CREATING AND DELIVERING BETTER SOLUTIONS

Sulfolane Impacted Soil and Groundwater Treatability Study

Vladimir Agatonovic, P.Geol. - EBA

Elena Vaisman, P.Chem. - U of C

EBA ENGINEERING CONSULTANTS LTD.

Outline

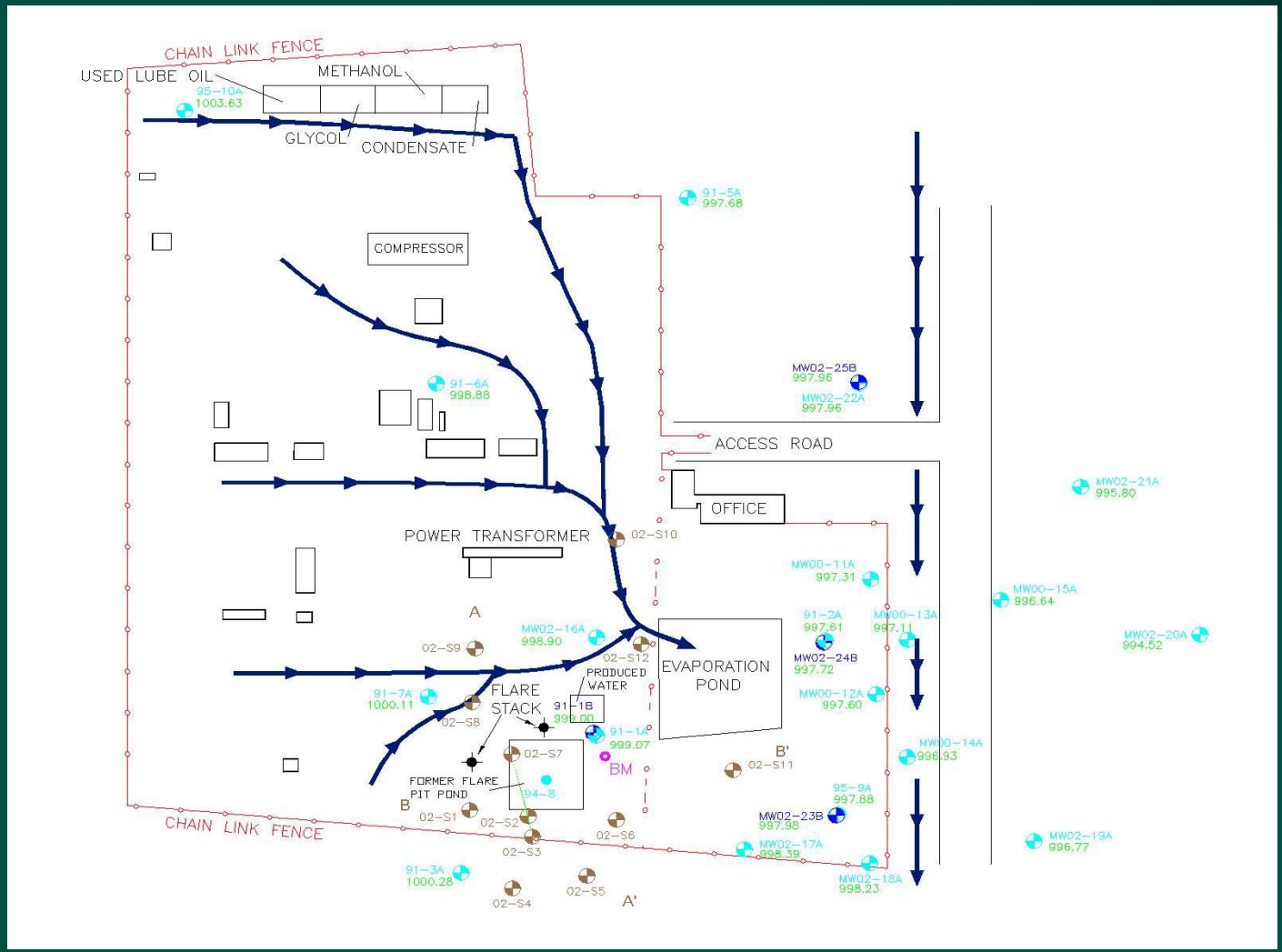
1. Introduction
2. Soil and Groundwater Quality Monitoring Results
3. Sulfolane – Sulfinol®
4. Laboratory Treatability Trial
5. Treatability Trial Results
6. Conclusions

