Investigation of Sulfolane Extraction, Analysis and Sorption/Desorption with Relevance to Alberta Forest Soils and Associated Groundwater
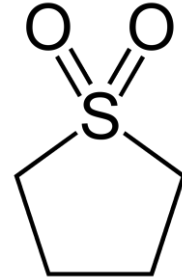
Presenters: Sheila Luther and Nahid Hassanvand-Gandaei

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

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Soil Extraction Methods - Literature Review

Methods	Advantages	Disadvantages
Soxhlet Extraction[1,2,10,13]	• Robust extraction method • Provides efficient extractions	• Long extraction times (16 to 24 hrs) • 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 • Water extractions - 92-104 % efficiency • Water extraction following a back extraction with water-saturated toluene • Toluene is especially favorable because sulfolane is used to extract aromatics	• Labour intensive – requires possibly centrifuging, filtering and volume reduction • Sample handling that is required could introduce error

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Water Extraction Methods - Literature Review

Methods	Advantage(s)	Disadvantage(s)
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)

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Analytical Methods - Literature Review

Instrument	Advantages	Disadvantages
Gas Chromatograph equipped Flame Ionization Detector (GC-FID)[12]	• 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[7]	• 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[3]	• Simple water extraction • Direct aqueous injection	• Sample preparation can be more prone to interferences • Potential for interference from salts

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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

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Stage 1 Study - Methods

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

* Not part of Stage 1 but were part of Stage 2 study.

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Stage 1 Study - Results

Soil Sulfolane - Site Replicates
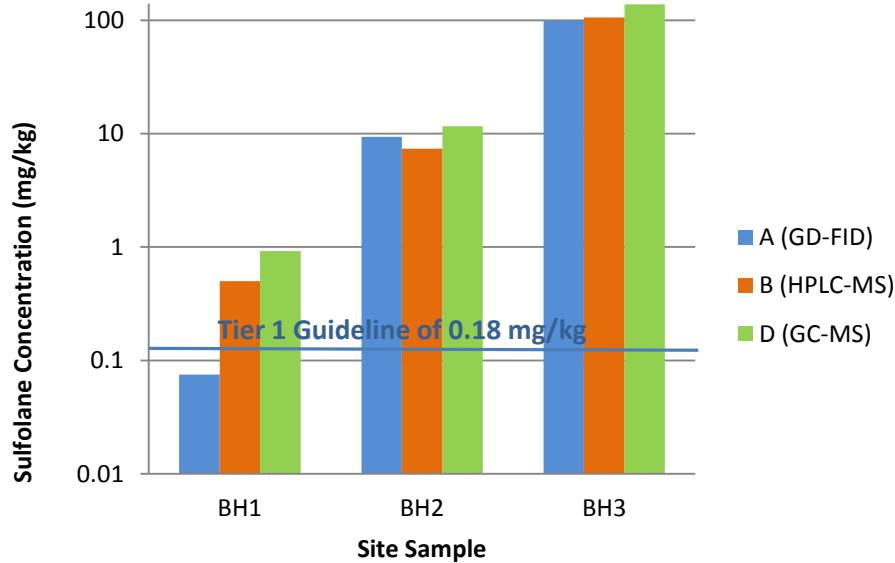
Groundwater Sulfolane - Site Replicates
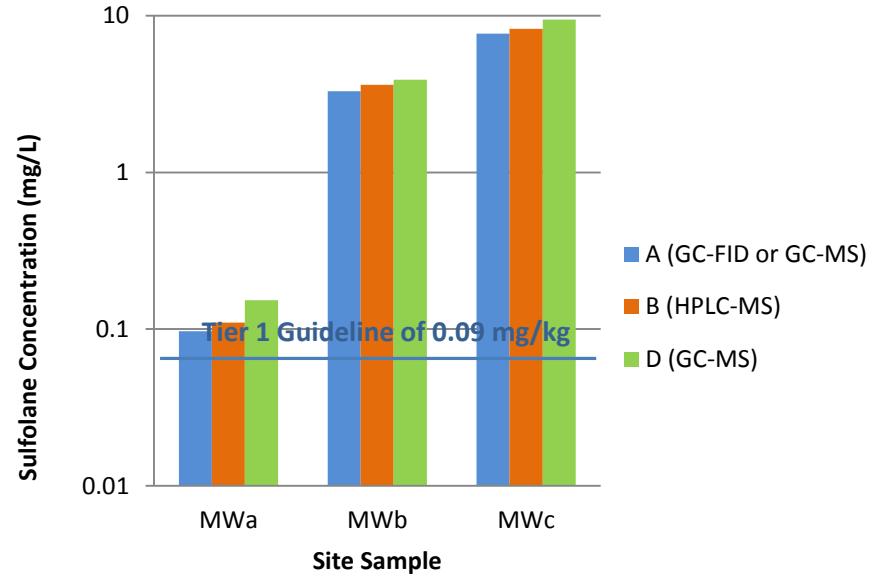
Z Score[14] for Data Evaluation

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

$$Z = \frac{(x - \overline{x})}{\sigma_x}$$

- 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.

