

Joint Industry Project (Stage 2) – Establishing Risk-Based Limits for Elemental Sulphur in Soil



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Remediation
Technologies
Symposium 2024

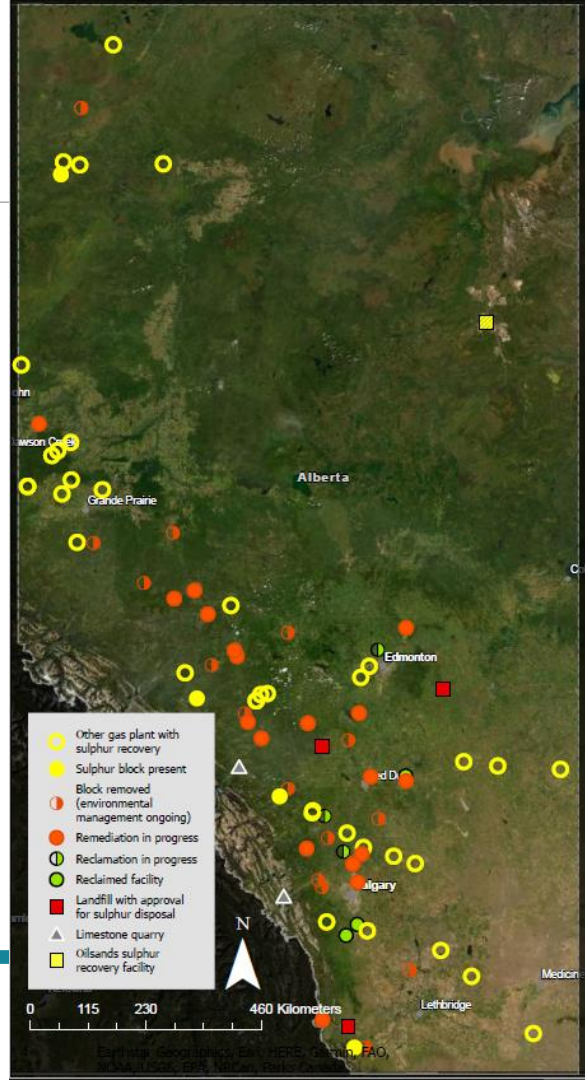
Outline

1. Project Background and Proponents
2. Research Outline
3. Research Findings and Application
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Stage 2 Background and Project Proponents

Distribution of Facilities with Historical or Current Sulphur Recovery in Alberta

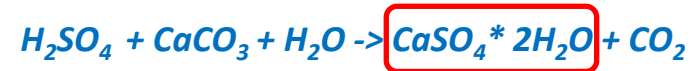
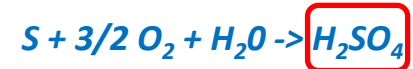
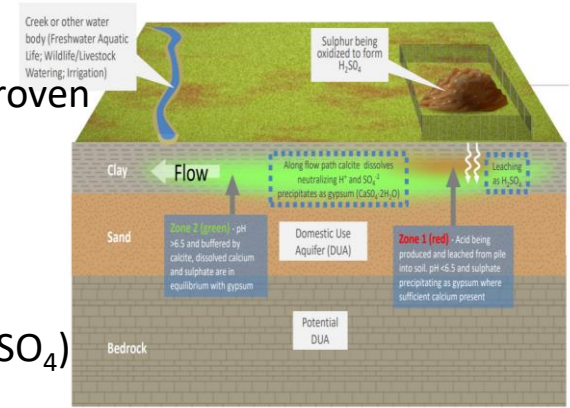
- Identified ~41 sour gas processing sites with current or historical sulphur blocks
 - 5 - block present
 - 31 - block removed- ongoing ES environmental management or remediation
 - 3 - reclamation in progress
 - 2 – reclaimed
- ~20 individual licensees have plants with existing or former blocks
- Additional potential impacts at oilsands, refineries, storage and handling facilities



Data from AER, ST-50A- Gas processing plants in Alberta, filtered by "GP Sulphur Recovery", February 2022

