Investigation of Sulfolane Extraction, Analysis and Sorption/Desorption with Relevance to Alberta Forest Soils and Associated Groundwater

Presenters: Sheila Luther and Nahid Hassanvand-Gandaei
Introduction

• Focus: extraction methods, analytical techniques and sorption/desorption behavior of sulfolane

• Motivated by site in forested area of Alberta with sulfolane plume

• During previous site assessments sulfolane has been encountered in unexpected areas, particularly in soil (≤1.5 mg/kg concentration)
Introduction (continued)

• Work completed:
  – literature review
  – laboratory and research studies
    • Stage 1: triplicate field samples submitted to 3 testing laboratories
    • Stage 2: spiked soil and groundwater samples submitted to several (3 to 5) testing laboratories
    • Stage 3: sorption/desorption studies
## Soil Extraction Methods - Literature Review

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| **Soxhlet Extraction**
  $^{1,2,10,13}$          | • Robust extraction method                                               | • Long extraction times (16 to 24 hrs)                                                                  |
|                          | • Provides efficient extractions                                         | • Large volumes of solvents                                                                            |
|                          |                                                                          | • Mostly required for water-insoluble and slightly water-soluble organics                               |
|                          |                                                                          | • Can extract non-target compounds from soil                                                             |
| **Shake Extractions**
  $^{3,4,11}$            | • Sulfolane miscibility in water allows for shorter extraction times     | • Labour intensive – requires possibly centrifuging, filtering and volume reduction                      |
|                          | • Water extractions - 92-104 % efficiency                                | • Sample handling that is required could introduce error                                                 |
|                          | • Water extraction following a back extraction with water-saturated toluene|                                                                                                          |
|                          | • Toluene is especially favorable because sulfolane is used to extract aromatics |                                                                                                          |
## Water Extraction Methods - Literature Review

<table>
<thead>
<tr>
<th>Methods</th>
<th>Advantage(s)</th>
<th>Disadvantage(s)</th>
</tr>
</thead>
</table>
| Separatory funnel/cold shake\(^5,6,7,11\) | • Low time requirement (3x2-min extraction)                                  | • Better for recovering water-insoluble and slightly water-soluble organics  
• Sulfolane is miscible in water and thus the extraction is likely to be subject to poor sulfolane recovery  
• Solvent evaporation can cause a bias towards higher concentrations |
| Liquid-liquid extractor\(^8,9\)   | • Improves extraction efficiency and removes emulsion problems                | • Large volume of solvent and extensive amount of time (18 – 24 hrs)                                                                                                                                              |
## Analytical Methods - Literature Review

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| **Gas Chromatograph equipped Flame Ionization Detector (GC-FID)**<sup>12</sup> | • Relatively inexpensive instrument  
• Direct aqueous injection - minimal sample handling required | • Non-selective detector results in risk of interferences by non-target compound  
• Higher detection limits (0.2 mg/L) |
| **GC-Mass Spectrometry**<sup>7</sup>             | • Ionize compounds and sort the ions based on their mass-to-charge ratio-identify origin of interference  
• Lower detection limits (for example: 0.001 mg/L) | • Potential for interference if petroleum hydrocarbons present as co-contaminant  
• Too many fragments when identifying for intermediates  
• Sample preparation typically requires extraction in an organic solvent |
| **High Pressure Liquid Chromatography (HPLC)-MS**<sup>3</sup> | • Simple water extraction  
• Direct aqueous injection | • Sample preparation can be more prone to interferences  
• Potential for interference from salts |
Stages 1 and 2 Study - Goals

1) to quantify variance in analytical results for sulfolane in soil and groundwater samples and determine to what degree they are similar or different

2) if different, to determine if differences occur more frequently under certain conditions such as organic or mineral soil, groundwater, certain concentrations (high, medium, low), or with certain analytical methods
Stage 1 Study - Methods