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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 ^{o}C to minimize microbial activity
- Soils were spiked to 100 mg/kg, 10 mg/kg and 0.5mg/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

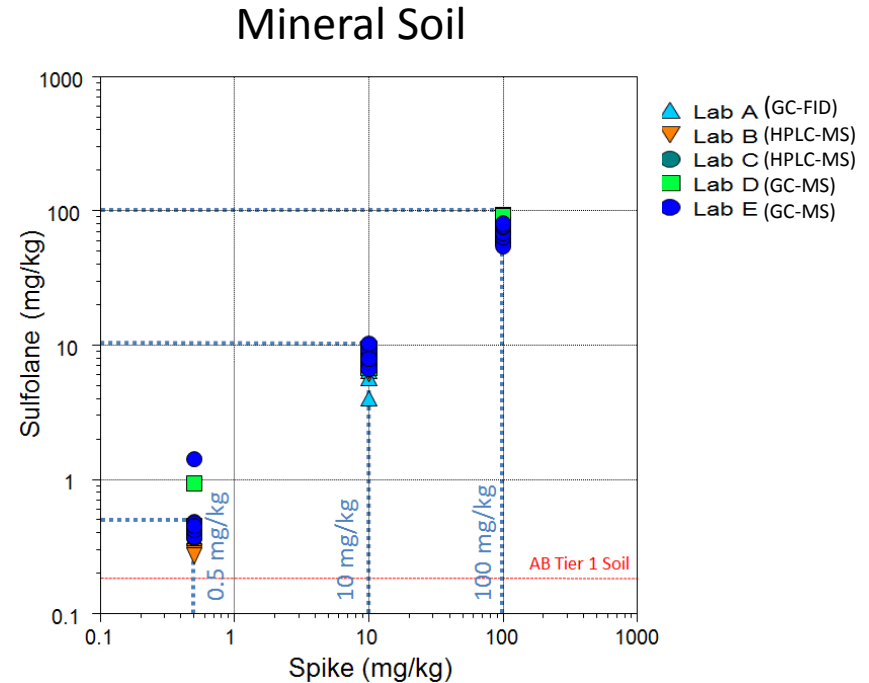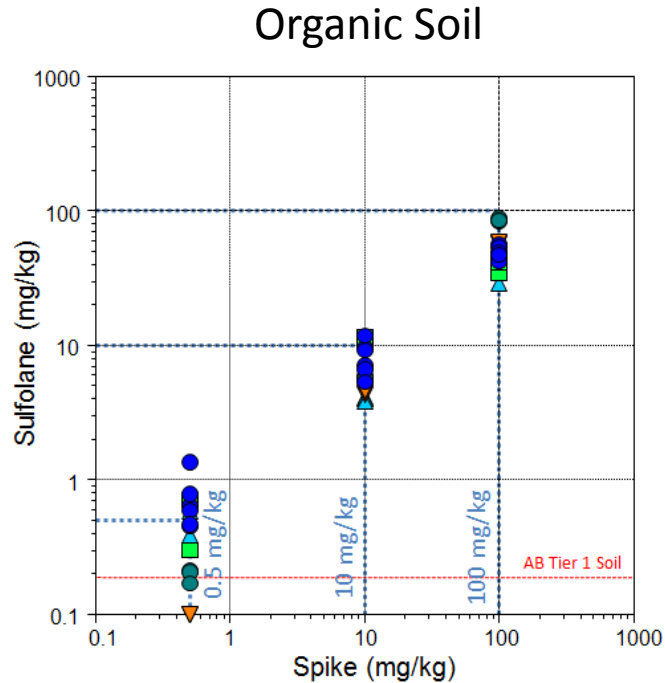A 3L stock solution of groundwater was prepared

- 0.1 mg/L
- 0.5 mg/L

Stage 2 Soil Material Characterization

Characteristic	organic	till
pH	4.94	7.51
Conductivity (dS/m)	0.36	1.1
Sodium Adsorption Ratio	0.55	0.57
Total Organic Carbon (mg/kg)	485000	9900
Texture	Peat	Clay (45%)
Cation Exchange Capacity (cmol+/kg)	160	20

