Schulich School of Engineering

Biodegradation of Sulfolane in Soil Using Aerobic Biopile Technology

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Successful Collaboration Between Academia and Industry – Breaking Open Sulfolane Remediation strategies

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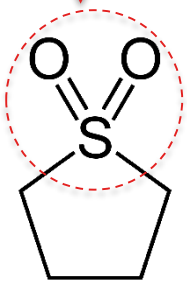
Outline

- Sulfolane Key Properties
- Environmental Standards
- Previous Sulfolane Presentations
- Development of Sulfolane Treatment Technology
- Aerobic Biodegradation of Sulfolane in Soil
- Lab Degradation of Sulfolane
- Pilot Demonstration-Biopiles
- Full Remediation on Sulfolane Contaminated soil

Sulfolane Key Properties

- Gas Sweetening
- Aromatics Extraction
- Textiles
- Production 18,000-36,000 tones[1]
- Soil and Groundwater contamination
- Ongoing Toxicity Studies (NTP)

Sulfonyl group



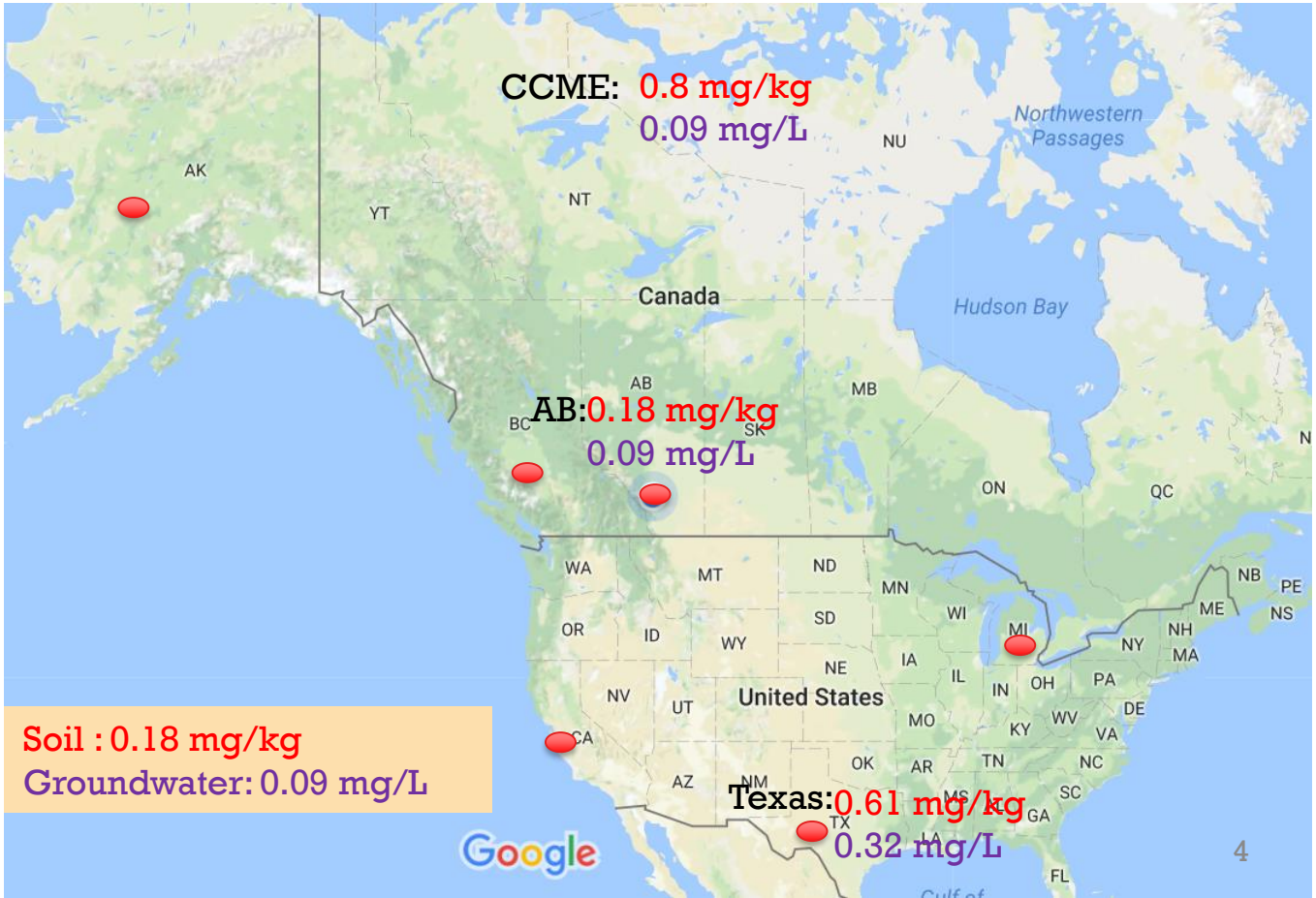
Cyclic structure

- ❑ Chemically stable
- ❑ Thermally stable
- ❑ Boiling Point: 287.3 °C [2]
- ❑ Vapor Pressure@20°C : 1.33 pa[3]
- ❑ Water Solubility@20°C: 1266 g/L[3]
- ❑ Soil Adsorption:
  - K_{oc}=0.07[3]
  - K_d(montmorillonite)=0.94L/kg[4]
  - K_d(kaolinite)=0.08 L/kg [4]

Environmental Standards

- Alberta
- BC
- Alaska
- Texas
- Louisiana
- California
- Michigan

Health Canada **interim** drinking water guideline: **0.04mg/L**.



