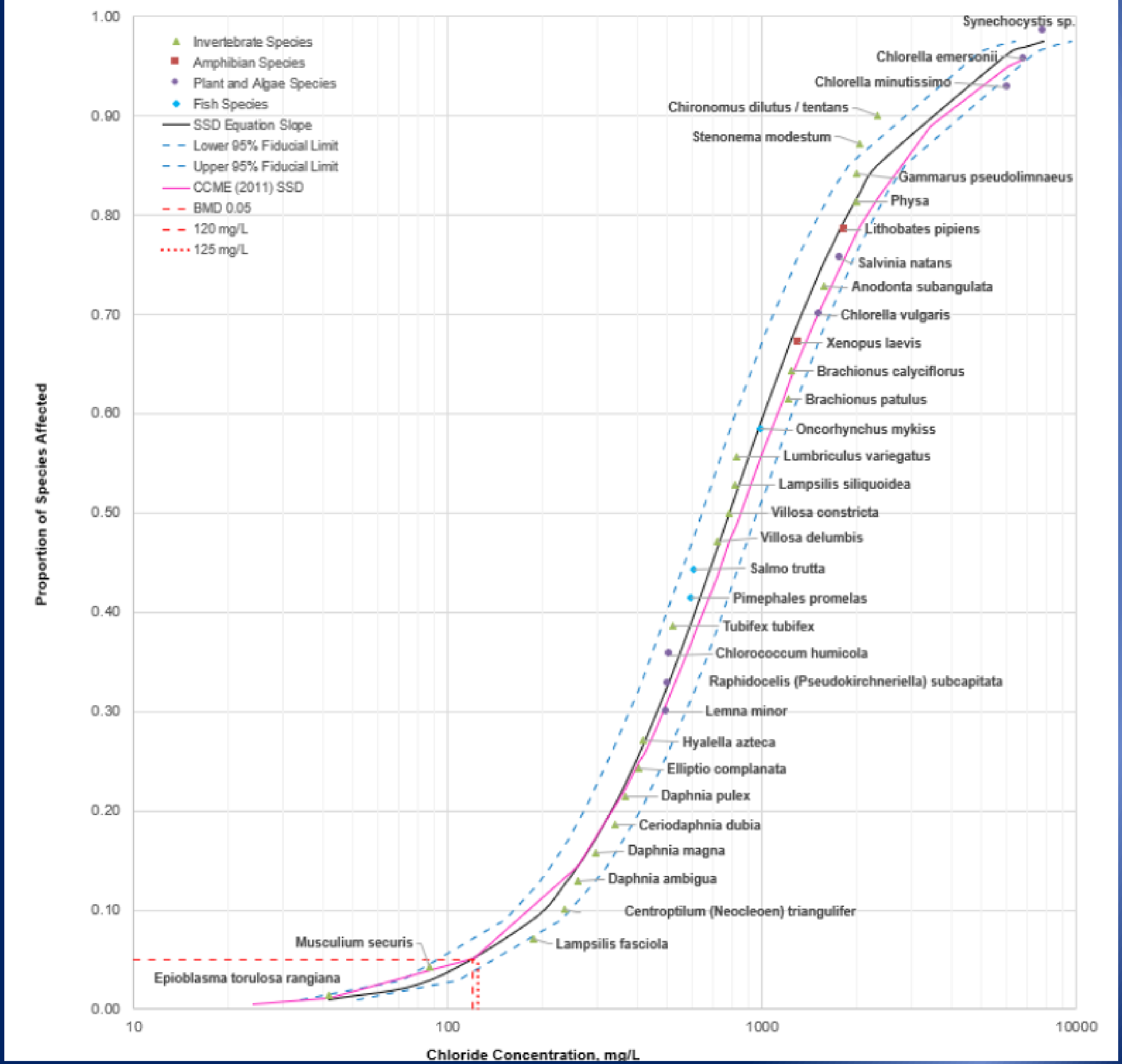
- All acceptable studies, low and no adverse effect concentrations, at toxicological study hardness levels

