



## ***In Situ* Bioventing Performance In Presence of Mixed Suite of Aerobically and Anaerobically Degradable Hydrocarbons**

*Prepared for:*

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Environmental Technologies

*Prepared by:*

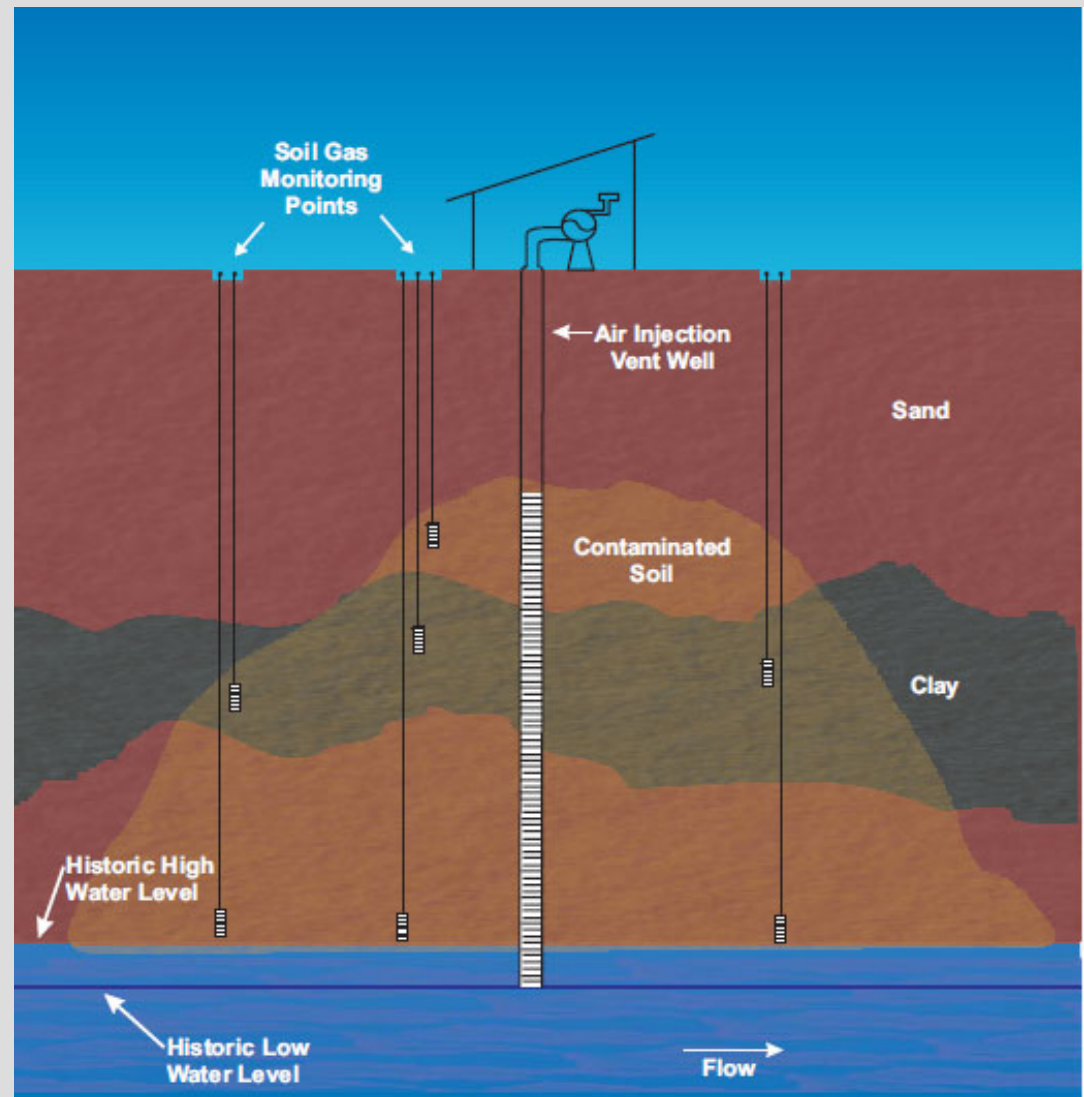


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# Bioventing Fundamentals

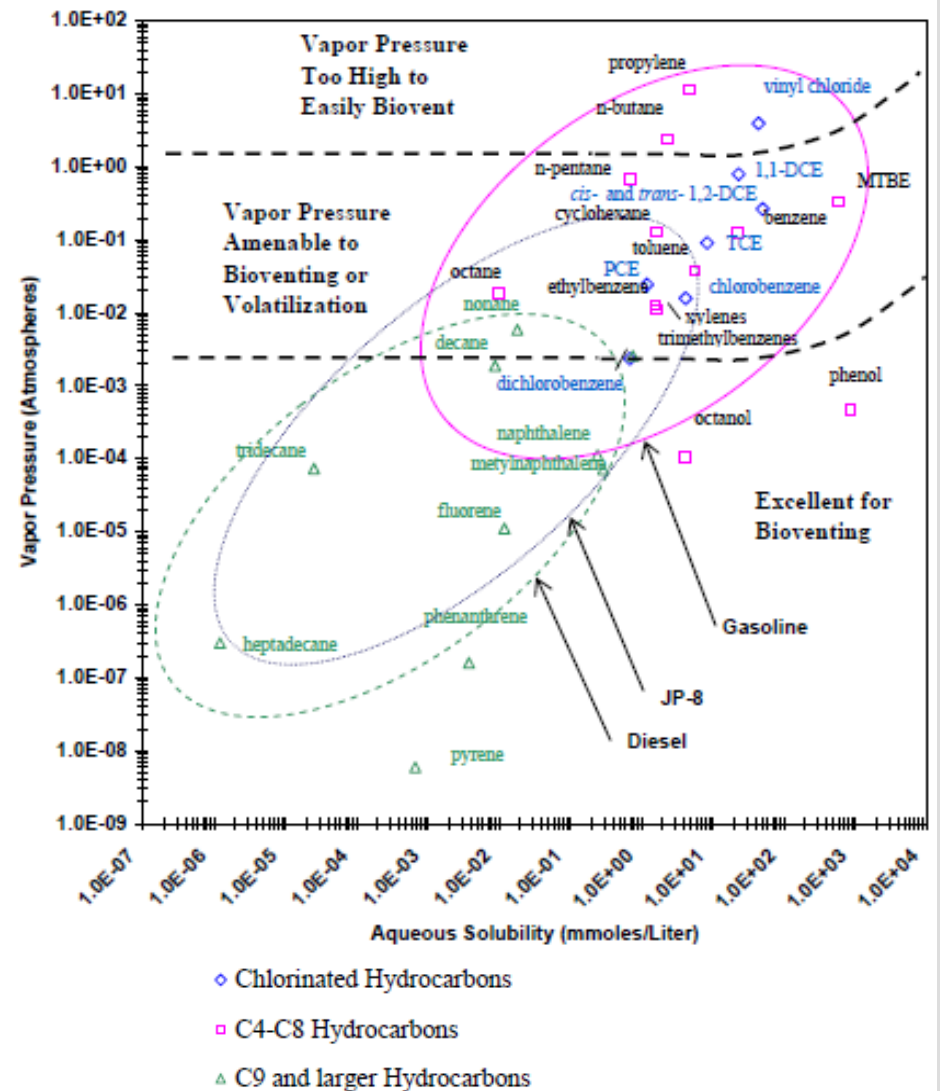
- Process of aerating soils to add oxygen to stimulate *in situ* biodegradation of wide-range of Hydrocarbons (HCs)
- As opposed to drawing vacuum with SVE, relies on injection of air into subsurface
- Operating at low air movement (pressure and injection rate) to minimize volatile migration or emissions



AFCEE (May 2004), Procedures for Conducting Bioventing Pilot Tests and LTM Bioventing Systems

# Bioventing Fundamentals (cont'd)

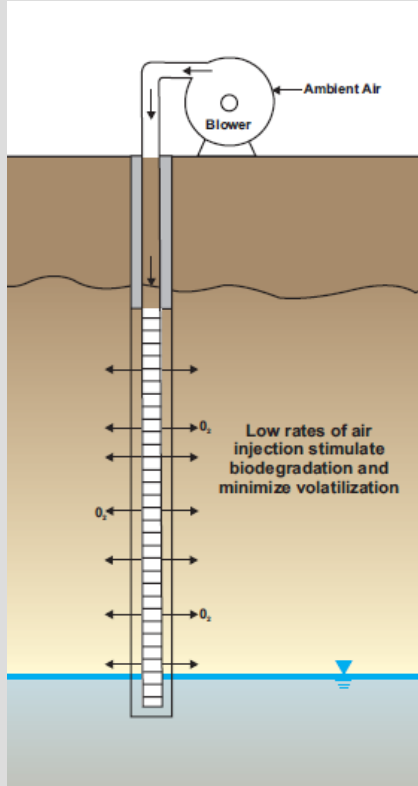
- Best suited for petroleum HCs with greater than 8 carbon atoms
  - ◆ Jet Fuels
  - ◆ Diesel
  - ◆ Heating Oil
- Amenable to aerobically degradable HC compounds with moderately low vapor pressure
  - ◆ Alkanes (C8+)
  - ◆ Aromatics
  - ◆ Chlorobenzene
  - ◆ Some Ketones
  - ◆ Others



