



Use of Anaerobic Reductive Dechlorination and Cement/Ferrous Iron System for the Remediation of Chlorinated VOCs

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Introduction

Green and sustainable remediation techniques were implemented in order to reduce the concentration of various chlorinated solvents at a site located in Indianapolis, IN.

The remedial design included enhanced biological reductive dechlorination injections, in conjunction with micron-scale zero valent iron (ZVI), in order to treat the chlorinated volatile organic compounds (CVOCs).

A combination of injection techniques and novel soluble organic hydrogen donors such as blue green algae and kelp, were utilized to treat the site. Through the use of algae and kelp, the remedial program is utilizing green and sustainable technologies in lieu of processed remedial materials.

The objective of the remedial design was to promote the conditions in-situ necessary for accelerated dechlorination via both abiotic and microbial processes. The remedial program was designed to mitigate off-site migration, treat sorbed and dissolved contamination, and create subsurface conditions that are ideal for biological reductive dechlorination.

An excavation was initially performed at the site, which was followed by backfilling of the subsurface with crushed brick and cement from a demolished building. A monitoring well, MW-9R, was afterwards installed in the middle of the area and that is the area where the remedial event was performed.

Chemistry

Researchers have shown that the reduction in CVOC concentrations is related with the simultaneous existence of cement and iron in the groundwater.

Portland cement (cement hereafter) is a common binder and can effectively immobilize contaminants. Hydration of cement produces calcium silicate hydrates ($\text{CaO-SiO}_2\text{-H}_2\text{O}$), which are nonstoichiometric colloidal gels that principally control the chemical environment in hydrated cement.

Chemistry

When Fe(II) is present in cementitious environments, high hydroxide ion concentration would be conducive to formation of iron solids such as Fe(II) hydroxide and Fe(II)-Fe(III) (hydr)oxides. These Fe(II)-Fe(III) (hydr)oxides are reported to form in concrete by corrosion of the embedded iron and can persist at pH up to 13.

It appears that the addition of Fe(III) to Fe(II)/cement systems increases PCE degradation, suggesting Fe(II)-Fe(III) (hydr)oxides might have been reactive agents (Rickard and Luther, 2007).

Cement has been found to catalyze or participate in the PCE degradation reactions over a pH range of 10.5-13.8, and the degradation kinetics can be described by a pseudo-first-order rate.

The degradation of tetrachloroethylene (PCE) by Fe(II) in the presence of cement hydration products has been observed in batch slurry reactors (Hwang and Batchelor, 2000).

