Green remediation of petroleum-impacted groundwater & soil: innovative technologies with low carbon footprints

Réhabilitation verte du pétrole-Impacté eaux souterraines et des sols: des technologies novatrices à faible émission de carbone footprints

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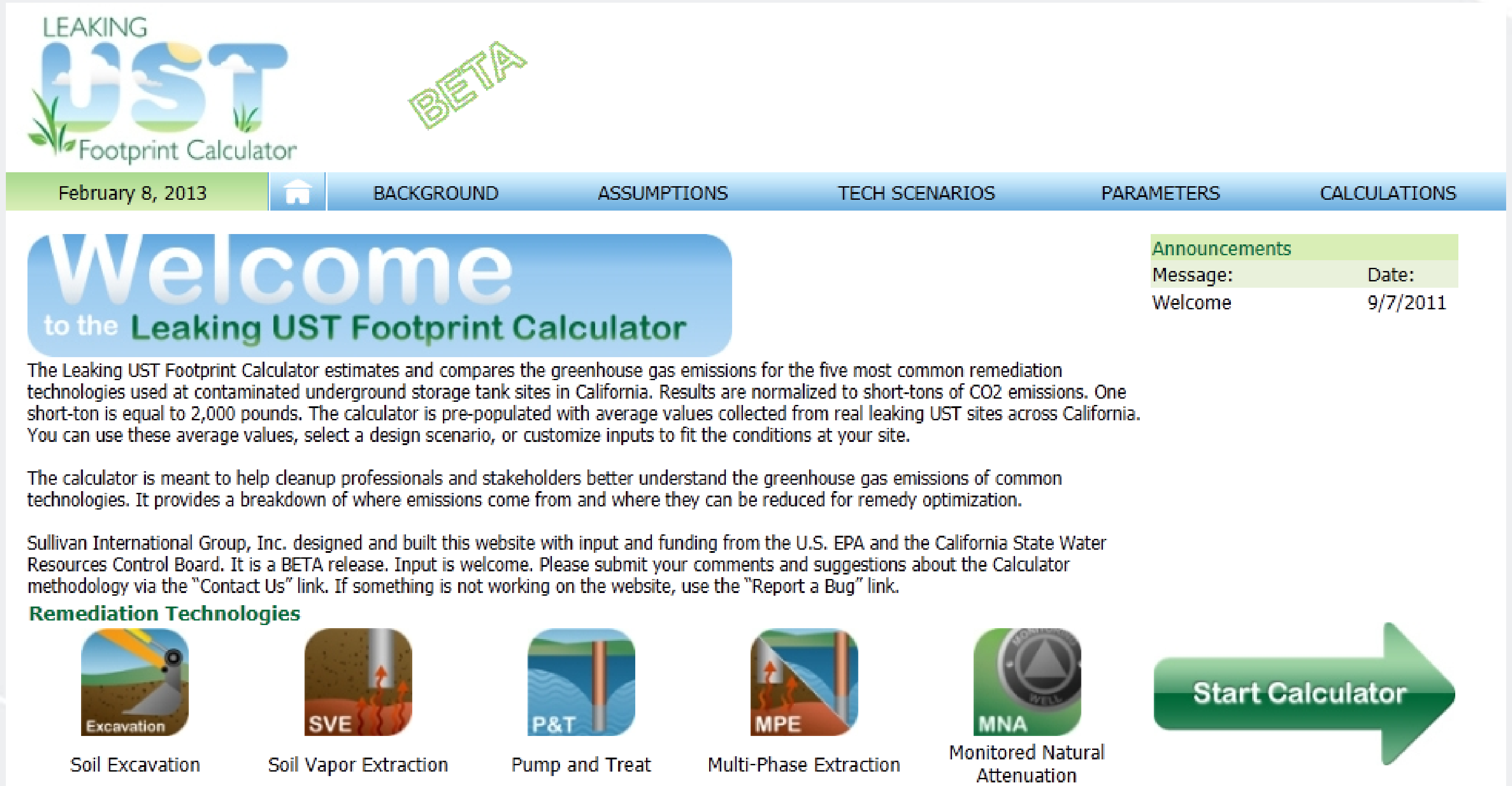
Today's presentation

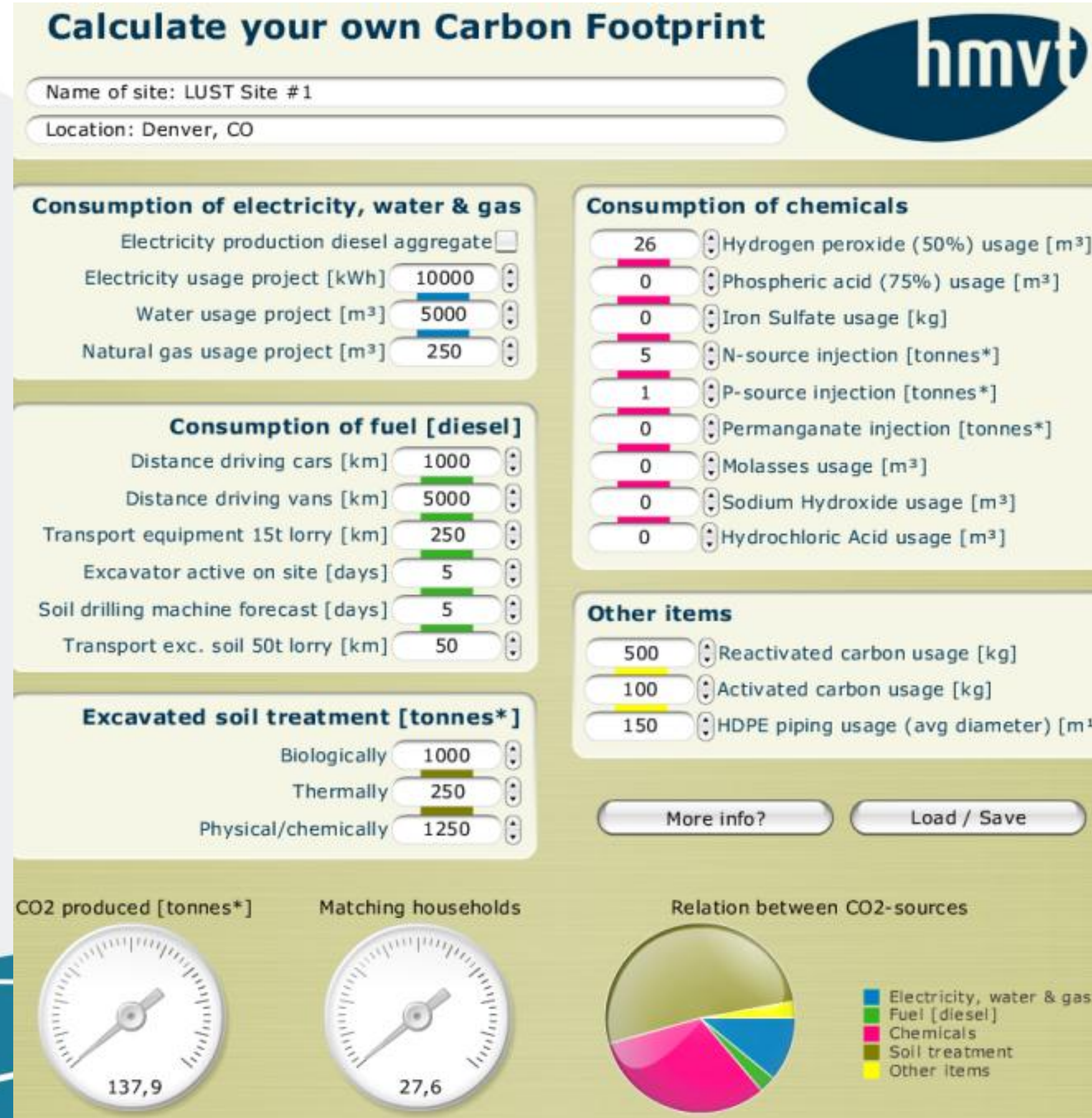
- **Green Remediation Technologies Overviews**
  - ✓ **Sulfate-Enhanced Biodegradation (SEB) Process**
    - *Utilizes sulfate-reduction biodegradation (SRB) natural attenuation processes and microbial populations to remediate petroleum hydrocarbons*
    - *Increases the in-situ concentration of the sulfate (SO_4) terminal electron acceptor through amendments of magnesium sulfate ($Mg\ SO_4$)*
  - ✓ **Enhanced Concentrating Oxygen Soil Vapor Extraction (ECO-SVE)**
    - *A remediation system which eliminates air emissions*
    - *Enhances in-situ bioremediation and extraction of volatile organic compounds (VOCs) from subsurface soils and groundwater*
  - ✓ **Carbon Footprints**

Carbon Footprint Calculators

http://www.hmvt.nl/sites/hmvt.nl/files/CO2_v0.5.swf



http://www.ustcalc.org/



Leaking Underground Storage Tank (LUST) Remediation Carbon Footprint Calculator

Leaking UST Footprint Calculator (source: US-EPA Region 9)

- Estimates and compares the greenhouse gas emissions for the <u>five most common LUST remediation technologies</u>

- Default, pre-populated average values collected from actual remediation experiences of California LUST sites.
- Results are normalized to short-tons of CO_2 emissions.