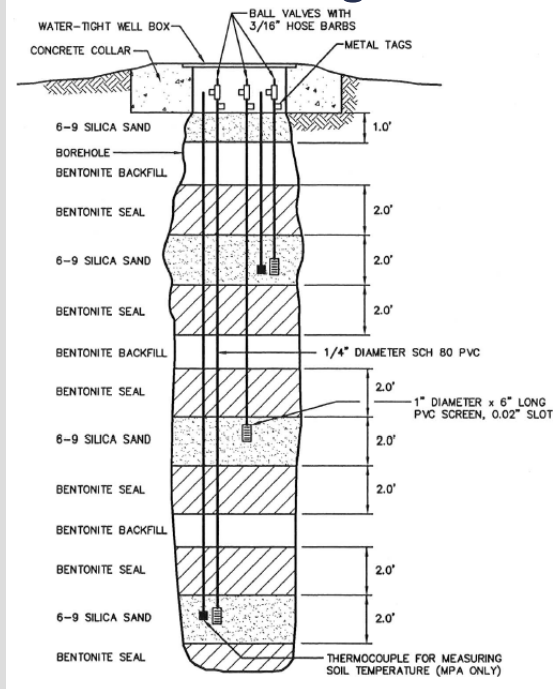
AFCEE (May 2004), Procedures for Conducting Bioventing Pilot Tests and LTM Bioventing Systems

# Respirometry Testing

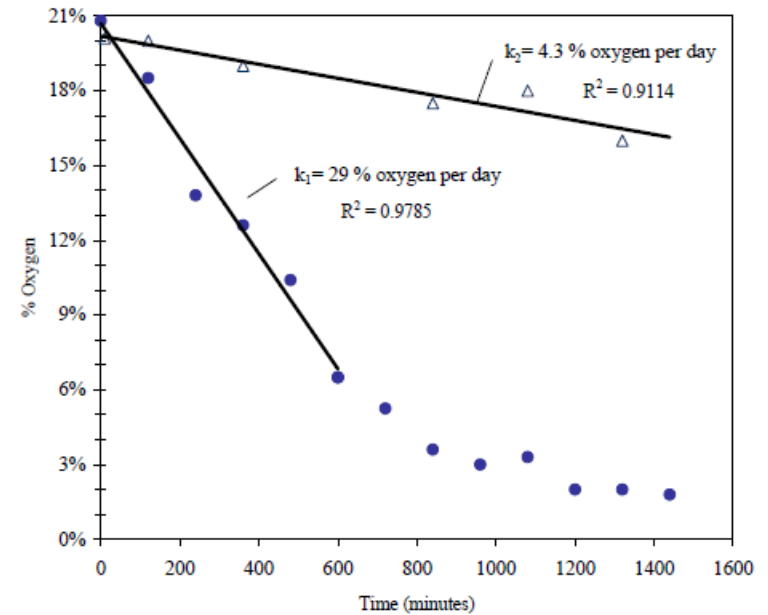
## Blower Shutdown



## Respirometry Testing



## Oxygen Utilization Rates



$$k_B = \frac{-k_o \theta_a \rho_{O_2} C}{100 (\rho_k)}$$

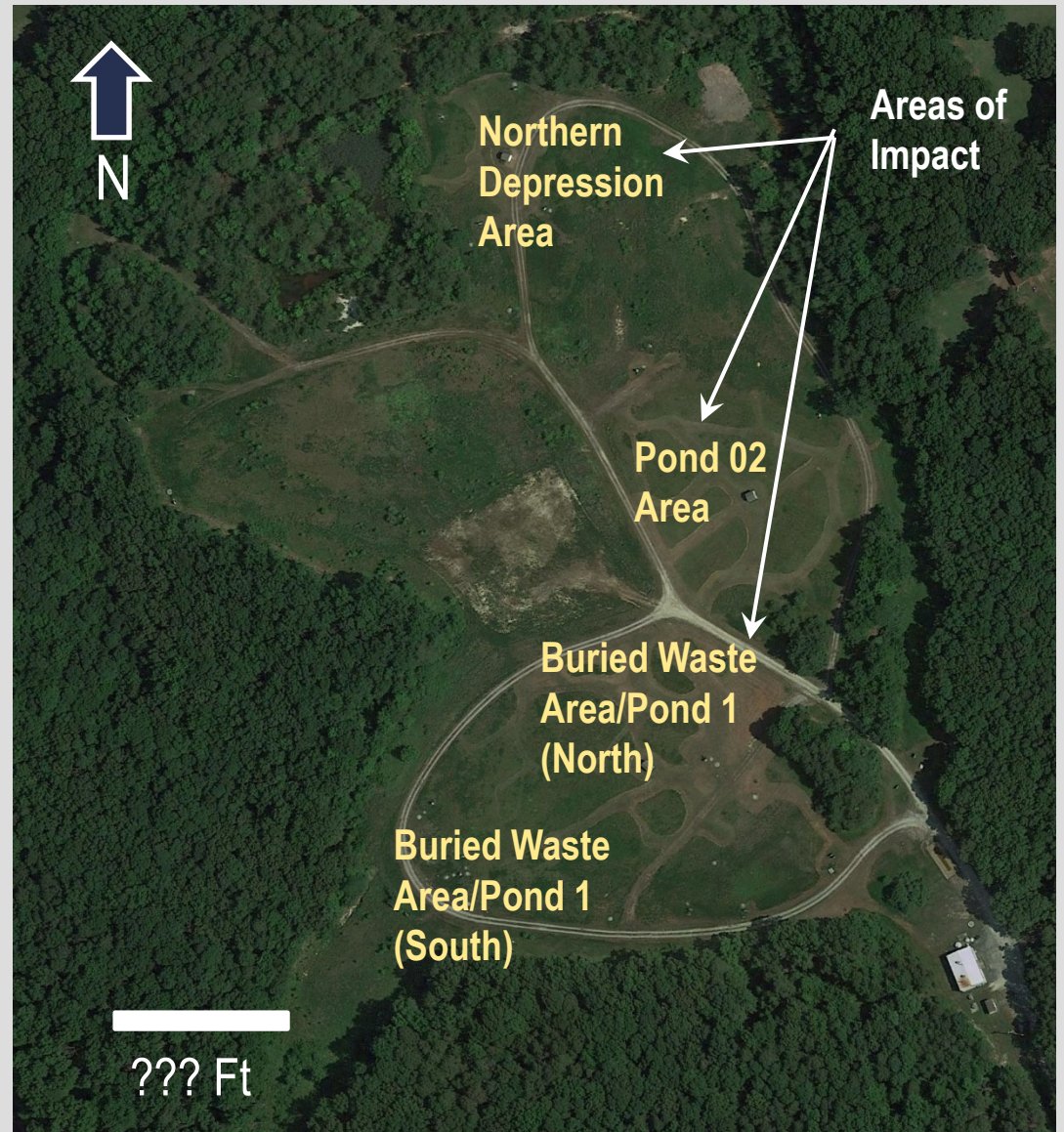
- where:
- $k_o$  = the rate of oxygen utilization (% oxygen/day)
  - $\theta_a$  = the gas-filled porosity of the soil (unitless)
  - $\rho_{O_2}$  = oxygen density (mg/L)
  - $\rho_k$  = the soil bulk density (g/cm<sup>3</sup>)
  - $C$  = hydrocarbon to oxygen ratio (1/3.5 or .29)
  - $k_B$  = the rate of hydrocarbon biodegradation (mg TPH/kg soil/per day)

- Rarely is Bioventing performance evaluated by comparing  $k_o$  or  $k_B$  to individual COC degradation rate estimates

AFCEE (May 2004), Procedures for Conducting Bioventing Pilot Tests and LTM Bioventing Systems