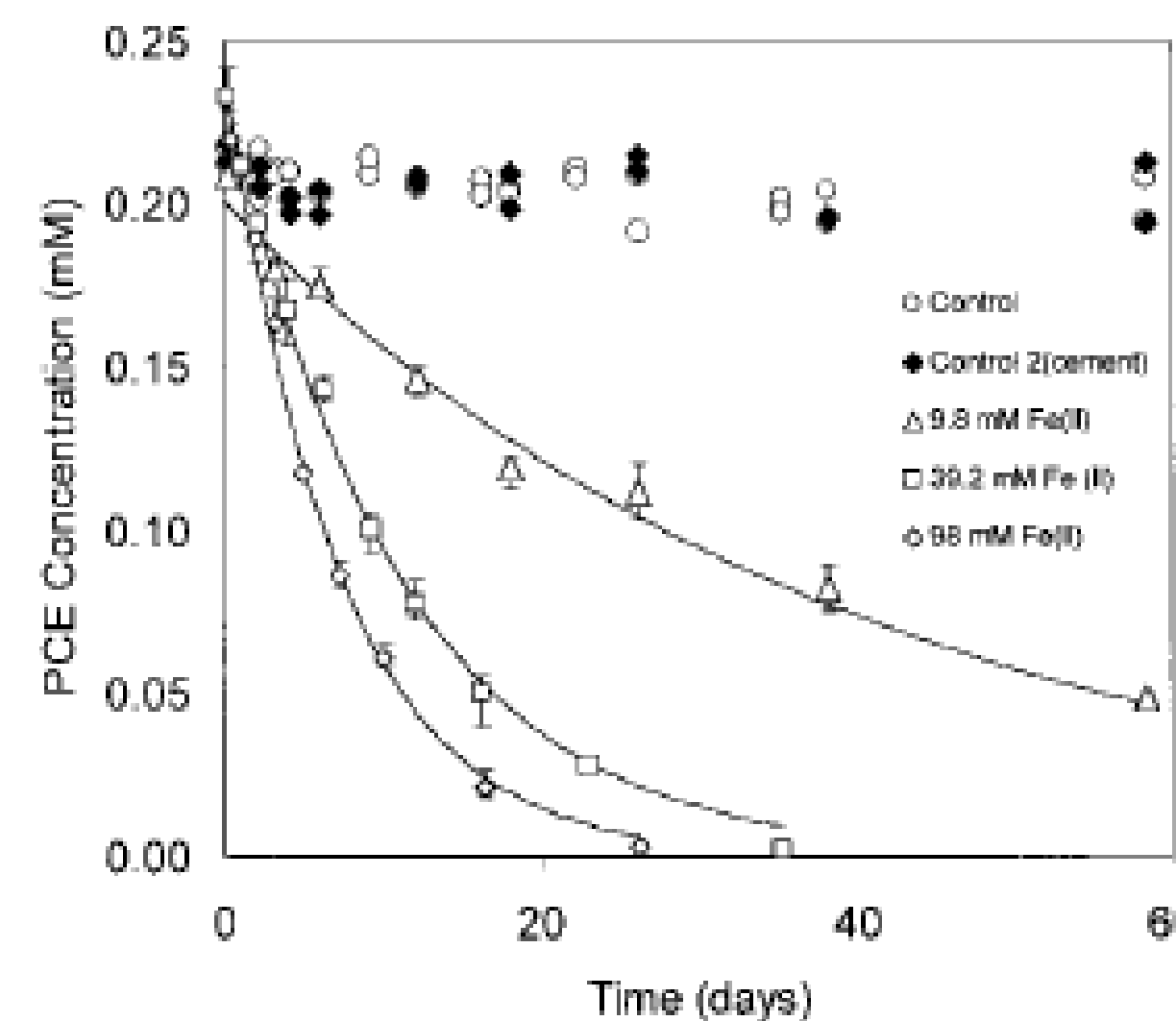


FIGURE 1. Kinetics of PCE reduction by Fe(II) in 10% cement slurries. The symbols represent the results from experiments on Fe(II) dose effect (exp. 1, 3, and 4 in Table 2). The error bars are ranges of measured PCE concentrations. Some error bars are smaller than the symbols. Lines represent first-order fits. $[\text{PCE}]_0 = 0.245 \text{ mM}$.

The distributions of the reduction products indicate that the major reduction pathway for PCE, TCE and 1,1-DCE is reductive-elimination, while for VC it is hydrogenolysis.

Chemistry

In fact, a 98% reduction of PCE concentration is achieved in a system with a pH of approximately 12. In this system, PCE is transformed to nonchlorinated products (acetylene, ethene, ethane) with acetylene being predominant, implying that elimination pathways were favored in the cement systems at high pH.

Half-lives of the chlorinated ethylenes in Fe(II)/cement systems ranged from 1.5 to 8.8 days, which were within life spans allowable in DS/S applications. The order of reactivity of the chlorinated ethylenes in the Fe(II)/cement systems was as follows: TCE > 1,1-DCE > PCE > VC.