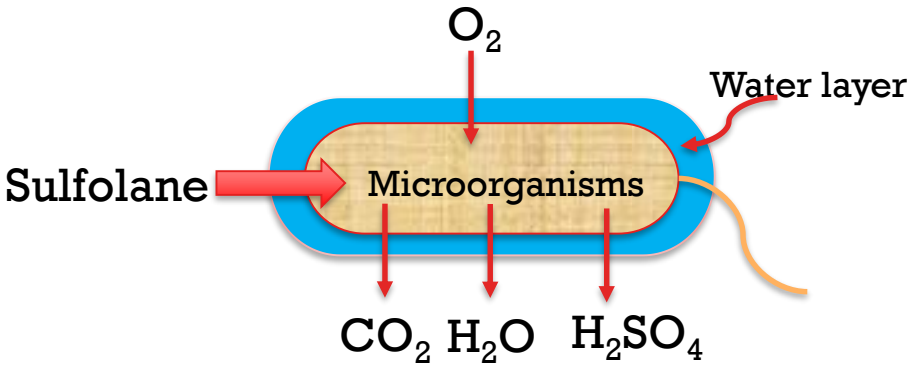
Previous Sulfolane Presentations

- EBA 2005 – Lab Scale
  - Soil: Bio-treatability
  - Groundwater: Bio-treatability; Chemical Oxidation
- Biogenie 2006 – Full Scale
  - Soil: Bio-treatability
- WorleyParsons Komex 2008 – Pilot and Full Scale
  - Groundwater: Bio-treatability
- Waterline 2016 – Pilot Scale
  - Soil: Bio-treatability; Chemical Oxidation
- Trium 2016 – Lab Scale
  - Groundwater: Chemical Oxidation
- Maxxam 2017 – Lab Scale
  - Laboratory Methods
- WorleyParsons 2017
  - Groundwater Remedial Options Review

Development of Sulfolane Treatment Technologies

Groundwater	Soil
▪ Advanced Oxidation – Lab and Field Pilot ▪ Bioremediation – Lab and Field Pilot ▪ Carbon Adsorption – Lab and Field Pilot ▪ Reverse Osmosis – Lab Scale ▪ Isotope Fractionation – Lab Scale ▪ Integrated Technology-Lab scale	▪ Bioremediation – Lab Scale, Field Pilot, Full Scale ▪ Soil Flushing & Washing – Lab Scale and Field Pilot ▪ In-Situ Chemical Oxidation (ISCO) – Lab Scale ▪ Oxygen Releasing Compounds (ORC) – Lab Scale and Field Pilot

Aerobic Biodegradation of Sulfolane in Soil



- N, P & micronutrients
- Proper pH
- Proper temperature

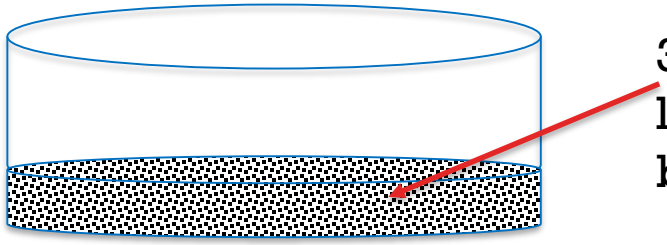
$$\text{Sulfolane} + 6.5\boldsymbol{O_2} \rightarrow 4CO_2 + 3H_2O + H_2SO_4$$