# Site Background

- Former Sand and Gravel Quarry (NPL Site)
- Unpermitted Dumping of Drums and Industrial Waste
- COCs: VOCs, SVOCs, Metals, PCBs
- 3 Treatment Areas: ~15 acres
- Remedial Approach
  - ◆ Principal Threat Materials –  $10^{-4}$  Risk or Greater
    - Liquid Waste Removal (completed in 1976)
    - Buried Drum Removal (completed in 1992)
    - Excavation/Thermal Treatment (completed in 2010)
  - ◆ Low-Level Threat Materials –  $10^{-4}$  to  $10^{-6}$  Risk
    - Bioventing (completed in 2017)
    - Anaerobic Bioremediation (Future)



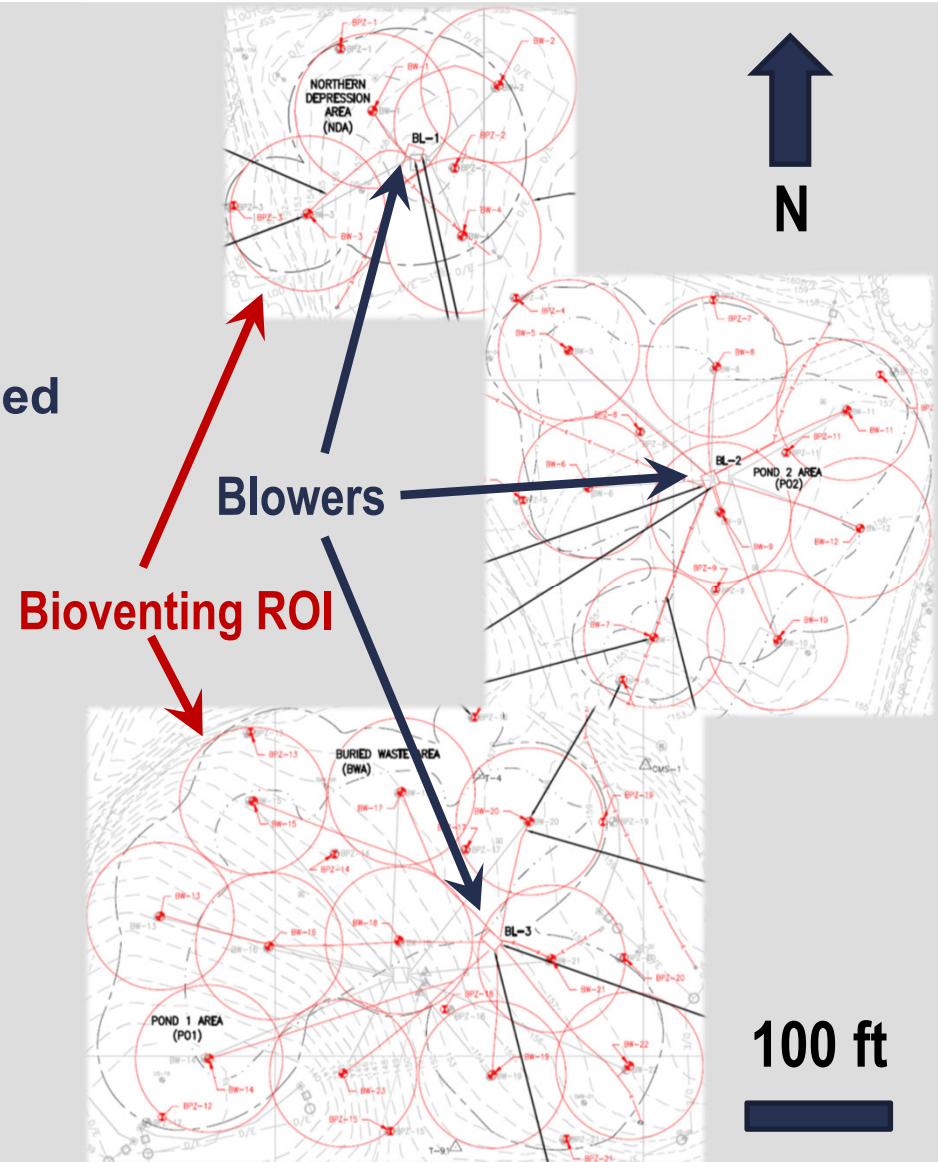
# Bioventing Summary

## ■ System Components

- ◆ 3 Blowers with VFDs
- ◆ 21 Bioventing wells (50 foot ROI)
  - Some nested w/ different screened intervals
- ◆ 27 Monitoring points (1-in. piezometers) with varying screened intervals in homogeneous sand aquifer

## ■ System Operation

- ◆ Flow: 11 to 18 cfm per well
- ◆ Pressure: 10 to 30 in. H<sub>2</sub>O
- ◆ Alarm (High Temp and Pressure) / Radio
- ◆ Full-time operation (except during respiration testing)
- ◆ Duration: 2011 - 2016



# Site COCs That Primarily Aerobically Biodegrade

| <b>Contaminants of Concern (COCs)</b> | <b>Molecular Weight (g/mole)</b> | <b>Aerobic Biodegradation Half Life* (days)</b> | <b>1<sup>st</sup> Order Aerobic Biodegradation Rate (1/days)</b> |
|---------------------------------------|----------------------------------|---|--|
| 1,4-Dichlorobenzene                   | 147                              | 42  | 0.0165   |
| Benzene                               | 78                               | 13  | 0.0533   |
| Chlorobenzene                         | 113                              | 143   | 0.0048   |
| Toluene                               | 92                               | 15  | 0.0478   |
| Methylene Chloride                    | 85                               | 42  | 0.0165   |
| Vinyl Chloride                        | 62                               | 118   | 0.0059   |

\*Suthersan S.S., 1997. Remediation Engineering Design Concepts, CRC Press, Boca Raton, FA.

# Site COCs That Primarily Anaerobically Biodegrade

| <b>Contaminants of Concern<br/>(COCs)</b> | <b>Molecular<br/>Weight<br/>(g/mole)</b> | <b>Aerobic<br/>Biodegradation<br/>Half Life*<br/>(days)</b> | <b>1<sup>st</sup> Order Aerobic<br/>Biodegradation<br/>Rate (1/days)</b> |
|---|--|---|--|
| 1,1,1-Trichloroethane**                   | 133                                      | 207   | 0.0034   |
| 1,1-Dichloroethane**                      | 99                                       | 105   | 0.0066   |
| 1,1-Dichloroethene**                      | 97                                       | 156   | 0.0044   |
| 1,2-Dichloroethane**                      | 99                                       | 140   | 0.0050   |
| Carbon Tetrachloride**                    | 154                                      | 360   | 0.0019   |
| Chloroform**                              | 119                                      | 118   | 0.0059   |
| Cis-1,2-Dichloroethene**                  | 97                                       | 118   | 0.0059   |
| Tetrachloroethene**                       | 166                                      | 360   | 0.0019   |
| Trichloroethene**                         | 131                                      | 341   | 0.0020   |

\*Suthersan S.S., 1997. Remediation Engineering Design Concepts, CRC Press, Boca Raton, FA.

\*\*COCs biodegrading faster under anaerobic than aerobic conditions.