  - *Lampsilis fasciola* used to be on the SSD closer to *epioblasma torulosa rangiana*

  - *Now shifted 'right' on the SSD – reason, same researcher, same species, same lab – order of magnitude different in toxicological response*

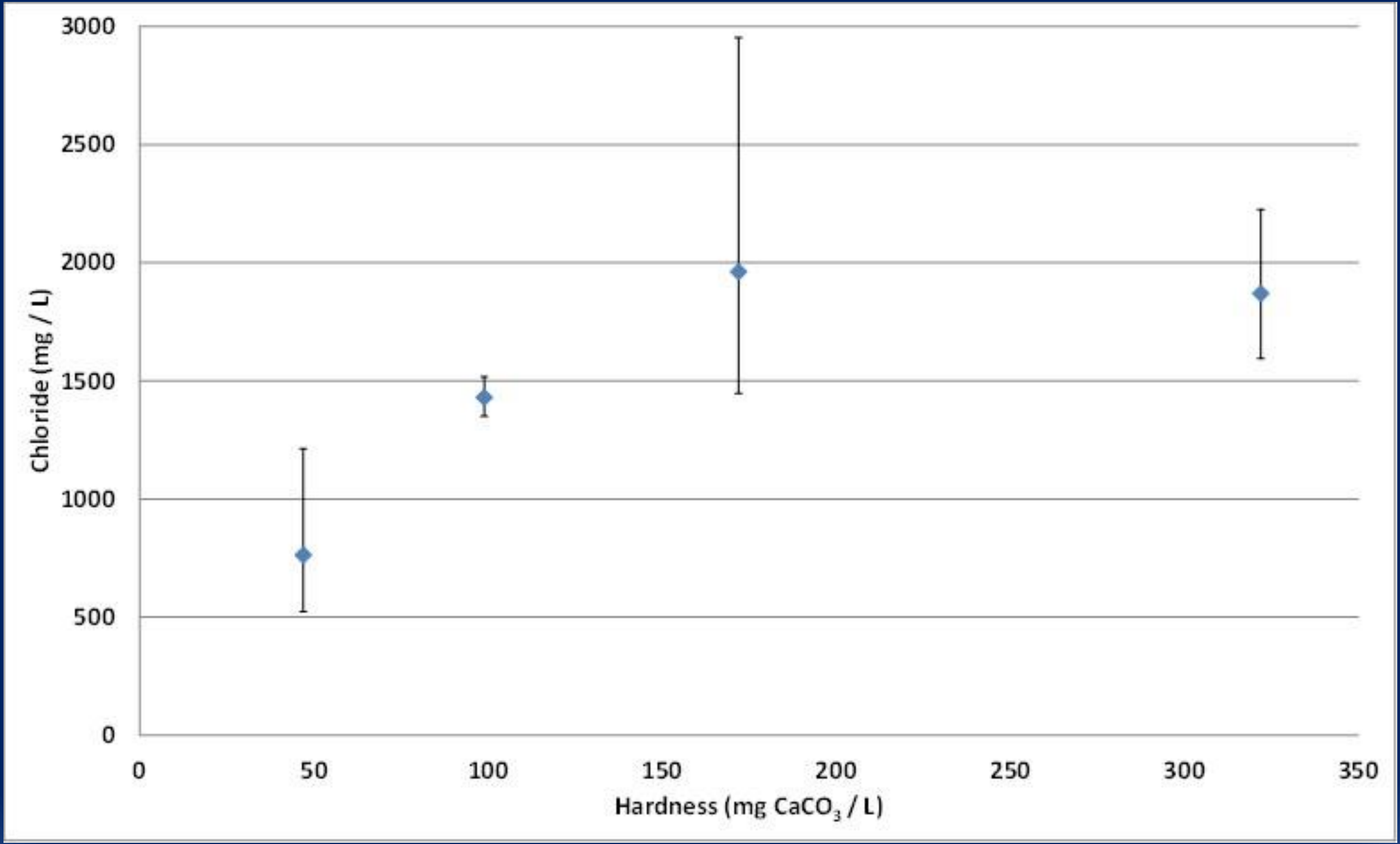
  - *geometric mean taken for the SSD as per CCME*

