# SULFOLANE IMPACTED SOIL AND GROUNDWATER TREATABILITY STUDY

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## ABSTRACT

During the long-term groundwater quality monitoring, elevated concentrations of dissolved organic carbon (DOC) were reported at two of the gas processing plants located in Alberta. The concentrations of petroleum hydrocarbons (PHC) were several orders of magnitude less than the DOC concentrations, or were not detected. Glycols and amines were included in the analytical schedule to observe if the analytical results of any of these could be correlated to the DOC concentrations detected. They returned non-detectable concentrations. A plant site historical product inventory was conducted to determine if the presence of any other products at the site could cause elevated DOC concentrations. The result of the review detected that, in 1992, existing amine process replaced the Sulfinol® process. The Sulfinol® gas sweetening method involves a combination of chemical and physical processes. It also utilizes diisopropanolamine (DIPA) as a chemical solvent. DIPA interacts with sour gas via its central nitrogen atom.

In 2000, sulfolane analyses were added to the existing groundwater quality analytical schedule to address the results of the historical plant operations. More than a half of the groundwater monitoring wells reported concentrations of sulfolane above the background concentrations. There were no guidelines for the maximum allowable concentrations (MAC) of sulfolane in soil and groundwater at that time. In 2004, EBA, conducted several laboratory treatments trials for the remediation of the soils and groundwater impacted by sulfolane in preparation for the site remediation. In 2005, Canadian Council of ministers of Environment (CCME), and Alberta Environment (AENV) adopted the Canadian Association of Petroleum Producers (CAPP) guidelines.

The soil treatability study investigated potential for bio-cell or bioreactor option. The bio-treatability trial conducted at the Hydroqual Laboratories showed that significant decrease in the sulfolane concentrations in soil occurred after 78 days of treatment.

The groundwater treatability trials were conducted at TIPML and the Ecoterra Solutions Inc. facilities. The TIPML conducted three trial utilizing mineralization, UV treatment and combination of both of the methods. The combination of mineralization and UV irradiation achieved 95% sulfolane removal ratio. Ecoterra conducted an aeration trial utilizing micro bubbles technology (GLR) in conjunction with slurry mixing and nutrient amendments and achieved 73% of sulfolane removal ratio.

## INTRODUCTION

In the last 20 years, soil and groundwater quality assessments, monitoring and remediation programs were conducted on numerous oil and gas facilities in Alberta. During that time, several thousands of analytical results were reviewed and compared against regulatory guidelines and standards. The most common compounds for compliance monitoring are petroleum hydrocarbons (PHC) and salts (produced formation water). The PHC with established guidelines for benzene, toluene, ethylbenzene and xylenes (BTEX) and four product group fractions. Chloride concentration is the best indicator parameter to monitor formation water impacts. In addition, there are a few other general indicator parameters, which are regularly monitored to determine if other site-specific parameters should be included in the analytical schedule. One of these is Dissolved Organic Carbon (DOC), which is an indicator parameter of the presence of hydrocarbons in soil and/or groundwater.

During the long-term monitoring, elevated concentrations of DOC were reported at two of the gas plants located in Alberta where the soil and groundwater quality was monitored for over one decade. The concentrations of PHC were several orders of magnitude lower than DOC concentrations or not detected. Glycols and amines were included in the analytical schedule to observe if the analytical results of these compounds could be correlated to the DOC concentrations, but returned non-detectable concentrations. The plant site historical product inventory review was conducted to determine if the presence of other products at the site could cause elevated DOC concentrations. The result of the review detected that, in 1992, existing amine process replaced the Sulfinol® process. The Sulfinol® gas sweetening method involves a combination of chemical and physical processes. It also utilizes diisopropanolamine (DIPA) as a chemical solvent. DIPA interacts with sour gas components via its central nitrogen atom.

In 2000, sulfolane was added to the existing analytical schedule to address the results of the historical plant operations. More than a half of the monitoring wells reported concentrations of sulfolane above the background concentrations. There were no guidelines for the maximum allowable concentrations (MAC) of sulfolane in soil or groundwater at that time.

