#### **REMEDIATION TECHNOLOGIES SYMPOSIUM 2025**

Session: Data Analysis, Shaughnessy Friday October 17th, 9:40am

METHANOL - NOW YOU SEE IT, NOW YOU DON'T

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#### **Brief Background**

#### Anthropogenic sources

- Municipal
  deicing of airplanes at airports
- Agricultural crop stimulant increasing yield and water efficiency
  - solvent for herbicides, biofuel for agricultural machinery
  - feedstock for producing fertilizers and pesticides
- Industrial
  Oil and gas activities (solvent and deicer)
- Residential
  cleaning products, windshield washer, paint thinner
- Natural body 0.5 mg/kg body weight (human); excreted in breath, urine

#### GUIDELINES

- CCME (2017) Soil
  - Coarse Soil 4.6 mg/kg
    Fine Soil 5.6 mg/kg (all land uses)
  - Limiting pathway groundwater check
- EPA (2024)
  - Coarse Soil 11 mg/kg
    Fine Soil 37 mg/kg (all land uses)
  - FAL protection
    DUA protection
  - Groundwater 19 mg/L (coarse/fine, all land uses)

#### Oil and Gas Contaminated Site Work Sources

- Methanol tanks, spheres, lines
  - Well sites, batteries, facilities
  - Photo from Reddit



- Doing hydrocarbon investigations and methanol
  - Terra cores and methanol vials
  - (photo from ALS Global)



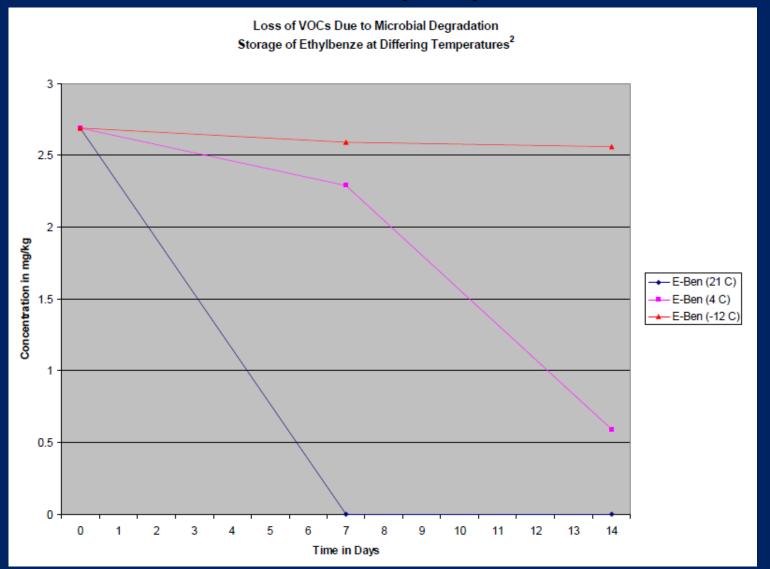
- Laboratory work supporting investigations
  - Common lab solvent



- Background / other
  - Peat soils beneath pads (highly anaerobic, still an anthropogenic impact)
  - Breath

#### Oil and Gas Contaminated Site Work Sources

 Terracore and methanol vial method introduction to contaminated site work was very important (Exova material)

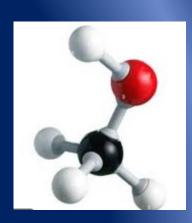


# Physical/Chemical Properties & Environmental Behaviour

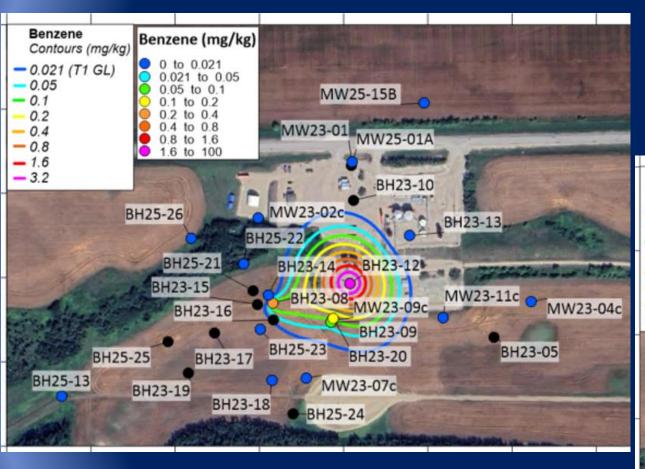
- Comparisons of properties with benzene and F1
  - Unitless Henry's Law (Partitioning from Groundwater or Soil Water to Air)
    - Methanol 0.0002 Benzene 0.225 F1 Aliphatics C6–C8 50
    - Will you detect methanol in soil vapour? Unlikely
    - Will you detect methanol in field screening with a PID or OVA? Unlikely!
  - Organic Carbon Partition Coefficient
    - Methanol 0.27 Benzene 81 g/mL F1 Aliphatics C6–C8 3,981
    - In a soil sample is methanol bound to soil? Only a little bit, mostly in water
    - Will methanol transport further in groundwater than benzene? YES, although half life is important, benzene ~ 1 year, methanol 0.67 year