Residual Sulphur Management Challenges

- Closing former Sulphur storage sites is an issue in Alberta:
 - Current guidelines are not set up to support closure
 - Landfilling S is really expensive – should be done when **risk** is proven
- Elemental S (ES) is a problematic COPC:
 - Widespread and variable distribution at former sour gas plants
 - Challenging to characterize due to heterogeneity - field and lab
 - Risk of ES oxidation, resulting in formation of sulphuric acid (H_2SO_4)
 - Can result in SO_4 plume formation
- Foothills soils typically contain abundant $CaCO_3$ that is available for buffering acidic effects

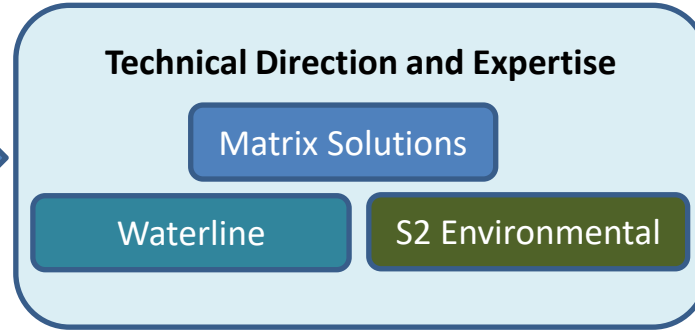


Residual Sulphur Management Stage 2 - Project Structure Overview

Steering Committee



Project Team



Key Stakeholders



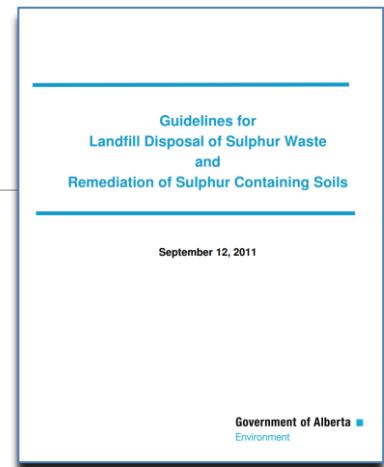
Project deliverables

- Best Practices Document
- Excel-based Calculator Tool
- Lab Study Report

Research Outline

Current Regulatory Guidance/ Limits

1. Soil with >500 mg/kg Elemental Sulphur (ES) is considered S-waste, to be treated onsite or disposed in a dedicated Class II landfill cell, encapsulated in limestone
 - Is there truly a risk of acidic leachate associated with soil at ES ≥ 500 mg/kg? If not, what is the threshold?
2. Soil exceeding 4% Total Sulphur (TS) cannot be treated onsite and must be landfilled
 - What is the justification for 4% (40,000 mg/kg) maximum TS?



Research Recommendations from Stage 1

1. Sulphur is a unique CoPC – practitioners expressed a need for additional guidance for effective site characterization
2. Data integration support is required for making sense of the various soil characteristics and parameters that influence acidification and needed amendment
3. We currently need to analyze both ES and TS, resulting in two datasets that rarely jive – is there a way to streamline analyses?

Research Findings and Application

Research Project Overview

Best Practices Document

- **Establish soil/waste stream sampling requirements** (e.g., soil testing frequency, timing, analytical requirements, and/or specific parameters)

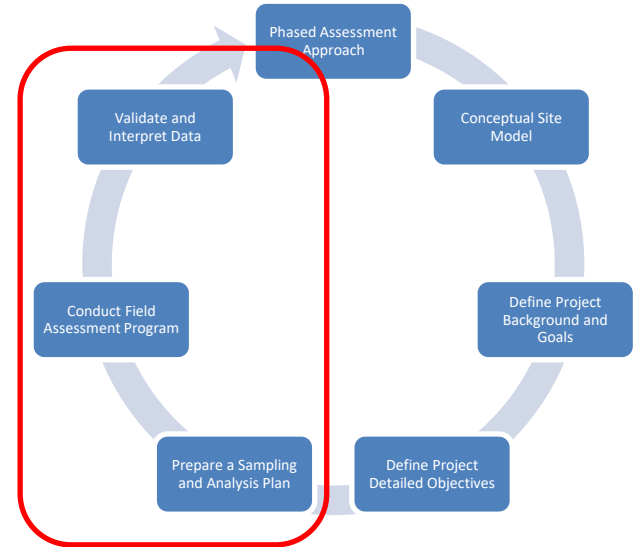
Calculator

- **Develop an Excel-based calculator**, with analytical data for inputs, to calculate whether soil has adequate acid neutralization capacity or if an acid neutralization amendment is required to maintain or reach target pH levels.

