Reduced Sulfur Compounds in Sediments and Soil

AGAT Laboratories

Canadian Science and Technology in Action Coast to Coast

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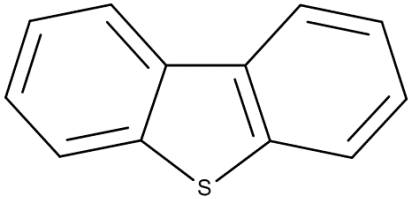
Applications of the Study

- Determine potential health concerns.
  - Short term: lung issue; long term: chronic hazard.
- Determine the remediation progress on site.
- Risk assessment is required for sites exposed to sour crude spills.

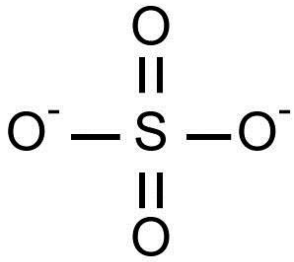
Applications of the Study

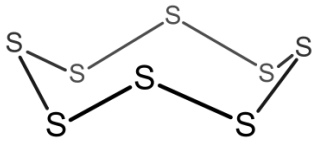
- Aromatic sulfur compounds can cause immediate human toxicity
  - i.e. Dibenzothiophene.
- General sulfur exposure may cause complicated health issues.
- Catalytic role in other hazardous reactions such as formation of methylmercury when sulfides remain in soil.
- There is a potential bioaccumulation in some plants (studies specifically done on Camphor tree).



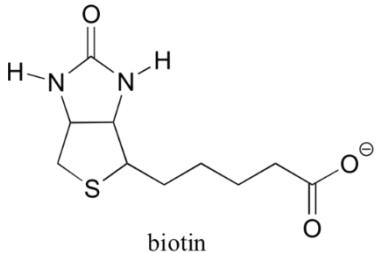
Sulfur Chemistry

Common Sulfurs Groups

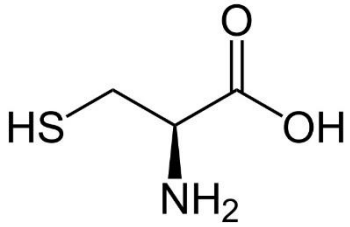




- Elemental Sulfur
- Oxidized Sulfur (Inorganic Sulfur)
- Reduced Sulfur (Organosulfur Compounds)
- Biological Sulfur Compounds (proteins, amino acids, vitamins, enzymes, etc).



biotin

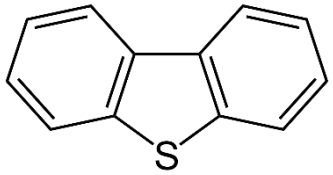


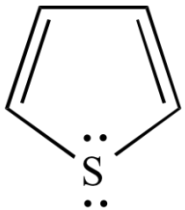
Cysteine

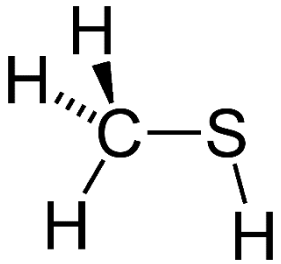
Sulfur Chemistry

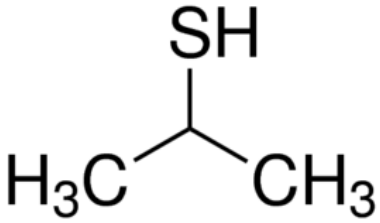
Reduced Sulfur Compounds (Organosulfur Compounds)

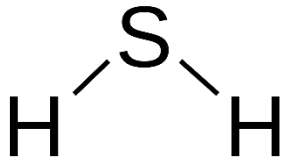
- Hydrogen Sulfide (H_2S)
- Thiols (R-S-H)
- Mercaptans (R_1-S-R_2)











Sulfur Chemistry

Hydrogen Sulfide (H_2S)

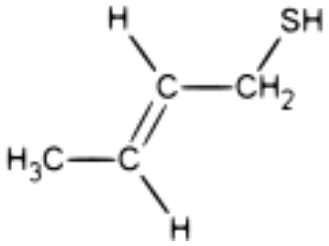
- The most commonly discussed RSC (Reduced Sulfur Compound).
- Typically present as a gas, though *very* soluble in water and reacts rapidly with transition metals.

$$H_2S \longleftrightarrow HS^- + H^+ \longleftrightarrow S^{-2} + 2H^+$$

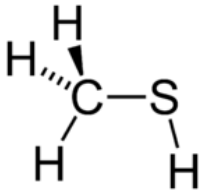
- Well known for being a poisonous gas and having a noxious odor.
- Produced in high volumes in many oil and gas fields.