  - *Why such a different result?*



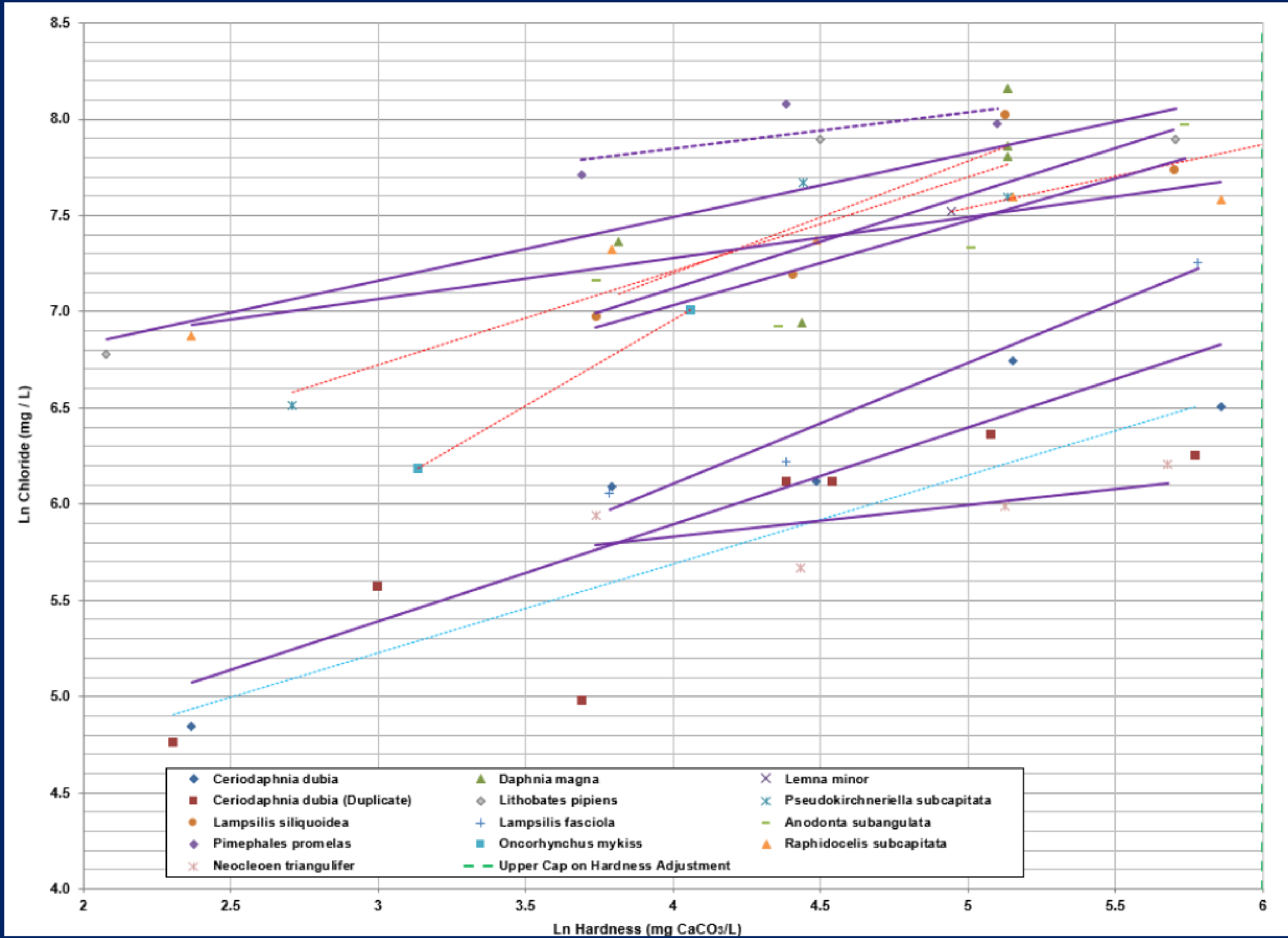
Chronic Chloride Guideline Derivation

- Example of hardness toxicity relationship
- Gillis (2011) – *Lampsilis siliquoidea* (fatmucket mussel)
- Error bars represent 95% confidence interval