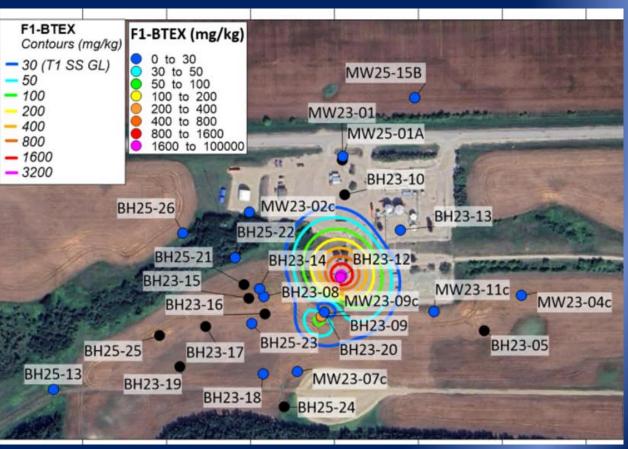
#### TABLE C-6. CHEMICAL PARAMETERS

	Koc (ml/g)	Source	H' dimensionless	Source	Da (cm²/s)	Source	Solubility (mg/L)
Trifluralin	9,682	ORNL (2006)	0.00421	ORNL (2006)	1.49E-02	ORNL (2006)	0.184
Other Organics	·						
Aniline	45	ORNL (2006)	8.26E-05	ORNL (2006)	7.00E-02	ORNL (2006)	36000
Di-n-butyl phthalate	1,460	ORNL (2006)	0.000074	ORNL (2006)	4.38E-02	ORNL (2006)	11.2
Dichlorobenzidine	7,489	ORNL (2006)	2.09E-09	ORNL (2006)	1.94E-02	ORNL (2006)	3.1
Diethanolamine	***1.9	AENV (2010a)	2.20E-12	AENV (2010a)			miscible
Diethylene glycol	0.018	AENV (2010b)	5.30E-09	AENV (2010b)			miscible
Diisopropanolamine	*** 2.2	CCME (2006b)	7.00E-06	CCME (2006b)			870000
Ethylene glycol	0.0072	EC (1999b)	2.50E-06	EC (1999b)	0.108	ORNL (2006)	miscible
Hexachlorobutadiene	994	ORNL (2006)	0.421	ORNL (2006)	5.61E-02	ORNL (2006)	3.2
Methanol	0.27	CCME (2017)	0.0002	CCME (2017)	0.15	CCME (2017)	miscible

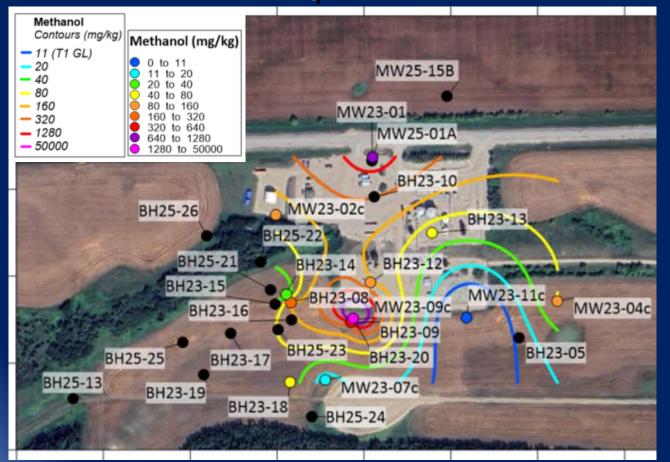


Benzene and F1 impacts in soil somewhat extensive near the facility





- Methanol impacts more extensive than benzene and F1-BTEX as per diagram
- Or are they?
- Perfect split duplicates samples taken
- distinct workstation and sampling equipment from hydrocarbons
- distinct coolers for transport





• Results?