Sulfur Chemistry

Thiols and Mercaptans



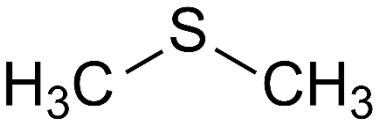
- Regularly produced by different plants and animals:
  - 2-butene-1-thiol is produced by skunks.
  - Methylmercaptan is produced from decaying plant matter.
- Regularly found in crude petroleum.
  - Due in part to diagenesis of sulfur containing compounds.
  - Methylmercaptan is added to petroleum gases as an odorant.



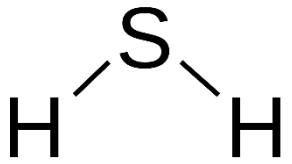
Sulfur Chemistry

Anthropogenic Sources

- Pulp Mills
- Petroleum Production
- Waste Treatment Plants



(Dimethyl Sulfide)



(Hydrogen Sulfide)

Sulfur Analysis

- Historically there's been a lack of commercially utilized methods for reduced sulfur compounds in environmental samples (soil and water).

- However there are regularly used methods for petroleum (UOP 791, ASTM D5504, ASTM D5623)

- Upon receiving regular requests for this analysis AGAT took it upon itself to build some new methods to accommodate the need.

Sulfur Analysis

Current Sulfur Scans in Petroleum and Air

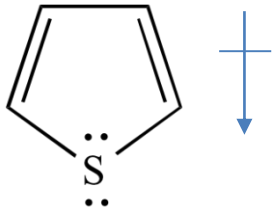
Hydrogen Sulfide	Ethyl Methyl Sulfide
Carbonyl Sulfide	Thiophene
Methyl Mercaptan	i-Butyl Mercaptan
Ethyl Mercaptan	Diethyl Sulfide
Dimethyl Sulfide	n-Butyl Mercaptan
Carbon Disulfide	t-Butyl Methyl Sulfide
2-Propyl Mercaptan	Dimethyl Disulfide
t-Butyl Mercaptan	Diethyl Disulfide
1-Propyl Mercaptan	

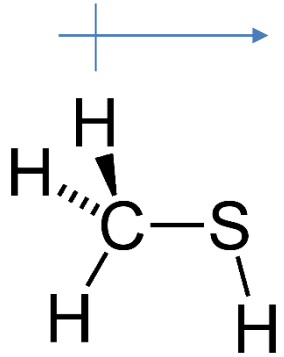
Sulfur Analysis

Extractions

As a part of R&D on this subject we tried multiple different extraction solvents.

- Hexane
- Toluene
- DCM (Dichloromethane)
- Chloroform (Trichloromethane)
- Amine (Monoethanolamine / MEA)





Sulfur Analysis

Extractions

To narrow the variables, we kept the extraction to only moderate agitation via a ‘hand – shaking’ method at ambient temperatures.

Future consideration may involve hot extractions or higher intensity agitations (ie. paint shaker).

Sulfur Analysis

Instrumentation

- Utilized gas chromatography with a Sulfur Chemiluminescent Detector (GC-SCD).
- Ability to detect sulfur species at a low detection limits with very little interference.

Sulfur Analysis

Sulfur Analysis

Results / Trends on Raw Condensate

- Raw results obtained from a crude condensate found to have 6,221 ug/g Total Organic Sulfur with H_2S removed.