Introduction

- Active Sour Gas Plants
- Gas Sweetening
- Gas Dehydration
- Treatment

Products : Condensate and Natural Gas

Site Plan


CHAIN LINK FENCE
USED LUBE OIL
METHANOL
95-10A
1003.63
GLYCOL
CONDENSATE
91-5A
997.68
COMPRESSOR
91-6A
998.88
MW02-25B
997.96
MW02-22A
997.96
ACCESS ROAD
MW02-21A
995.80
OFFICE
POWER TRANSFORMER
02-S10
MW00-11A
997.31
MW00-15A
996.64
A
MW02-16A
998.90
02-S9
02-S12
PRODUCED WATER
EVAPORATION POND
91-2A
997.61
MW00-13A
997.11
MW02-20A
994.52
MW02-24B
997.72
91-7A
1000.11
FLARE STACK
02-S8
91-1B
996.00
MW00-12A
997.60
91-1A
999.07
02-S7
BM
B'
02-S11
MW00-14A
996.93
FORMER FLARE PIT POND
94-8
95-9A
997.68
B
02-S1
02-S2
MW02-23B
997.98
02-S6
MW02-17A
998.39
MW02-19A
996.77
CHAIN LINK FENCE
02-S3
91-3A
1000.28
MW02-18A
998.23
02-S4
02-S5
A'

Physical Settings

Topography and Drainage:

- Porcupine Hills (1,600 masl).

Geology:

- Fill/gravel 0.5 m.
- Silty Clay Till – 2.5 m to 9.2 m, sand lenses.

Hydrogeology:

- Shallow water table at 1.7 m to 3.4 m.
- Groundwater flows towards east.
- Bulk hydraulic conductivity 1.02 E-5 cm/s to 1.41E-7 cm/s.

Soil and Groundwater Quality

Under the Alberta Environment Approval to Operate:

- Soil Management Program – Alberta Environment Soil Monitoring Directive (1996) – every five years.
- Groundwater Quality Monitoring Program initiated in 1991 – annually.

Soil

- Elevated concentrations of petroleum hydrocarbons (PHCs) detected – benzene, toluene, ethylbenzene, and xylenes (BTEX) and F_1, F_2, and F_3.
- Elevated chloride concentrations detected.

Groundwater

Historically elevated concentrations of:

- PHC – BTEX and F_1 and F_2.
- Dissolved Organic Carbon (DOC).
- Chlorides.
- Sulphate (naturally occurring).
- Nitrites and Nitrates.
- Total Dissolved Solids (TDS).

The DOC and PHC concentrations do not correlate.

