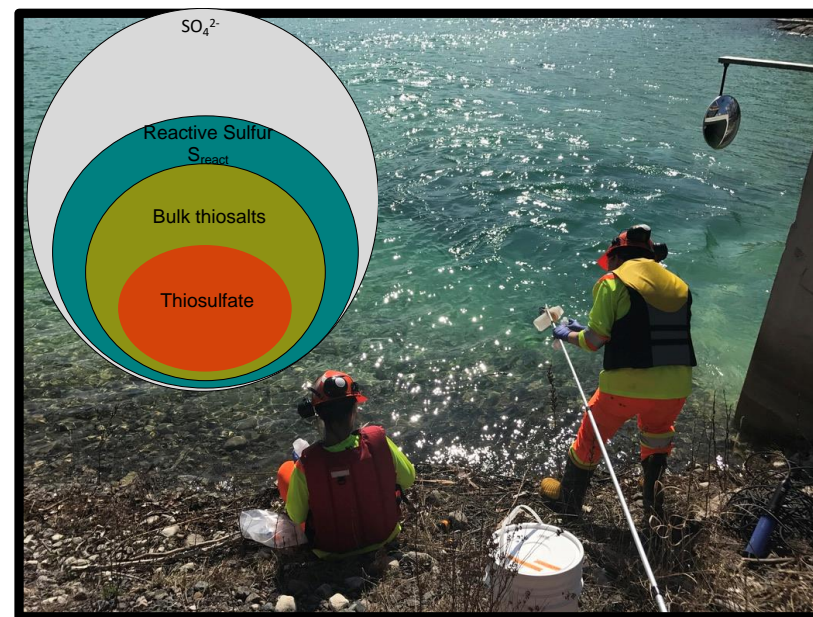




Cost-Effective Mass Balance Approach to Monitor Thiosalt Risks for the Mining Industry

Reactive Sulfur

Kelly Whaley-Martin*, Tara Colenbrander Nelson, Lauren Twible and Lesley Warren (University of Toronto)
Chad Jarolimek, Josh King and Simon Apte (CSIRO)
Stephanie Marshall (ERM)
Sam McGarry (Glencore, Sudbury INO),
Shirley Neault and Landice Yestrau (Hudbay Minerals)
Peter Mercer (Rambler Metals and Mining) and
Helga Sonnenberg (EcoReg Solutions)



Mine Wastewater Solutions Project

Genome Canada LSARP
ON MRI ORF-RE



MEND
NEDEM



GenomeCanada



Ontario Genomics



GenomeQuébec



Ontario
MINISTRY OF RESEARCH & INNOVATION

HUDBAY GLENCORE
SUDBURY INO



RAMBLER
METALS & MINING PLC

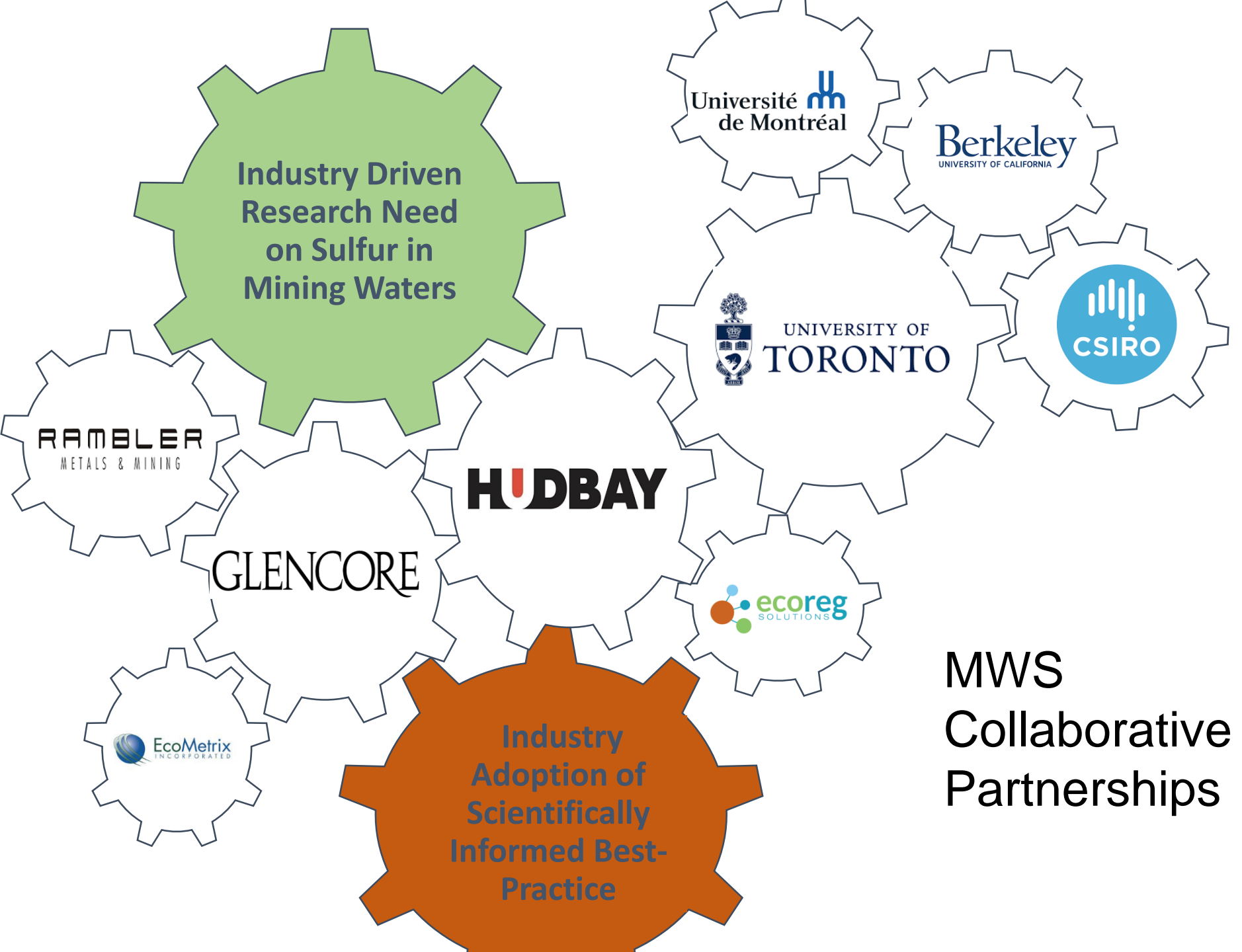


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MWS
Collaborative
Partnerships

| The Risk |

Dissolved reactive sulfur compounds in mining impacted waters are a global challenge

Reactive Sulfur Compounds

Water Flow Paths
↓

- Processing Waters
- Tailings Reservoir Caps
- Polishing/Setting Ponds
- Regulated Discharge Points
- Downstream Environments



| The Risk |

Dissolved reactive sulfur compounds in mining impacted waters are a global challenge

Oxidation



- Oxygen Consumption
- Acidity/Metal Release

Reactive Sulfur
Compounds

Potential
Environmental Impacts

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- Penalties
- Shutdowns

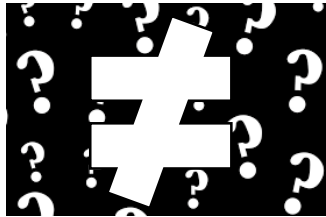


Analytical Definitions and Terminology Matter!