Leaking UST Footprint Calculator

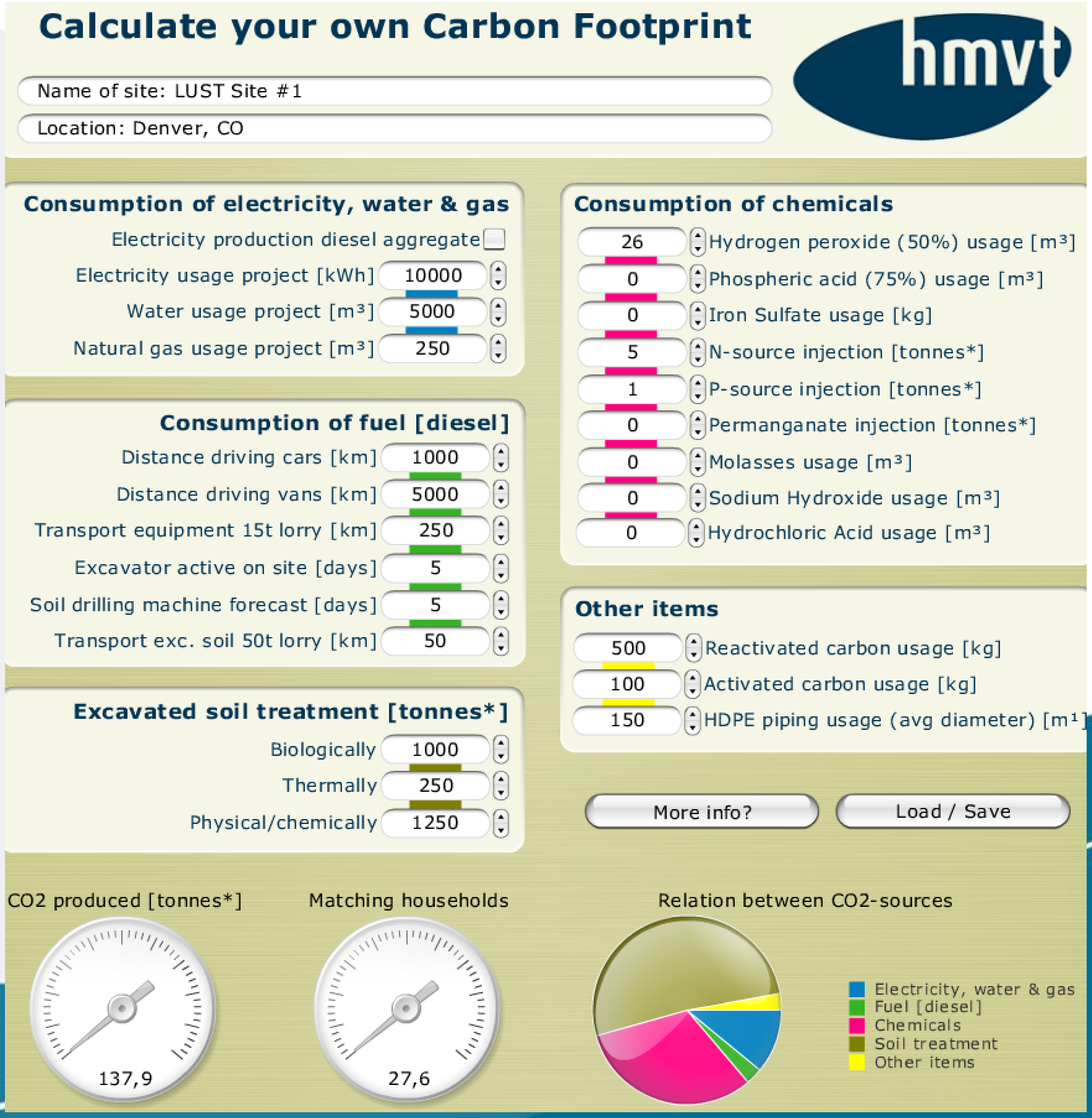
- Considers emissions that result from direct cleanup work, such as electricity generation, transportation to the site, and energy consumed treating water.

  - ✓ Does not quantify the carbon footprint of processes associated with the manufacture of materials used in the remediation technology, such as the manufacture of heavy equipment and PVC piping for monitoring wells.

HMVT Carbon Footprint Model

http://www.hmvt.nl/sites/hmvt.nl/files/CO2_v0.5.swf

- ✓ More completely quantifies the carbon footprint of materials used in the remediation technology and their manufacturing processes, such as PVC piping for monitoring wells, periodic GAC replacement, and chemical reagents.