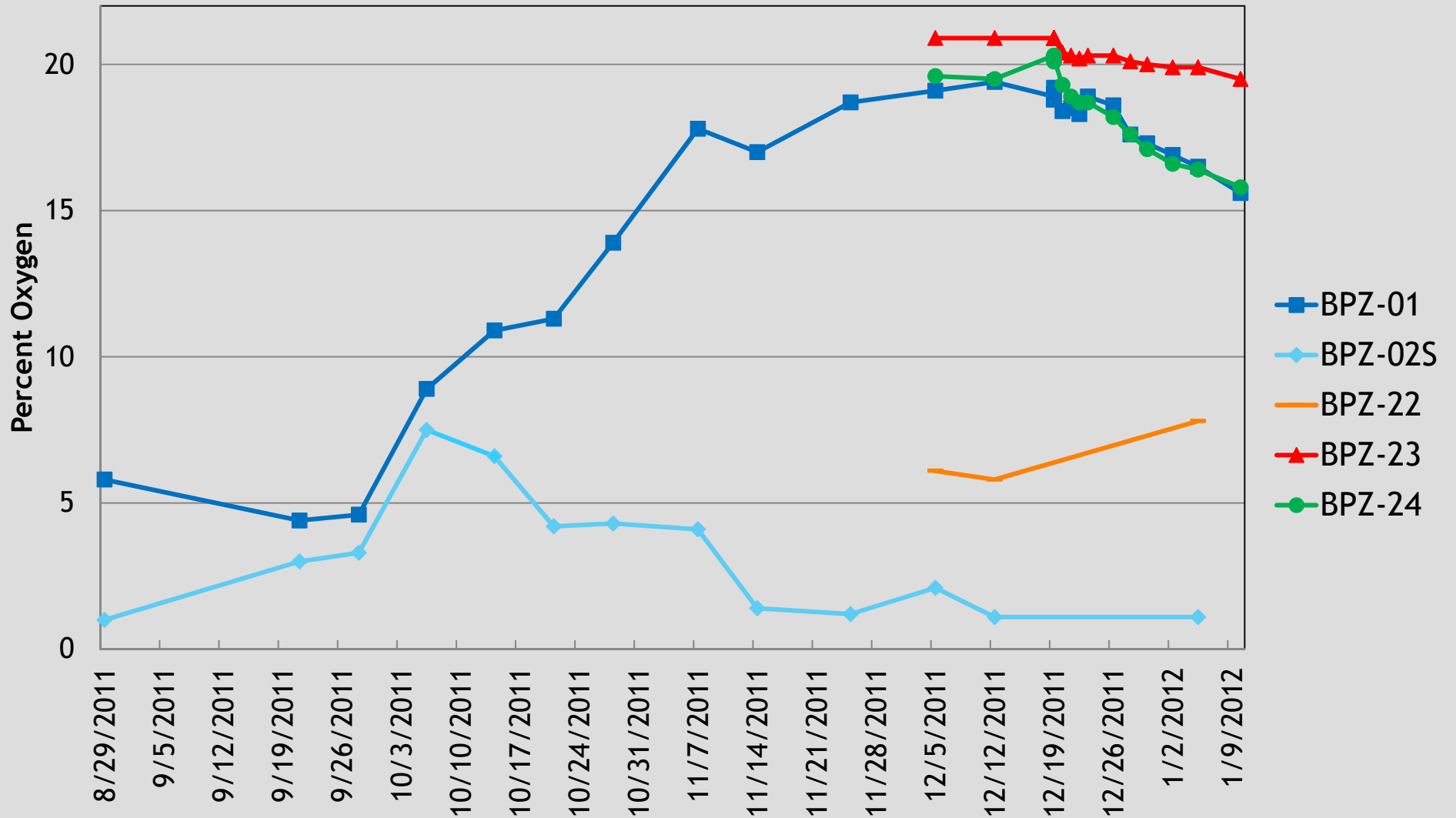


# Baseline Evaluation

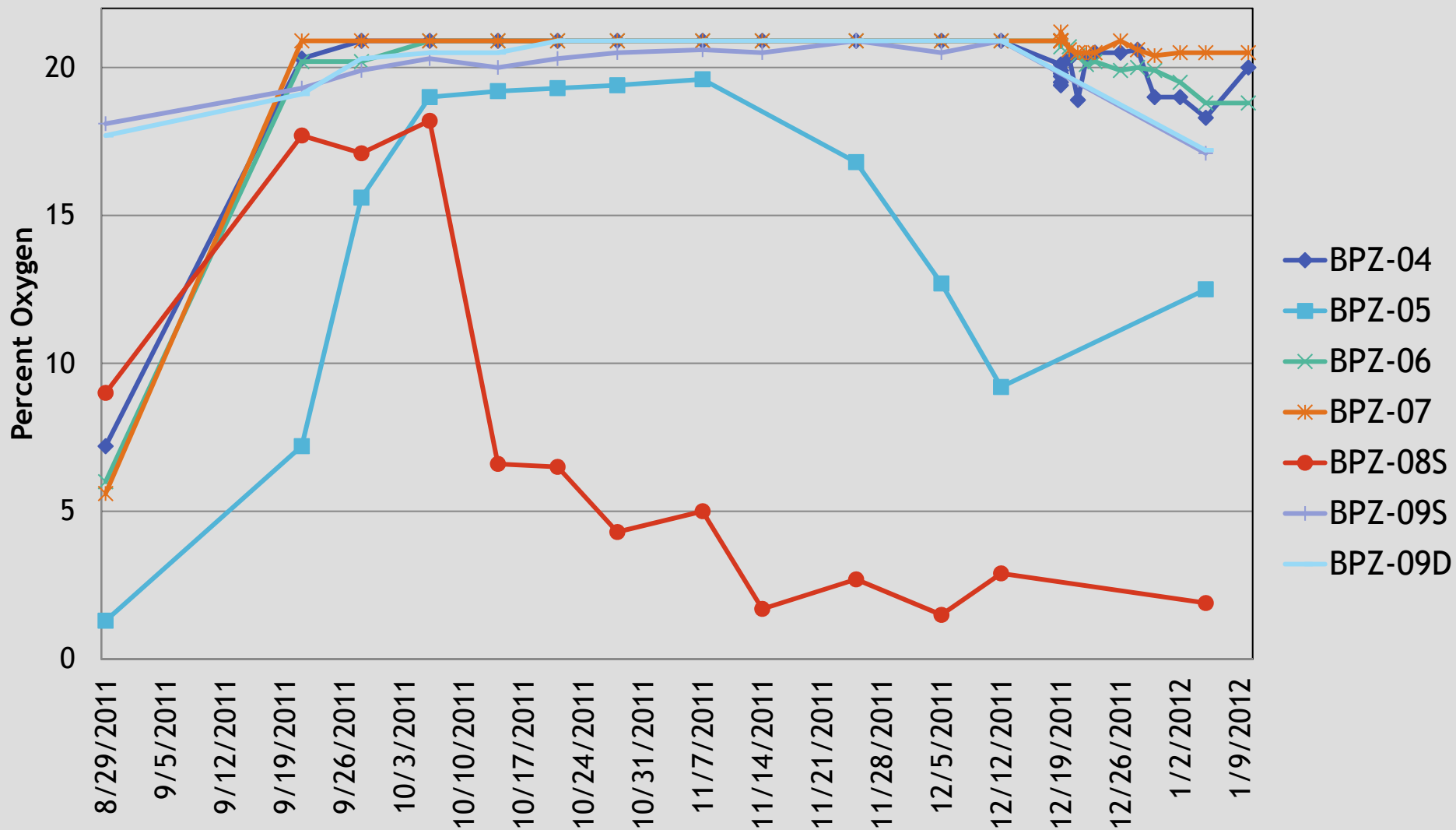
- **Baseline O<sub>2</sub> Concentrations**
  - ◆ **Active Biodegradation Areas vs Non-Active Biodegradation Areas**
- **O<sub>2</sub> vs CO<sub>2</sub> Relationship**
  - ◆ **Low O<sub>2</sub> corresponding to high CO<sub>2</sub>**
  - ◆ **High O<sub>2</sub> corresponding to low CO<sub>2</sub>**
- **Total VOCs vs O<sub>2</sub> and CO<sub>2</sub> Concentration**
  - ◆ **Distinctive patterns not apparent excepting a few locations:**
    - ◆ **BPZ-10 (high TVOCs, low O<sub>2</sub>)**
    - ◆ **BPZ-14S (low TVOCs, higher O<sub>2</sub>)**

| Location | TVOC (ppm) | CO <sub>2</sub> (%) | O <sub>2</sub> (%) |
|----------|------------|---------------------|--------------------|
| BPZ-1    | 264        | >5.0                | 5.8                |
| BPZ-2S   | 26.4       | >5.0                | 1                  |
| BPZ-2D   | NC         | NC                  | NC                 |
| BPZ-3    | NC         | NC                  | NC                 |
| BPZ-4    | 9.4        | >5.0                | 7.2                |
| BPZ-5    | 49.9       | >5.0                | 1.3                |
| BPZ-6    | 100        | >5.0                | 6                  |
| BPZ-7    | 32.5       | >5.0                | 5.6                |
| BPZ-8S   | 25.7       | >5.0                | 9                  |
| BPZ-8D   | NC         | NC                  | NC                 |
| BPZ-9S   | 29.6       | 1.78                | 18.1               |
| BPZ-9D   | 28.8       | 2.19                | 17.7               |
| BPZ-10   | 273        | >5.0                | 0.4                |
| BPZ-11S  | 61.8       | 3.96                | 16.9               |
| BPZ-11D  | 55.1       | 3.82                | 16.4               |
| BPZ-12   | 85.8       | >5.0                | 0.3                |
| BPZ-13   | 29.5       | >5.0                | 1.9                |
| BPZ-14S  | 17         | 3.72                | 16.4               |
| BPZ-14D  | NC         | NC                  | NC                 |
| BPZ-15   | 115        | >5.0                | 1.6                |
| BPZ-16   | 85.5       | >5.0                | 2.1                |
| BPZ-17S  | 25.4       | 3.51                | 17.6               |
| BPZ-17D  | NC         | NC                  | NC                 |
| BPZ-18   | 58.9       | 2.73                | 17.2               |
| BPZ-19   | 57.6       | >5.0                | 8.6                |
| BPZ-20   | 13.8       | >5.0                | 3.9                |
| BPZ-21   | 11.8       | >5.0                | 2.3                |

