



Field-Scale Treatability Study for Enhanced In Situ Bioremediation of Explosives in Groundwater: BioBarrier Installation and Hot Spot Treatment Using DPT Injection

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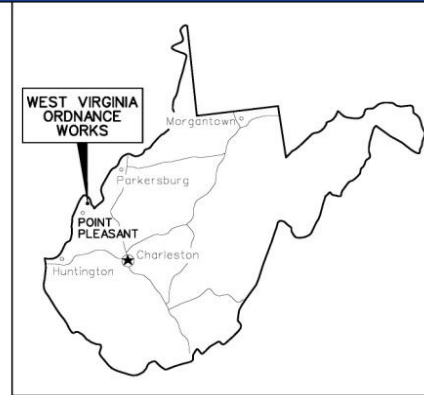
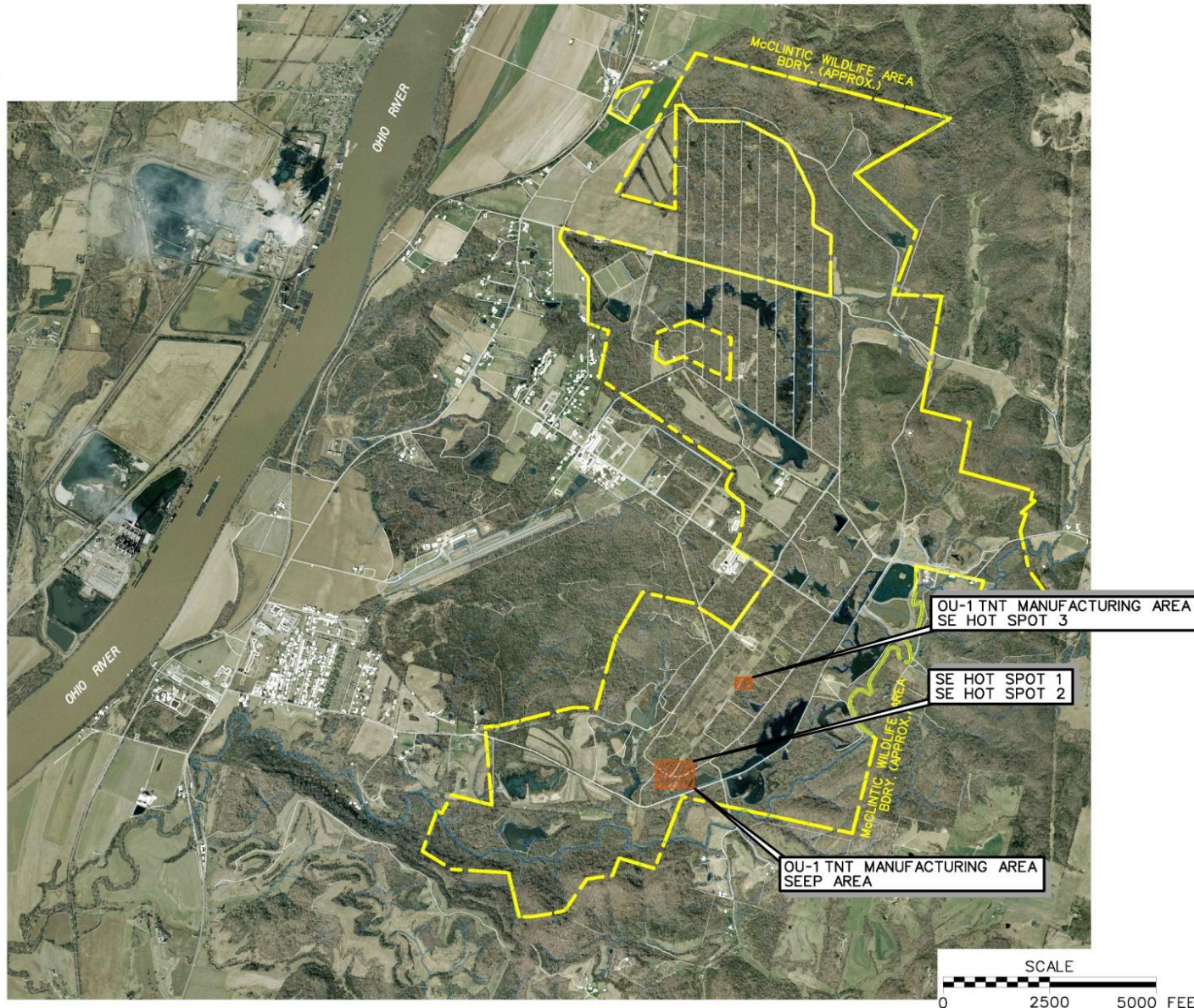
- ▶ Introduction
- ▶ Technology Description
- ▶ Carbon Source Comparison
- ▶ BioBarrier
- ▶ SE Hot Spot 1
- ▶ SE Hot Spot 2
- ▶ SE Hot Spot 3
- ▶ Conclusions

- ▶ West Virginia Ordnance Works (WVOW) was a TNT manufacturing facility from 1942-1945
- ▶ The WVOW site is located on the east bank of the Ohio River, six miles north of Point Pleasant, WV
- ▶ WVOW included 12 TNT production lines
- ▶ TNT production resulted in soil and groundwater contamination
- ▶ Complete decontamination was not achieved, so portions were transferred to the state of West Virginia for use as a wildlife management reserve
- ▶ The site is now the McClintic Wildlife Management Area

WVOW TNT Manufacturing Area



WVOW TNT Manufacturing Area



LEGEND

 EISB GROUNDWATER STUDY AREAS

FIGURE 1-1
SITE LOCATION MAP

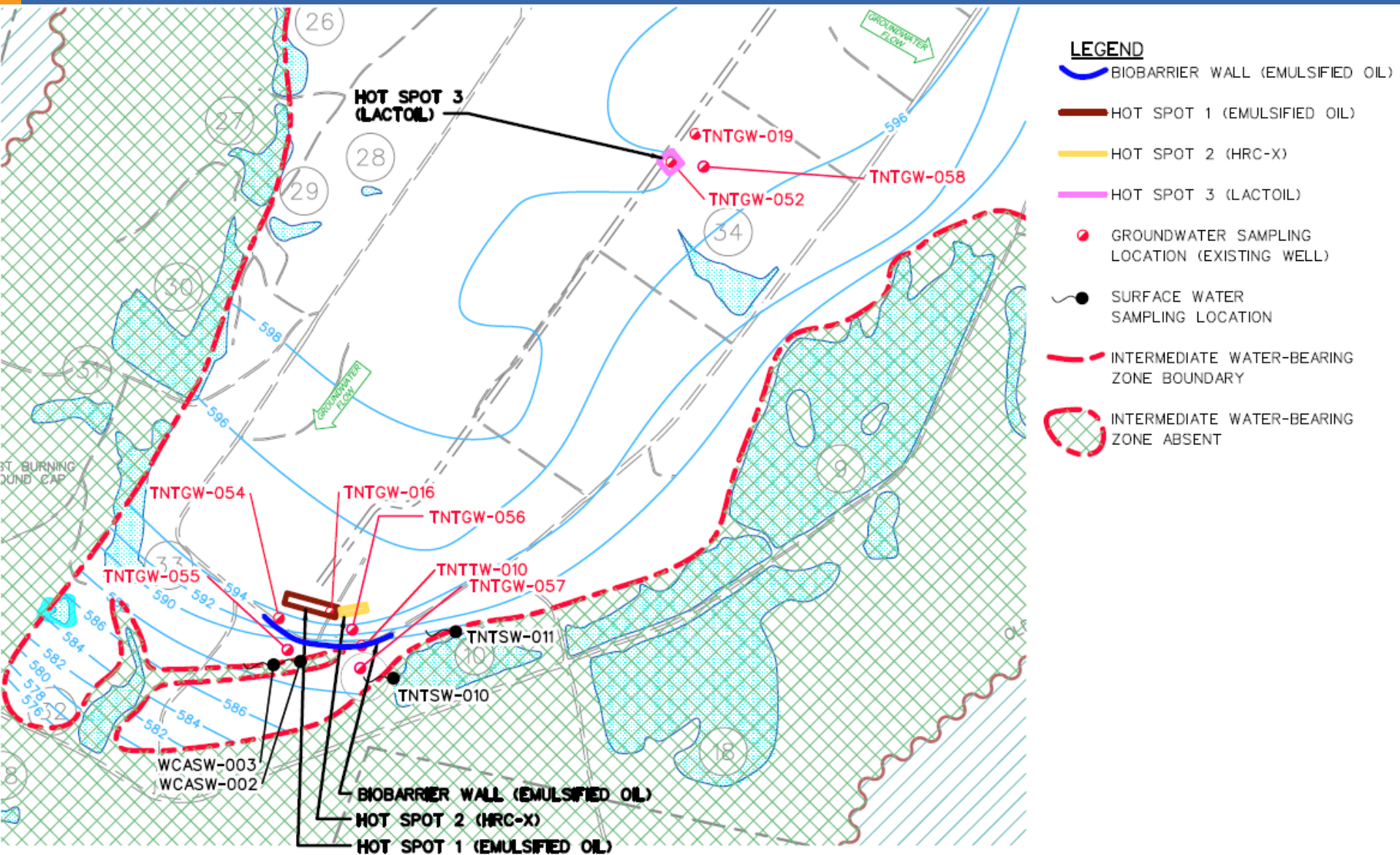
THE EISB TREATABILITY STUDY
WORK PLAN
WEST VIRGINIA ORDNANCE WORKS
MASON COUNTY, WEST VIRGINIA

 a world of Solutions™

- ▶ Four study areas; Seep Area, SE Hot Spot 1, SE Hot Spot 2, and SE Hot Spot 3
- ▶ Primary chemicals of concern (COCs) include: 2,4,6-Trinitrotoluene (TNT), 2,4-Dinitrotoluene (2,4-DNT), 2,6-DNT, 2-Amino-4,6-DNT (2ADNT), and 4-Amino-2,6-DNT (4ADNT)
- ▶ Enhanced in situ bioremediation (EISB) was selected for field-scale evaluation
- ▶ Three different carbon sources are being compared for their effectiveness: SRSTM -Emulsified Vegetable Oil (Terra Systems, Inc.), HRC-XTM (Regenesis), and LactOilTM (JRW)
- ▶ The study is focused only on groundwater treatment

