Equilibrium Environmental Inc.

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Water Hardness Ion Mixtures and Chloride Toxicity Towards Aquatic Life

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Banff, Alberta

Anthony Knafla, M.Sc., DABT, P.Biol
FWAL Group










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    Linda Eastcott (Imperial Oil Ltd)

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

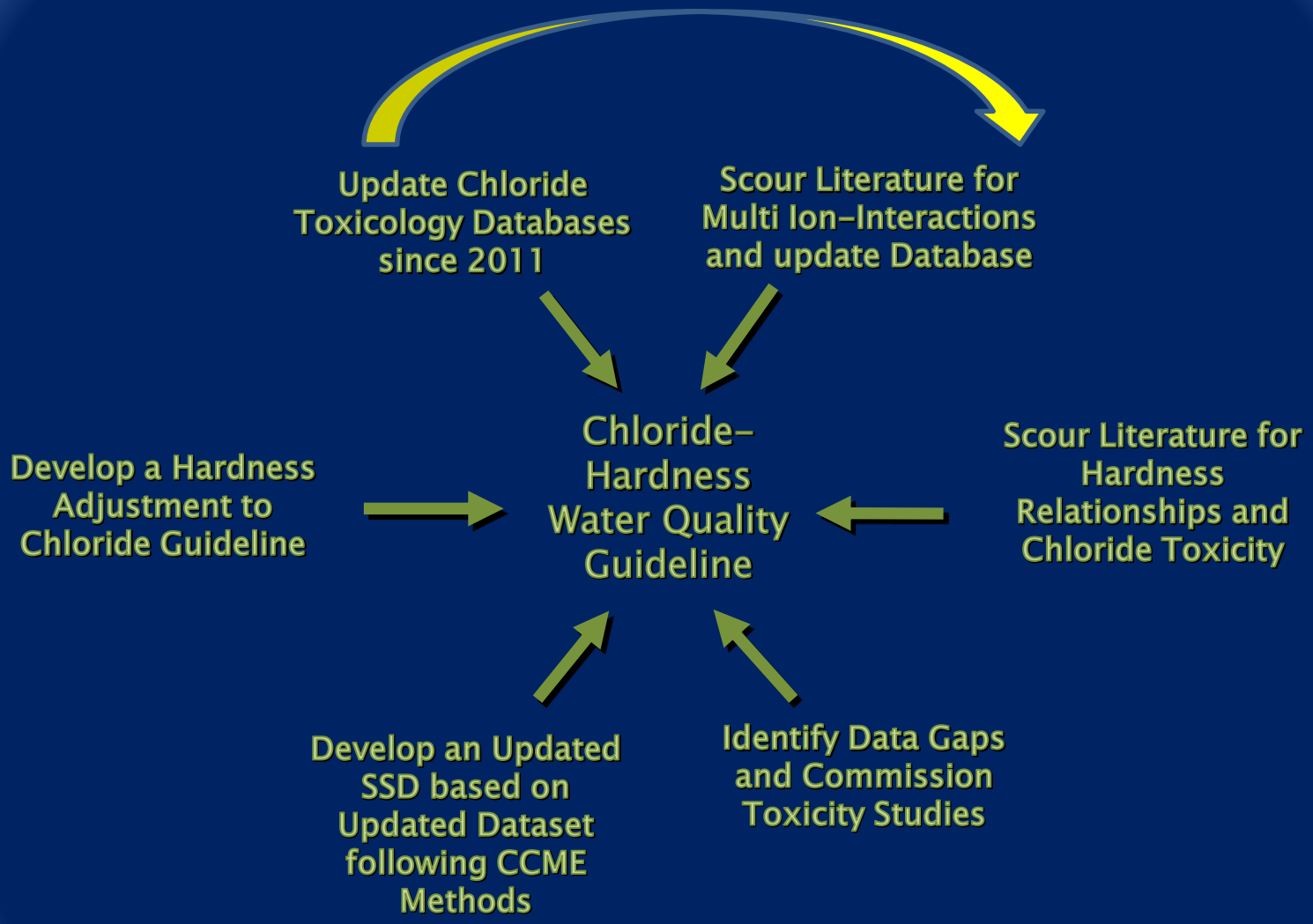
- EQUILIBRIUM SCIENTIFIC STAFF
  - Anthony Knafla

- ADDITIONAL CONTRIBUTIONS
  - Ian McIvor (previous work)

Brief Background

- Natural Sources of Chloride
  - Marine evaporite, weathered geological material, wildfires, sea spray
- Anthropogenic sources
  - Road salts for winter motorist safety
    - Single largest use of salt, Major loading in urban areas
  - Industrial effluents , irrigation drainage, municipal waste water, etc.
  - Oil and gas activities (produced water)
  - Salt blocks, manure applications
- Ambient chloride Concentrations
  - Lakes & Rivers – typically < 100 mg/L
- CCME (2011) guideline derived a chronic guideline of 120 mg/L
  - Indicated that adjusting for water hardness may be appropriate, however, some data are equivocal and more study needed
- In Alberta, Saskatchewan, and NE British Columbia, chloride aquatic life guideline is a major driver of remediation at oil and gas impacted sites due to produced water releases
  - Driver for funding of research for hardness influence on chloride toxicity to petition to CCME for updating a national guideline