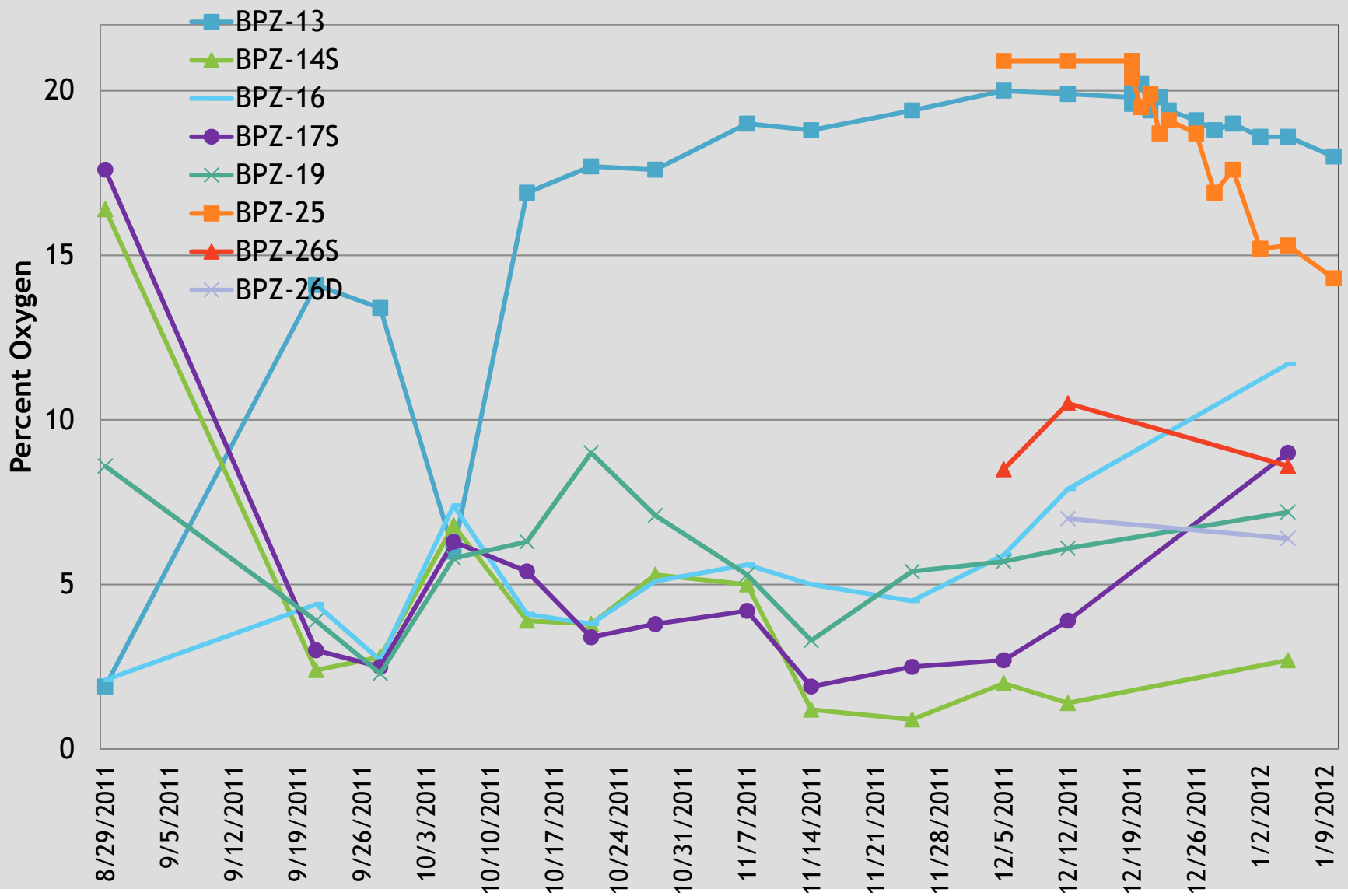
# Northern Depression Area Percent Oxygen vs Time