- From heavily contaminated site to barely contaminated site
- Base method is GC-FID
- Also ran via GC-MS - distinct results and impact areas
- This should not happen

Note formaldehyde

Borehole	Sample Date	Depth	Methanol GC/FID	Methanol GC/FID Batch A	Methanol GC/FID Batch B	Methanol GC/MS Batch B	Formaldehyde
		m	mg/kg	mg/kg	mg/kg		mg/kg
SEQG 2024- coarse soil (<3 m)			11				NG
SEQG 2024- coarse soil (<3 m)			11				NG
MW25-01A	22-Mar-25	9		43.2	0.25	9.0	0.005
	22-Mar-25	15		51.2	0.25	2.9	5.6
	22-Mar-25	18		84	4.9	7.4	185
	17-Mar-25	6		0.25	0.25	5.1	0.005
BH25-13	17-Mar-25	7		0.25	0.25	13.1	286
	18-Mar-25	24		1.1	0.25	4.0	196
	13-Mar-25	3		52	0.25	7.3	2.11
	13-Mar-25	5.5		123	11.1	9.6	6.05
	13-Mar-25	9		438	0.25	1.2	9.73
	13-Mar-25	12		432	7.9	30.5	1.2
	13-Mar-25	15		657	0.25	26.3	0.19
	14-Mar-25	18		26.6	0.25	6.3	285
	14-Mar-25	40		32.2	0.25	8.6	4.8
	19-Mar-25	9		18.7	0.25	3.2	252
	19-Mar-25	12		15.4	0.25	13.2	121
	19-Mar-25	9		197	0.25	8.4	163
	19-Mar-25	12		16.8	0.25	7.0	207
	19-Mar-25	21		9.9	0.25	2.6	204
	23-Mar-25	36		3.1	11.3	7.5	212

- Second site example of four in total
- Soil samples submitted at different time intervals March and April results beyond hold times by up to two months
- Some variability between methods, contaminated to not contaminated, but samples beyond hold times are not considered valid for contaminated sites
- Persistence in samples demonstrated

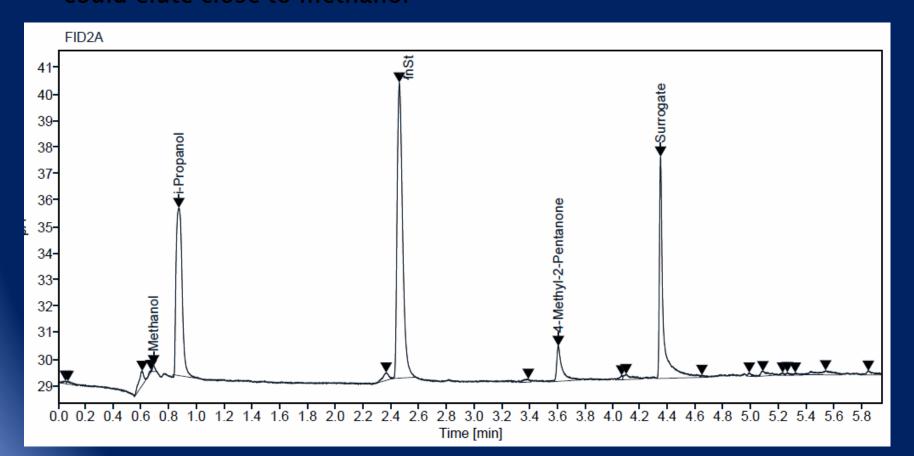
Methanol Analysis on February 2025				Methanol Analysis	Methanol Analysis on April 2025		
BH ID	Depth	EEI Field Screening Results	Lab 1 (GC-FID)	Lab 2 (GC- MS)	Lab 1 (GC-FID)	Lab 1 (GC-FID)	Lab 2 (GC-MS)
		mg/L	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Albei	Alberta Tier 1 Guideline						
BH25-05	0.5		80		10	17.9	6.4
BH25-05	3	0.7	<1.0	0.6			-
BH25-05	6	-0.1	1.2	0.6			-
BH25-05	9	-0.1	18		16	9.1	33.2
BH25-05	12		60		32	27.2	25.6
BH25-05	15		<1.0	0.6			-
BH25-05	18		<1.0	0.6			
BH25-06	0.5		180		46	56.4	40.1