Sulfur oxidative processes are **often intimately connected** with toxicity/**regulatory failures**

MDMER regulations **don't currently regulate** SO_4^{2-} or **reactive S compounds** in Canadian discharged mine waters...but the term “thiosalts” is an industry-adopted term

Reactive Sulfur
Compounds



Thiosalts

| Analytical Definitions and Terminology Matter! |

Chemical Definition: Reduced sulfur oxyanions formed during milling (grinding, aeration and flotation circuits)



(Thiosalt Consortium/CANMET)

Thiosalts

Analytical Definitions: Serious ambiguity/variation on around how “thiosalts” are measured from mine to mine and/or between commercial laboratories

->leading to “Apples” and “Oranges” data comparisons



| Analytical Definitions and Terminology Matter! |

“Bulk Thiosalts”

Acidimetric Titration (HgCl_2
Titration)

“Thiosalts”

Ion Chromatography

Thiosalts



“Apples”



Originally proposed in 1911
(Feld), later modified in 1976
(Noranda Research centre)



“Oranges”



Commercial labs report “thiosalt”
numbers but often they are only
measure thiosulfate



Acidimetric Titration (Bulk Thiosalts)

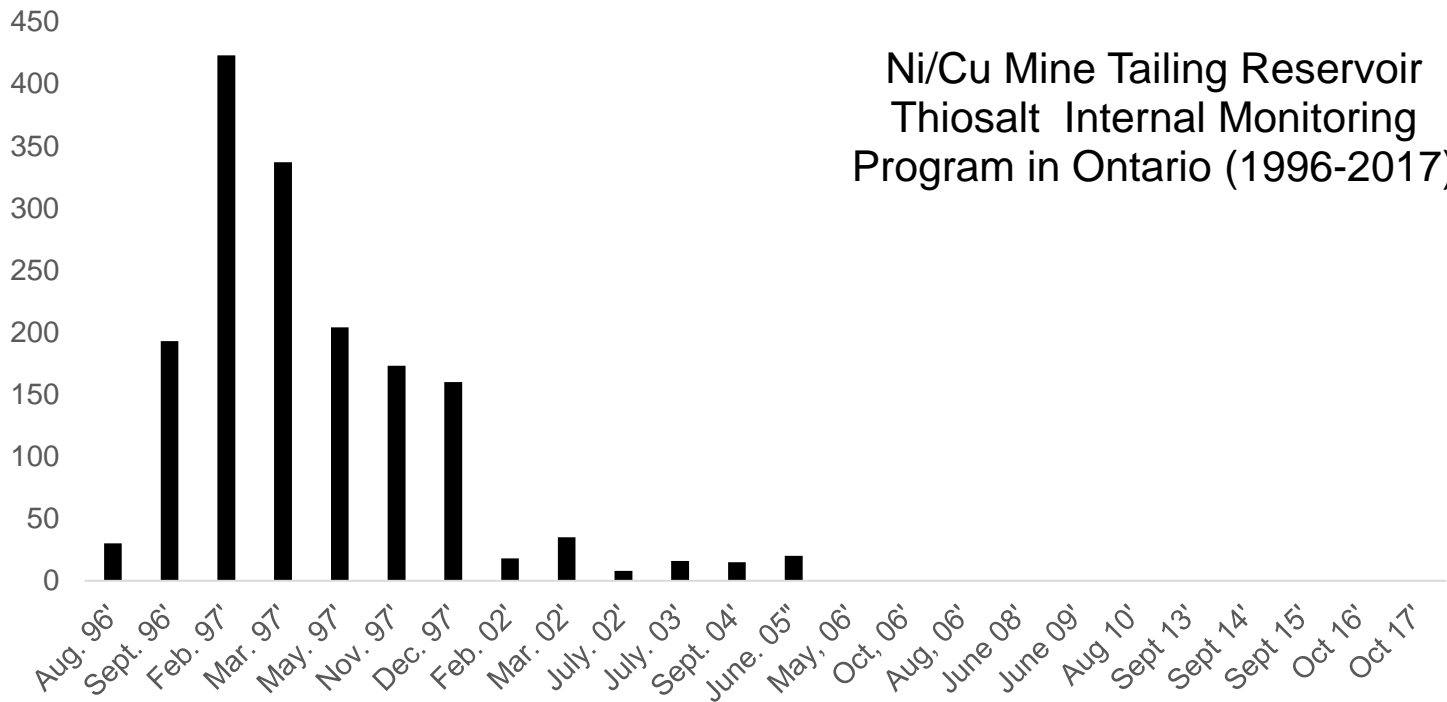


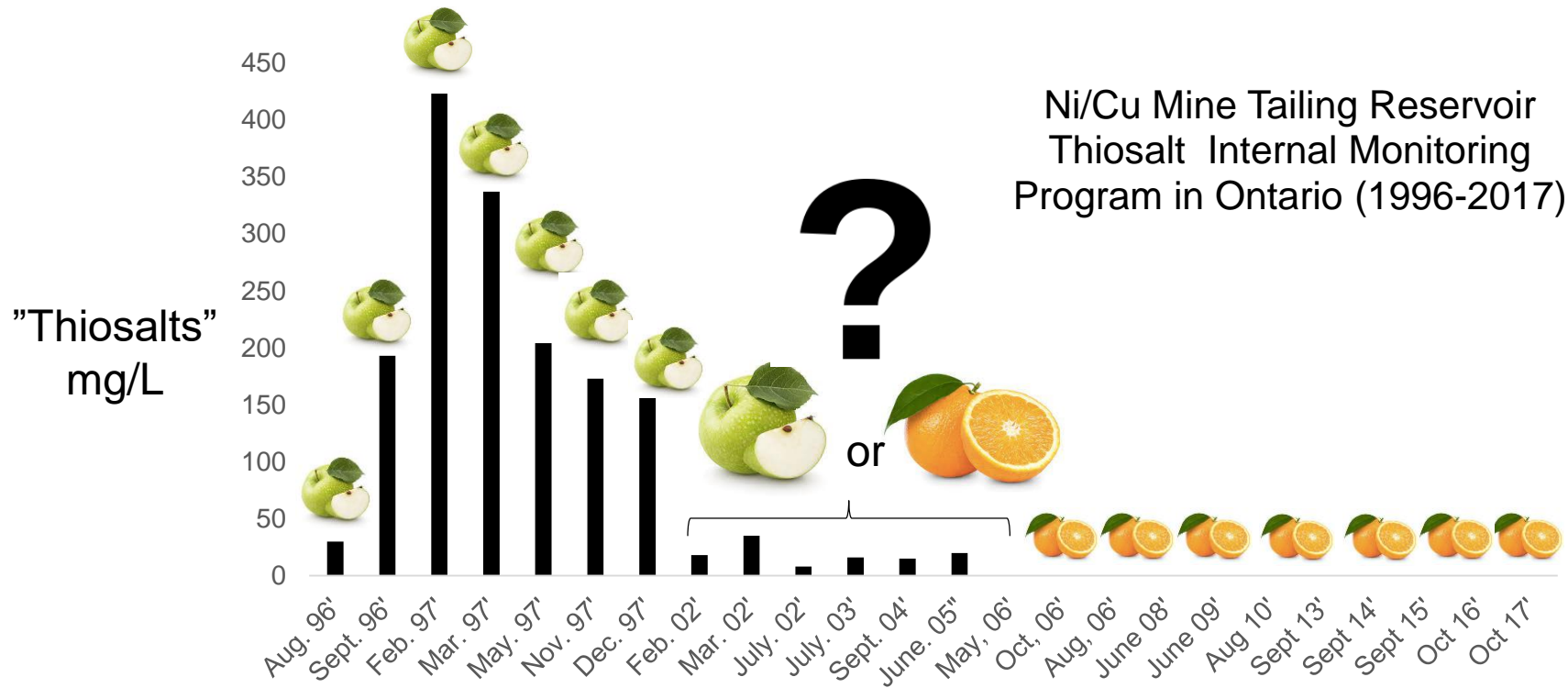
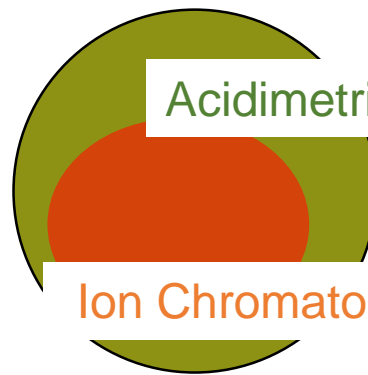
Ion Chromatography (Thiosulfate)