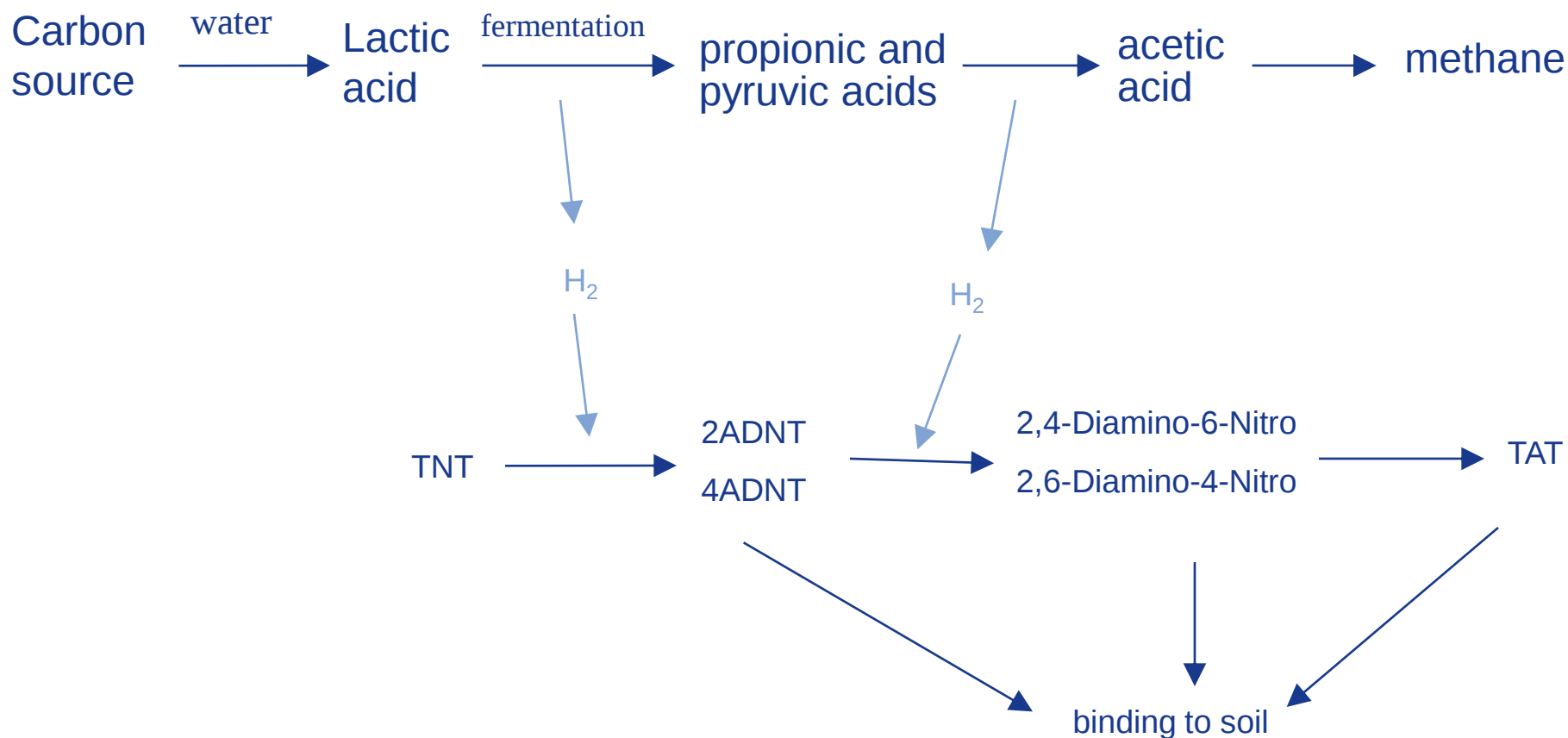
- ▶ Baseline sampling was performed prior to injection of the carbon source in the study areas
- ▶ Nine wells and four seep locations were sampled
- ▶ Performance sampling was conducted quarterly after injection for one year followed by the first of two semi-annual sampling events
- ▶ One remaining semi-annual sampling event is planned for the end of August 2012
- ▶ A comprehensive evaluation report will be prepared at the conclusion of the study

WVOW TNT Treatability Study Area



- ▶ EISB is a process where a reducing environment is created for indigenous microorganisms
- ▶ A carbon source is injected into the aquifer, which provides an energy source for indigenous microorganisms
- ▶ As carbon is consumed, O_2 is depleted until the system becomes anaerobic
- ▶ After O_2 is consumed, anaerobic fermentation begins and H_2 is released into the system
- ▶ H_2 is consumed in competing reactions – reduction of electron acceptors and reduction of nitroaromatics

Carbon Source Degradation and TNT Biodegradation Pathway



- ▶ SRS, Emulsified Vegetable Oil was used for the Seep Area (BioBarrier) and SE Hot Spot 1
- ▶ HRC-X was used for SE Hot Spot 2
- ▶ LactOil was used for SE Hot Spot 3

► SRS, Emulsified Vegetable Oil

- SRS is a slow release substrate comprised of a mixture of emulsified oil (50-70%) and sodium lactate (< 5%) manufactured by Terra Systems, Inc.
- Fast-release lactate creates reducing conditions soon after injection to kick-start the bioactivity
- Emulsified oil dissolves slowly, releasing hydrogen to maintain reducing conditions, providing a longevity of three to five years
- Emulsified oil is immobile after adsorbing to soil particles
- SRS has the consistency of milk and comes ready for injection
- Applied at the Seep Area to form long lasting BioBarrier and at SE Hot Spot 1, which has a high groundwater flow velocity



- ▶ Hydrogen Release Compound (extended release formula)
 - A proprietary polylactate ester manufactured by Regenesis Bioremediation Products, Inc.
 - A viscous material that slowly releases lactic acid
 - High viscosity at ambient temperature – needs to be heated for injection
 - Relatively immobile and does not migrate; ideal for aquifers with steep hydraulic gradients and/or high flow velocities
 - Extended release formula remains active for multiple years
 - Applied at SE Hot Spot 2, which has a high groundwater flow velocity
 - Provides a side-by-side comparison with SRS at SE Hot Spot 1

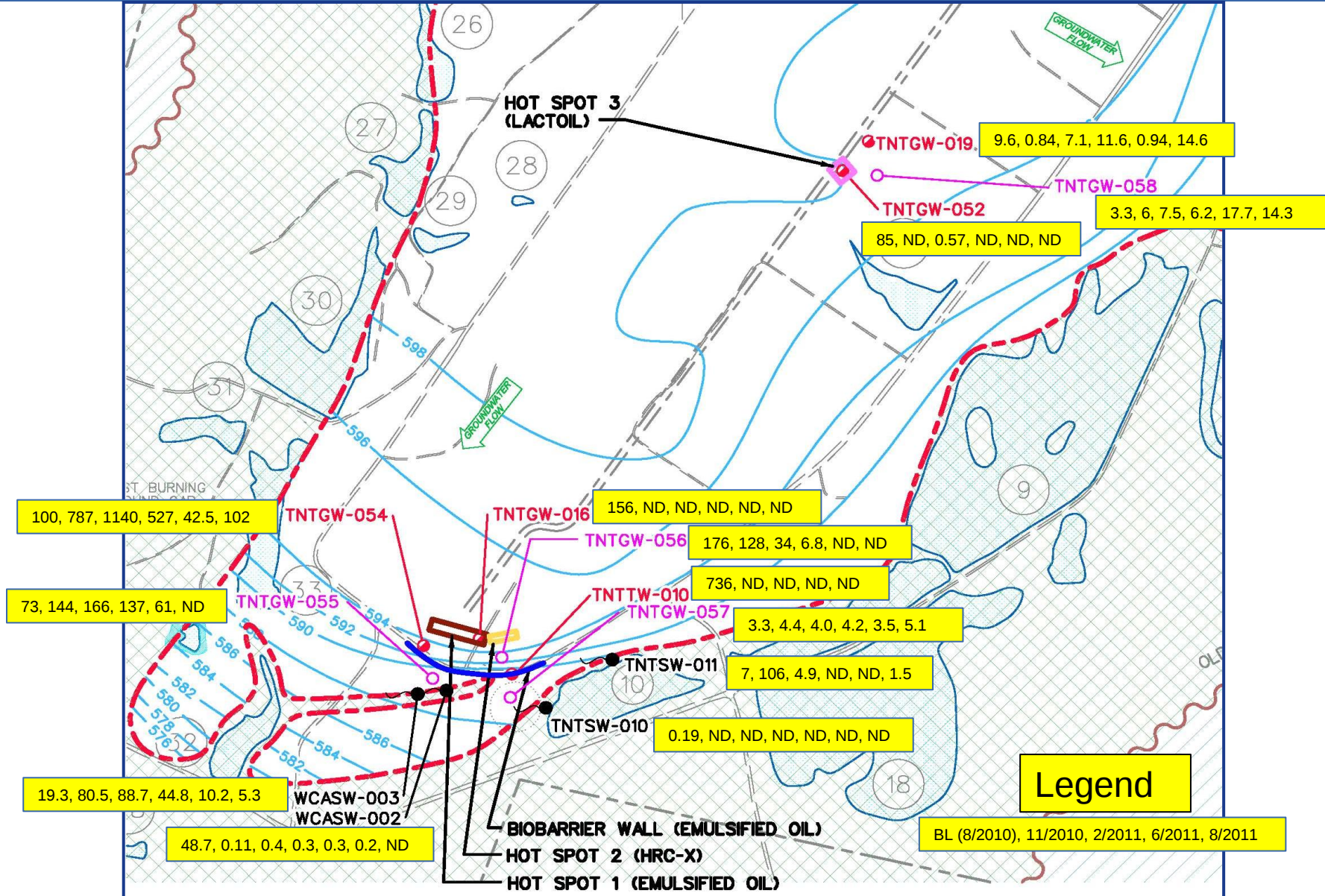


► LactOil

- A mixture of ethyl lactate (40%) and vegetable oil (40%) manufactured by JRW
- Ethyl lactate generates more metabolic acids per unit weight than sodium lactate. It has the potential to reduce pH, thus requiring pH buffering
- One micrometer oil droplet compared to 5-10 micrometers in common emulsified oil, moves through pore space more easily, but also has a shorter active life
- Applied at SE Hot Spot 3 where COC concentrations are lower and longevity is not as critical



