

Combined Remedies to Expedite Remediation of a Carbon Tetrachloride Source Zone at an Active Grain Elevator Facility

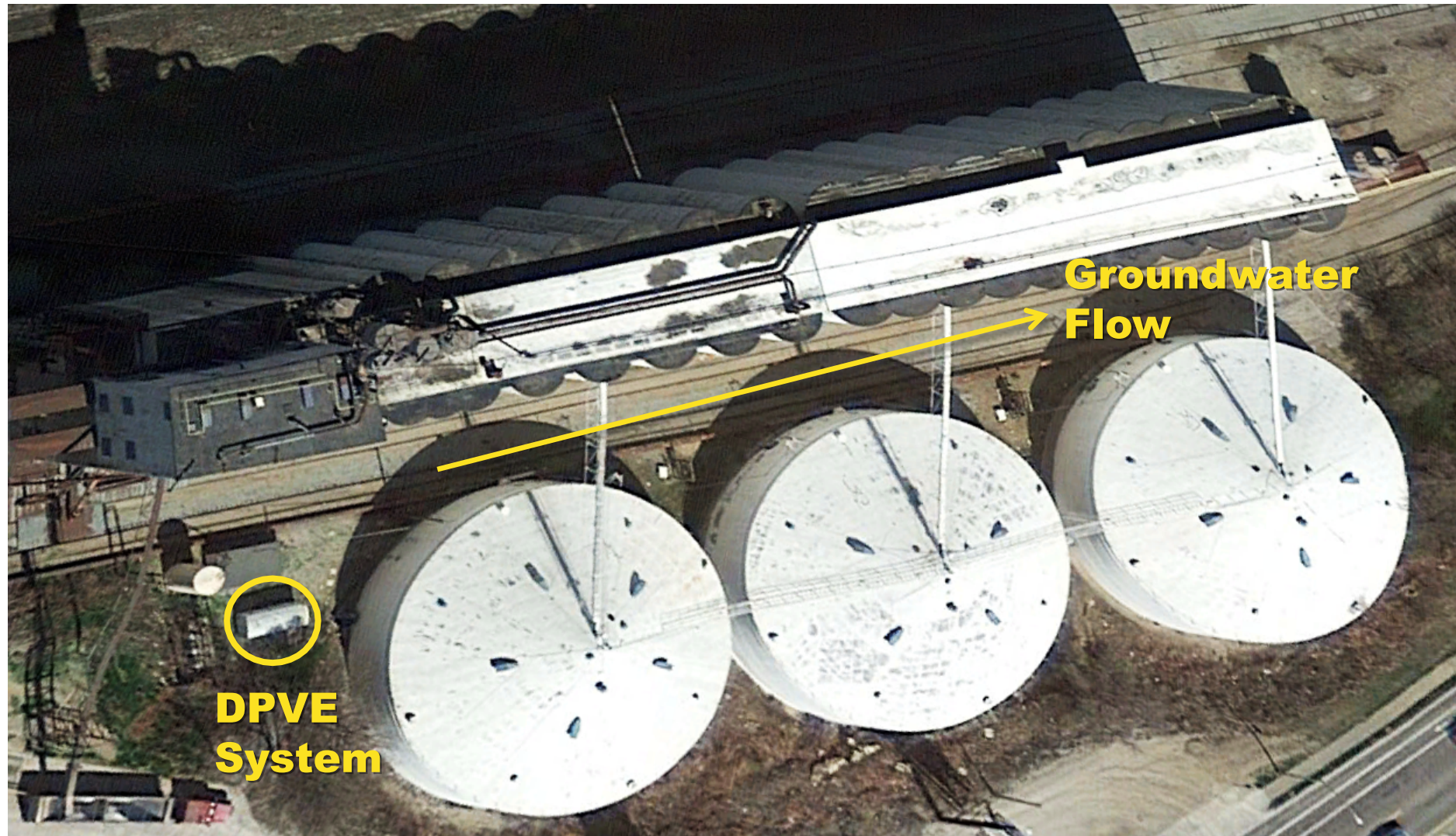
Eric Dulle, PE

June 6, 2024
2024 Chlorinated Conference
Denver, CO

SITE REMEDIATION PRESENTATION OVERVIEW

- ▶ Active Grain Elevator Facility - Kansas City, Kansas
- ▶ 80/20 Fumigant Mixture – Carbon Tetrachloride and Carbon Disulfide – Used in 70s and 80s
- ▶ Leaks from AST Discovered in 90s – Groundwater and Soil Impacts
- ▶ Site Enters KDHE Voluntary Cleanup Program: 2000
- ▶ DPVE System Installation & Operation: Dec. 2007 to 2019
- ▶ Surfactant Enhanced Extraction (SEE) Pilot Study: Spring 2015
- ▶ SEE Full-Scale: Fall 2016
- ▶ In-Situ Chemical Reduction: 2020

SITE LAYOUT



SITE CHALLENGES

- ▶ Limited vehicle access led to creative equipment placement



SITE CHALLENGES

- ▶ DPVE system installed by crane

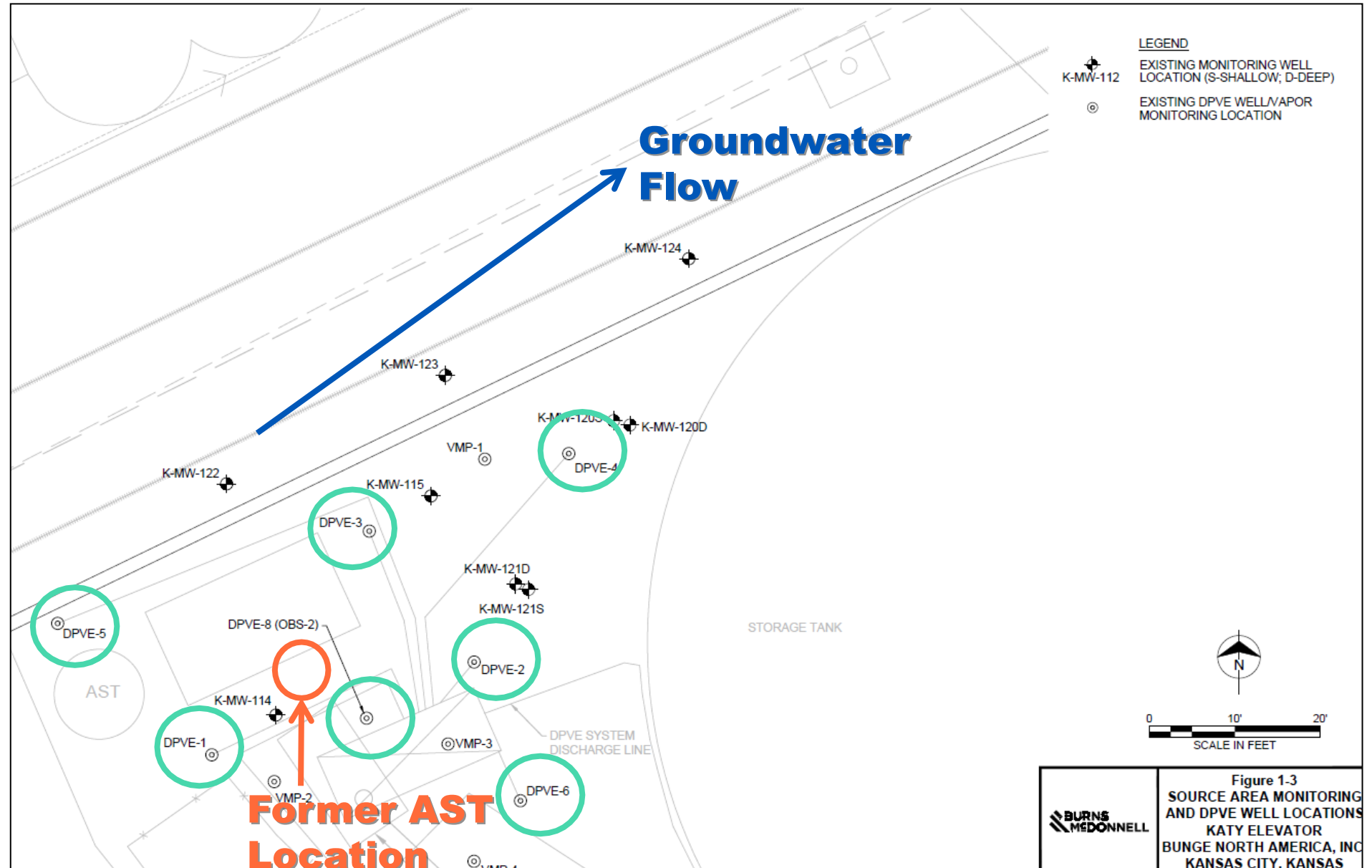


SITE CHALLENGES

- ▶ DPVE system situated adjacent to substation, railroad tracks, and elevator infrastructure