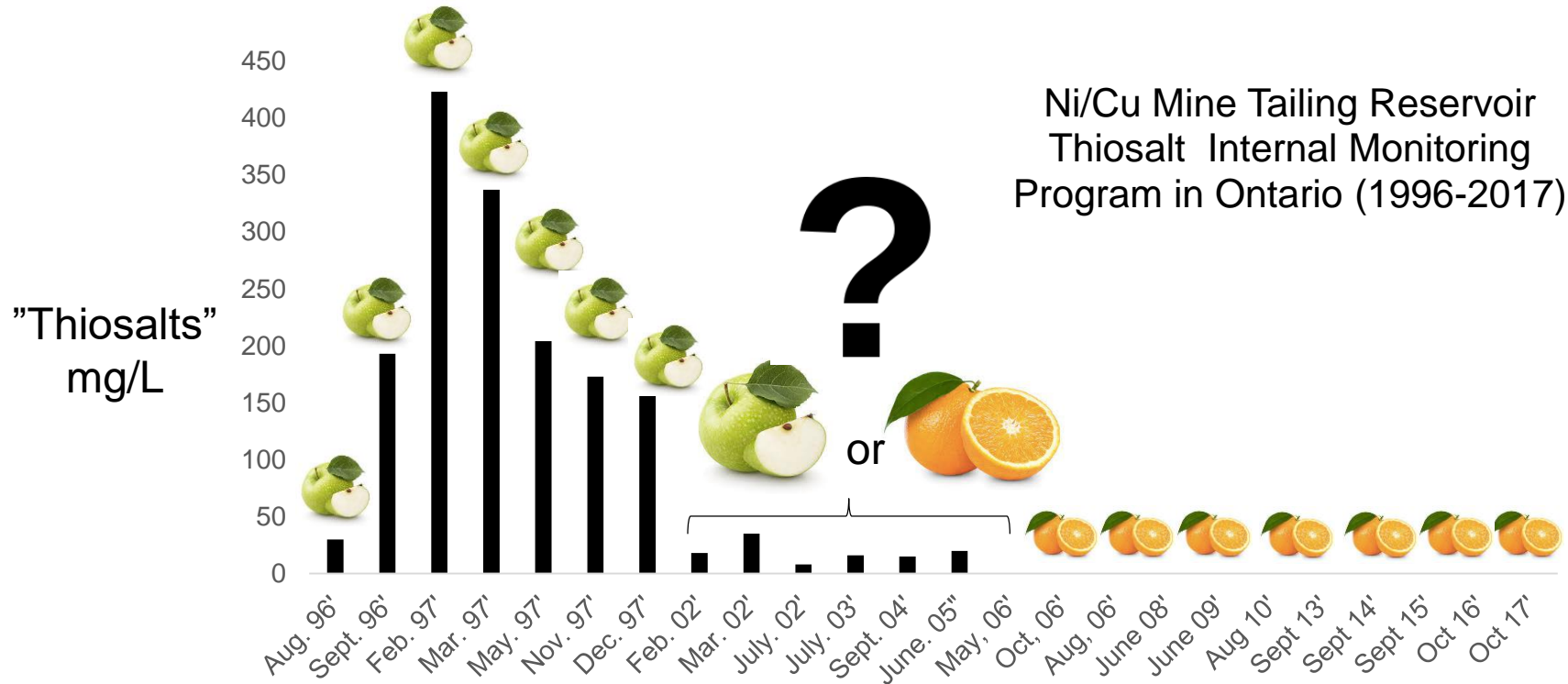
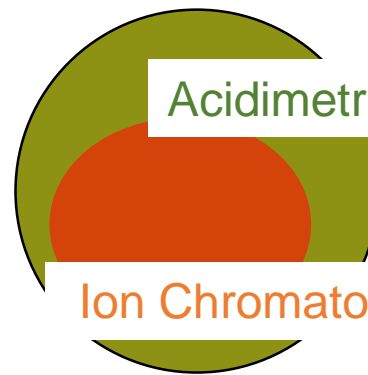
"Thiosalts"
mg/L

Ni/Cu Mine Tailing Reservoir
Thiosalt Internal Monitoring
Program in Ontario (1996-2017)





The commercial laboratory was asked.... they stated *"to the best of their knowledge there had been no change in thiosalt methodology over time"*
-Subsequently, when an overview of the analytical method used was asked for, **two SOPs were sent for both Acidimetric Titration and Ion Chromatography**



Ambiguity on analytical definitions, unknown changes to methodologies and lack of information sharing can lead to

→ **Incomparable data sets**

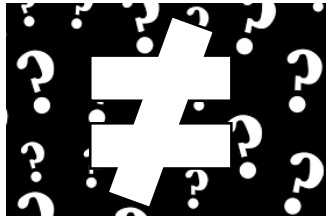
→ Misinterpretation of “thiosalt” concentrations over time/space

Analytical Definitions and Terminology Matter!

Sulfur oxidative processes are **often intimately connected** with toxicity/**regulatory failures**

MDMER regulations **don't currently regulate SO_4^{2-} or reactive S compounds** in Canadian discharged mine waters...but the term “thiosalts” is an industry-adopted term

Reactive Sulfur
Compounds

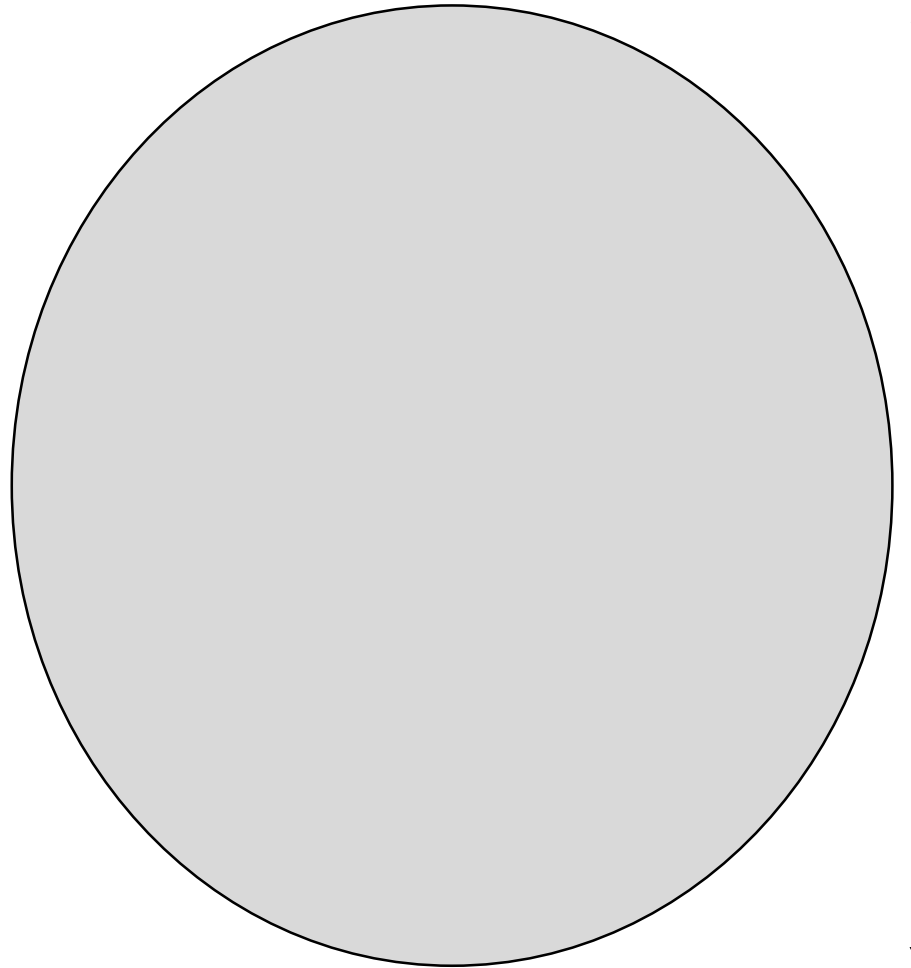


Thiosalts

| Analytical Definitions and Terminology Matter! |

Reactive Sulfur
Compounds

Aqueous sulfur pools can be comprised of many different inorganic and organic sulfur compounds