TNT Concentration Trends to Date

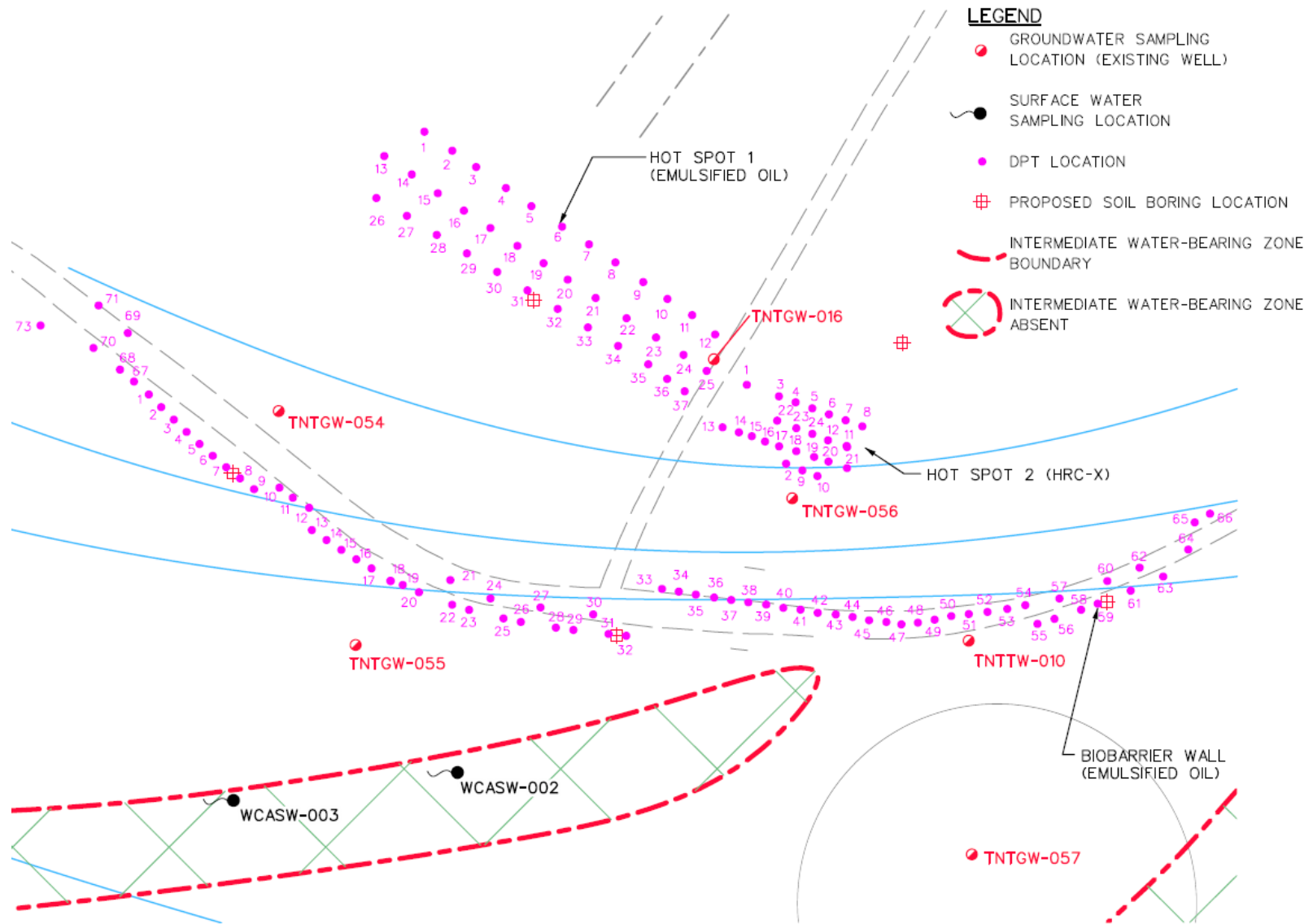


Seep Area – BioBarrier Installation

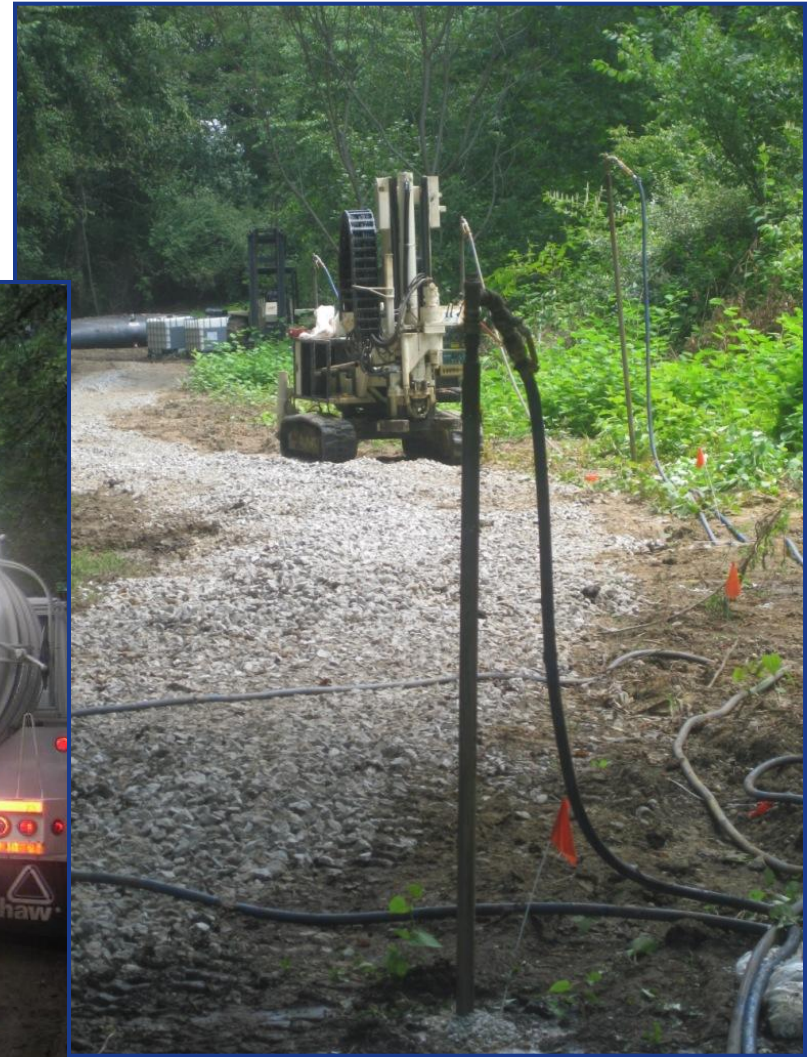


- ▶ SRS injected in a linear pattern perpendicular to groundwater flow
- ▶ Forms a long-lasting BioBarrier to intercept groundwater flow and prevent downgradient migration of COCs to the seeps
- ▶ BioBarrier consists of 72 injection points with a 10-foot spacing
- ▶ A total of 32,791 lbs of SRS was mixed with potable water to provide 20,000 gallons of solution for injection
- ▶ 197 lbs of yeast extract was added as a nutrient
- ▶ ~308 gallons of solution (35% of available pore volume) was injected at each point
- ▶ A target injection interval of 10-18 feet below ground surface was adjusted 10 feet deeper for a few points based on lithology
- ▶ Surfacing occurred at several injection points due to local lithologic variations