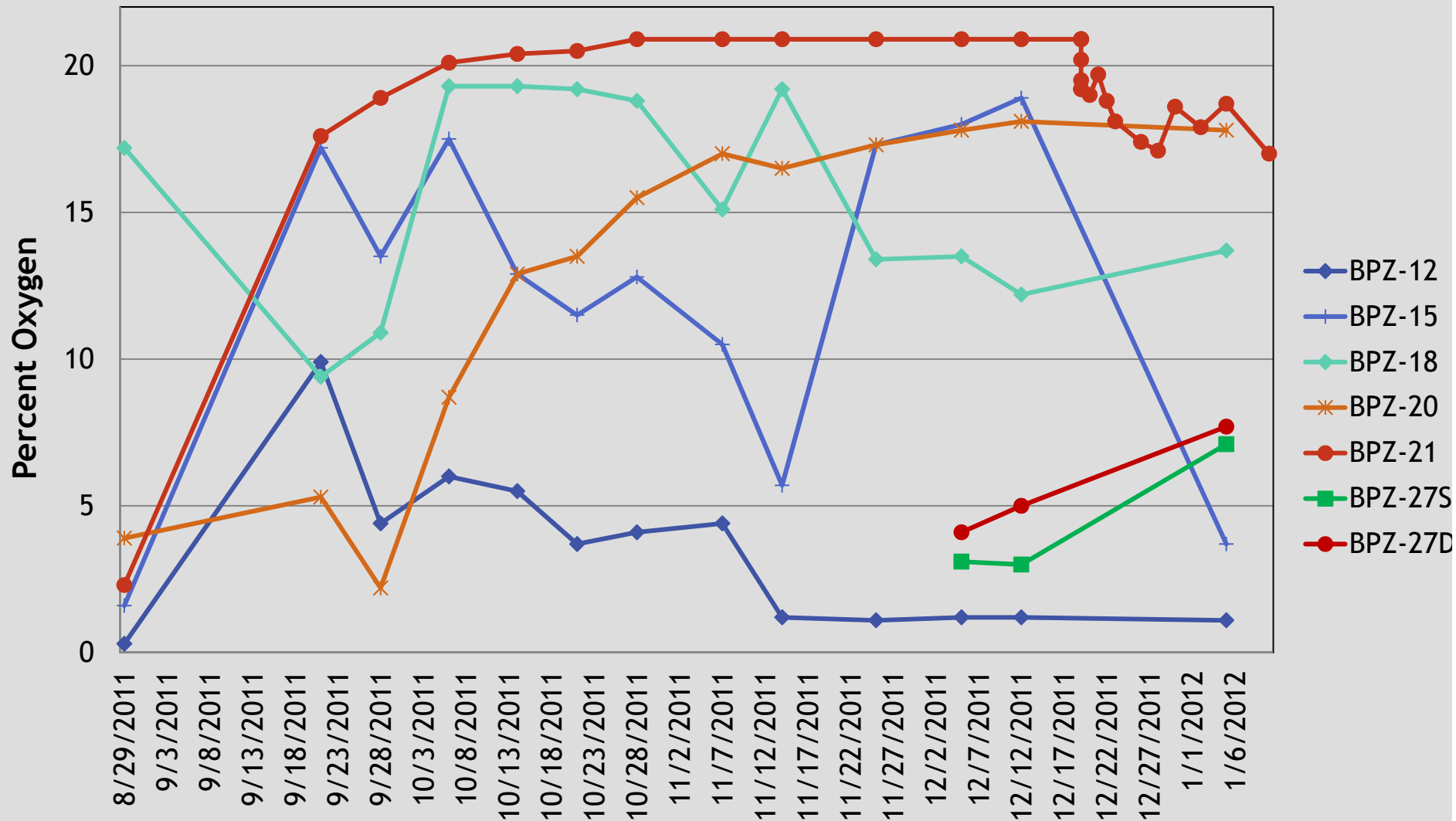
# Pond 02 Area Percent Oxygen vs Time



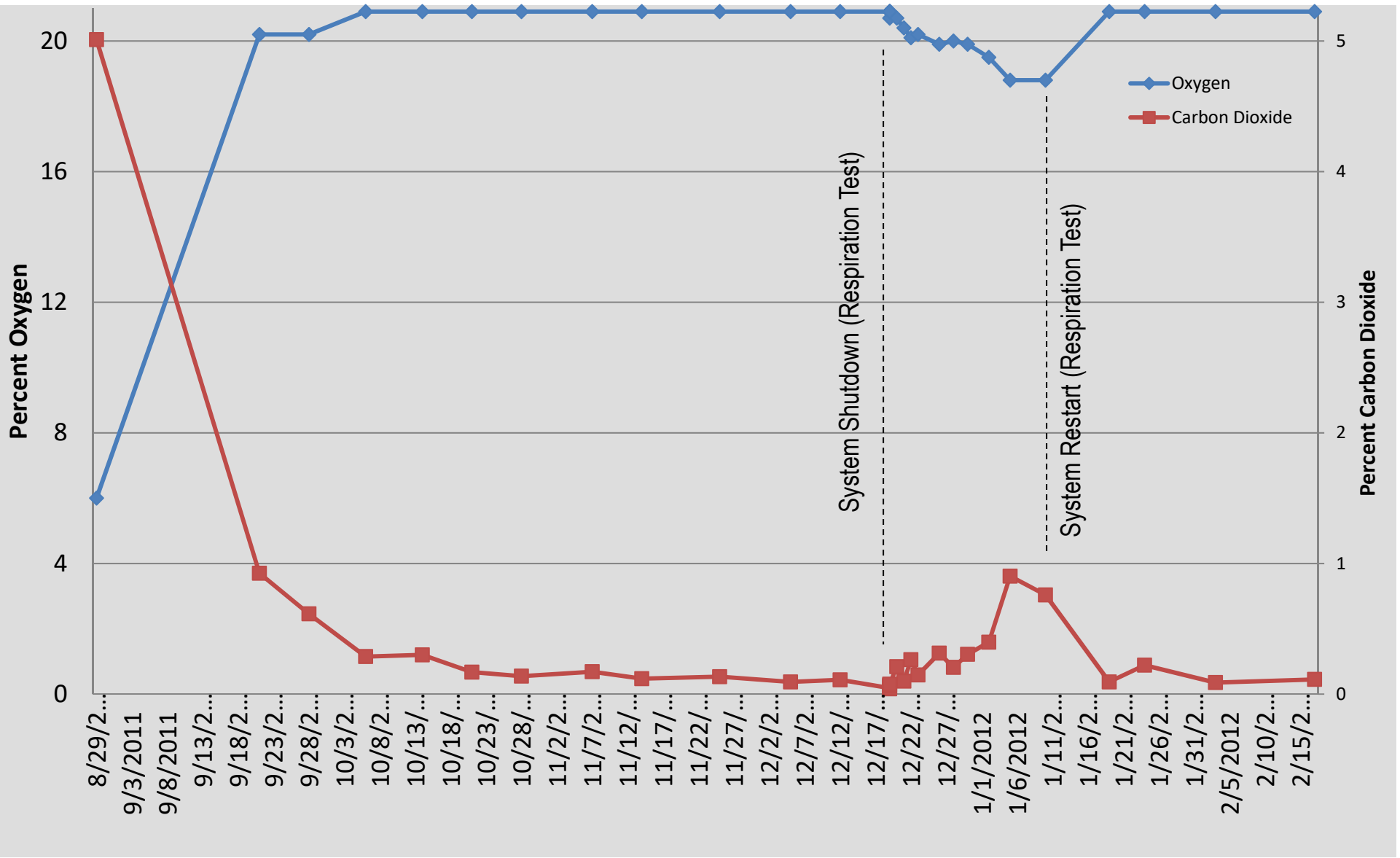
## Buried Waste Area/Pond 01 (North) Percent Oxygen vs Time



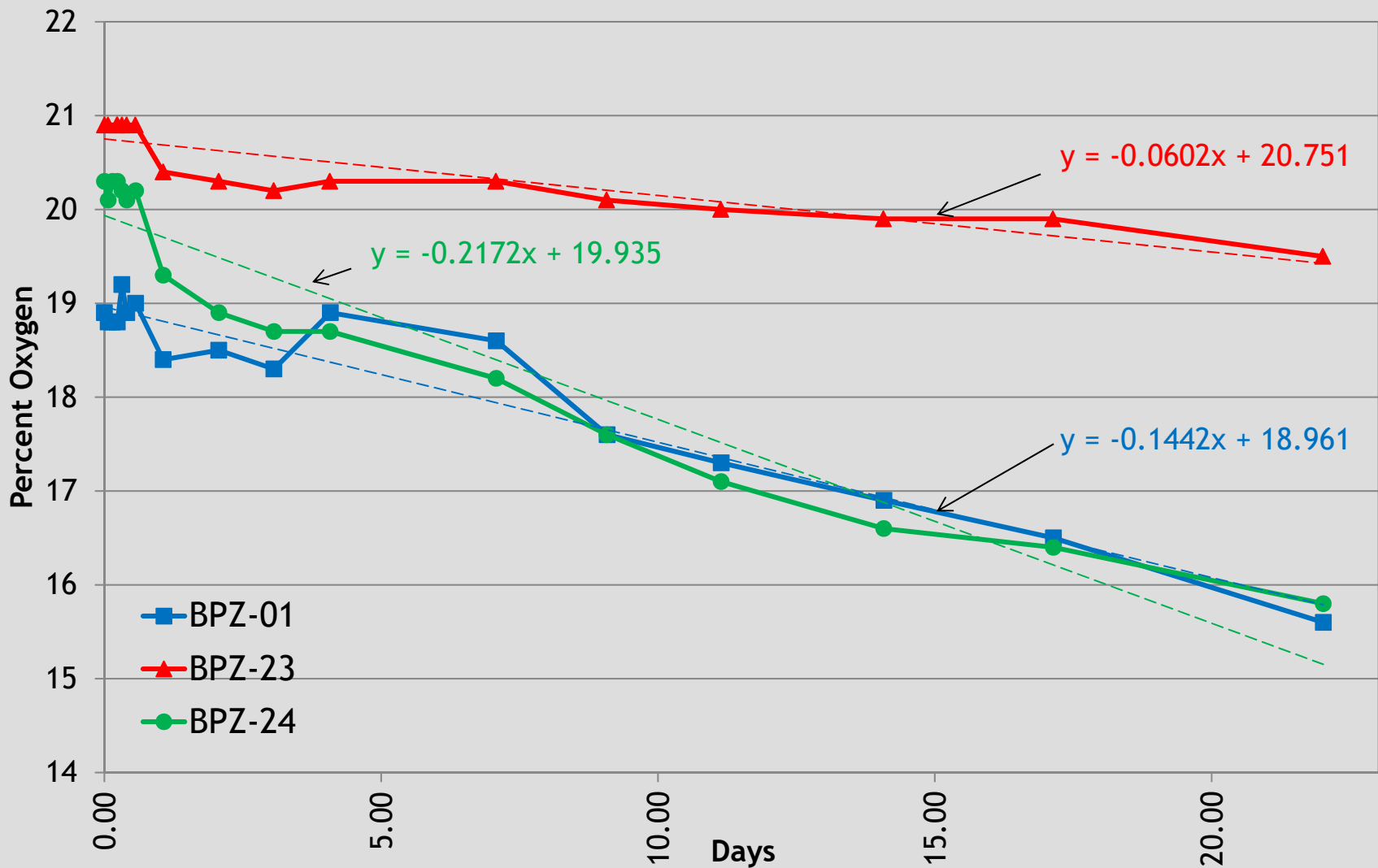
# Buried Waste Area/Pond 01 (South) Percent Oxygen vs Time