Lab Investigation:
- Treatability study
- Optimization

Pilot Demonstration:
- Evaluation
- Modification

Full Remediation:
- Modification

Lab Study: Experimental Setup

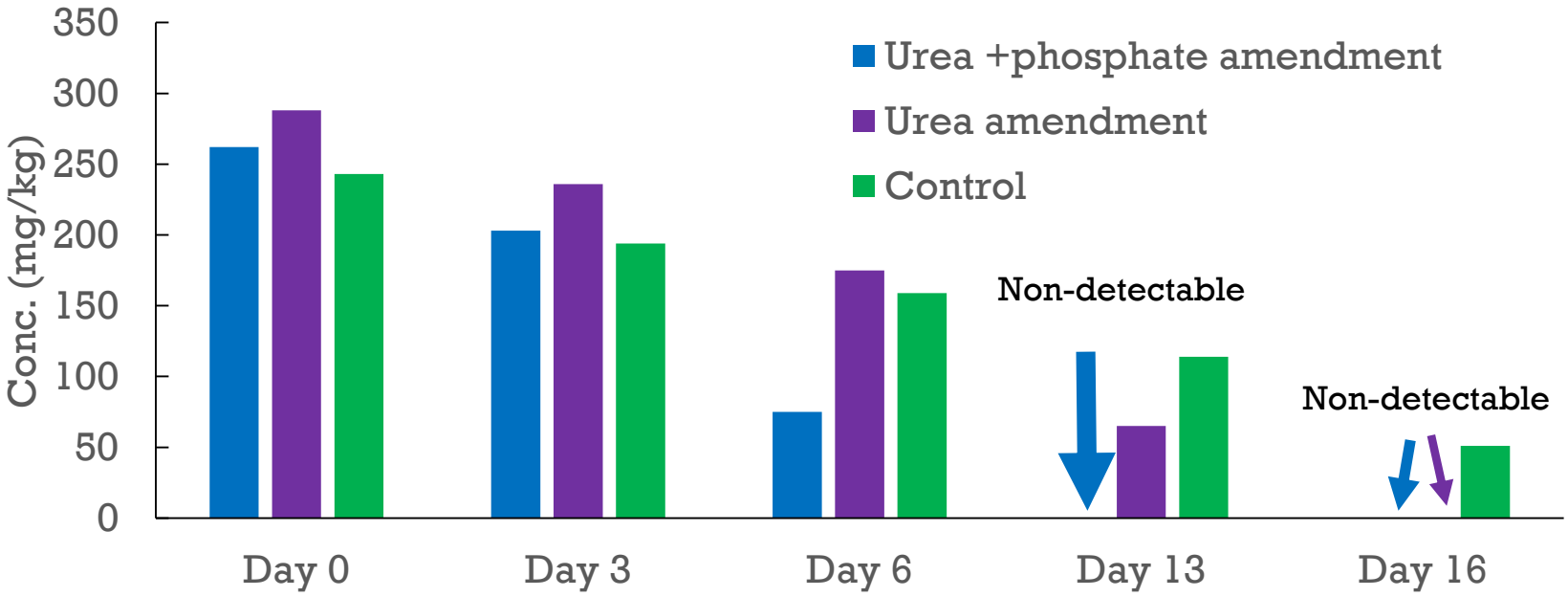


300 g of soil was loosely packed in a beaker (**ø= 15 cm**)

- Moisture : 18%
- Oxygen: exposed to atmosphere
- Temperature: 22 °C
- Nutrients : different conditions

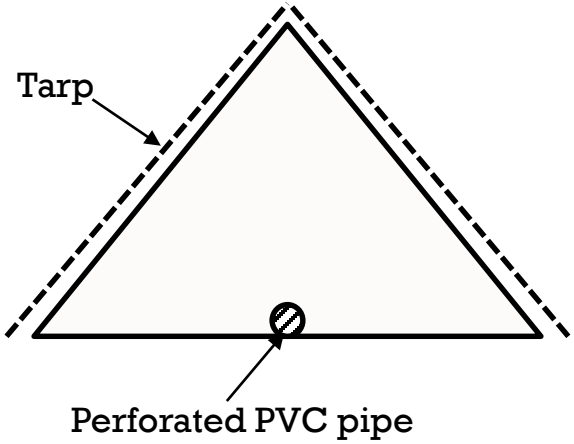
Soil Texture	
Physical properties	Value
Sand percentage	8.3
Silt percentage	43.0
Clay percentage	48.6
Texture	Silty Clay

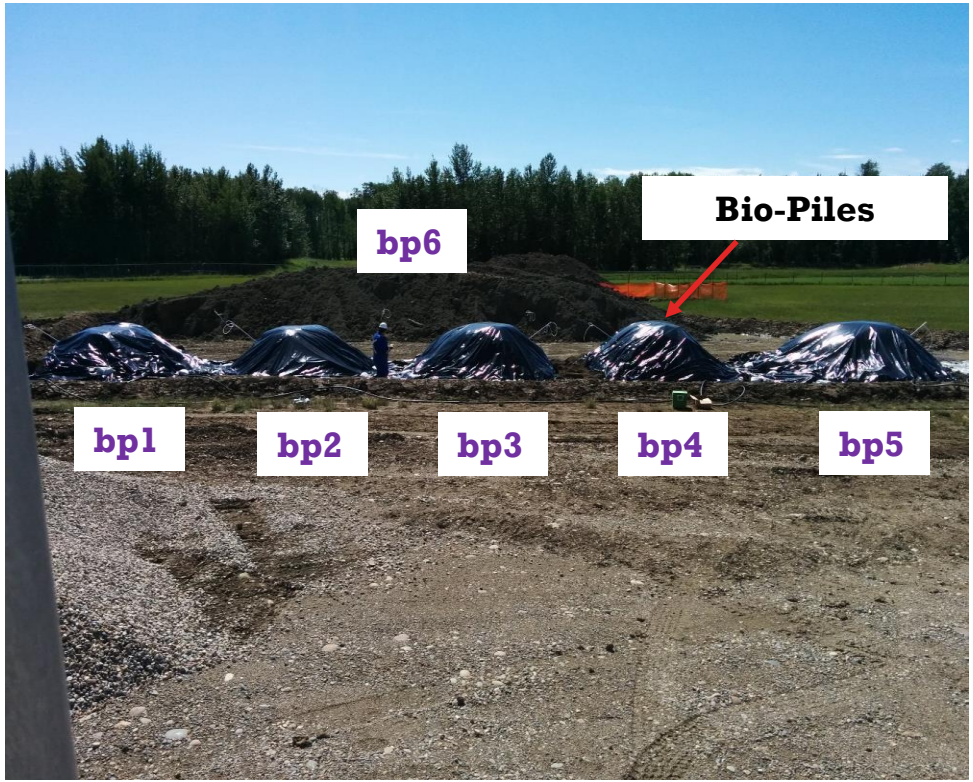
Lab Study: Different Lab Conditions



- Sulfolane metabolized microorganisms were present in the contaminated soil.
- N-P amendment samples yield the best degradation results.

