SOVEREIGN CONSULTING INC.
AN ENVIRONMENTAL SERVICES FIRM

# Calculation of Biodegradation Rates above and below the Water Table

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# Background

*Background*

- Former Refinery over 500 acres with widespread historical LNAPL impacts
- Interim hydrocarbon recovery system implemented as primary remedial system with declining performance over 15 years
- Implemented pilot-scale bioremediation systems (biovent, biosparge, AS/SVE) to show greater effectiveness given current site conditions

*Focus of Presentation*

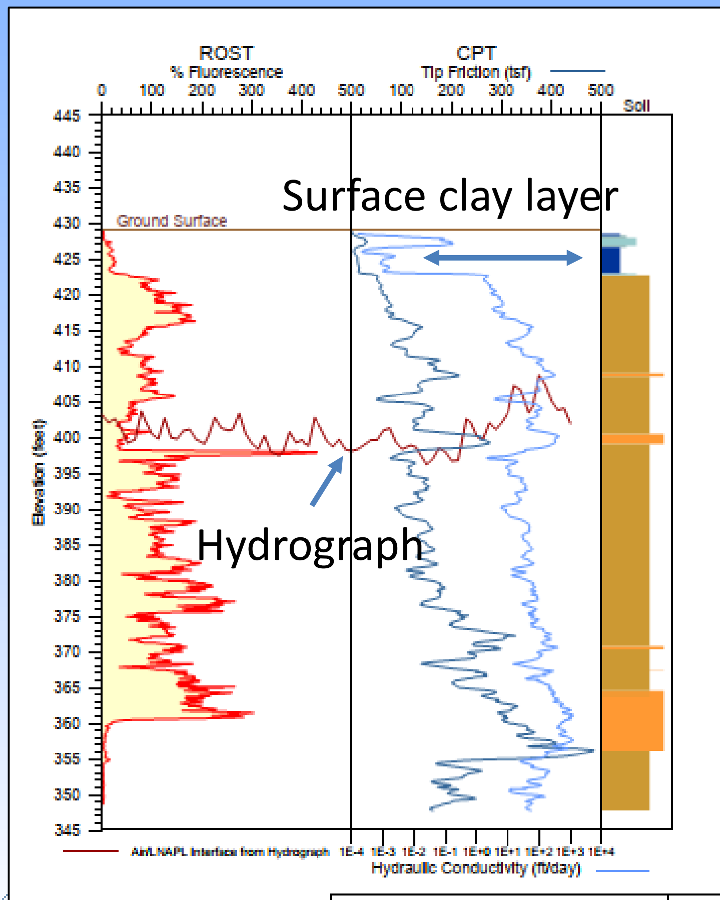
- Methods developed to calculate biodegradation rates associated with system operations above and below water table
- Development of key parameters for evaluating bioremediation system performance

# Site/Project Background

- Bioventing is being applied to an area with weathered gasoline LNAPL impacts above and below the water table to enhance biodegradation

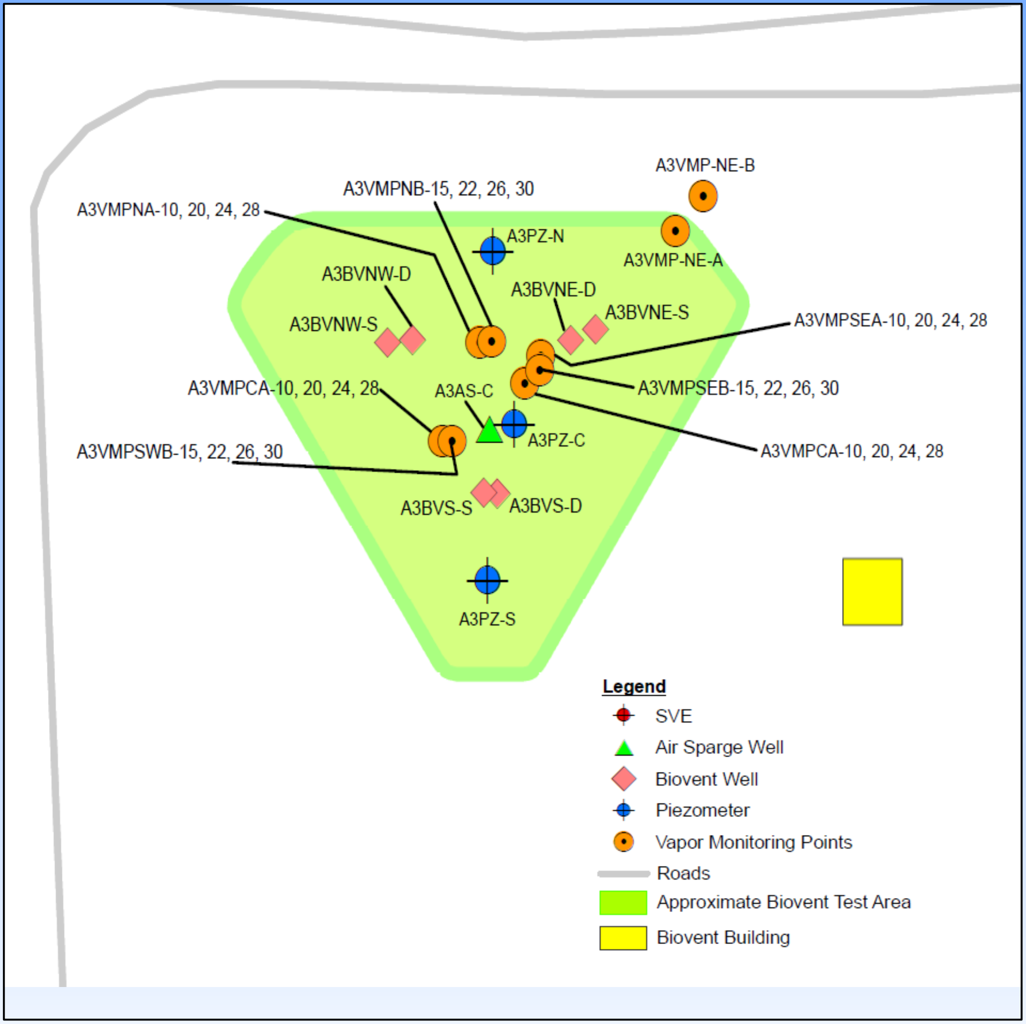
30 ft vadose zone

Smear zone 40 ft below water table due to historical Pumping (~20 feet in bioventing zone)



