Surfactant Enhanced Extraction to Expedite Remediation of Carbon Tetrachloride Source Zone at an Active Grain Elevator Facility

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Site Remediation Presentation Overview

- Grain Elevator Kansas City MO Enters Voluntary Cleanup Program: April 2000
- DPVE System Installation & Startup: Dec. 2007 to 2014 (Soil Phase II)
- Surfactant Enhanced Extraction (SEE) Pilot Study: Spring 2015
- SEE Full Scale: Fall 2016
- Observations continue into 2017

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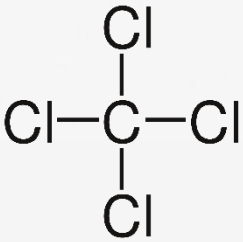
Chlorinated Solvents: A Forensic Evaluation (2013) Brian Murphy and Roberto D. Morrison

5.6.2 Fumigants

The use of carbon tetrachloride as a fumigant for stored grains commenced prior to World War I (WWI). During WWII, the use of carbon tetrachloride as a grain fumigant increased. Carbon tetrachloride was used in a number of liquid pesticide formulations, primarily in fumigants, along with other active ingredients, including ethylene dibromide, carbon disulfide and ethylene dichloride.[78] These fumigants controlled insect infestations in grains during storage, transfer, milling, distribution, and processing.

Carbon tetrachloride persisted as a pesticide in stored grain until 1970 although it was banned in US consumer products. In 1977–1978, 3.6 million liters of fumigant containing carbon tetrachloride were applied to grains stored on farms; the total estimated amount of carbon tetrachloride used in fumigants in 1978 was 28 million pounds.[79] In 1984, it was estimated that 98% of liquid fumigant formulations contained carbon tetrachloride while 2% was used to fumigate grain mill equipment. Carbon tetrachloride formulations were more widely used at smaller grain elevators than at large elevators. In 1984 approximately 70% of the grain stored at large grain elevators in the US, including terminal elevators, was treated with aluminium phosphate formulations, rather than carbon tetrachloride.[80]



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Background Information

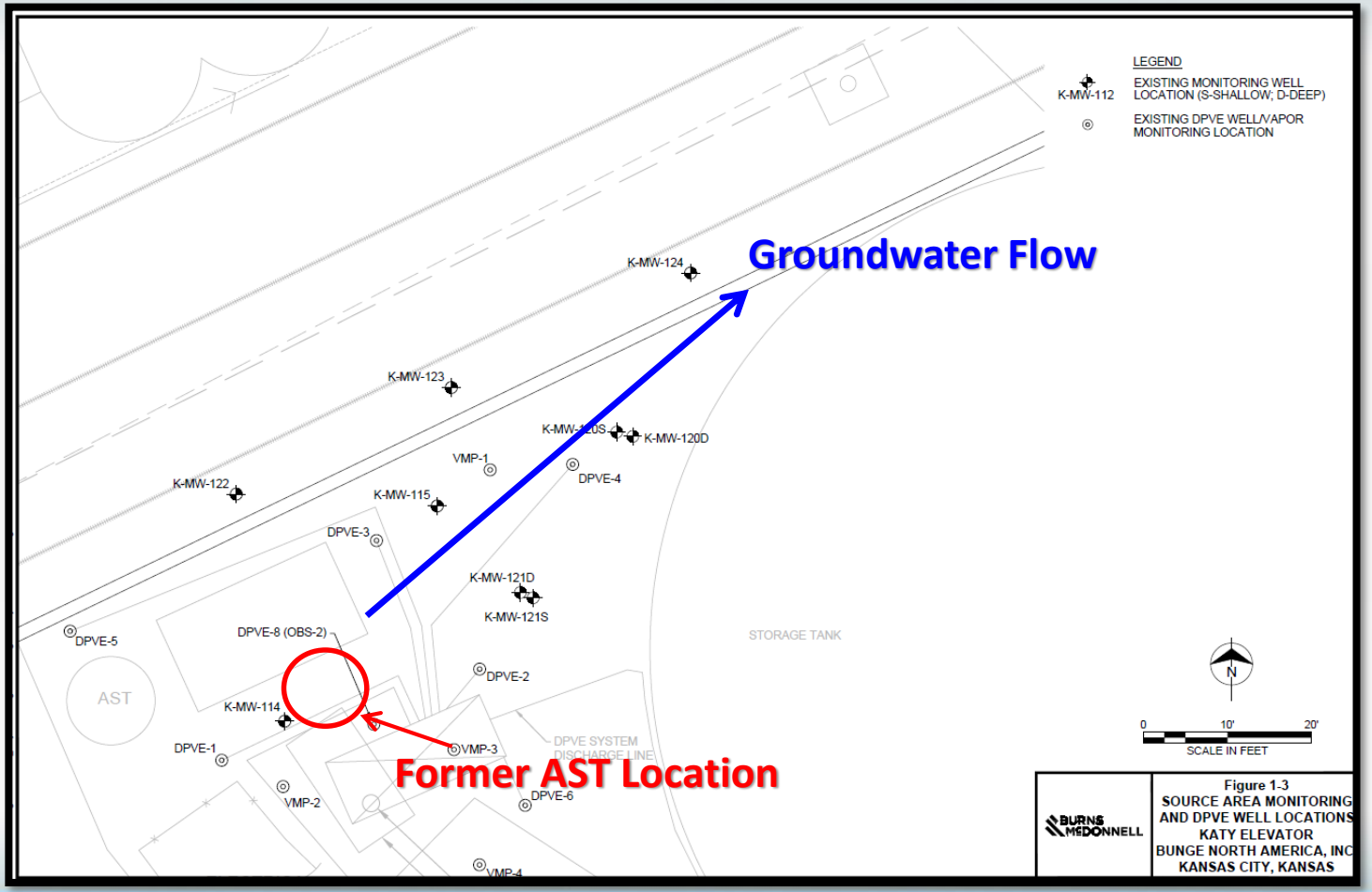
- The site is located in Kansas City, Kansas and currently operates as an active grain elevator facility for many decades.
- The site entered into the Voluntary Cleanup and Property Redevelopment Program (VCPRP) in 2000 following groundwater and soil detections of grain fumigant constituents of concern (COCs), including carbon tetrachloride, in the vicinity of a former fumigant aboveground storage tank (AST).
- Following source area investigation and groundwater plume delineation activities, dual-phase vacuum extraction (DPVE) was implemented in 2007 for the removal of COCs in source area soils and groundwater. Groundwater was encountered at the site approximately 7 to 8 feet (2.13 to 2.44 m) below ground surface (bgs).
- Lithology within the targeted source zone generally consists of well sorted, loose, silty-sand to depths ranging from approximately 13 to 17 feet (3.96 to 5.18 m) underlain by silty clay.

Background Information (Continued):

- After approximately 6 years of DPVE operation, resulting in the removal of over 9,000 pounds of total VOCs, a subset of source area extraction wells continued to exhibit elevated COC groundwater concentrations.
- Additional investigation (2014) was conducted to assess the nature and extent of residual COC mass in the source area and provide data required for the evaluation of alternatives that could expedite source area remediation.
- The investigation results indicated significant sorbed-phase COC mass, generally limited to the shallow, sandy interval of an area bound by the DPVE wells exhibiting elevated COC concentrations. Light non-aqueous phase liquid (LNAPL) heavily impacted with the site COCs was also identified.
- Surfactant enhanced extraction (SEE) was subsequently identified as the optimal source zone remedial alternative because of the technology's ability to quickly and efficiently remove a concentrated, but relatively isolated, shallow zone of contaminant mass.

Site Layout

Site Layout



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Site Challenges

Due to limited vehicle access, in the vicinity of the former AST, and proposed treatment system location.

So placement of equipment became creative!

How creative?

Site Challenges

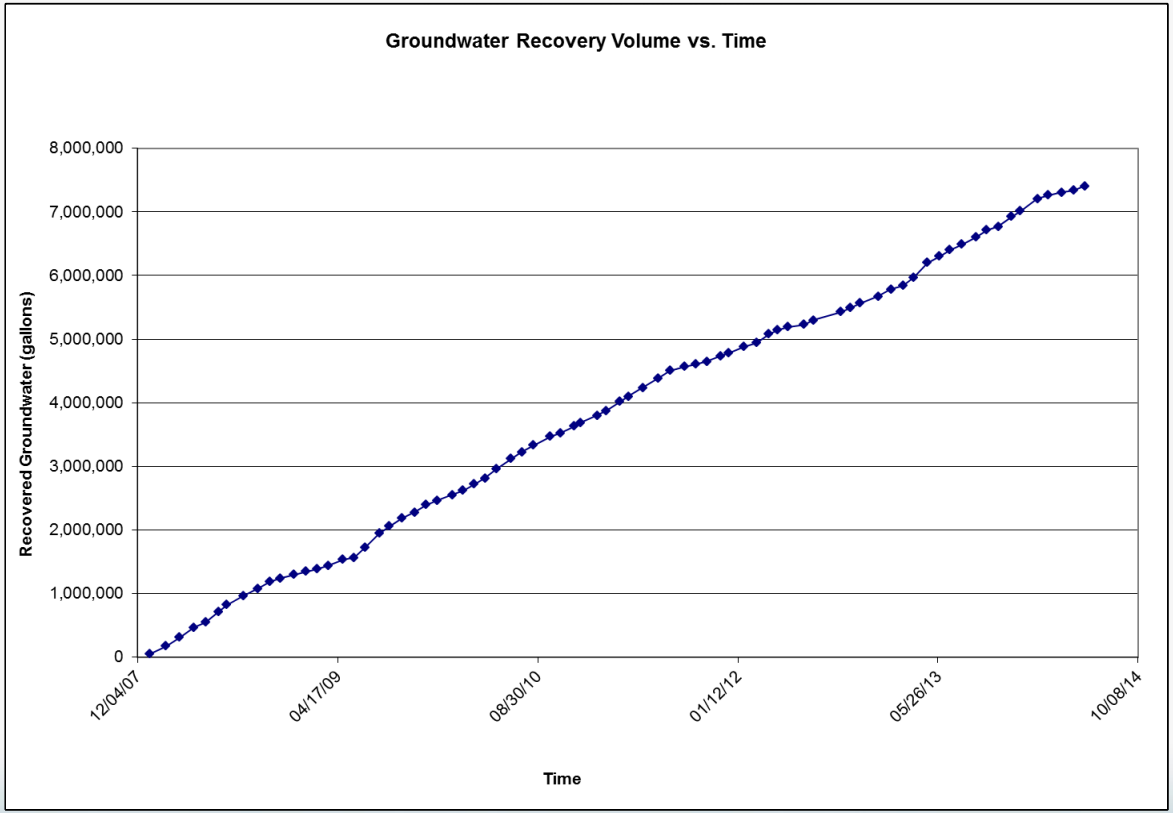
Why drive when you can fly…

Site Challenges

A Happy Camper!

DPVE Performance – Summary (2007 to 2014)

- Plume size and concentration reduction
- Vapor-Phase Removal: 9,100 pounds (690 gal. as CT)
- Dissolved-Phase Removal: 33 pounds (as CT)
- Groundwater Recovered/Treated: 7.5 Million Gallons



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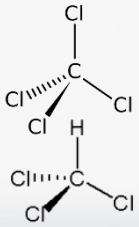
Source Area Conditions (Ca. 2006 to 2014)

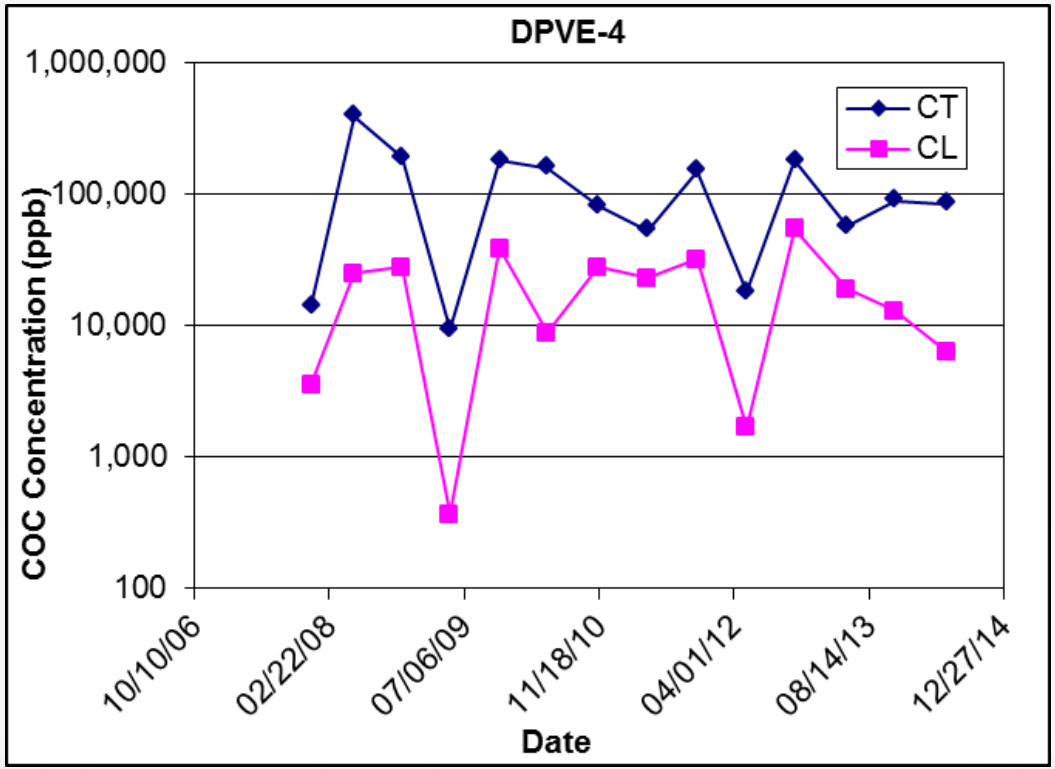
- Continued variability and persistence in source area DPVE wells

Could significant mass remain in the soil?