Round Robin Testing – Field Soil and ES-Spiked Soil

- **Test soil** from former sulphur storage sites and spiked soils with round robin testing at three commercial laboratories
- Compare results for ES and TS, and determine range of accurate ES detection

Focus of Best Practices



Best Practices Document

- Objectives- to provide direction for:
 1. Sampling rigour to enable risk-based limit justification; and
 2. Assessment considerations above and beyond existing guidance

APPENDICES

- APPENDIX A Geochemical Considerations for Plume Assessment
- APPENDIX B Regulatory Guidance and Guideline Summary
- APPENDIX C Laboratory Study for Residual Sulphur Management Project – Stage 2
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Proposed Analytical Protocol

Recommended parameters:

- ES (if > 500 mg/kg → CCE)
- pH (if $<$ background → Lime requirement)
- EC and/or sulphate
- Metals (selective)
- Soil texture (selective)



Amendment Requirement and Potential Acidification Calculator

Legend for Calculator Inputs

xx	User entry from laboratory results
xx	User entry with dropdown
xx	Automatically calculated

Part 1 - ACID PRODUCING POTENTIAL - Use if Elemental S > 500 mg/kg (*requires soil CCE analysis)			
Factor	Parameter	Unit	Number
Acid Producing Potential:	Elemental S (ES; mg/kg)	mg/kg	500
	ES Neutralization Requirement	%	0.16
	Lab-reported CCE	%	0.00
	Net Neutralization Requirement	%	0.16
	Safety Factor	%	20
	Neutralization Safety Factor Increment	%	0.03
RESULT 1	Neutralization Requirement including Safety Factor	%	0.19

*Run 'calcium carbonate equivalent'

Part 2 - DEPRESSED SOIL pH - Use if Soil pH < pH Target (*requires Lime Requirement analysis by lab)			
Factor	Parameter	Unit	Number
Depressed Soil pH Scenarios	pH Target	-	6.80
	Soil pH	-	5.00
	Buffer pH (Sikora/SMP)	-	6.10
	Soil type	-	Fine
RESULT 2	Neutralization Requirement (T CCE/T soil)x100 ⁻³	%	1.21

*Run 'lime requirement'

Part 3 - COMBINED - Use if ES > 500 mg/kg and Soil pH < pH Target (*requires Lime Requirement analysis by lab)			
Factor	Parameter	Unit	Number
RESULT 3	Lime Requirement including Safety Factor Threshold	%	1.40

Part 4 - Use if ANA CCE is not 100% (e.g., fly ash, crushed concrete ⁴)			
Factor	Parameter	Unit	Number
Neutralization requirement for alternate ANA	Acid neutralizing agent (ANA) CCE	%	70.00
RESULT 4	Alternative Neutralization Requirement	%	2.01

Apply to amend with limestone alternatives

- Underpinned by recommended Best Practices and laboratory study
- Tested by Joint Industry proponents

Calculator Demo

Amendment Requirement Calculator

https://waterline.sharepoint.com/.../ResidualSulphurManagement-JointIndustryProject/_layouts/15/Doc.aspx?sourceidococ=%7B85DA40A2-D3FA-4FE4-A734-20A516901194%7D&file=Amendment%20Requirement%...

