MORE THAN A DECADE OF CHALLENGES AND SUCCESS: ENHANCED IN SITU REDUCTIVE DECHLORINATION OF TRICHLOROETHENE/1,1,1-TRICHLOROETHANE SOURCE AREA IN FRACTURED BEDROCK

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INTRODUCTION

In 2003, a pilot test was initiated to demonstrate in situ reductive dechlorination (IRD) of chlorinated volatile organic compounds (VOCs) at a Pennsylvania Superfund site with a fractured carbonate aquifer, using methanol, ethanol, and lactate amendments, and a commercial microbial culture KB-1. By 2005, pilot injections were suspended due to excess levels of nutrients nearly toxic to the microbial community. The inefficient degradation rates led to more extensive laboratory microcosm studies. A microbial culture capable of degrading trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) was grown in Site groundwater, and initial bioaugmentation was conducted in 2006. Based on the success of the resumed pilot with nutrients and lactate only, a full-scale biorecirculation system was implemented in 2010. After achieving within two years the complete IRD of high concentrations of TCE, cis-1,2-dichloroethene (cDCE) and TCA to end-products, challenges posed by variable groundwater flow conditions and precipitation/biofouling on well screens resulted in the near complete loss of in situ electron donor concentrations. As a result, additional diagnostic testing and well rehabilitation efforts were employed in an attempt to restore biostimulation, confirm the robustness of the dehalorespiring culture, and restore IRD rates.

BACKGROUND

Solvent Recycling Facility (Carbonate Valley, PA)

COMPLICATING FACTORS

- Groundwater in fractured dolomite/limestone aquifer of Pennsylvania
- Depth to groundwater: ~80-90 ft, seasonal variations up to ~30 ft
- Source zone "thickness" ~35 ft (upper bedrock zone)
- Groundwater flow through source zone ~30 to 60 gpm (43,000-86,000 gpd)
- Fracture zone/well yields: 0.5 to 30 gpm (median 3 gpm)
- Treat source zone containing over ~80,000 ppb of trichloroethene (TCE), 1,1,1 trichloroethane (1,1,1-TCA) and other chlorinated ethenes/ethanes
- Dehalococcoides mccartyi (Dhc) inhibited by 1,1,1-TCA and high methanol (2005). Note: vinyl chloride (VC) and ethene not present prior to bioremediation
- A period of abnormally low groundwater flow (2012–2013) adversely affected the typically continuous and effective distribution of electron donor

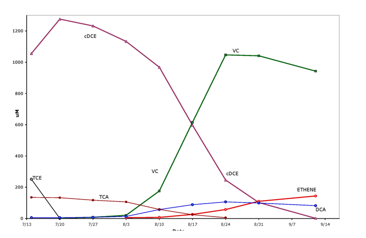
KEY IMPLEMENTATION STEPS

LABORATORY MICROCOSM STUDY (2005–2006)

Objective: Culture a TCA tolerant TCE degrading consortium using Site groundwater capable of degrading methanol and ethanol and TCE/TCA

- Conducted microcosm with Site groundwater and TCE, cDCE, and TCA concentrations of 42,000, 94,000 and 17,000 ppb (residual source area concentrations)
- Bacteria culture added contained 1,1,1-TCA-tolerant Dhc ethenogenes, Dehalobacter, fermenters, acetogens, sulfate-reducing bacteria, and methanogens
- **First ever** demonstration of complete degradation of TCE/cDCE and 1,1,1-TCA **concurrently**, using lactate and BCI culture

Malvern TCE Superfund Site
Microcosm Study: Microcosm #7 (Bioaugmented)



AISB PILOT TEST (2006–2010)

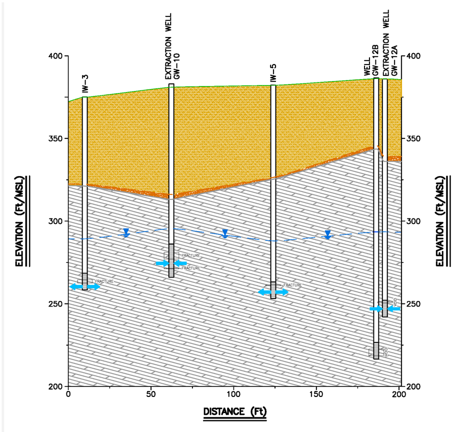
AISB FULL-SCALE DESIGN (2009–2010)