CT – Carbon Tetrachloride

CL – Chloroform





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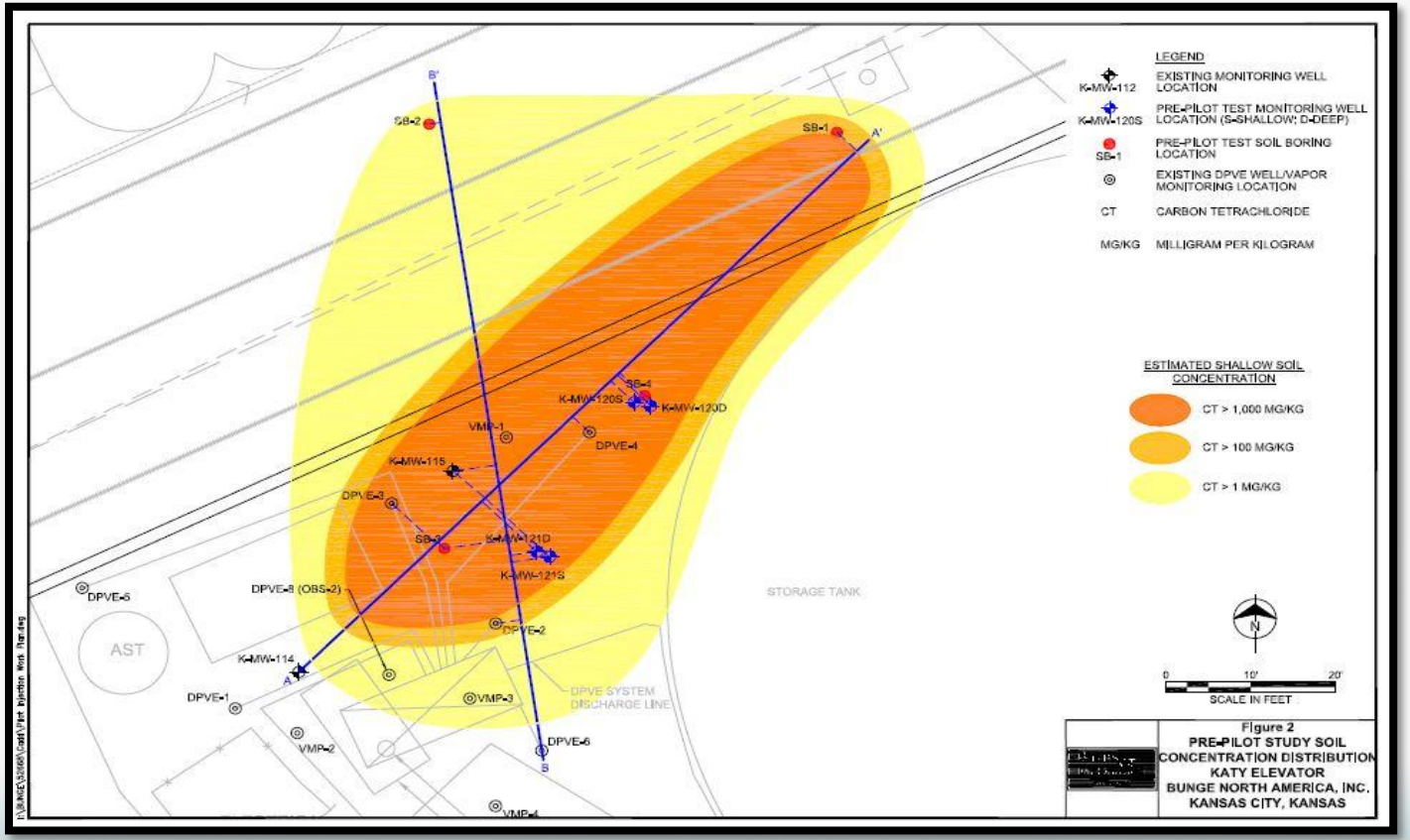
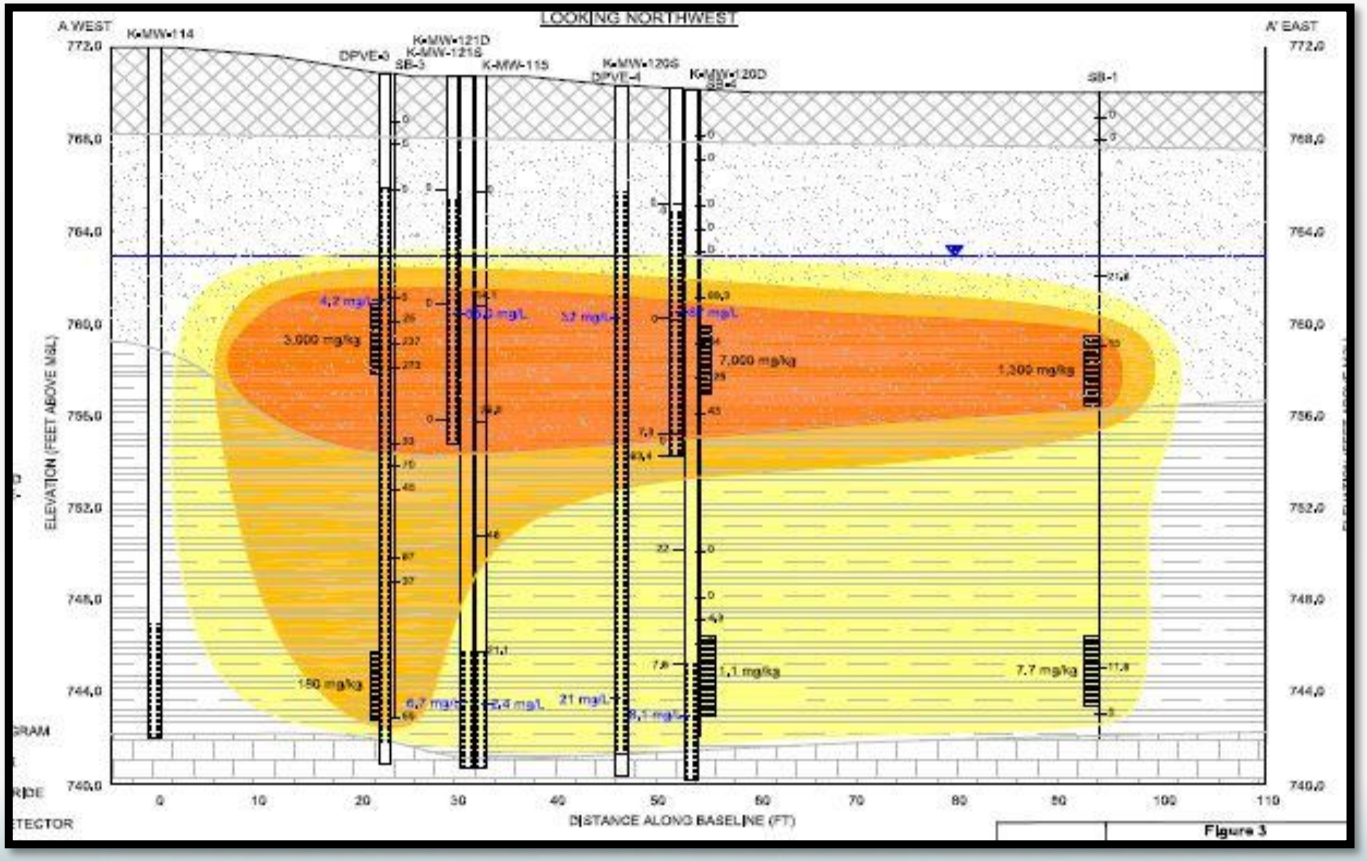
2014 Investigation Soil Results

Sample Name	SB-1/SS-1	SB-1/SS-2	SB-2/SS-1	SB-2/SS-2	SB-3/SS-1	SB-3/SS-2	SB-4/SS-1	SB-4/SS-2
Sampling Date	07/21/14	07/21/14	07/21/14	07/21/14	07/21/14	07/21/14	07/21/14	07/21/14
Sample Depth	10-13	24-26	10-13	23-28	10-13	23-28	10-13	23-28
COCs								
Carbon Tetrachloride (µg/Kg)	1,300,000	7,700	31,000 J*	16,000	3,000,000	180,000	7,000,000	1,100
Chloroform (µg/Kg)	11,000	15,000	350 J*	4,400	30,000	21,000	19,000	150
Methylene Chloride (µg/Kg)	ND (1,100)	ND (350)	ND (270) UJ	ND (340)	ND (2,700)	220 J*	ND (2,600)	ND (550)
Chloromethane (µg/Kg)	ND (430)	ND (140)	ND (110) UJ	ND (140)	ND (1,100)	ND (140)	ND (1,100)	ND (220)
Carbon Disulfide (µg/Kg)	790 J*	ND (350)	96 J*	480	180,000	28,000	42,000	ND (550)
Degradation Parameters								
Total Organic Carbon (mg/Kg)	4,600	3,400	2,200	3,800	3,400	10,000	2,600	3,800
AVS (µmol/g)	0.036	ND (0.028)	ND (0.019)	0.72	ND (0.020)	1.11	ND (0.020)	ND (0.022)
Bioavailable Iron (mg/Kg)[(1)]	NS	NS	75	239	295	538	308	412
Miscellaneous Inorganic Parameters								
Manganese (mg/Kg)	8.3	420	11	390	20	290	260	94

2014 Investigation Results (Soil)



2014 Investigation Results (Soil) A-A Cross Section



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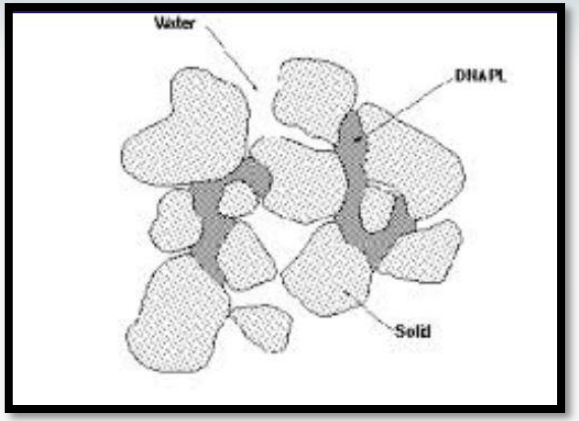
2014 Investigation Results

Source Zone Nature & Extent

- Soil data provides additional insights into mass distribution
- Shallow soil CT conc.'s ranged from 1,300 to 7,000 mg/kg>
  - Indicative of NAPL ganglia and/or concentrated sorbed phase mass
- NAPL ganglia explain variable groundwater concentrations with "Slugs" of COC mass indicative of *back-diffuse* within source zone during DPVE operation

Why does significant mass remain???