- triplicate soil samples collected at 4 locations with varying sulfolane concentrations
- samples distributed to 3 commercial testing laboratories for analysis of sulfolane in soil
- triplicate groundwater samples collected at 3 locations with varying sulfolane concentrations
- samples distributed to 3 commercial testing laboratories for analysis of sulfolane in groundwater
## Stage 1 Study - Methods

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Sample Matrix</th>
<th>Instrumentation</th>
<th>Extraction Method</th>
<th>Detection Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Soil</td>
<td>GC/FID</td>
<td>water mechanical extraction</td>
<td>0.15 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>GC/FID</td>
<td>direct injection</td>
<td>0.2 mg/L</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>GC/MS</td>
<td>DCM liquid-liquid separatory funnel extraction</td>
<td>0.001 mg/L (low level)</td>
</tr>
<tr>
<td>B</td>
<td>Soil</td>
<td>HPLC/MS</td>
<td>acidified water extraction</td>
<td>0.10 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>HPLC/MS</td>
<td>diluted with glacial acetic acid</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>C*</td>
<td>Soil</td>
<td>HPLC/MS</td>
<td>organic free water extraction</td>
<td>0.005 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>HPLC/MS</td>
<td>no extraction, direct analysis</td>
<td>0.002 mg/L</td>
</tr>
<tr>
<td>D</td>
<td>Soil</td>
<td>GC/MS</td>
<td>DCM soxhlet extraction</td>
<td>0.05 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>GC/MS</td>
<td>DCM:ethyl ether mixture liquid-liquid partitioned in a stir flask extraction</td>
<td>0.003 mg/L</td>
</tr>
<tr>
<td>E*</td>
<td>Soil</td>
<td>GC/MS</td>
<td>DCM soxhlet extraction</td>
<td>0.010 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>GC/MS</td>
<td>DCM cold shake</td>
<td>0.005 mg/L</td>
</tr>
</tbody>
</table>

* Not part of Stage 1 but were part of Stage 2 study.
Stage 1 Study - Results

**Soil Sulfolane - Site Replicates**

<table>
<thead>
<tr>
<th>Site Sample</th>
<th>BH1</th>
<th>BH2</th>
<th>BH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfolane Concentration (mg/kg)</td>
<td>A (GD-FID)</td>
<td>B (HPLC-MS)</td>
<td>D (GC-MS)</td>
</tr>
<tr>
<td>Tier 1 Guideline of 0.18 mg/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Groundwater Sulfolane - Site Replicates**

<table>
<thead>
<tr>
<th>Site Sample</th>
<th>MWa</th>
<th>MWb</th>
<th>MWc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfolane Concentration (mg/L)</td>
<td>A (GC-FID or GC-MS)</td>
<td>B (HPLC-MS)</td>
<td>D (GC-MS)</td>
</tr>
<tr>
<td>Tier 1 Guideline of 0.09 mg/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Z Score\textsuperscript{14} for Data Evaluation

- Parameters:
  - Mean (x)
  - Standard deviation (sigma - \sigma)
  - Relative standard deviation (RSD)

\[Z = \frac{(x - \bar{x})}{\sigma_x}\]

- Z-score indicates how many standard deviations the data is away from the mean.
- An optimum Z-score for this study was considered to be within the range of -2 to +2.
Stage 1 Study – Findings and Discussion

• All Z-scores satisfactory within -2 to +2 range.
• Soil RSDs ranged from 18% to 85%. Highest RSD (85%) for <1 mg/kg.
• Groundwater RSDs ranged from 8% to 24%. Highest RSD (24%) for concentrations of <0.2 mg/L.