- Different solvents showed different efficiencies:

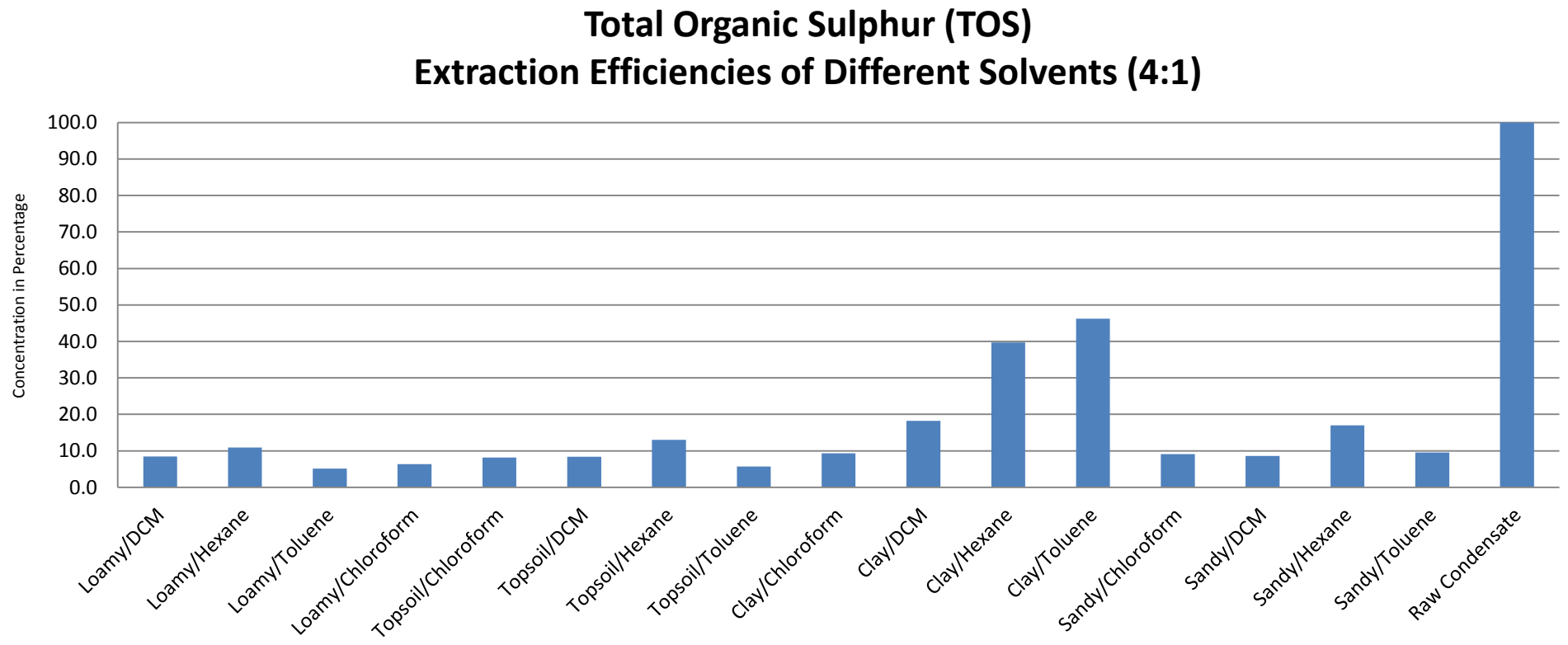
Sample	Normalized TOS (ug/g)
Condensate	6221
Toluene + Condensate	3784
Hexane + Condensate	3724
DCM + Condensate	1708
Chloroform + Condensate	1704