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Water Characterization

Characteristics	Water
pH	7.90
Total Dissolved Solids (mg/L)	310
Dissolved Organic Carbon (mg/L)	3.1

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Stage 2 Study - Results

Organic Soil · Mineral Soil

Lab A (GC-FID)
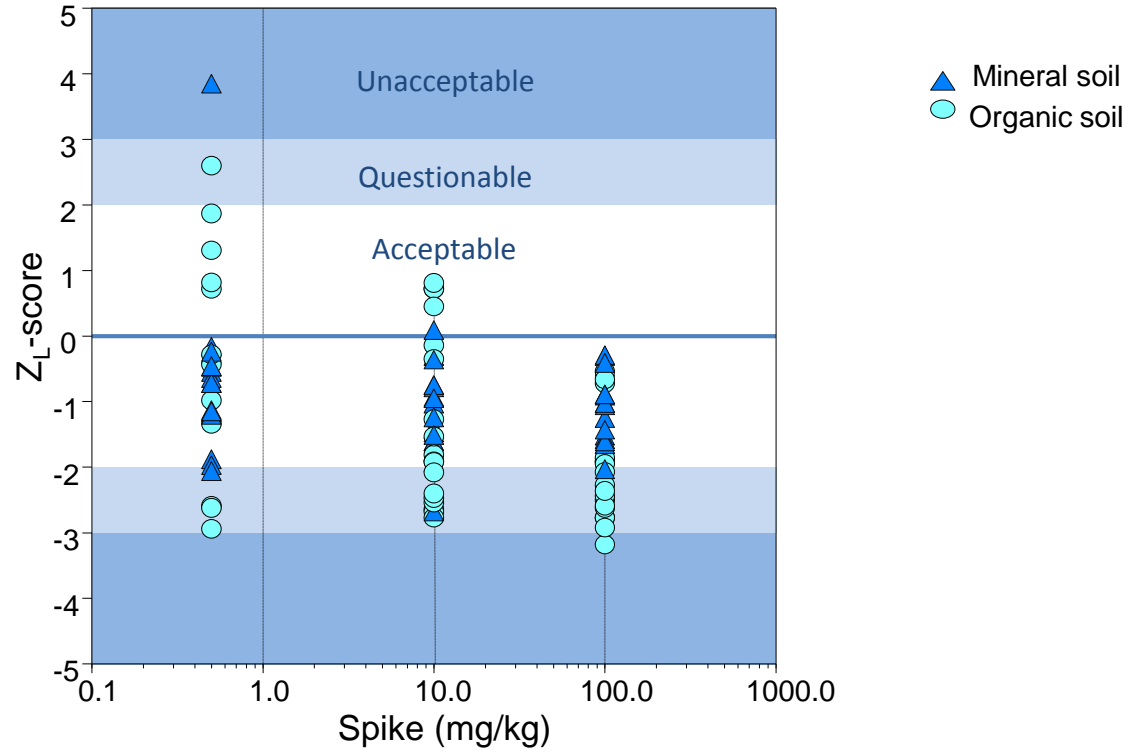Lab B (HPLC-MS)
Lab C (HPLC-MS)
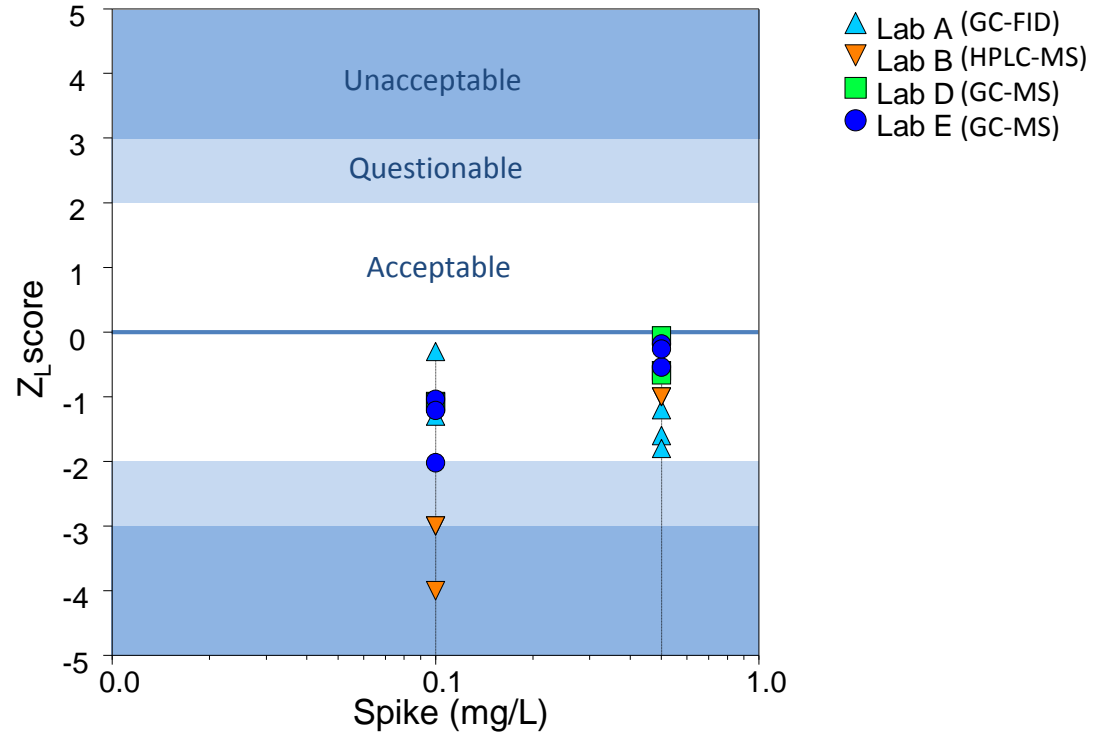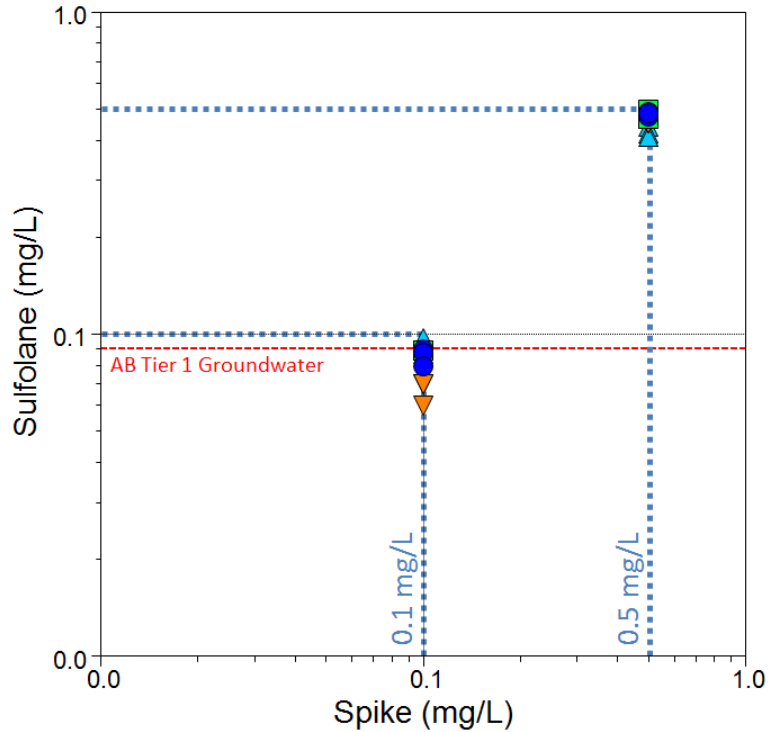Lab D (GC-MS)
Lab E (GC-MS)