Chronic Hardness Adjustment

- Next step – analyze chloride toxicity as a function of water hardness

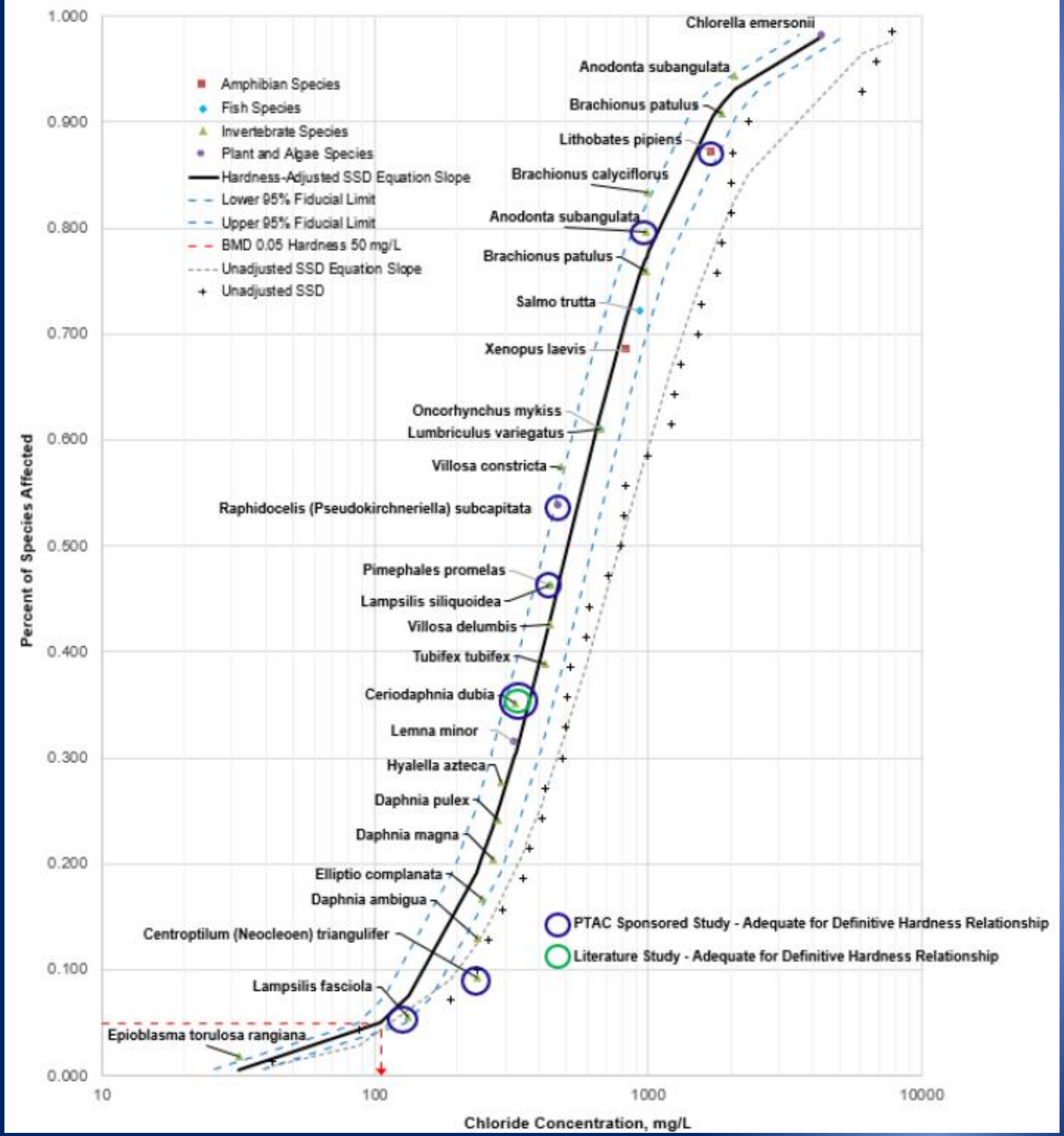


Hardness Adjusted Long-Term SSD Derivation