## BACKGROUND

The purpose of the annual groundwater quality monitoring program is to determine if the plant activities are affecting the local groundwater quality. Since the installation of the initial groundwater monitoring well network (1991), groundwater samples have been collected and analyzed for the following compounds: Chloride, Nitrite + Nitrate as Nitrogen ($NO_2$ + $NO_3$ as N), Dissolved Organic Carbon (DOC), Dissolved Kjeldahl Nitrogen (DKN), Total Dissolved Solids (TDS), Total Petroleum Hydrocarbons (TPH), and Benzene, Toluene, Ethylbenzene and Xylenes (BTEX). For the last few years, petroleum hydrocarbons (PHC) have been detected in the vicinity of the former flare pit and east of the evaporation pond. Also, during the fall 2001 groundwater sampling event, elevated concentrations of sulfolane were detected in the same area.

In 2002, additional groundwater investigation programs were conducted in an attempt to delineate aerial extent of the groundwater with elevated concentrations of sulfolane. Subsequently, 11 groundwater monitoring wells were installed east of the former flare pit at the plant site and off the plant site on the agricultural land (Figure 1).

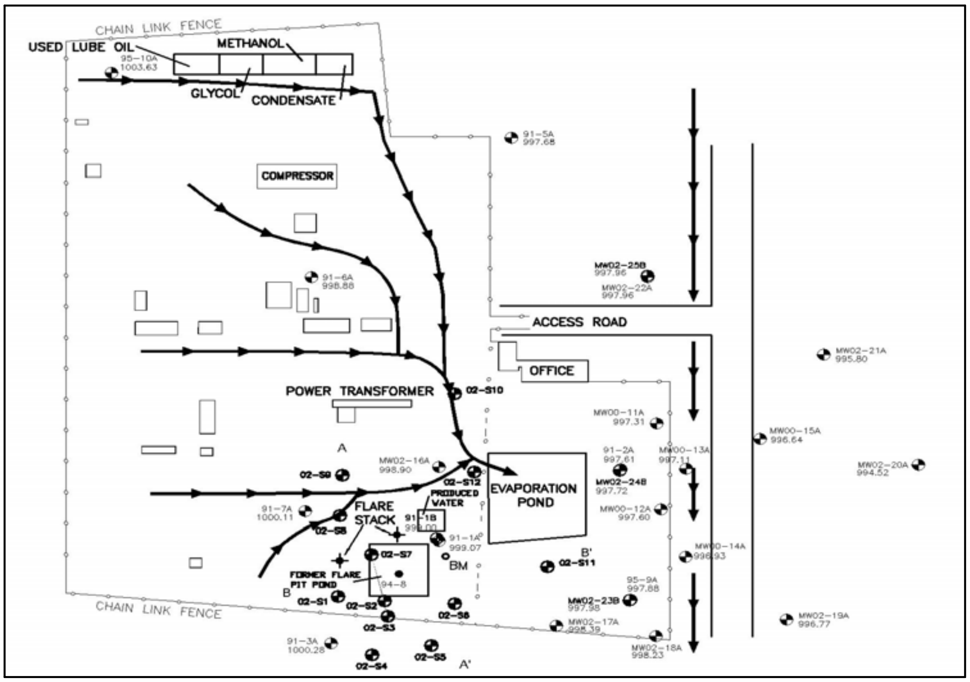


Figure 1 Plant Site Groundwater Monitoring Network

In addition to the groundwater investigation, in 2003, a detailed soil quality assessment program was conducted to determine the volume of soil with elevated concentrations of sulfolane and PHC, considered a secondary source of impact, in the vicinity of former flare pit area. A total of 54 soil samples were collected from 11 locations. It was estimated that approximately 9,600 $m^3$ of soil had concentrations of sulfolane greater than 500 mg/kg. The secondary source reduction was recommended.

In 2004, the groundwater quality investigation continued further east off the plant site. Additional 5 shallow and 3 deep wells were installed to delineate the aerial extent of the groundwater with concentrations of sulfolane greater than the background concentration, assumed to be 0.5 mg/L. Two of the 2004 monitoring wells returned concentrations of sulfolane greater than the assumed background concentration.