Amendment Requirement Calculator

Legend for Calculator Inputs

- xx User entry from laboratory results
- xx User entry with dropdown
- xx Automatically calculated

Part 1 - ACID PRODUCING POTENTIAL - Use if Elemental S > 500 mg/kg (*requires soil CCE analysis)

Factor	Parameter	Unit	Number
Acid Producing Potential:	Elemental S (ES; mg/kg)	mg/kg	500
	ES Neutralization Requirement	%	0.16
	Lab-reported CCE	%	0.00
	Net Neutralization Requirement	%	0.16
	Safety Factor	%	2.0
Neutralization Safety Factor Increment	%	0.03	
RESULT 1	Neutralization Requirement including Safety Factor	%	0.19

Instructions/Description

Enter lab-reported elemental sulphur (ES) concentration for sample in question

Required % CCE to buffer the reserve acidity of elemental S to maintain existing pH based on stoichiometric ratio of 3.2:1 (CCE to ES)

Enter lab-reported CCE in %

Calculated neutralization surplus or deficit taking into account required and actual CCE

Safety factor to consider additional buffering needs*

Neutralization requirement increment associated with safety factor.

Green = excess buffering capacity including safety factor; Red = insufficient buffering including safety factor; where red, add neutralization requirement to offset acidification potential.

Part 2 - DEPRESSED SOIL pH - Use if Soil pH < pH Target (*requires Lime Requirement analysis by lab)

Factor	Parameter	Unit	Number
Depressed Soil pH Scenario:	pH Target	-	5.60
	Soil pH	-	3.00
	Buffer pH (Silkora/SMP)	-	6.10
	Soil type	-	Fine
RESULT 2	Neutralization Requirement (T CCE/T soil)x100 ³	%	0.54

Enter the desired soil pH target based on environmental regulations and/or site-specific requirements

Enter lab-reported soil pH as measured and reported by the lab; if no pH neutralization is required, enter the same value for pH target as soil pH

Analyze lime requirement at the testing laboratory to obtain this result; buffer pH may be reported as Silkora or SMP pH as it is interpreted that each are functionally equivalent. Ensure the buffer pH is reported, as lime requirement is dependant on the target pH, which may vary.

Select fine or coarse grained soil based on the definition in the Alberta Tier 1 guidelines (EPA, 2024).

Result of 0 = no active acidity/lime requirement; Result > 0 = lime requirement to achieve soil pH to target assuming product is 100% CCE, T/T converted to % of CCE applied based on 20 cm soil depth and soil type.

Part 3 - COMBINED - Use if ES > 500 mg/kg and Soil pH < pH Target (*requires Lime Requirement analysis by lab)

Factor	Parameter	Unit	Number
RESULT 3	Lime Requirement including Safety Factor Threshold	%	0.73

Accounts for required %CCE (100% potency) needed to buffer reserve acidity with safety factor threshold and active acidity (if applicable). Note: Application of >12.8% CCE may not be advisable based on logistics of incorporation and potential soil structure impact

Part 4 - Use if ANA CCE is not 100% (e.g., fly ash, crushed concrete)

Factor	Parameter	Unit	Number
Neutralization requirement for alternate ANA	Acid neutralizing agent (ANA) CCE	%	70.00
RESULT 4	Alternative Neutralization Requirement	%	1.05

Actual CCE % of ANA product (limestone or other) obtained from manufacturer or via lab testing; if 100% CCE, enter 100 here.

% of ANA material to add on mass/mass basis. If number is negative, no ANA addition is required. Note: Application of >12.8% CCE may not be advisable based on logistics of incorporation and potential soil structure impact.

Notes:

*Acid Producing Potential = where a soil does not exhibit depressed pH, it is required to evaluate potential oxidation of ES to H₂SO₄. Calculations are provided in AENV (2011). In cases where there are other acidifying sulphur minerals present, such as pyrite, these would also need to be included in the overall sulphur concentration.

The safety factor was introduced to ensure that residual buffering capacity is maintained in the case that a soil's acid neutralization capacity is consumed by reaction with H₂SO₄. The safety factor accounts for issues such as heterogeneity, complexity of soil chemistry/geochemistry, difficulty to achieving even amendment rates over entire area and depth requiring amendment. 20% of the ES concentration is provided as a default, but this value should be reconsidered based on site specific considerations and data.