Research Method – Guideline Development



Chloride Cation–Specific Differences

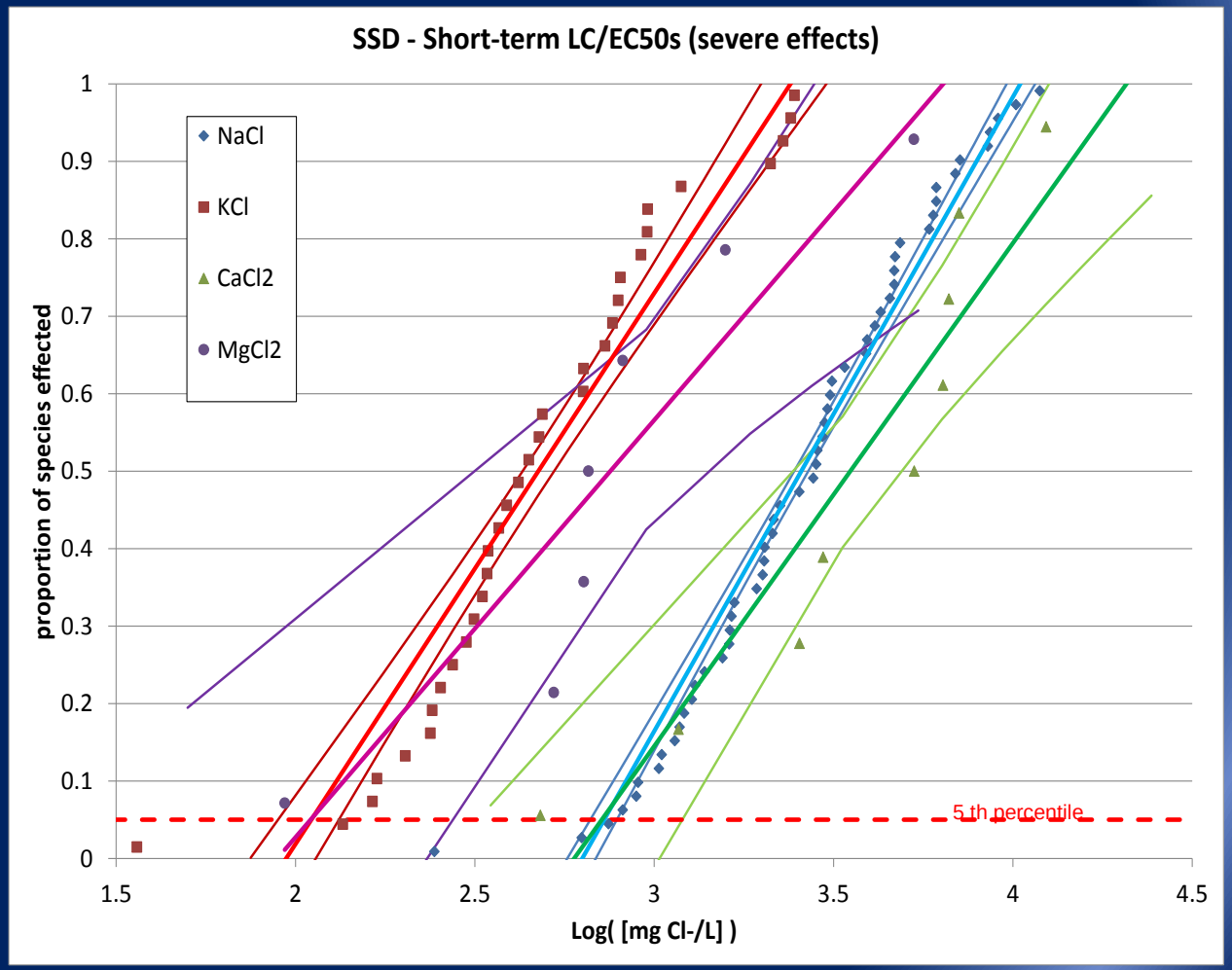
- The is a clear different in toxicity between different cations associated with chloride
- Requires some evaluation of cation toxicity
- There is also evidence of a complex interaction for mixtures of salt ions

KCl different in toxic potency compared to $CaCl_2$, $MgCl_2$, and NaCl

KCl considered distinct toxicant ion pair – excluded from dataset – needs to be addressed separately