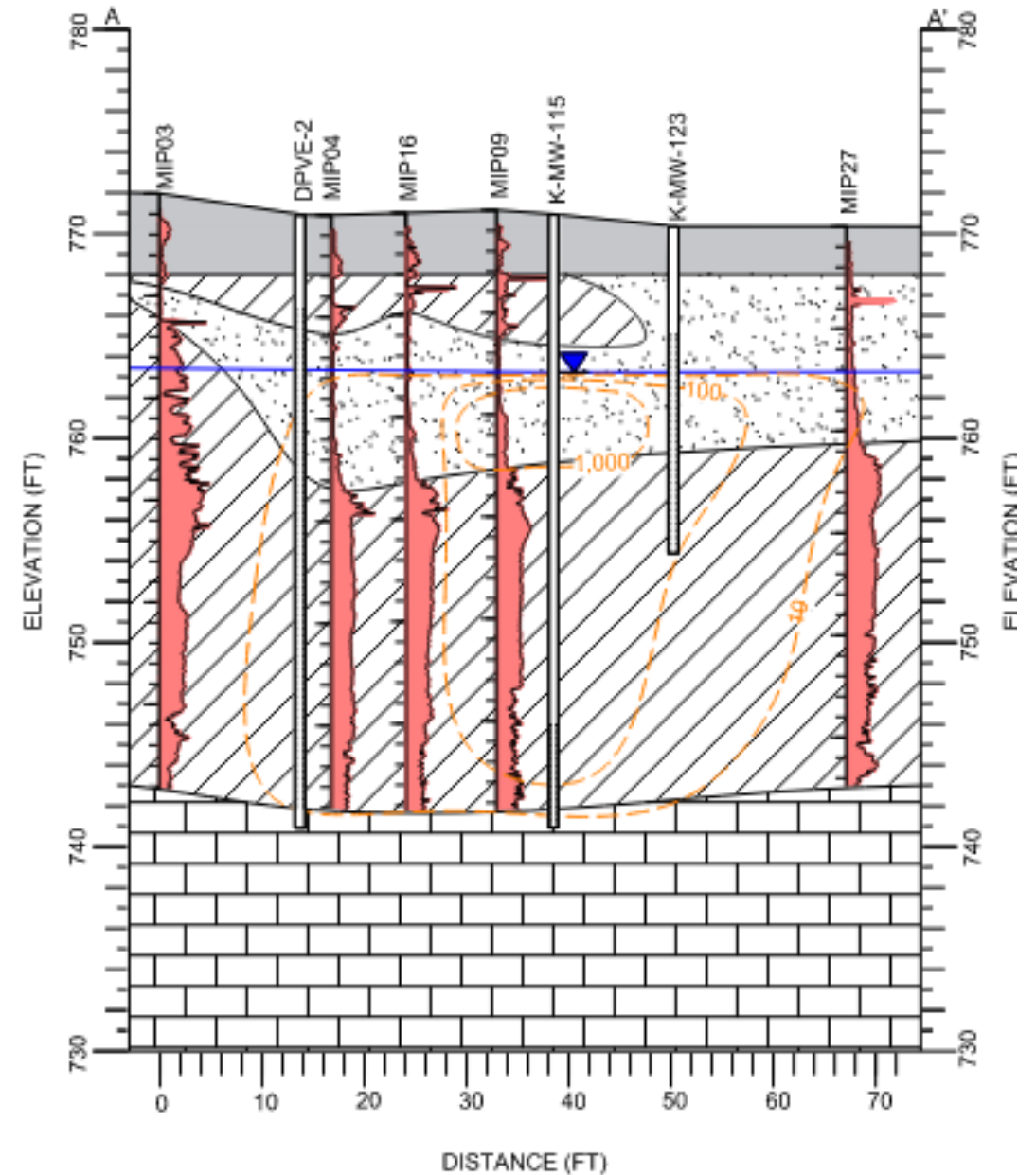


SITE LAYOUT

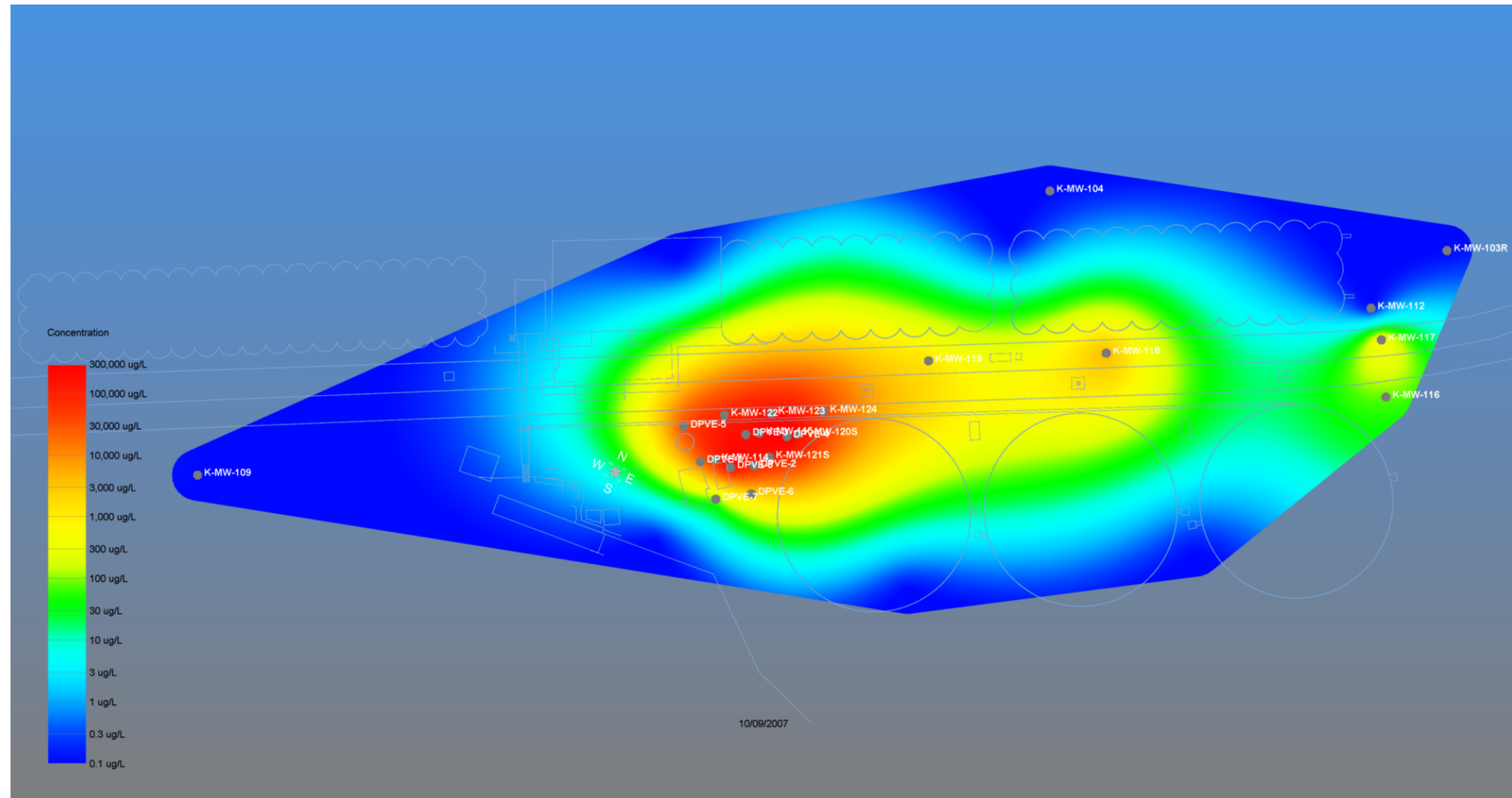


CONCEPTUAL SITE MODEL

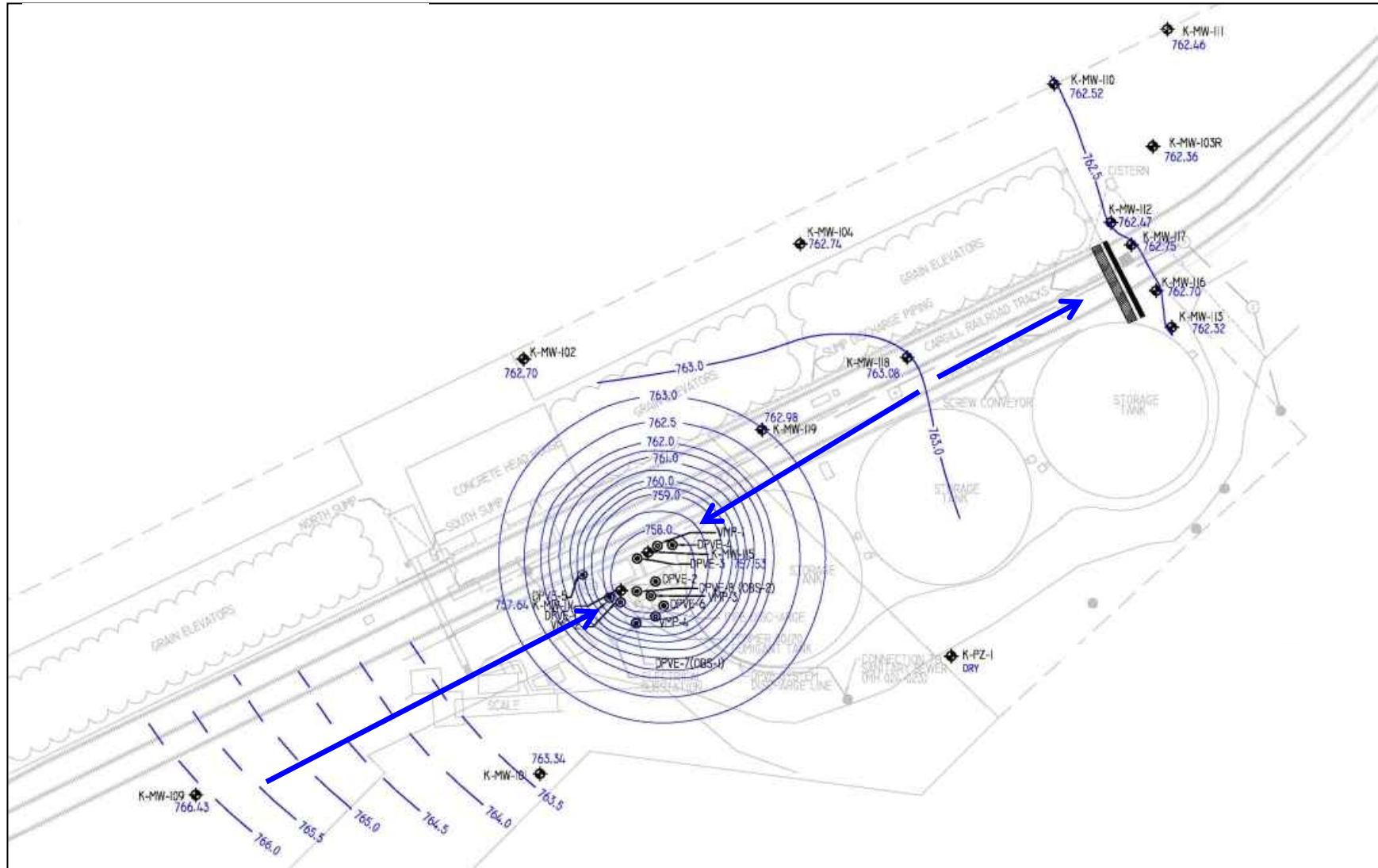
- ▶ MIP/EC
- ▶ High conductivity sand zone
 - Slight variations in EC responses – higher and lower conductivity ‘channels’
- ▶ Low conductivity clay layer
- ▶ Low hydraulic gradient
 - Extended contact time



DPVE PERFORMANCE – SUMMARY (2007 – 2014)

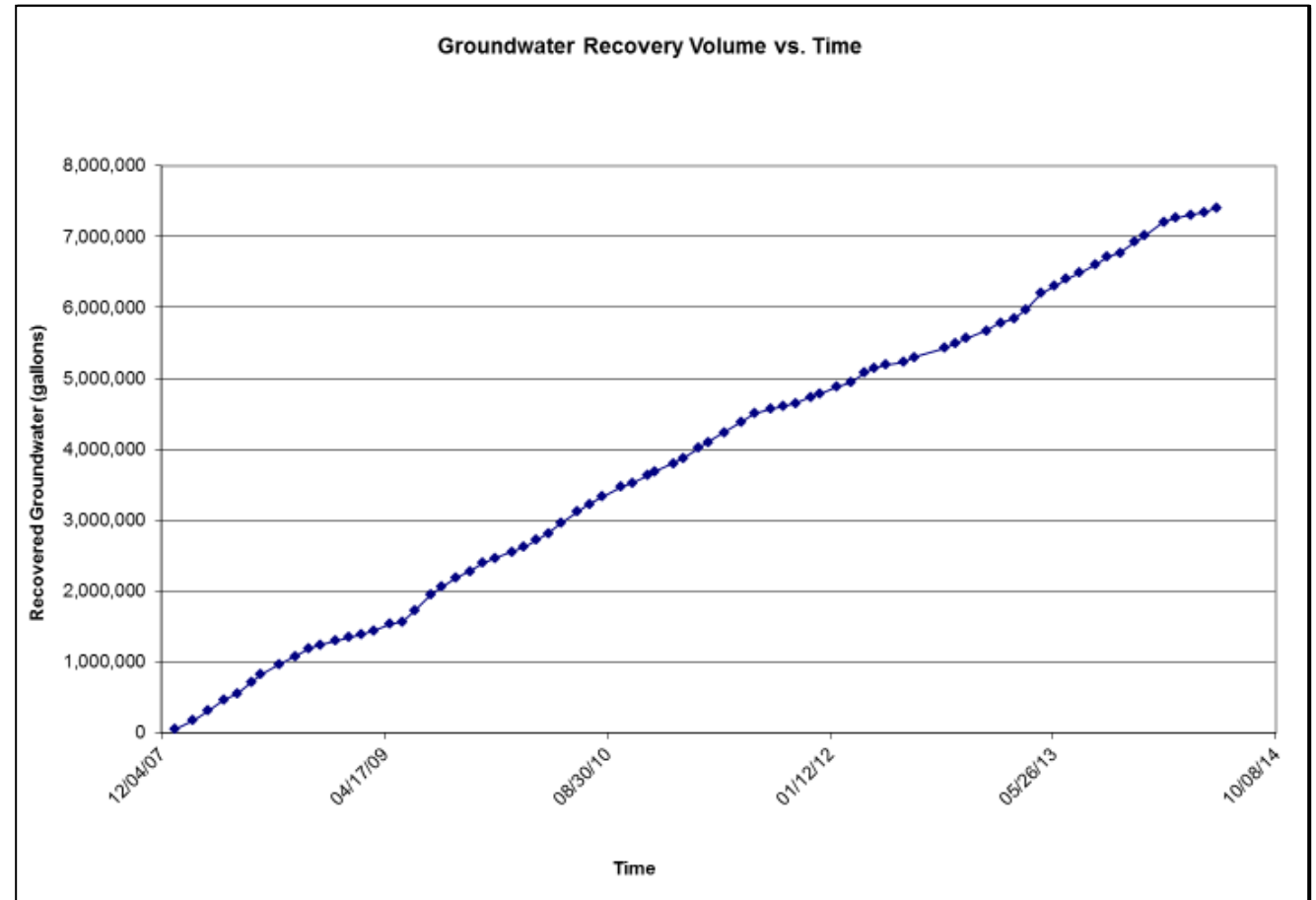


DPVE PERFORMANCE – HYDRAULIC CONTROL AND CAPTURE



DPVE PERFORMANCE – SUMMARY (2007 – 2014)

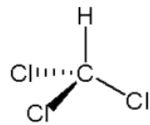
- ▶ Plume size and concentration reduction
 - Vapor-Phase Removal:
 - 9,100 pounds (690 gal. as CT)
 - Dissolved-Phase Removal:
 - 33 pounds (as CT)
 - Groundwater Recovered/Treated:
 - 7.5 million gallons