BioBarrier Layout



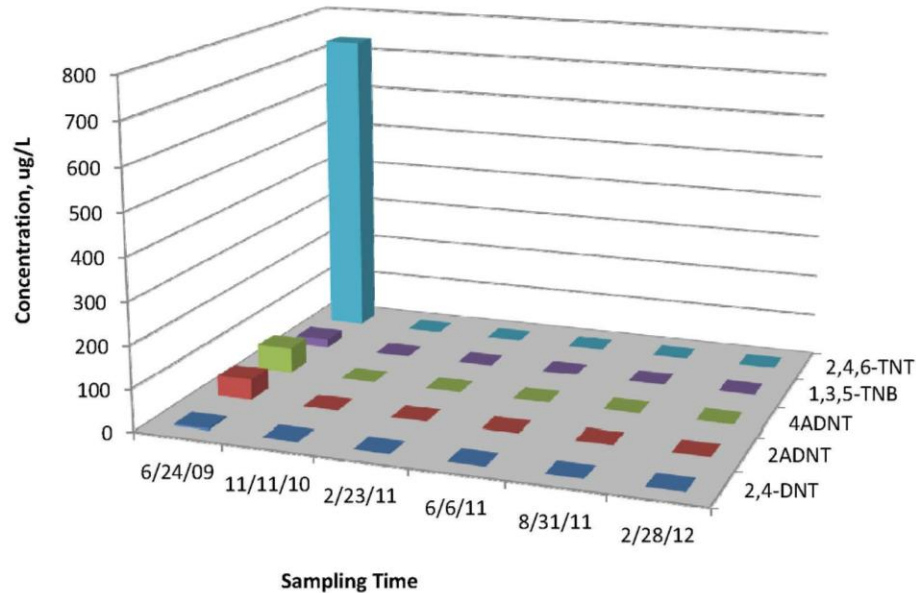
BioBarrier - SRS Mixing and Injection



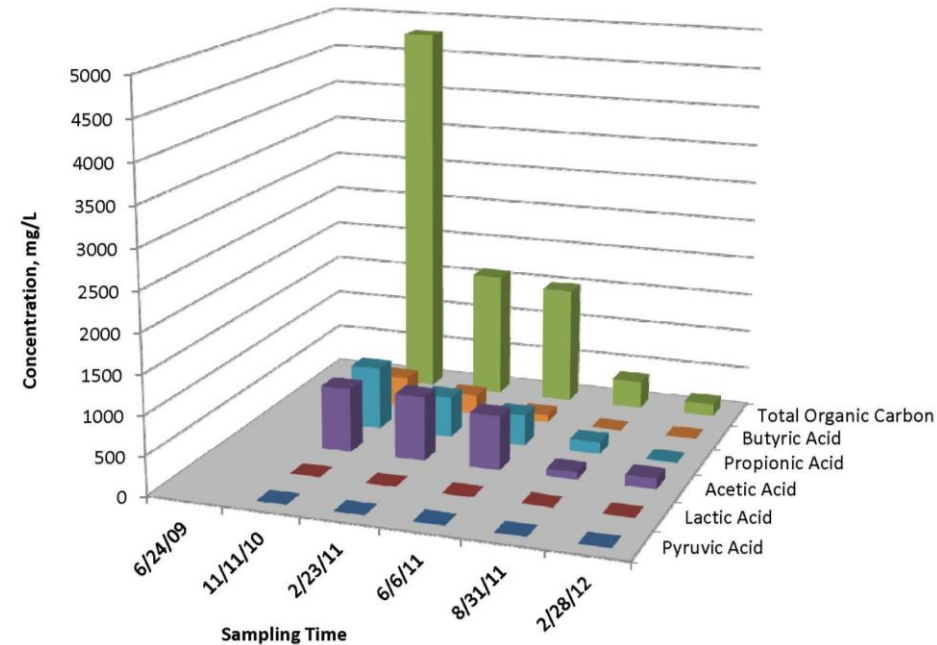
SRS Injection for BioBarrier



TNTTW-010 -- TNT Series

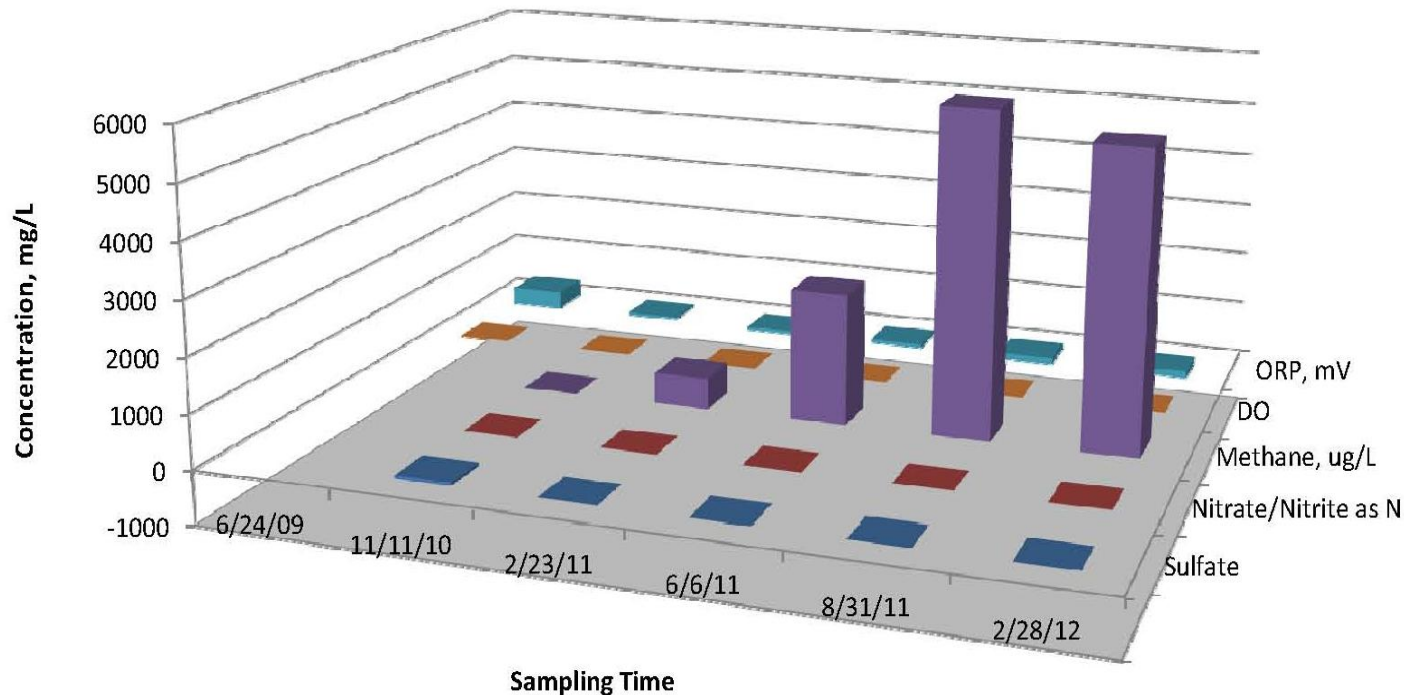


TNTTW-010 -- Metabolic Acids and TOC



- ▶ TNT series compounds decreased to below detection limit of 20 ug/L three months after injection and has remained near non-detect
- ▶ TOC increased to 4,800 mg/L, and gradually decreased to 156 mg/L
- ▶ Metabolic acids increased to 820 mg/L, then decreased to ~100 mg/L

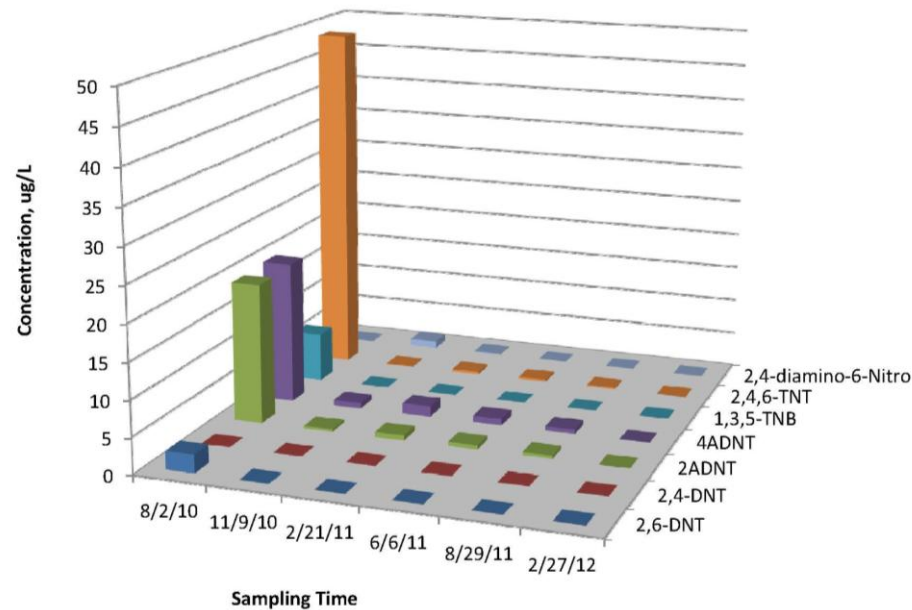
TNTTW-010 -- Geochemistry



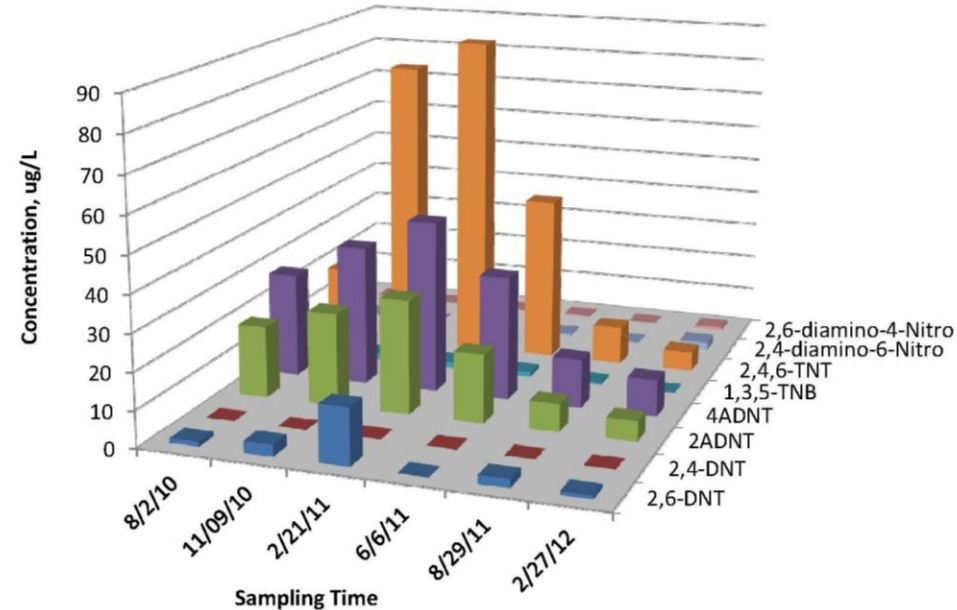
- ▶ ORP dropped from 326.7 to -128.3 mV, then increased to -122.1 mV
- ▶ DO dropped from 9.7 to 0.72 mg/L
- ▶ Sulfate dropped from 59.9 to 1.2 mg/L
- ▶ Methane increased from 1.4 to 5,940 ug/L, then dropped to 5,480 ug/L