Pilot Study: Setup of Soil Bio-Piles





Details of Soil Piles

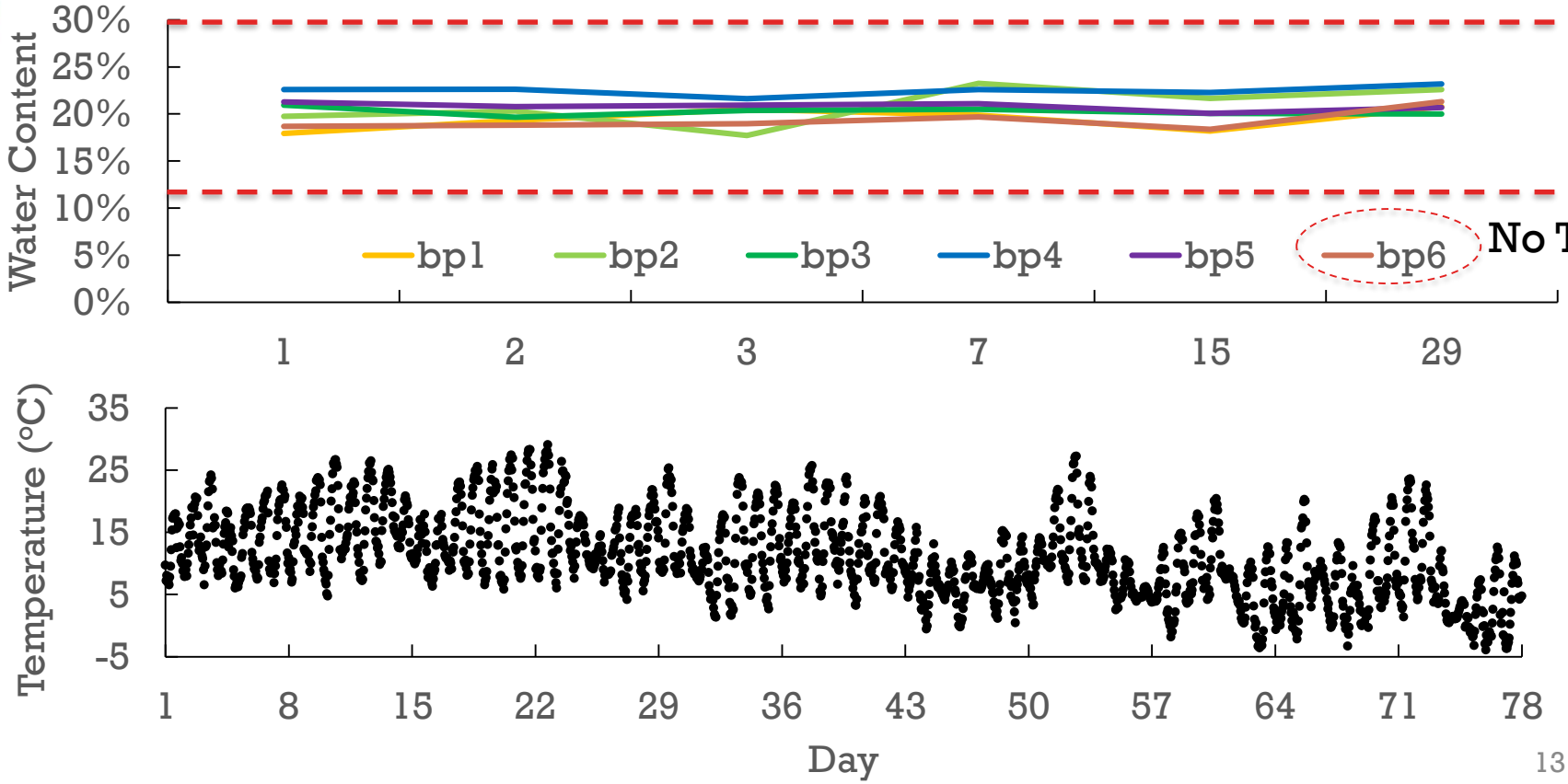
Soil pile	Size of pile (m^3)	Covered with Tarps	Nutrient Amendment			Aeration
			Nitrogen nutrient	Phosphate nutrient	Alfalfa green	
bp 1	25	Yes	Yes	NO	NO	Yes
bp 2	25	Yes	Yes*	Yes	NO	Yes
bp 3	25	Yes	Yes	Yes	NO	Yes
bp 4	25	Yes	NO	NO	Yes	Yes
bp 5	50	Yes	NO	NO	NO	Yes
bp 6	500	No	NO	NO	NO	NO