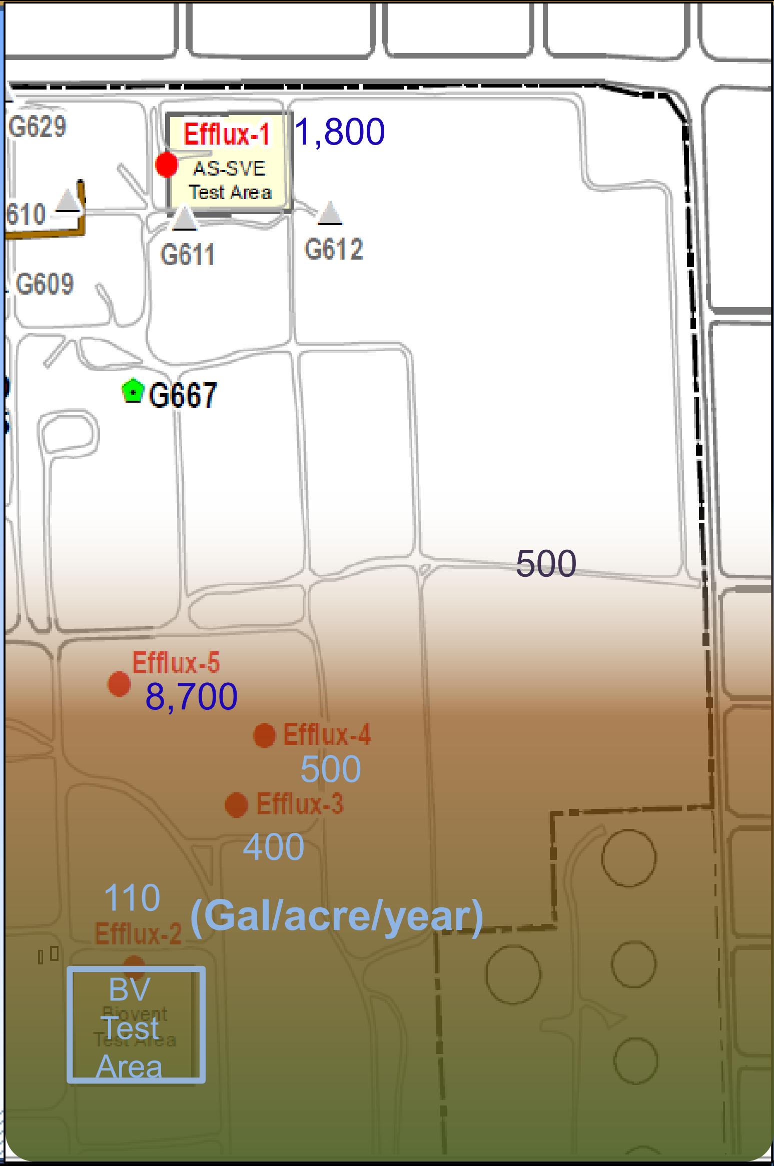

# Site/Project Background

- 6 biovent wells in 3 nested pairs (shallow and deep)
- Operated at a range of 5-12 scfm
- Monitored through 4 nested vapor monitoring points (VMPs) and 3 groundwater monitoring wells
  - Up to 8 vertical depths in each VMP



# Initial Background Degradation Rates

- Background rates estimated using surface efflux of $CO_2$
- $CO_2$ produced through natural degradation contained by clay in southern portion of site
- Relies on 1-dimensional vertical gas transport to represent biodegradation rate, but $CO_2$ efflux is not consistently 1-dimensional
- Recently Garg et al. (2017) compiled rates from various sources yielding a range of NSZD rates between 700 to 2800 Gal/acre/yr



# Initial Respiration Testing

- During baseline soil gas monitoring in all areas, anaerobic conditions existed
  - <1% oxygen, >60% methane, >10% carbon dioxide
- Periodic respiration testing conducted to evaluate system performance using established guidance
- O2, CO2, and CH4 were monitored in VMPs during periods of shutdown
  - Initially only oxygen utilized to calculate aerobic respiration

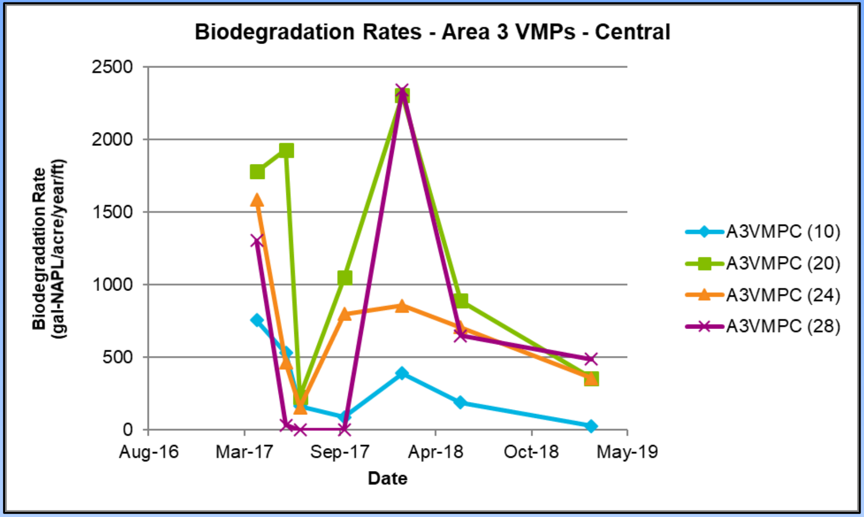
$$k_B = \frac{-k_{O_2}/100 \cdot \theta_g \cdot \rho_{O_2} \cdot S_{O_2}}{\rho_{bulk}}$$