Contact time increases sorption and concentration

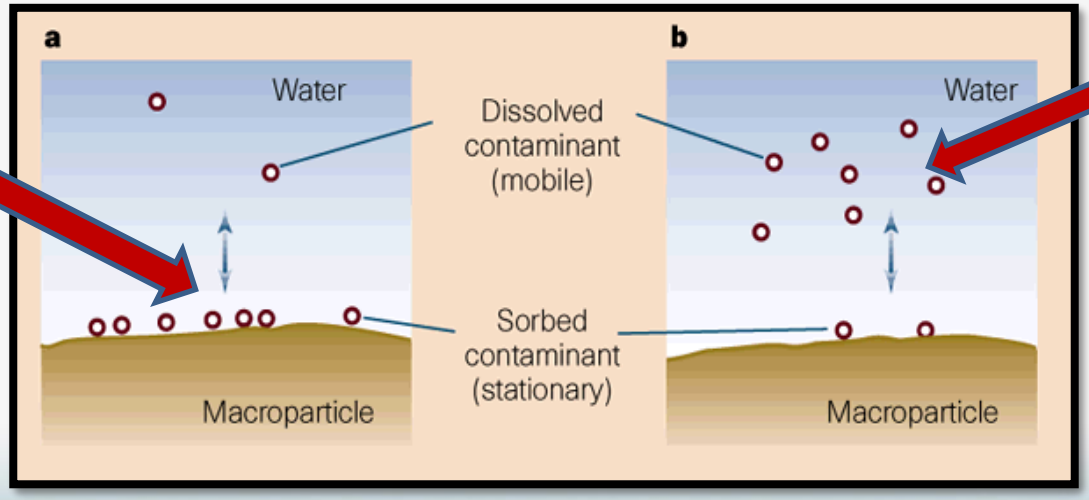
- CT typically discontinued in the mid-1960s
- Desorption rate is < adsorption rate
  - Koc (CT soil organic carbon-water partitioning coefficient): 251 L/Kg
    - Compare to vinyl chloride: 8.5 L/Kg
- Elevated organic carbon concentrations in sand zone
- Source zone periphery rapidly remediated by DPVE
  - Minimal contact time in these areas

Koc measures the mobility of a substance in soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil. A very low value means it is highly mobile in soil. Koc is a very important input parameter for estimating environmental distribution and environmental exposure level of a chemical substance

Sorption Verses Availability

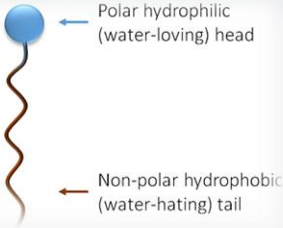
Normally hydrophobic organic chemicals exhibit limited solubility in groundwater. As a result these contaminants (Vapor, Dissolved, or NAPL) *Phase Partition* and sorb (i.e., absorb and adsorb) onto soil or bedrock surfaces. This image shows how contaminant sorption effecting their Availability and Mobility for in-situ and ex-situ remediation. SEE opportunity.

Sorbed Reduced Availability



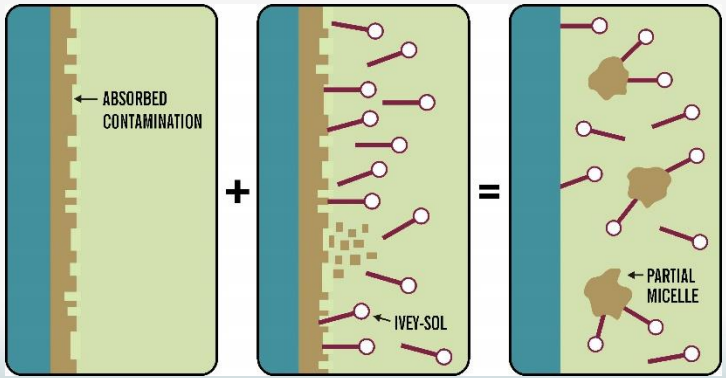
Desorbed Increased Availability

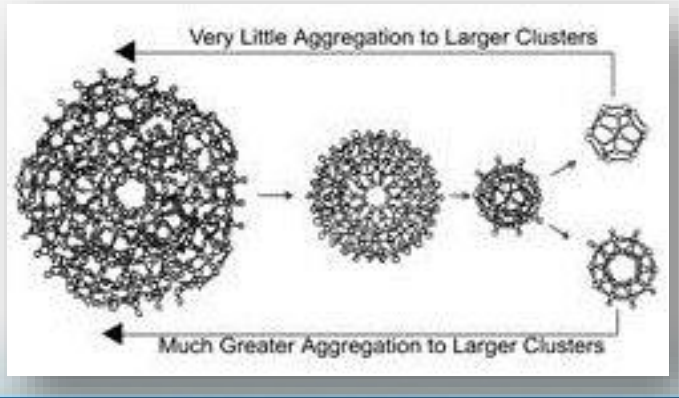
Surfactant Enhanced DPVE



How it works

- Surfactants are structured with a hydrophilic head and hydrophobic tail
- Hydrophobic tail attracts and attaches to organic portion of CT (carbon molecule)
- Hydrophilic head attracted to groundwater making CT miscible (Ivey-sol® effective below CMC)
- Lowers surface tension by reducing H_20 cluster size (73 to < 30 Dynes) improves '*apparent*' K

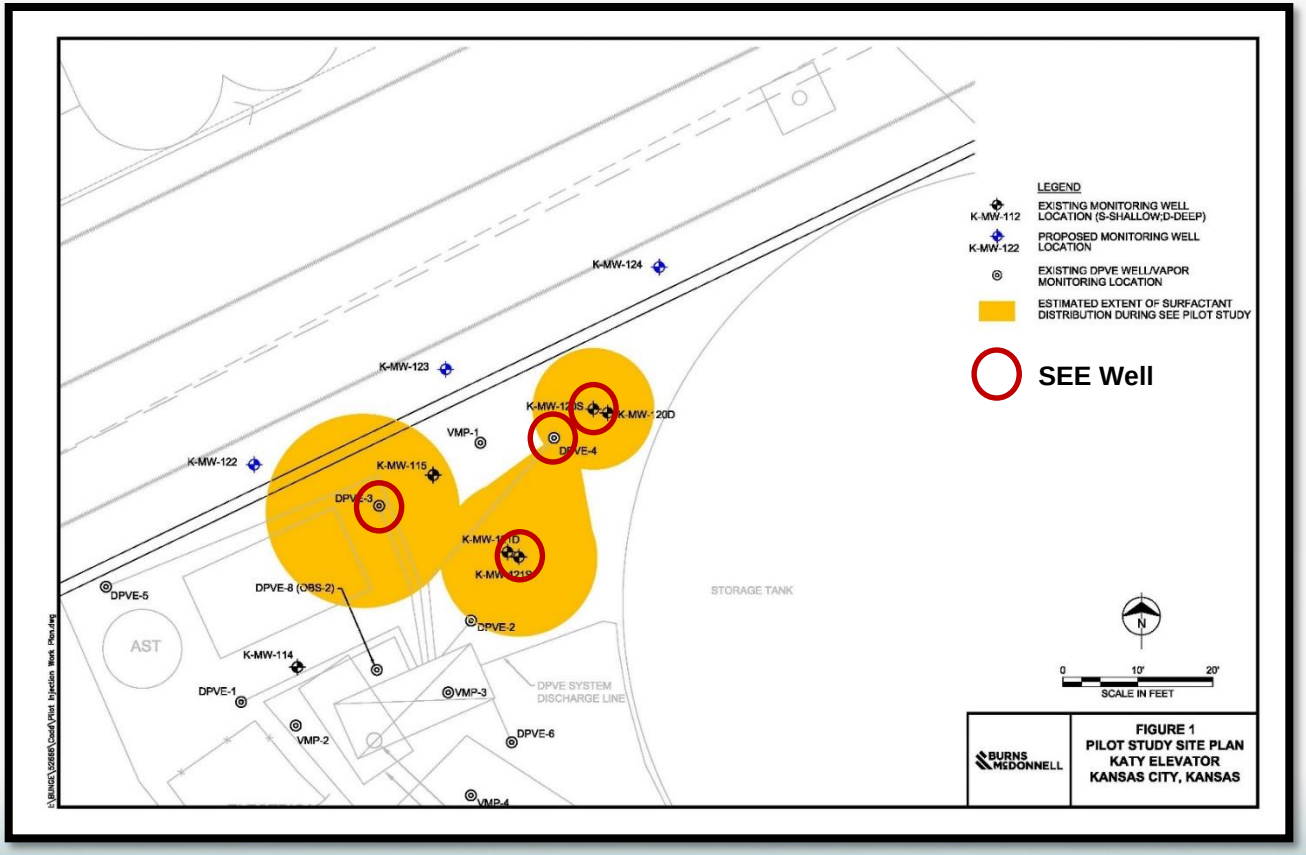




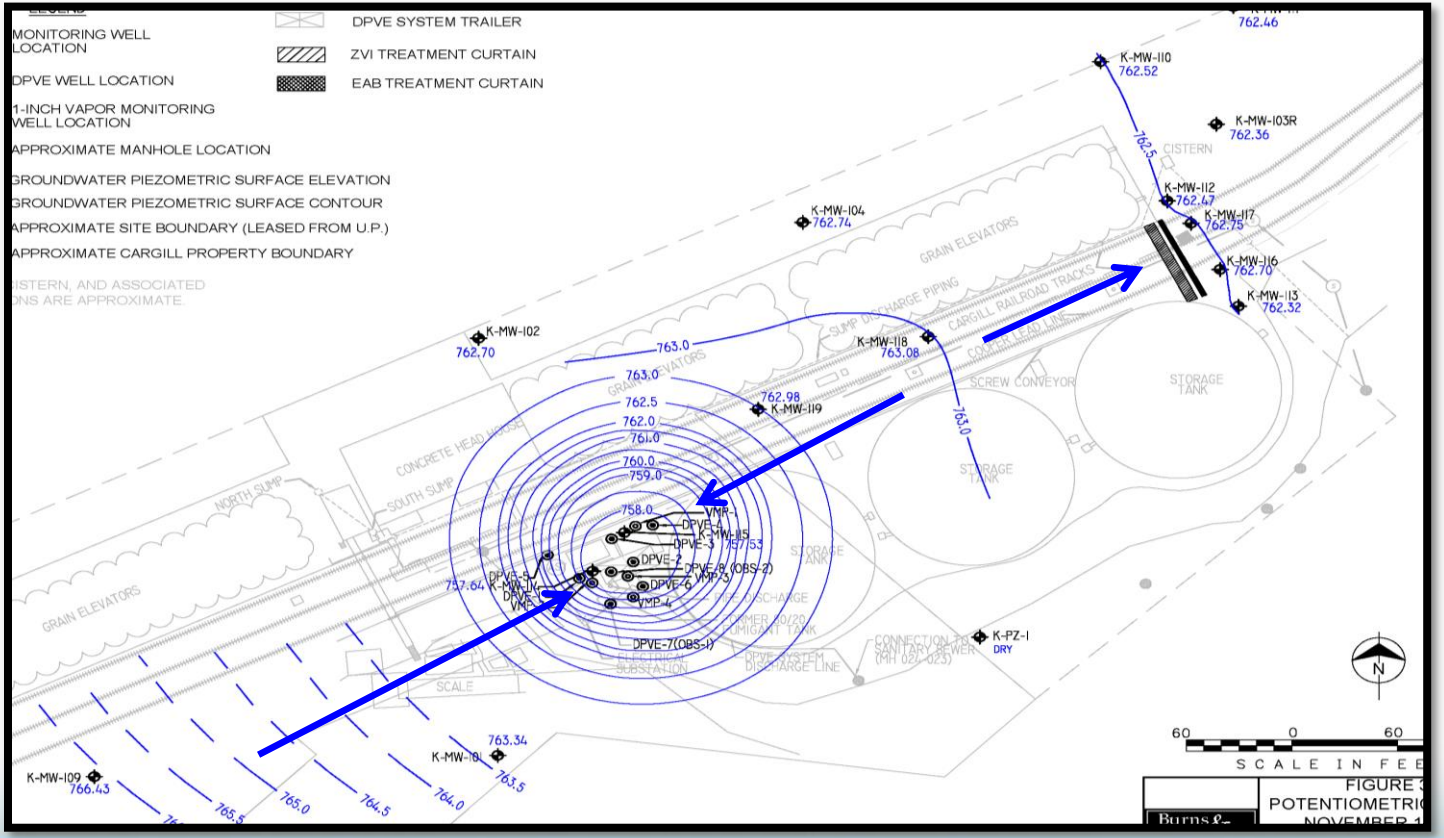
SEE Pilot Study Overview

SEE Pilot limited to:

- DPVE-3
- DPVE-4
- K-MW-120S
- K-MW-121S



DPVE Performance – Hydraulic Control and Capture

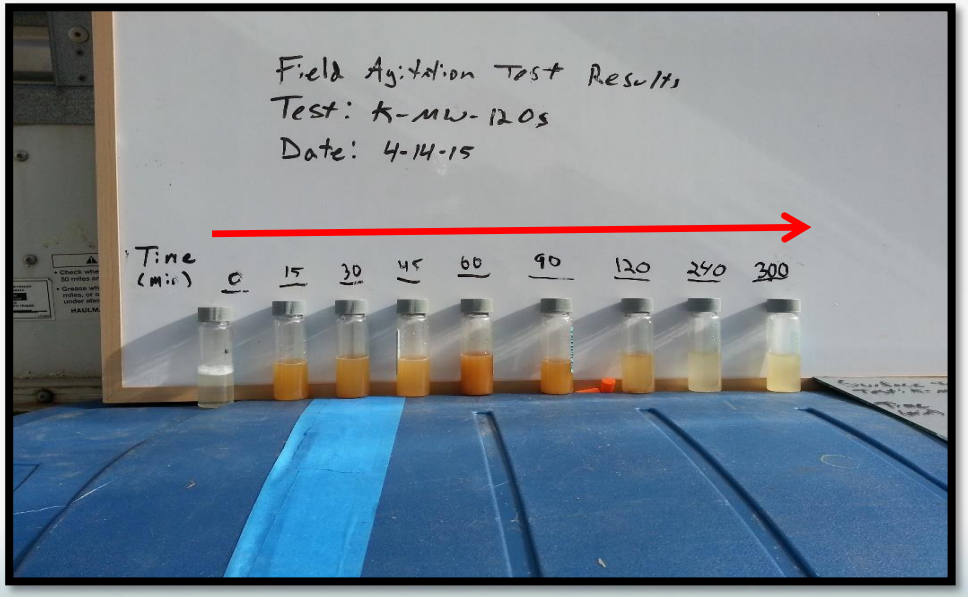


SEE Pilot Study Overview

Mixing Ivey-sol 20 L into 980 L of Water
1:50 Dilution For Application

SEE Pilot Study Overview

- SEE Pilot Test Begins Spring 2015 - Approx. 30 days
- Tests conducted at K-MW-120s, K-MW-121s, DPVE-3 and DPVE-4
- 1 Drum (55 Gal.) Surfactant Used



Field surfactant test (FST) observations at DPVE after injection into K-MW-120. Also had field PID VOC observations correlated with FST trends…they used multiple lines of evidence to aid observations & sample selection to laboratory…trends held.

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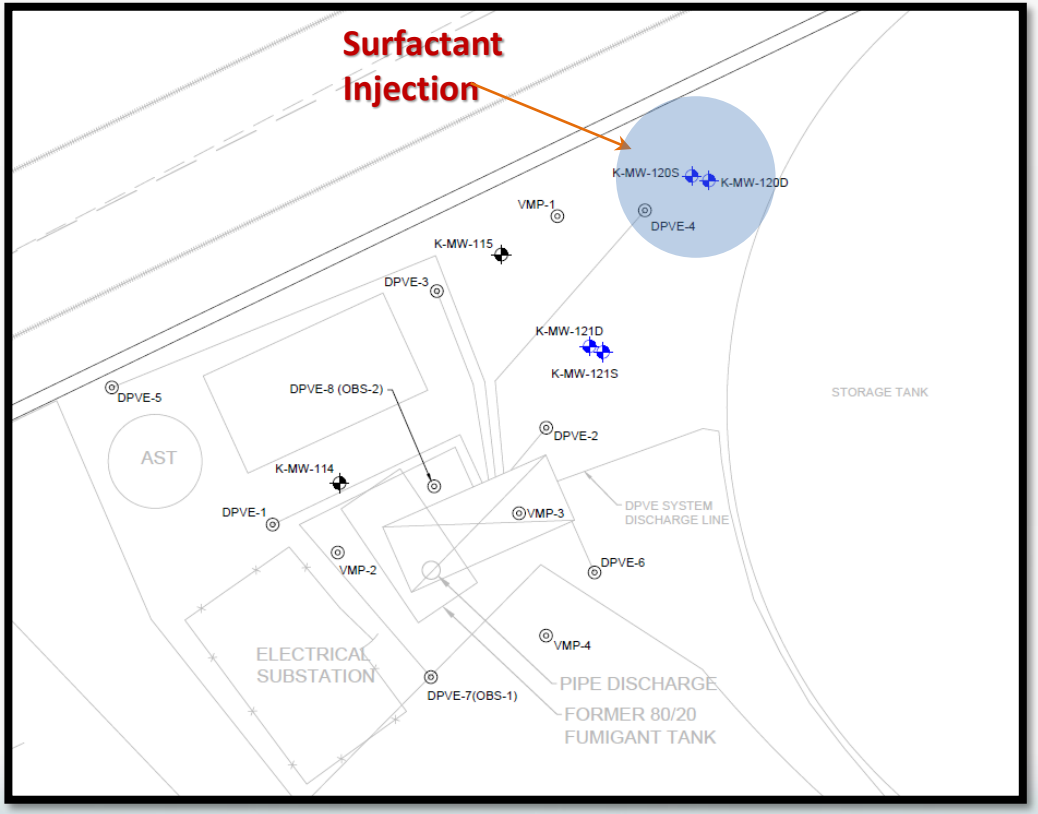
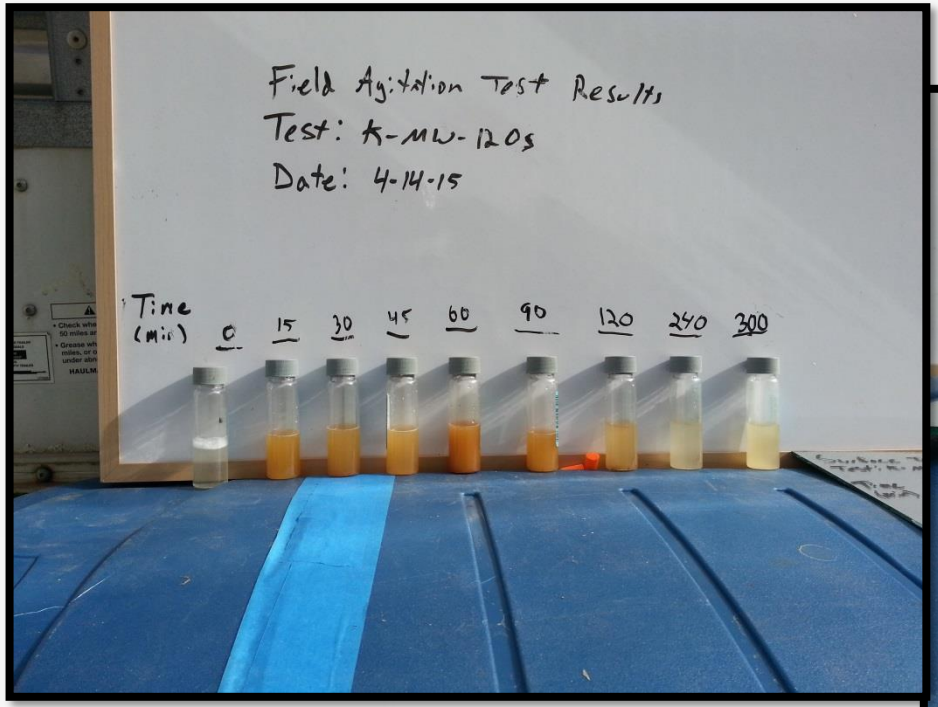
Test #1: K-MW-120s Push-Pull

- April 13 - 15, 2015
- 270 gal. water/5 gal. surfactant (1:50)
- Residence time: 20 hours
- Surfactant present in DPVE-4 (idr verification)

After 20 hours turned on DPVE system…



Test #1: K-MW-120s Push-Pull



Field Agitation Test Results

Surface Tension Test Results

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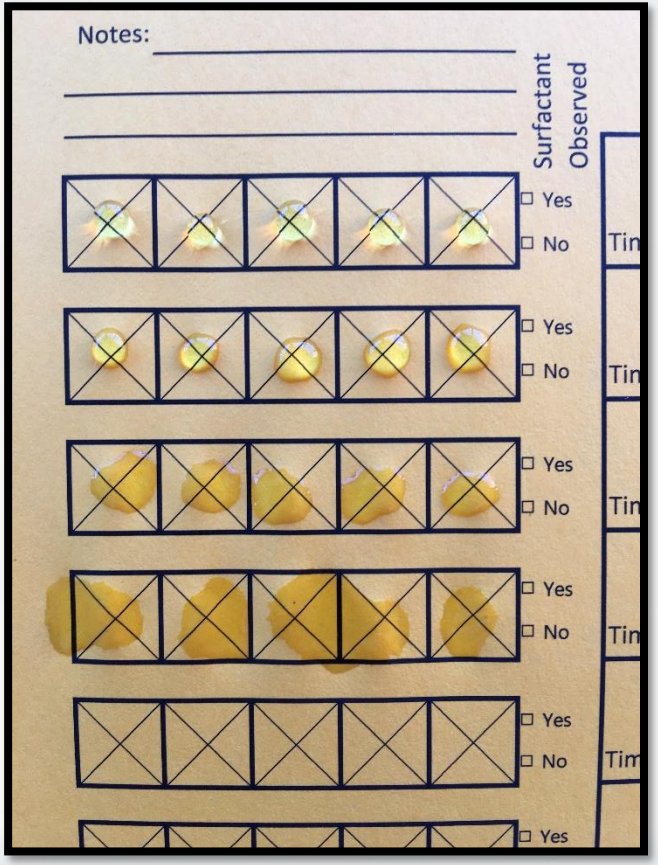
Real-Time Field Surfactant Test

Base Line Through Increasing Surfactant and COC concentration Field Testing In Real-Time

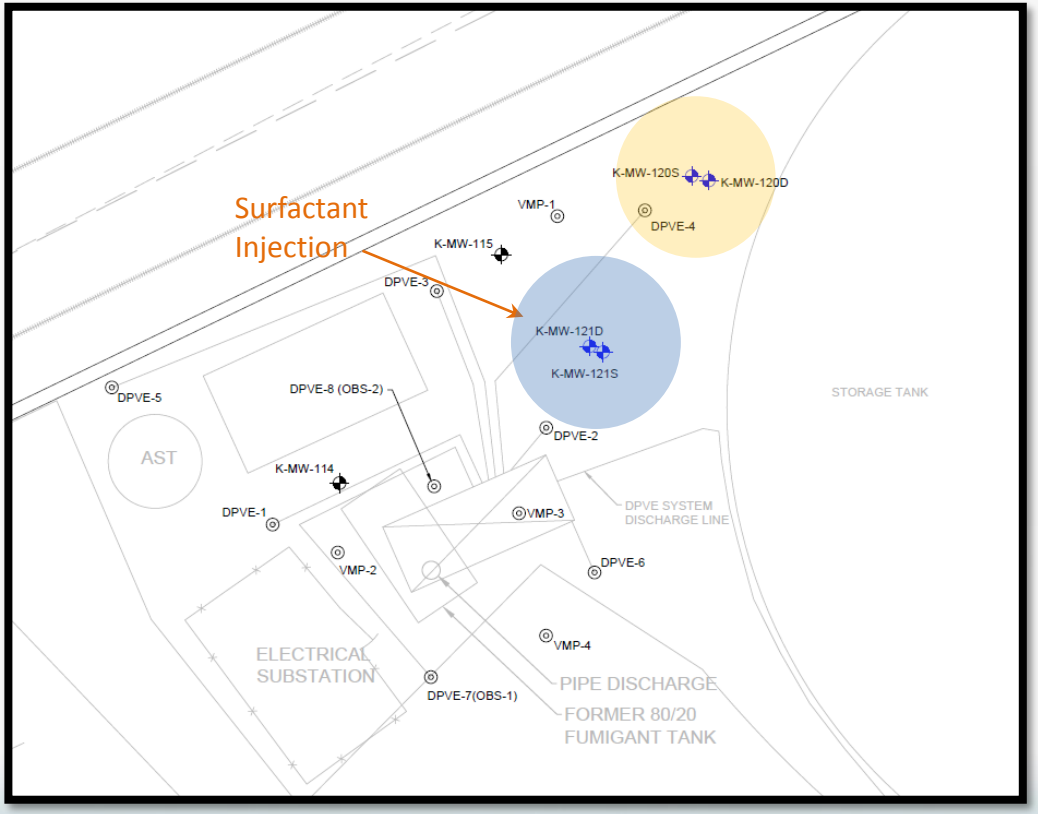
Demonstration of the field surfactant test at booth our following talk.