MgCl dataset is weak

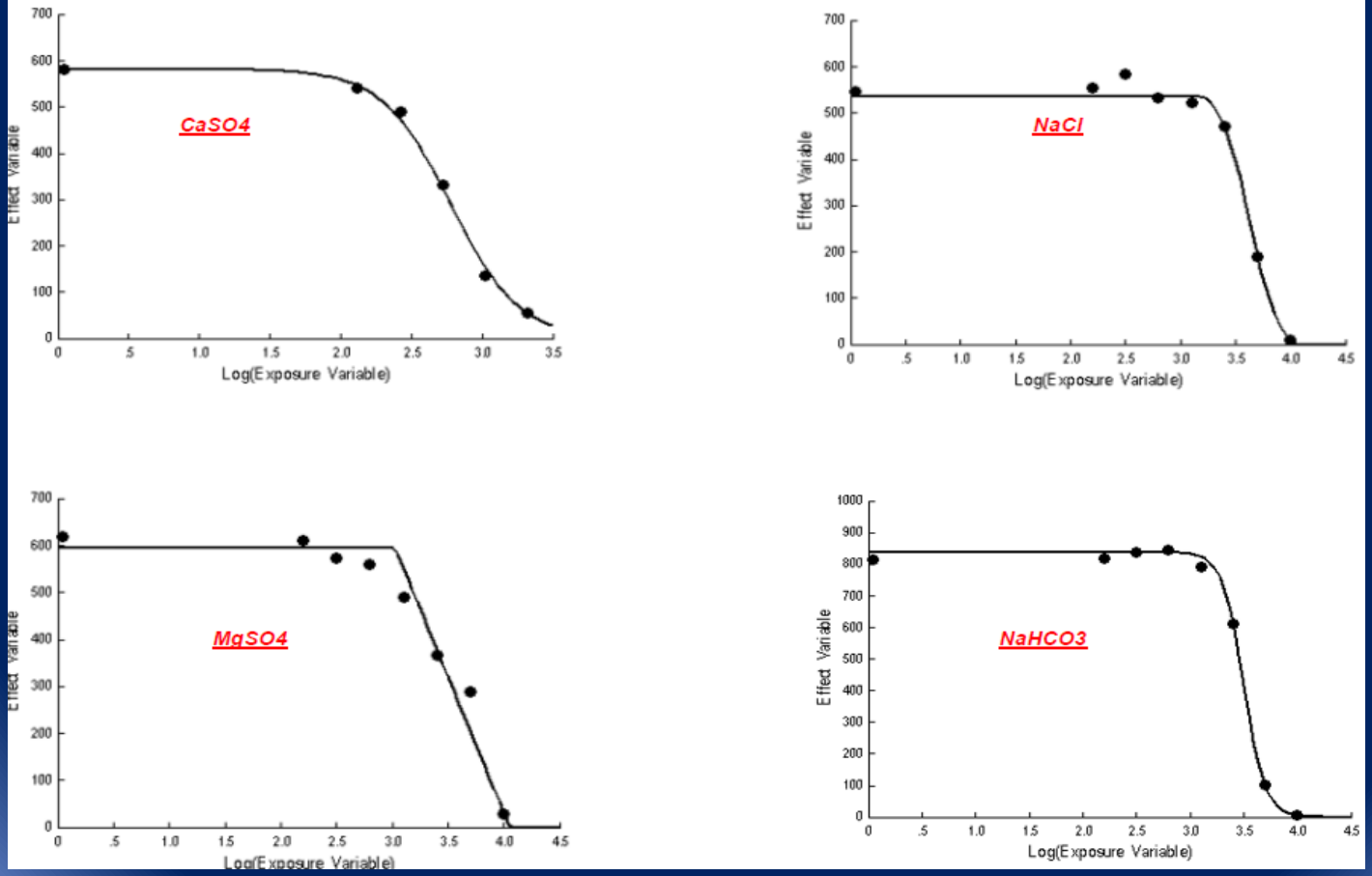
NaCl & $CaCl_2$ toxicity is similar



Also Exploring Anion Differences and Ion Pair Differences

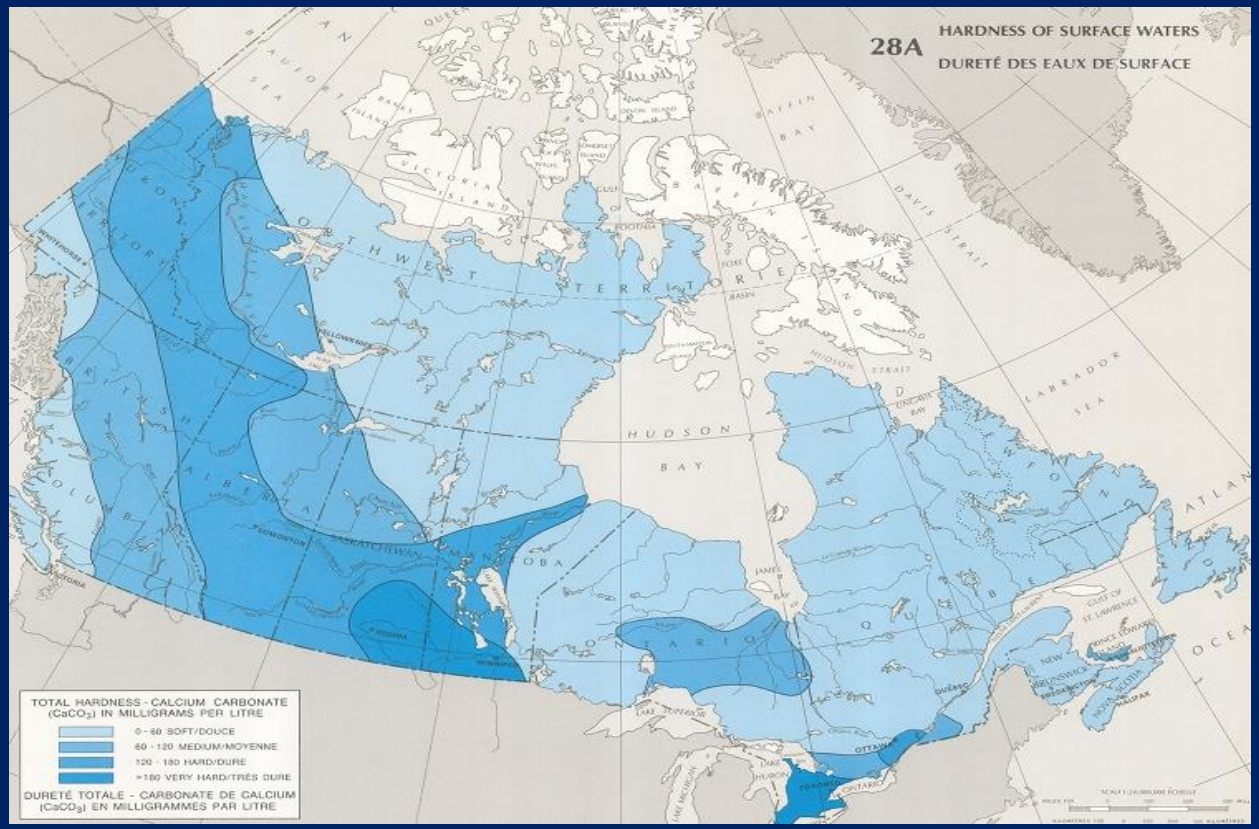
- The is a clear different in toxicity between different cations
- Seeing notable differences between ion combinations and looking for some unifying mechanisms or explanations
- Found nutrient status can be a major factor (for algae)

Figure 14. Multi Salt – 10 x Nutrient Supplement – CaSO4, NaCl, MgSO4, & NaHCO3



Hardness Relationship – Chloride Toxicity

- Variable water hardness in Canada (NRCAN, 1978)
- If chloride toxicity varies with hardness, then guideline across Canada should vary



Hardness = Sum of polyvalent cations

$(Ca^{2+}$ & $Mg^{2+}) = 2.5[Ca^{2+}] + 4.1[Mg^{2+}]$

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)