Sulfur Analysis

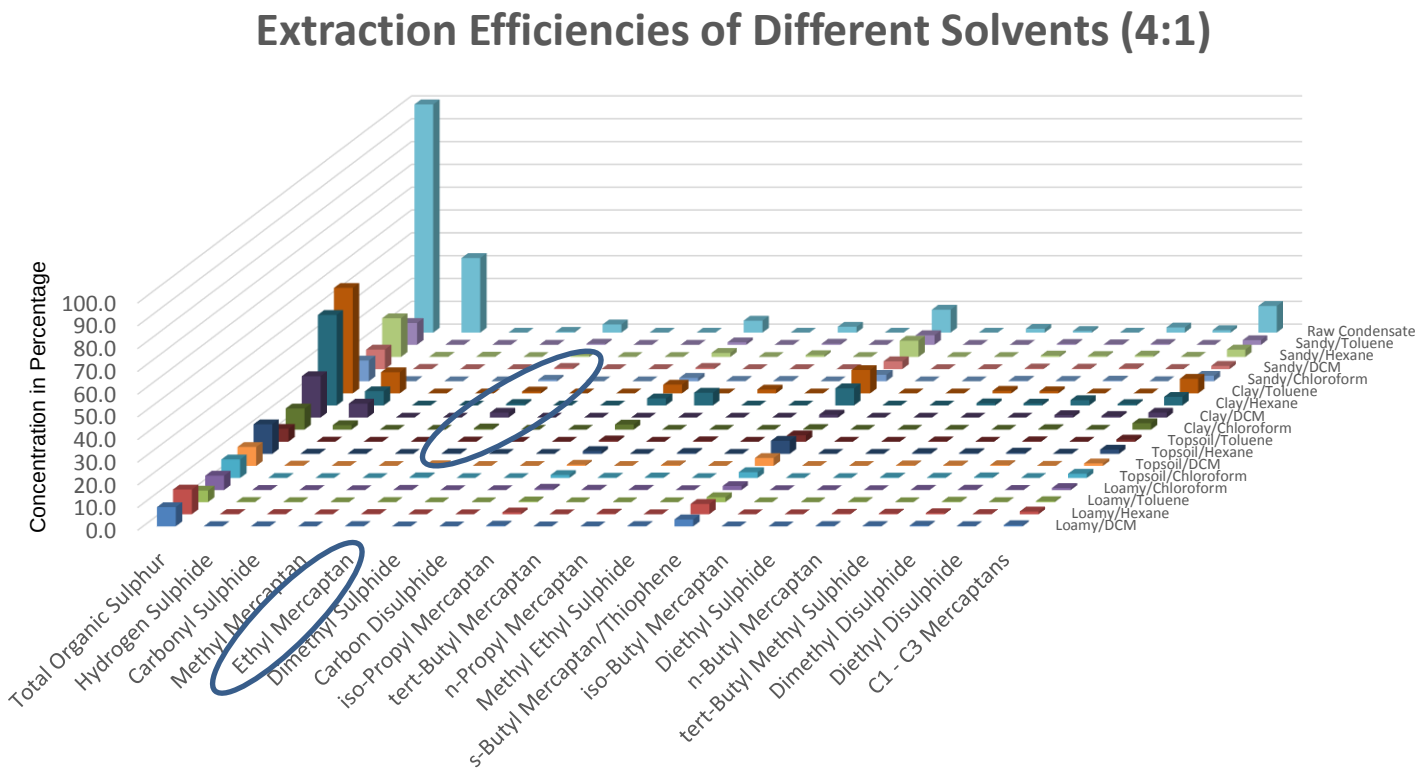
Results / Trends on Soil spiked with Condensate

- 5 grams of soil was spiked with 5 grams of condensate (our standard).
- Extracted with a 4:1 ratio of each solvent at 4°C.