BioBarrier Results

WCASW-002-- TNT Series

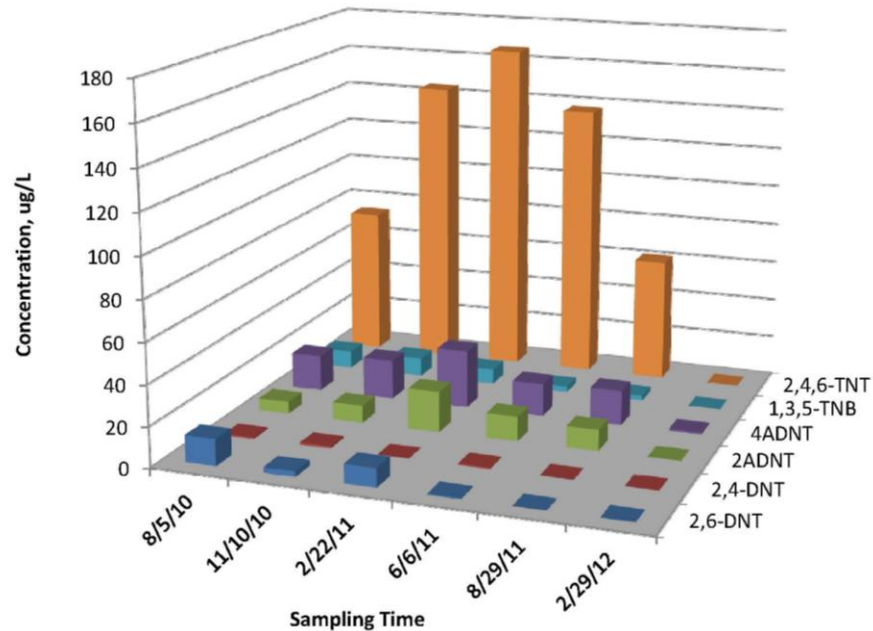


WCASW-003-- TNT Series

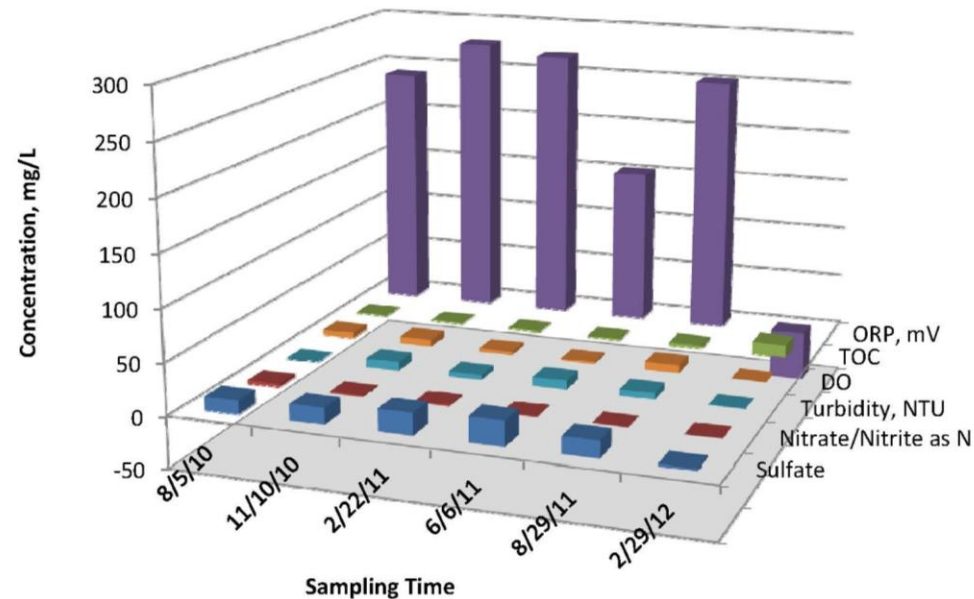


- ▶ More than 90% reduction of TNT series immediately downgradient at the seep location (WCASW-002)
- ▶ Further downgradient at seep location WCASW-003, initial increase in TNT series followed by a steady decrease
- ▶ No evidence of reducing conditions (i.e., no metabolic acids detected)

TNTGW-055-- TNT Series

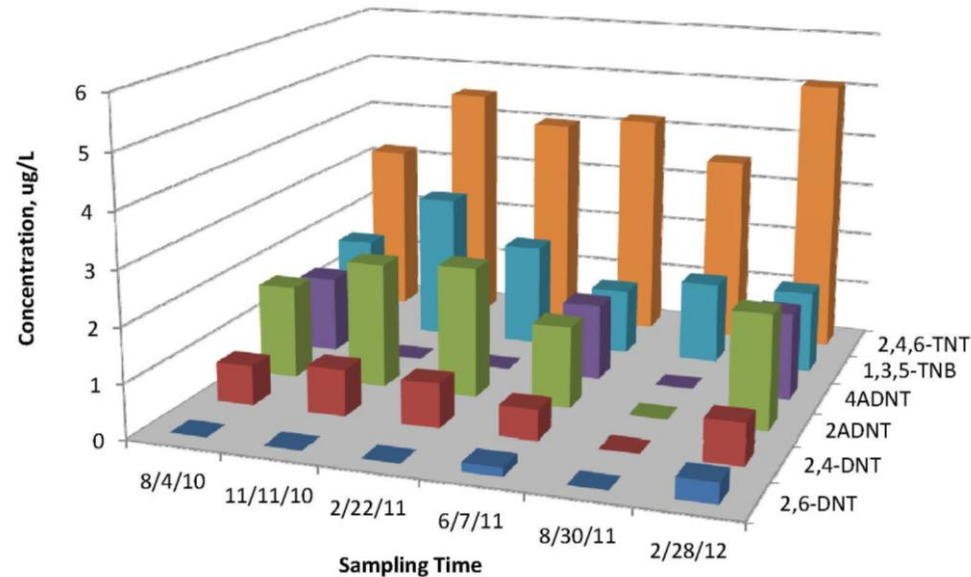


TNTGW-055 -- Geochemistry

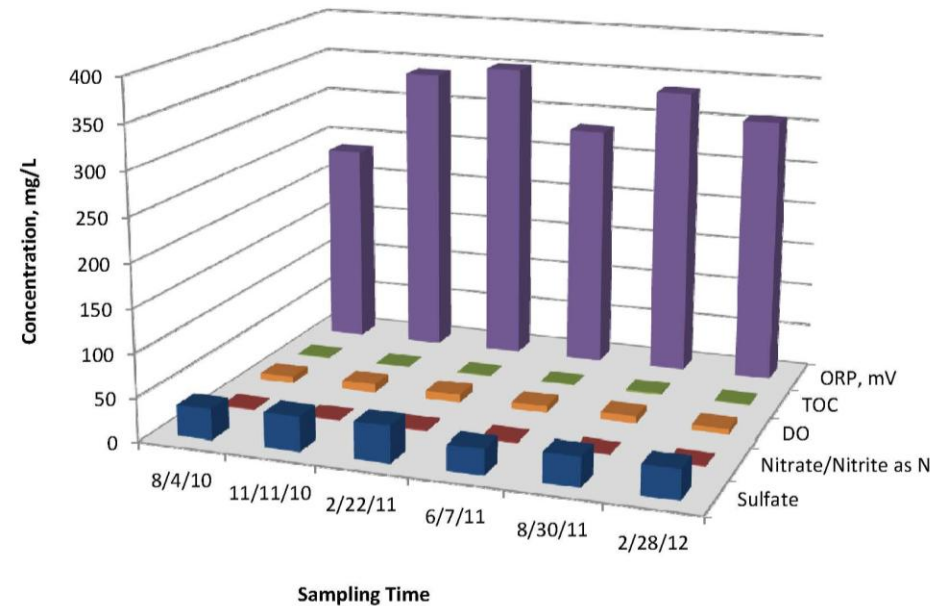


- ▶ TNT concentration increased from 73 ug/L to 166 ug/L then began a steady decrease to near non-detect
- ▶ Reducing conditions observed in 2/29/12 sampling with ORP dropping to -47.8 mV
- ▶ No metabolic acids detected

TNTGW-057-- TNT Series



TNTGW-057 -- Geochemistry



- ▶ Minor fluctuation in TNT Series at low concentrations
- ▶ No reducing conditions observed
- ▶ No metabolic acids detected

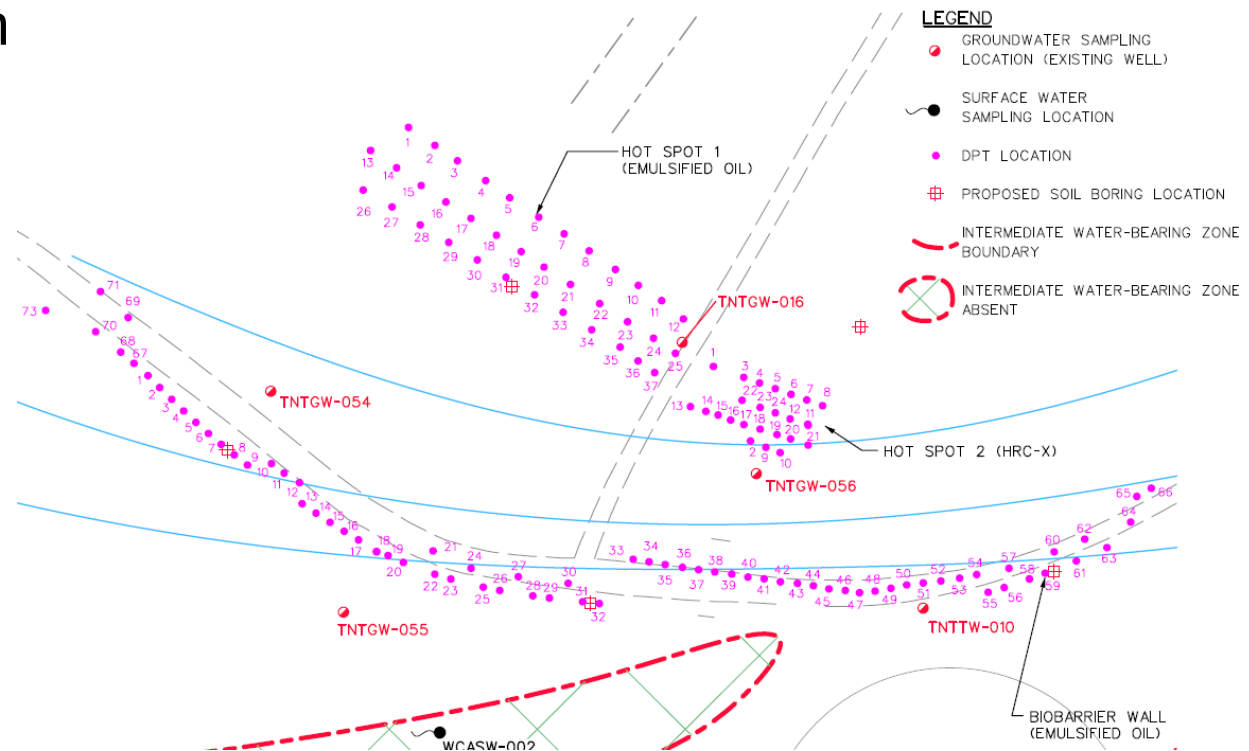
SE Hot Spot 1 Area

- ▶ SRS
- ▶ Located upgradient of the western portion of the BioBarrier
- ▶ High TNT concentration (156 ug/L), and relatively high groundwater flow rate (0.5 feet/day) → suitable for SRS
- ▶ A total of 17,867 lbs of SRS was mixed with potable water to provide 11,400 gallons of solution for injection at 37 points
- ▶ 107 lbs of yeast extract was added as a nutrient
- ▶ ~308 gallons of solution was injected at each point