Discussion
• Higher concentrations, as encountered at facility source area, likely to be more reliable than lower concentrations, as found at periphery of the site.
Stage 2 Study (Spiking) - Methods

Soils
Dried and ground soils used
- Autoclaved 2x30 mins at 121 °C to minimize microbial activity
- Soils were spiked to 100 mg/kg, 10 mg/kg and 0.5 mg/kg
  - Used a spray bottle
  - Hand mixed to fully coat soils with solution
- Heterogeneity minimized
  - Used a sample splitter
  - Rolled soils on ground in a bucket
- Brine solution was used to spike till soils (1500 mg/kg NaCl)

Groundwater
A 3L stock solution of groundwater was prepared
- 0.1 mg/L
- 0.5 mg/L
## Stage 2 Soil Material Characterization

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>organic</th>
<th>till</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.94</td>
<td>7.51</td>
</tr>
<tr>
<td>Conductivity (dS/m)</td>
<td>0.36</td>
<td>1.1</td>
</tr>
<tr>
<td>Sodium Adsorption Ratio</td>
<td>0.55</td>
<td>0.57</td>
</tr>
<tr>
<td>Total Organic Carbon (mg/kg)</td>
<td>485000</td>
<td>9900</td>
</tr>
<tr>
<td>Texture</td>
<td>Peat</td>
<td>Clay (45%)</td>
</tr>
<tr>
<td>Cation Exchange Capacity (cmol+/kg)</td>
<td>160</td>
<td>20</td>
</tr>
</tbody>
</table>
## Water Characterization

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.90</td>
</tr>
<tr>
<td>Total Dissolved Solids (mg/L)</td>
<td>310</td>
</tr>
<tr>
<td>Dissolved Organic Carbon (mg/L)</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Stage 2 Study - Results

Organic Soil

Mineral Soil

![Graphs showing results for Organic Soil and Mineral Soil with different detection methods: GC-FID, HPLC-MS, GC-MS.](image)
Sulfolane Spiking Study

- Acceptable uncertainties chosen as,
  - Extraction uncertainty $u_{ex} = \pm 20\%$
  - Analytical uncertainty $u_{an} = \pm 10\%$
- $Z_L$-score$^{14}$ used to measure “acceptable” deviation from expected results

$$Z_L score = \frac{(x_i - x_{expected})}{\sqrt{(u_{ex})^2 + (u_{an})^2}}$$
Soil Spiking Results

- Mineral soil
- Organic soil

<table>
<thead>
<tr>
<th>Spike (mg/kg)</th>
<th>ZL-score</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-5</td>
</tr>
<tr>
<td>1.0</td>
<td>-4</td>
</tr>
<tr>
<td>10.0</td>
<td>-3</td>
</tr>
<tr>
<td>100.0</td>
<td>-2</td>
</tr>
<tr>
<td>1000.0</td>
<td>-1</td>
</tr>
</tbody>
</table>

- Acceptable
- Questionable
- Unacceptable
Groundwater Spiking Study

![Graph showing the results of a groundwater spiking study.](image)

- **Spike (mg/L)**: The x-axis represents the spike concentration in mg/L.
- **Z-score**: The y-axis represents the Z-score, which is used to determine the acceptability of the results.
- **Acceptable**, **Questionable**, and **Unacceptable** regions are marked on the graph.
- **Lab A (GC-FID)**, **Lab B (HPLC-MS)**, **Lab D (GC-MS)**, and **Lab E (GC-MS)** are indicated by different symbols on the graph.
Stage 2 Study - Findings and Discussion

Soil
- Sulfolane results for organic soils show greater scatter compared to mineral soils, especially at <1 mg/kg sulfolane in soil
- Soil variability may be related to sample preservation, heterogeneity and/or extraction related sources of error.
- When low concentrations analyzed in organic soils, frequently had to have detection limit raised.
- Both organic and mineral soils results show negative bias, possibly due to extraction inefficiencies

Groundwater
- The majority of analyses at 0.1 – 0.5 mg/L sulfolane in groundwater lie within the acceptable range
- Groundwater data less variable than soils data.
- Groundwater results also show negative bias
Stage 2 Study – Discussion (continued)

Potential Sources of Error
• Sample heterogeneity
• Sulfolane loss from sample through biodegradation
• Incomplete extraction
• Particulates or other interfering constituents in extractant
• Sulfolane concentration increase after extraction due to evaporation of solvent
• Interferences potentially affecting detectors:
  – Natural organics
  – Organic parameters present as co-contaminants
  – Salts naturally present or co-contaminants
  – Wide ranging sulfolane concentrations
Stage 2 Study – Supplemental Work