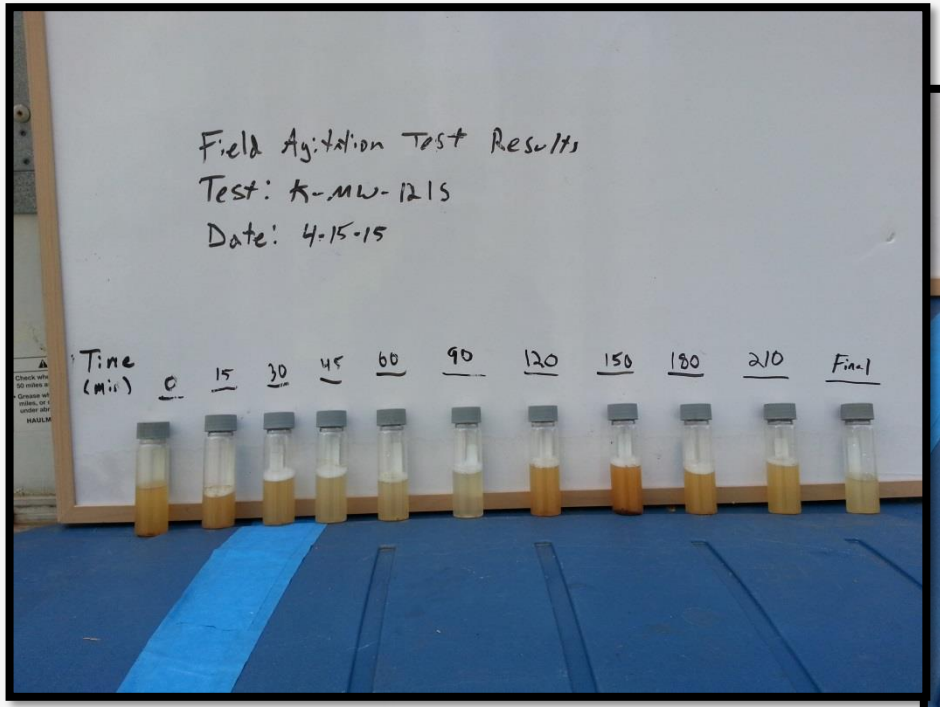
Test #2: K-MW-121s Push-Pull

- April 15 - 16, 2015
- 540 gal. water/10 gal. surfactant (Increased Volume)
- Residence time: 5 hours
- Surfactant not present in observation wells

DPVE-2 idr was less due to shorter residence time…time affects idr…low groundwater gradient.



Test #2: K-MW-121s Push-Pull



Field Agitation Test Results

Surface Tension Test Results

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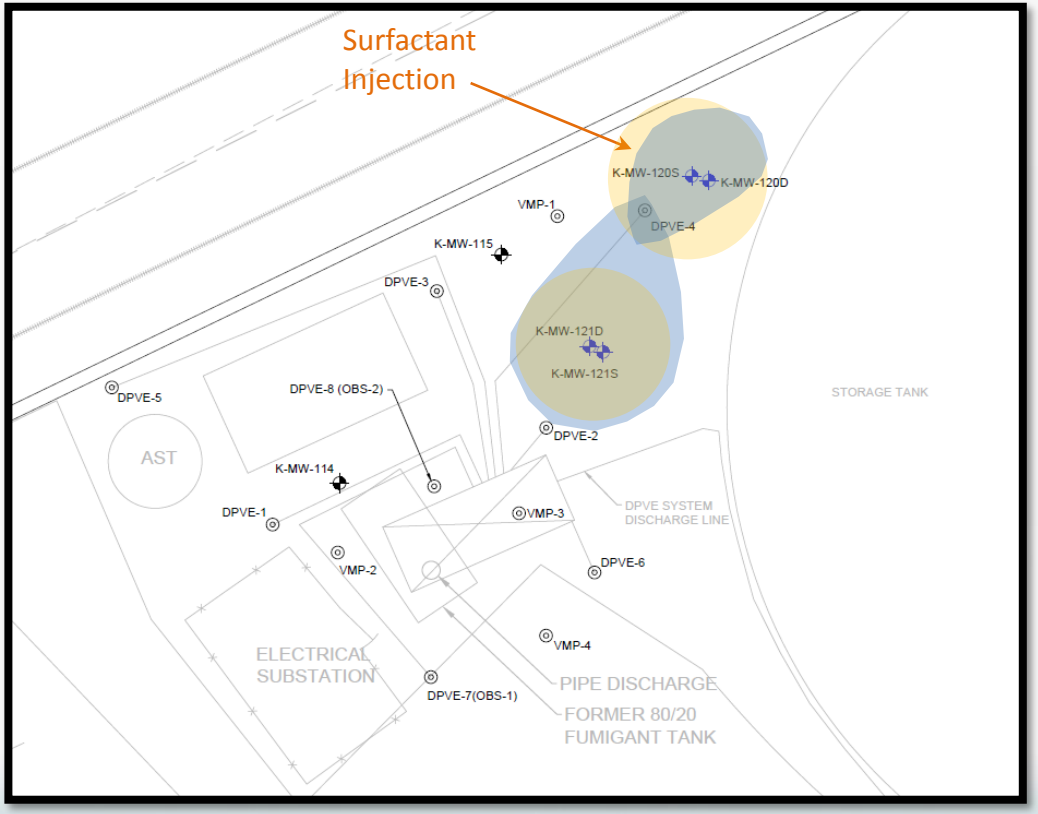
Test #3a: DPVE-4 Point-to-Point

- April 16 - 22, 2015
- 540 gal. water/10 gal. surfactant injected at K-MW-120s and 121s
- Groundwater extracted from DPVE-4
- Residence Time: N/A

Injected away from extraction well to wash through aquifer 'point-to-pint' application.



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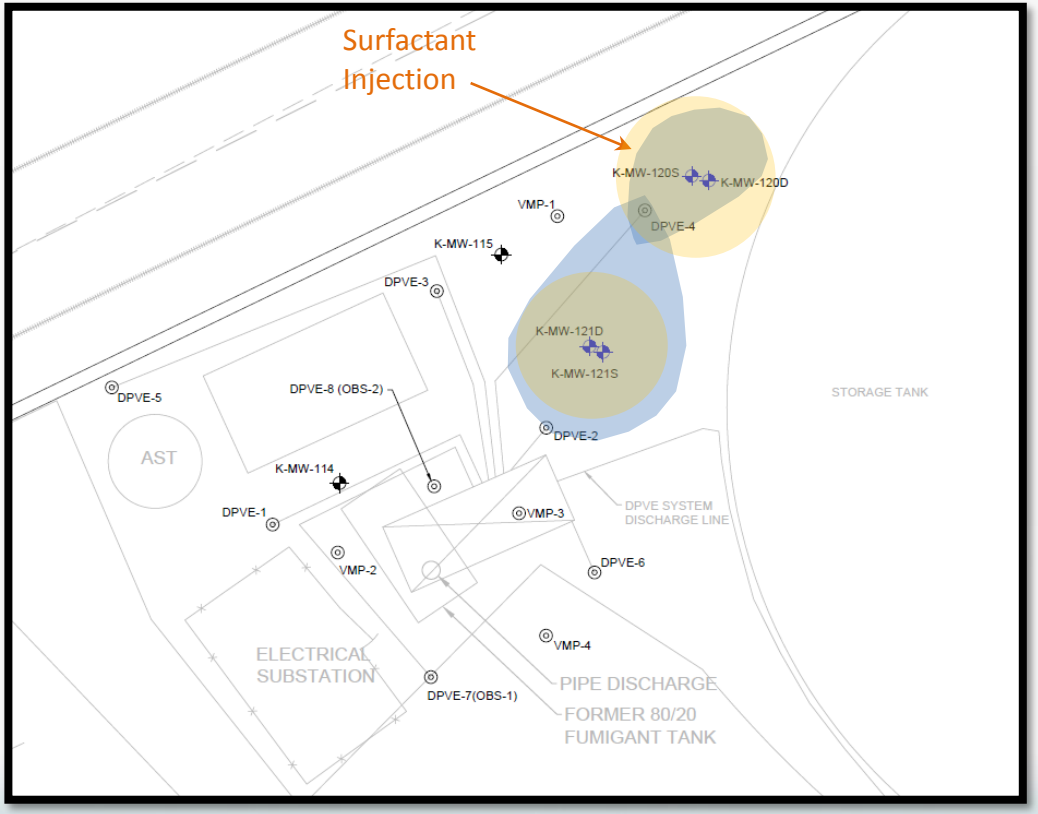
Test #3b: K-MW-120s and K-MW-121s Pull

- April 22 – May 7, 2015
- After 6 days, trace surfactant still present in K-MW-120s and 121s
- Groundwater extracted from K-MW-120s and 121s
- Residence time: 6 Days

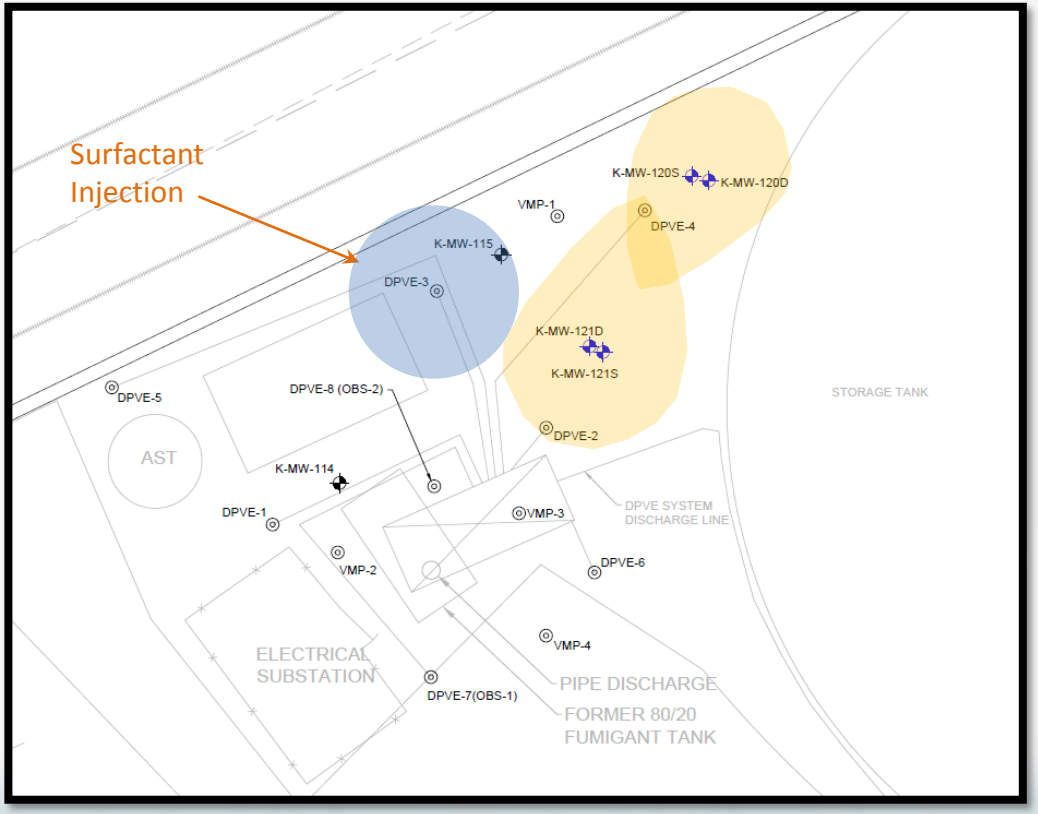
After a week still seeing Ivey-sol so decided to pull from wells injected into…most effective think due to mixing in-situ push-push and contact time.



Test #4: DPVE-3 Push-Pull

- May 7- 14, 2015
- 540 gal. water/15 gal. surfactant
- Residence time: 4 days
- Surfactant not present in observation wells

Push-pull at DPVE-3 using higher volume and slightly higher [Ivey-sol].