Pumping to control and facilitate distribution of donor/nutrients for source treatment through AISB

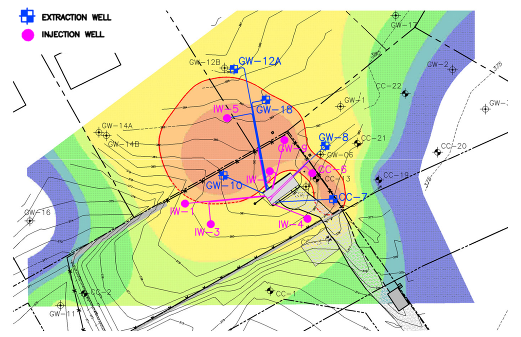
- **USEPA issues remedy change document (August 2009) based on laboratory/pilot results!**
- Accelerated in situ biological treatment (AISB) to degrade chlorinated VOCs throughout the source zone (and enhance dissolution)
- Groundwater extracted and amended with nutrients and re-injected in the source area creating *some* groundwater recirculation/treatment "cells"
- Groundwater to be bioaugmented with TCE/TCA degrading culture initially, and as necessary
- Natural Attenuation to address downgradient VOC plume beyond AISB treatment zone

AISB AMENDMENTS

- 3 to 7 gpm extraction/injection flow (~0.5 to 1.5 gpm per well)
- Donor: Sodium Lactate (60%)
  - » Target in situ concentration: 700 to 800 mg/L
  - » Injection rate: 22 mL/min
  - » Daily usage: ~4.1 gal/day
  - » Usage in 2 years: ~2,900 gallons
- Nutrients: Miracle Gro™ and Potassium Tri-poly-phosphate (KTPP) (source of ammonia-N and phosphate)
  - » Target in situ concentrations: 1mg/L each
  - » Injection rate: 22 mL/min
  - » Usage in 2 years: Miracle Grow ~1,050 gallons; KTPP ~660 gallons
- Vitamin B12: ~5 grams / week
- 76 L of TCE/TCA degrading bacteria culture (BCI developed in Site groundwater) and as necessary
- Natural Attenuation to address downgradient VOC plume beyond AISB treatment zone



Remediation Well Cross Section



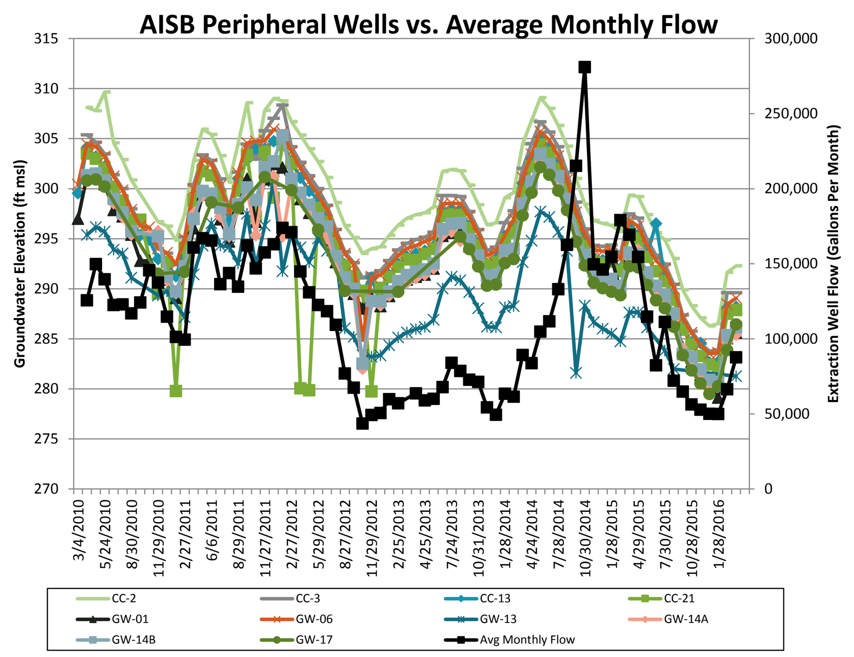
Exterior of treatment building

Interior of treatment building

Extraction well vault

CHALLENGES AND DIAGNOSTIC TESTING

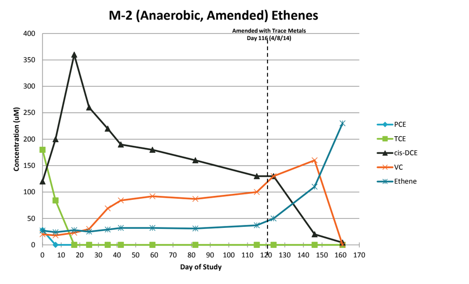
AISB PERIPHERAL GROUNDWATER ELEVATIONS VS. AVERAGE MONTHLY FLOW



GW-10 DIAGNOSTIC TESTING: 2013–2014

Results:

- Microcosm amended with lactate confirms that Dhc/Dhb culture is present and functioning
- Bioaugmentation of Site groundwater was not shown to be necessary based on results
- Results indicate that the **addition of trace minerals significantly increased the reduction of cDCE and production of ethene**



TRACE MINERAL NUTRIENT EVALUATION

Results indicated that trace mineral nutrients would be restored to the system upon restoring flow and donor distribution to the wells.

		GW-10 Microcosm Trace Nutrient Addition	Miracle Gro Solution	Nutrient Tank Mixture	GW-10 Groundwater
Mineral Nutrients					
Boron	mg/l	0.02	23.3	11.3	0.0267 J
Calcium	mg/l	0.37	13.7	10.3	37.6
Cobalt	mg/l	0.21	0.0093 J	0.0246 J	0.0062
Copper	mg/l	0.05	94.3	41.6	0.0035 J
Iron	mg/l	--	229	82.2	2.88
Magnesium	mg/l	--	16.4	8.34	38.3
Manganese	mg/l	0.14	59.4	27.2	1.57
Molybdenum	mg/l	0.04	0.751	0.357	N.D.
Nickel	mg/l	0.06	0.0254 J	0.0447 J	0.0030 J
Potassium	mg/l	--	13,700	25100	17.9
Selenium	mg/l	0.03	0.0449 J	< 0.1	< 0.0048
Sodium	mg/l	--	297	251	102
Tungsten	mg/l	0.05	NA	NA	NA
Zinc	mg/l	0.24	68.8	30.6	0.0063 J

SYSTEM OPTIMIZATION EFFORTS

Extraction Well Rehabilitation

GW-10 rehabilitation conducted in July 2014:

- Physical surging first followed by pumping test
- Overnight sulfamic acid treatment followed by surging and pumping test
- Flow increased significantly and no negative effects on groundwater pH

GW-8, GW-12A, GW-18 rehabilitation conducted in August 2014:

- Overnight sulfamic acid treatment with manual brushing of well screens

GW-12A biomaterial observed during rehabilitation

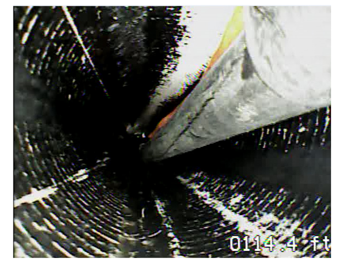
Purge water from rehabilitation activities

Biomaterial observed at Well GW-18 During OTV Logging

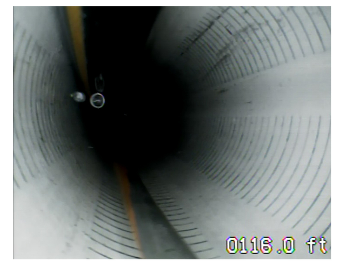
Injection Well Rehabilitation

Rehabilitation of the AISB injection wells was conducted in February and March 2015.