Total S: all sulfur compounds

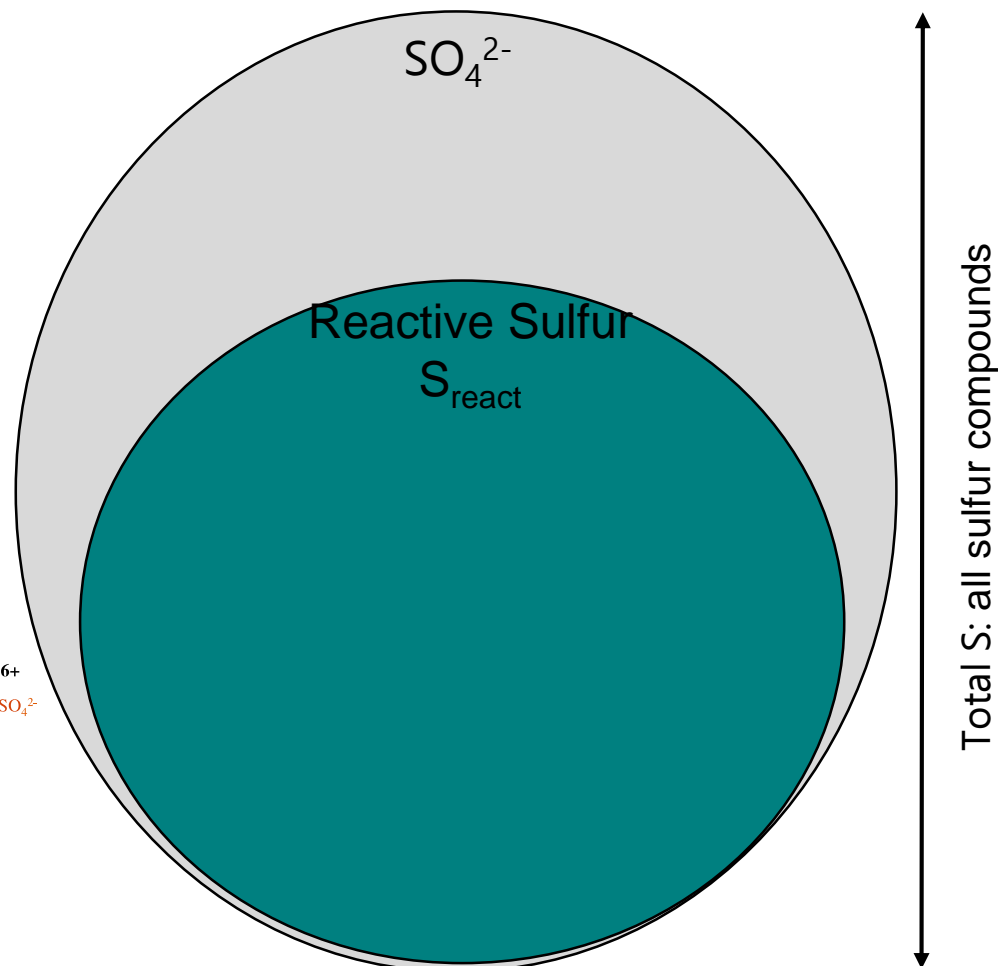
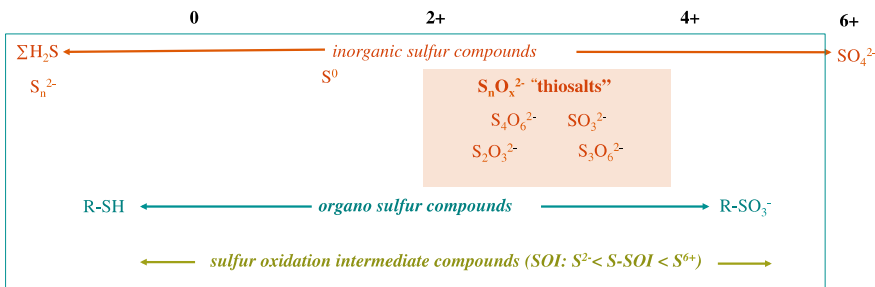


Complex Sulfur Pools are Present in Mining Water

Reactive Sulfur Compounds

Aqueous sulfur pools can be comprised of many different inorganic and organic sulfur compounds

POSSIBLE OXIDATION STATES FOR SULFUR AT EARTH'S SURFACE

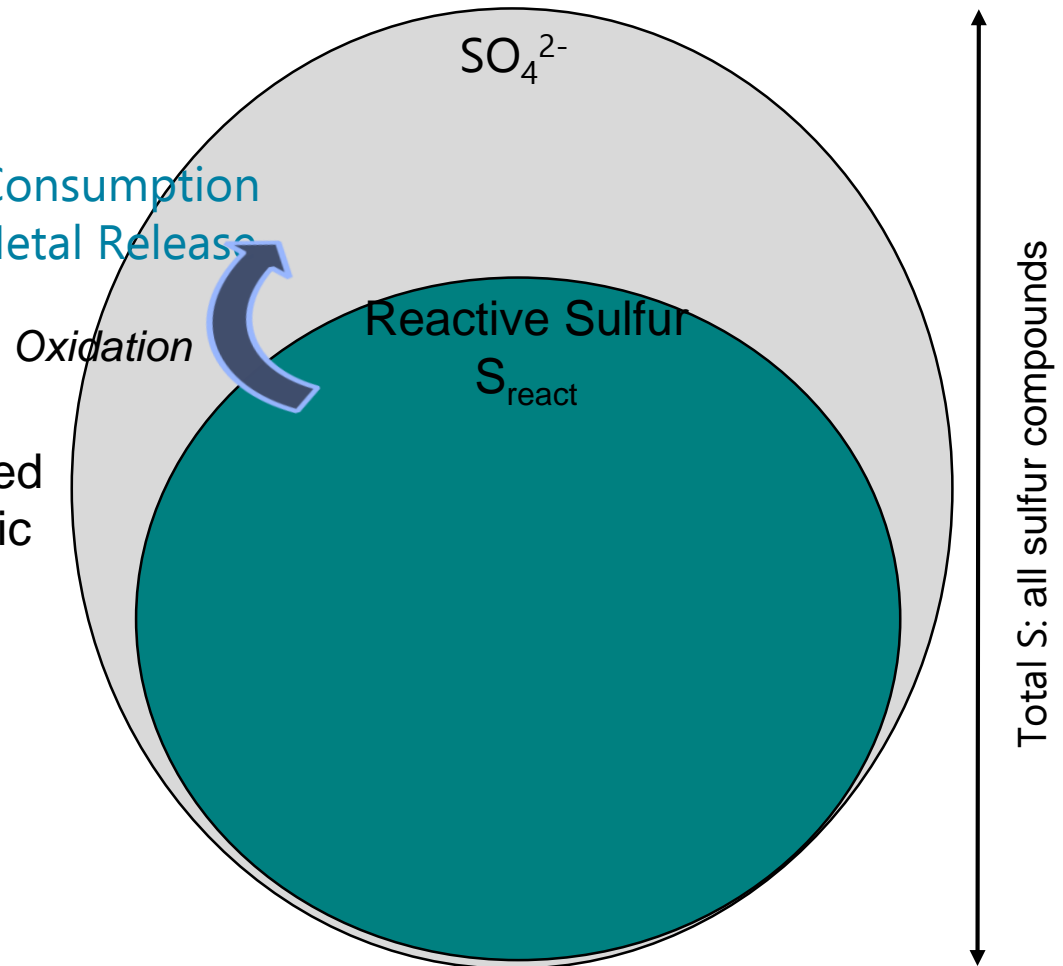


Complex Sulfur Pools are Present in Mining Water

Reactive Sulfur Compounds

- Oxygen Consumption
- Acidity/Metal Release

Aqueous sulfur pools can be comprised of many different inorganic and organic sulfur compounds



Cost-Effective Mass Balance Approach to Monitor Dissolved Sulfur Risks for the Mining Industry

→ Defined a new S method:

→ Reactive Sulfur (S_{react})

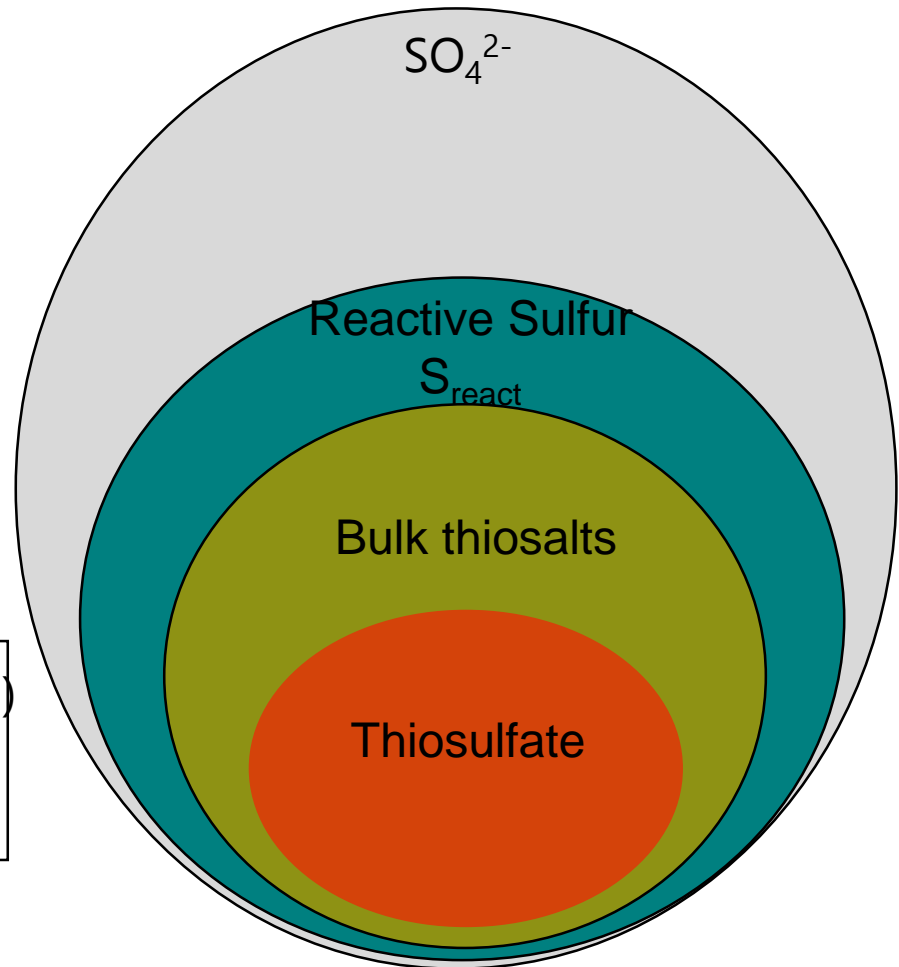
$$S_{\text{react}} = \text{Total S} - \text{S-SO}_4^{2-}$$

→ Compare S_{react} to Current Methods

S_{react}
VS.