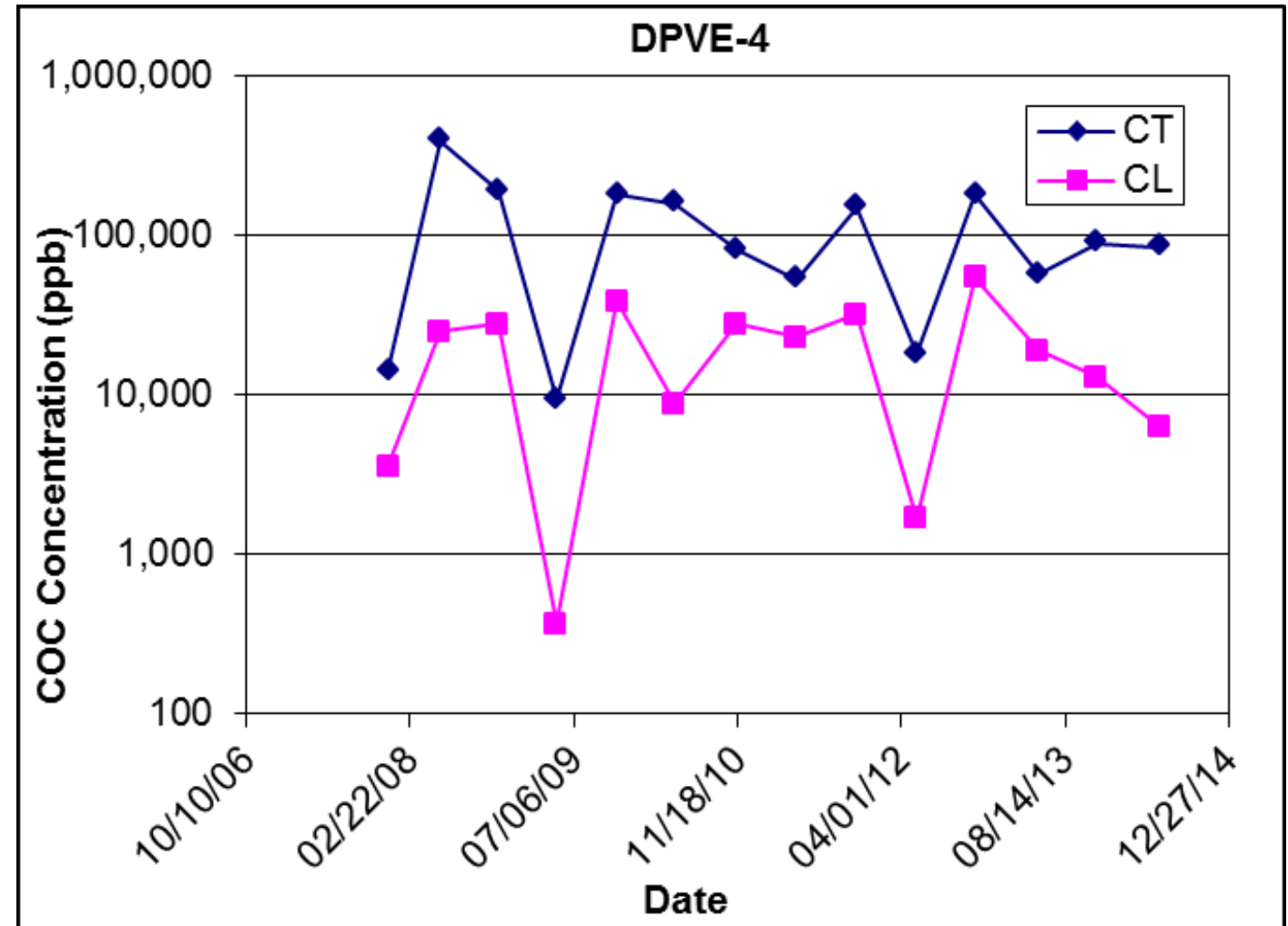
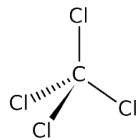
SOURCE AREA CONDITIONS (2006 – 2014)

- ▶ Continued variability and persistence in source area DPVE wells
- ▶ Could significant mass remain in the soil?

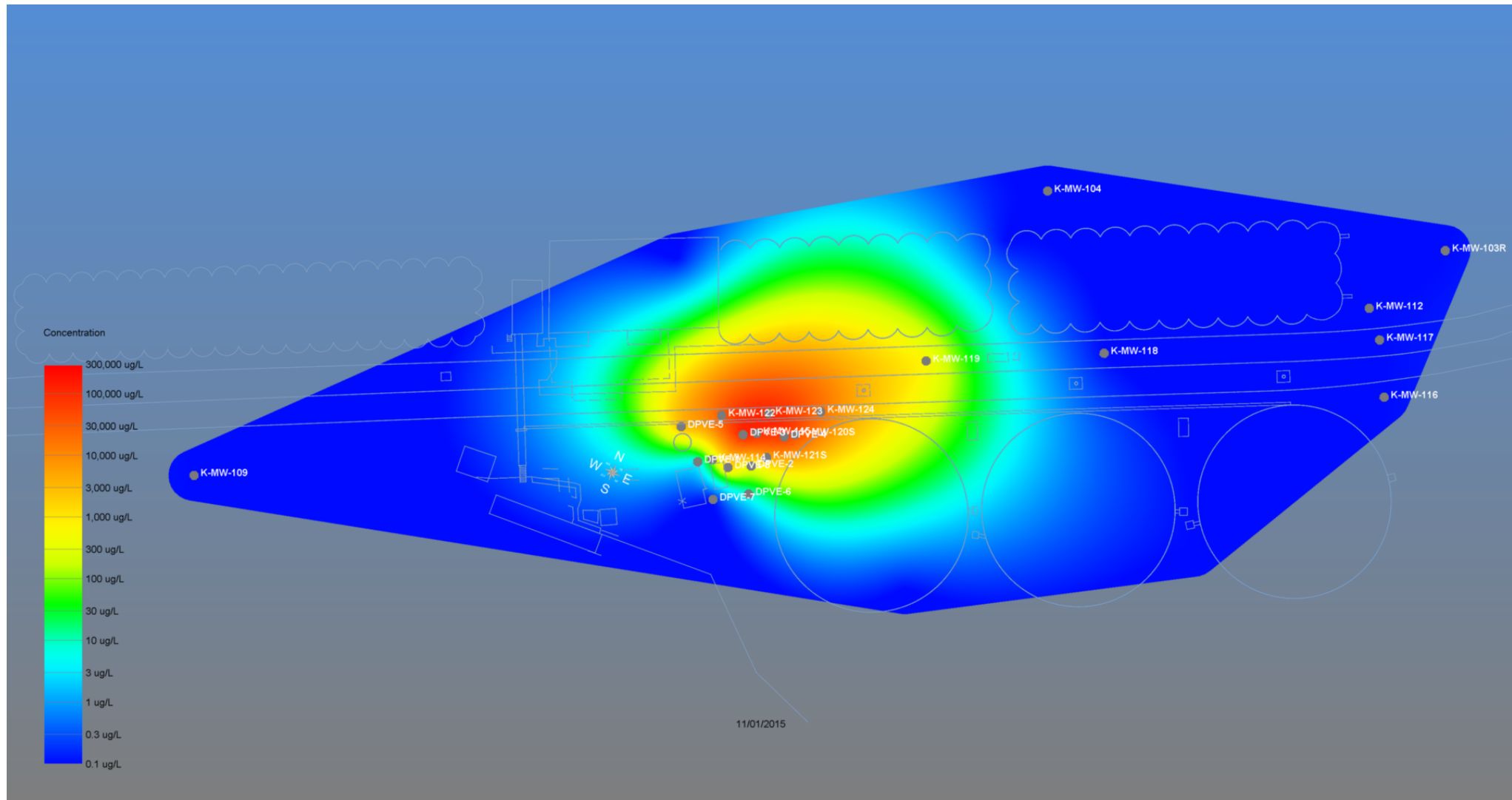
CT – Carbon Tetrachloride



CL - Chloroform



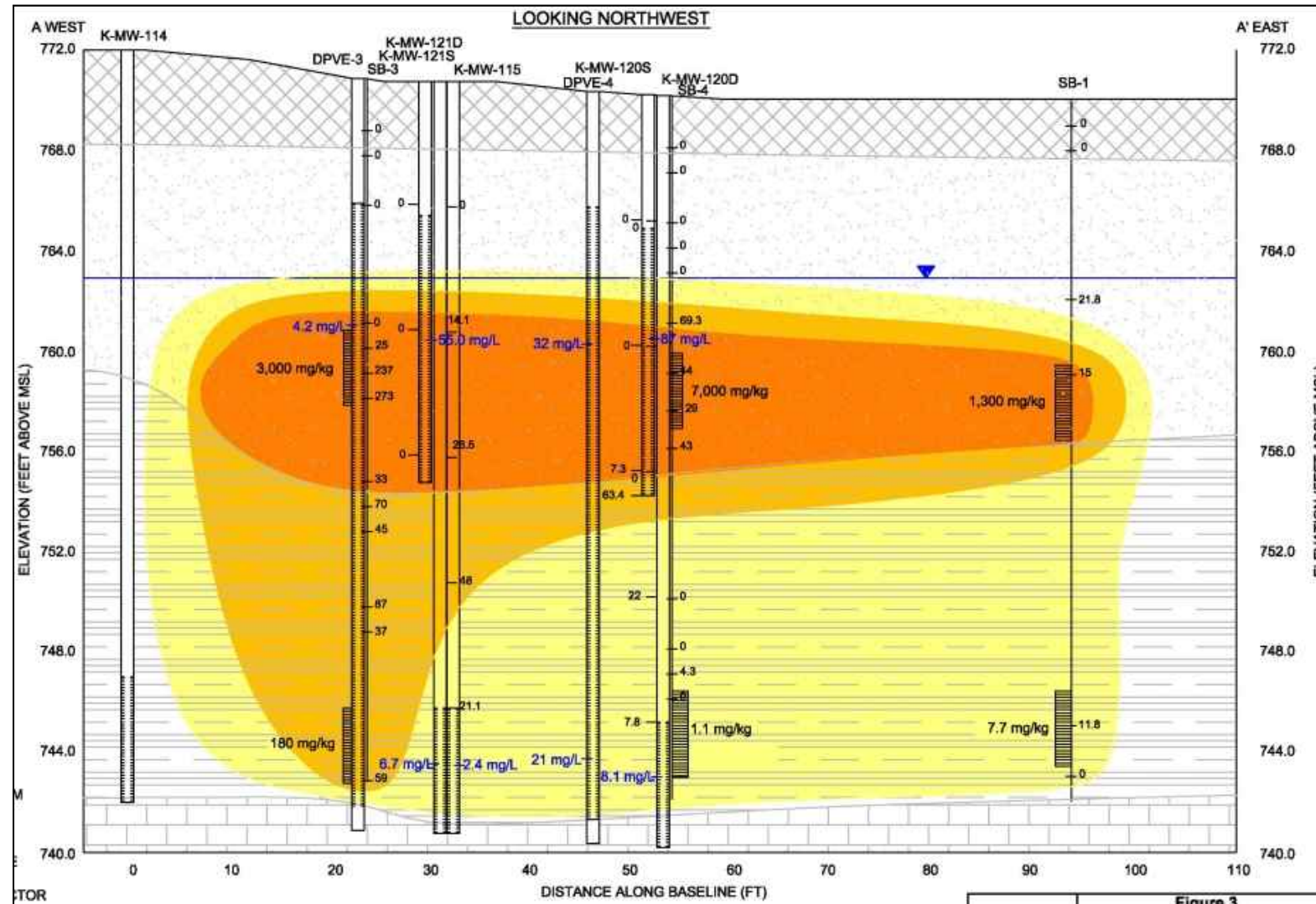
DPVE PERFORMANCE – SUMMARY (2007 – 2014)



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 SOIL INVESTIGATION RESULTS



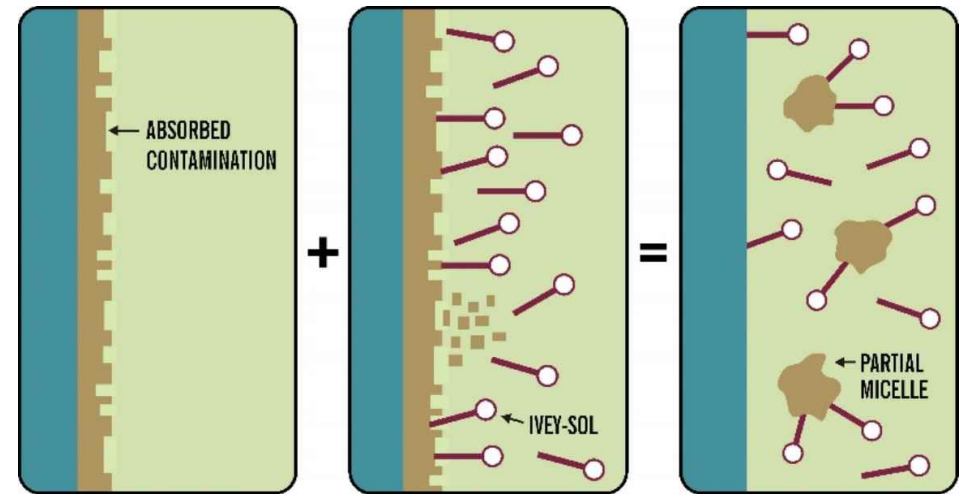
WHY DOES SIGNIFICANT MASS REMAIN?