SE Hot Spot 1 Area

- ▶ 250-foot × 50-foot injection grid
- ▶ ~200 feet upgradient of the western portion of the BioBarrier (~ one year of groundwater travel time)
- ▶ Total of 37 injection points aligned in three parallel rows
- ▶ Target depth interval of 10-18 feet below ground surface, adjusted accordingly based on changes in elevation

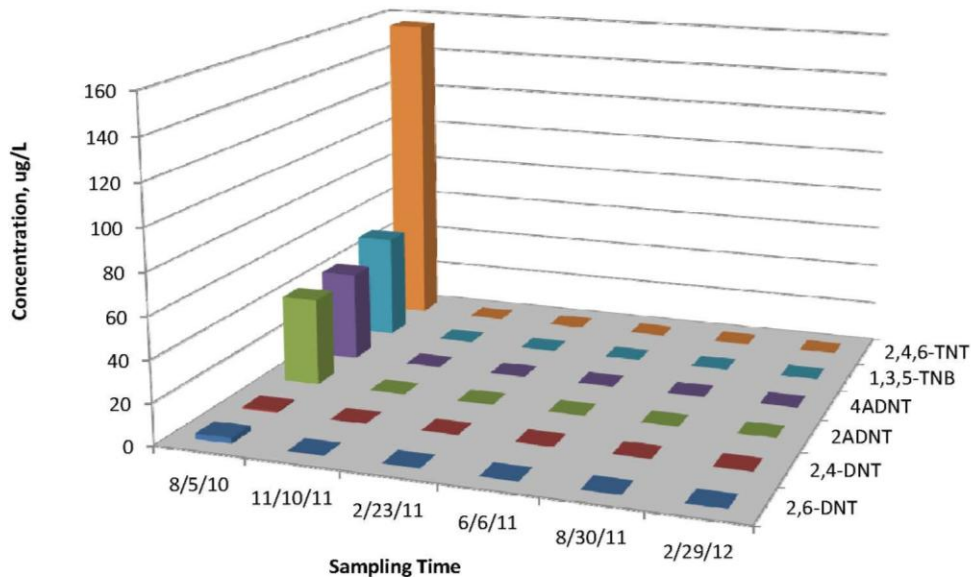


SE Hot Spot 1 - SRS Mixing and Injection

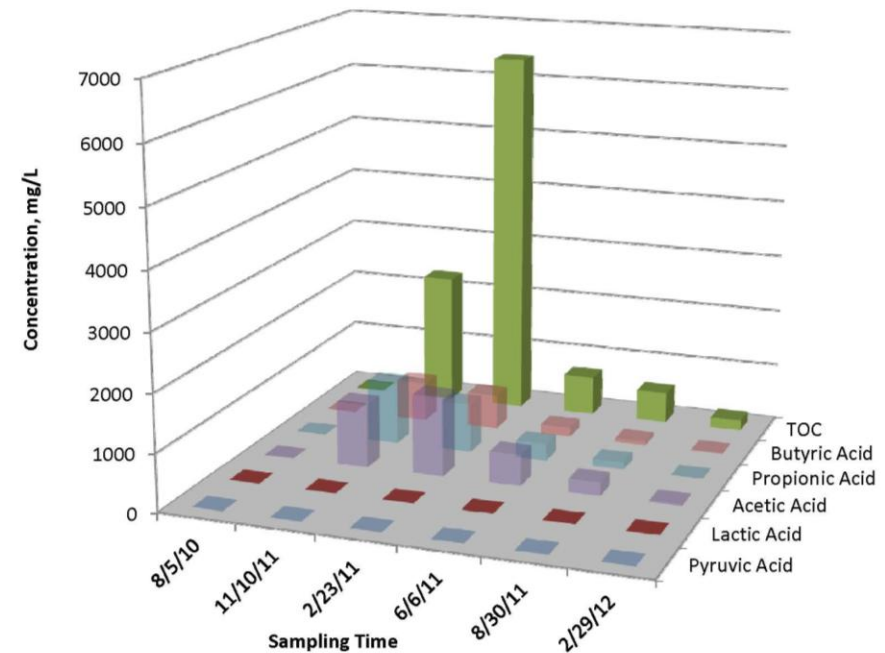


SE Hot Spot 1 Results

TNTGW-016 -- TNT Series



TNTGW-016 -- Metabolic Acids and TOC



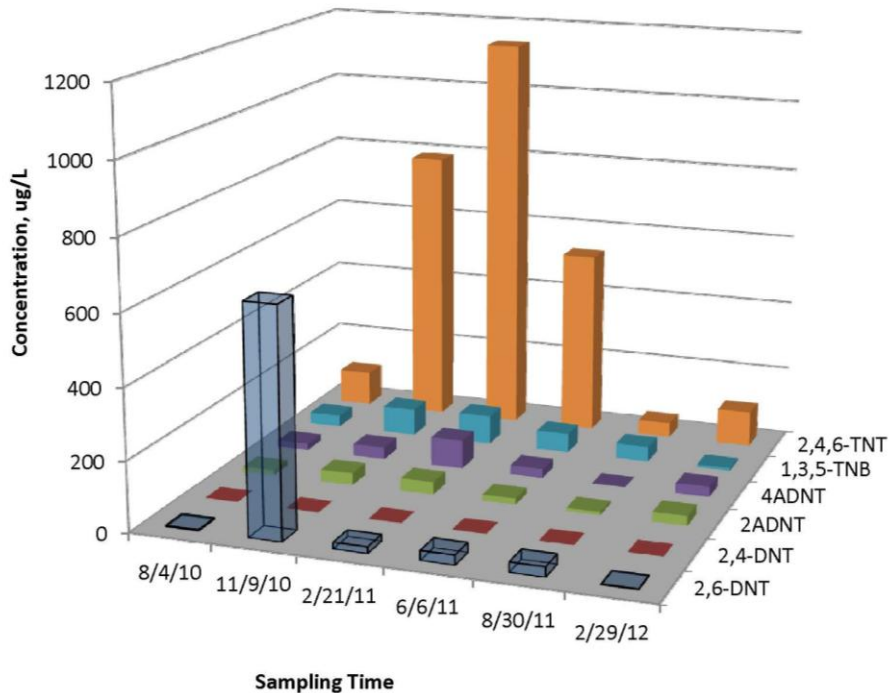
- ▶ TNT series concentration decreased to below detection limit of 20 ug/L three months after injection and has remained near non-detect
- ▶ Metabolic acids detected after 3 months and increased by 6 months then began to drop
- ▶ TOC peaked at 6,400 mg/L 6 months after injection then rapidly dropped

3D bar chart showing Concentration (mg/L) vs. Sampling Time for various parameters. The chart displays data for 8/5/10, 11/10/11, 2/23/11, 6/6/11, 8/30/11, and 2/29/12. Parameters include ORP (mV), DO, Methane, Nitrate/Nitrite as N, and Sulfate. The highest concentration is 256.6 mg/L for Sulfate on 2/23/11.

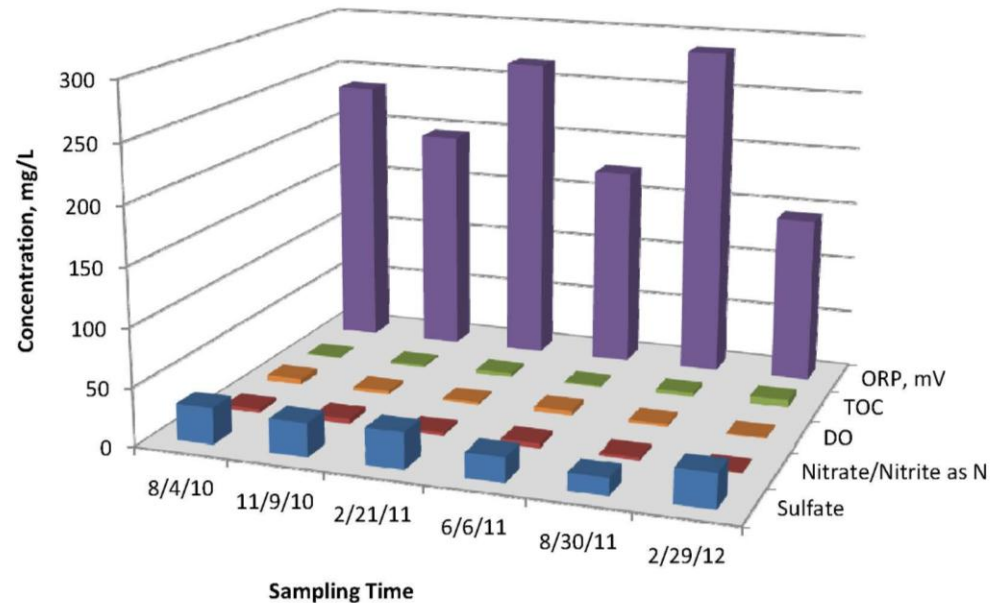
Sampling Time	ORP, mV	DO	Methane	Nitrate/Nitrite as N	Sulfate
8/5/10	~60	~5	~5	~5	~5
11/10/11	~10	~10	~10	~10	~10
2/23/11	~10	~10	~10	~10	256.6
6/6/11	~10	~10	~10	~10	~10
8/30/11	~10	~10	~10	~10	~10
2/29/12	~10	~10	~10	~10	~10