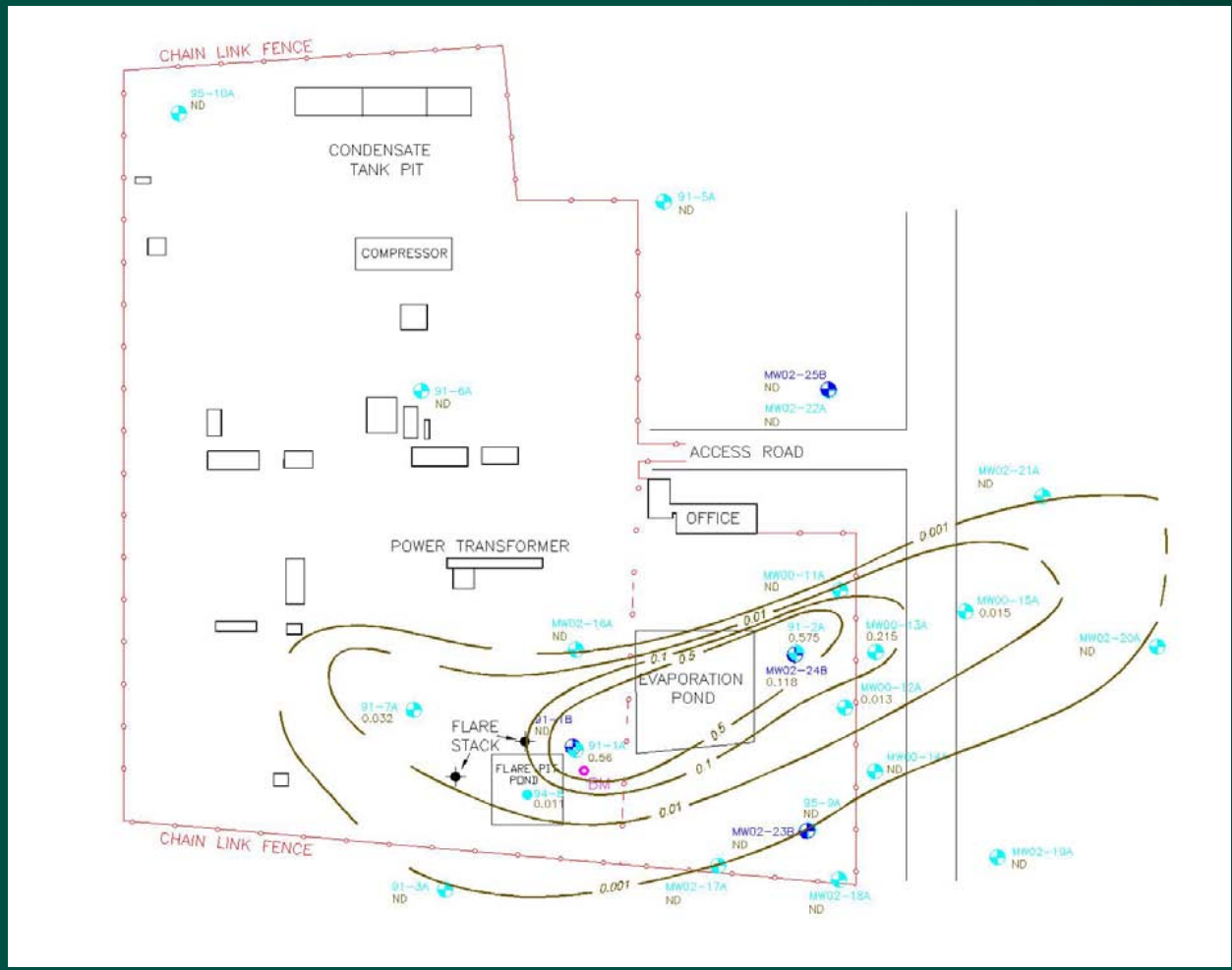
Assessment

- Resolution of elevated concentrations of DOC initiated the plant site product inventory review.
- Product review detected that, in 1992, existing amine process replaced Sulfinol process.
- Sulfinol process was mixture of Sulfinol® and DIPA.
- In 2000, Sulfolane analyses were added to the regular annual groundwater quality monitoring.