- ▶ CT discontinued in the 1980s
 - Contact time increases sorption
 - 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
- ▶ Elevated CT discovered in LNAPL
- ▶ Source zone periphery rapidly remediated by DPVE
 - Minimal contact time in these areas

SURFACTANT ENHANCED DPVE

How It Works

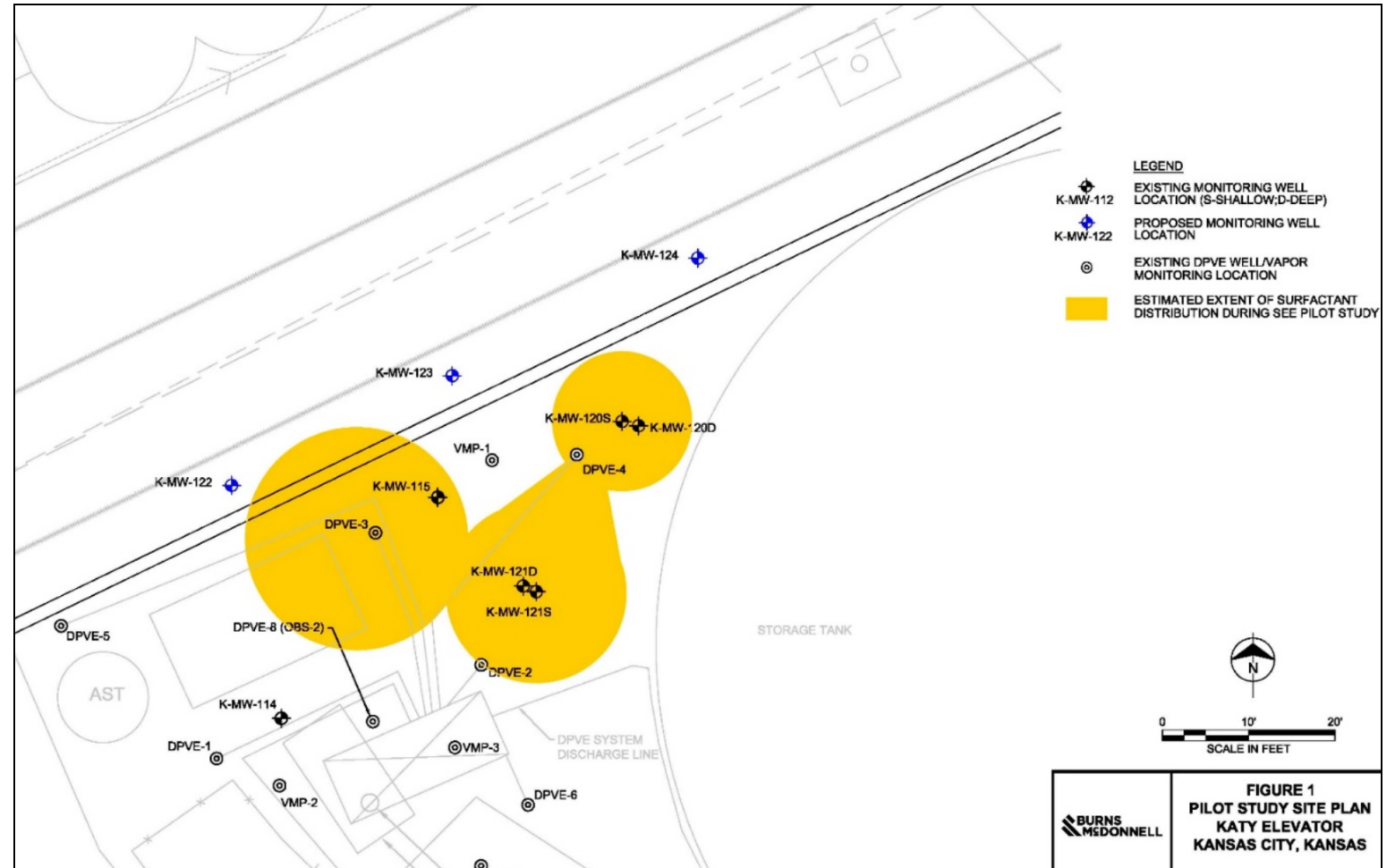
- ▶ Surfactants are structured with a hydrophilic head and hydrophobic tail
- ▶ Hydrophobic tail attracts and attaches to organic portion of CT (carbon)
- ▶ Hydrophilic head attracted to groundwater making CT miscible
- ▶ Lowers surface tension by reducing H₂O cluster size (73 to < 30 Dynes) improves 'apparent' K



SEE PILOT STUDY OVERVIEW

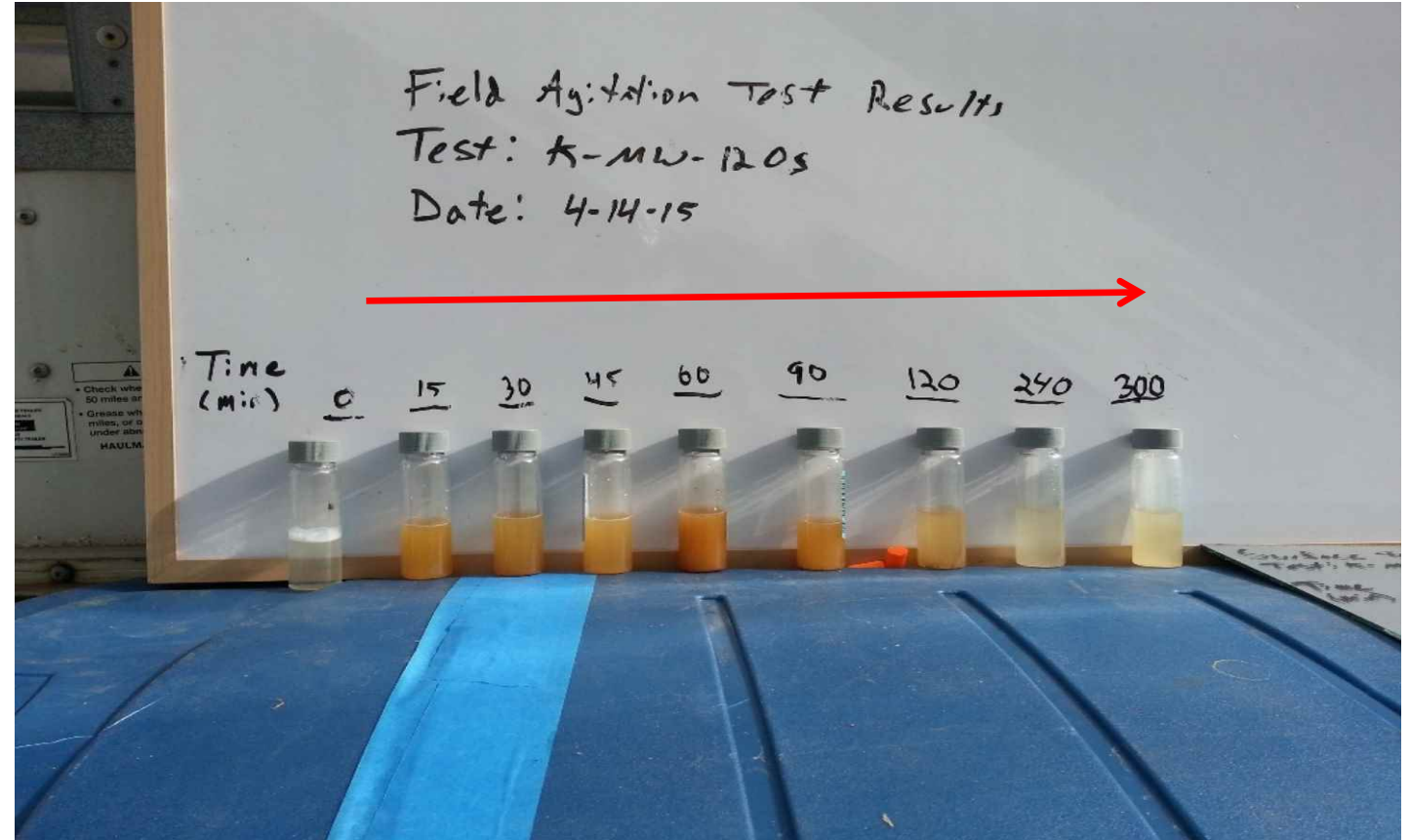
SEE Pilot Limited To:

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



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



FULL-SCALE SEE

- ▶ August through November 2016
- ▶ 275 Gallons Ivey-sol 106 Surfactant Formulation
 - Mixed with conservative tracer for distribution observation
- ▶ Applied Push-Pull and Point-to-Point Flushing Techniques
- ▶ Monitored recovery progress via real-time tracer testing and using the Ivey-sol field surfactant test sheets

FULL-SCALE SEE



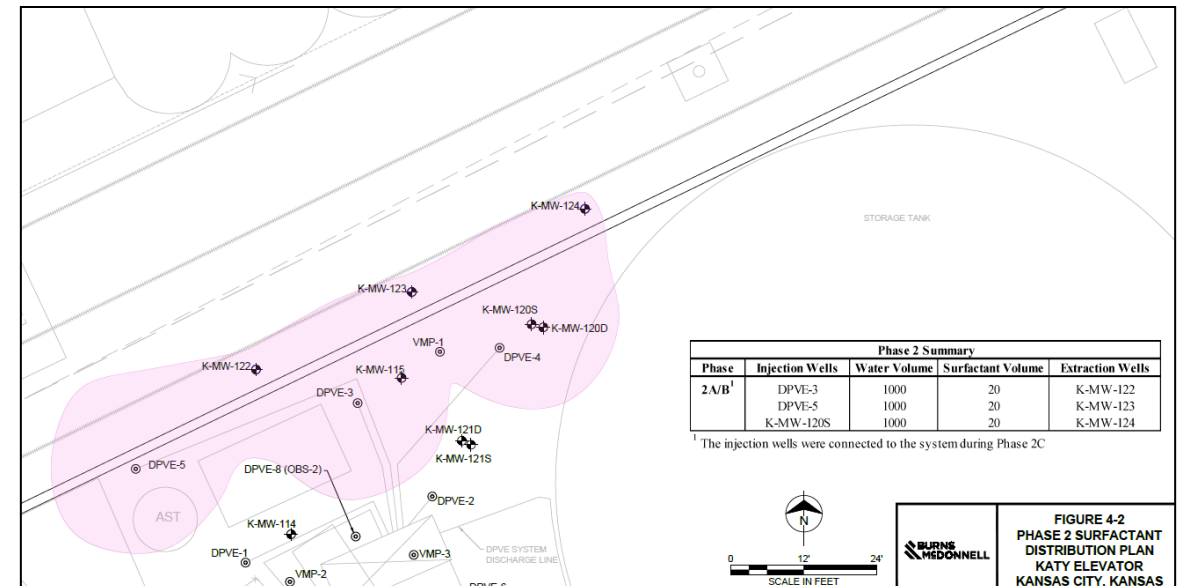
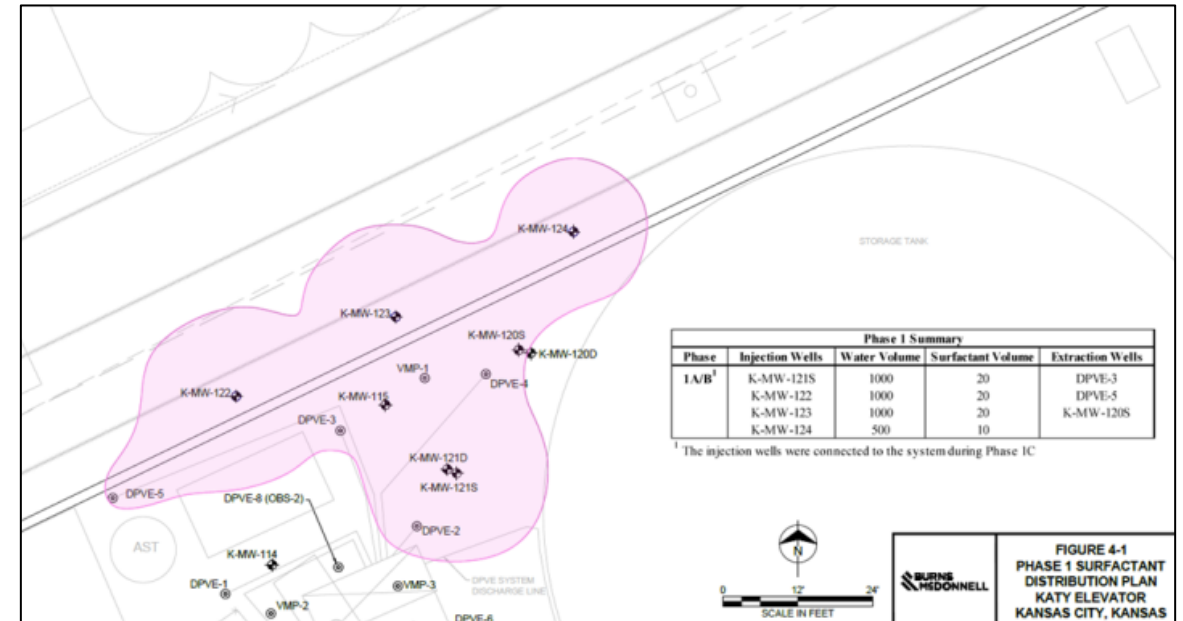
Aquafluor Meter: Measures intensity of fluorescence