Workbook Statistics

93%

Laboratory Study

Objective: Examine available laboratory methods to support assessing risk of S impacts

Hypotheses:

- Where Elemental Sulphur (ES) has weathered in soils over time, Total Sulphur (TS) will be greater than ES due to gypsum/SO₄ - particularly at lower concentrations
- Labs using sequential dilution and consistent preparation methods could report ES concentrations over 4% within a 70% to 130% variability
- Differences in reported concentrations will, in some cases, be attributable to laboratory methods

Round Robin – Field Soil Analysis

- Samples from stockpiled soil at a former S management and slating area
- Wide variability in ES concentrations- lab-reported and visual
- Highly calcareous soils (natural; >25% CCE in some cases)
- No contaminants other than sulphur and its oxidation products
- Extensive field sample homogenization

OB1



Row 2



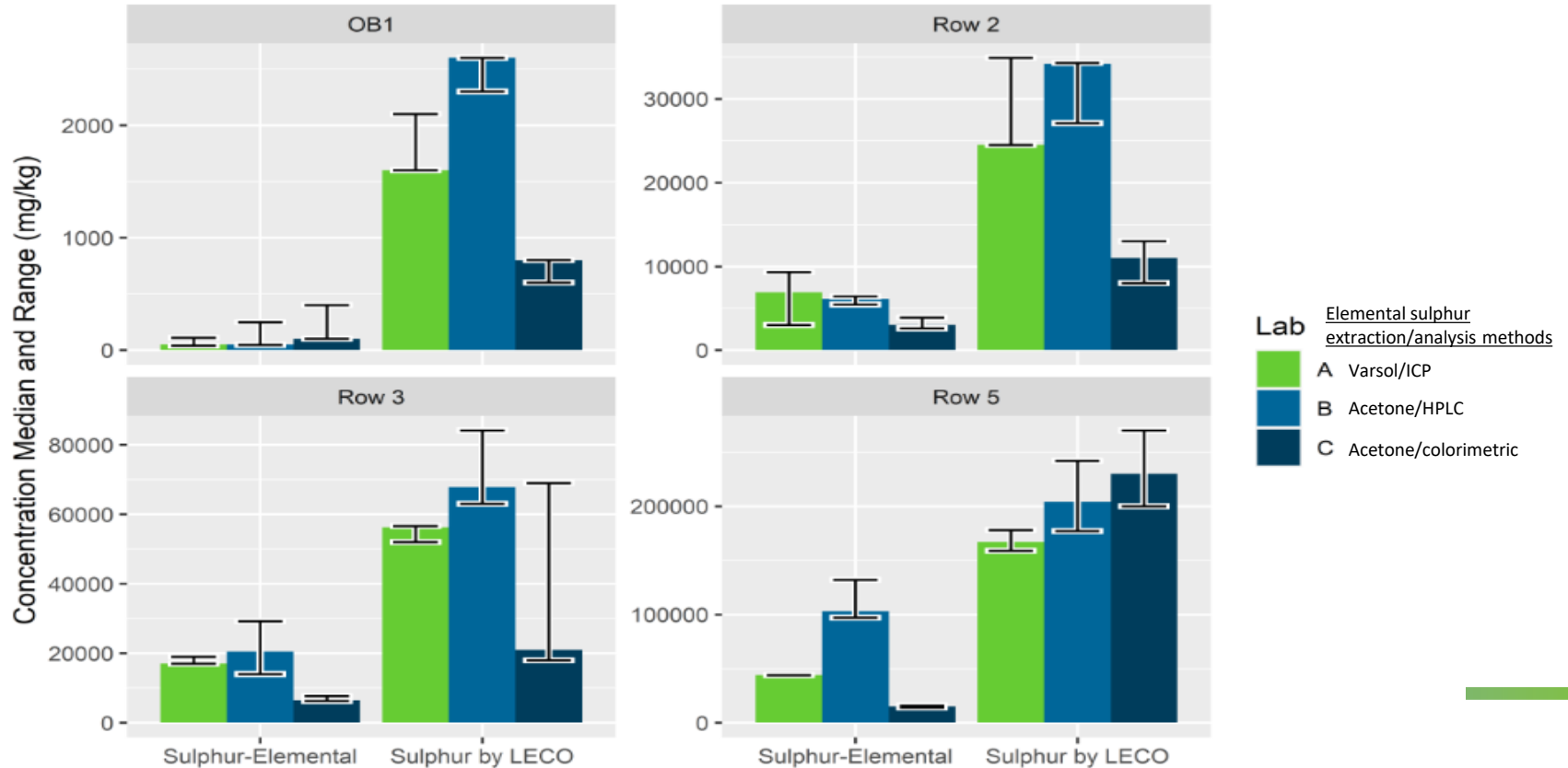
Row 3



Row 5



Field Soils: TS and ES Analysis Results



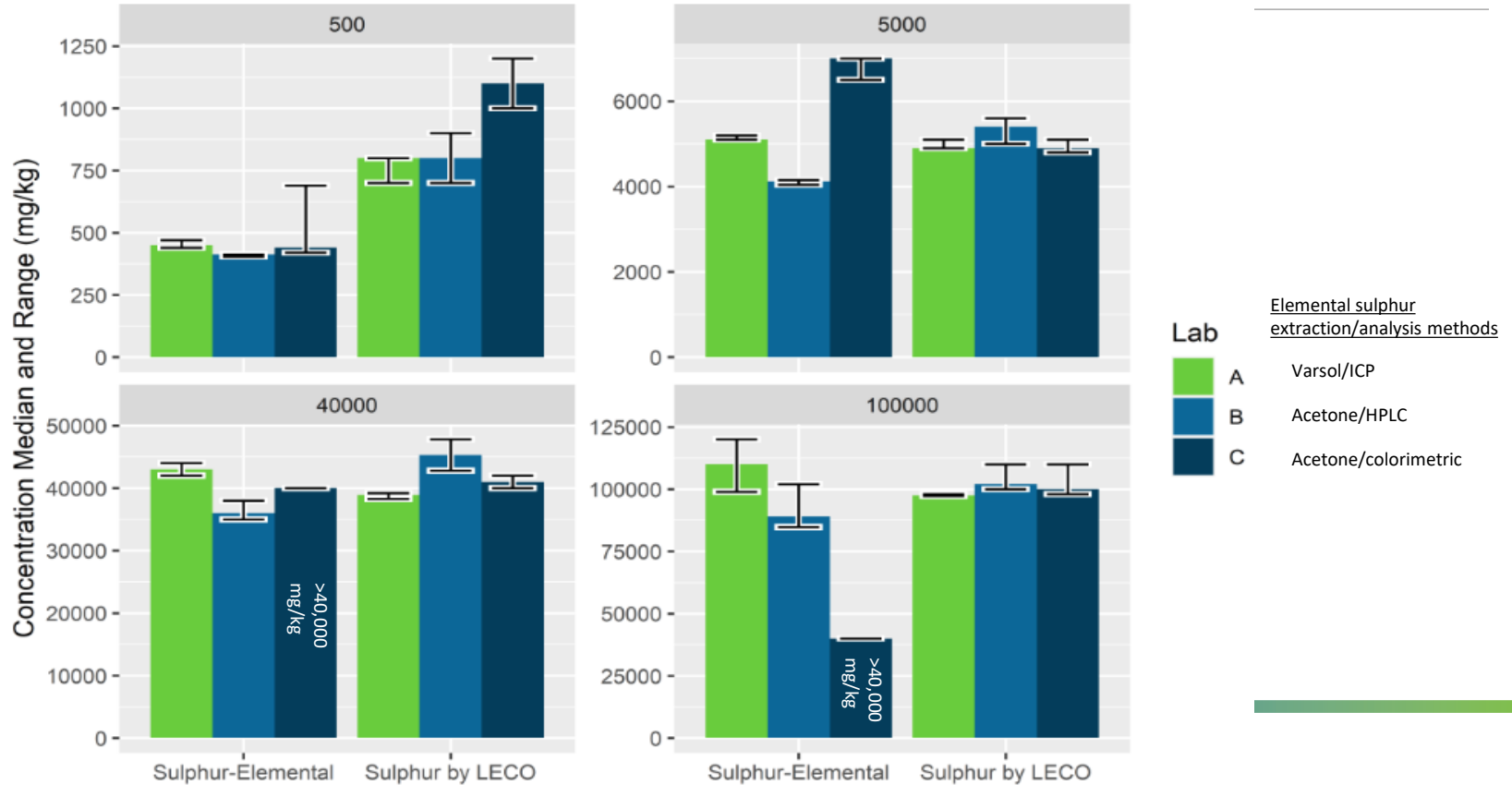
Field Soil – Round Robin Summary

- Surprisingly large differences in results!!
- Elemental Sulphur:
 - Some variability within labs (range between triplicates)
 - Concentration bias for [Lab C] < [Lab A] < [Lab B]
 - Cost differential between methods
- Total Sulphur:
 - Observed variability between labs (consistent LECO method)
- **Sample heterogeneity** likely a big issue

Round Robin – Spiked Soil Analysis

- Fine-grained soil from a non-industrial site (contained low concentration of TS; ~1,000 mg/kg)