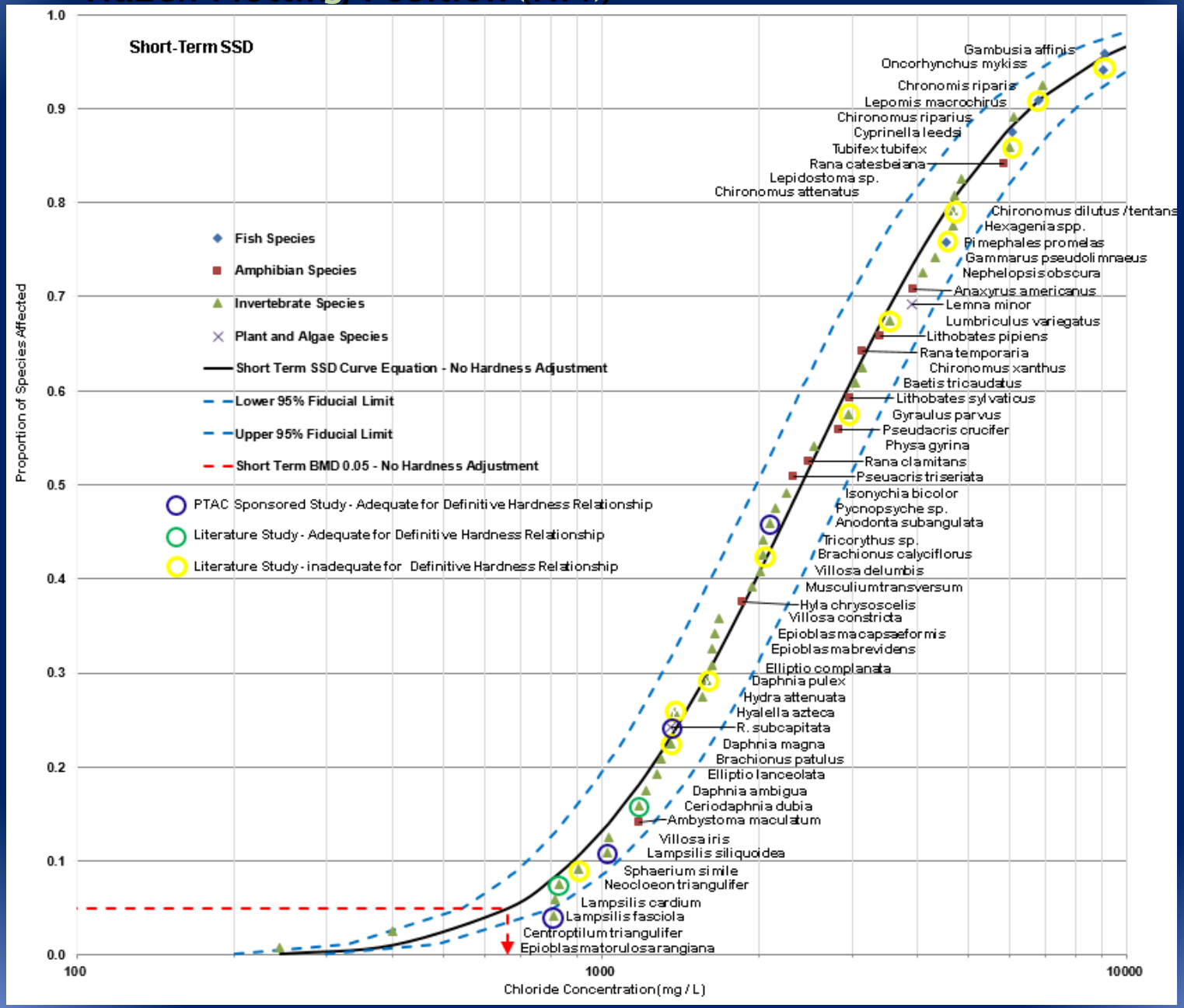
- Elphick (2011) published a means of evaluating reduced chloride toxicity due to increasing hardness

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
  - >200 studies
  - 2077 entries: Unacceptable: 16%;
    NaCl: 37%; KCl: 12% ; $CaCl_2$: 4%;
    $MgCl_2$: 1%; multiple ions: 30%

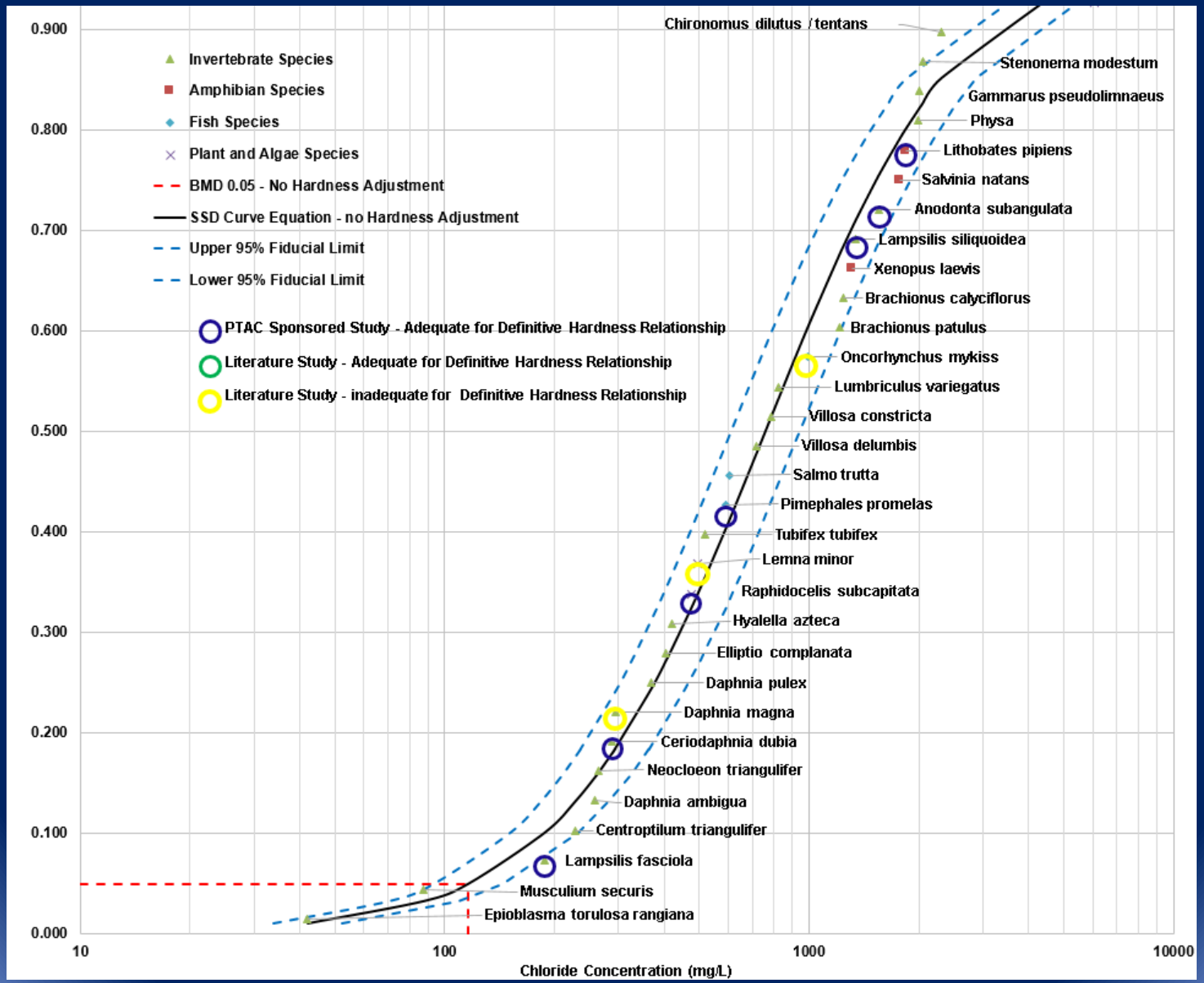
Short-Term Chloride Guideline Derivation