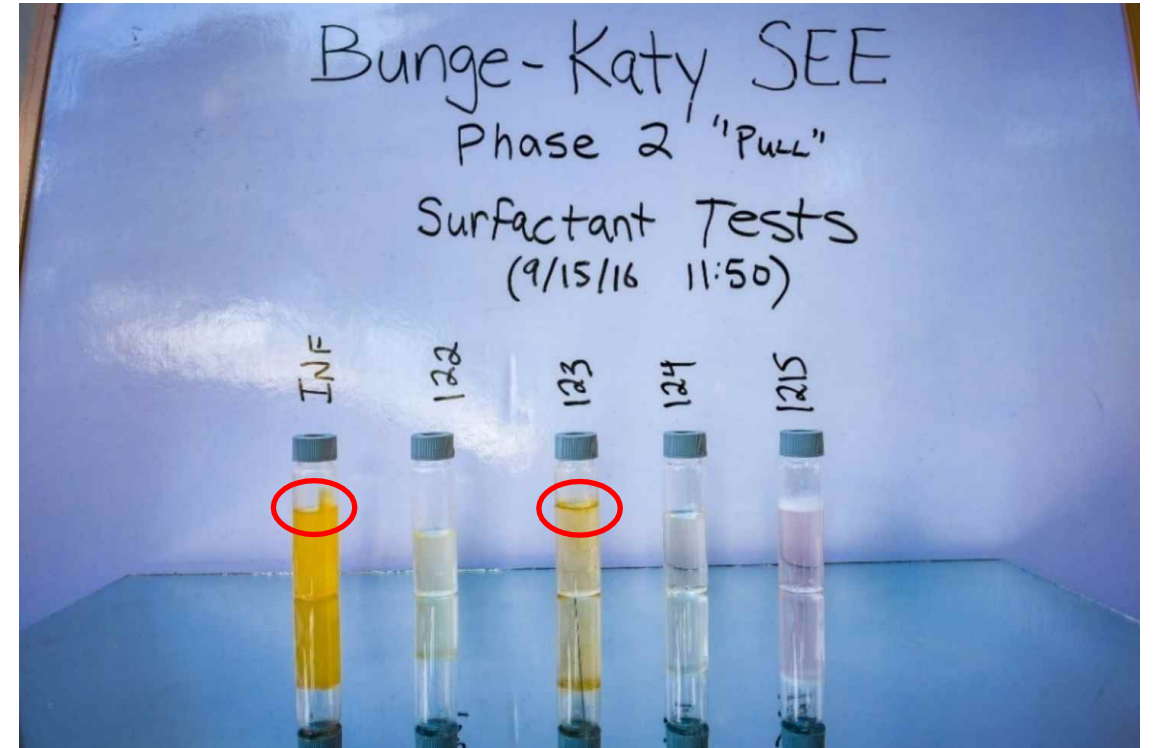
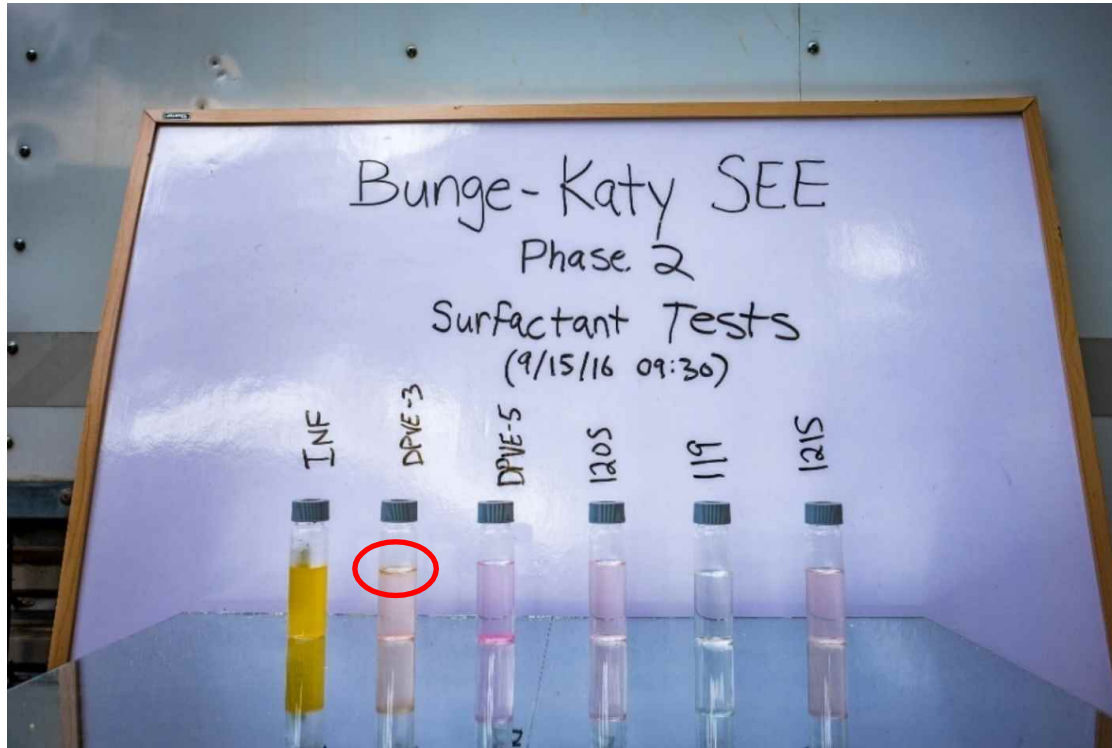
Diluted Ivey-sol in water with tracer added – pre-injection mixing.

FULL-SCALE SEE

- ▶ Three additional wells – K-MW-122 through 124 – Installed to facilitate surfactant delivery to the northern portion of the source area
- ▶ A total of 5 SEE phases were conducted to target the most heavily impacted portion of the source area

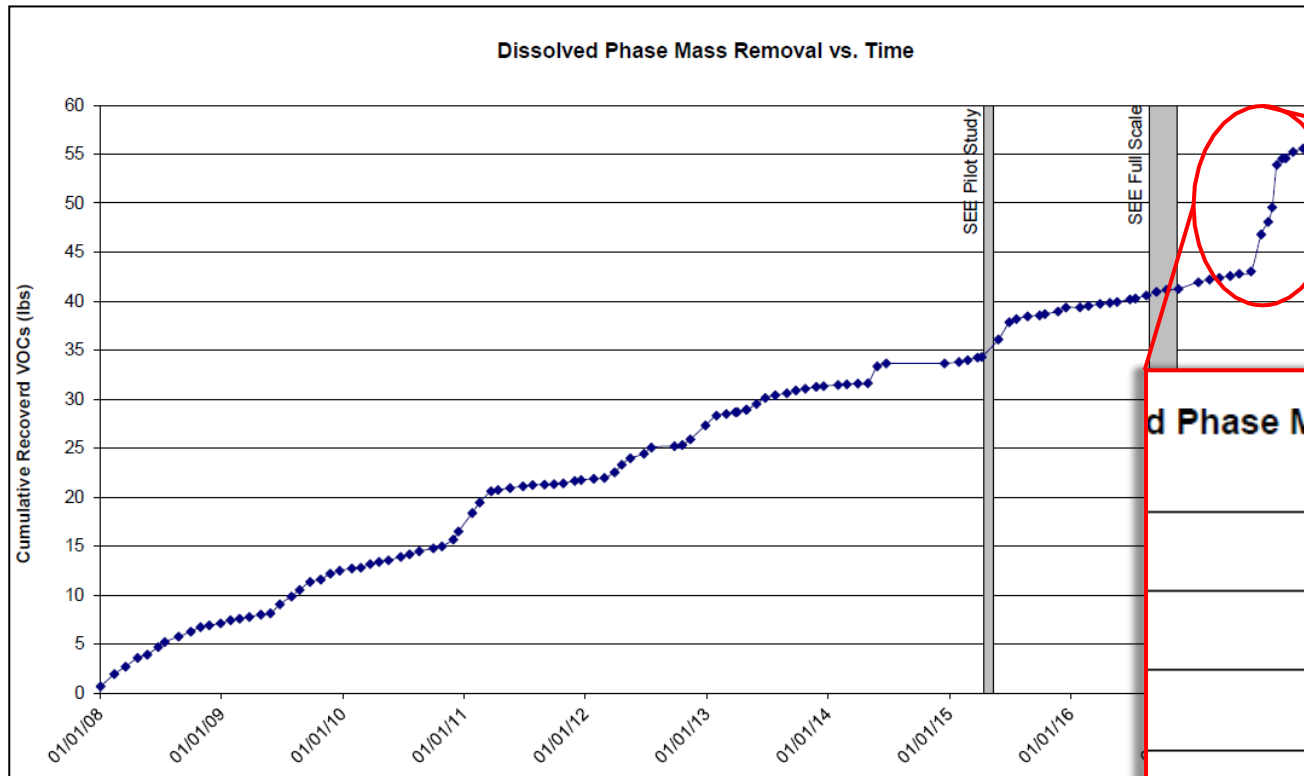


FULL-SCALE SEE



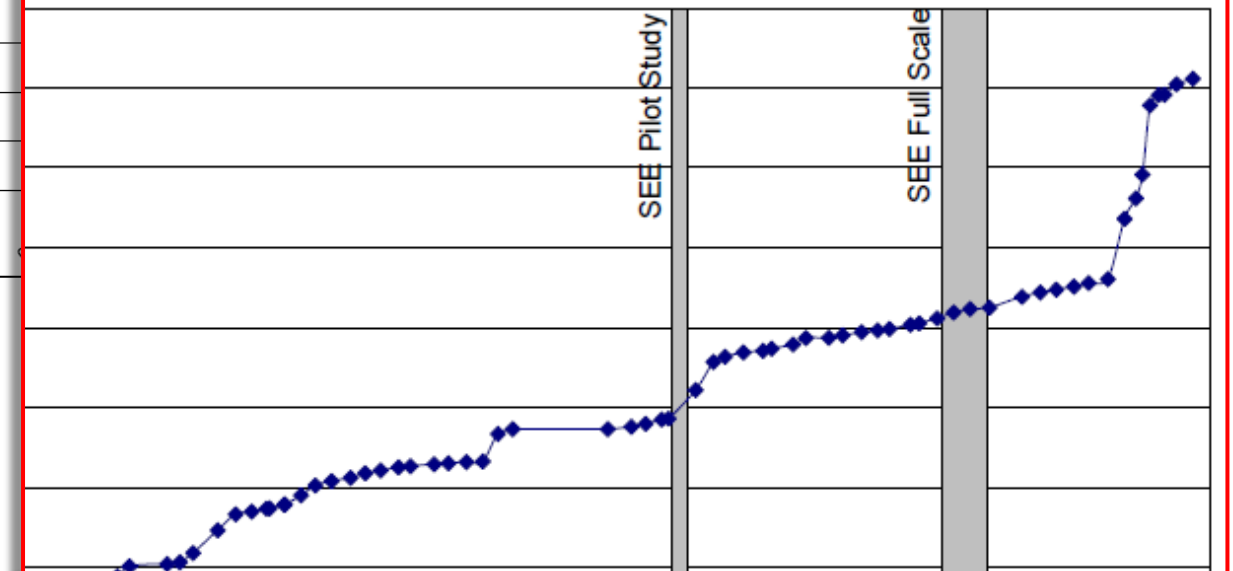
*Influent samples indicative of LNAPL which was heavily concentrated with COCs.
Note: 119 was downgradient, lack of tracer confirmed hydraulic control of SEE area.*

FULL-SCALE SEE



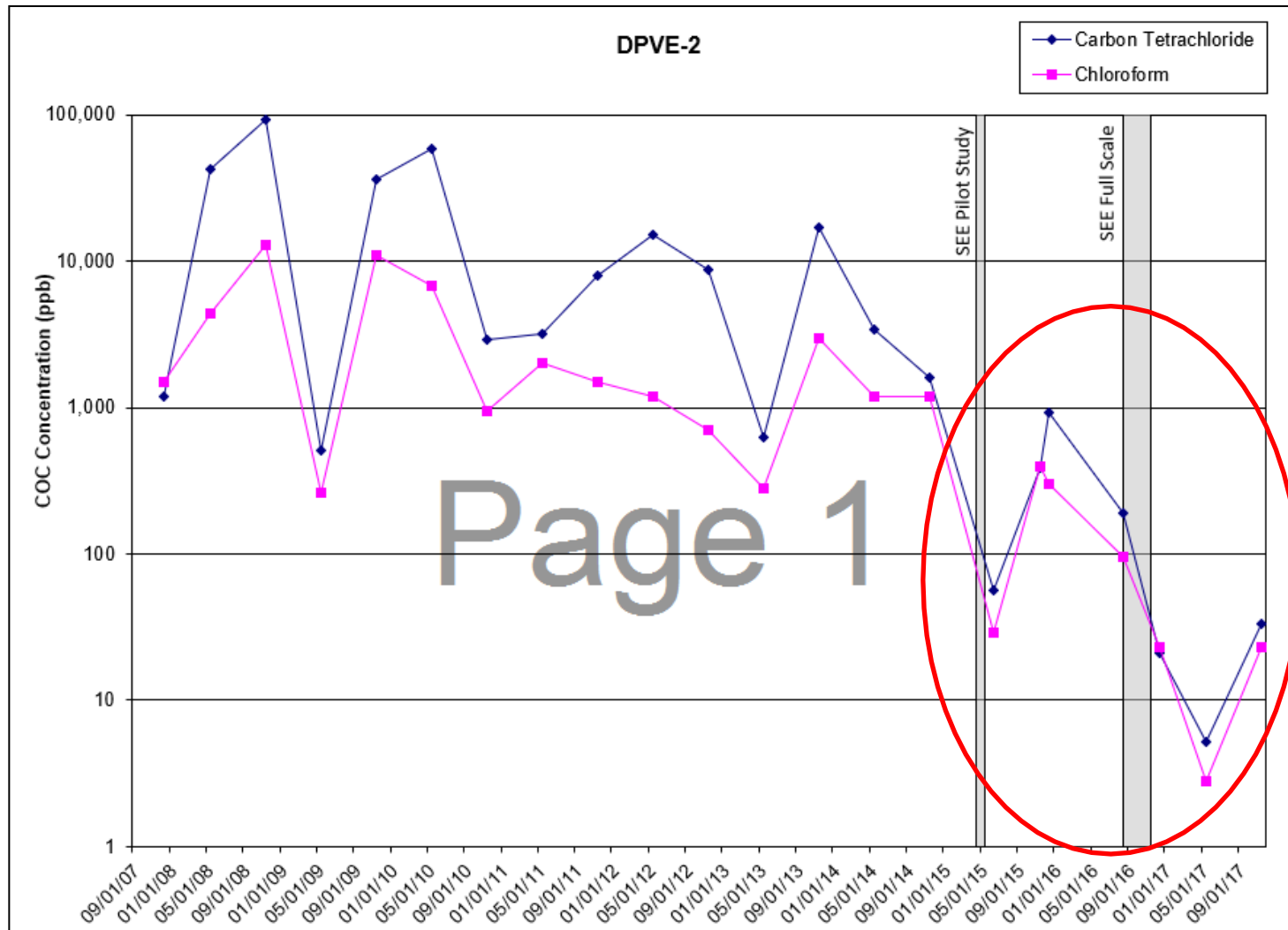
25% of the total mass recovered since 2007 was during the 12-month post-SEE period.