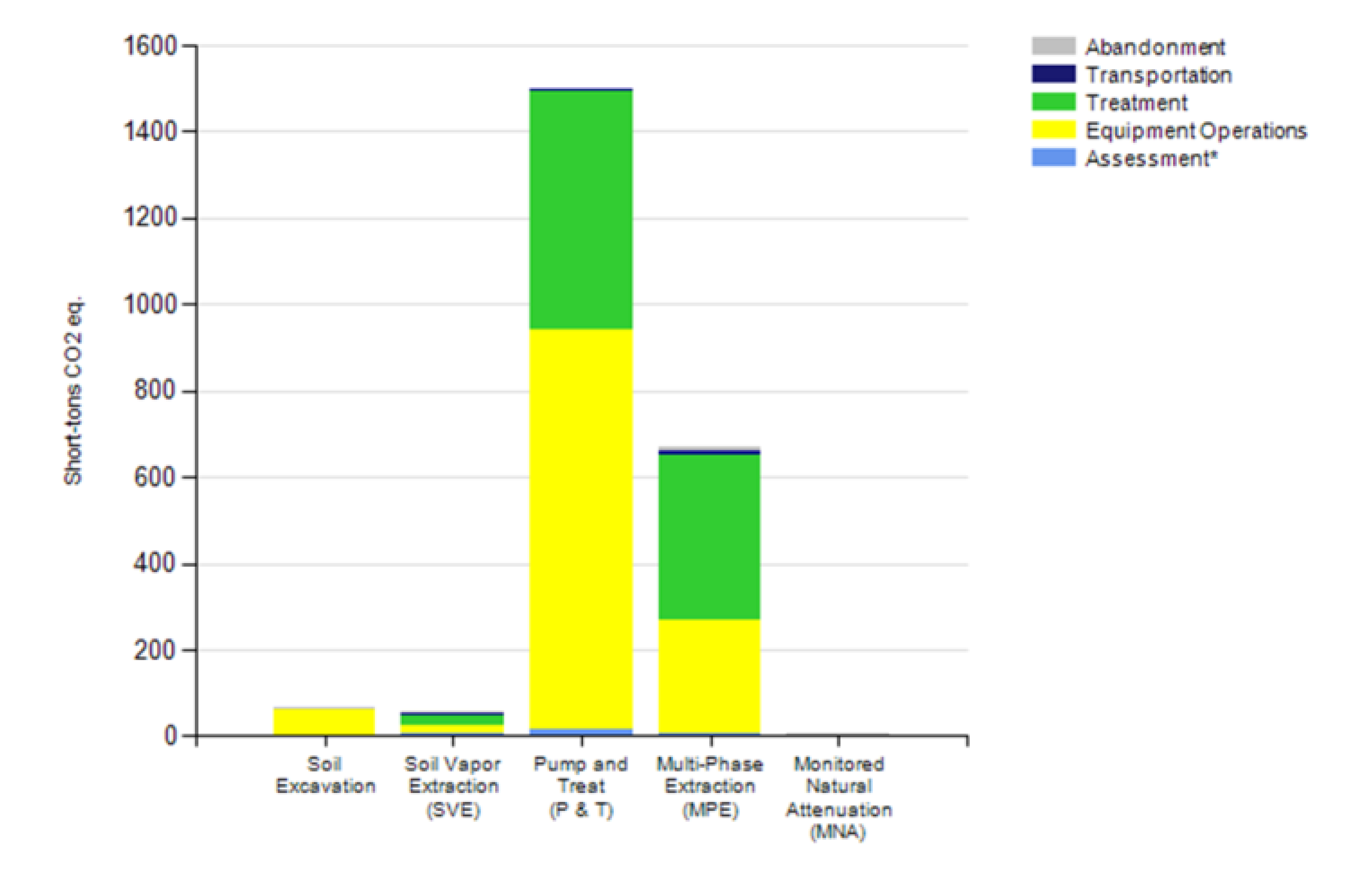


Carbon Footprint Estimations for Technologies

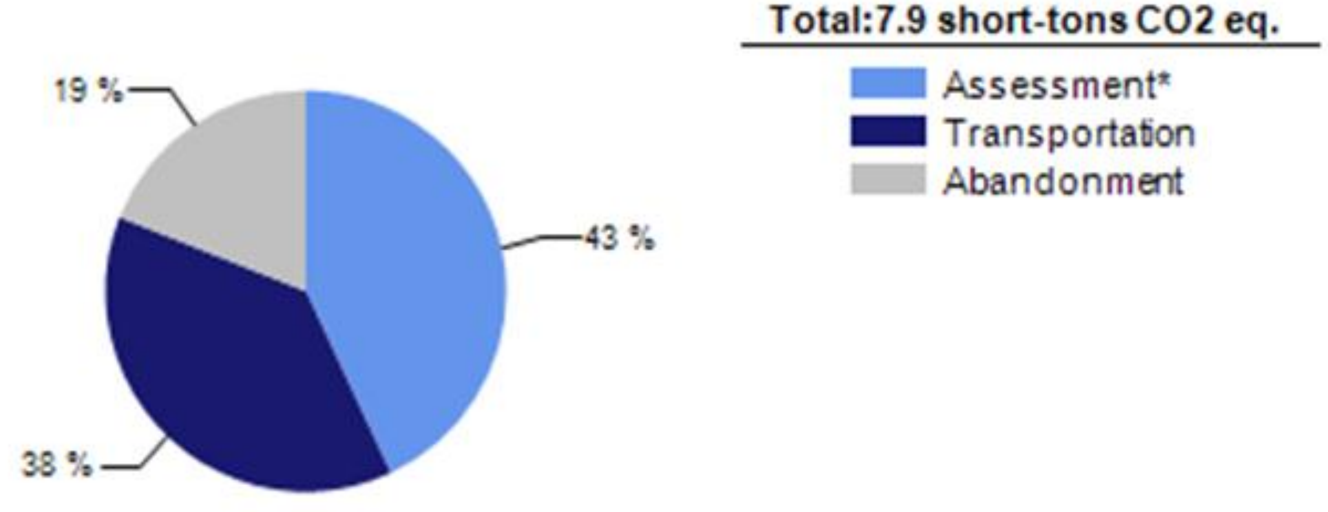
Technology	Duration	Short-tons CO2 eq.	Metric tons CO2 eq.	Cars on the road for one year	Acres of forest needed to sequester carbon
Excavation	19.4 days	70.5	64.0	12.2	0.6
ECO-SVE	**1.0 years**	**57.8**	**52.4**	10.0	0.5
P & T	6.0 years	1504.0	1364.4	260.9	12.9
MPE	3.0 years	667.7	605.7	115.8	5.7
SEB-MNA	**6.0 years**	**7.9**	**7.2**	1.4	0.1

http://www.epa.gov/cleanenergy/energy-resources/calculator.html

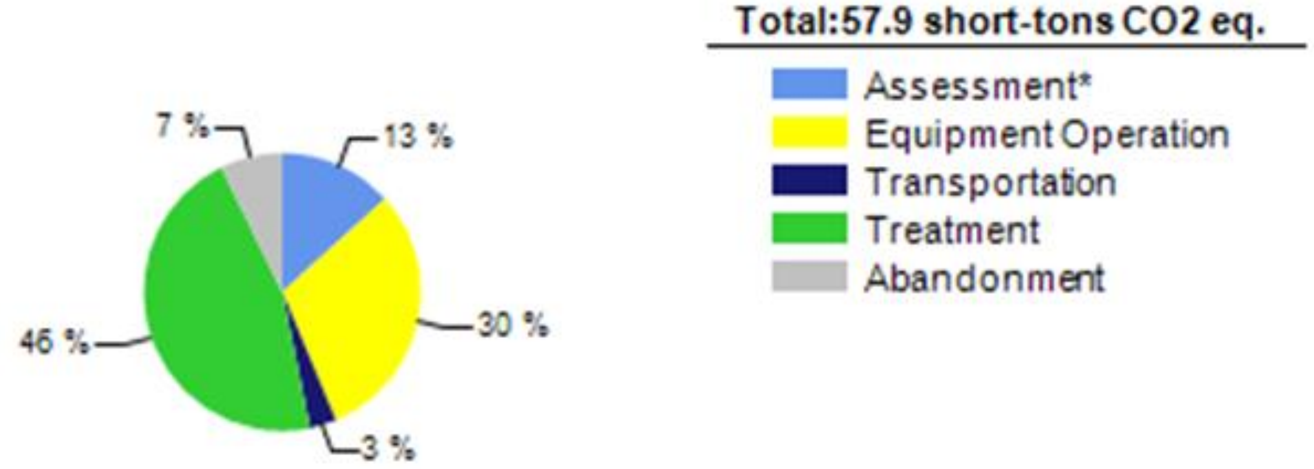
Carbon Footprint Estimations for Technologies



Sulfate-Enhanced Biodegradation - MNA



ECO - SVE



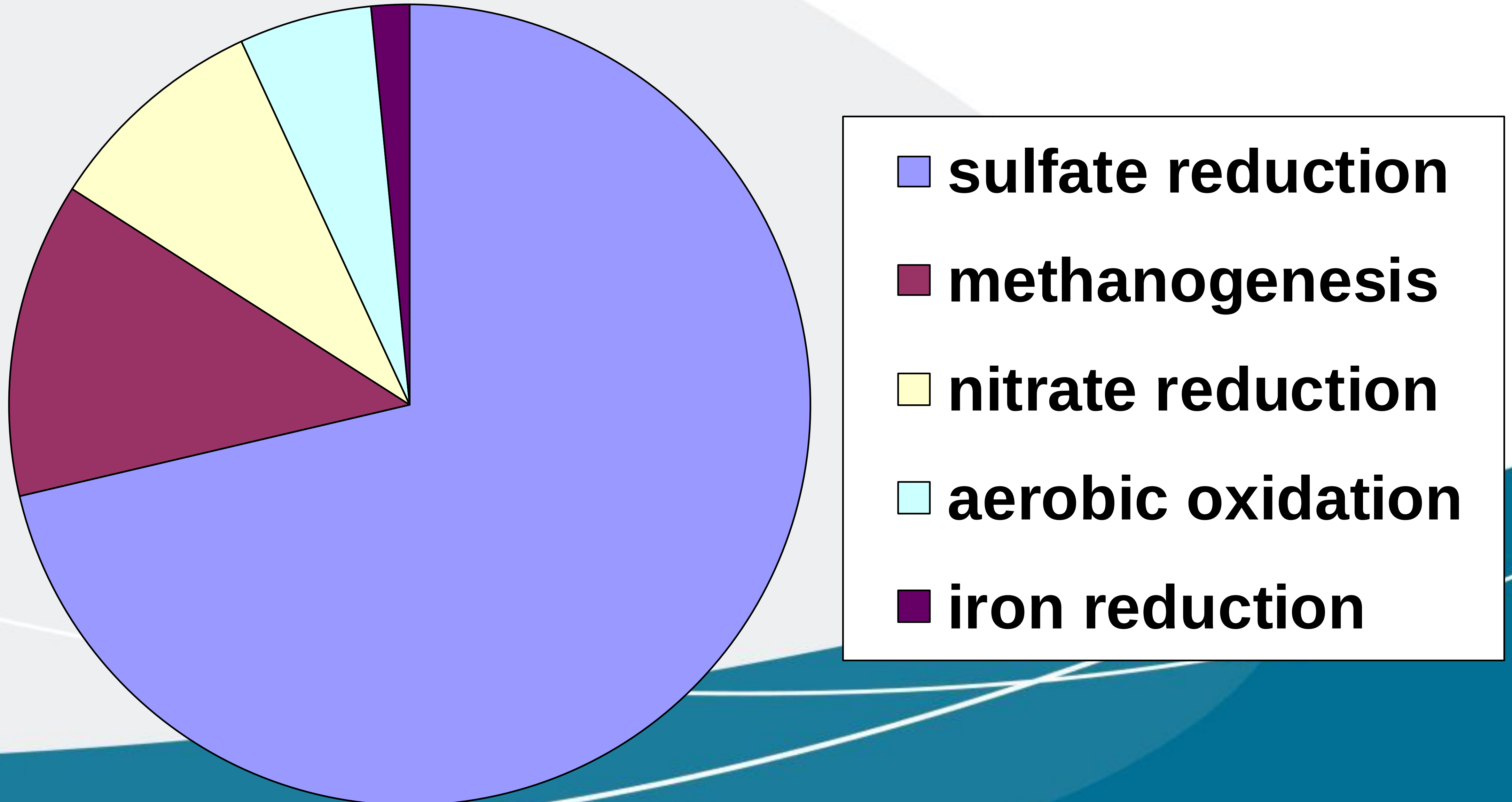
Sulfate-Enhanced Biodegradation (SEB)

- **Petroleum Hydrocarbon + $MgSO_4$ + Dissolved Iron → Iron Sulfide + H_2O + $MgCO_3$ + CO_2**
  - ✓ Iron Sulfide and Magnesium Carbonate are insoluble and immobile
  - ✓ 4.7 grams of Sulfate utilized per gram of BTEX degradation

- **US Patent 7,138,060 issued in November 2006**

Significance of Sulfate in MNA

Sulfate Reduction is the predominant electron-accepting process for monitored natural attenuation of hydrocarbons



What's really happening during MNA?