SE Hot Spot 1 Results

TNTGW-054-- TNT Series



TNTGW-054 -- Geochemistry



- ▶ TNT concentration increased from 99.8 ug/L to 1,140 ug/L 6 months after injection, dropped to 42.4 ug/L after 12 months, then increased to 102 ug/L after 18 months
- ▶ No metabolic acids detected until 18 months after injection when a small detection of Butyric acid was detected at 7.5 mg/L
- ▶ No significant TOC noted and no reducing conditions observed

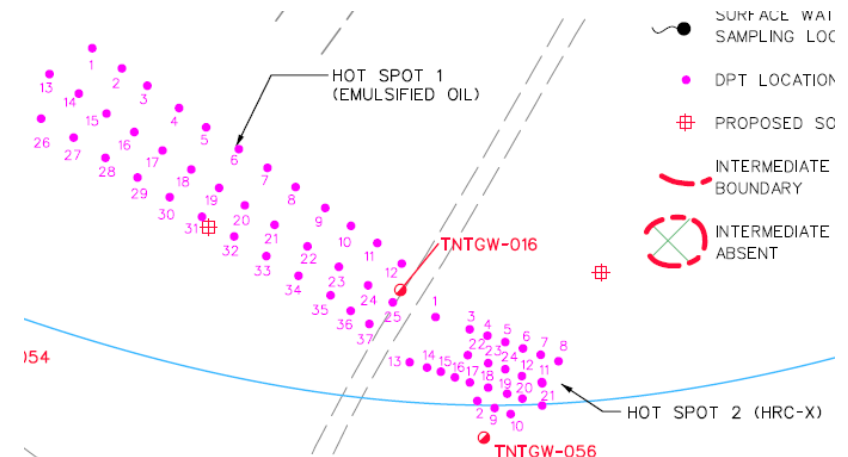
SE Hot Spot 2 Area

- ▶ Located upgradient of the central portion of the BioBarrier
- ▶ High TNT concentration (156 ug/L) and relatively fast groundwater flow (0.5 feet/day)
- ▶ HRC-X selected for this area → side-by-side comparison with SRS (SE Hot Spot 1)
- ▶ A total of 810 lbs of HRC-X was injected through 24 points (~34 lbs for each point)
- ▶ HRC-X was heated to 160 F in a hot water bath to reduce viscosity prior to injection; no dilution required



SE Hot Spot 2 - HRC-X Injection

- ▶ A 100-foot × 50-foot injection grid
- ▶ ~180 feet upgradient of the BioBarrier (~ one year of groundwater travel time from SE Hot Spot 2 to BioBarrier)
- ▶ Total of 24 injection points spaced on 10-foot centers, aligned in four rows based on accessibility, in a staggered configuration
- ▶ Target depth interval of 3-8 feet below ground surface at the lowest elevation points, adjusted accordingly at higher elevations



SE Hot Spot 2 – HRC-X Heating

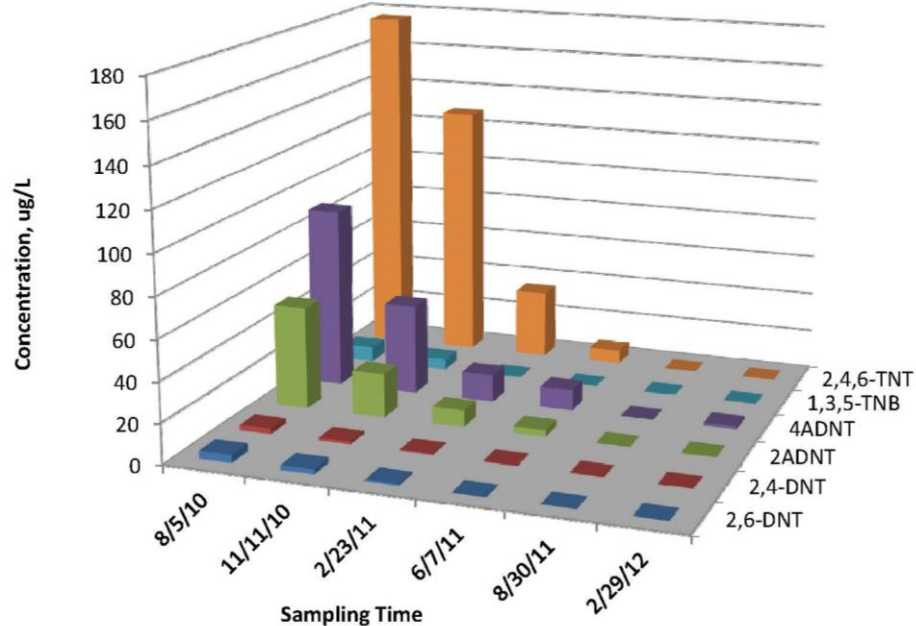


SE Hot Spot 2 – HRC-X Injection

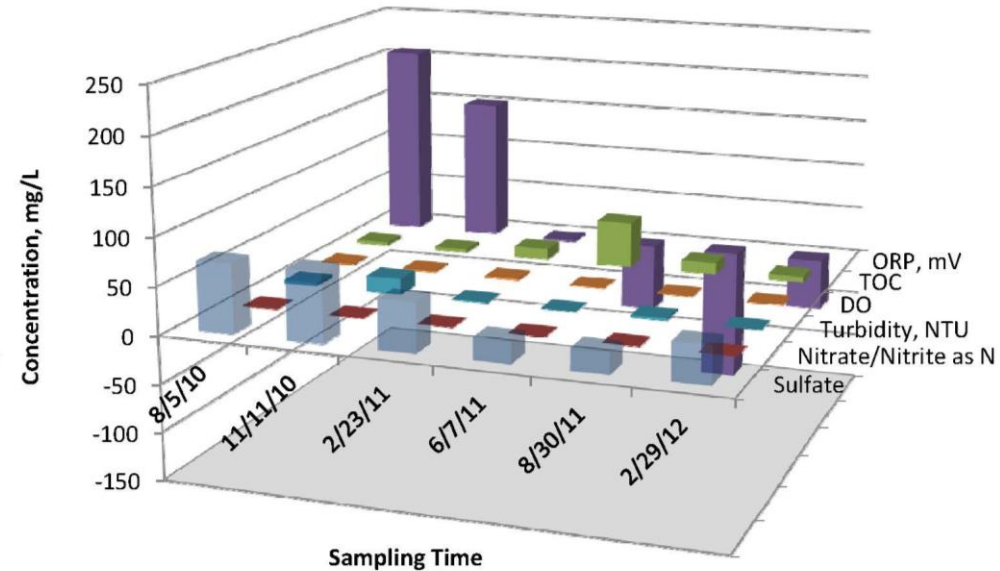


SE Hot Spot 2 Results

TNTGW-056-- TNT Series



TNTGW-056 -- Geochemistry



- ▶ Decrease in TNT from 176 ug/L to non-detect
- ▶ Steady decrease in ORP from 206.9 mV to -144.1 mV followed by a rebound to -54.6 mV
- ▶ Decrease in sulfate from 72 mg/L to 22.4 mg/L followed by a slight increase 38.7 mg/L

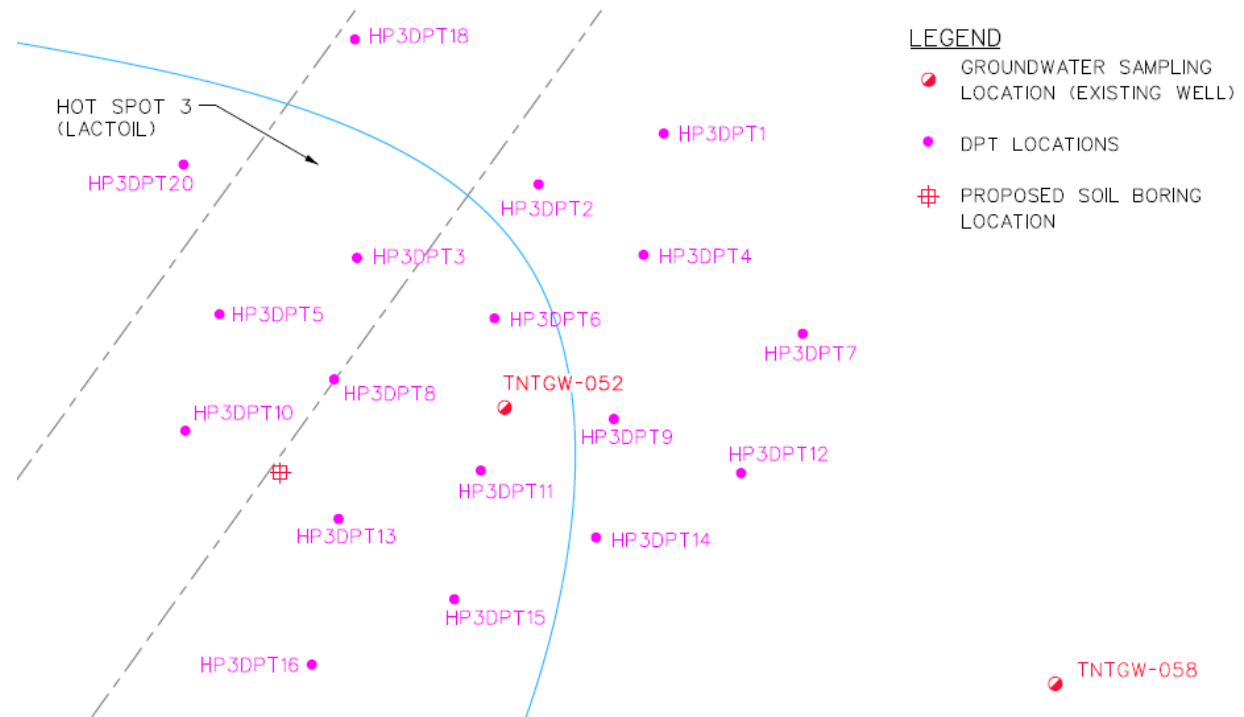
SE Hot Spot 3 Area - LactOil Injection



- ▶ Soil treatment (blending/removal) was conducted previously in this area
- ▶ Groundwater flow velocity 0.58 feet/day at nearby well TNTGW-019
- ▶ Relatively low TNT concentration (85 ug/L) – no critical requirement on carbon source longevity
- ▶ LactOil with relatively short life-span was selected as the carbon source
- ▶ A total of 5,714 lbs of LactOil was mixed with potable water to produce 3,500 gallons of solution for injection through 18 points (~200 gallons at each point)
- ▶ 34 lbs of yeast extract was added as a nutrient
- ▶ 300 lbs of NaHCO_3 added as a pH buffer