- Powdered ES samples were mixed into soil at concentrations of 500, 5,000, 40,000 and 100,000 mg/kg by Lab A
- Spikes and controls sent to 3 laboratories for analysis in triplicate

Spiked Soils: TS and ES Analysis Results



Spiked Soil – Round Robin Summary

- Much less variability within and between labs than in field study
- Generally good agreement between ES and TS at $[ES] > 500 \text{ mg/kg}$
- Lab C could not report ES above 40,000 mg/kg
- Labs A and B, using varsol extraction/ICP and acetone extraction/HPLC respectively and sequential dilution were able to **accurately report ES concentrations to 100,000 mg/kg**
- Differences in preparation, sampling and extraction effort at labs are likely still sources of variability

Lab Study Conclusions

- Surprising variability in field sample round robin
 - Differences largely due to sample heterogeneity as well as methods
 - Best Practices for sample collection and lab protocols important
- Colorimetric method for ES analysis not as useful for these sites as varsol or acetone extraction followed by ICP or HPLC with sequential dilution
 - Allowable ES test methods should be expanded to include varsol extraction
 - Sample preparation should be an important focus
- Evaluation of risk at sites could be focused on assessment of **reduced and mobile forms of Sulphur**
 - Should not be based on 4% TS alone - decisions should be made based on ES/SO₄/pyrite concentrations



Conclusions

RSM Stage 2 Project Outcomes

- Best Practices guidance available to support sampling and analytical protocol at ES-impacted sites