Dissolved Phase Mass Removal vs. Time



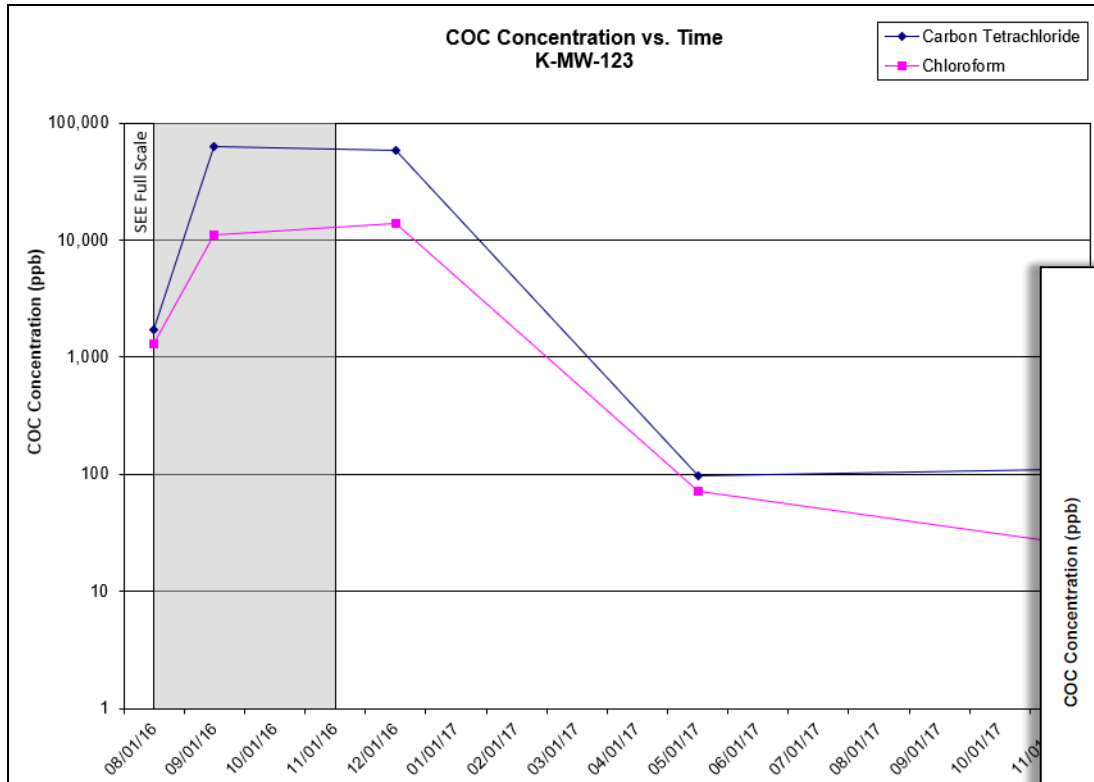
Influent groundwater concentrations up to 30,000 ug/L observed – 5x the highest concentrations ever observed during DPVE operations.

FULL-SCALE SEE

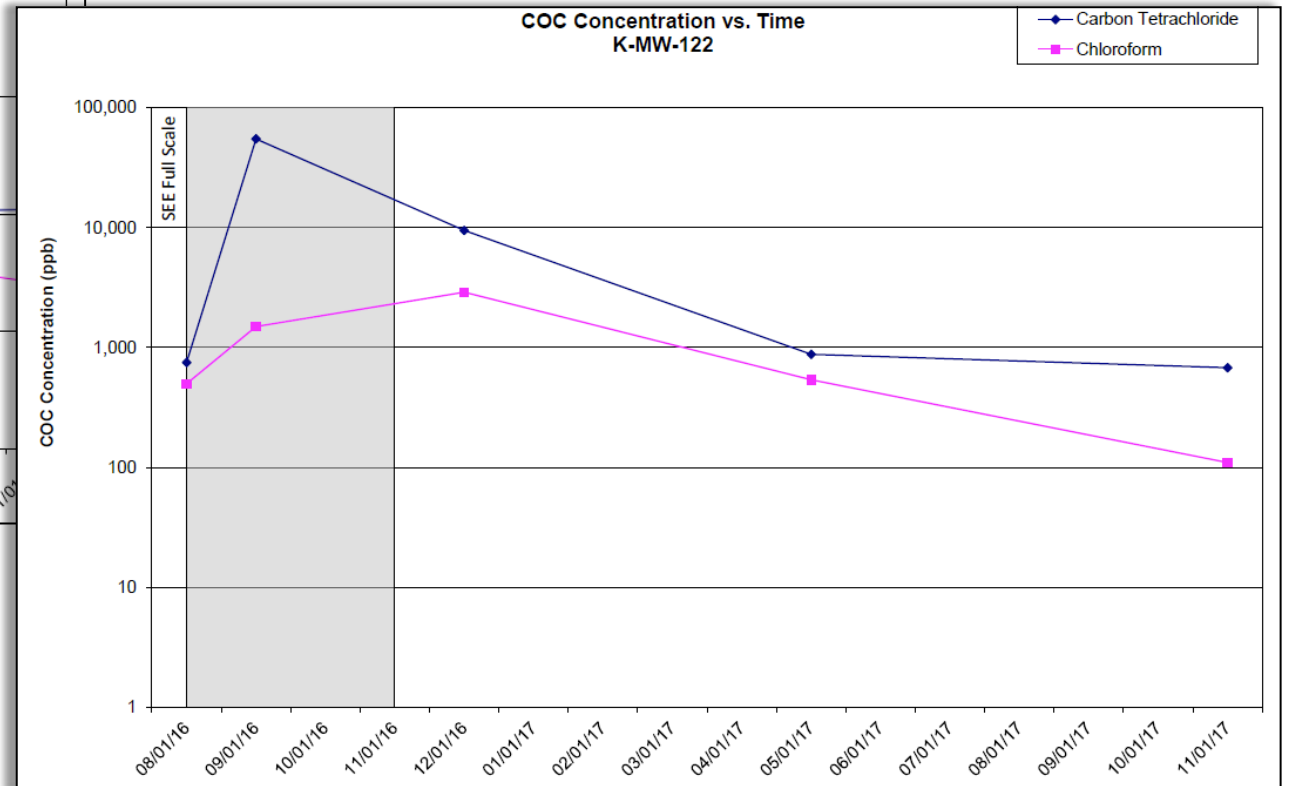


DPVE-2, located in the southern portion of the source area, demonstrated 2 order of magnitude COC reduction following the SEE pilot scale

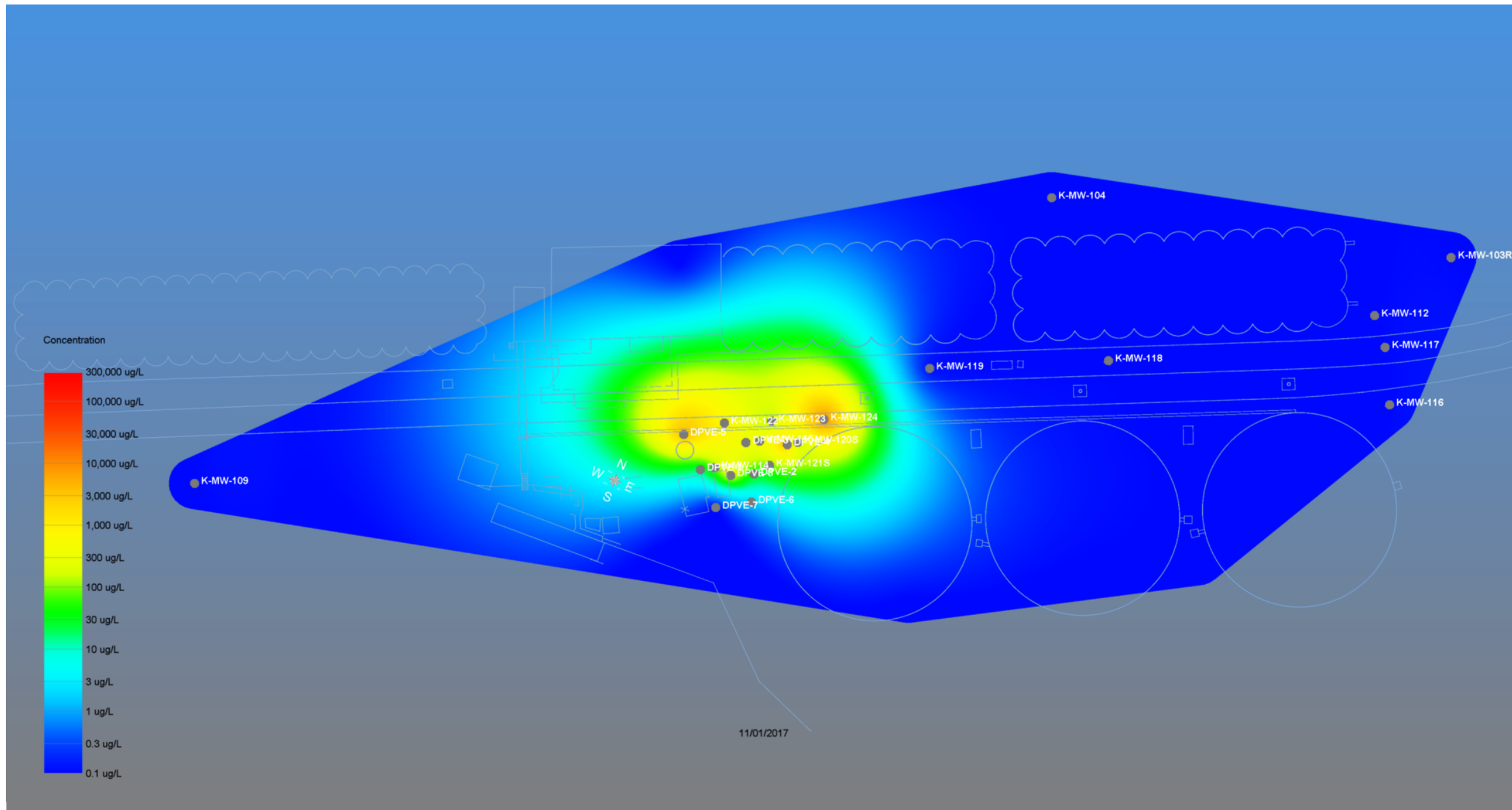
FULL-SCALE SEE



K-MW-123 demonstrated 3 order of magnitude COC reduction following full-scale SEE

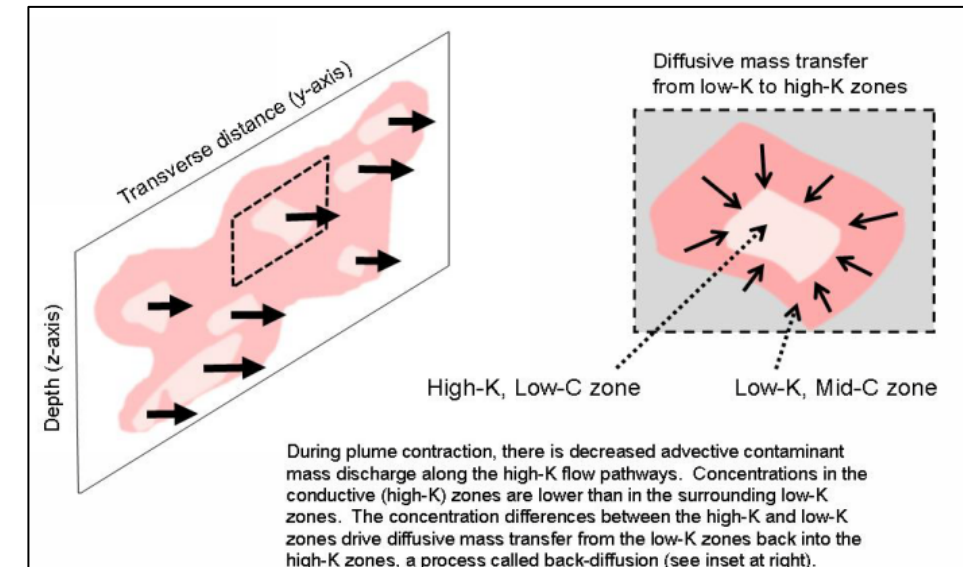
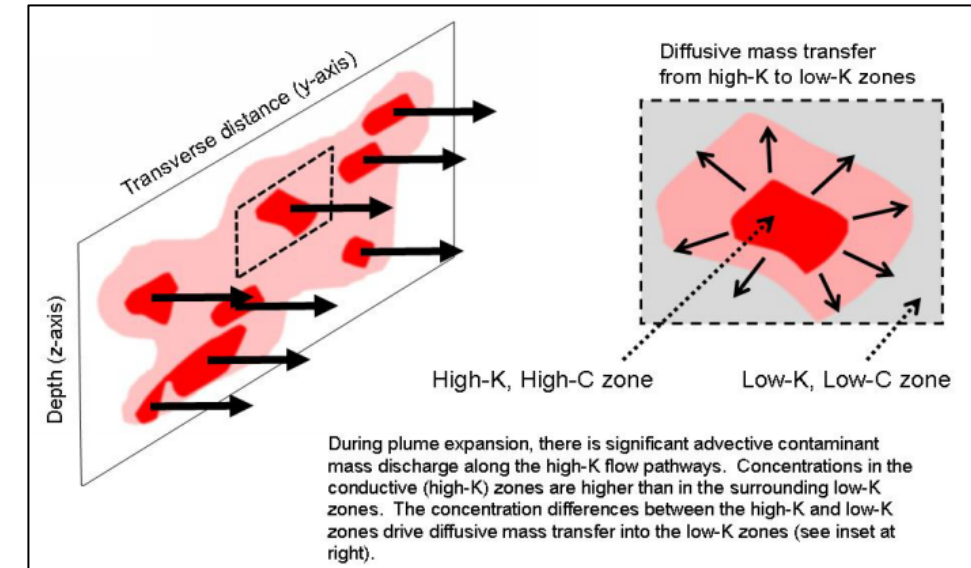