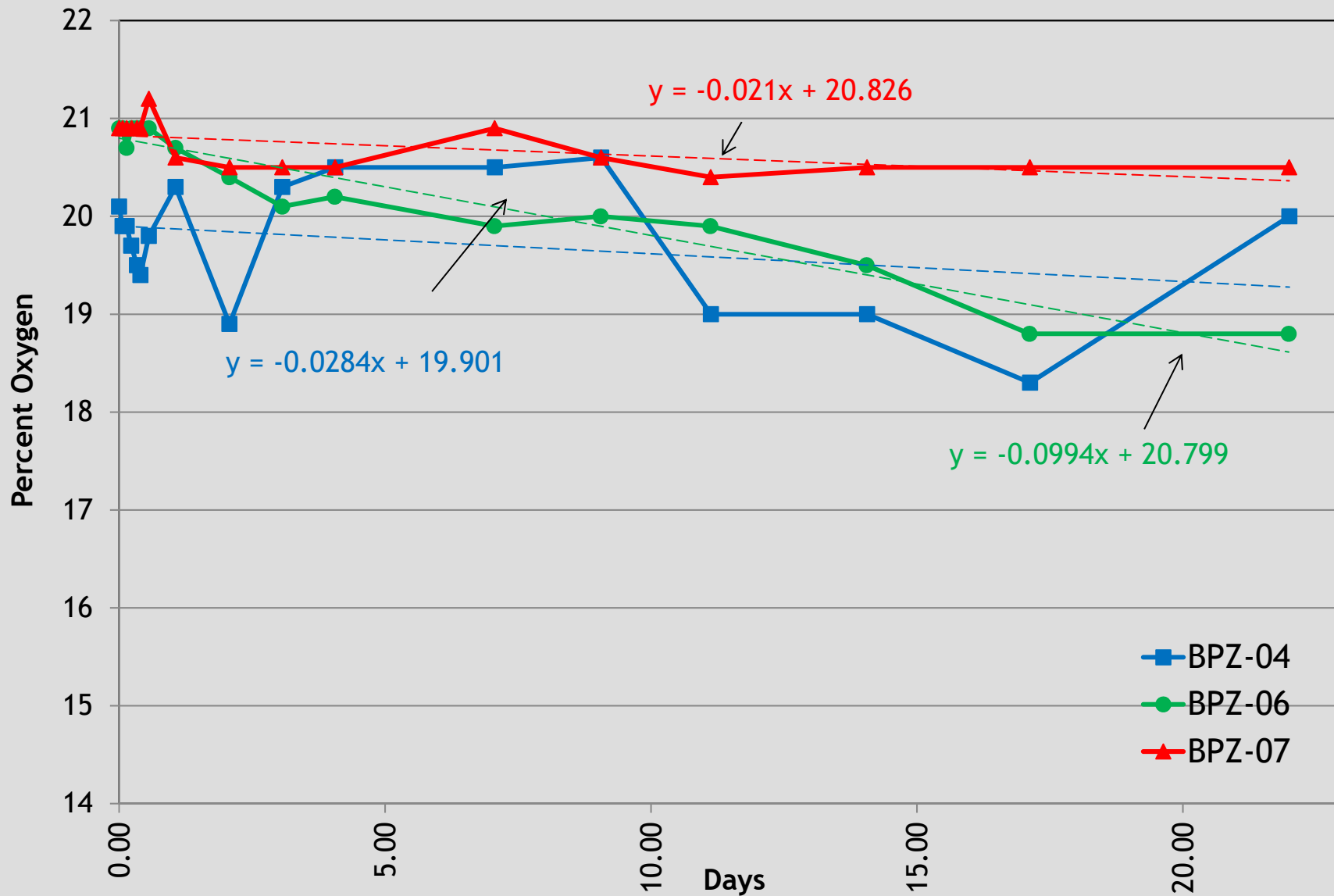
# BPZ-06 (Pond 02 Area) Percent Oxygen and Carbon Dioxide vs Time



# NDA Oxygen Utilization December 2011 Respirometry Test

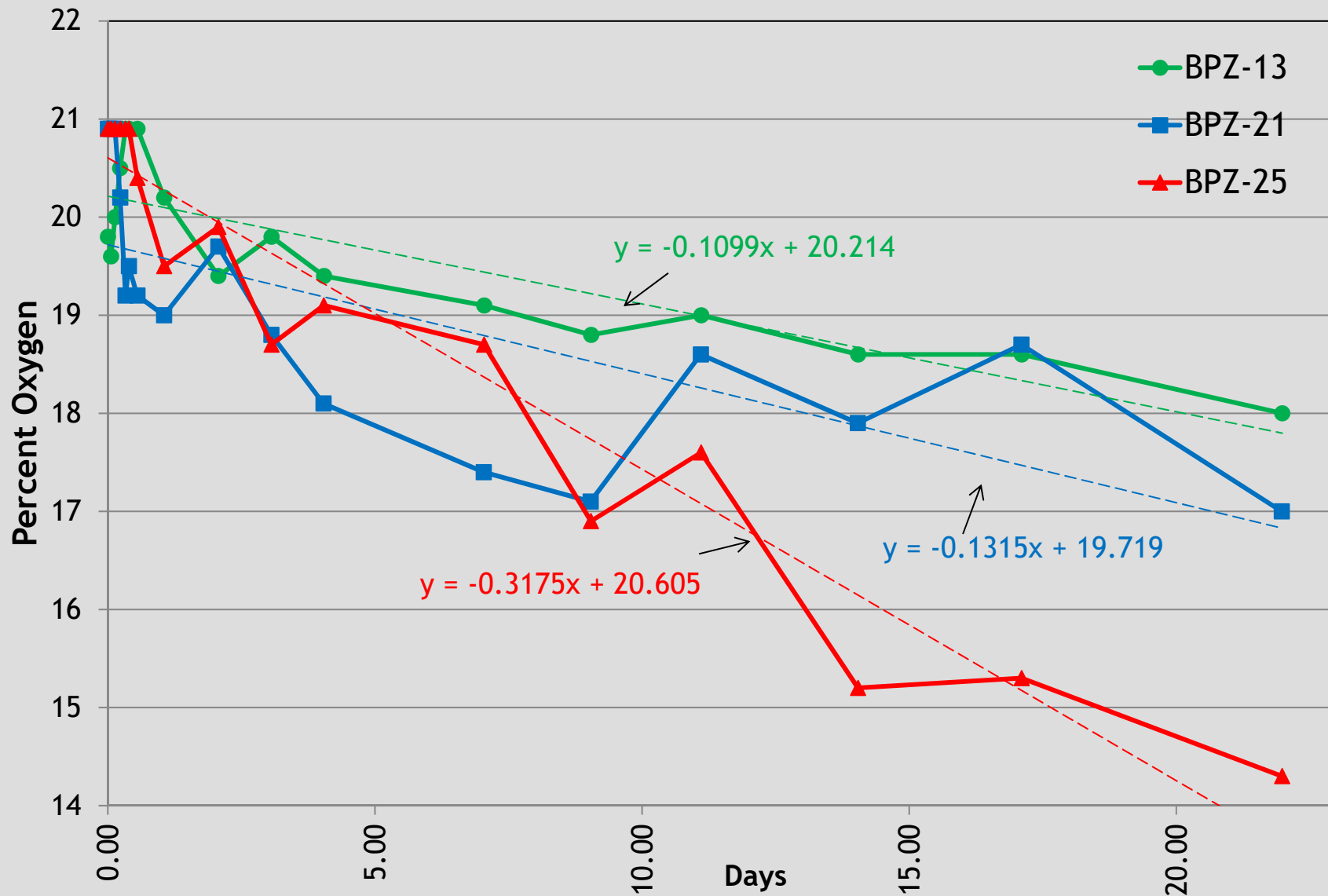


# P02 Oxygen Utilization December 2011 Respirometry Test





# BWA/P01 Oxygen Utilization December 2011 Respirometry Test



# In Situ Oxygen Utilization Rates<sup>1</sup>

|  | NDA<br>(%/day)   | PO2<br>(%/day)    | BWA/PO1<br>(North)<br>(%/day) | BWA/PO1<br>(South)<br>(%/day) | Background<br>(%/day) |
|--|------------------|-------------------|-------------------------------|-------------------------------|-----------------------|
| Range of %<br>O <sub>2</sub> Utilization<br>Rate   | -2.1 to<br>-0.03 | -2.4 to<br>-0.015 | -1.03 to<br>-0.01             | -0.95 to<br>-0.0012           | -0.56 to<br>0         |
| Average of %<br>O <sub>2</sub> Utilization<br>Rate | -0.36            | -0.22             | -0.16                         | -0.26                         | 0                     |

**Overall Average Oxygen Utilization Rate<sup>2</sup> = -0.25%/day**

1. Oxygen Utilization Rates measured from March 2014 through September 2015

2. Average Utilization Rate without background

# Site-Specific Oxygen Utilization Rate

$$k_B = \frac{-k_o}{100} \frac{\theta_a \rho_{O_2} C}{(\rho_k)}$$

where:  $k_o$  = the rate of oxygen utilization (% oxygen/day)

$\theta_a$  = the gas-filled porosity of the soil (unitless)

$\rho_{O_2}$  = oxygen density (mg/L)

$\rho_k$  = the soil bulk density (g/cm<sup>3</sup>)

$C$  = hydrocarbon to oxygen ratio (1/3.5 or .29)

$k_B$  = the rate of hydrocarbon biodegradation (mg TPH/kg soil/per day)

| $\theta_a$ | $\rho_{O_2}$ | $\rho_k$ | $C$  |
|------------|--------------|----------|------|
| 0.25       | 1300         | 1.8      | 0.29 |

|             | $k_o$        | $k_B$        |
|-------------|--------------|--------------|
| NDA         | -0.36        | -0.19        |
| PO2         | -0.22        | -0.12        |
| BWA/PO1 (N) | -0.16        | -0.08        |
| BWA/PO1 (S) | -0.26        | -0.14        |
| <b>Avg</b>  | <b>-0.25</b> | <b>-0.13</b> |