The plant site groundwater quality monitoring network is presented on Figure 1.

## GEOLOGY AND HYDROGEOLOGY

The regional study area was defined as the area lying within a 5 km radius of the plant site. Information on regional bedrock and surficial geology and hydrogeology was compiled from various public sources. Information on regional groundwater use and quality was obtained from the Alberta Environment Water Well Drilling Report database.

### Regional Geology

Upper Cretaceous continental deposits of the St. Mary River and Bearpaw Formations underlie the regional study area. These deposits comprise of sandstone, shale, siltstone, mudstone, ironstone beds, and thin coal beds.

Surficial geology in the regional study area includes Quaternary sand and gravel, and other unconsolidated sediments (clay, sand, silt).

### Regional Hydrogeology

A total of 29 shallow domestic water supply wells are reportedly located within a 3 km radius of the plant site. These water wells meet industrial, domestic and livestock watering needs. The total depth of the domestic water wells range from 9 to 87 m, and their production rates range from 9 to 182 L/min. The static water levels appear to be below 30 m for the majority of the wells. Based on static water levels, these wells draw water from sources that are much deeper than the shallow water table at the plant site.

The closest shallow off-site domestic water well is located approximately 1.2 km east of the plant site.

The local groundwater quality, by potable standards, is poor with an average total dissolved solids content (TDS) of about 2,500 mg/L, ranging from <1,000 mg/L to 5,000 mg/L. The hydrochemical character is also quite variable with a significant sulphate component ranging from 131 mg/L to 1,449 mg/L and chloride concentrations ranging from 18 mg/L to 207 mg/L.

### Topography and Drainage

The investigated area lies on the western edge of the Interior Plains. The highest elevation of the area is more than 1,600 m above sea level (m.a.s.l.) and is located in the southwest corner of the Porcupine Hills. The lowest point, where the Bow River leaves the area to the southeast, is 732 m above sea level (m.a.s.l.). The area has a variety of geomorphological structures, such as canyon-like river valleys, buried river valleys, smooth or pitted round moraine surfaces combined with eskers, gravel flats and level lacustrine plains. This area is a part of the South Saskatchewan River drainage basin.

There are a number of lakes in the area. Some among them (McGregor Lake, Travers Reservoir and Little Bow) are man-made. Most of the other lakes and sloughs in the area are of glacial origin.

### Site Geology and Drainage

The maximum depth reached by boreholes drilled on the site was 11.0 m below ground surface (bgs). Geological sediments encountered beneath the site consist mainly of silty clay till with some sand lenses. The clay till is highly heterogeneous.

The plant site topography is gently sloped towards east (4%). The plans site surface runoff water is collected and stored at the plant site.

### Plant Site Hydrogeology

The thickness of Quaternary deposits in the plant site area, as documented by Alberta Environment water well records, is estimated to be in the order of 30 m. The dominant surficial deposit consists of clay tills with silty sand lenses and layers. The clay till bulk hydraulic conductivity, based on slug test results, range from $1.02 \times 10^{-5}$ to $1.41 \times 10^{-7}$ cm/s.

The water table lies from 0.88 to 2.96 m (bgs) and exhibits seasonal fluctuations with elevations generally lower in the autumn.

## GROUNDWATER QUALITY

The plant site groundwater quality has been monitored for the last fifteen years. The plant site groundwater quality was assessed by comparing the analytical results from the groundwater monitoring network to the assumed background concentrations and Canadian Council of ministers of Environment (CCME) 2003 Canadian Drinking Water Quality Guidelines (CDWQG).

The time series chat of Benzene and Sulfolane concentrations are presented on Figures 2 and 3, respectively.