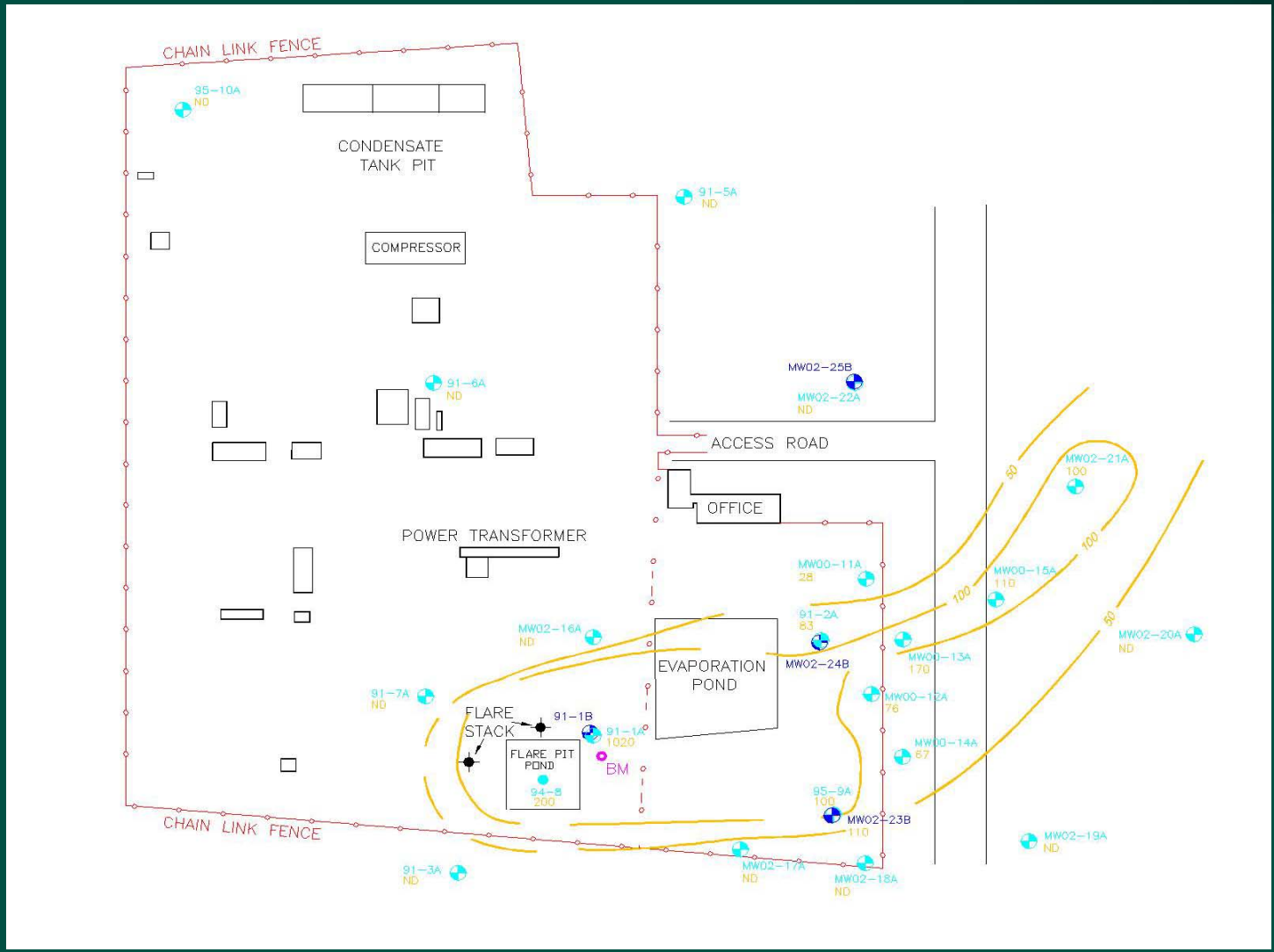
Assessment continued...

- Half the monitoring wells returned concentrations of sulfolane greater than background concentrations.
- In 2002, soil and groundwater with elevated concentrations of PHC and Sulfolane were partially delineated in the vicinity of the former flare pit and east of the Evaporation Pond.
- Sulfolane was detected in all collected soil samples in the vicinity of former flare pit.