K-MW-122 demonstrated 2 order of magnitude COC reduction following full-scale SEE



IN-SITU CHEMICAL REDUCTION

- ▶ DPVE and SEE highly successful in liberation and recovery of concentrated mass in high conductivity channels
- ▶ Desorption/diffusion continues
- ▶ Soil/aquifer matrix data support biotic reductive dichlorination via iron-reducing bacteria



IN-SITU CHEMICAL REDUCTION

- ▶ Shut down DPVE system
- ▶ Innovative Environmental Technologies (IET)
- ▶ Provectus Provect-IR60
 - 60% ZVI; 40% Carbon Source
 - 10 Micron ZVI
- ▶ Amendment-Water Ratio ~30%
- ▶ 24,000 lbs
- ▶ Shallow Sand Zone

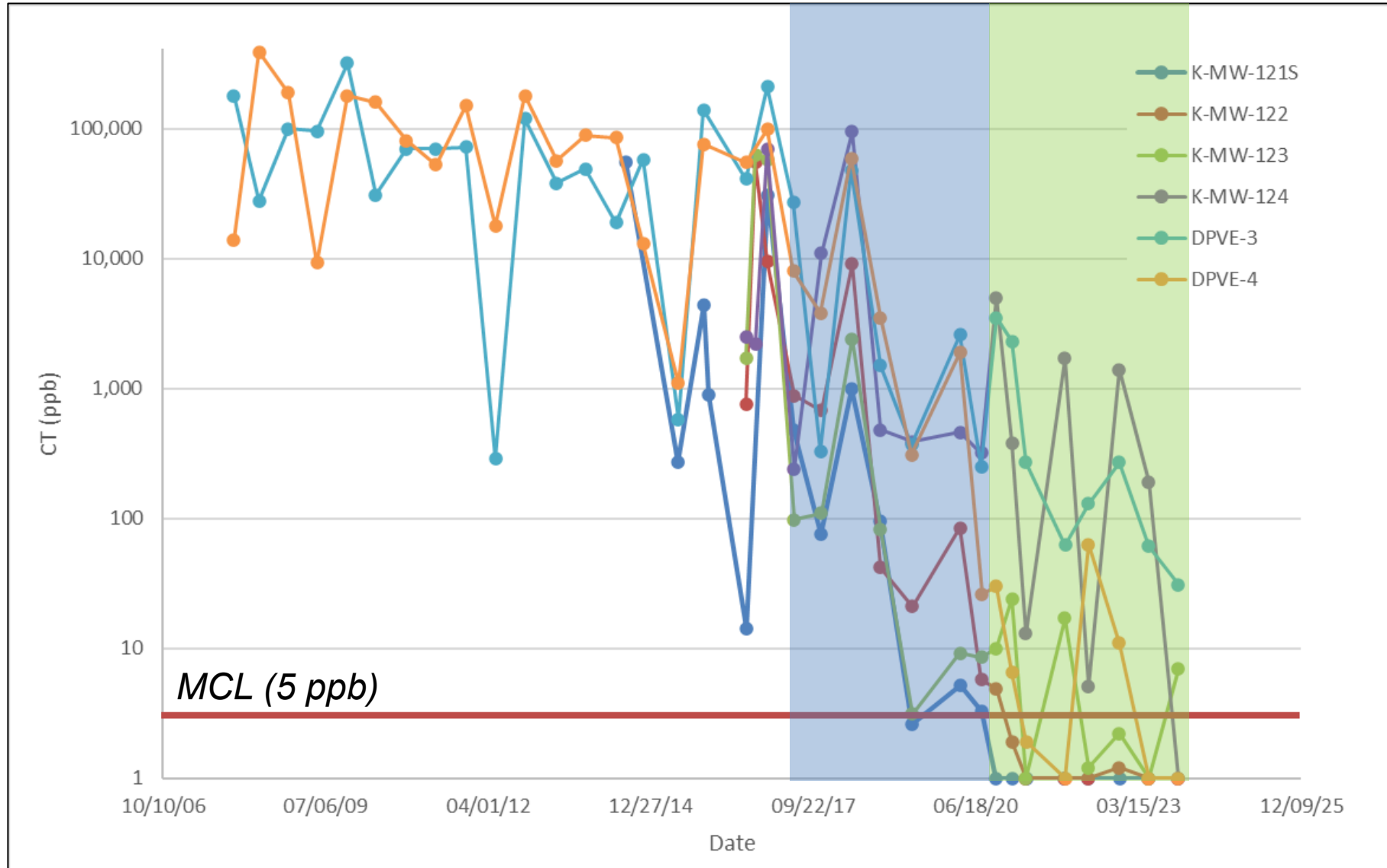


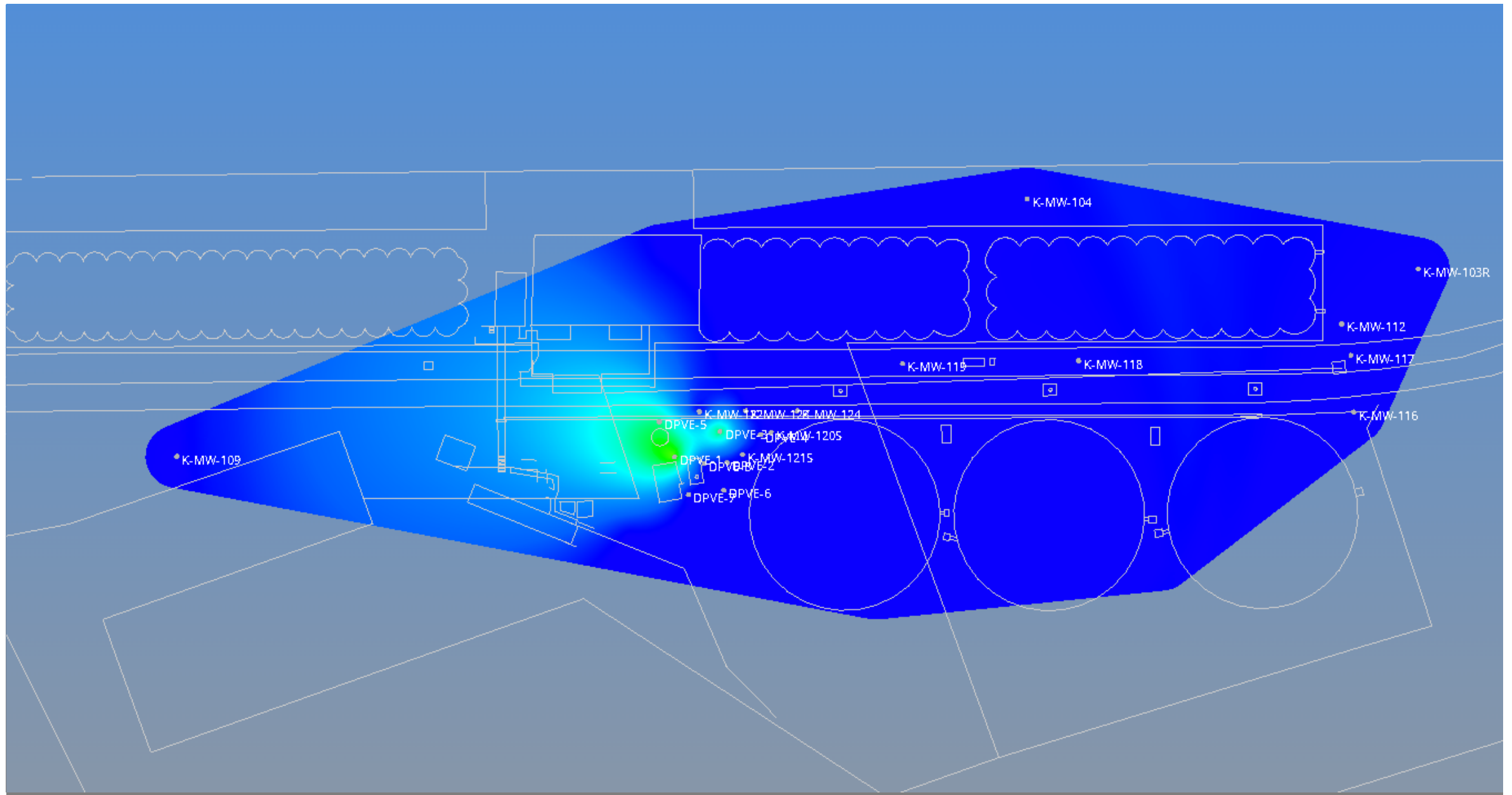
IN-SITU CHEMICAL REDUCTION

- ▶ Some daylighting
 - Switched to Bottom-up
- ▶ 10+ foot ROI



IN-SITU CHEMICAL REDUCTION RESULTS





IN-SITU CHEMICAL REDUCTION RESULTS

- ▶ Only 1 of 6 Shallow Source Area Monitoring Wells exceed KDHE RSK of 5 ug/L
 - 6.9 ug/L at K-MW-123
- ▶ KDHE approval to cease DPVE system
- ▶ Evidence of continued biodegradation
 - Elevated TOC and iron; Reduced DO and ORP
 - Elevated CF and MC

Get In Touch With Us!

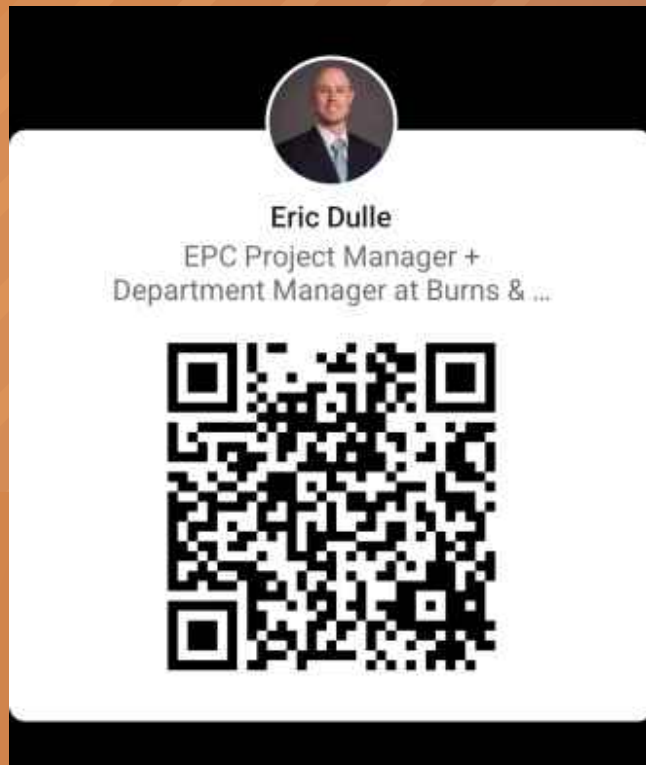


Eric Dulle, PE | Burns & McDonnell

Phone | 314-375-3288

Email | edulle@burnsmcd.com

Web | Web: www.burnsmcd.com



Will Moody | Provectus

Phone | 908-581-6291

Email | will.moody@provectusenv.com

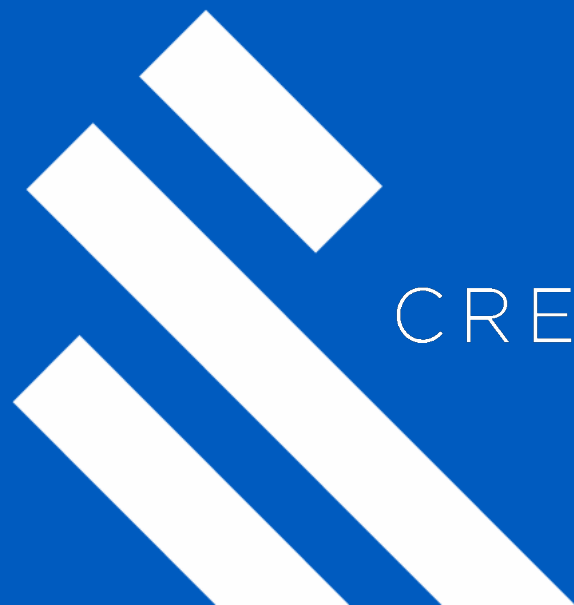
Web | www.provectusenvironmental.com

**George (Bud) Ivey
| Ivey International Inc.**

Phone: 250-203-0867

Email: budivey@iveyinternational.com

Web | www.iveyinternational.com



CREATE AMAZING.