- Anaerobic processes dominate hydrocarbon natural attenuation
- Terminal electron acceptors control *in-situ* biodegradation rates
- Sulfate provides many advantages
  - ✓ High solubility
  - ✓ Low health risk
  - ✓ Economical

Process Overview

- Nearly saturated aqueous MgSO4 solution utilized
  - ✓ ~15-25% w/v
- Periodic amendments (3 to 6 month intervals)
- Applied by gravity flow
  - ✓ Ground surface applications
  - ✓ Application wells or trenches
  - ✓ Via infiltration galleries
  - ✓ Fed into former SVE wells

Sulfate Application

- Easy to apply
- Minimal health and safety risk
- Minimal site disruption

Site Selection Criteria

- Conditions inside GW plume vs. background
  - *Depleted* ***Dissolved Oxygen (DO)***
  - *Decreased* ***Nitrate (NO_3)***
  - *Elevated* ***Dissolved Iron (Fe^{2+})***
  - *Decreased* ***Sulfate (SO_4)***
- Confirm presence of Sulfate-Reducing bacteria

  - Optional line of MNA evidence

Site Selection Criteria

- Potentially useful for product sheens
- Effective within saturated zone
- Effective for petroleum hydrocarbons including BTEX, MTBE, and TBA

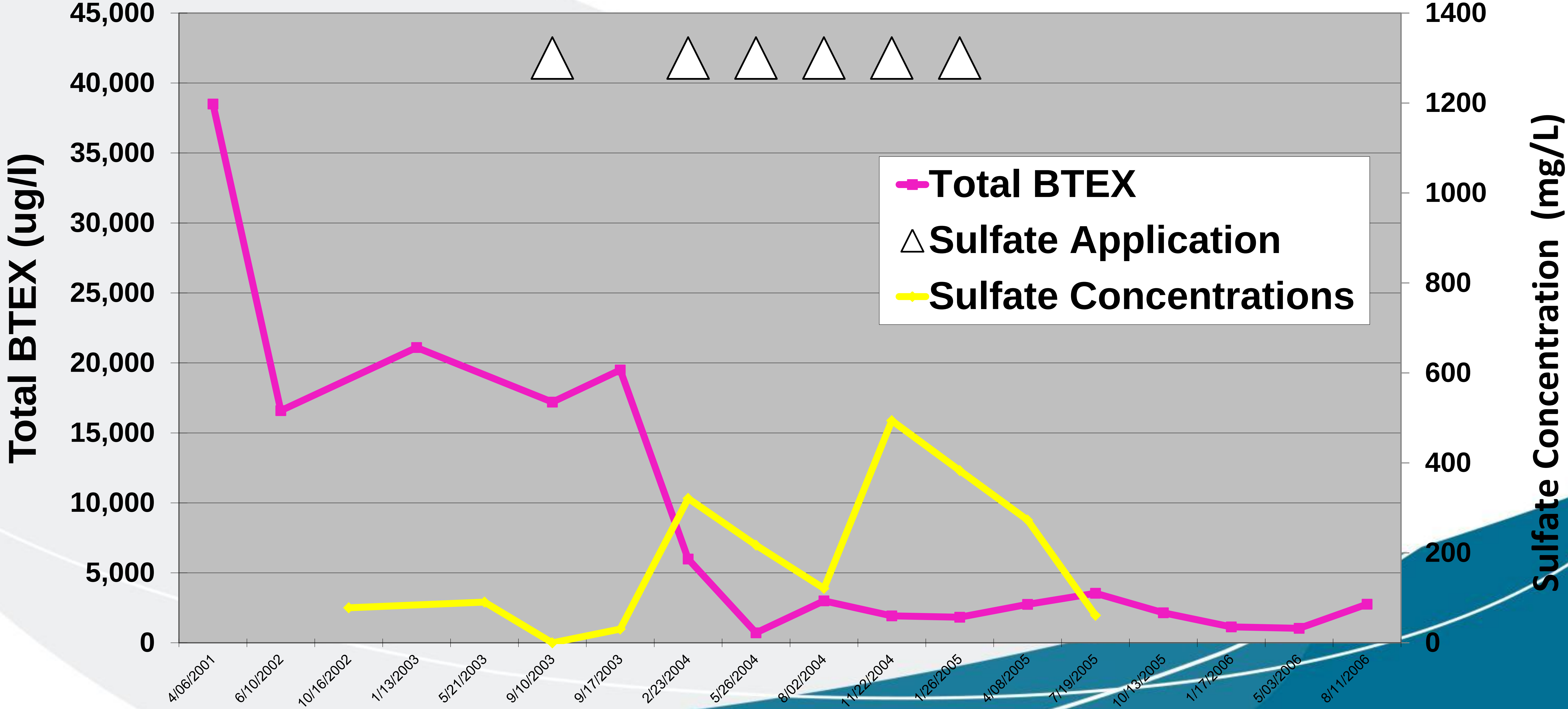
Petroleum Hydrocarbon Case Study

- Former gas station releases in 1992 and 2001
- Geology: silty clay with sand fill
- Groundwater 1 to 2 feet bgs (0,5 meter)
- LPH was last encountered in March 2003

Petroleum Hydrocarbon Case Study

- Prior remediation attempts were unsuccessful
  - *high vacuum total fluids extraction*
  - *oxygen bio-sparging*
  - *bioaugmentation*
  - *monitored natural attenuation*
- <u>Six (6) Sulfate amendments</u> were surface-applied over a two year period

Source Area Well



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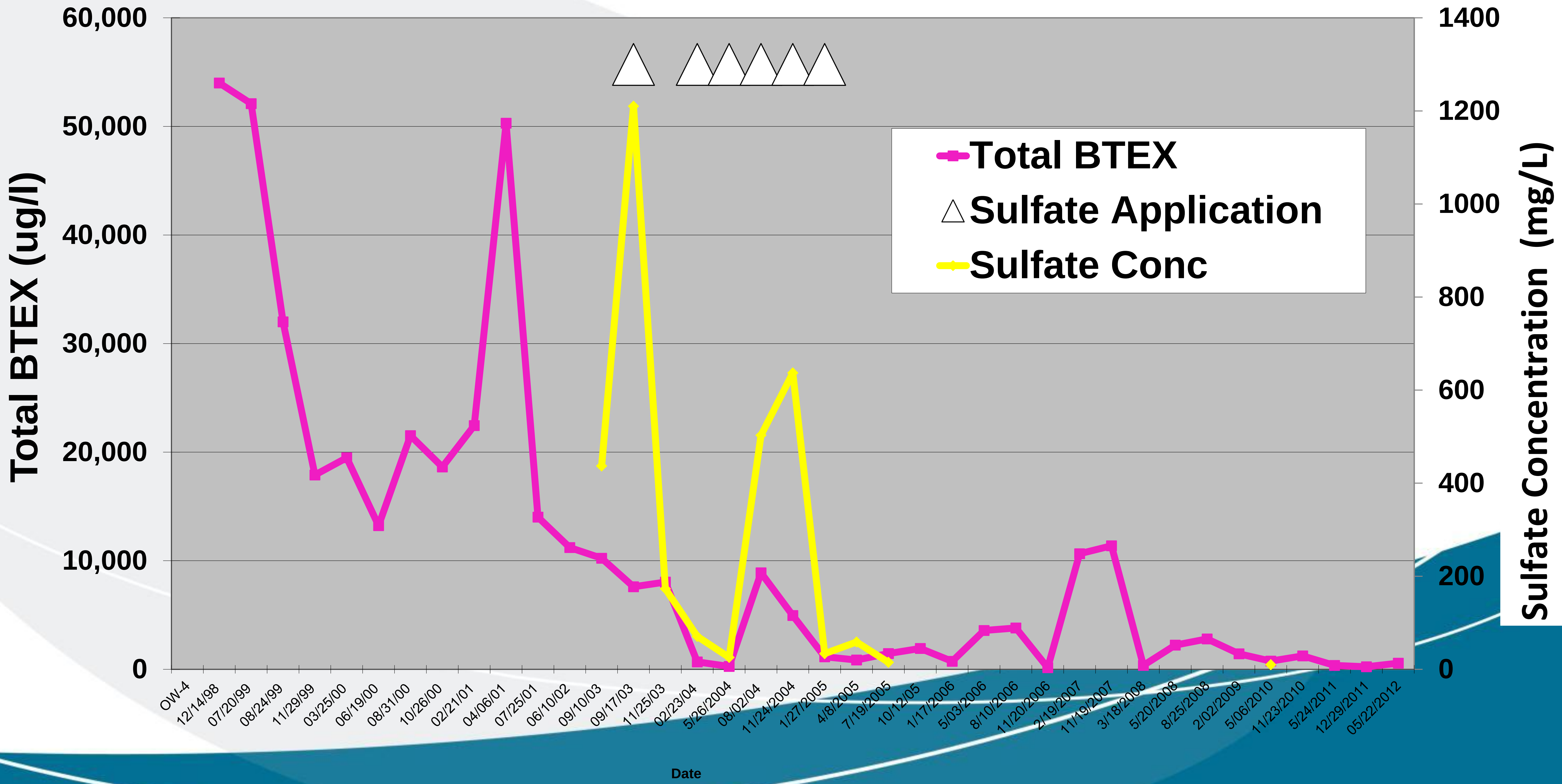
Down Gradient Well



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Common Misconceptions

- Biodegradation requires aerobic conditions
- Anaerobic Biodegradation is too slow
- Hydrogen Sulfide gas will be generated
- Sulfate solution amendments increase plume migration
- SEB produces a Sulfate ‘contaminant plume’