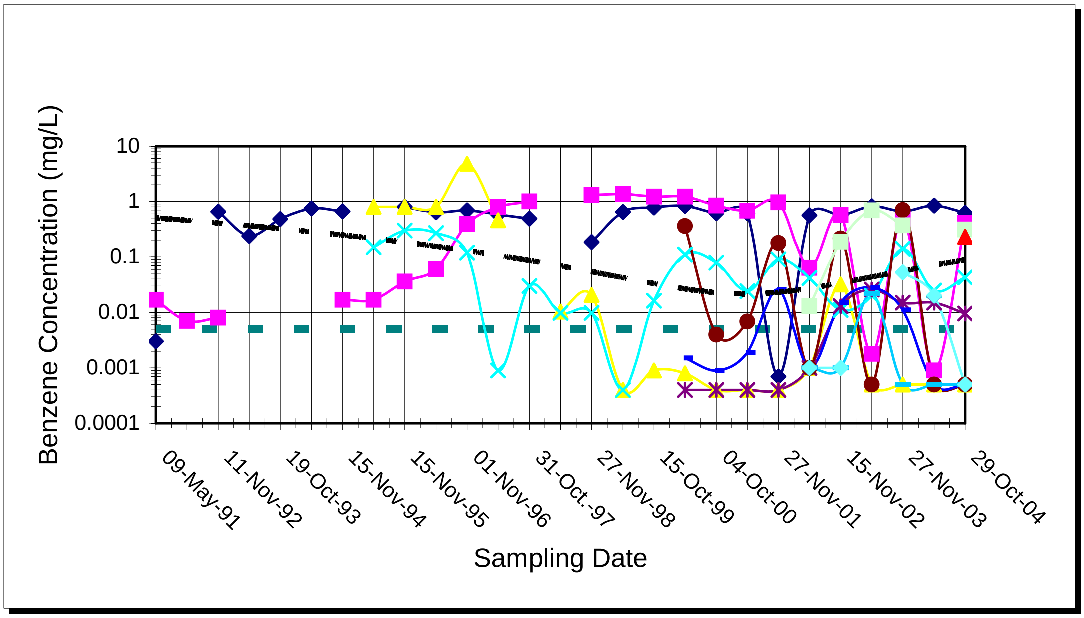


Figure 2. Time Series Plot of Benzene Concentration

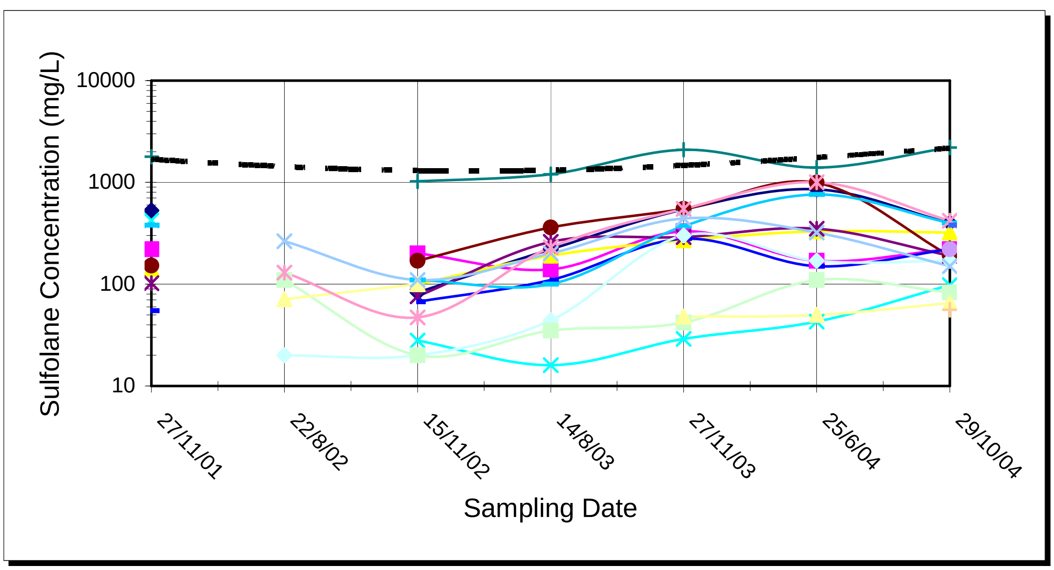


Figure 3. Time Series plot of Benzene Concentration

Figure 4 presents the sulfolane concentration distribution map for autumn of 2004.