- Analytical results can be used in a calculator for evaluating risk of acidification and needed amendment (limestone or other) supporting:
 - Onsite amendment requirements
 - Potential landfilling at Class II vs. dedicated cell with limestone
- Recommendations put forward for sample homogenization
 - Evaluate benefits and feasibility
 - Recommendation includes use of spiked soil standards
- Analytical methods proven for ES to $\geq 100,000$ mg/kg – could use TS analysis strategically for sulphate-based CSM
 - Requires AEPA method acceptance confirmation

Recommended Risk-Based “Limits”

1. Is there risk of acidic leachate associated with soil at $ES \geq 500$ mg/kg?
If not, what is the threshold?
 - Soil will acidify at 500 mg/kg if there is no buffering; in soils where we generally find sulphur, there often is buffering capacity that should be analyzed
 - Consider potential acid generation with actual pH and buffering capacity
 - Ideal for landfills to consider buffering and pre-amendment vs. 500 mg/kg
2. Soil exceeding 4% Total Sulphur (TS) cannot be treated onsite and must be landfilled
 - If 4% (40,000 mg/kg) **ES**, there may be challenges in amending
 - If majority of the TS component is **gypsum (inert)**, this should not dictate that soil be disposed offsite

Thank you!

- Funders and steering committee
- Regulatory advisors
- Laboratories – AGAT, BV and Element
- Calculator development: Eric Pringle and Andrew Schietzsch, Waterline Resources
- Technical review: Lindsay Oiffer, Matrix Solutions