Benzene Concentration Distribution Map 2002



Sulfolane Concentration Distribution Map 2002

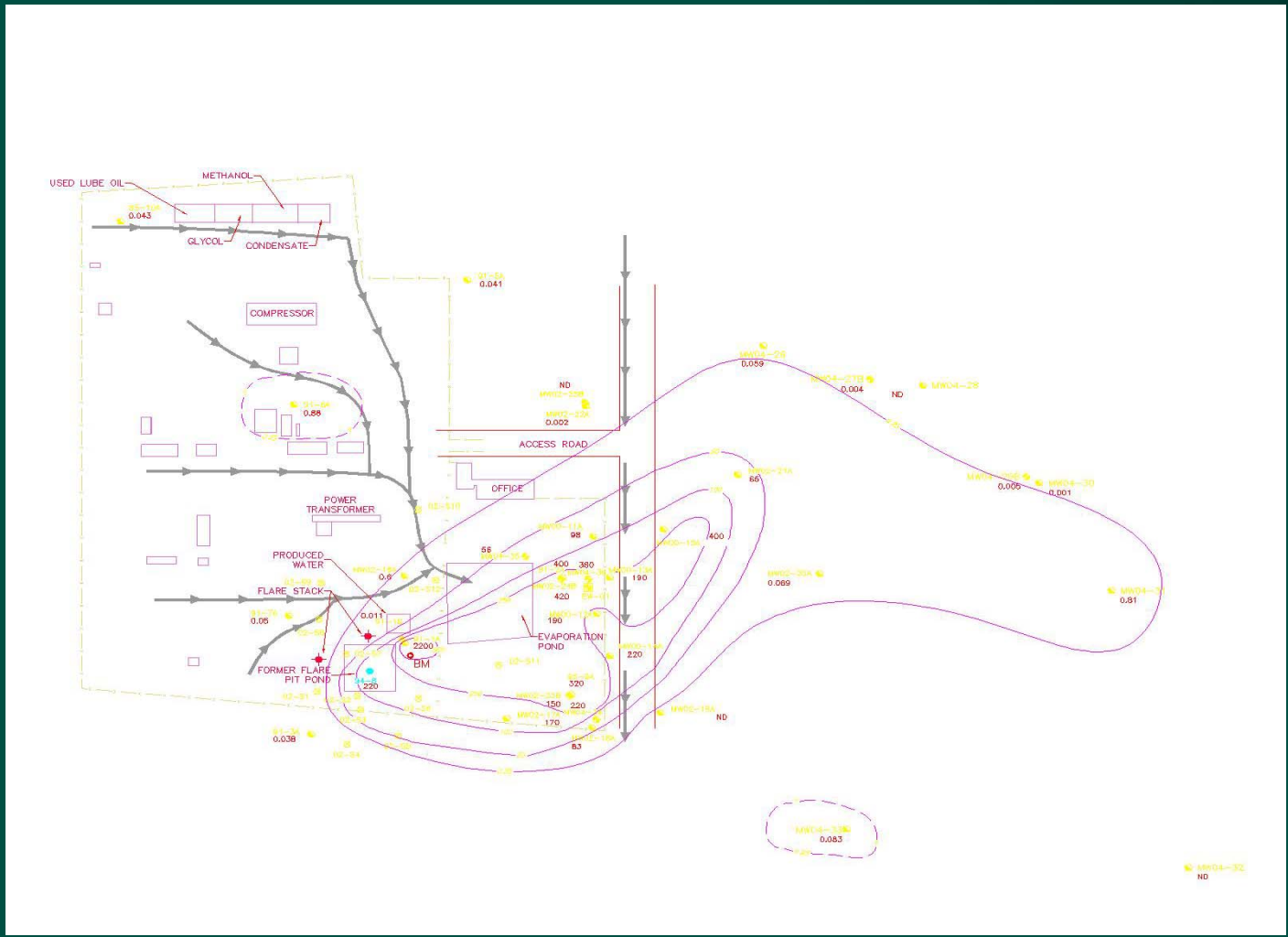


Assessment continued...

- In 2004, additional groundwater quality monitoring wells were installed to further delineate the groundwater with concentrations of sulfolane greater than background concentrations.

- One groundwater extraction well and one observation well were installed to determine hydrogeological properties of a shallow water-bearing zone.

Sulfolane Concentration Distribution Map 2004



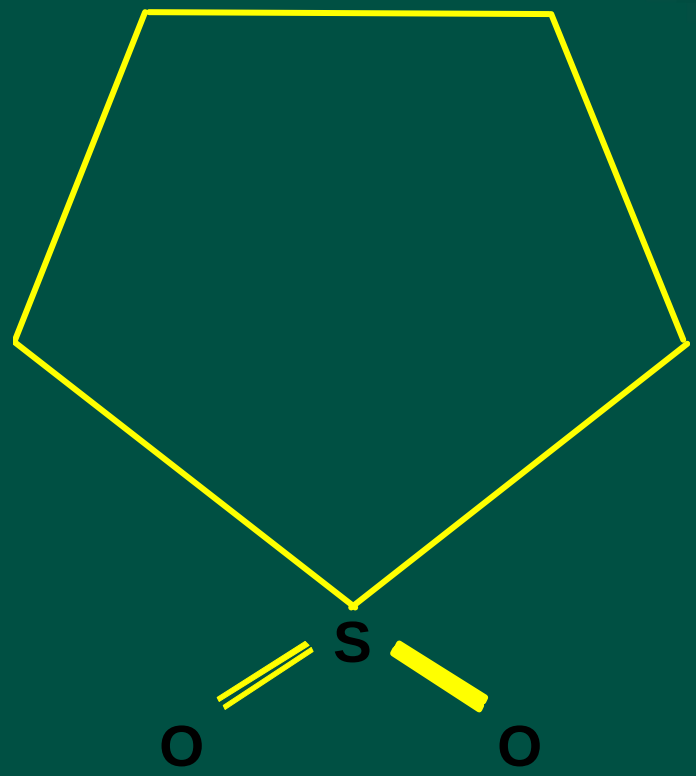
Assessment continued…

- In 2005, the Canadian Council of Ministers of the Environment (CCME) and Alberta Environment adopted the Canadian Association of Petroleum Producers (CAPP) guidelines for sulfolane: in soil (2.3 mg/kg) and groundwater (0.26 mg/L).