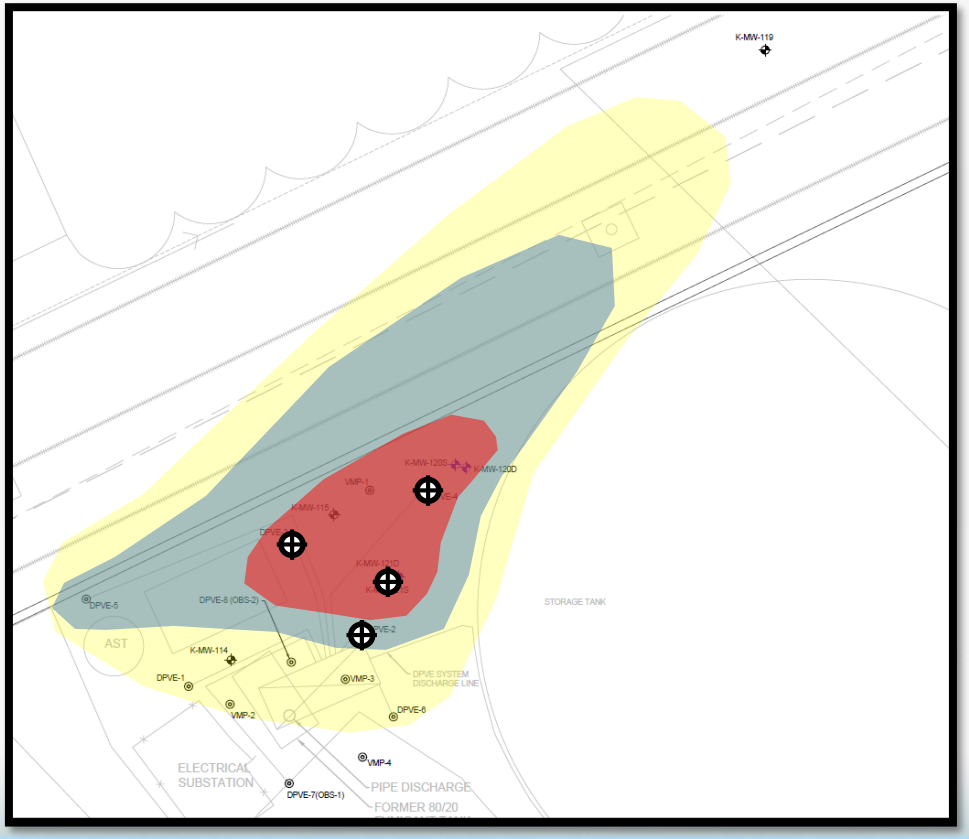


Pilot Study Results

- Test #1 – Slight increase in mass removal
  - Minimal injection volume
- Test #2 – Greater increase in mass removal
  - Minimal residence time
- Test #3a/3b – Influent groundwater concentration (8,100 ug/L) *highest ever recorded by over 50-percent*
  - Increased residence time and aquifer mixing
- Test #4 – *Influent groundwater concentrations 4x greater than average (>> 400% Increase)*
  - Increased residence time and injection volume

Pre-SEE Pilot Study Plume Conditions – Shallow Zone

50,000 ug/l
1,000 ug/l
10 ug/l



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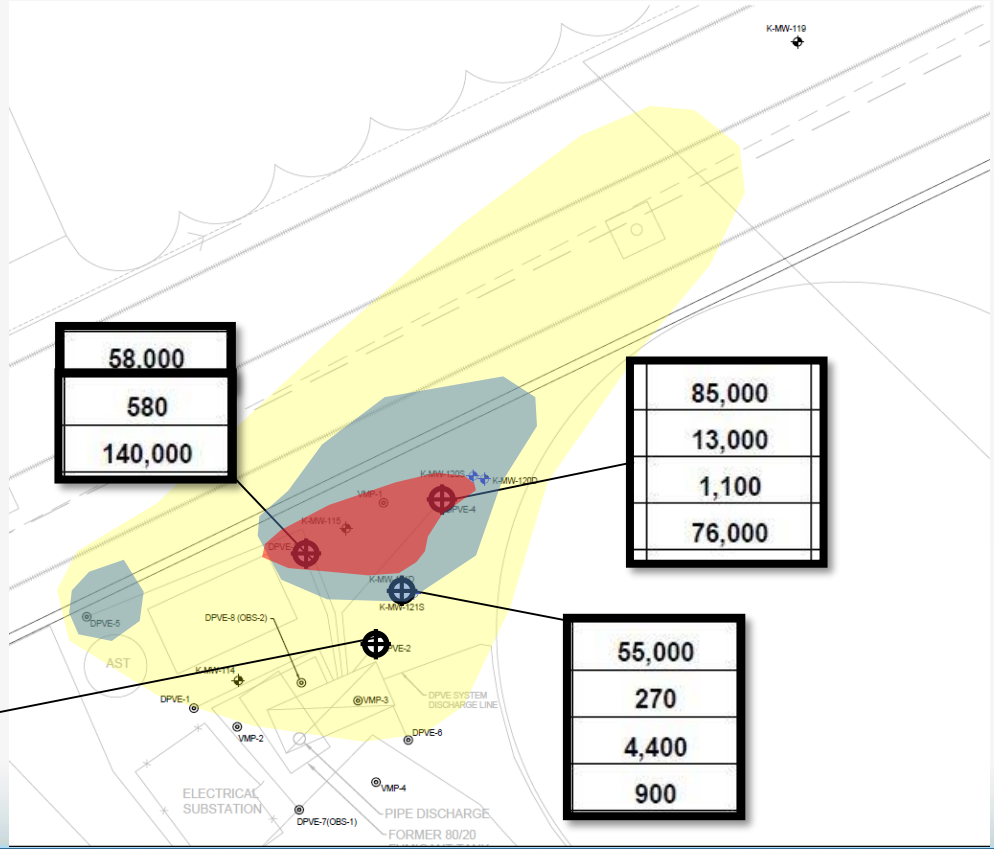
Post Pilot-scale Plume Conditions – Shallow Zone

50,000 ug/l
1,000 ug/l
10 ug/l



Sustained mobility yielding mass recovery in heart of plume…at active RW

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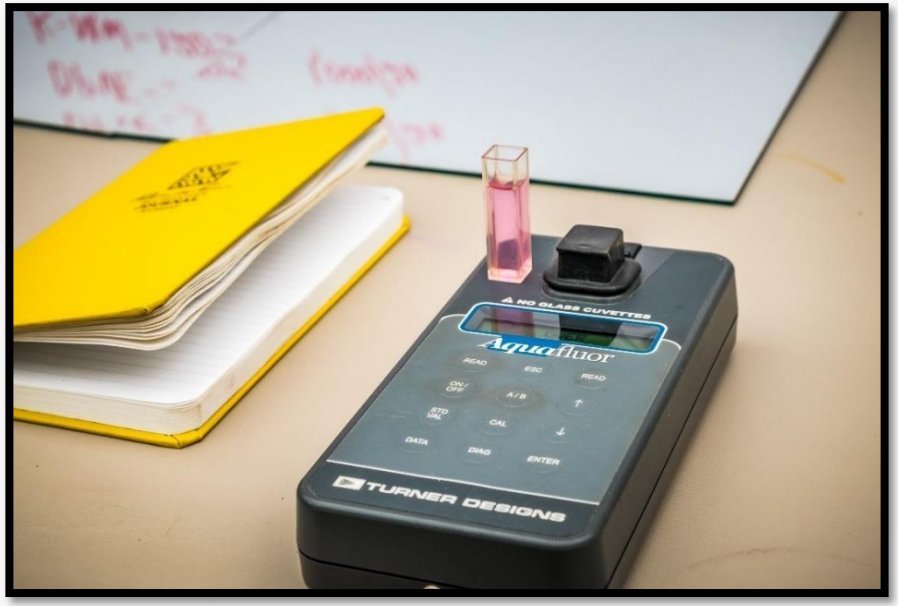
Full-Scale SEE

- August through November 2016
- 275 Gallons Ivey-sol 106 (Cl) Surfactant Formulation
  - Mixed with conservative tracer for distribution observation
- Applied *Push-Pull* and *Point-to-Point* Ivey-sol Flushing
- Monitored in-situ applications via real-time tracer testing and using the Ivey-sol field surfactant test sheets.

Full-Scale SEE



Aquaflour Meter: measures intensity of fluorescence.

Diluted Ivey-sol in water with tracer added – pre injection mixing.

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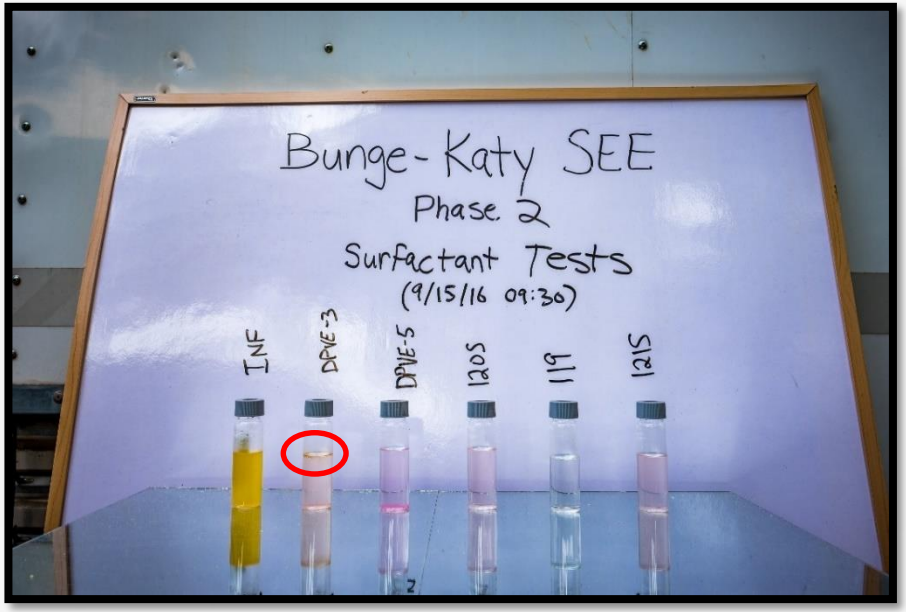
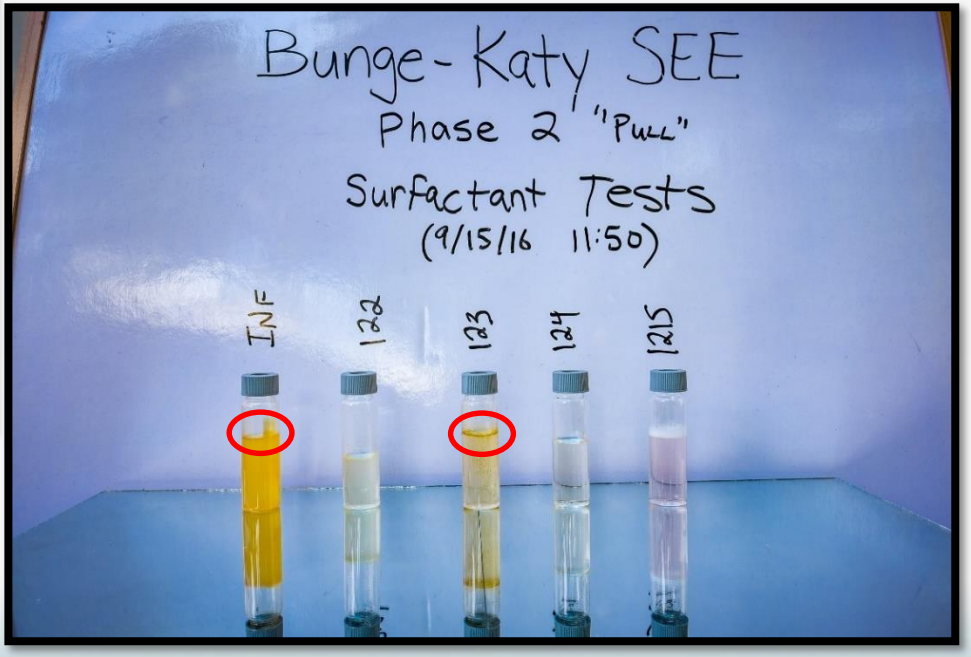
Full-Scale SEE





Indicative of LNAPL which was loaded with COC…got both CT & TPH. 119 was down gradient no tracer of surfactant confirming hydraulic control.