- Hazen Plotting Position (HPP)



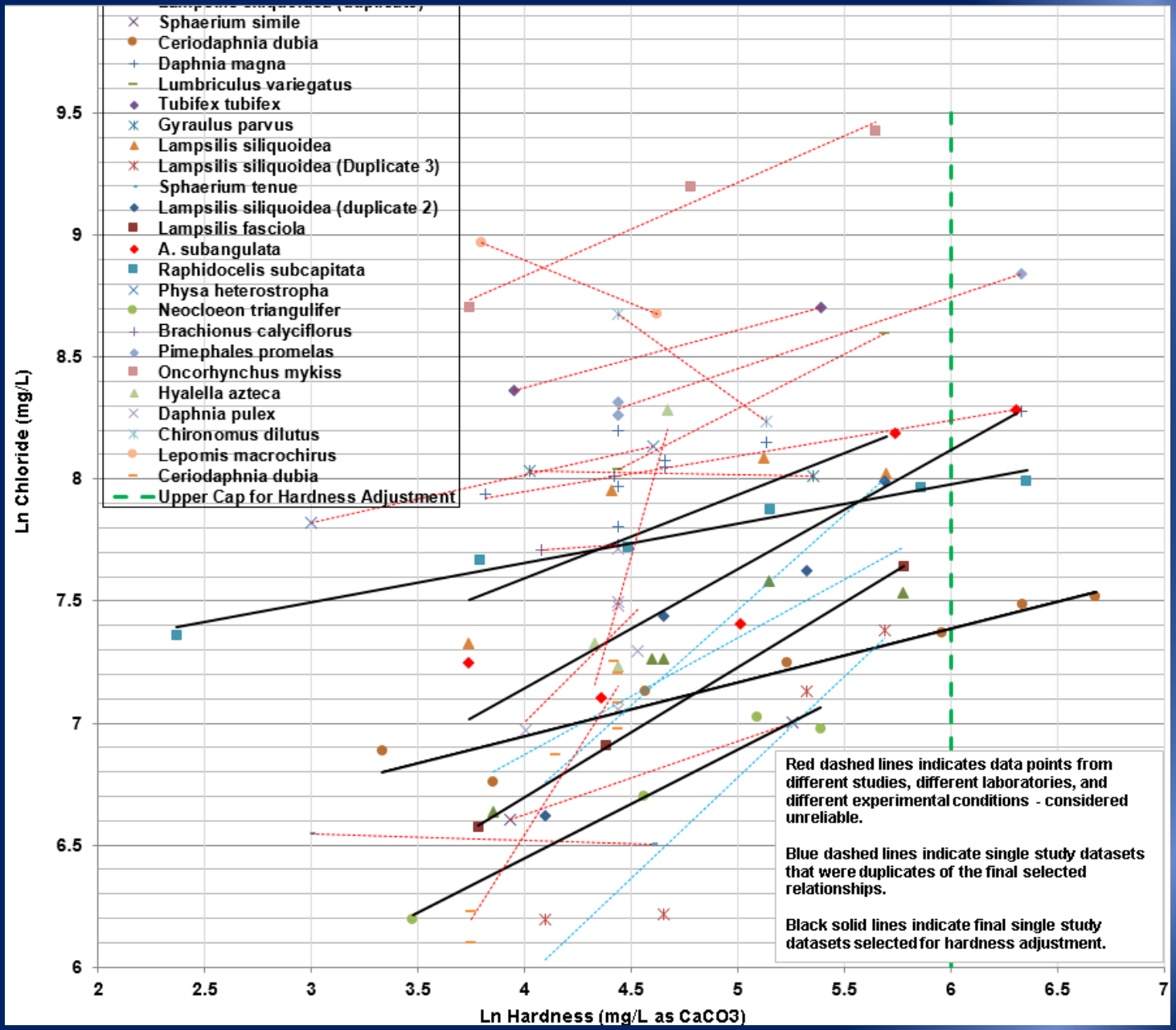
Long-Term Chloride Guideline Derivation

- Previous literature data was inadequate for hardness adjustment based on EPA and other guidance for a chronic endpoint



Short-Term Hardness Adjustment

- Clear relationships between increasing hardness and decreasing chloride toxicity – to a point
- studies not showing relationships frequently had study design issues and often were not targeted to evaluated hardness relationships