Bulk Thiosalts (Acidimetric Titration)

Thiosulfate (Ion Chromatography)



Cost-Effective Mass Balance Approach to Monitor Dissolved Sulfur Risks for the Mining Industry

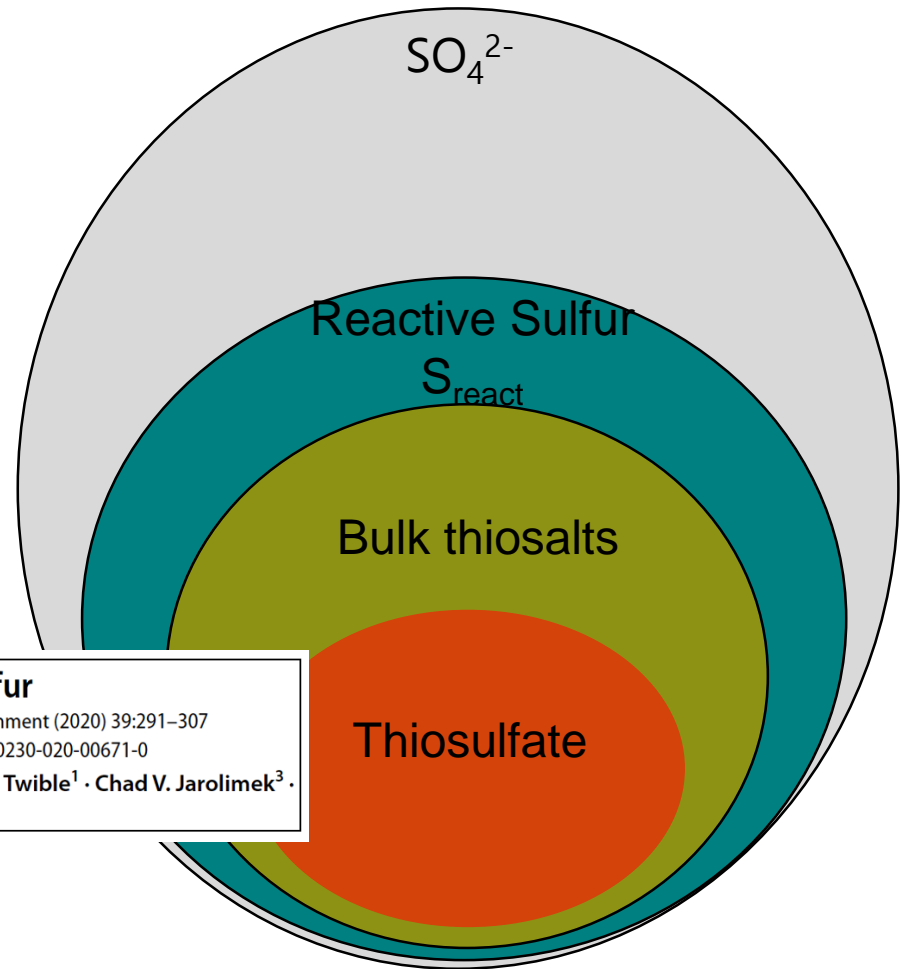
Mass-Balance Approach

→ defined a new S method: reactive sulfur(S_{react})

Reactive Sulfur S_{react}

(total S – sulfate)

- More conservative of risk
- Economical
- Calculable with current monitoring data
- Directly comparable across mines



A Mass-Balance Tool for Monitoring Potential Dissolved Sulfur

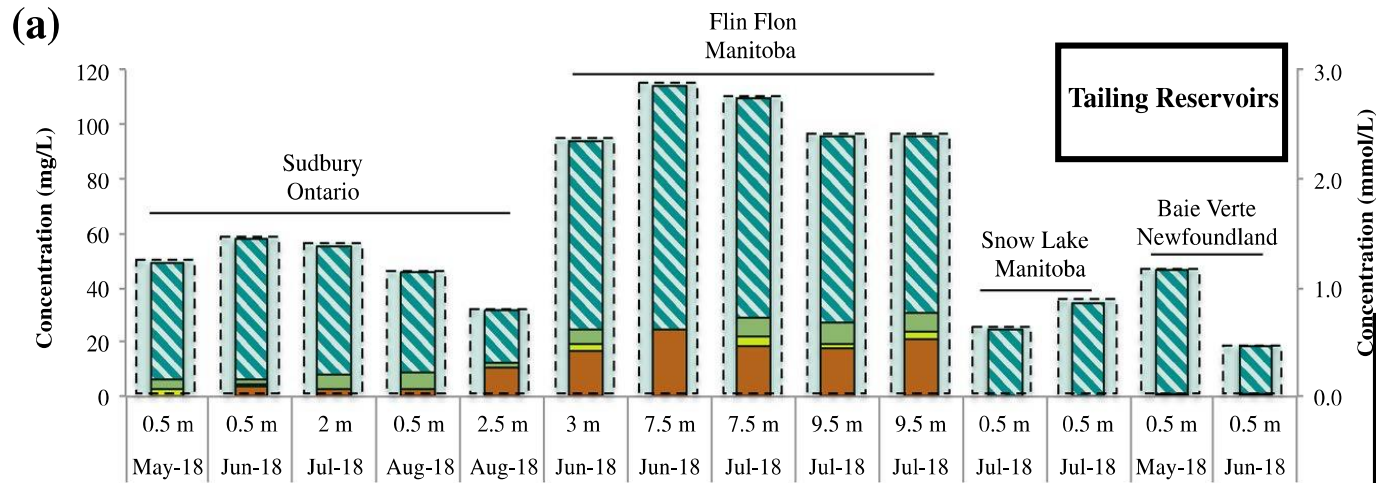
Oxidation Risks in Mining Impacted Waters

Mine Water and the Environment (2020) 39:291–307

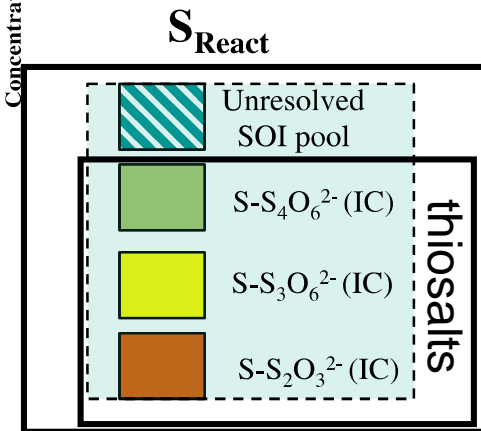
<https://doi.org/10.1007/s10230-020-00671-0>

Kelly Whaley-Martin¹ · Stephanie Marshall² · Tara E. Colenbrander Nelson¹ · Lauren Twible¹ · Chad V. Jarolimek³ · Josh J. King³ · Simon C. Apte³ · Lesley A. Warren¹

S_{react} speciation across 4 mines (i.e. How much of S_{react} = sulfur oxyanions?)