Sulfur Analysis



Sulfur Analysis

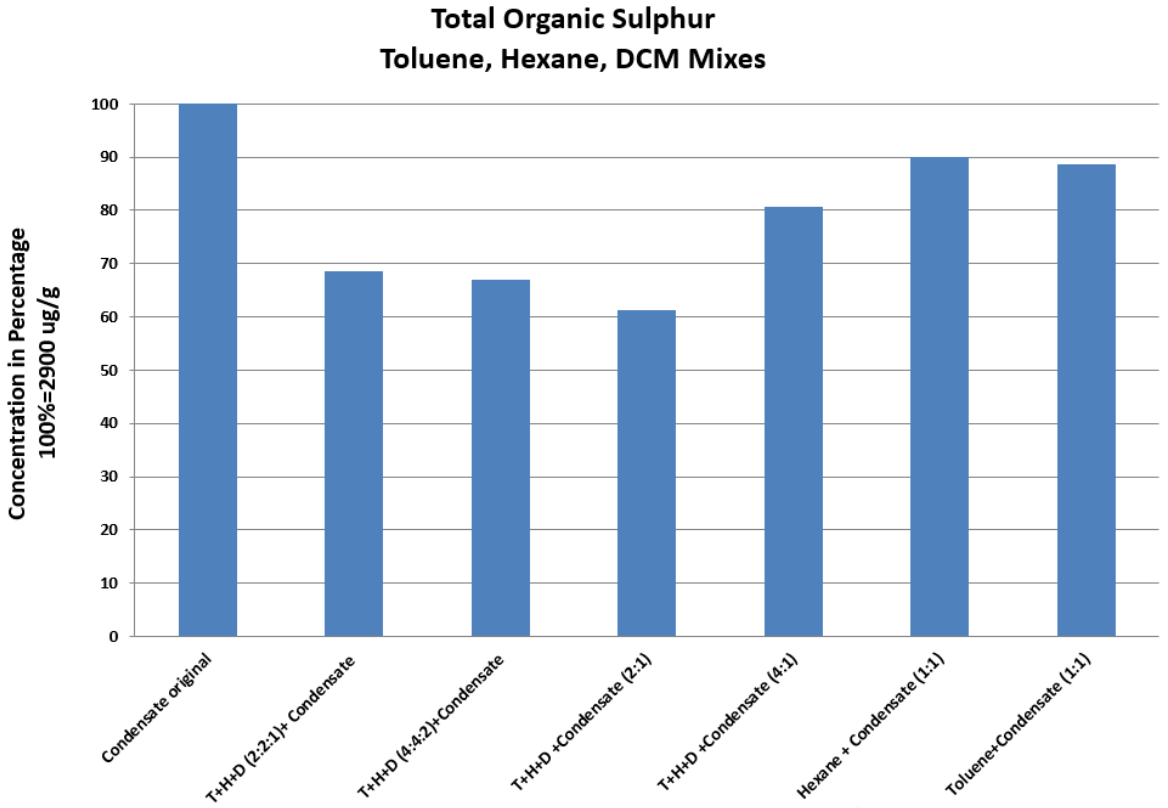


Sulfur Analysis

Results / Trends on Soil spiked with Condensate

- 5 grams of soil was spiked with 5 grams of condensate (our standard).
- Extracted with a varying ratio of each of the solvents.