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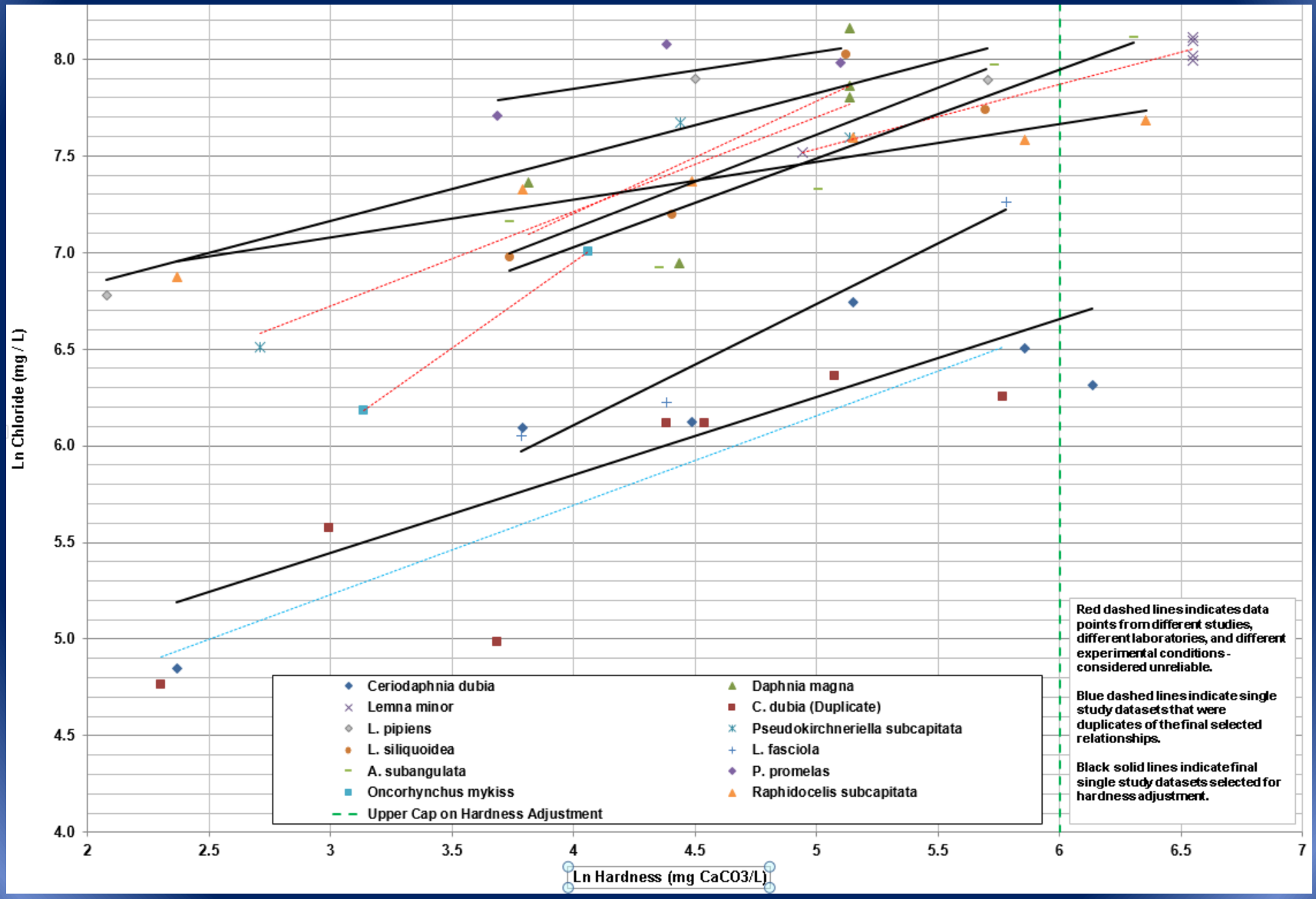
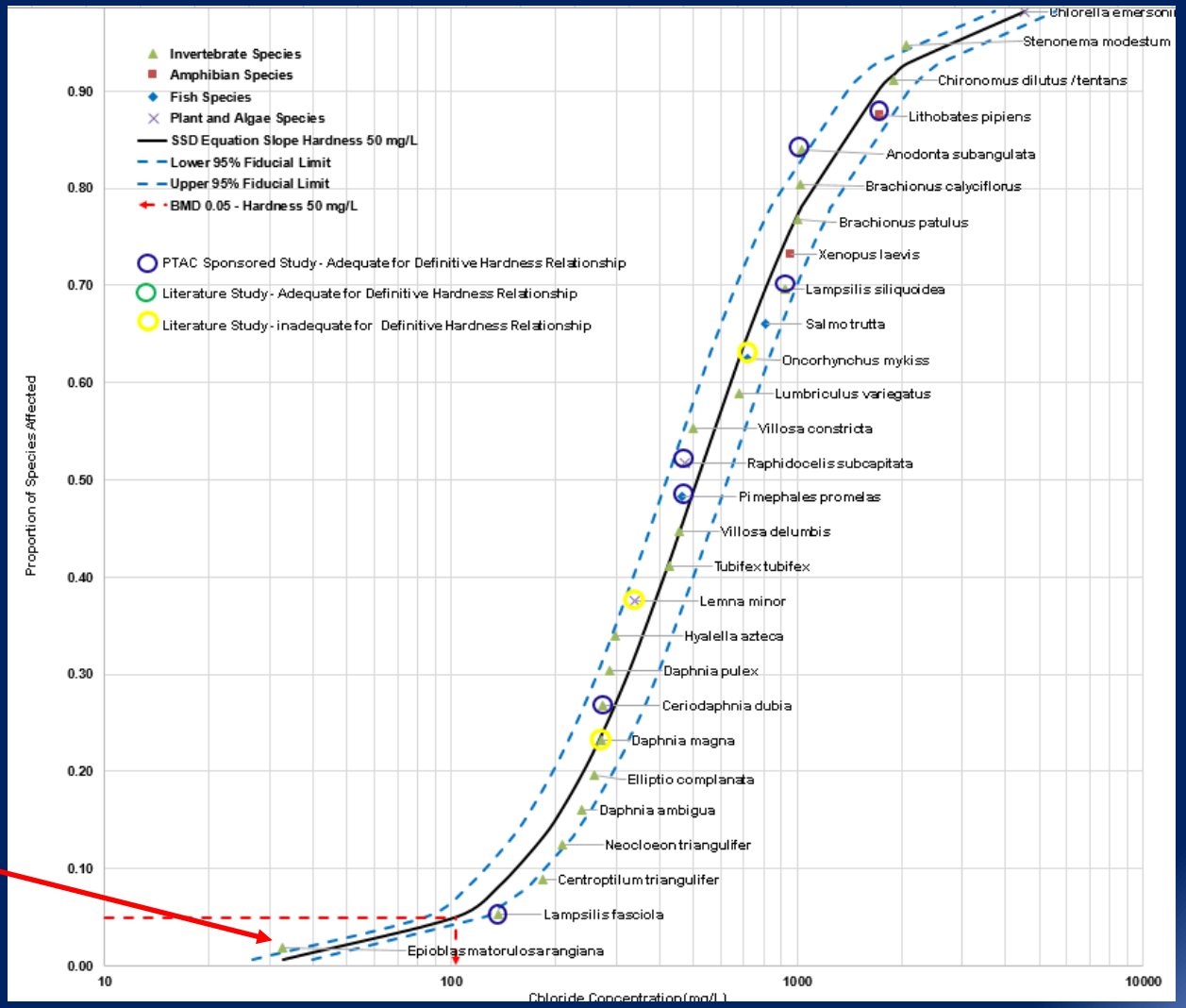