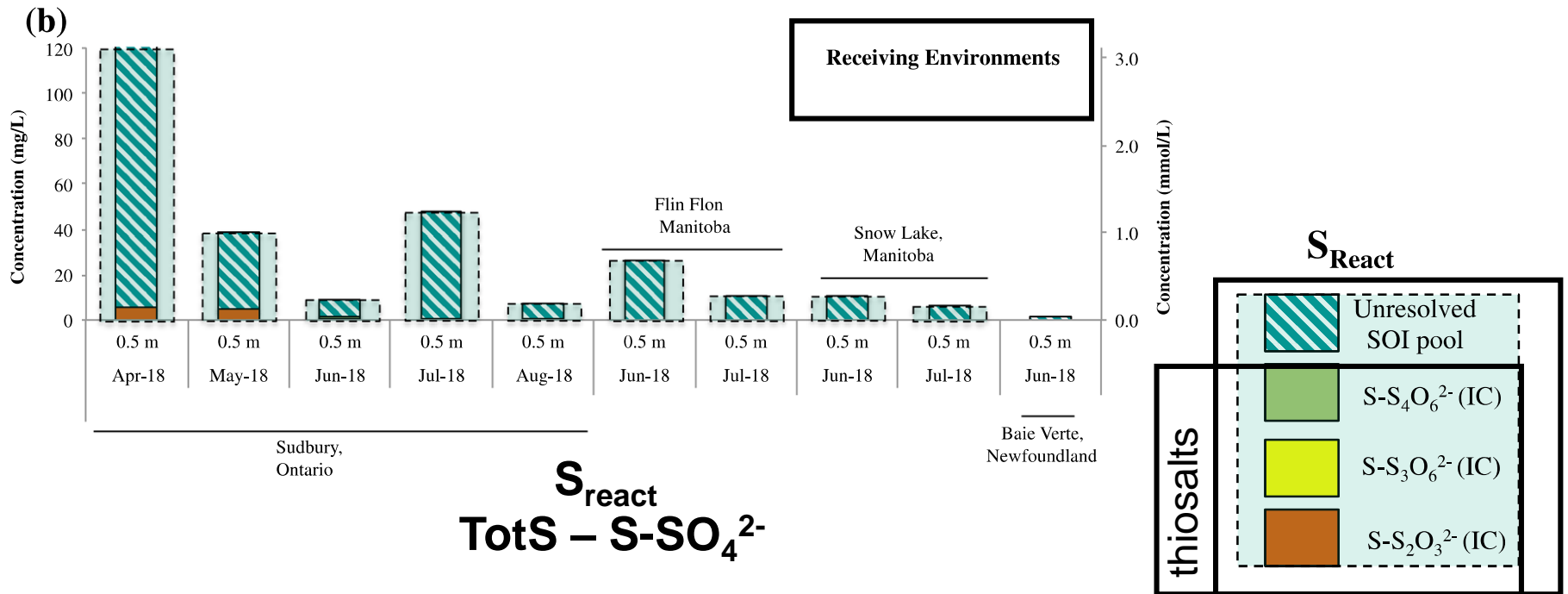


$$S_{\text{react}} = \text{TotS} - S - \text{SO}_4^{2-}$$



[Thiosalts] $\ll S_{\text{react}}$ in tailings reservoirs

Thiosulfate ($S_2O_3^{2-}$)
Trithionate ($S_3O_6^{2-}$)
Tetrathionate ($S_4O_6^{2-}$)



Thiosulfate ($S_2O_3^{2-}$)
 Trithionate ($S_3O_6^{2-}$)
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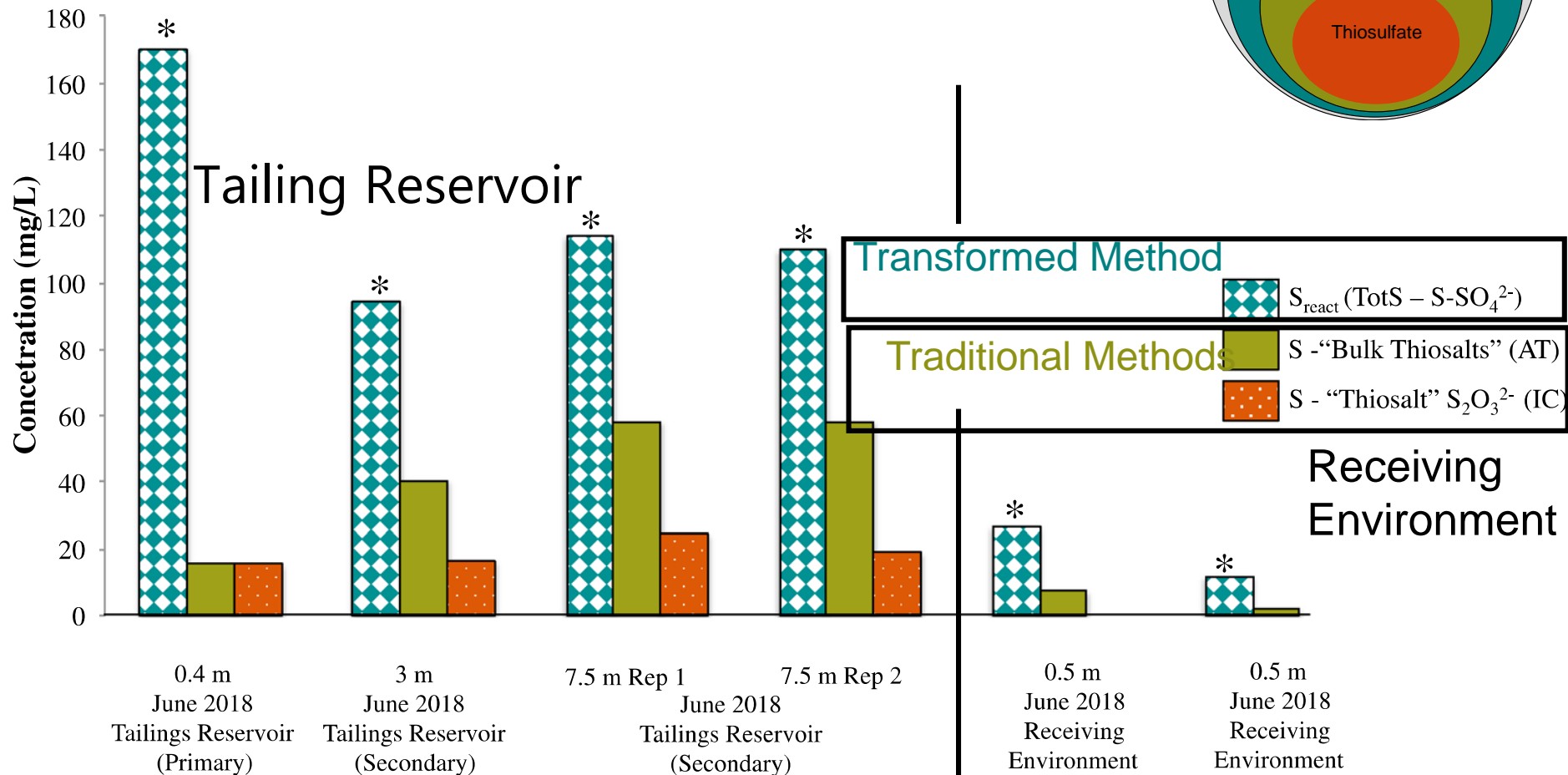
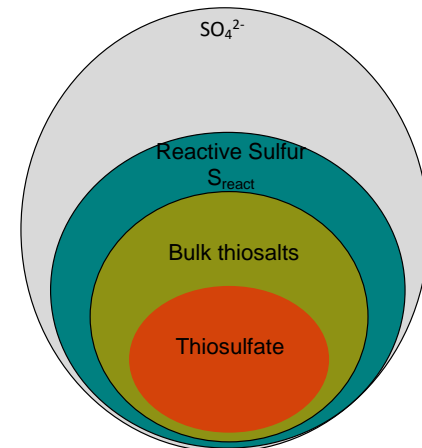
From 2014-2018, ~70 mine water sites →
 Thiosulfate was on average only 4% of overall S pools!