- Figure is guideline and SSD at a hardness of 50 mg/L
- Driver is one of the mussel species that can't be tested in Canada

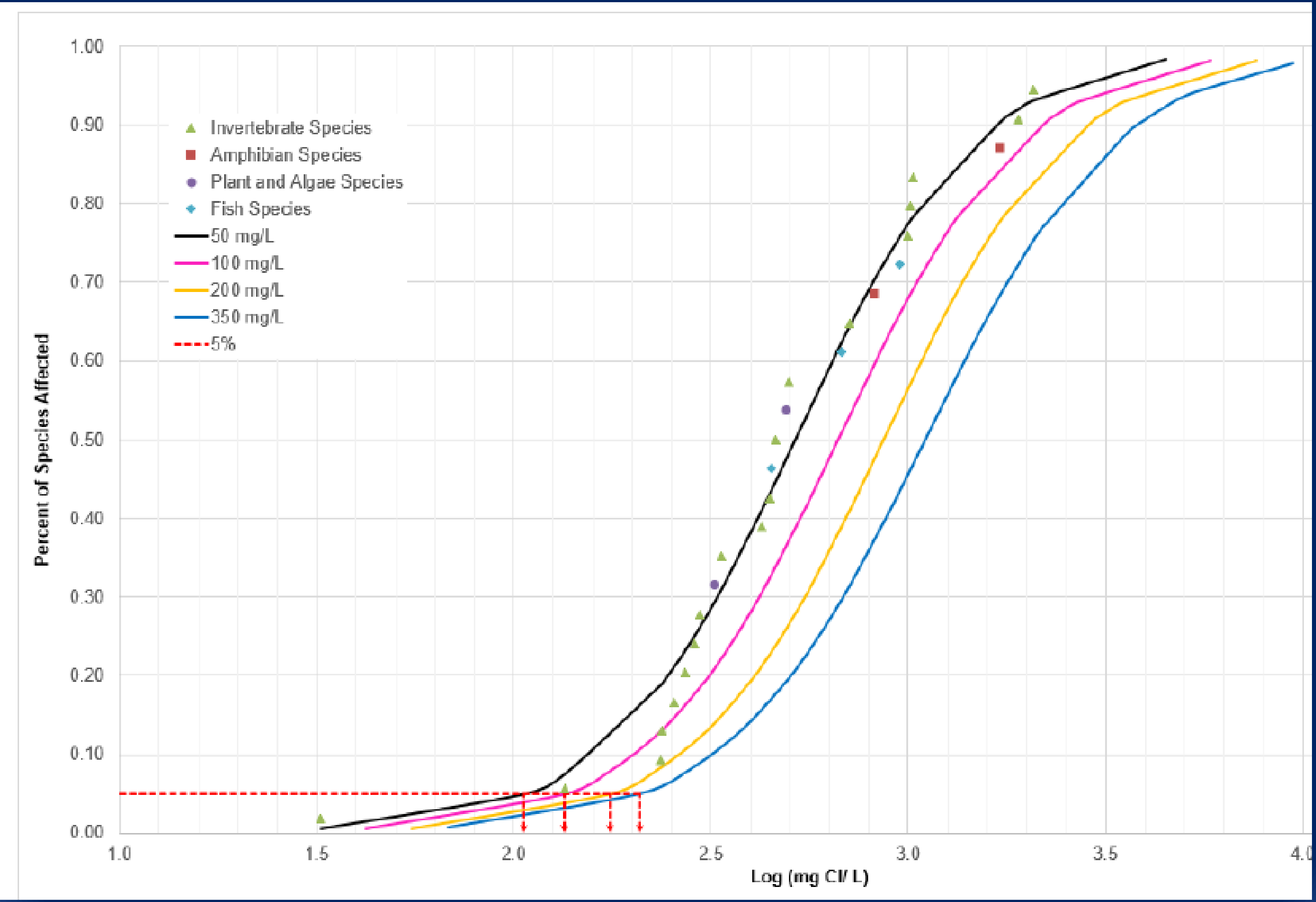
Long-term WQG = $exp^{[0.38\ (\ln(hardness)) + 3.18]}$