Hardness Adjusted Long-Term SSD Derivation

- Following adjustment, order of species can change due to hardness conditions under which the experiments were conducted
- Driver is still one of the mussel species that is 'untestable'



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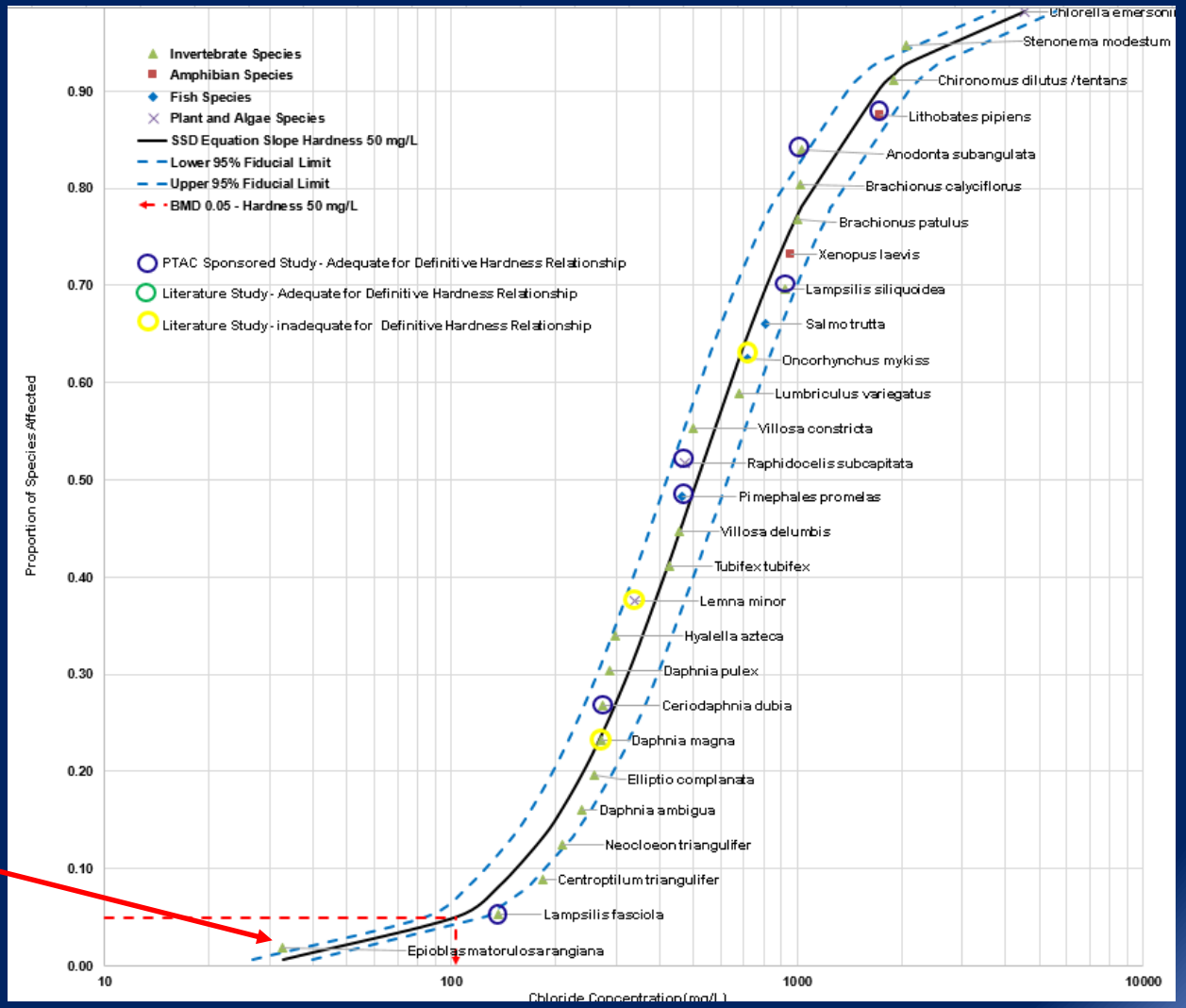
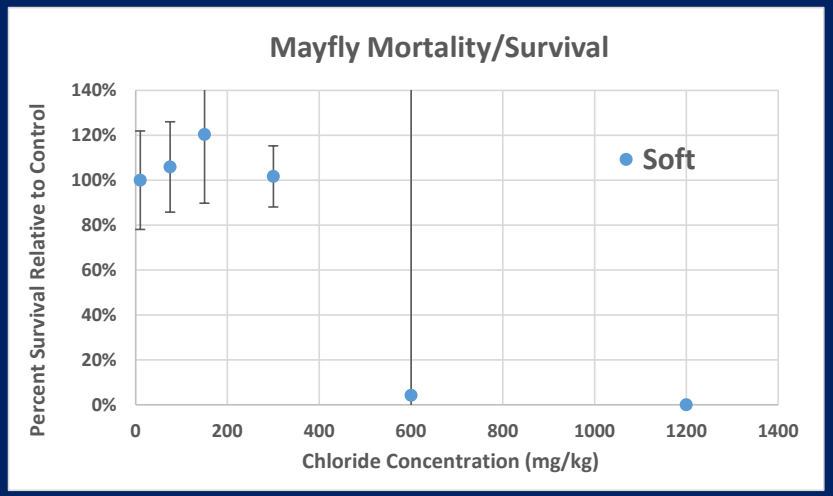
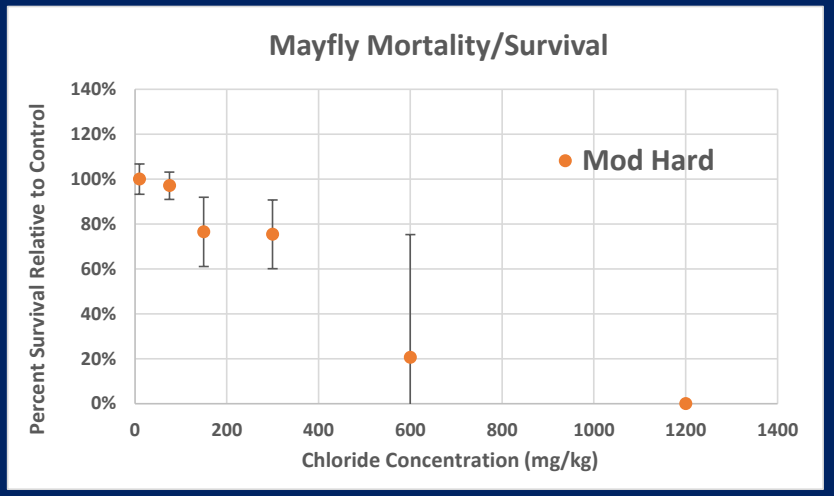
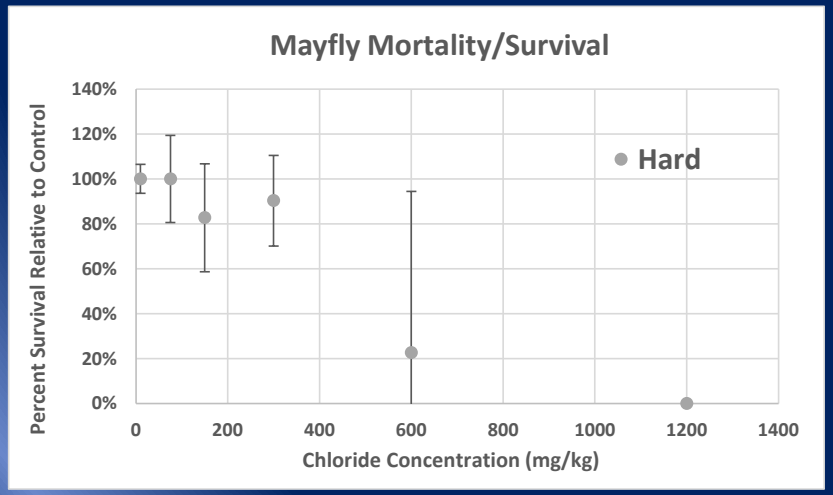