- Overnight sulfamic acid treatment with manual brushing of well screens



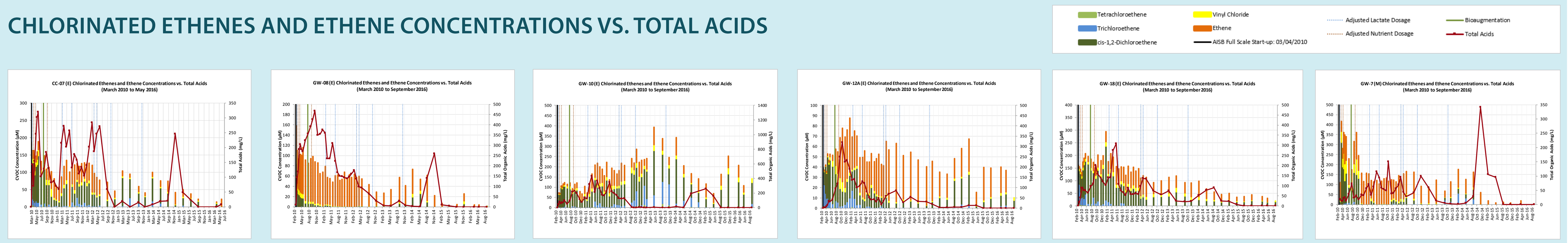
Down hole OTV inspection: BEFORE rehab



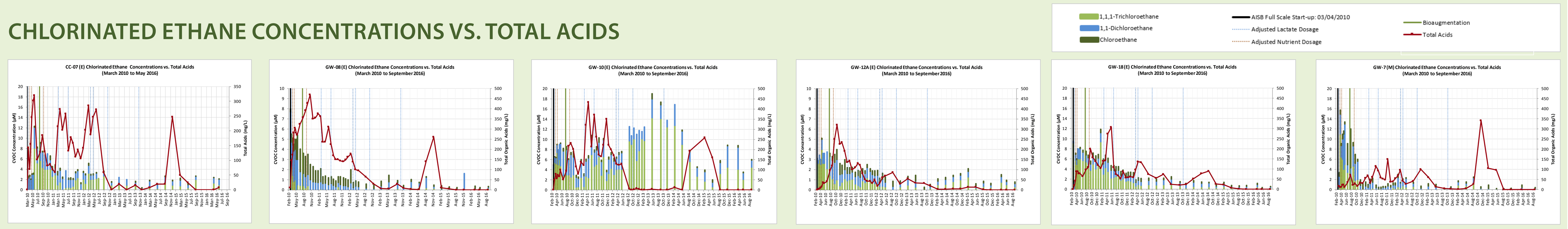
Down hole OTV inspection: AFTER rehab

RESULTS AFTER SIX YEARS OF FULL-SCALE OPERATIONS

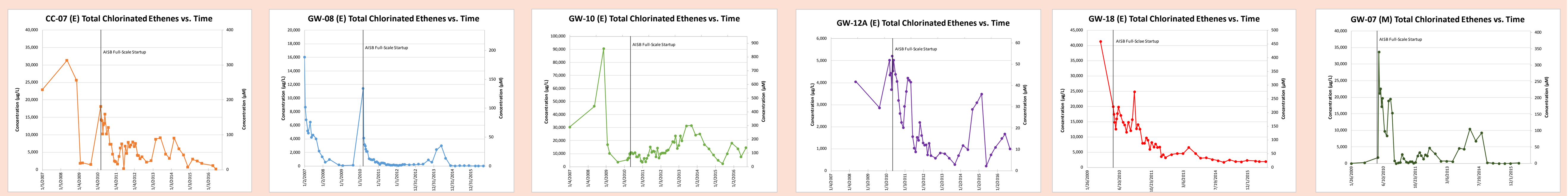
CHLORINATED ETHENES AND ETHENE CONCENTRATIONS VS. TOTAL ACIDS



CHLORINATED ETHANE CONCENTRATIONS VS. TOTAL ACIDS



TOTAL CHLORINATED ETHENE CONCENTRATION OVER TIME (PPB VS. MOLAR)



PERCENT REDUCTION OF TOTAL CHLORINATED VOLATILE ORGANIC COMPOUNDS (CVOCS)

% Reduction of Total Chlorinated Volatile Organic Compounds (CVOCs) — Source Area Wells

Well	Well Type	Date	Historical Max Prior to Full-Scale (March 2010)	Average Concentration Prior to Treatment[1]	Current Average Concentration[2]	% Reduction from Historical Maximum	% Reduction from Prior to Treatment
CC-07*	Extraction	06/23/2004	34,390	30,310	1,047	97.0%	96.5%
GW-07*	Monitoring	04/12/2006	84,035	6,225	143	99.8%	97.7%
GW-08*	Extraction	10/31/2006	28,715	28,250	9	100.0%	100.0%
GW-10*	Extraction	11/12/2008	92,858	53,125	12,009	87.1%	77.4%
GW-12A	Extraction	05/07/2008	4,641	3,934	1,318	71.6%	66.5%
GW-12B	Monitoring	05/07/2008	1,728	1,294	378	78.1%	70.8%
GW-18	Extraction	08/21/2009	43,156	43,171	2,010	95.3%	95.3%
Average						89.8%	86.3%
Weighted Average						94.2%	89.8%