Sulfolane

- Sulfolane ($C_4H_8O_2S$) – common trade name for an organic chemical tetrahydrothioprene 1,1 -- dioxide, colourless, very polar, highly soluble in water, and extremely stable.
- Sulfinol® – solvent developed by Shell in early 1960s for extracting aromatics from hydrocarbons; second major application is in the process of 'sweetening' natural gas.
- Sulfinol® is slightly heavier than water (1,060 g/L).

Sulfolane



Laboratory Trials

Soil:

- Bio-treatability.

Groundwater:

- Bio-treatability.
- Chemical Oxidation (Mineralization).

Soil Trial

- Five soil samples collected.
- Sulfolane concentrations ranged from 350 mg/kg to 3,400 mg/kg.
- Two samples with highest concentrations of sulfolane were homogenized – 1,400 mg/kg.
- Samples for analytical analyses collected on days 0, 15, 30, 45, 63, and 78.

Soil Trial

7 Bio-reactors:

- Control – no additives.
- Sterile.
- Condensate impacted.
- Ammonia nitrogen (83 mg/kg).
- Ammonia nitrogen (232 mg/kg).
- Ammonia phosphate (83 mg/kg).
- Ammonia phosphate (232 mg/kg).

Oxygen concentrations maintained >10%.

Groundwater Trials

Bio-treatment:

- Aeration (GLR micro-bubbles®) and nutrient amendment.

Chemical Oxidation:

- H_2O_2.
- UV radiation.
- Combination of both of the methods.

Groundwater Trials

Aeration Trial:

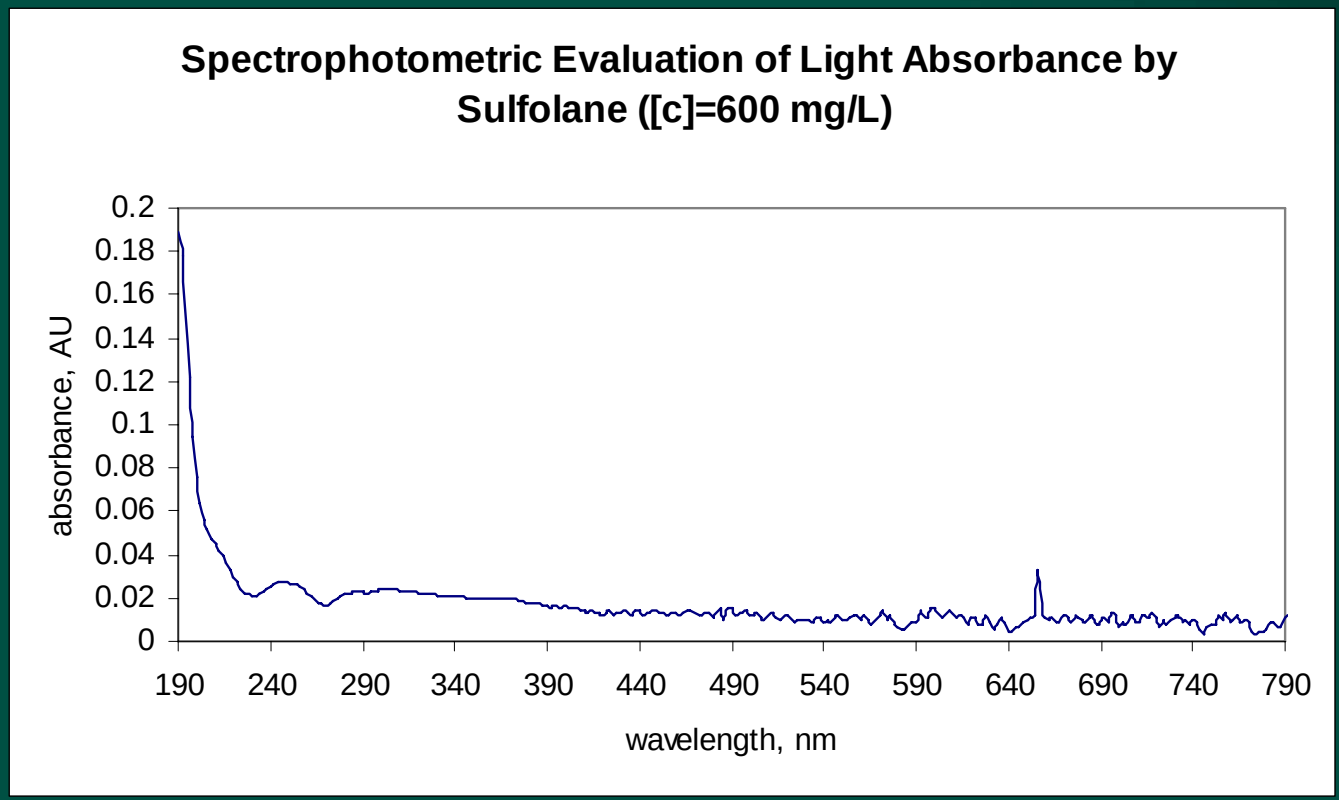
- 24–hour trial.
- Continuous aeration - O_2>7.7 mg/L.
- Nutrient - Ammonia phosphate.
- Samples collected at 0, 8, and 24 hours.