Hardness ($mg\ CaCO_3/L$)	Long-term WQG ($mg\ Cl^-/L$)
Current derivation	($exp^{[0.38(\ln(hardness)) + 3.18]}$)
5 (very soft)	44
50 (soft)	106
100 (moderately soft)	138
200 (moderately hard)	180
350 (hard)	222



Hardness Adjusted Long-Term SSD Derivation

- Essentially a family of curves based on hardness level



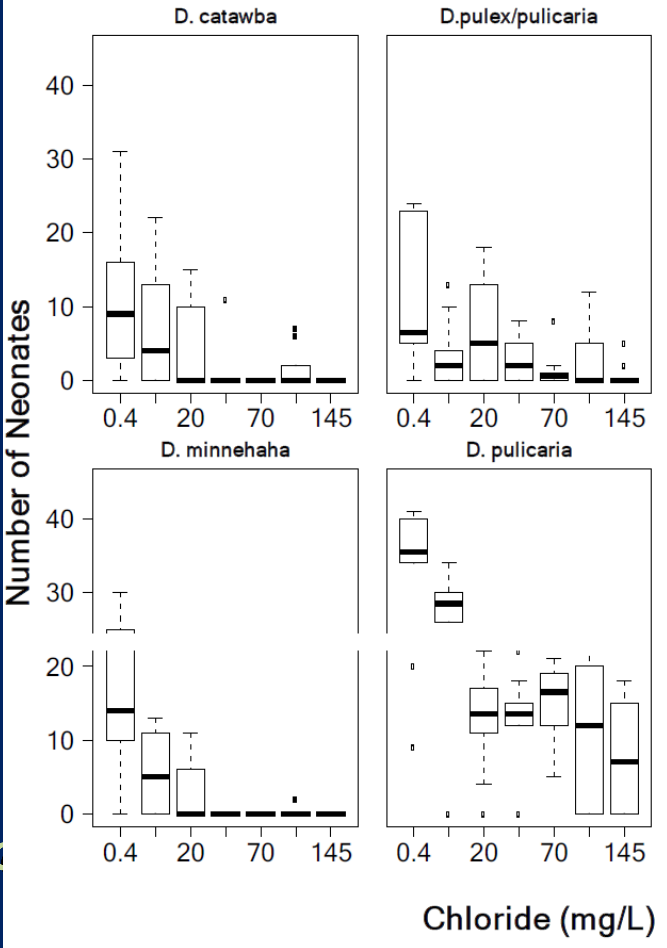
Demonstration of Hardness Important for Data Derived from Soft Water Experiments