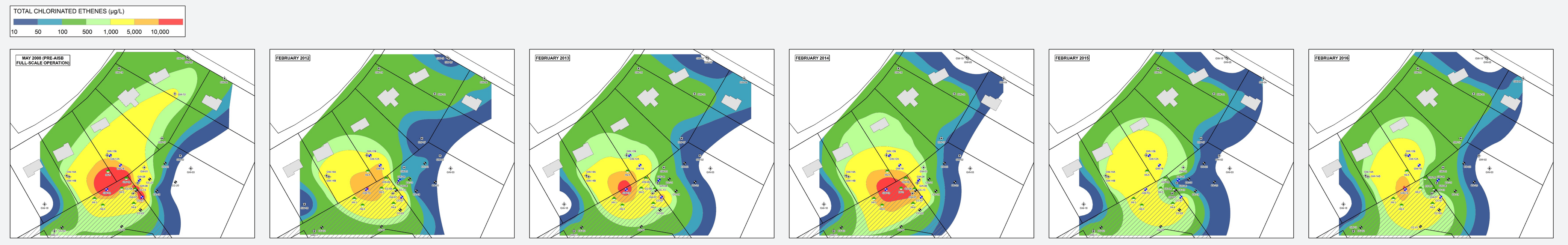
Notes:
All results in ug/L
CVOCs include PCE, TCE, cDCE, VC, 1,1,1-TCA, 1,1-DCA
1/2 detection limit was used for calculations, as appropriate
[1] - Average concentration prior to treatment takes the average of up to three data points collected prior to the start of treatment, pilot test or full-scale. This may include a time range of several years due to infrequent data collection.
[2] - The average concentration of the most recent three data points through March 2016. For source area wells, the average is based on a time range of six months
* - Indicates well was part of the pilot testing

% Reduction of Total Chlorinated Volatile Organic Compounds (CVOCs) — Downgradient Monitoring Wells

Well	Well Type	Date	Historical Max Prior to Full-Scale (March 2010)	Average Concentration Prior to Treatment[1]	Current Average Concentration[2]	% Reduction from Historical Maximum	% Reduction from Prior to Treatment
CC-13	Monitoring	09/29/2004	2,210	1,066	134	93.9%	87.4%
CC-21	Monitoring	11/23/2004	3,928	1,689	121	96.9%	92.8%
GW-01*	Monitoring	02/21/2001	31,990	26,135	376	98.8%	98.6%
GW-06	Monitoring	08/18/2004	5,506	1,209	799	85.5%	33.9%
GW-13	Monitoring	10/19/2007	2,338	1,507	325	86.1%	78.5%
GW-04	Monitoring	09/30/2004	389	266	86	77.8%	67.6%
GW-05	Monitoring	05/08/2008	513	226	9	98.3%	96.1%
Average						91.1%	79.3%

Notes:
All results in ug/L
CVOCs include PCE, TCE, cDCE, VC, 1,1,1-TCA, 1,1-DCA
1/2 detection limit was used for calculations, as appropriate
[1] - Average concentration prior to treatment takes the average of up to three data points collected prior to the start of treatment, pilot test or full-scale. This may include a time range of several years due to infrequent data collection.
[2] - Average concentration of most recent three data points through March 2016. For downgradient monitoring wells, average is based on a time range of one year
* - Indicates well was part of the pilot testing

TOTAL CHLORINATED ETHENE ISOCONCENTRATION MAPS



CONCLUSIONS AND RECOMMENDATIONS

- Seasonal groundwater conditions and in-well biofouling resulted in lower system flow that caused significantly diminished organic acid concentrations.
- Overall, extraction well rehabilitation efforts significantly improved system flow and donor distribution in the aquifer.
- With the return of organic acids, VOC levels of parent compounds and cDCE have decreased and VC and ethene concentrations have increased, which indicates that biodegradation activity has resumed at most locations.
- The resumed biodegradation of both chlorinated ethenes and ethanes indicates Dhc and Dhb remain viable in the aquifer.
- The locations which have shown a lag in organic acids reestablishment have also shown less biodegradation activity.
- Additional optimization efforts will be performed after groundwater elevations rise within the historical operational range.

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