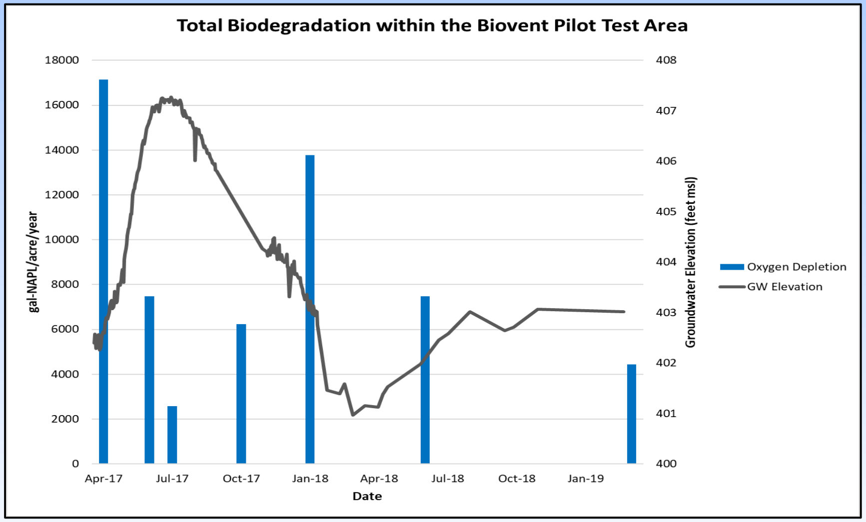
| | |
|---|---|
| $k_B$ | = Rate of aerobic biodegradation (mg-HC/kg-soil/day) |
| $k_{O2}$ | = Measured oxygen utilization rate (vol%-$O_2$/day) |
| $\theta_g$ | = Gas-filled soil pore space |
| $S_{O2}$ | = Stoichiometric mass ratio of hydrocarbon to oxygen (0.29 g-HC/g-$O_2$) |
| $\rho_{O2}$ | = Density of oxygen gas (1,330 mg/L) |
| $\rho_{bulk}$ | = Soil bulk density |
| $\rho_n$ | = LNAPL Density |
| $b_{n\_vz}$ | = Smear Zone Thickness |

**Unit Conversion:**

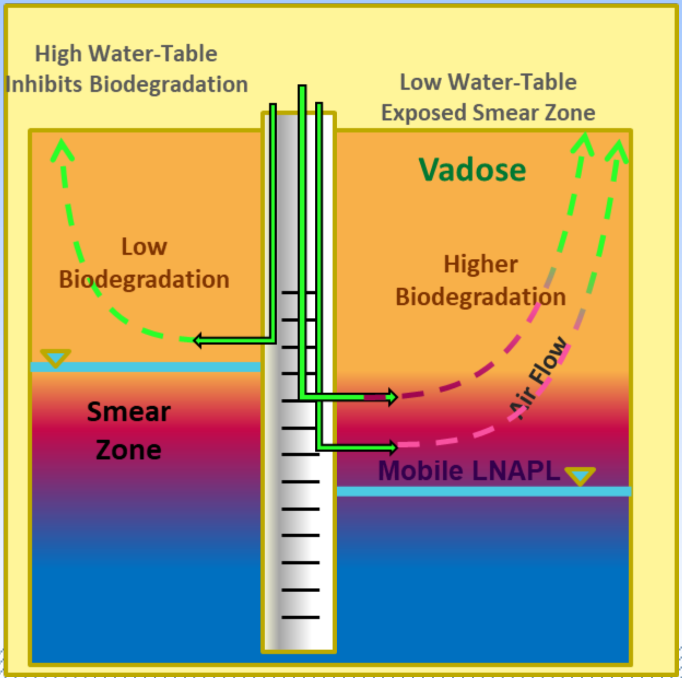
$$\frac{Gal\ NAPL}{Acre}/Year = k_B \cdot bn_{\_vz} \cdot (\rho_{blk}/\rho_n) \cdot (1.28e5)$$