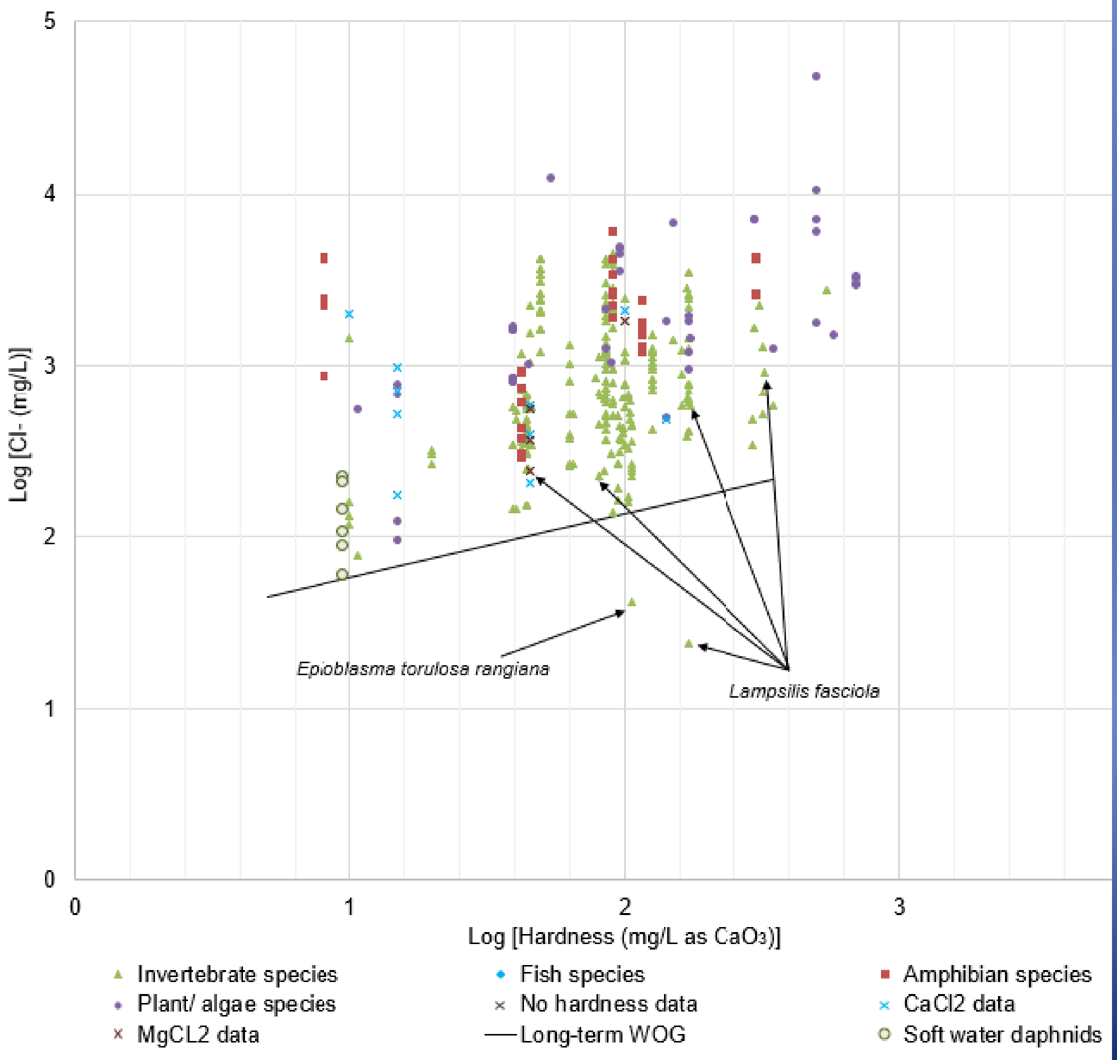
- Evaluate protectiveness of the guideline
- Two points below line

- *Lampsilis fasciola*
  same testing, same lab different result
  Geometric mean taken