Advantages - Sulfate-Enhanced Biodegradation

- Naturally occurring
- High solubility
- Easily applied as an aqueous solution
- Results are surprisingly rapid
- Minimizes site disturbance
- No long term operation and maintenance

Another Green Remediation Alternative

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ECO- SVE

Enhanced Concentrating Oxygen Soil Vapor Extraction

- Remediation system which eliminates air emissions
  - ✓ no air permits needed
- Enhances extraction of VOC's from the subsurface soils and groundwater
- Stimulates *in-situ* bioremediation of subsurface groundwater and vadose soils

ECO- SVE

- Creates a slight net vacuum between the subsurface and the atmosphere by extracting more air than is injected
  - ✓ Causes atmospheric air to be drawn into the subsurface
  - ✓ Eliminates the potential for fugitive emissions

- Utilizes pressure swing adsorption to separate VOCs, Nitrogen, Oxygen and Carbon Dioxide into separate vapor streams
  - ✓ Re-injected oxygen enhances the bioremediation process

ECO- SVE

- O_2 is injected into the impacted areas (GW or vadose) to enhance aerobic bioremediation
  - ✓ Air stripping (volatilization) benefit, but not a primary driver
- N_2 and CO_2 can be injected to create anaerobic conditions
- Goal is not to extract, the goal is to make a gentle circulatory system that primarily destroys contaminants *in-situ*
  - ✓ Mass removal by SVE occurs, but adds cost

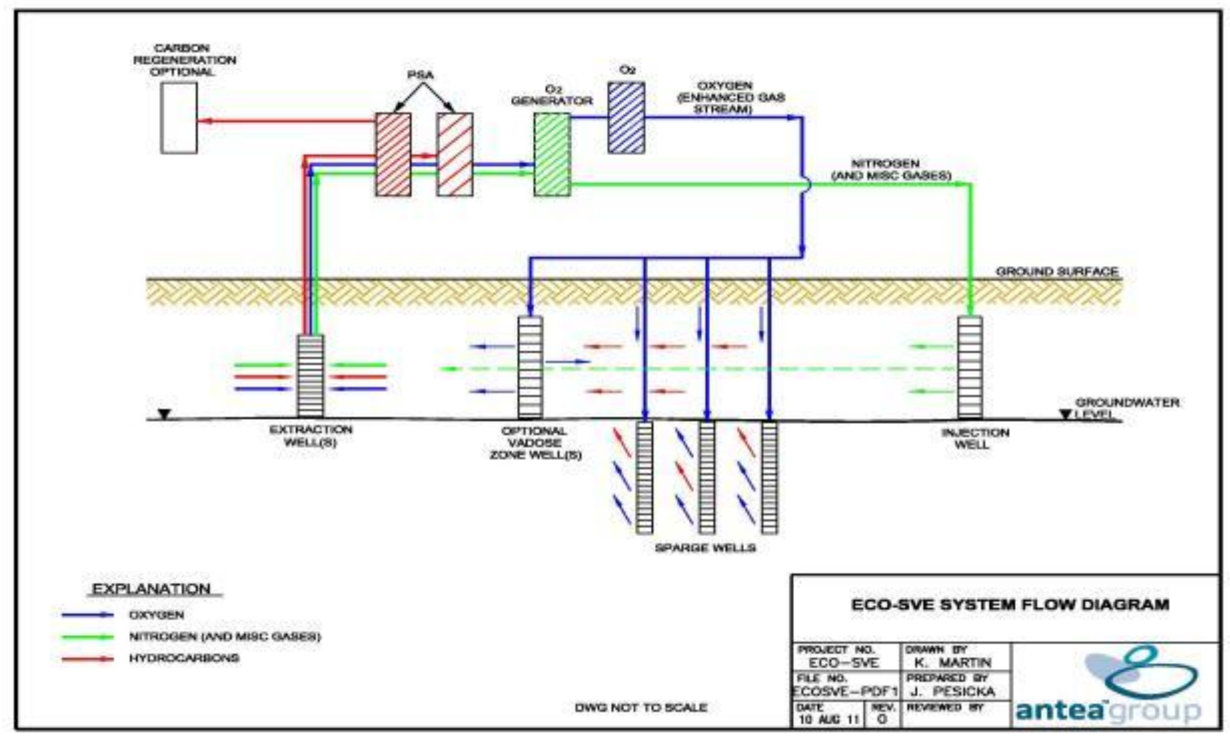
Key Components

- Vapor Extraction Pump
- Injection Pump (may be same as above)
- Pressure Swing Adsorbers (may be more than one adsorbent type)
- Optional - VOC and Water Condenser
- Water and liquid transfer pumps as necessary
- Extraction and Injection wells

Process Description

- VOC's/Gases extracted from subsurface
- All Vapors enter pressure swing absorber (PSA)
- VOC's, N_2, CO_2, O_2 adsorbed in or passed through each PSA, based on desired configuration
- VOC's, desorbed and condensed along with water (additional equipment required)
- Other gases re-injected

- **US Patent 8,210,772 issued July 2012**



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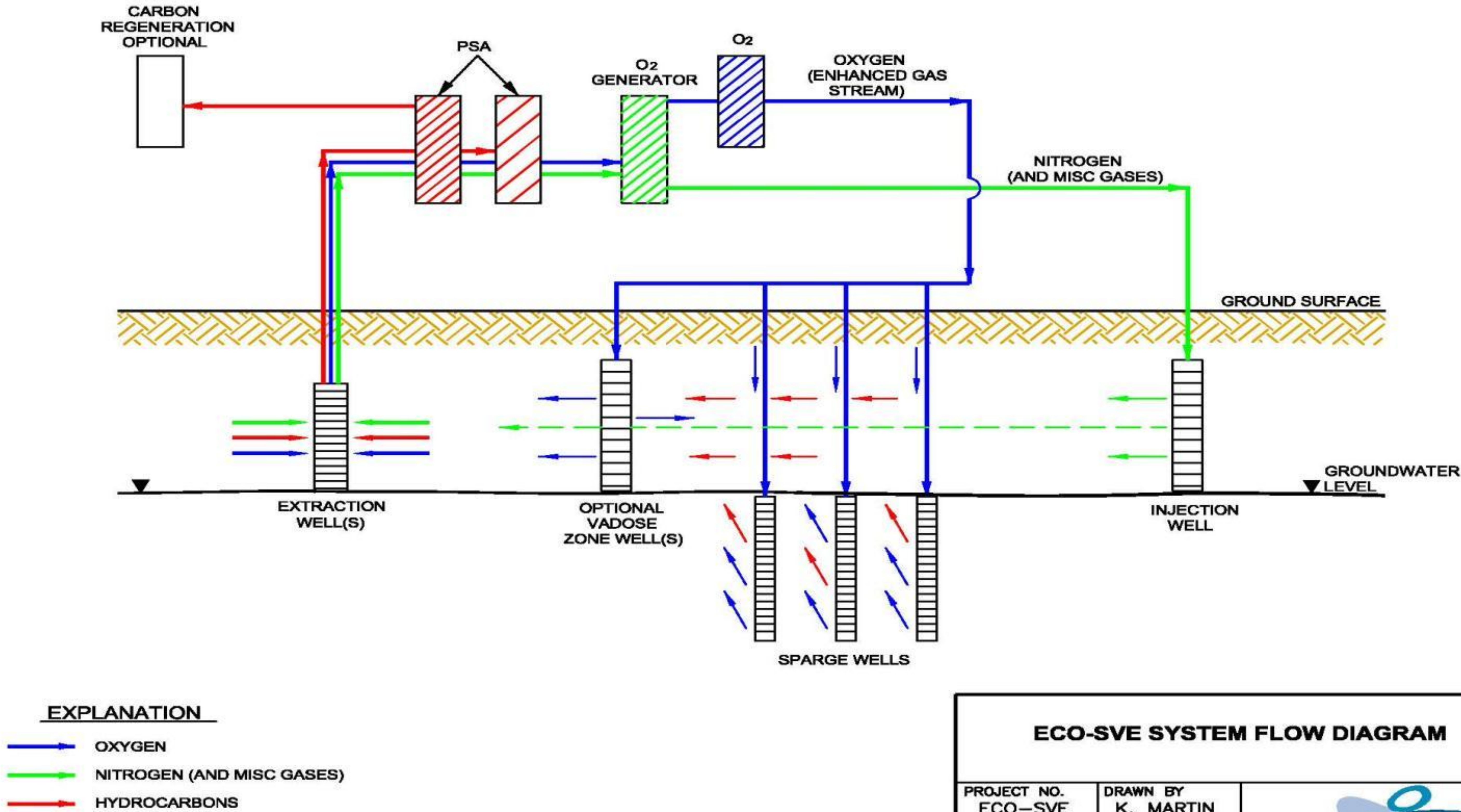