Sulfur Analysis

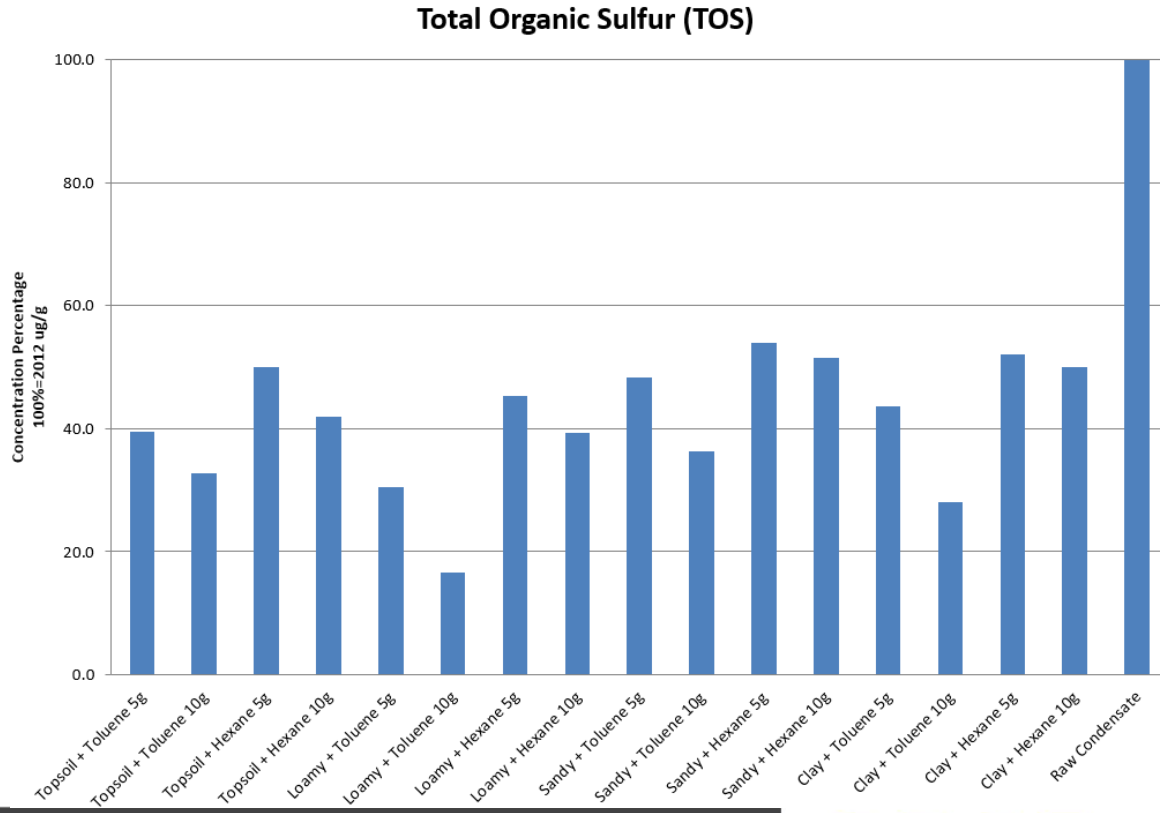


Sulfur Analysis

Results / Trends on Soil spiked with Condensate

- 5 grams of soil was spiked with 5 grams of condensate (our standard).
- Extracted with a 1:1 ratio and 2:1 ratio of each of the solvents.