* The amount of nitrogen added in bp 2 was only 1/10 of that in bp1

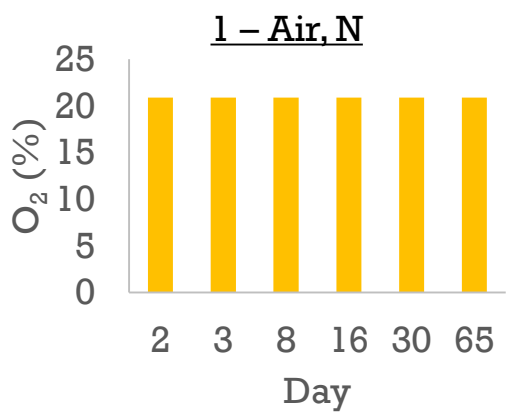
Sample Collection and Analysis

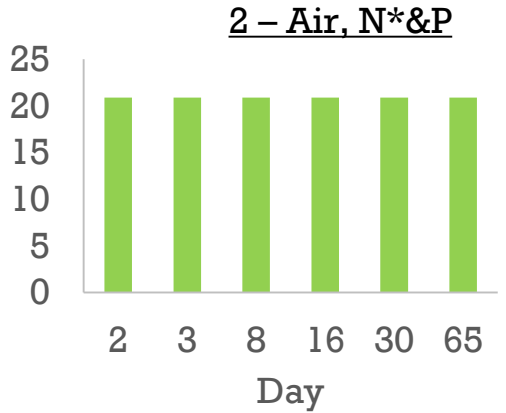
- Six random samples were collected from each soil pile
- CO_2, O_2 and water moisture content were monitored.
- Temperature data was obtained from Alberta Climate Information service