SEE PILOT STUDY OVERVIEW

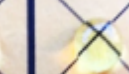
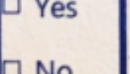
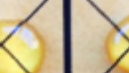
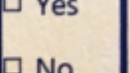
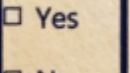
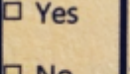
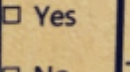
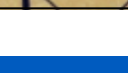
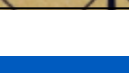
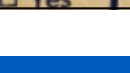
- ▶ Mixing 5 gal Ivey-sol into 250 gal of Water
- ▶ 1:50 Ratio For Application
- ▶ Installed temporary GAC



REAL – TIME FIELD SURFACTANT TEST

- ▶ Real-time field surfactant testing - measuring water surface tension

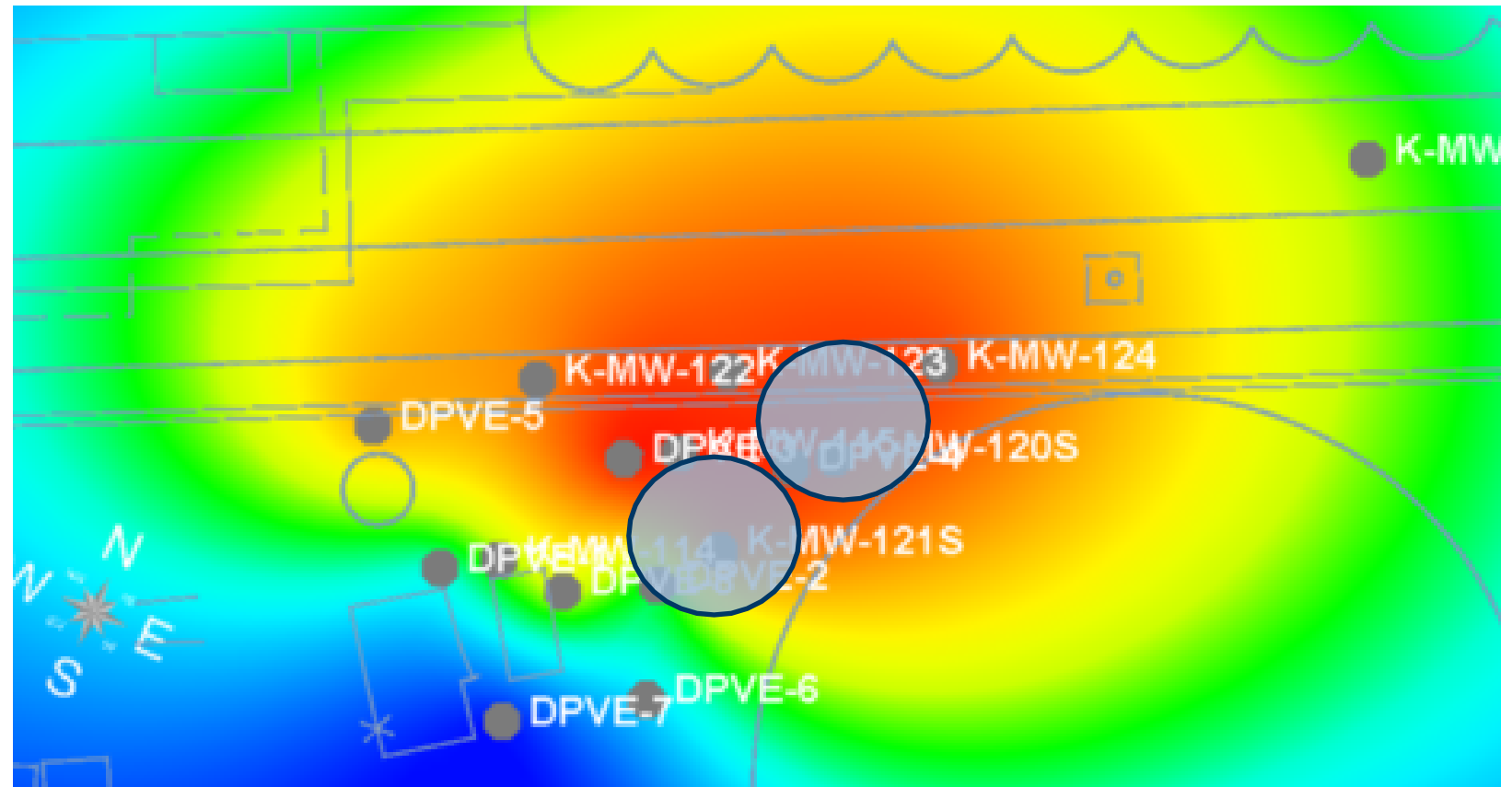
Notes: _____

					Surfactant Observed	
					☐ Yes ☐ No	Tim
					☐ Yes ☐ No	Tim
					☐ Yes ☐ No	Tim
					☐ Yes ☐ No	Tim
					☐ Yes ☐ No	Tim
					☐ Yes	

PILOT STUDY RESULTS

Test 1 and 2

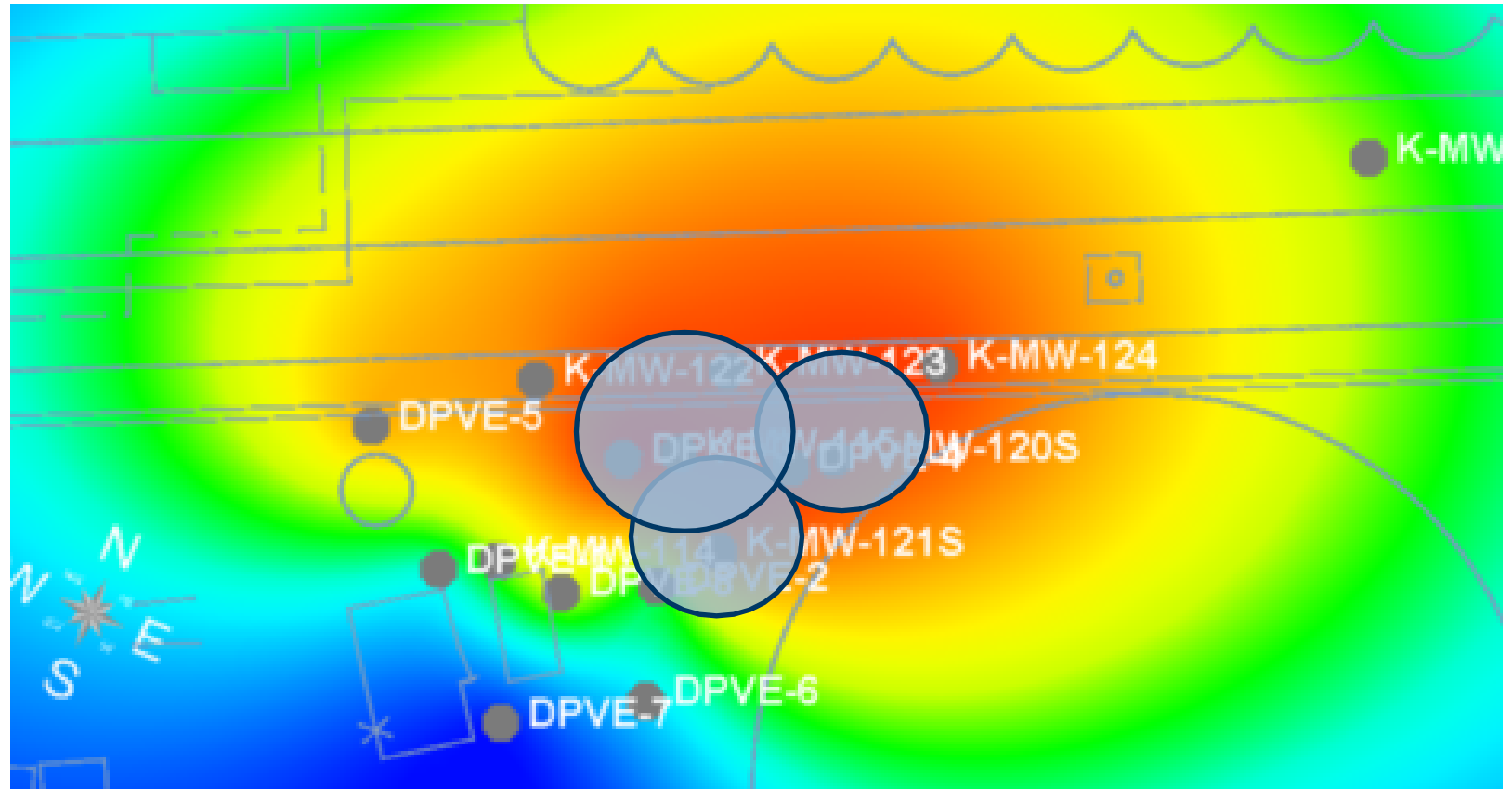
- ▶ Push-Pull Tests at shallow monitoring wells
- ▶ Modest increase in mass removal observed



PILOT STUDY RESULTS

Test 3 and 4

- ▶ Point-To-Point Tests
- ▶ Influent groundwater concentrations (8,100 ug/L) highest ever recorded by over 50-percent
- ▶ Influent groundwater concentrations 4x greater than average



PILOT STUDY RESULTS

- ▶ Highly elevated and highly variable influent concentrations
- ▶ Recovery of high concentration “slugs” over short periods of time

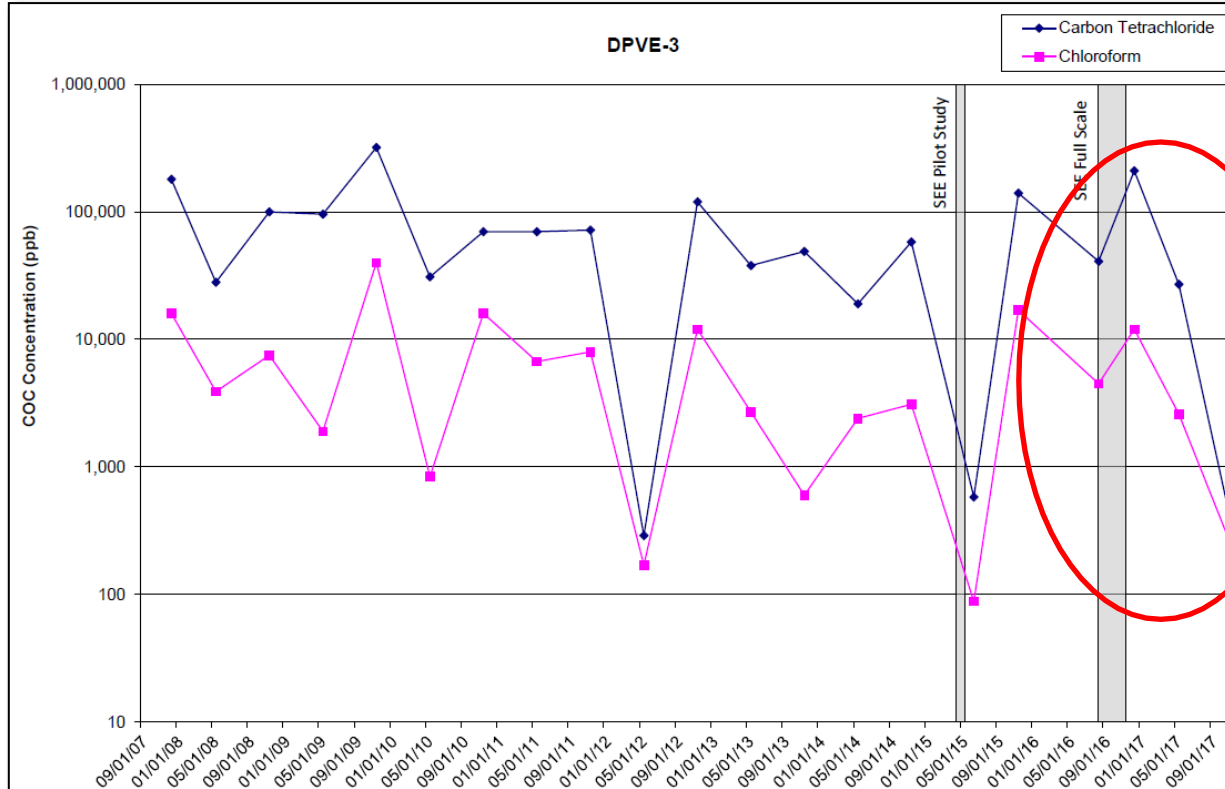
Sample Collection Date	Sample Collection Time	Sample Location	Carbon Disulfide (µg/L)	Chloroform (µg/L)	Methylene Chloride (µg/L)	Carbon Tetrachloride (µg/L)	Total VOC (µg/L)
Pilot Test #2: K-MW-121S Push-Pull							
04/15/15	1027	Baseline Treatment Influent	12	200	ND (10)	590	602
	1345	Treatment Influent	45 J	140	ND (50)	4,400	4,585
	1535	Treatment Influent	ND (10)	510	ND (10)	960	1,470
	1645	Treatment Influent	29	280	ND (25)	570	879
	1450	AS Effluent	ND (5.0)	17	ND (5.0)	10	27
	1452	GAC Effluent	ND (5.0)	ND (1.0)	ND (5.0)	ND (1.0)	ND (12.0)
04/16/15	0825	Treatment Influent	63	480	ND (25)	1,500	2,043
	0827	AS Effluent	25	420	ND (25)	1,200	1,645
	0830	GAC Effluent	NA ¹				

FULL-SCALE SEE RESULTS

- ▶ 98% CT Reduction in Source Area Shallow Monitoring Wells
 - K-MW-120S, 121S, 122 through 124
- ▶ 92% CT Reduction in Source Area DPVE wells
 - DPVE-3 and 4
- ▶ Significant reductions in LNAPL thickness
 - No measurable LNAPL in March 2018

FULL-SCALE SEE

DPVE-3 demonstrated 3 order of magnitude COC reduction following full-scale SEE



DPVE-4 demonstrated 2 order of magnitude COC reduction following full-scale SEE