$[\text{Thiosalts}] \ll S_{\text{react}}$ in receivers

Undetected S is making it's way through different treatment systems

Whaley-Martin et al., 2020

S_{react} More Conservative of Risk than IC and AT methods



* Significantly different $p < 0.05$

Flin Flon, Manitoba

Snow Lake, Manitoba

HUBBAY

GLENCORE
SUDBURY INO

Whaley-Martin et al., 2020



Utilizing the Science to Lead Adoption of Best-Practice In the Industry

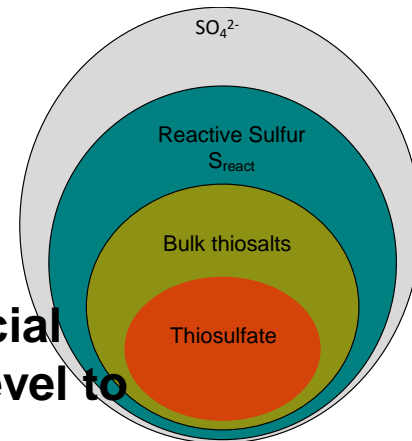


Electively adopting this methodology to improve their sulfur monitoring capabilities throughout treatment systems

- **Cost Analysis**

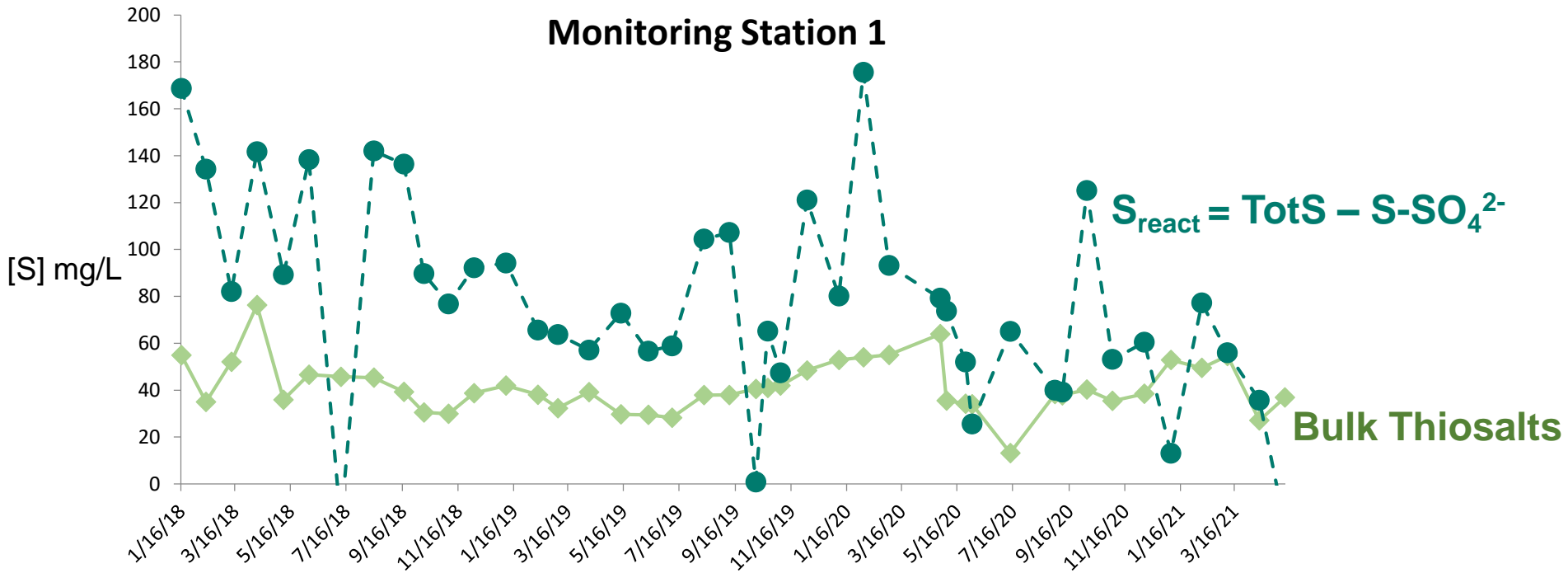
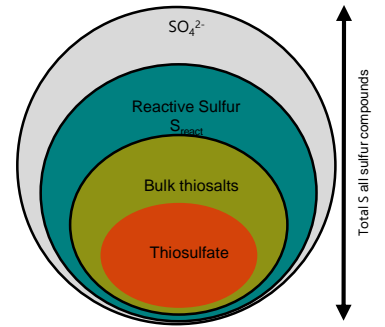
Acidimetric Titration ~\$160
VS
Reactive S ~\$13

- Hudbay (Flin Flon) currently **has attained provincial approval to use this approach at the regulatory level to replace the traditional acidimetric titration**



Comparing methods over time

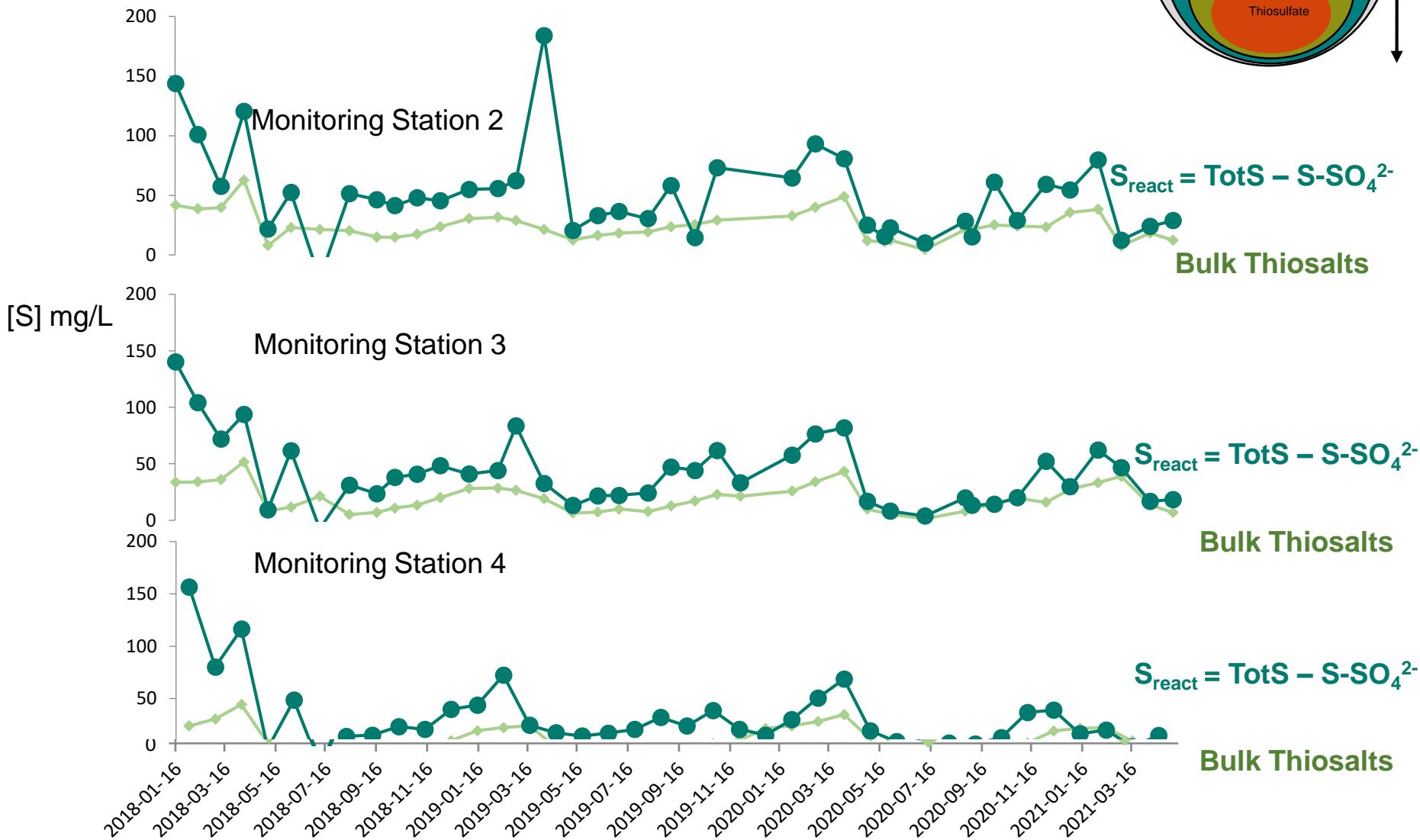
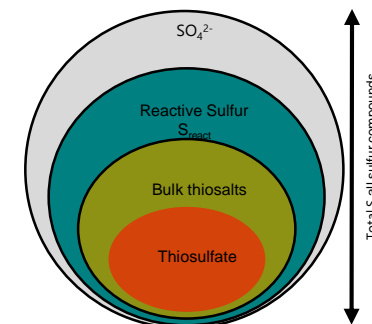
S_{react} vs. Bulk Thiosalts (Acidimetric Titration)