- *Epioblasma torulosa rangiana*
  single study, not reproduced – drives the SSD

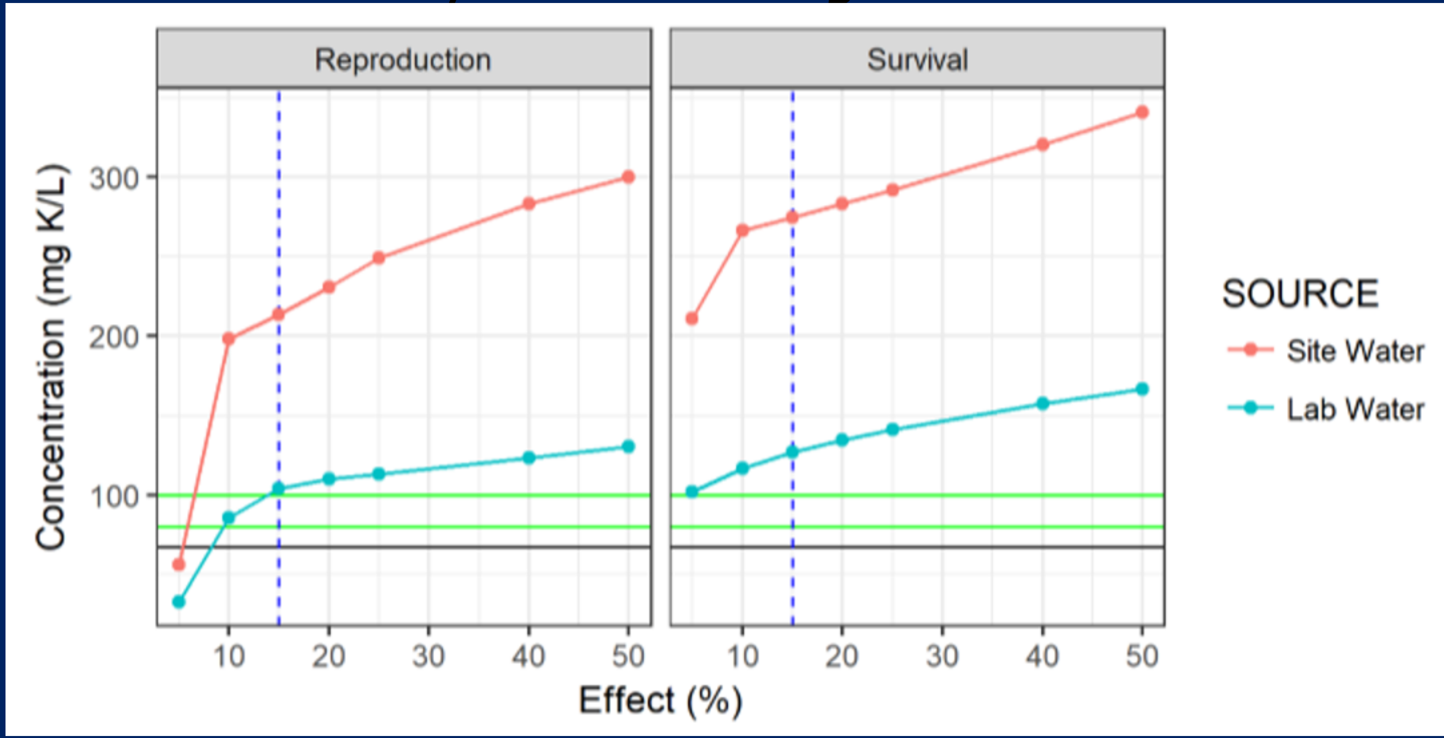
- Arnott et al (2020) – recent soft water daphnid data





Lab Water Versus Field Water

- Consistently, lab water toxicity experiments produce effects at lower concentrations than field water
  - Results shown below d. Magna, but same results seen for multiple frog, mussel, and other species
  - All studies used here are lab water experiments – implies that for a number of species, there is an added level of conservatism (good)
  - For non-lab cultured species used in toxicity testing (e.g., wild type), clear difference in toxicity depending on source water of collection
  - Implies a built in safety factor to the guidelines



Fin.

Questions?