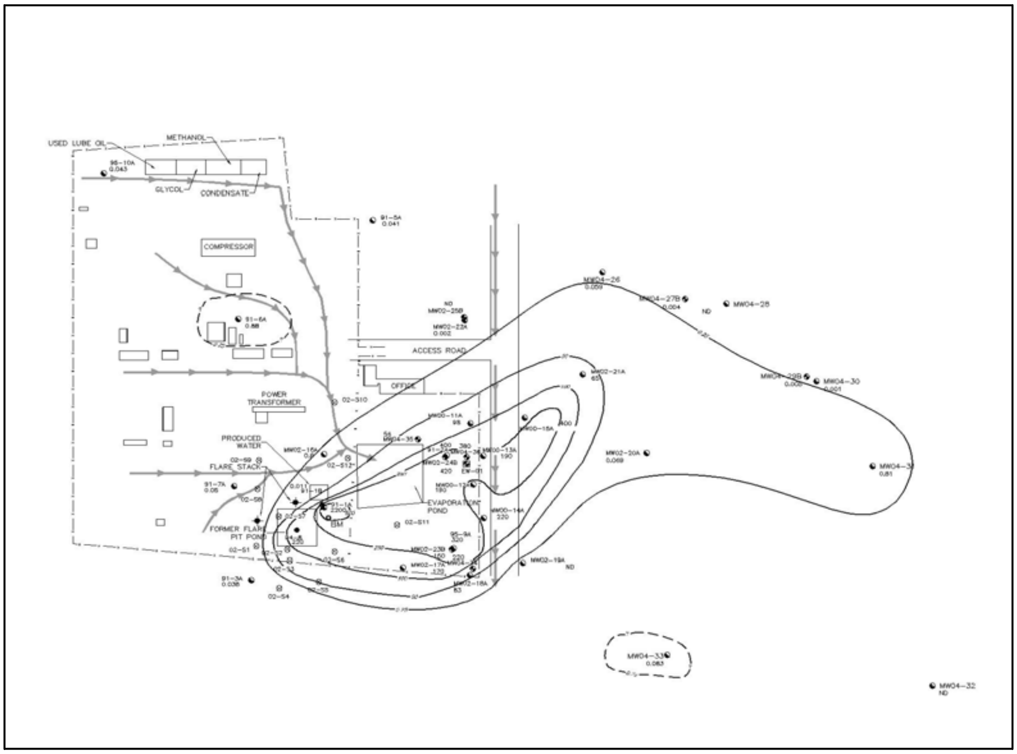


Figure 4 Sulfolane Concentration Distribution Map

Based on these result the sulfolane impacted soil and groundwater laboratory trials have been scheduled.

## SULFOLANE DEGRADATION TRIAL

Sulfolane ($C_4H_8O_2S$) is common trade name for an organic chemical – tetrahydrothiophene 1,1-dioxide which is colourless, very polar, highly water soluble and extremely (chemically and thermally) stable compound. It was used in variety of industrial purposes, principally developed by Shell in early 1960's for extracting aromatics from hydrocarbon mixtures such as petroleum naphtha, pyrolisys gasoline or coke-oven light oil [1,2]. Its second major application is in the process of "sweetening" of natural gas streams such as, Sulfinol® and Sulfreen® processes, where it acts as the physical solvent for removal of sour components (acid gases) [3].

Sulfolane is known to have leached into groundwater through spills, landfills and unlined surface storage ponds. It was determined that Sulfolane mobility in soil is very high [4,5]. Thus, due to sulfolane high water solubility, stability and high mobility in soil and groundwater, poses a risk for an off-site impacts.

In 2005 CCME and AENV adopted CAPP guidelines for the maximum allowable concentration of sulfolane in soil and groundwater 2.3 mg/kg and 0.26 mg/L, respectively.