# Initial Respiration Testing

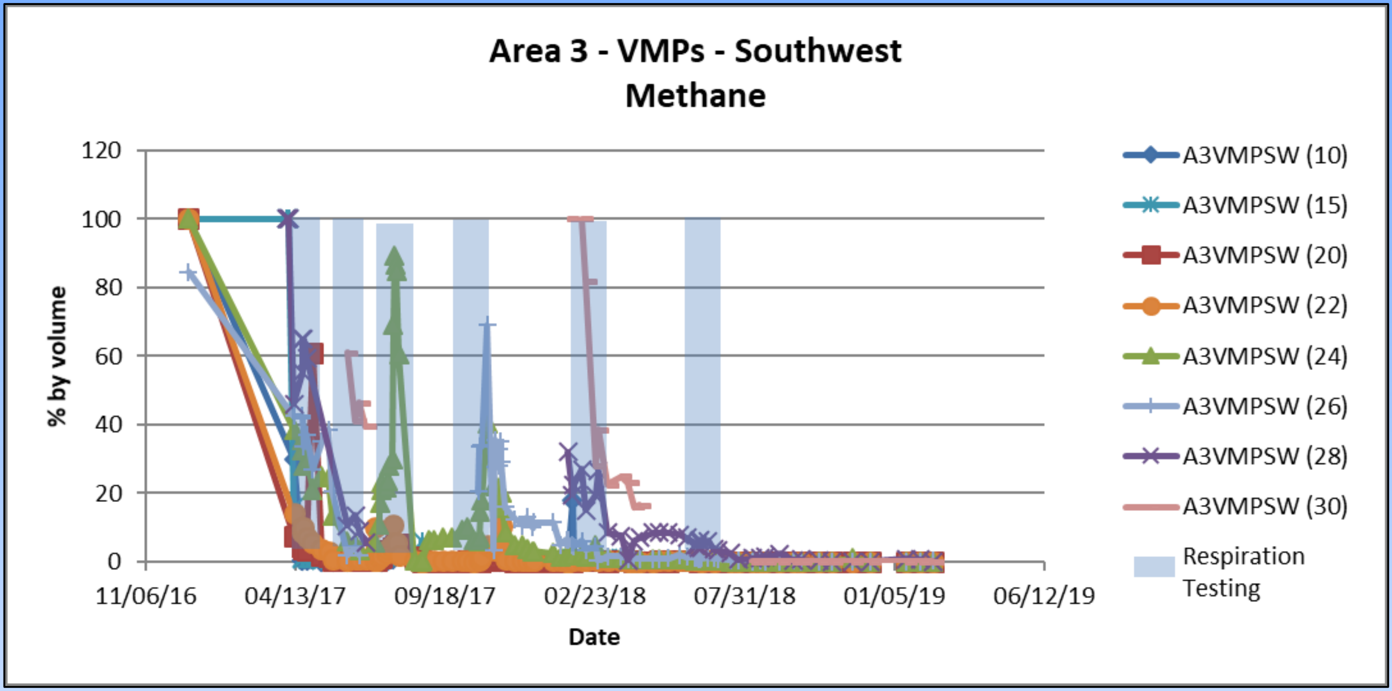



- Earliest apparent respiration rates highest in shallow vadose zone
- Over time rates higher in deeper vadose zone and during lower water table periods



# Initial Respiration Testing




- *How is methane impacting testing and calculations?*
  - Initial oxygen depletion
  - Continuous methane generation from impacted saturated zone

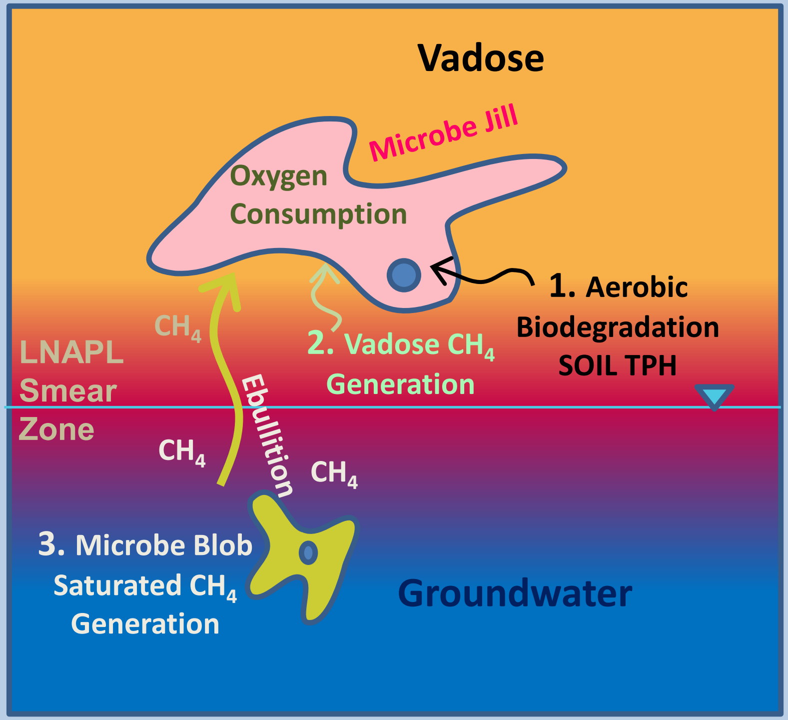
# Biodegradation in Vadose and Saturated Zones

- Oxygen Ultimately Utilized by:
  1. Aerobic Soil PHC Degradation
  2. Methane Generation Vadose Zone
  3. Methane Ebullition Saturated Zone

- *During respiration testing, oxygen depletion in the presence of methane cannot necessarily be attributed to aerobic biodegradation*

- Utilized both methane and oxygen respiration calculations to estimate total biodegradation rates within the biovent area

**Respiration Testing, No Air Flow from System & Oxygen Remains from Recent Operation**



# Total Biodegradation Rate: Calculations

- Equations used for calculating degradation rates during respiration testing:

Respiration Rate from Oxygen Depletion

$$k_{O2}\ (\text{mg-HC/kg-soil/day}) = R_{dO2} \cdot \theta_g \cdot \rho_{O2} \cdot S_{O2} / 100 / \rho_{blk}$$

Respiration Rate from Methane Generation

$$k_{CH4}\ (\text{mg-HC/kg-soil/day}) = R_{CH4m} \cdot \theta_g \cdot \rho_{CH4} \cdot S_{CH4} / 100 / \rho_{blk}$$