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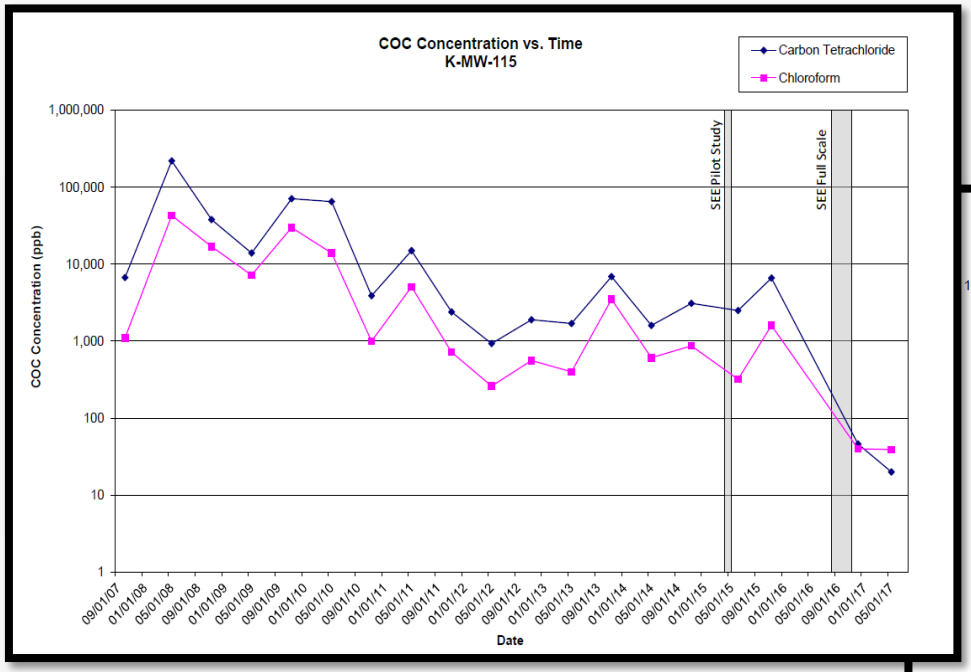
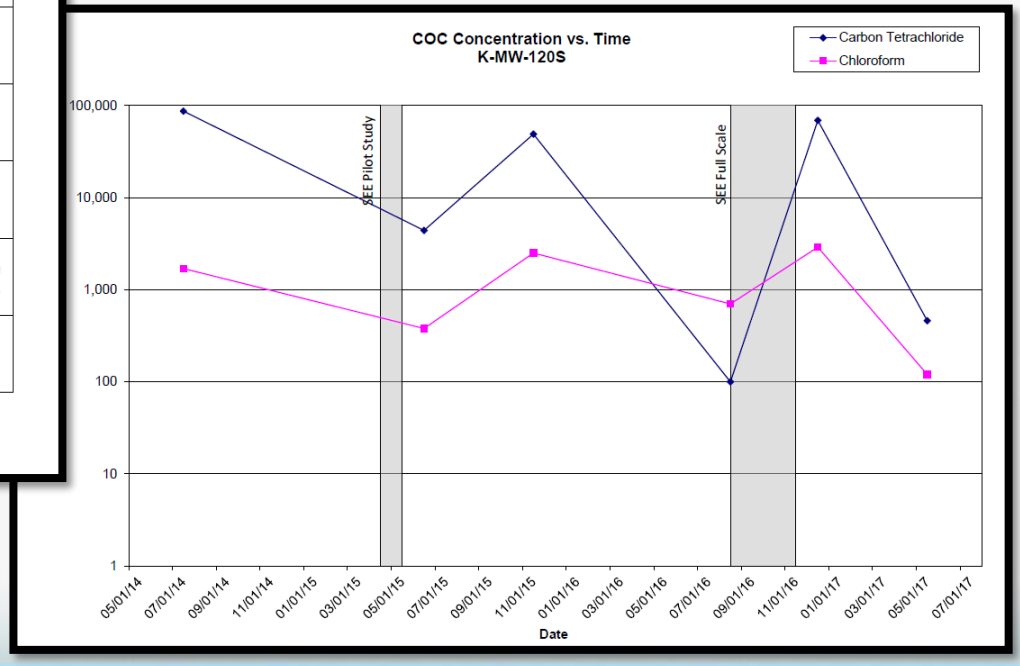
Full-Scale SEE



K-MW-120s install in 2014 for pilot…Log scale 100K to <1K 2017-2017 due to pilot & full scale 3+ order of magnitude [COC] reductions



Log scale 2011-2015 flat then Ivey-sol applications yields significant [COC] 2+ order of magnitude reductions.

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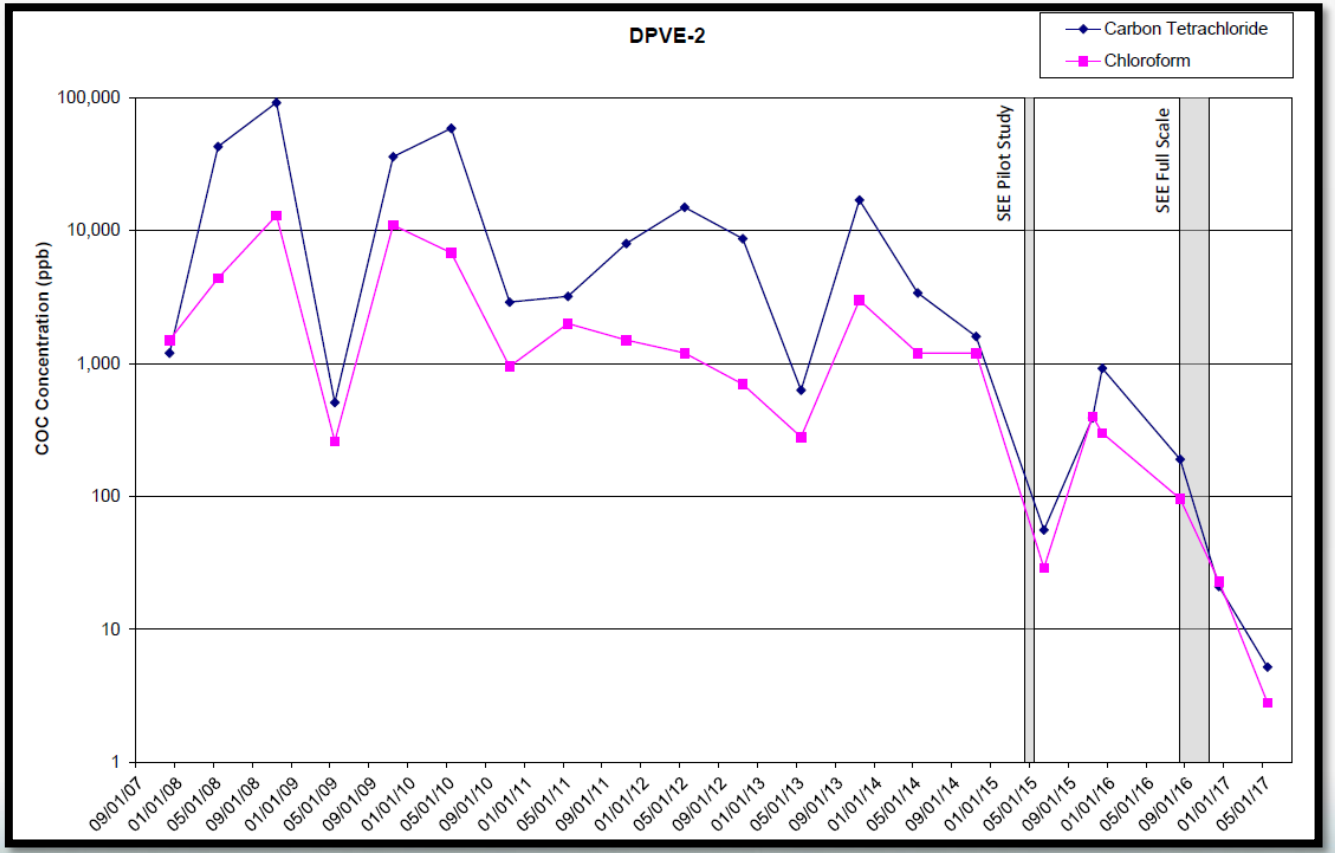
Full-Scale SEE

1-year of periodic pilot scale CT clean-up did more than they could accomplish in 7+ years

Almost down to the 5 ppb clean-up goal.

November 2017 sampling event scheduled.



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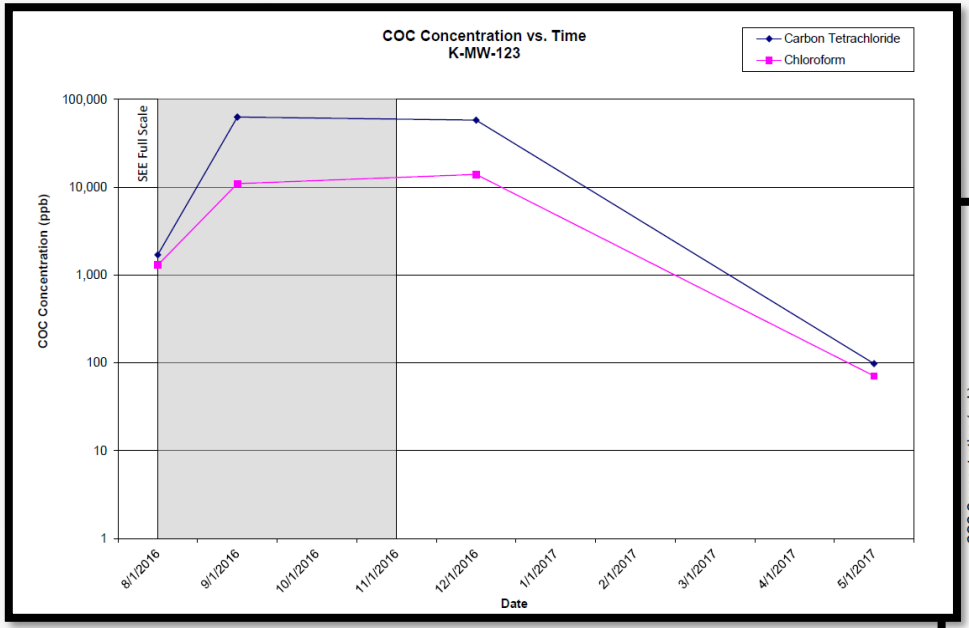
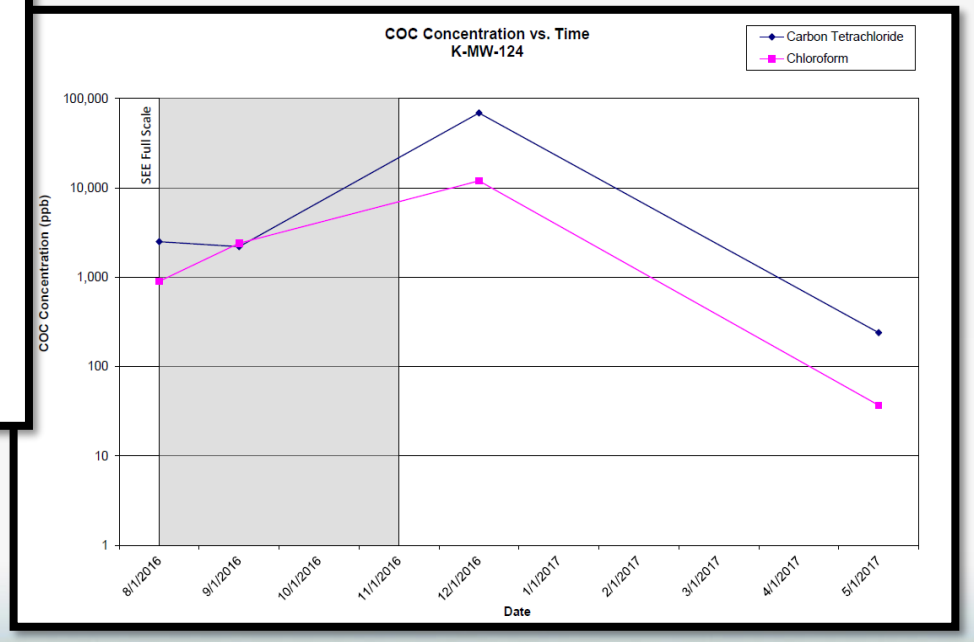
Full-Scale SEE



At these wells installed in Aug. 2015 for full scale…baseline through Ivey-sol applications yielded significant orders of magnitude drops in [COC].