• Collected leachate of the organic soil
• Filtered, spiked with sulfolane and extracted with DCM.
• Analyzed by GC-MS in Selective Ion Mode (SIM) and SCAN Mode\textsuperscript{15}.
  • SIM analyses specific m/z ion peaks of a specific compound and provides greatest sensitivity of target compound
  • SCAN monitors a broad rage of m/z ion peaks. Lower sensitivity compared to SIM, no better than GC-FID
Potential Interferences Identified

- 2-butynyl hydrazine
- 1,1-dimethyl-2-octyl-Cyclobutane
- Allyl methallyl ether
- Stearic acid hydrazide
- Butyric acid hydrazide

[Link to NIST Webbook]
Stage 3 - Goal

• The sorption and desorption of sulfolane in organic and mineral soils is also being studied to further evaluate the transport behaviour of sulfolane in different soil matrices that are relevant to the subject site
Stage 3 - Sorption/Desorption - Literature Review

• Limited published data\textsuperscript{16,17}
• Batch-Type Procedures\textsuperscript{18,19}
• Need to consider factors such as:
  • Air-drying vs oven-drying
  • Constant temperature
  • Headspace
  • Microbial activity
Sorption/Desorption: 4°C – 48 hrs

Fig. 1: Sorption of Sulfolane on Organic Soil

Fig. 2: Desorption of Sulfolane from Organic Soil

\[
y = 2.8999x + 94.081 \\
R^2 = 0.9962
\]
Stage 3 Study – Discussion

- $K_d$ of organic (peat) soil = 2.9 L/kg
  - Ratio of amount sorbed per mass of solid to the amount of the sorbate remaining in solution at equilibrium
  - Previous studies have not addressed peat soils, mostly focused on soils with about 3% organic content with a mineral base
  - Results indicate peat based soil sorbs sulfolane more than mineral soils (max. uptake by mineral soils reported a $K_d$ of 0.94 L/Kg by montmorillonite)
  - Higher concentrations of sulfolane need to be spiked onto the peat soil to determine the maximum uptake capacity of the soil
- 48 hrs is an arbitrary standardized time line and a longer experimental time is required to fully understand the mechanisms of sorption and desorption
Conclusions

• Stage 1 and 2 studies generally showed acceptable results for sulfolane analysis in soil and groundwater.
• More variability was present in soils and particularly organic soils.
• Also more variability was present at lower concentrations.
• There is potential for interference from some natural organic compounds when using GC-FID or GC-MS.
• Longer experimental times are needed to fully understand the mechanisms of sorption/desorption.
Recommendations

• Suggestions for consultants and testing laboratories to minimize sources of error:
  – Conduct pre-sampling discussions with testing laboratories of any potential concerns, such as natural or introduced potential interfering constituents or wide ranging sulfolane concentrations in sample lot.
  – Laboratory may consider using sulfolane spiking of samples to help prevent false positives possibly being detected by GC-FID analysis.
  – Increase and target field QC sampling especially targeting lower concentrations
  – Increase vigilance to sample preservation and keeping samples with zero headspace, away from light, and at 4C once sampled.
  – Where possible, minimize sample storage time.
Recommendations

• Suggestions for consultants and testing laboratories to minimize sources of error (continued):
  – Expect possible detection limit concerns when analyzing low concentrations in organic soils; some testing laboratories are reporting without these concerns flagged. Discuss with preferred testing laboratory in advance to determine if this can be addressed.
  – Once data received, promptly review data for any potential anomalous results, as could occur when there are unexpected results based on history of site and field conditions, or failing QC sample results. Request re-checks where applicable.
Recommendations

• CCME Version 4 Suggestions\(^1\):
  – Update to include the various options for analyzing sulfolane presented
  – Make clear that detection method, in some instances, may be affected by interferents
  – Require testing laboratories to consider organic soils when developing testing methods
  – Evaluate if sample holding times and sample preservation listed are sufficient
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References

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