**Overall  $k_B$  = -0.13 mg Hydrocarbons (HCs)/kg soil/per day**

# Estimated Mineralized HCs

## ■ NDA

- ◆ Soil Volume = 480,000 cu ft
- ◆ Soil Mass = 20,784,000 Kg
- ◆ HCs Mineralized = 7,069 Kg

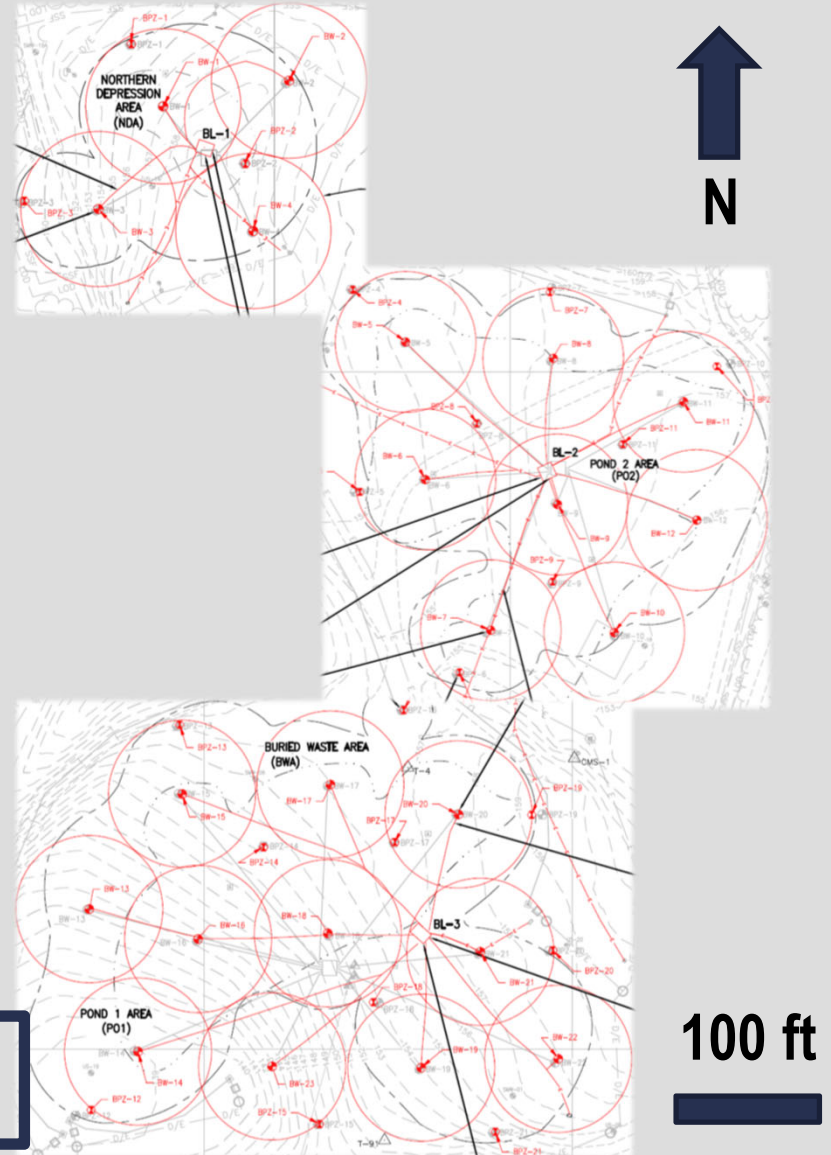
## ■ PO2

- ◆ Soil Volume = 870,000 cu ft
- ◆ Soil Mass = 37,671,000 Kg
- ◆ HCs Mineralized = 7,920 Kg

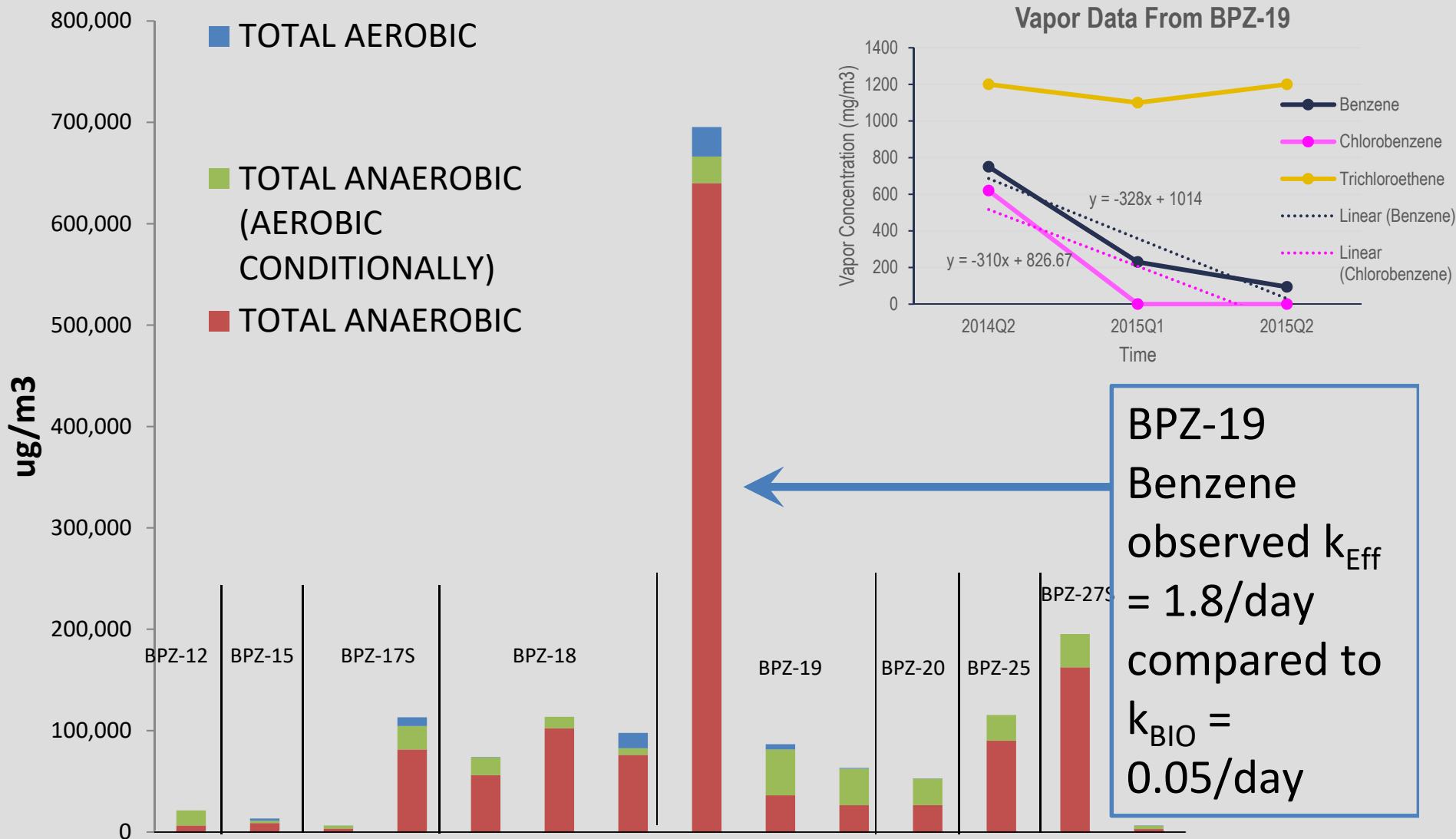
## ■ BWA/PO1

- ◆ Soil Volume = 1,050,000 cu ft
- ◆ Soil Mass = 45,465,000 Kg
- ◆ HCs Mineralized = 2,489 Kg

**Total HCs Mineralized = 17,479 Kg**



# Trends of Aerobically and Anaerobically Degradable HCs in Vapor Samples from BWA/PO1



# Conclusions

- ✓ Although Oxygen Utilization Rates are often used to empirically calculate Hydrocarbon Degradation Rates, many bioventing actions are not planned to confirm these conclusions with temporal soil and/or groundwater analytical data.
- ✓ Percent Oxygen Utilization of Hydrocarbons is expected to be low for Sites undergoing prior cleanup with thermal treatment.
- ✓ Even for homogeneous aquifer settings, *in situ* bioventing performance, as measured by Oxygen Utilization via Respirometry, can be highly variable.
- ✓ Effective decay constants ( $K_{\text{eff}}$ ), as expected, are observed to be higher than literature-based biodegradation rate constants because they incorporate additional processes including volatilization and vapor dispersion.



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