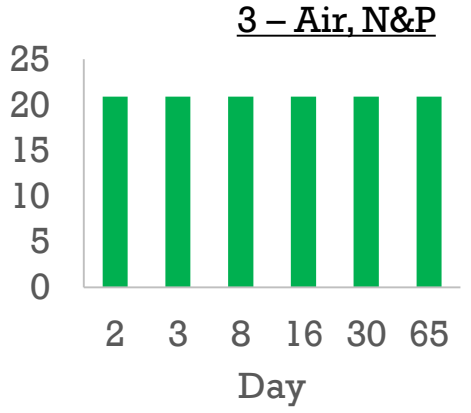
Water Content & Temperature

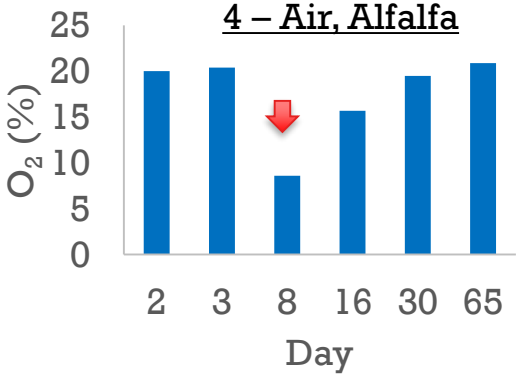


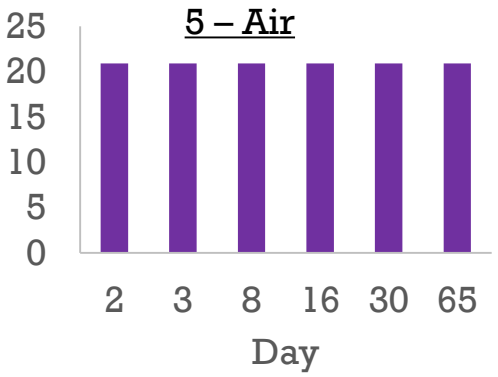
Oxygen

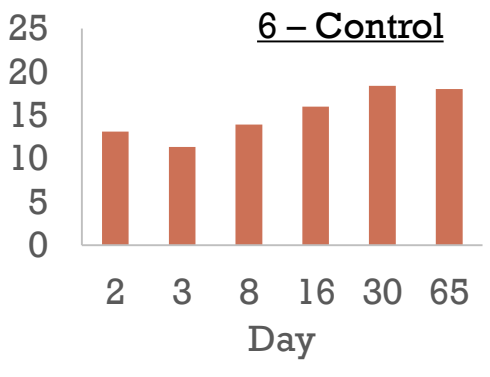

1 – Air, N
25
20
15
10
5
0
O_2 (%)
2 3 8 16 30 65
Day

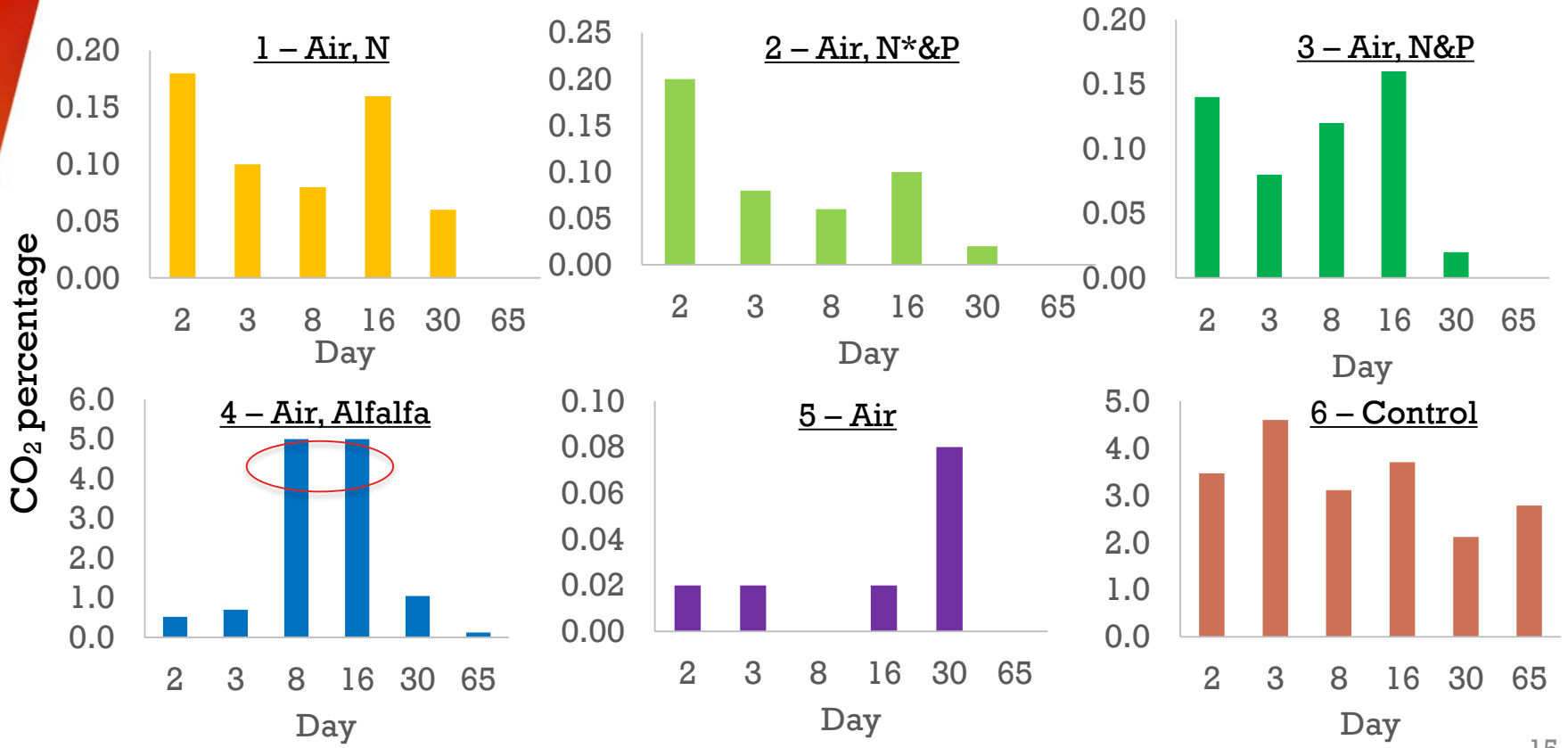

2 – Air, N*&P
25
20
15
10
5
0
2 3 8 16 30 65
Day


3 – Air, N&P
25
20
15
10
5
0
2 3 8 16 30 65
Day

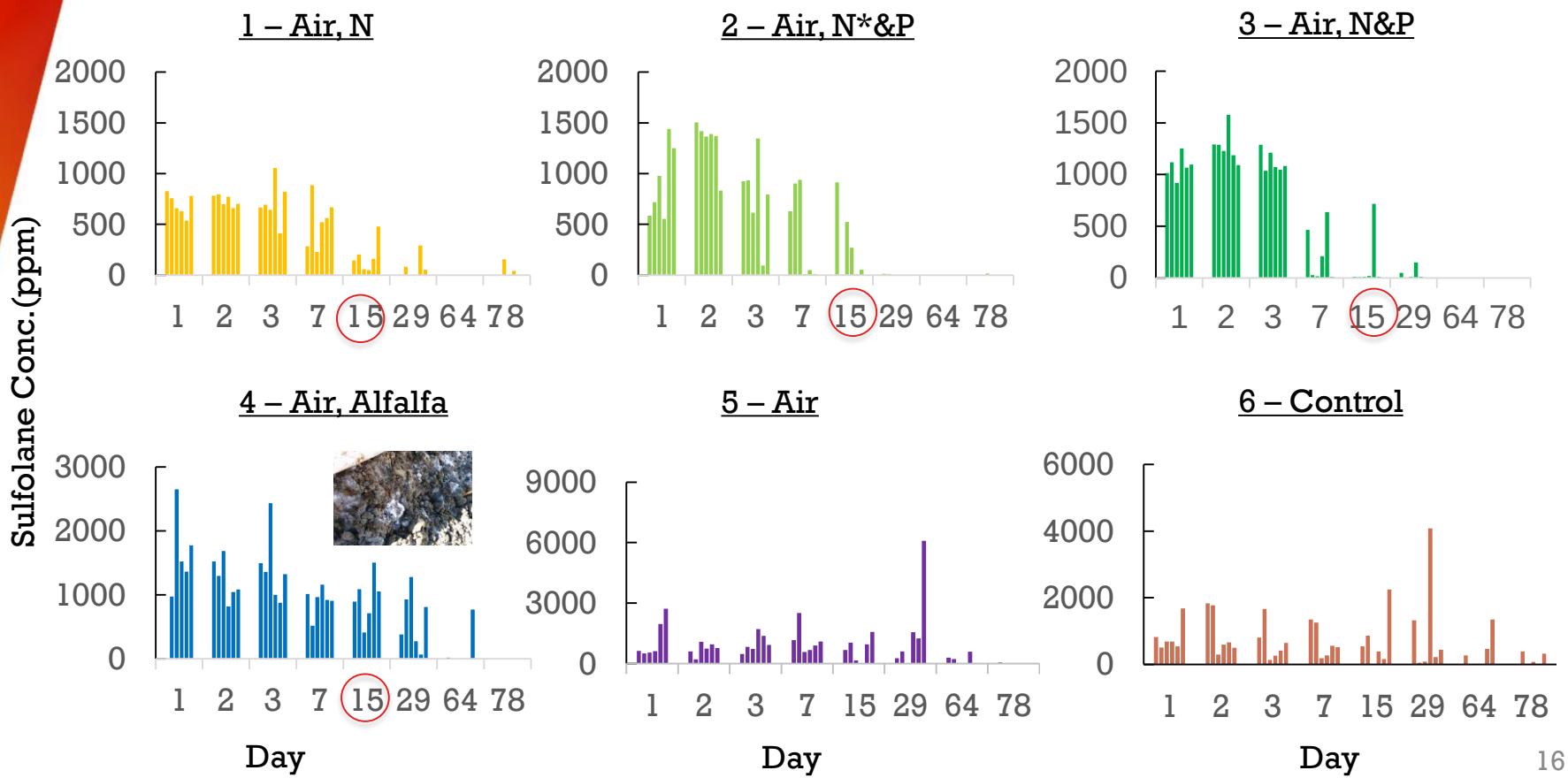

4 – Air, Alfalfa
25
20
15
10
5
0
O_2 (%)
2 3 8 16 30 65
Day


5 – Air
25
20
15
10
5
0
2 3 8 16 30 65
Day


6 – Control
25
20
15
10
5
0
2 3 8 16 30 65
Day


CO_2 percentage
1 – Air, N
0.20
0.15
0.10
0.05
0.00
2 3 8 16 30 65
Day
2 – Air, N*&P
0.25
0.20
0.15
0.10
0.05
0.00
2 3 8 16 30 65
Day
3 – Air, N&P
0.20
0.15
0.10
0.05
0.00
2 3 8 16 30 65
Day
4 – Air, Alfalfa
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2 3 8 16 30 65
Day
5 – Air