Groundwater Trials

Chemical Oxidation:

- 7-day trial.
- H_2O_2 concentration = 10 g/200 ml.
- UV radiation – 7 W UV bulb.
- $C_4H_8O_2S + 13H_2O_2 = 4CO_2 + H_2SO_2 + 16H_2O$.

Groundwater Trials



Results - Soil

Days	Control	Sterile	Ammonia 83 mg/kg	Nitrate 232 mg/kg	Ammonia 83 mg/kg	Phosphate 232 mg/kg
0	1,300	1,400	1,700	1,700	1,400	1,400
15	1,700	1,600	1,500	1,500	1,500	1,400
78	1,100	1,200	860	760	2.1	2.9

Results - Groundwater

Sample Description	Sulfolane (mg/L)	Removal Ratio (%)	Time (hours)
Blank	1,200 (1,800)		
Chemical oxidation	950	79	
UV Irradiated sample	1,000	83	
Chem. Oxidation + UV	13	99	168
Aeration + Nutrients	490	73	24

Results - Groundwater

Energy consumed by the samples was calculated using the following formula:

- $P = E_{photon} * I/S = 0.2$ m J/sec cm^2

Where:

- E_{photon} – energy of a single photon
- I – intensity of the photon flux in the system, and
- S – surface of irradiated vessel

Results - Groundwater

[Using the sun as source of UV radiation]

Based on commonly used potassium ferrioxalate system irradiation value, the estimated solar energy is:

$$E_{solar} = 3.5 \text{ mW/cm}^2$$

Therefore, a week of UV radiation in the lab will be equal to ***10 hours*** of sun exposure.

Conclusions

Soil:

- Sulfolane biodegradation is possible (bacteria require longer time to adjust to environment).
- After 78 days of incubation with ammonia phosphate fertilizer, the soil sample becomes non-toxic to Microtox®.
- Full sulfolane biodegradation occurred with an ammonium phosphate fertilizer.
- No obvious production of toxic by-products.

Conclusions

Groundwater:

- The sulfolane degradation occurred under the chemo-physical and biodegradation (aeration) processes.
- The chemical oxidation and UV irradiation trial achieved 95% removal of sulfolane after one week of treatment.
- The biodegradation treatment achieved 73% of sulfolane removal after 24 hours.

Conclusions

Chemical Oxidation:

- If field scale treatment utilizes sunlight, 10 hours of the daily light will be required.

Note: UV reactor should be considered as more effective method

Biodegradation:

- Field scale treatment would require a water treatment and storage facility.

Acknowledgements

Enviro-Test Laboratories Ltd.
University of Calgary, TIPML
Hydroqual Laboratories Ltd.
Ecoterra Solutions Inc.

Jeff Wilson, Ph. D., P. Biol.. Microbial Answers Inc.
Kathryn Bessie, P. Ag., EBA Engineering Consultants Ltd.

CREATING AND DELIVERING BETTER SOLUTIONS

THANK YOU

EBA ENGINEERING
CONSULTANTS LTD.