DWG NOT TO SCALE

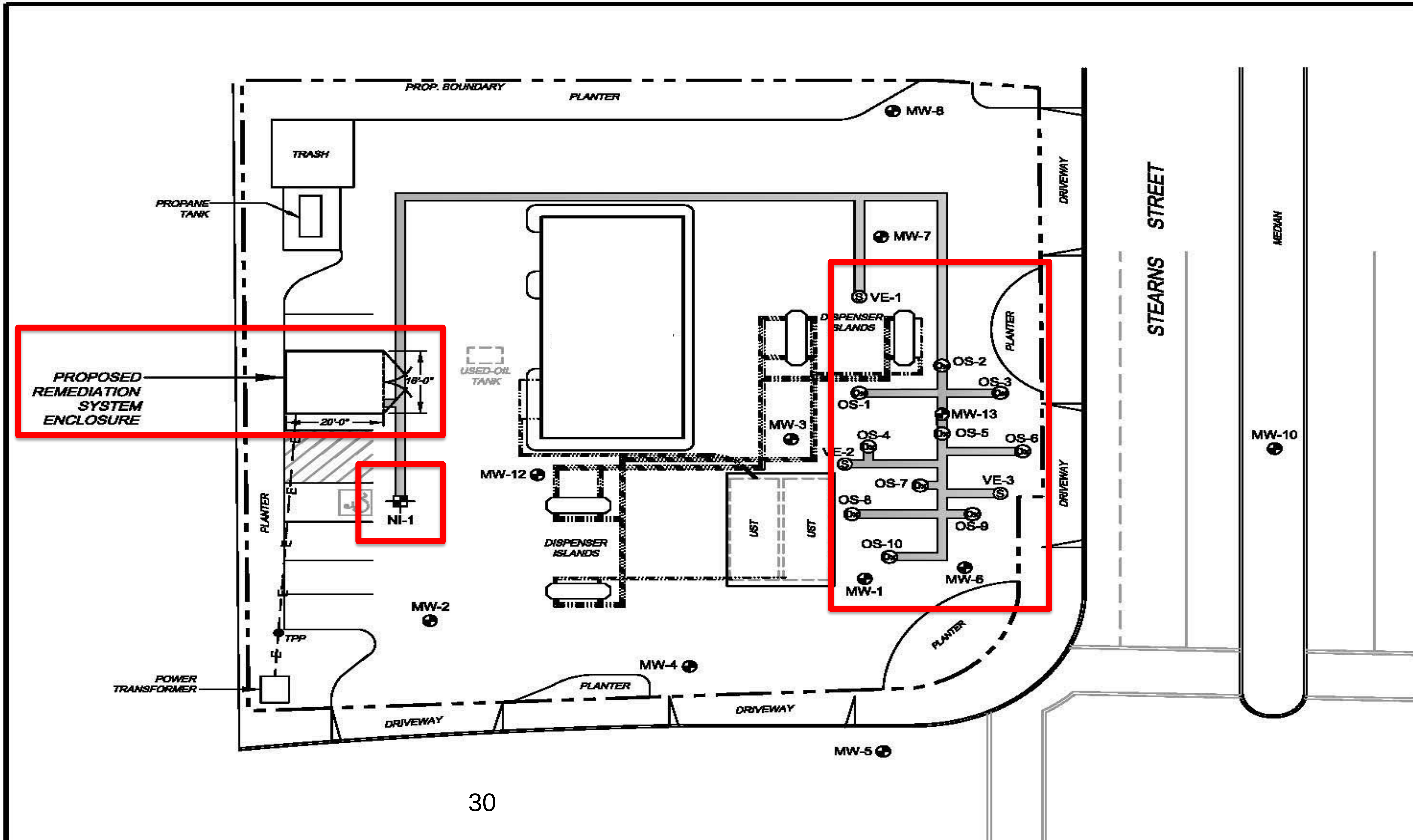
ECO-SVE SYSTEM FLOW DIAGRAM

PROJECT NO.		DRAWN BY
ECO–SVE		K. MARTIN
FILE NO.		PREPARED BY
ECOSVE–PDF1		J. PESICKA
DATE	REV.	REVIEWED BY
10 AUG 11	0	

antea group

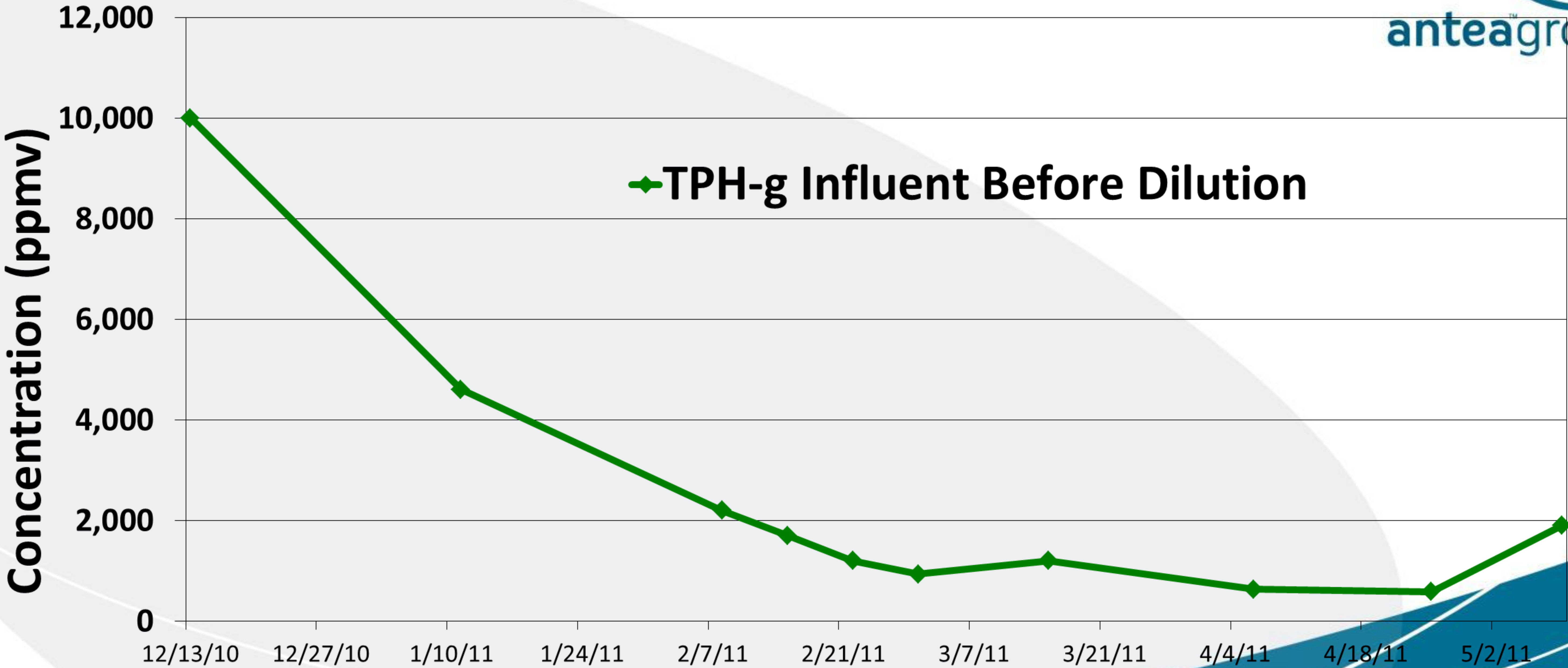
Case Study

- Hydrocarbon (gasoline range) impacted site
  - ✓discovered 1989
- Southern California
- Impacted soil and groundwater
- Depth to water 45 feet (13 m)
- Geology – silty sand/sand
- Impacts on site