0.10
0.08
0.06
0.04
0.02
0.00
2 3 8 16 30 65
Day
6 – Control
5.0
4.0
3.0
2.0
1.0
0.0
2 3 8 16 30 65
Day

Treatment Comparison



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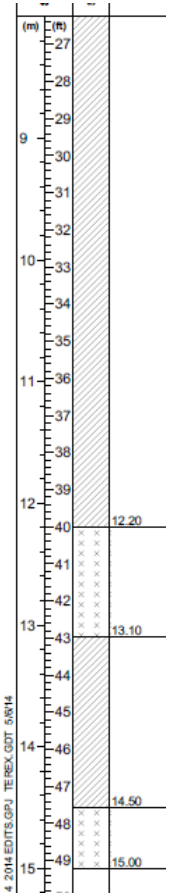
Summary of Degradation Kinetics

Soil Piles		BP1	BP2	BP3	BP4	BP5	BP6
		Air, N	Air, N*&P	Air, N&P	Air, Alfalfa	Air	Control
First Order Kinetics	K (Day^{-1})	0.09	0.09	**0.17**	0.03	NA	NA
	Half life (Day)	5.3	5.4	**3.0**	17.9	NA	NA
Zero Order Kinetics	Rate (mg/kg/Day)	24	26	**42**	17	NA	NA

The highest zero order degradation rate observed in lab was 220 mg/kg/day.


~26,000 m3
~8,000 m3
~20,000 m3

Full Scale Remediation – Year 1



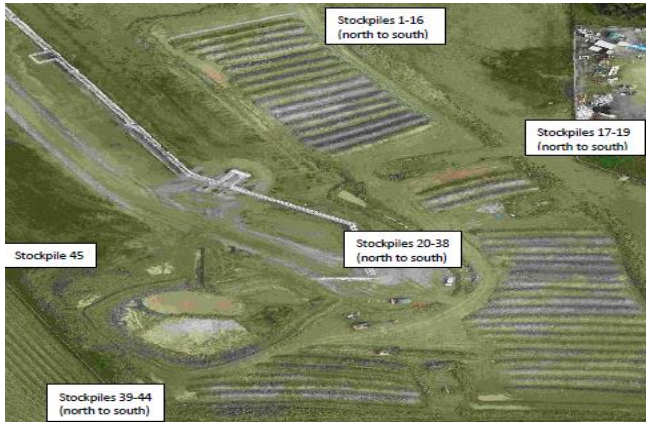
- Former Flare Pit
  - Sulfolane, DIPA, PHCs
  - Soil Texture
    - 23% Sand
    - 40% Silt
    - 37% Clay
  - Sulfolane [0.42 - 8170 mg/kg]
    - Average 364 mg/kg
  - Impacts 2 – 9 mbgs