Sulfolane Spiking Study

- Acceptable uncertainties chosen as,
    - Extraction uncertainty u_{ex} = ±20%
    - Analytical uncertainty u_{an} = ±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

Groundwater Spiking Study

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

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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

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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[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

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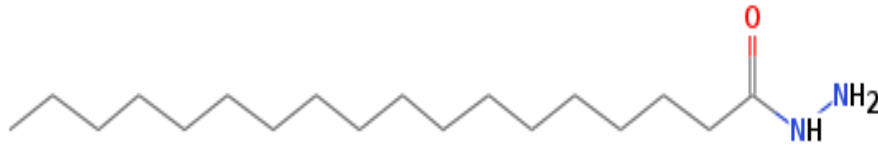# Potential Interferences Identified
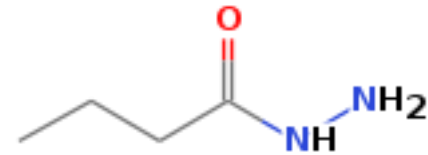
2-butenyl hydrazine

1,1-dimethyl-2-octyl-Cyclobutane
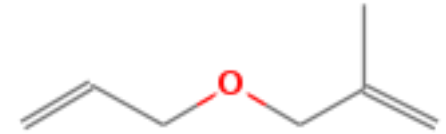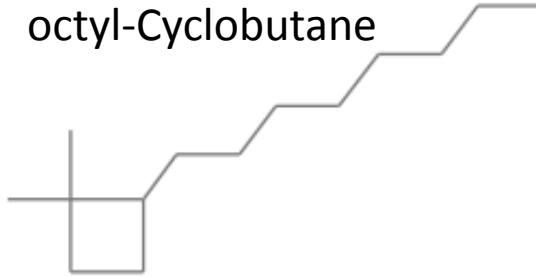
Allyl methallyl ether

Stearic acid hydrazide

Butyric acid hydrazide

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[16,17]

- Batch-Type Procedures[18,19]

- Need to consider factors such as:

  - Air-drying vs oven-drying

  - Constant temperature

  - Headspace

  - Microbial activity

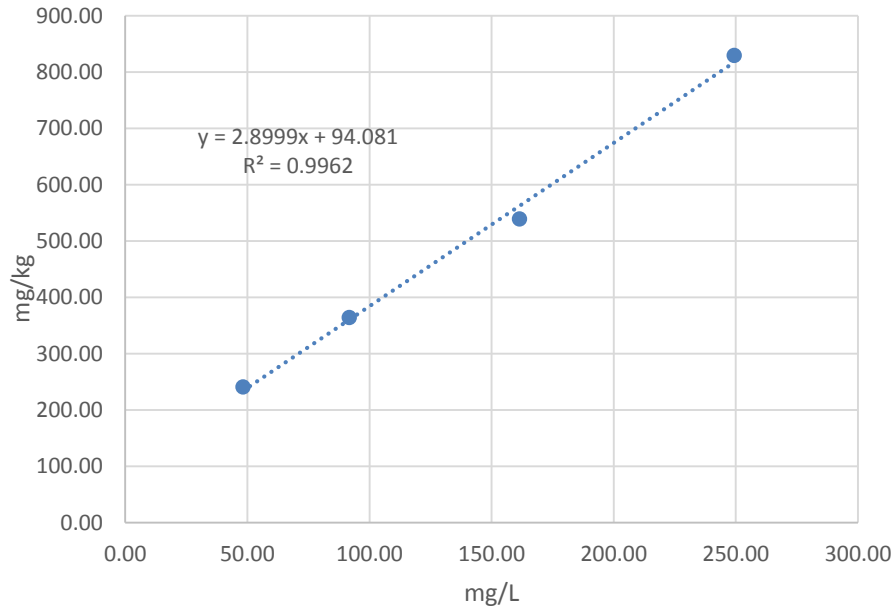# Sorption/Desorption: 4°C – 48 hrs
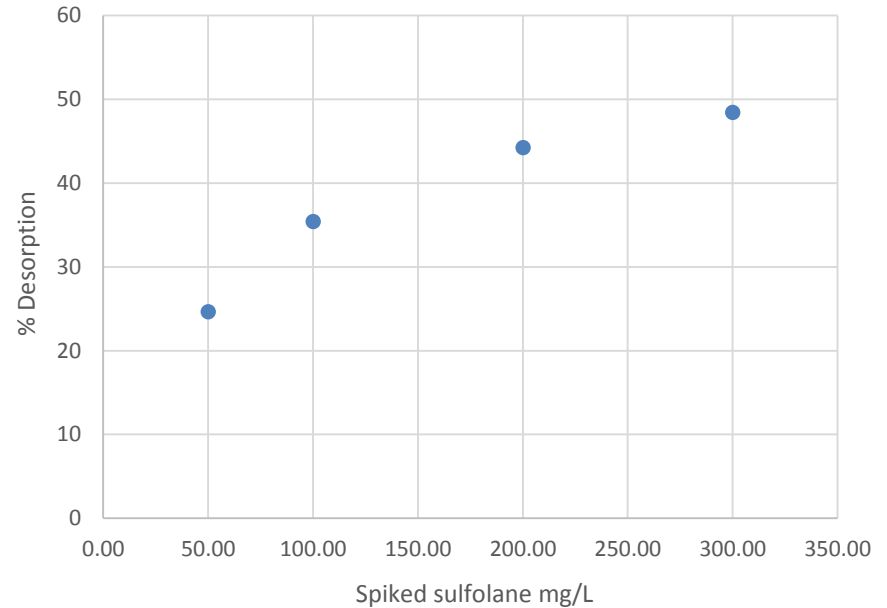

Fig.1: Sorption of Sulfolane on Organic Soil

$y = 2.8999x + 94.081$
$R^2 = 0.9962$

Fig.2: Desorption of Sulfolane from Organic Soil

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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

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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.

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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.

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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.

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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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