Comparing methods over time

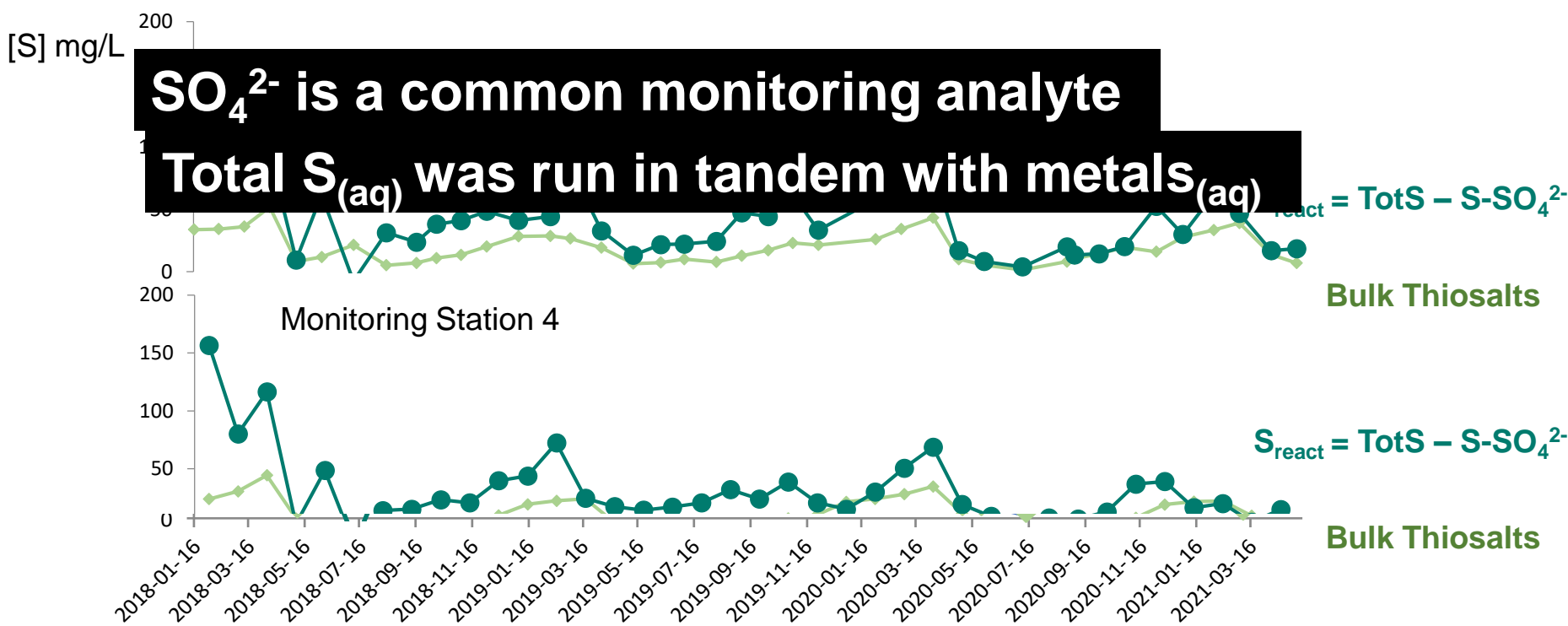
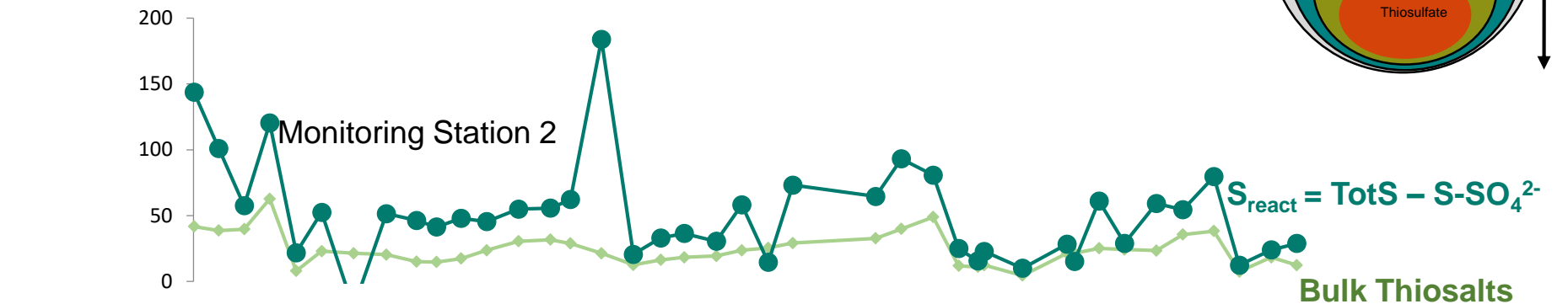
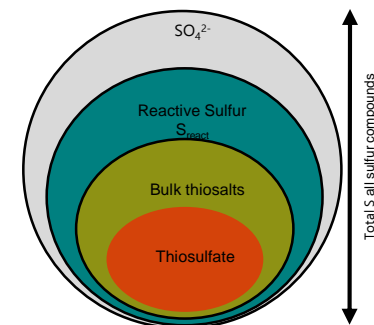
S_{react} vs. Bulk Thiosalts (Acidimetric Titration)





Comparing methods over time

S_{react} vs. Bulk Thiosalts (Acidimetric Titration)



SO_4^{2-} is a common monitoring analyte

Total $\text{S}_{(\text{aq})}$ was run in tandem with metals $_{(\text{aq})}$

| The Risk |

Dissolved reactive sulfur compounds in mining impacted waters are a global challenge

Oxidation



- Oxygen Consumption
- Acidity/Metal Release

Reactive Sulfur
Compounds

Potential
Environmental Impacts

Industry Liability
and Risk

- Water Flow Paths ↓
- Processing Waters
 - Tailings Reservoir Caps
 - Polishing/Setting Ponds
 - Regulated Discharge Points
 - Downstream Environments

- Toxicity Failures
- Penalties
- Shutdowns



|The Risk|

You can't manage what you can't detect.....

Dissolved reactive sulfur compounds in mining impacted waters are a global challenge

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| Call to Action |

Dissolved reactive sulfur compounds in mining impacted waters are a global challenge

Current language around "thiosalts" is problematic: ambiguity around its definition analytically

Mass-Balance Approach

Reactive Sulfur Compounds

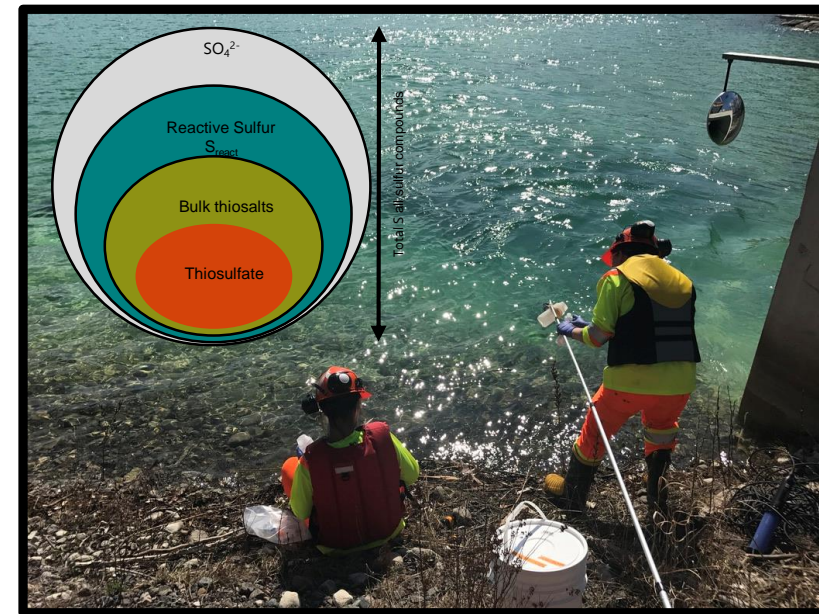
- Cost-effective** : reduced cost/more time points/replicates
- Part of many monitoring programs (also allows for historical delineation)
- More conservative of risk**: able to capture any inorganic or organic sulfur compounds that are "in play" for downstream microbial or abiotic oxidation
- Easy to calculate**





Questions/Insights?

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Dr. Simon Apte, Analytical Chemist, CSIRO

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simon.apte@csiro.au



Biography

Dr. Simon Apte's research focuses on the analysis of trace metals and the links between trace metal speciation and bioavailability in waters. Much of his current work is directed to understanding the impacts of mining on aquatic environments, the impact of hydraulic fracturing in the unconventional gas industry and the fate of nanomaterials in the environment.

Prior to joining CSIRO, Dr. Apte was a Research Scientist in the Environmental Chemistry Group, Water Research Centre in the United Kingdom (UK) from 1985 to 1990. He was Lecturer in Environmental and Analytical Chemistry, Department of Applied Sciences, University of Technology, Papua New Guinea from 1989 to 1990.