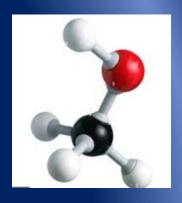
- Second site two locations were redrilled in exact same location
- Methanol is highly soluble, doesn't stick to soil, impacts should be quite diffuse and similar during redrills (would be different if binds strongly to soil leading to a greater risk of 'hot spots' for less mobile contaminants
- In 2023, concentrations were > 100 mg/kg
- In 2025, concentrations were below Tier 1 guidelines (11 mg/kg for coarse)
- To further complicate matters, all groundwater data from same impacted water bearing zone were all non-detect
- Observed at two other sites impacts in soil, not in groundwater, that doesn't work for a substance like methanol



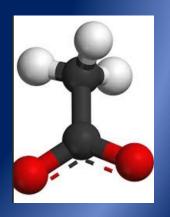
#### **Methanol Conundrum**

- Dig into literature and chemist's blogs
- Numerous reports of people trying to resolve issue of some unknown chemical co-eluting with methanol
  - Much of this literature from the biological field, not soil and groundwater
  - Some published studies suggest acetate, acetone, formaldehyde, ethanol could elute close to methanol









- Possibility of using PID but with non-standard eV bulb
  - Standard eV bulb of 10.6 will not detect methanol
  - Tried this in the field with 11.7 eV bulb should be able to catch methanol, unsuccessful
- Develop a field-workable spectrophotometric technique
  - Methods were mostly used in biological and alcoholic beverage producing industries
  - Multiple methods painstakingly tested
  - Many were not going to be effective in the field
  - Found one method that was effective in the field and wouldn't necessarily require an expensive portable spectrophotometer – could just provide a Yes/No answer for delineation

- EEI Field Screening Method modified published method and selection of equipment optimal for field use
- #1 Extract permeate from soil sample processed through a mudpress (easy if GW, step not needed)
- #2 combine permeate with enzyme cascade A and heat to 37 °C – optimal for enzyme activity



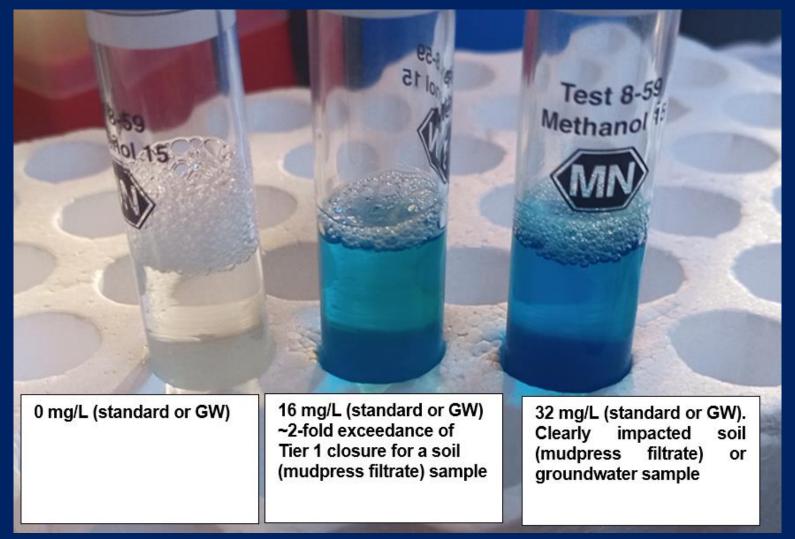


- #3 combine permeate with enzyme cascade A and heat to 37 °C – optimal for enzyme activity
  - Accuracy of reagent addition is important use calibrated pipettes, work fine in the field
- #4&5 more enzyme steps

 #6 - spectrophotometer such as Hach DR3900 reading - can get quantitative output of above or below Tier 1 guidelines (need to develop standard curve)



 #7 – Take your reading – quantitative output, BUT, also get a chromophore and can look at a simple Blue/Not Blue response for a hit/no hit



#### **Take Home Points**

- If you suspect methanol impacts at a site and need to collect samples,
  - Distinct work station
  - Distinct soil knives.
  - Distinct coolers.
  - Don't breathe too much on your samples!
  - Consider a field screening technique
  - Collect split duplicate samples and send to different labs
  - Consider running additional analytical techniques such as GC-MS or derivatization

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- Also analyze for formaldehyde
  - This is a one liner requirement in EPA (2024) Tier 1 doc
  - Guideline is very low compared compared to methanol, but is not listed in the Tier 1 document – check the Government of Alberta 2010 Methanol Document



Fin.

**Questions?**