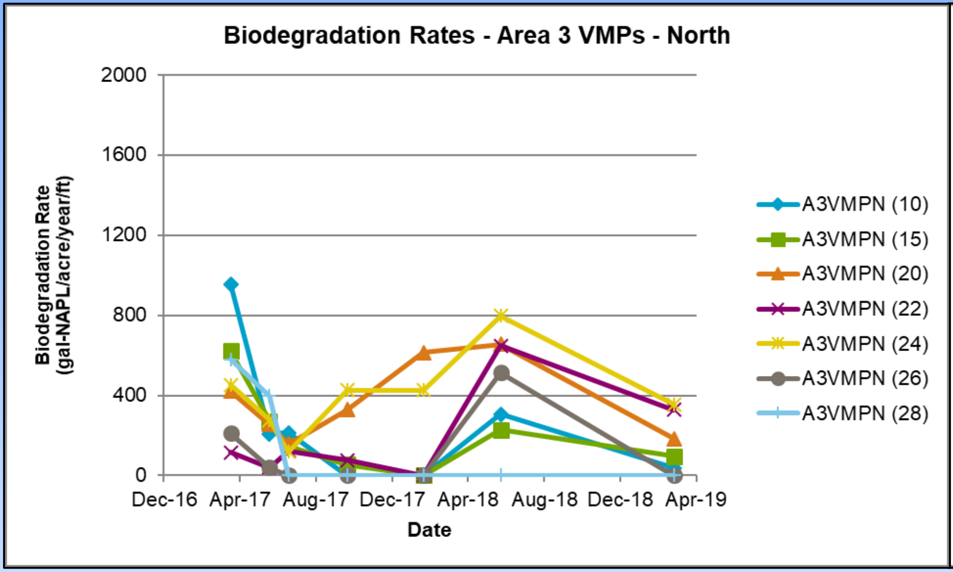
*Differences:*

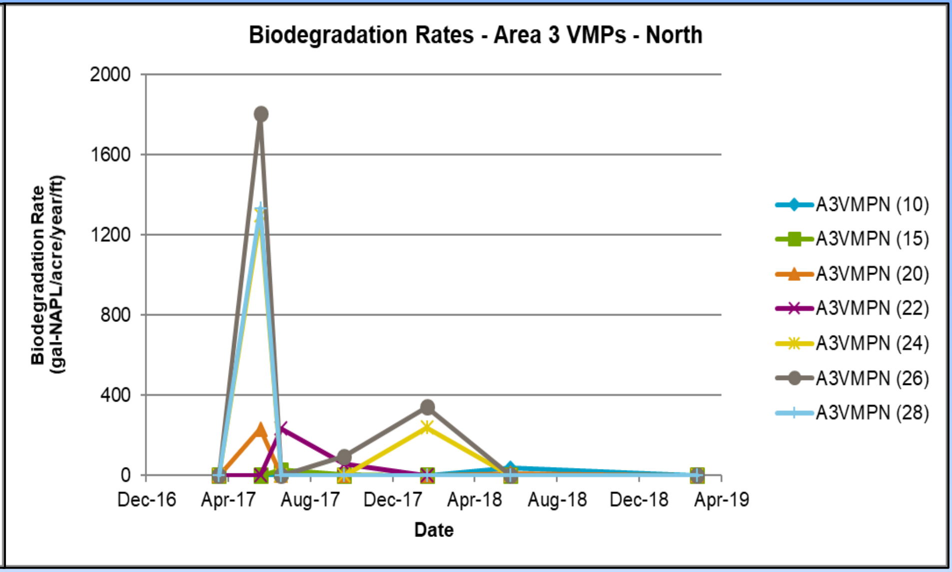
$R_{dO2}/R_{CH4m}$ = *Rate of oxygen depletion/methane generation*

$\rho_{O2}/\rho_{CH4}$ = *Oxygen/methane gas density*

$S_{O2}/S_{CH4}$ = *Stoichiometric coefficient for hydrocarbon degraded*

# Total Biodegradation Rate




**Respiration rates from Oxygen Depletion**

**Respiration rates from Methane Generation**

# Total Biodegradation Rate Calculations

Equations show contributions of biodegradation of hydrocarbons vs methane consumption by methanotrophic microbes

**Oxygen Respiration** $K_{O2gal\text{-}M} = K_{O2gal\text{-}BIO} + K_{O2gal\text{-}CH4}$

*i.e. Rate of oxygen respiration = Aerobic bio + Methane consumption*

**Methane Respiration** $K_{CH4gal\text{-}M} = K_{CH4gal\text{-}BIO} - K_{CH4gal\text{-}O2}$

*i.e. Rate of methane respiration = Anaerobic bio – Methane consumption*

# Total Biodegradation Rate Calculations

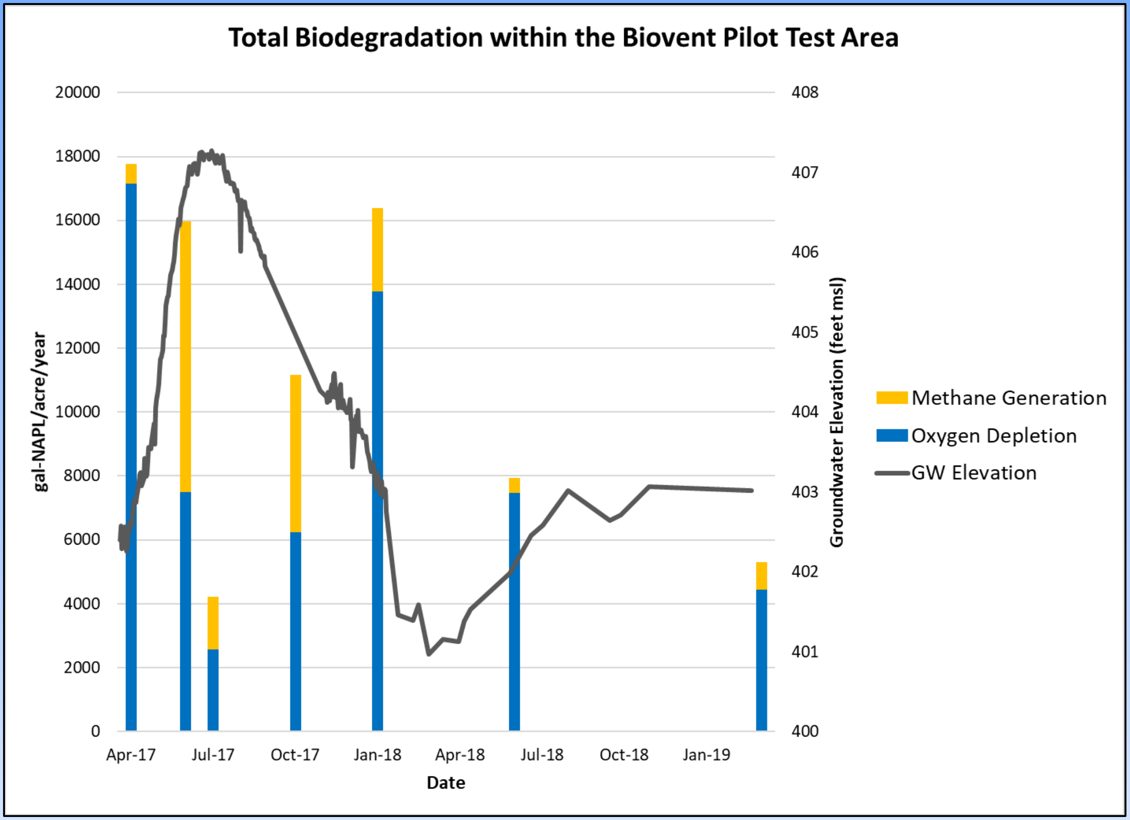
- ***Because the respiration test measured oxygen depletion and methane generation concurrently, $K_{CH4gal\text{-}O2}$ and $K_{O2gal\text{-}CH4}$ are equivalent.***