The sulfolane degradation trials for soil and groundwater were conducted utilizing chemical oxidation and aerobic bio-degradation.

## SOIL TREATABILITY TRIAL

The soil treatability trial was conducted at Hydroqual Labs. The soil treatability trial investigated a potential for bio-cell or bioreactor application. Five samples of soil from suspected sulfolane impacted area of the former flare pit were submitted for the analytical analyses. The sulfolane concentrations in those samples varied from 450 mg/kg to 3400 mg/kg. The two samples with the highest concentrations of sulfolane (moist sandy clay) containing a heterogeneous mixture of black and brown colour soil and a strong hydrocarbon and sweet odour were homogenized and prepared for treatability trial.

The initial treatability trial design incorporated seven treatments to evaluate the effectiveness of two organic fertilize amendments on enhancing the biodegradation of sulfolane and available hydrocarbons. The seven treatments included: untreated control, sterile control, condensate contaminated soil, 83 mg/kg Nitrogen based fertilizer (35:0:0), 232 mg/kg Nitrogen based fertilizer (35:0:0), 83 mg/kg Nitrogen Phosphate based fertilizer (28:14:14), and 232 mg/kg Nitrogen Phosphate based fertilizer (28:14:14). In addition, media toxicity analyses were conducted. The tests were conducted in 4-L polycarbonate bioreactors fitted with air-tight lids and oxygen sensors.

During the tests the oxygen concentrations were maintained at >10%. The soils in bioreactors were mixed weekly to provide proper soil aeration. The soil samples from the bioreactors were collected at 0, 15, 30, 45, and 78 day of the treatment. The soil samples were analyzed for CCME BTEX and F1 +F2, Nutrients, TKN, Available Ammonia Nitrogen, and Sulfolane.

## GROUNDWATER TREATABILITY TRIALS

The groundwater treatability trails were conducted at University of Calgary, Tomographic Imaging and Porous Media laboratory (TIPML) and at the Ecoterra Solutions Inc. facility.

The TIPML conducted three trials: sulfolane mineralization, UV irradiation and combination of both of the methods. Ecoterra conducted an aeration trial with fertilized amendment.

### Sulfolane Mineralization

The first trial with stoichiometric amount of hydrogen peroxide required for sulfolane degradation, was intended for simulation of in-situ groundwater remediation. Mineralization of sulfolane by hydrogen peroxide is presented by the following reaction:

$$C_4H_8O_2S + 13\ H_2O_2 = 4\ CO_2 + H_2SO_2 + 16\ H_2O$$

Three groundwater samples with concentrations of sulfolane in range of 800 to 1,000 mg/L were used for this trial. In addition, the groundwater samples contained hydrocarbons that could use hydrogen peroxide for their own degradation. Since, the amount of hydrocarbons present in the samples varied significantly five times larger amount (that required by stoichiometry) of hydrogen peroxide was applied.

**UV Irradiation**

Before commencing UV irradiation experiments, spectrophotometer evaluation of light absorbance by sulfolane solution was performed to identify the possibility of photolysis. The result was that sulfolane solution did not show any absorption of the light in the visible region, only UV region seemed to be active indicating that direct photolysis of sulfolane was most probable under the UV irradiation.

**Mineralization and UV Irradiation**

In this trial combination of both of the previously conducted experiments were combined. However it is known that UV irradiation initiates significant production of hydroxyl radicals from hydrogen peroxide. Hydroxyl radicals act as a potent oxidant because if it's high oxidation potential and non-selective reactivity. As an example the oxidizing strength of common oxidizers in water such as $OH^-$ , $O_3$, $Cl_2$, $ClO^-$ are 2.8 V, 2.1 V, 1.4 V, and 0.9 V, respectively. Therefore, various water treatment technologies (ozonation, direct photolysis, $H_2O_2$) inherently produce some amount of hydroxyl.

In combined experiment the groundwater sample was treated with 50 ml/L of 30% $H_2O_2$ in a rotation setup under UV irradiation for a week. Irradiation was achieved using a 40W fluorescent bulb with emission centered at 350 nm.