SE Hot Spot 3 Area

- ▶ A 80-foot × 80-foot injection grid
- ▶ Sixteen injection points in four staggered rows
- ▶ Due to surfacing at some points, two points were added in the field to achieve the design injection volume
- ▶ Target depth interval of 10-15 feet below ground surface at the lowest elevation points was adjusted accordingly at the higher elevation points

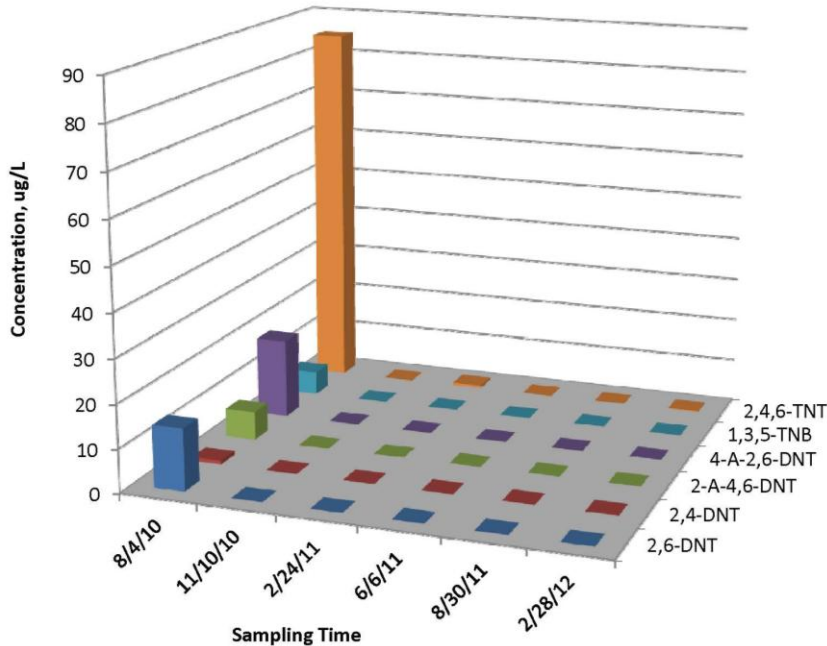


SE Hot Spot 3 - LactOil Injection

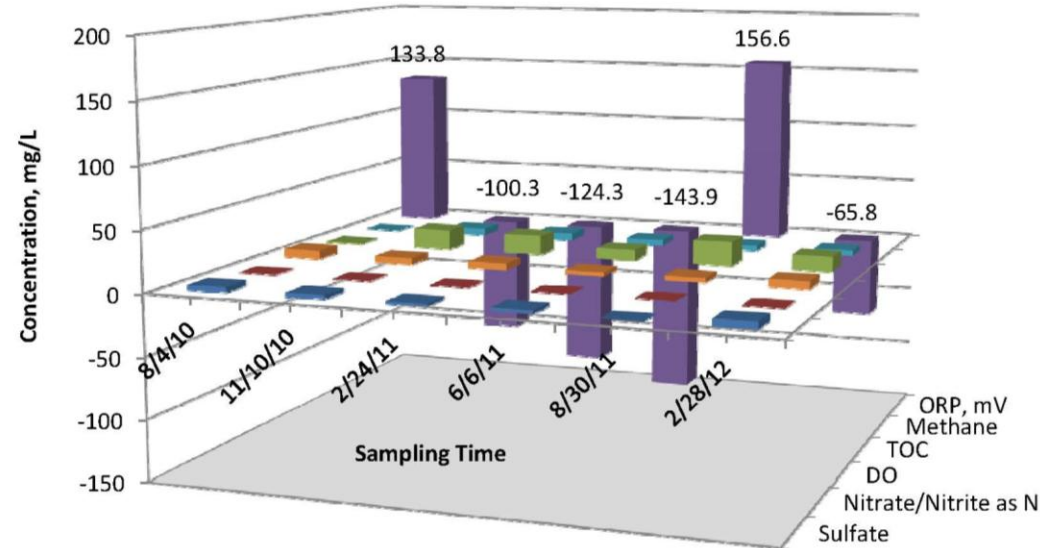


SE Hot Spot 3 Results

TNTGW-052 -- TNT Series



TNTGW-052 -- Geochemistry



- ▶ TNT series concentration decreased to below detection limit of 0.20 ug/L three months after injection and has remained near non-detect
- ▶ ORP decreased for 9 months, spike upward, then decreased again
- ▶ TOC increased slightly
- ▶ No metabolic acids detected to date
- ▶ Methane increased to 6.24 mg/L (6,240 ug/L) and has remained above 4.5 mg/L (4,500 ug/L)

Comparing Performance

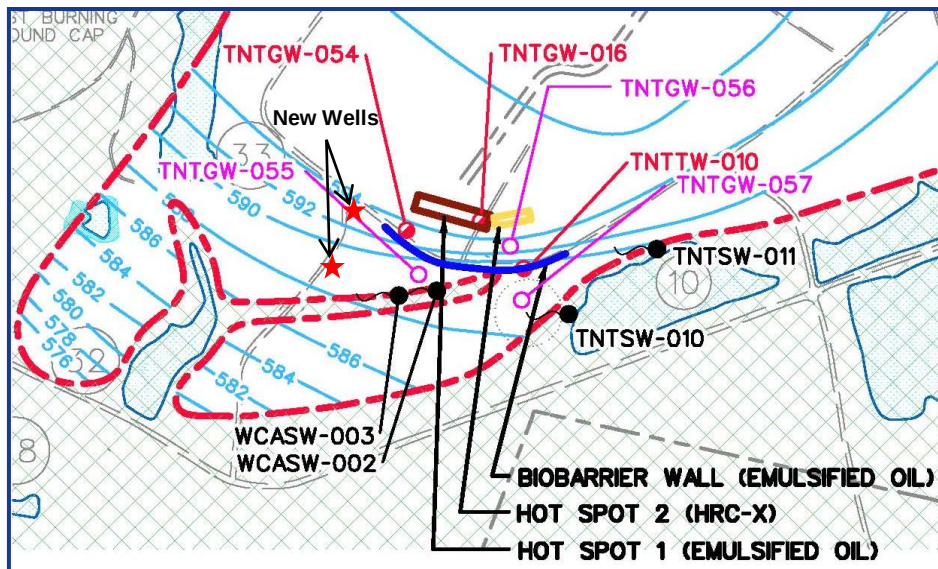
Parameters	SRS		HRC-X	LactOil
	TNTTW-010	TNTGW-016	TNTGW-056	TNTGW-052
Sulfate, mg/L	1.2	<1	22.4	2.1
Nitrate/Nitrite as N, mg/L	<0.05	<0.1	<0.05	< 0.05
Methane, µg/L	5,940	8,880	547	6,240
ORP, mV	-128.3	-91.5	-144.1	-143.9
DO, mg/L	0.72	0.57	0.46	3.46
TOC, mg/L	4,800	6,400	49.3	20.3
Pyruvic Acid, mg/L	10.9	< 1	< 0.1	< 0.1
Lactic Acid, mg/L	<10	< 10	< 1	< 1
Acetic Acid, mg/L	824	1,380	< 1	< 1
Propionic Acid, mg/L	797	1,080	< 1	< 1
Butyric Acid, mg/L	4,800	687	< 1	< 1

- ▶ Both SRS and LactOil decreased TNT series compounds to below detection limits within the injection grids
- ▶ Down-gradient of HRC-X injection grids showed a steady decrease of TNT series throughout the study
- ▶ All three substrates successfully created reductive conditions at the designed dosing rates
- ▶ LactOil generated a spike of methane and lowest ORP early on providing a short bloom of electron donors
- ▶ SRS generated two orders of magnitude higher TOC and metabolic acids – long-lasting slow release carbon source

- ▶ EISB is shown to be effective for treatment of groundwater contaminated with nitroaromatics
- ▶ Carbon source selection was based on several factors
 - Hydraulic gradient and groundwater flow velocity
 - Contaminant concentrations
- ▶ The designed dosing rates of carbon sources were able to create reducing conditions within the injection zones
 - Negative ORP values
 - Decreasing DO and sulfate
 - Increasing methane and metabolic acids
 - Contaminants decreased to below detection limits
- ▶ No downward trend in concentration observed downgradient of SRS injection area in the first two quarterly sample rounds
- ▶ Downward trend in concentration observed at the seep location nearest the BioBarrier, and down gradient of the HRC-X treatment area
- ▶ Pilot-scale field application provides valuable information for carbon source selection and full-scale design parameters

What Next?

- ▶ Install 2 new monitoring wells west of TNTGW-054 and TNTGW-055
- ▶ Collect baseline samples for new wells
- ▶ Inject HRC-X in target zone west of TNTGW-054
- ▶ Complete last semi-annual performance samples (including new wells)
- ▶ Collect two more rounds of performance samples from TNTGW-054, TNTGW-055, and two new wells



Questions?





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