- Summing oxygen respiration and methane respiration equations yields total biodegradation rate regardless of methane consumption:

$$K_{CH4gal\text{-}M} + K_{O2gal\text{-}M} = K_{CH4gal\text{-}BIO} - K_{CH4gal\text{-}O2} + K_{O2gal\text{-}BIO} + K_{O2gal\text{-}CH4}$$

$$= K_{CH4gal\text{-}BIO} + K_{O2gal\text{-}BIO}$$

# Total Biodegradation Rate




- Ratio of oxygen depletion to methane generation changes over time
- Heat generated by degradation in vadose zone extends far below water table, increasing anaerobic biodegradation

# Oxygen Utilization during Operations-Biovent

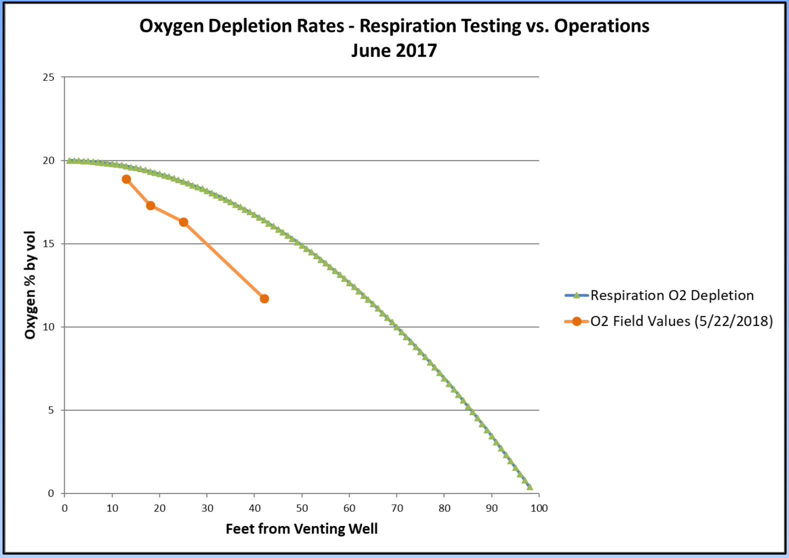
- Oxygen depletion rates calculated during respiration testing were compared to oxygen readings in VMPs during operations

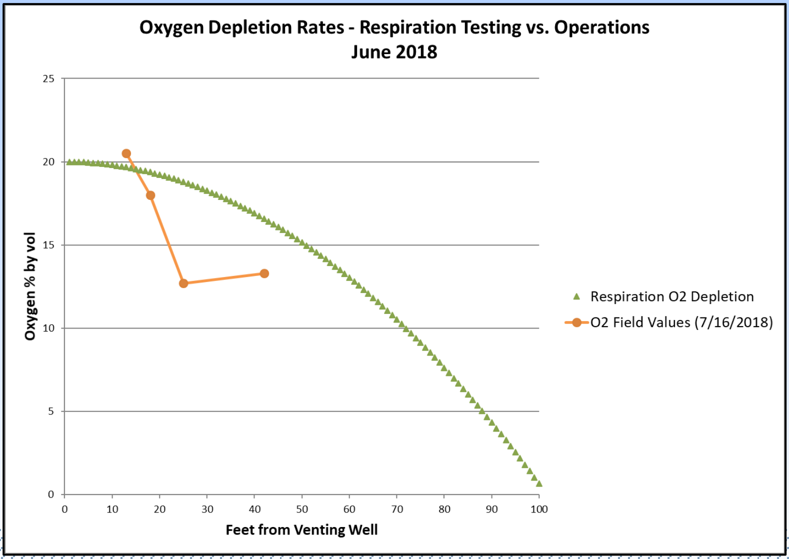
- Modeled oxygen % at radius r and oxygen depletion $k_{O2}$:

$$O_2(r) = .209 - \left(\frac{\pi r^2 h \theta_g}{Q_a}\right) k_{O_2}$$

*Where:* $\mathbf{k_{O2}}$ *= oxygen depletion rate*

- <u>Field readings can be used to calculate oxygen depletion rates without requiring respiration testing</u>
  - Immediate response