Full Scale Remediation – Year 1

- Former Flare Pit
  - Excavated June & July 2016

Full Scale Remediation – Year 1

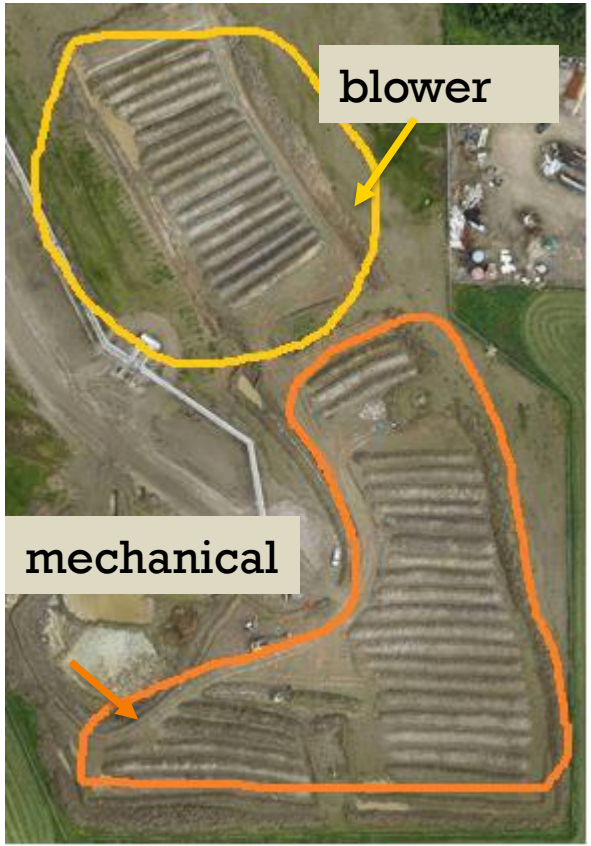
- ~8000 m^3 soil placed in windrows
  - volume assessed with drone
- Per m^3 of soil: 0.1 kg MAP and 0.29 kg urea
  - based on TOC and 100:5:1- C:N:P
- Oxygen
  - blower aeration
  - mechanical aeration



Blower Aeration – Year 1

blower

Full Scale Remediation – Year 1

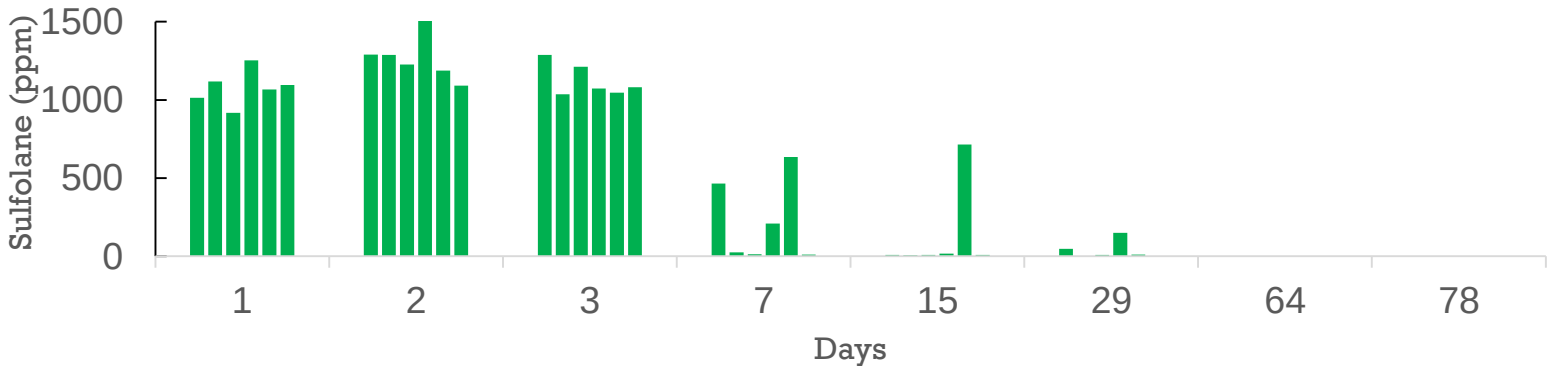


- Mechanical aeration
  - July and August
- Blower aeration
  - 24/7
- Based on half-life from pilot: ~35 days to clean soil with 346 mg/kg of sulfolane.
- 81 days between excavation and confirmatory samples
- 2 of 44 windrows exceeded sulfolane guideline

Ongoing Remediation

Summary

- Aerobic biodegradation of sulfolane was observed both in the lab and in the field.
- The addition of nutrients and forcing aeration enhanced sulfolane degradation (Pilot).
- Supplemented with both "N" and "P" nutrient resulted the best sulfolane degradation rate, the half-life is 3 days (optimal pilot conditions)
- Mechanical and forced aeration were both successful in full scale



References

[1] CCME. 2006. Canadian Environmental Quality Guidelines for Sulfolane:Water and Soil.

[2] Kirk-Othmer. 1999. Encyclopedia of Chemical Technology. Fourth Edition, 1999. John Wiley & Sons.

[3] Shell Chemicals Europe Limited. 1994. Sulfolane Data Sheet, Shell Chemicals UK Ltd.

[4] Luther, S.M., Dudas, M.J. and Fedorak, P.M. 1998. Sorption of sulfolane and diisopropanolamine by soils, clays and aquifer materials. *Journal of contaminant hydrology*, *32*(1), pp.159-176.

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Thank you!

Questions?