Sulfur Analysis

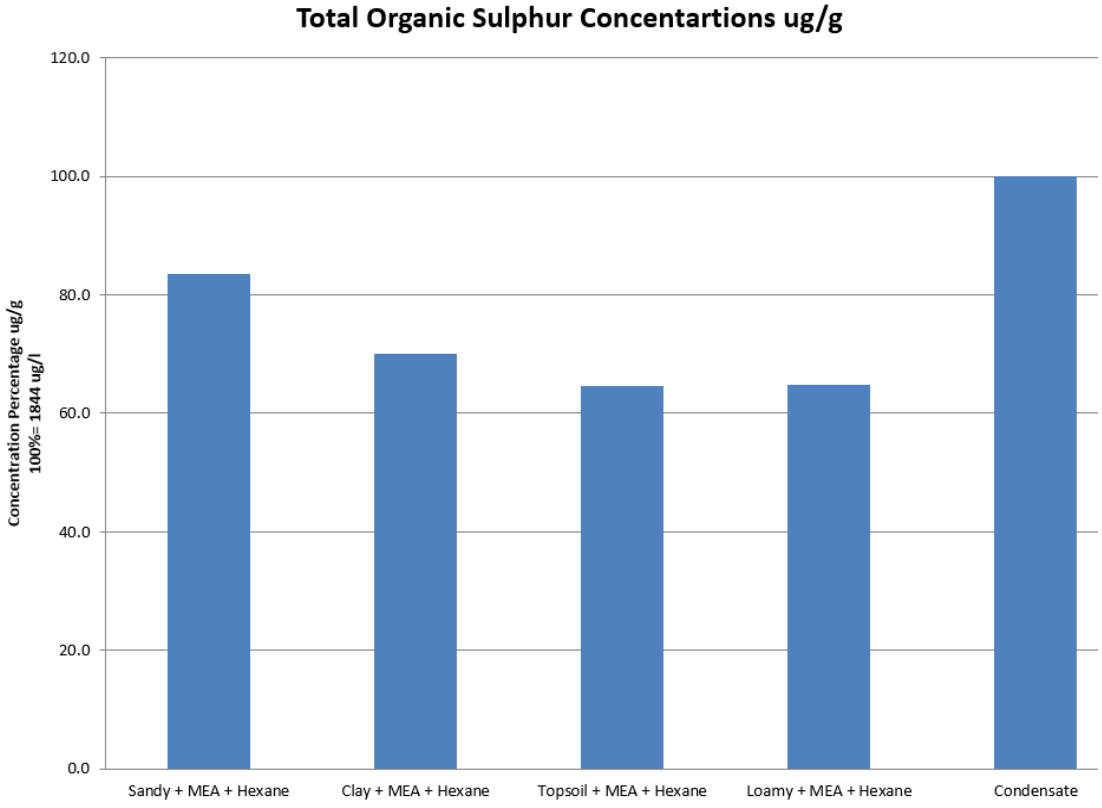


Sulfur Analysis

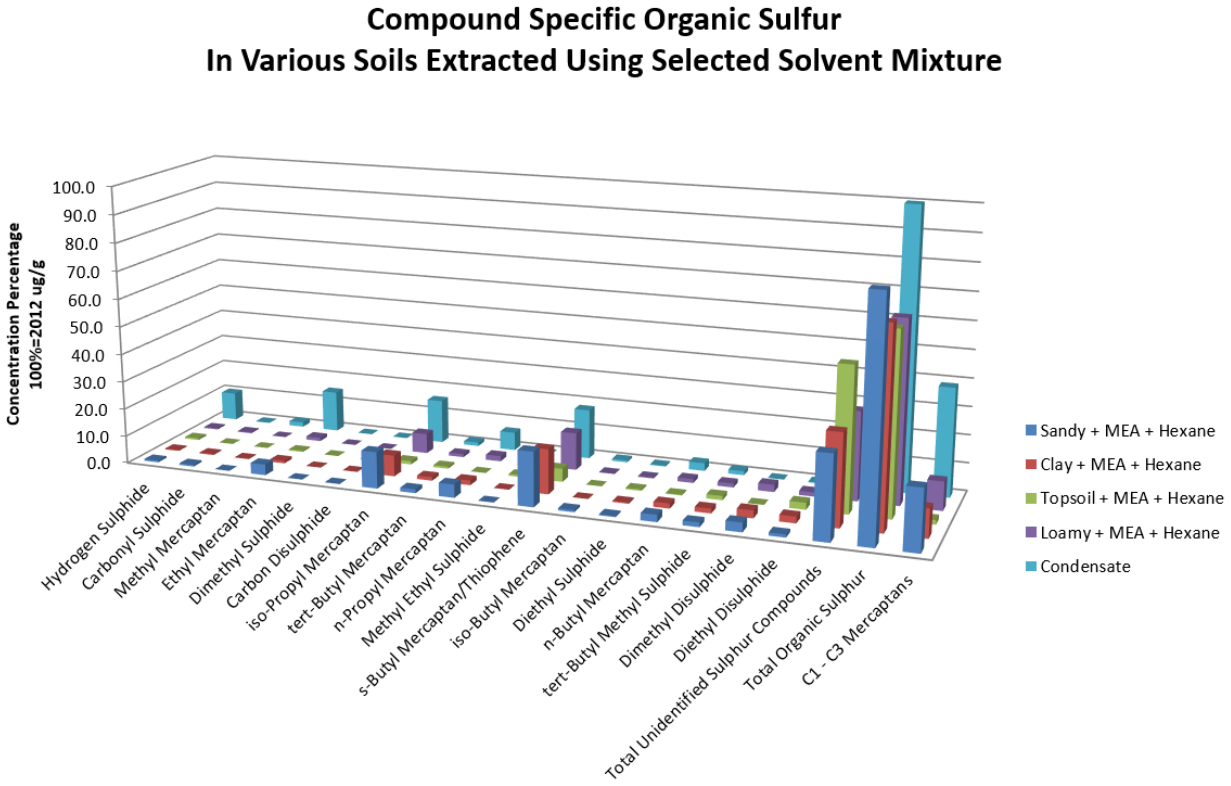
Results / Trends on Soil spiked with Condensate

- 5 grams of soil was spiked with 5 grams of condensate (our standard).
- Extracted with a mix of solvent (Hexane) and Amine (MEA)

Sulfur Analysis



Sulfur Analysis



Sulfur Analysis

Concluding Remarks

- It was found that Hexane with the addition of an Amine was the most effective solvent mixture.
    - Some sulfur compounds showed preference for polar solvents.

- Applicable scenarios for utilizing this methodology include:
    - Soil Background Studies
    - Initial Spill Response
    - Useful for determining EH&S Efforts for Onsite Exposure / Releases

Sulfur Analysis

Steps forward

- Finalize testing and validate a finalized method.
- Review publication of method to allow for standardization.
- Obtain feedback from industry on applications and need.
- Review expanding to Reduced Sulfur in Water Analysis.

Thank You

Questions and Discussion