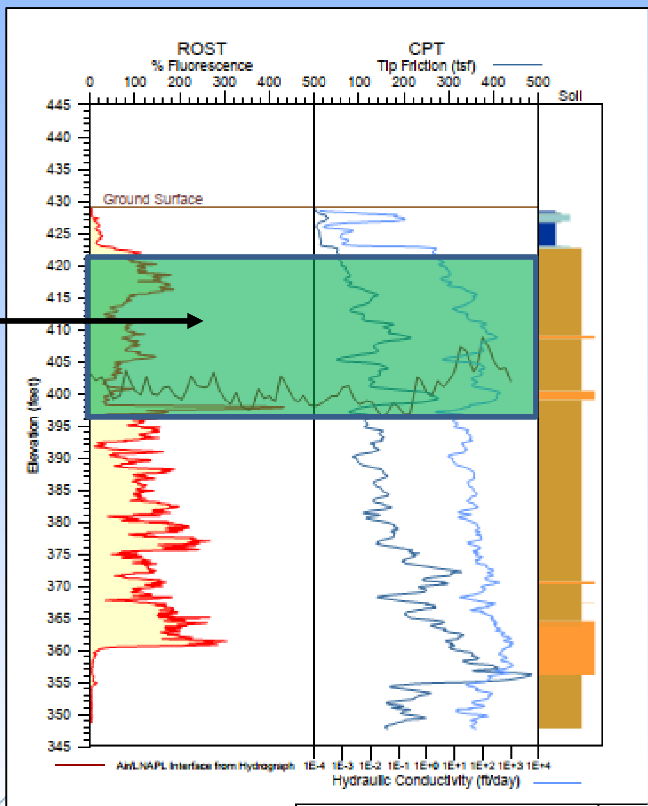


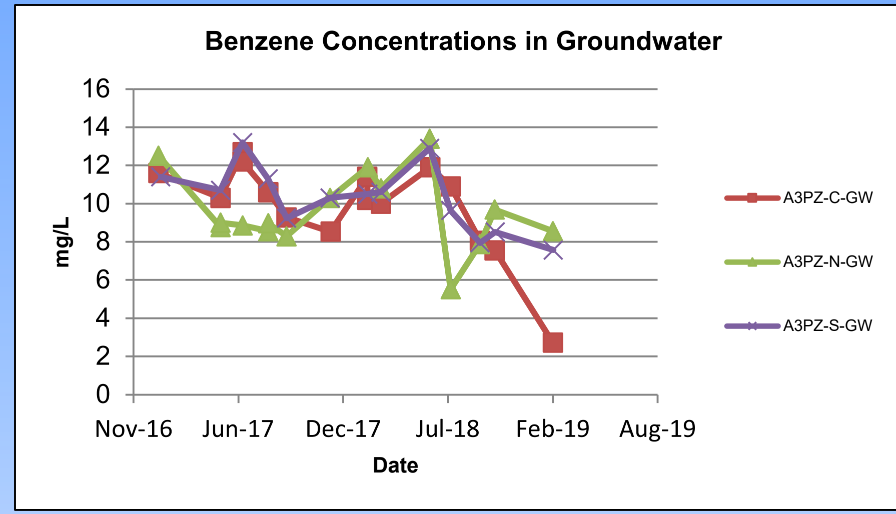



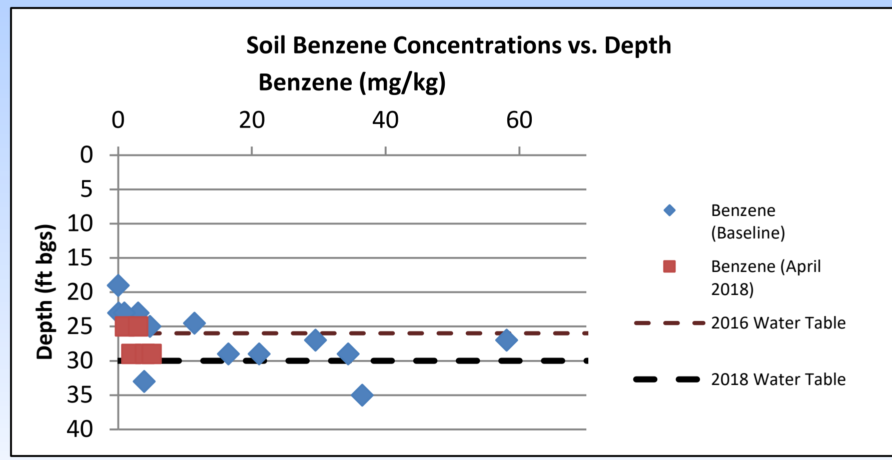
# Impact on Benzene Concentrations

- Effective results on benzene concentrations in groundwater beyond expectations

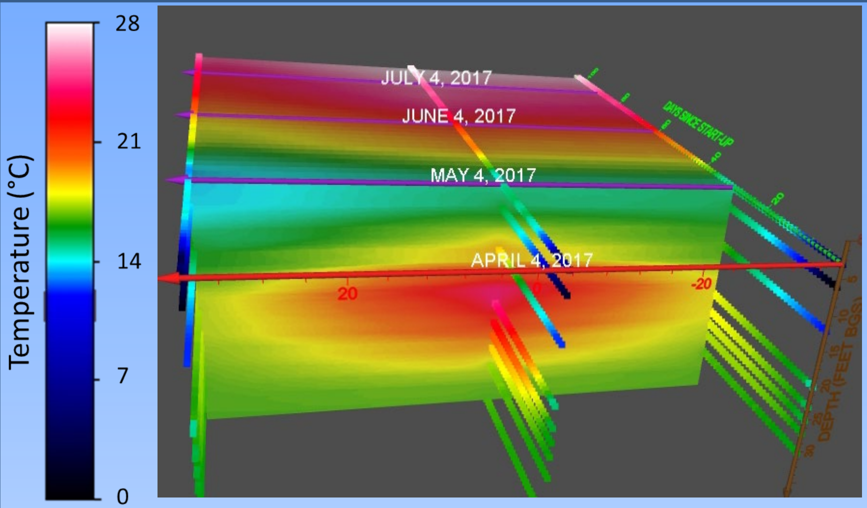
Biovent Zone



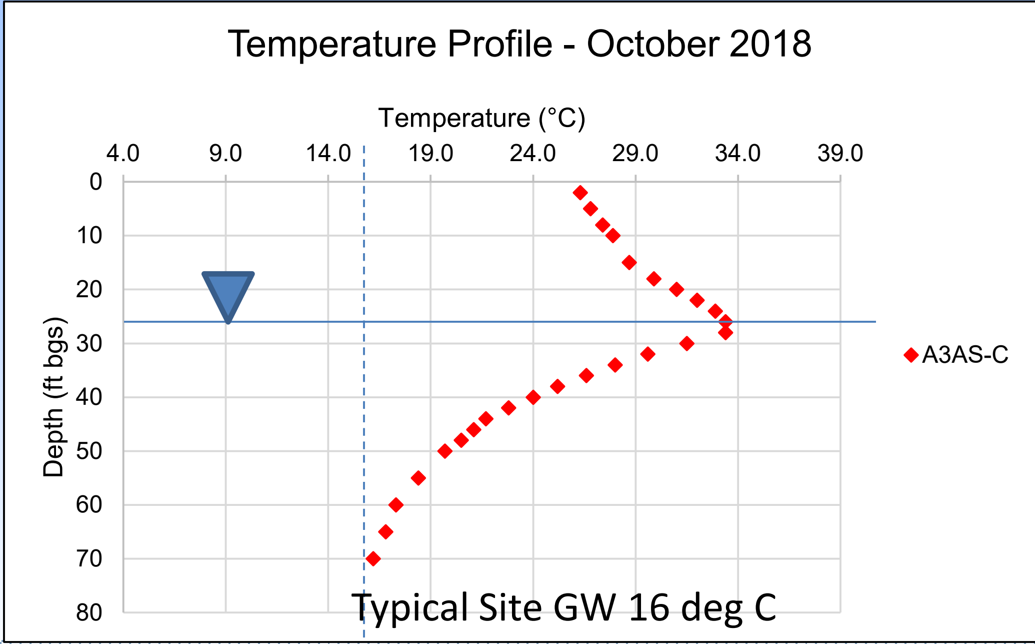



# Temperature Effects




- Temperature increase extends well below water table and could impact anaerobic biodegradation rates