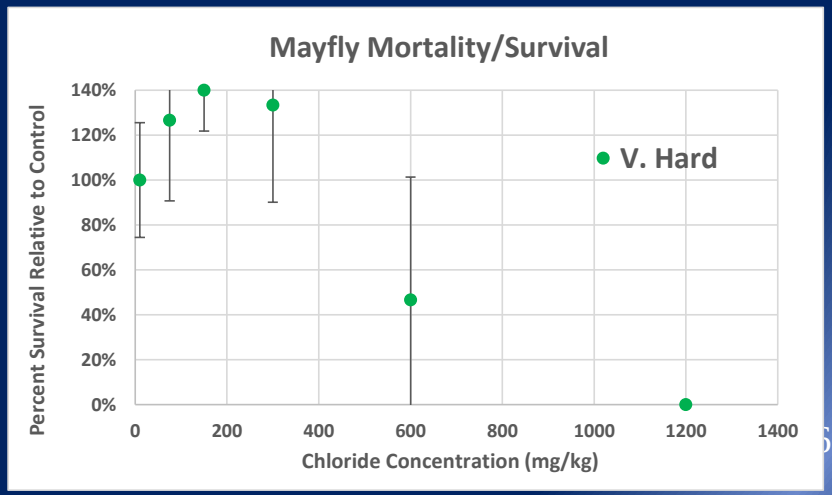
HOT OFF THE PRESS! MAYFLY TOXICITY

- Nautilius environmental completed Mayfly toxicity testing as it was determined by the FWAL team that having an EPT species is critical
- General pattern of decreased chloride toxicity with increasing hardness observed (preliminary results) – mayfly don't like soft & very hard water (had higher control mortality)



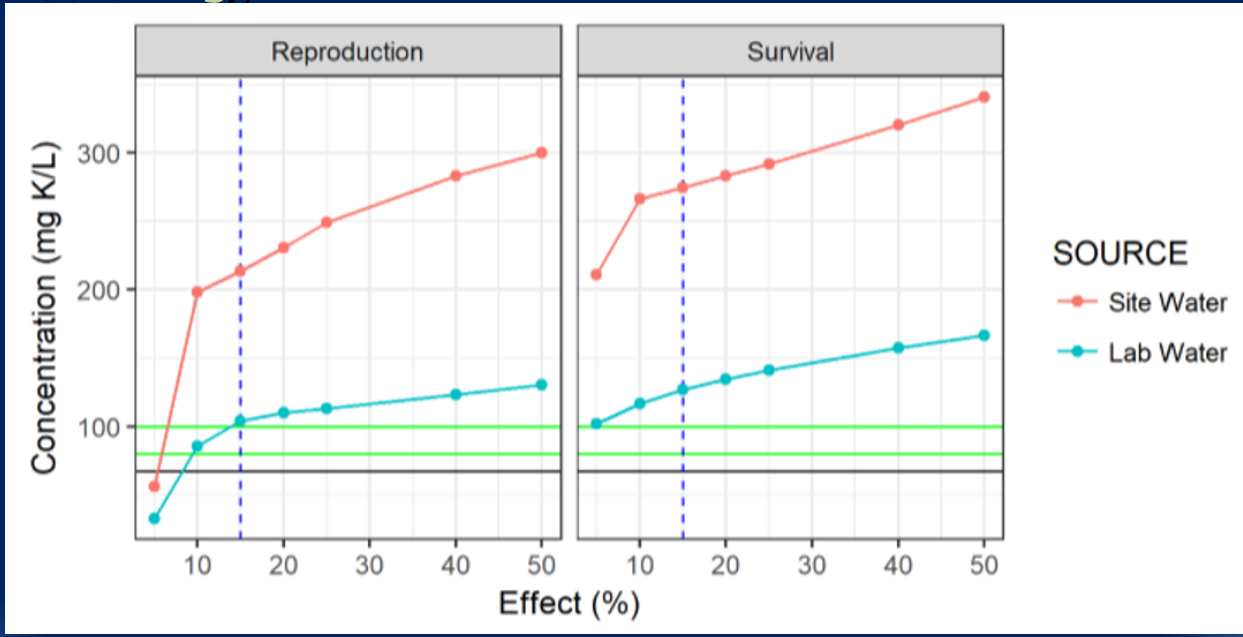






Some Points to Consider

- 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
    - Sensitive mussel species re-tested by same author just different source of mussels had an EC_{10} in the 100s of mg/L rather than in the 10s of mg/L



Fin.

Questions?