**Aeration Trial**

The aeration trial was conducted utilizing micro bubbles technology® in conjunction with slurry mixing and two fertilizer amendments previously applied in the soil treatability trial. This trial was conducted at 15$^{o}$C ambient temperature and constant mixing for 24 hours. The average dissolved oxygen concentration in the water sample was 7.7 mg/L.

**SUMMARY OF RESULTS**

**Soil**

The homogenized soil sample is toxic to Microtox® and remains toxic with no addition of fertilizer after 78 days of incubation. However, after 78 days of incubation with ammonia phosphate fertilizer the sample of soil becomes non-toxic to Microtox®.

The hydrocarbons presented in the soil sample were biodegraded before sulfolane in the treated samples. The sulfolane degrading bacteria required longer time to adapt than the hydrocarbon degrading bacteria.

Full sulfolane biodegradation occurred with ammonium phosphate addition of 83 mg/kg and 232 mg/kg. There was no obvious production of toxic by-products.

**Groundwater**

The following table summarizes the sulfolane degradation trial results.

| Sample Description | Sulfolane (mg/L) | Removal Ratio (%) | Time (hours) |
|---|---|---|---|
| Blank | 1200 (1800*) | | |
| Mineralization | 950 | 21 | 168 |
| UV Irradiated sample | 1000 | 17 | 168 |
| Mineralization + UV | 63 | 95 | 168 |
| Aeration + Nutrients | 490* | 73 | 24 |

**Chemo-physical Treatment**

The combination of mineralization and UV irradiation revealed the highest ratio of sulfolane removal (95%) under the chemo-physical treatment after one week of treatment. Significant production of gases was observed during this experiment.

In order to estimate the time required for similar field application under the sunlight, the assessment of UV energy consumed in the lab trial was required. This value can be compared to the solar energy ($W/cm^2$) and the time of the field experiments is calculated based on the known lab trial time as follows:

Energy, P, consumed by the sample during the lab experiment was estimated using the following equation:

$$P = E_{photon} * I/S = 0.2\ (m\ J/s\ cm^2)$$

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

Energy of single photon can be approximated as:

$$E_{photon} = h\upsilon = hc/\lambda = 5.67*10^{-19}\ (J/photon)$$

Where
- h is a Plank constant; $h = 6.62*10^{-34}$
- $c = 3*10^8$ m/s, and
- $\lambda = 350$nm

The intensity of the photon flux, $I$ = 2.25*$10^{16}$ (photons/s) was measured previously by ferrioxalate actinometry [6].

Therefore, solar energy required was calculated using the following formula;

$$E_{solar} = \mathbf{0.2\ m\ W/cm^2} \quad and\ E_{\lambda,400nm} = \mathbf{3.5\ mW/cm^2}$$

Thus, the week of UV irradiation on the lab will be equal to:

$$7\ days * (0.2\ m\ W/cm^2/3.5\ mW/cm^2) = \mathbf{10\ hrs}\ of\ sun\ exposure.$$

## Biodegradation Treatment

The bioremediation treatment (aeration in conjunction with slurry mixing and ammonia phosphate amendments) and resulted in decrease of initial sulfolane concentrations of 1800 mg/L to 490 mg/L in 24 hours. Therefore, 73% of sulfolane was removed from the groundwater sample

## CONCLUSIONS

The sulfolane treatability in soil samples was achieved utilizing aerobic conditions and ammonia phosphate fertilized amendments, after 78 days of treatment.

The groundwater impacted by sulfolane degradation occurred under the chemo-physical and biodegradation (aeration) processes.

The mineralization and UV irradiation treatment achieved 95% removal of sulfolane after one week of treatment. If field scale treatment utilizes sunlight, 10 hours of the daily light would be required. However, UV reactor should be considered as well.

The biodegradation treatment achieved 73% of sulfolane removal after 24 hours. The field scale treatment would require the water treatment and storage facility.

Based on these results, the field scale trials for soil and groundwater treatment should be scheduled. More aggressive methods should be considered in order to minimize the time required the successful treatment.