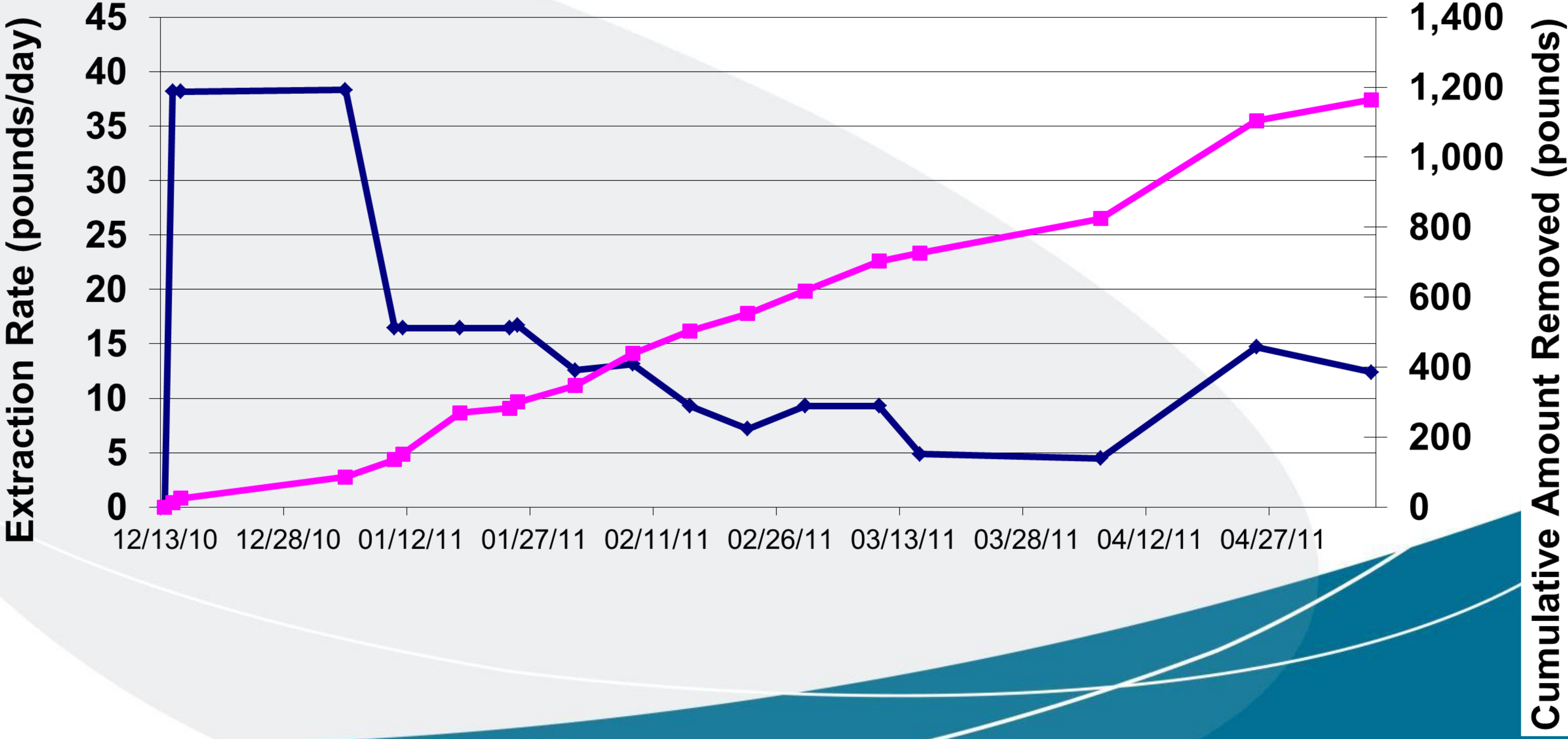


PROP. BOUNDARY
PLANTER
MW-8
TRASH
PROPANE TANK
MW-7
VE-1
DISPENSER ISLANDS
PLANTER
DRIVEWAY
STEARNS STREET
MEDIAN
PROPOSED REMEDIATION SYSTEM ENCLOSURE
16'-0"
20'-0"
USED-OIL TANK
OS-2
OS-3
OS-1
MW-13
MW-3
OS-4
OS-5
OS-6
VE-2
MW-10
MW-12
NI-1
OS-7
VE-3
OS-8
OS-9
PLANTER
DISPENSER ISLANDS
UST
UST
DRIVEWAY
OS-10
MW-1
MW-6
MW-2
TPP
PLANTER
POWER TRANSFORMER
MW-4
PLANTER
DRIVEWAY
DRIVEWAY
MW-5

Vapor Concentration - Extraction



Mass Removal – Extraction Only



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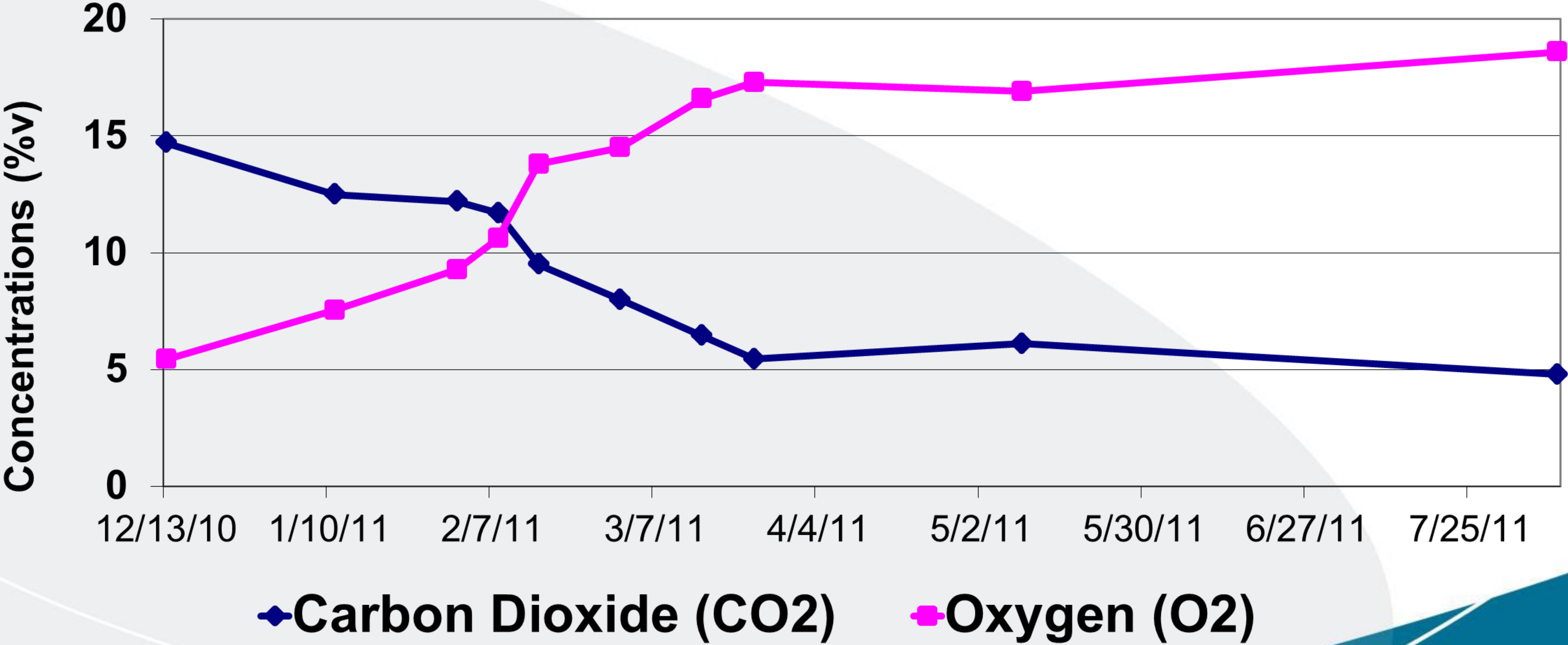
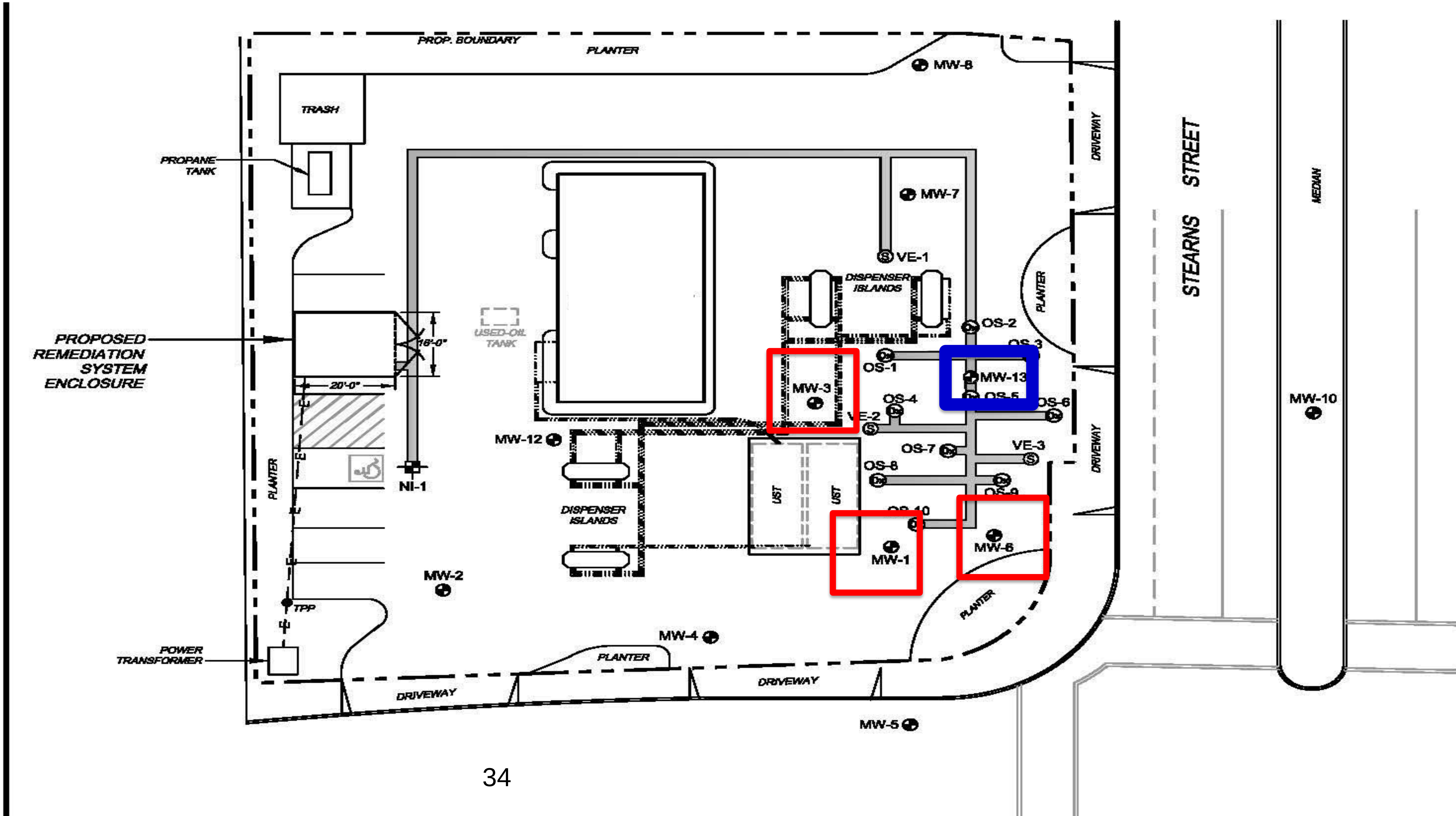
TPH – Extraction Rate ... TPH – Cumulative Removed