- Temperature a lagging indicator compared to response of soil gases but help illustrate effects

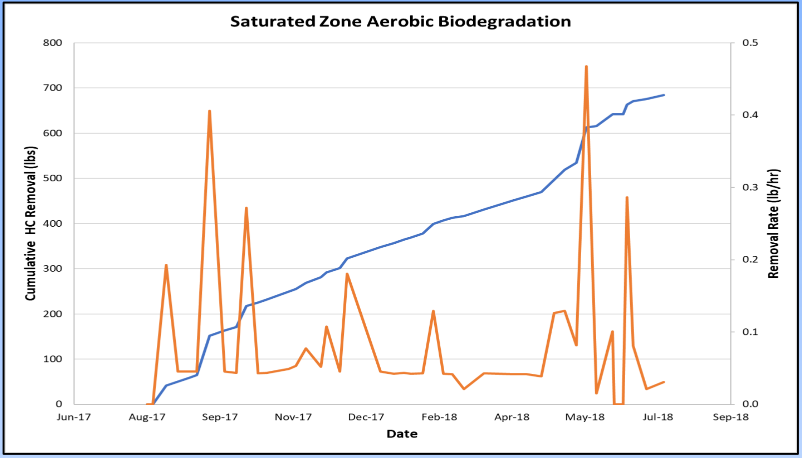


# Oxygen Utilization during Operations - Biosparge

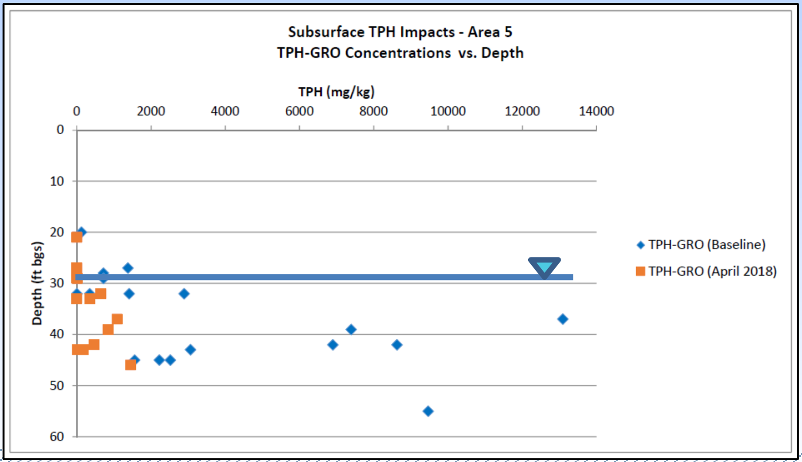
- Vadose zone respiration calculated using VMPs similar to biovent

$$HC\left(\frac{lb}{hr}\right) = \frac{(.209-[O_2])Q_a * 60832}{37800} * 0.29$$

- Decrease in oxygen between sparge well and VMPs immediately above water table assumes oxygen depletion through aerobic bio in saturated zone




- Rapid utilization after shutdown makes DO harder to measure using down-hole meter
- Stoichiometric calculation to calculate hydrocarbon removal; rates in saturated zone limited compared to vadose zone (~215 gal/acre/yr)




- **<u>Biosparge rates can create bioventing conditions in vadose zone</u>**
  - **<u>Bioreactor to treat sparged vapors</u>**

# Key Lessons

***Background degradation***

- Respiration testing needs to account for $CH_4$ contribution to understand true aerobic degradation rates
- While $CO_2$ efflux methods can be used to estimate background degradation prior to system operation, these rely on 1D transport
- Methane respiration testing provided a useful analog of saturated zone/background degradation during system operation

# Key Lessons

***System Enhanced Biodegradation***

- Utilized combined oxygen and methane respiration to calculate total biodegradation rate
- Soil gases from VMPs can potentially provide an immediate response of biodegradation rates using either operational data or respiration testing
- Oxygen utilization another measure of aerobic biodegradation in saturated zone during biosparging or air sparging
  - Consider soil gases because dissolved gases transient
  - Sparge rates can create bioventing conditions in vadose zone
  - *Consider vadose zone a bioreactor for sparged vapors*

# Key Lessons

***System Enhanced Biodegradation***

- Temperature effects of bioremediation may have positive unintended consequences
  - Lagging indicator compared to soil gases due to heat capacity of soil

- Periodic assessment of COC concentrations in groundwater/soil can be triggered by conditions seen in field to document effectiveness
  - Decreases in oxygen depletion rates or temperatures
  - Geochemistry for biosparge (DO, ORP, SC)

- Utilize water table effects where possible – take advantage of current groundwater extraction system

# Possible Future Directions

***Background Degradation***

- Vadose - Measure $CH_4$/anaerobic respiration (i.e. NSZD) using nitrogen push pull tests with helium tracer
  - Similar concept used in landfill biocover design
  - Can work where 1D vertical soil gas transport not applicable

- Saturated – Measure $CH_4$ respiration using DI water, with tracer
  - $\Delta$ conductance measures diffusion/advection
  - $\Delta$ tracer measures ebullition fractionation beyond diffusion/advection
  - $\Delta$ $CH_4$ accounting for two factors measures saturated respiration rate

***System Degradation Rates***

- Calibrate model of degradation relating soil gases during operations to respiration rates during respiration testing

# Questions/Discussion

# Contact

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