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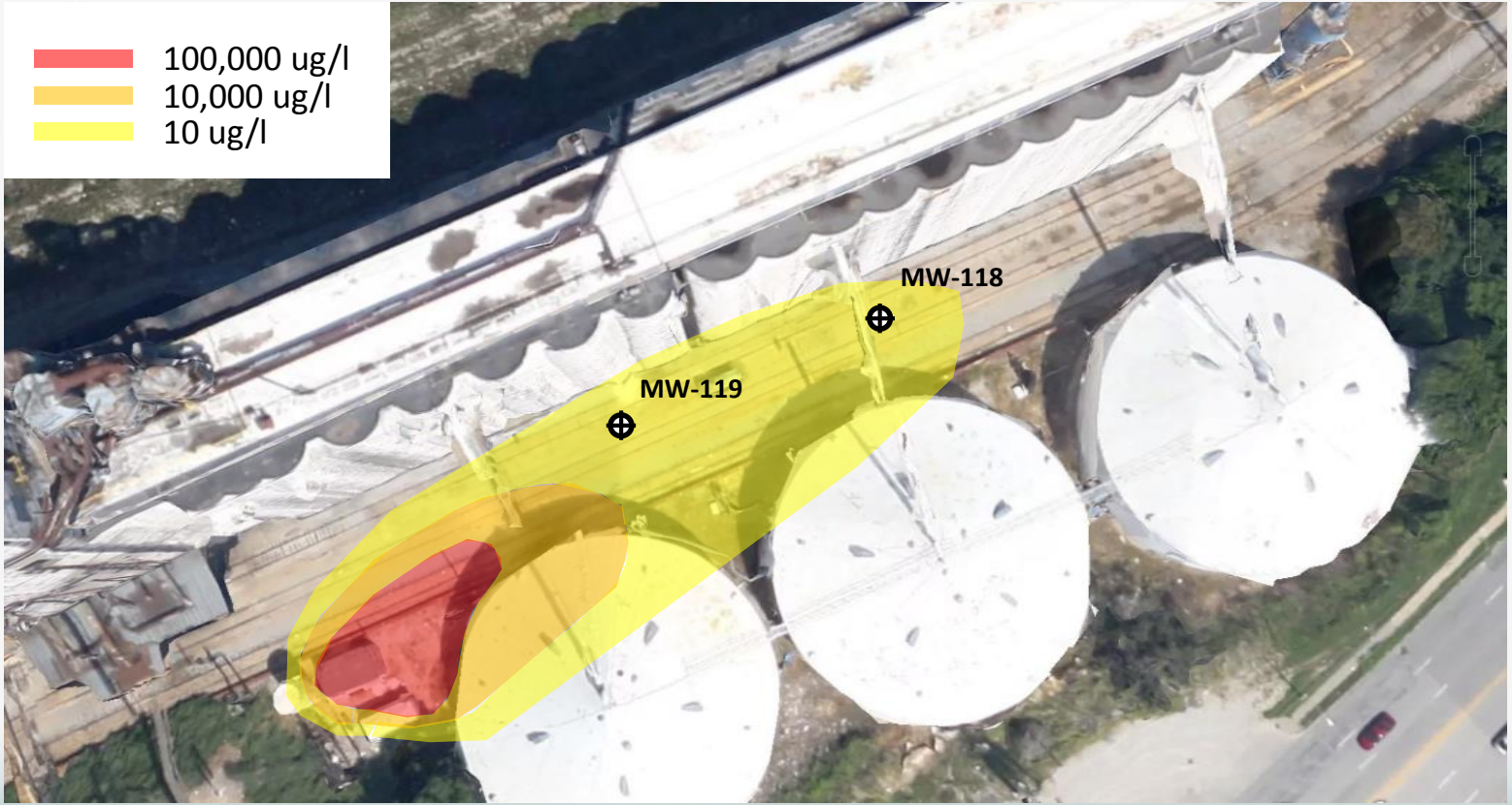
Original Plume Conditions



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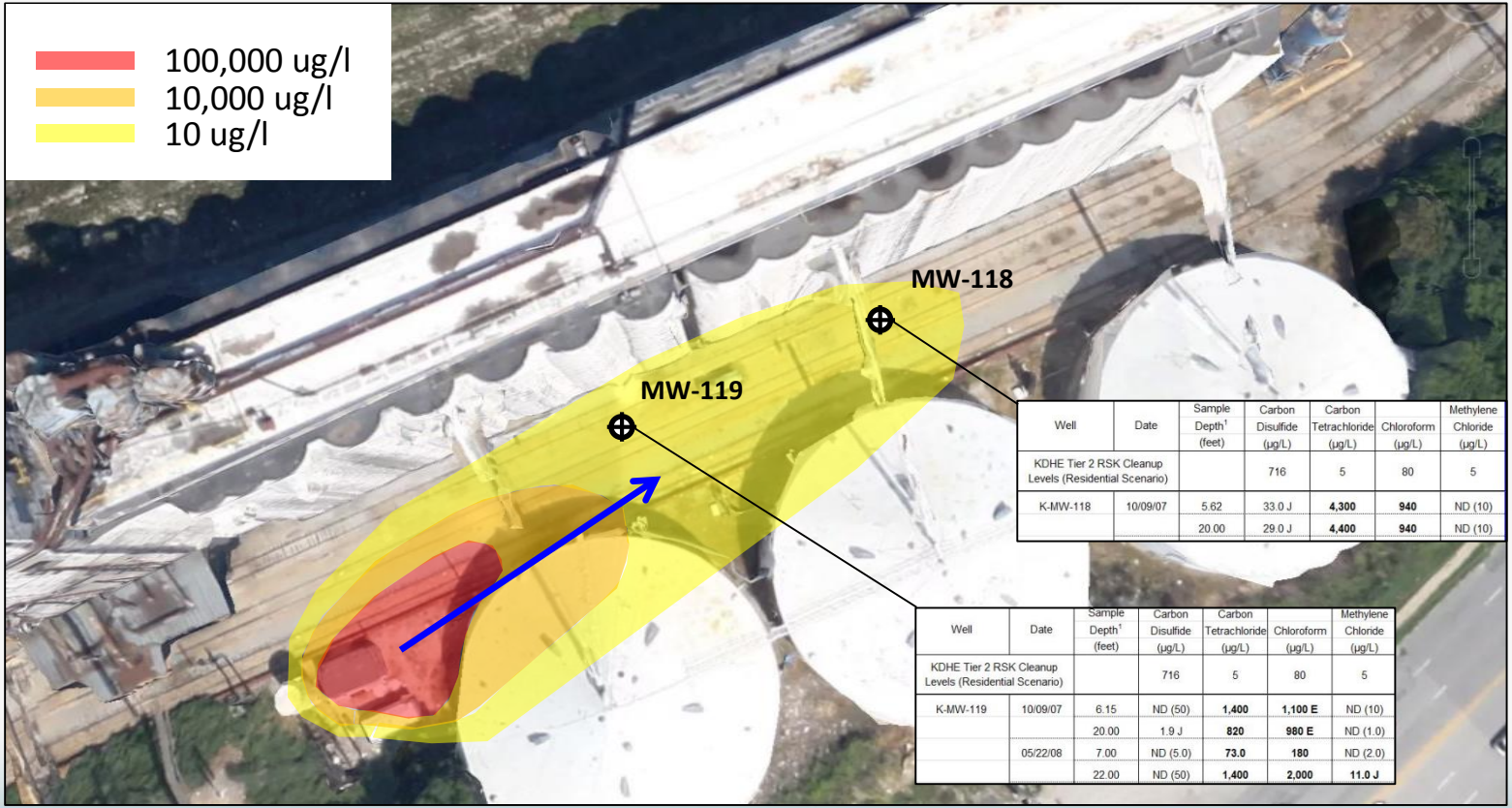
Pre-Remediation Plume Conditions



Well	Date	Sample Depth[1] (feet)	Carbon Disulfide (µg/L)	Carbon Tetrachloride (µg/L)	Chloroform (µg/L)	Methylene Chloride (µg/L)
KDHE Tier 2 RSK Cleanup Levels (Residential Scenario)			716	5	80	5
K-MW-118	10/09/07	5.62	33.0 J	**4,300**	**940**	ND (10)
		20.00	29.0 J	**4,400**	**940**	ND (10)

Well	Date	Sample Depth[1] (feet)	Carbon Disulfide (µg/L)	Carbon Tetrachloride (µg/L)	Chloroform (µg/L)	Methylene Chloride (µg/L)
KDHE Tier 2 RSK Cleanup Levels (Residential Scenario)			716	5	80	5
K-MW-119	10/09/07	6.15	ND (50)	**1,400**	**1,100 E**	ND (10)
		20.00	1.9 J	**820**	**980 E**	ND (1.0)
	05/22/08	7.00	ND (5.0)	**73.0**	**180**	ND (2.0)
		22.00	ND (50)	**1,400**	**2,000**	**11.0 J**

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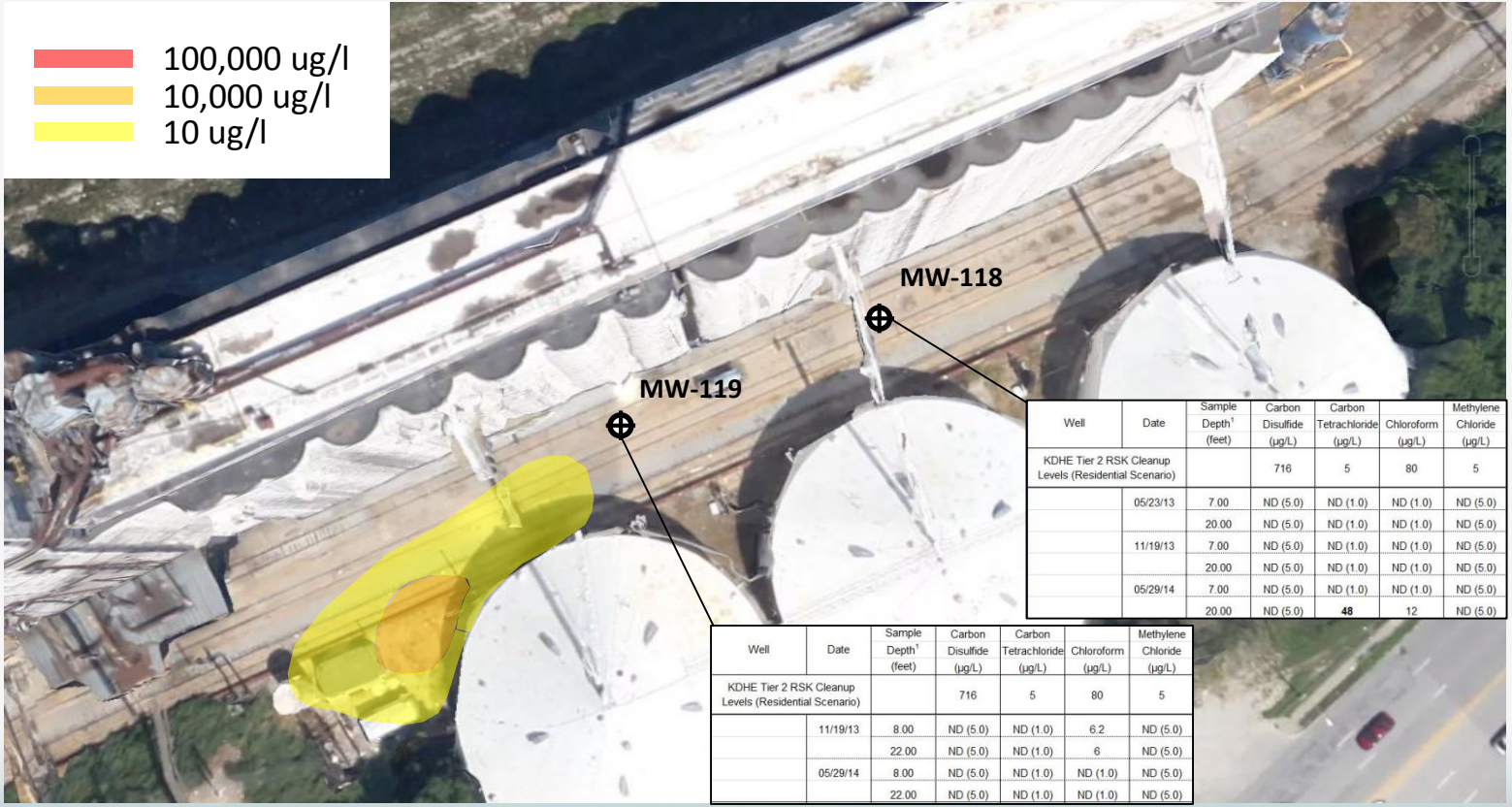
Post-DPVE SEE Remediation Plume Conditions (Pilot)



Well	Date	Sample Depth[1] (feet)	Carbon Disulfide (µg/L)	Carbon Tetrachloride (µg/L)	Chloroform (µg/L)	Methylene Chloride (µg/L)
KDHE Tier 2 RSK Cleanup Levels (Residential Scenario)			716	5	80	5
	05/23/13	7.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
		20.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
	11/19/13	7.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
		20.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
	05/29/14	7.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
		20.00	ND (5.0)	**48**	12	ND (5.0)

Well	Date	Sample Depth[1] (feet)	Carbon Disulfide (µg/L)	Carbon Tetrachloride (µg/L)	Chloroform (µg/L)	Methylene Chloride (µg/L)
KDHE Tier 2 RSK Cleanup Levels (Residential Scenario)			716	5	80	5
	11/19/13	8.00	ND (5.0)	ND (1.0)	6.2	ND (5.0)
		22.00	ND (5.0)	ND (1.0)	6	ND (5.0)
	05/29/14	8.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)
		22.00	ND (5.0)	ND (1.0)	ND (1.0)	ND (5.0)

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Full-Scale SEE Results

- K-MW-115, 120S, 121S, and 123: ***99% reduction since pilot study***
- K-MW-124: ***90% reduction since pilot study*** DPVE-3 and DPVE-4 remain variable
  - Post-SEE monitoring indicate elevated COC mass mobilized during SEE activities still being recovered by these extraction wells
- They have seen further reductions in COC mass on site and next round of sampling is scheduled for November 2017.

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