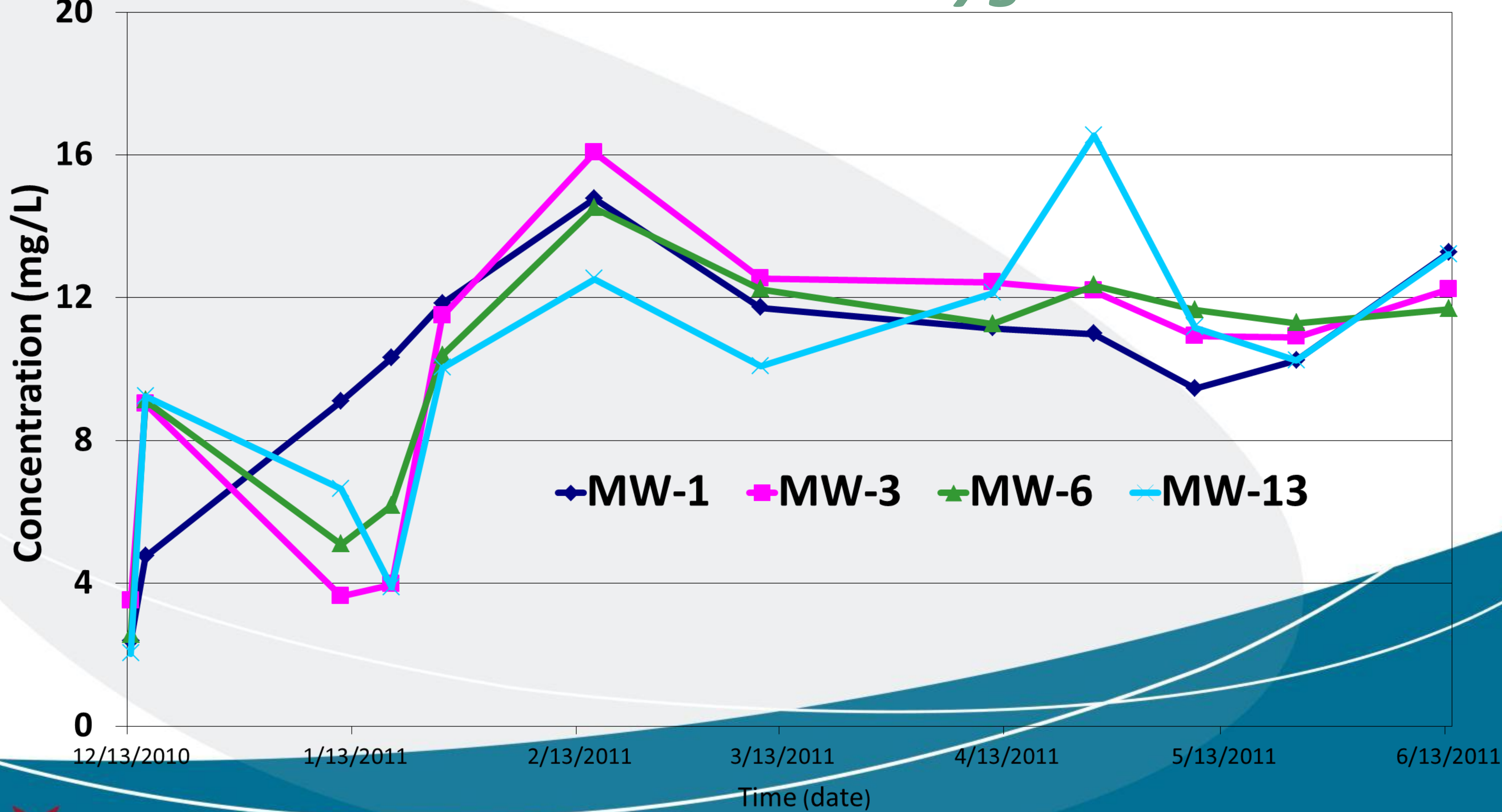
Influent Fixed Gases



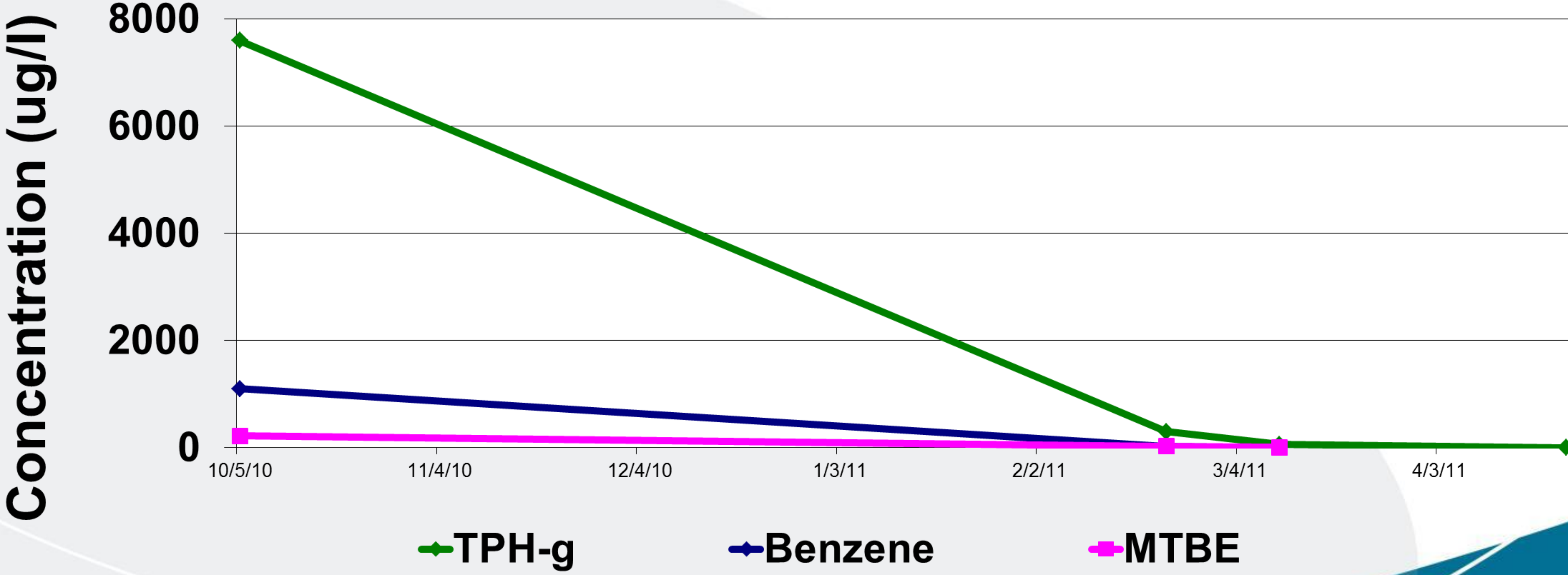
Groundwater Dissolved Oxygen & Concentrations



Groundwater Dissolved Oxygen



Groundwater Concentrations



System Advantages

- Enhanced bioremediation
- Reduction in energy costs
- Recycling of VOC's rather than destruction
  - ✓ optional equipment required
- Unaffected by the level of VOC's in extracted gas stream

- Relatively low carbon foot print w/o emissions

System Advantages

No Combustion – No Off-Gas

- No catalytic or thermal combustion
- No high temperature processes
- No supplemental fuel
- No air exhaust or emissions

- Cost Savings
  - ✓ Lower electrical & fuel costs
  - ✓ Lower flow rates / lower energy cost

Cost Advantages

- Other Cost Savings
  - ✓ No permit application fees
  - ✓ No annual permit fee
  - ✓ No emission monitoring labor costs
  - ✓ No emission analytical costs
  - ✓ Reduced O&M site visit costs
  - ✓ Expedited site clean up times

Ideal sites for ECO-SVE

- Locations with stringent air permit & discharge issues
  - ✓ Cost to air discharge
  - ✓ Exhaust or nuisance issues
  - ✓ Monitoring requirements
  - ✓ Stakeholder issues
- Anywhere Air Sparge/Soil Vapor Extraction is applicable
- No Liquid Phase Hydrocarbons (LPH)

Summary: Green Remediation Options

Unique technological approaches:

- Sulfate-Enhanced Biodegradation (SEB)
  - ✓ Very low carbon footprint
- ECO-SVE
  - ✓ Eliminates key air emissions stream
  - ✓ Promotes *in-situ* destruction of contaminants
  - ✓ Relatively low carbon footprint