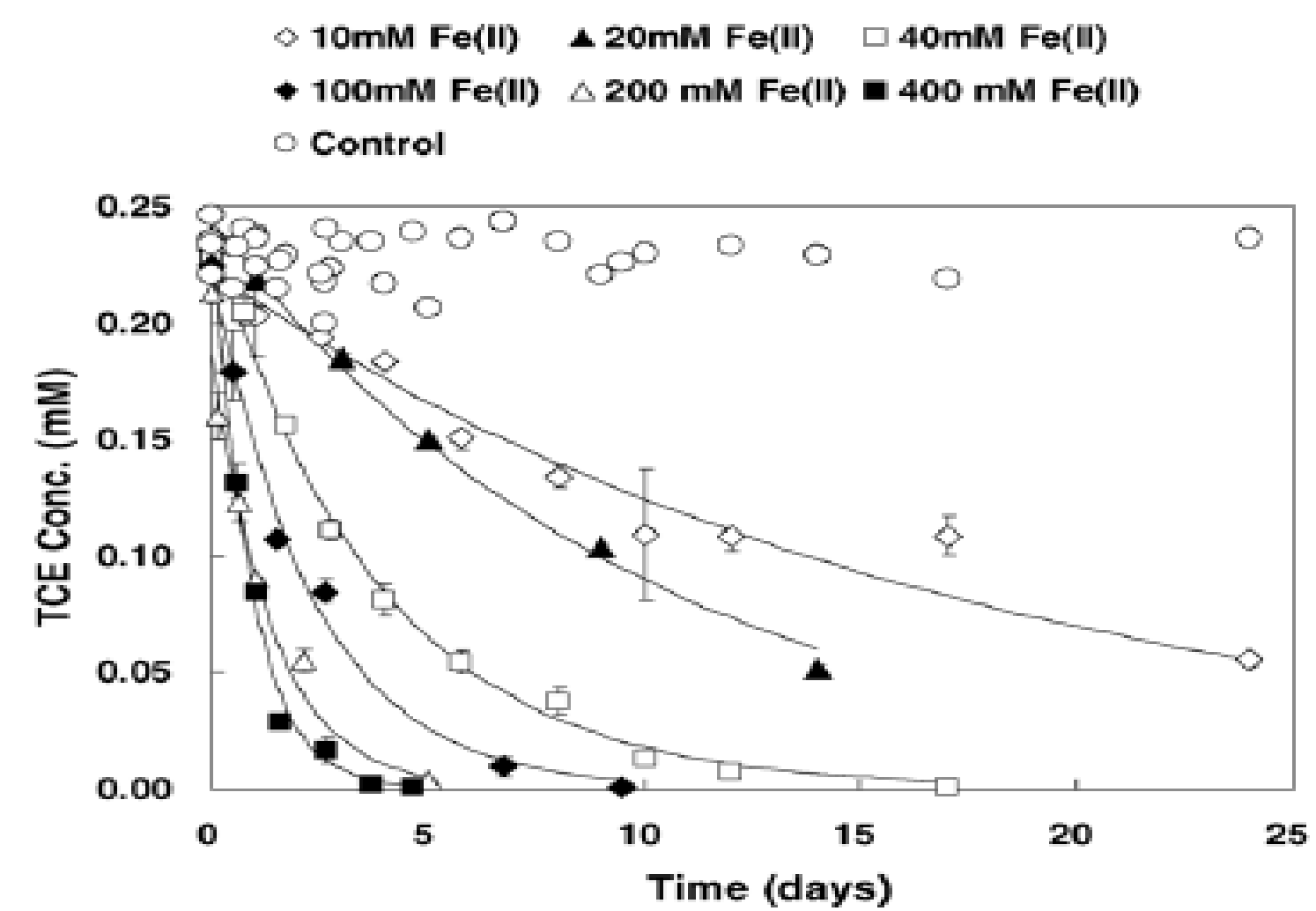
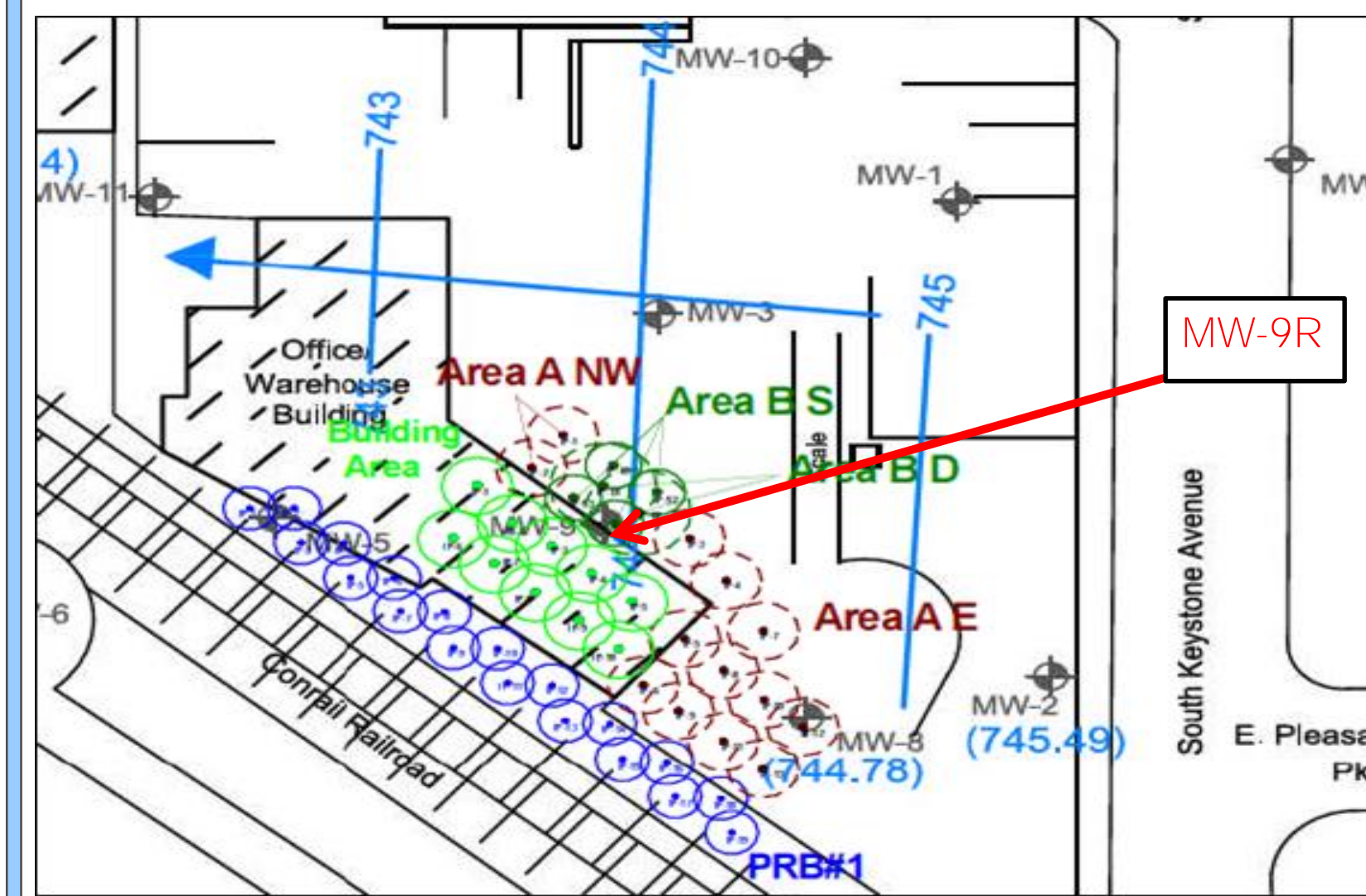


Fig. 2. Kinetics of TCE reduction in Fe(II)/cement systems containing various amounts of Fe(II). The error bars represent ranges of measured concentrations of TCE. Curves represent pseudo-first-order fits.

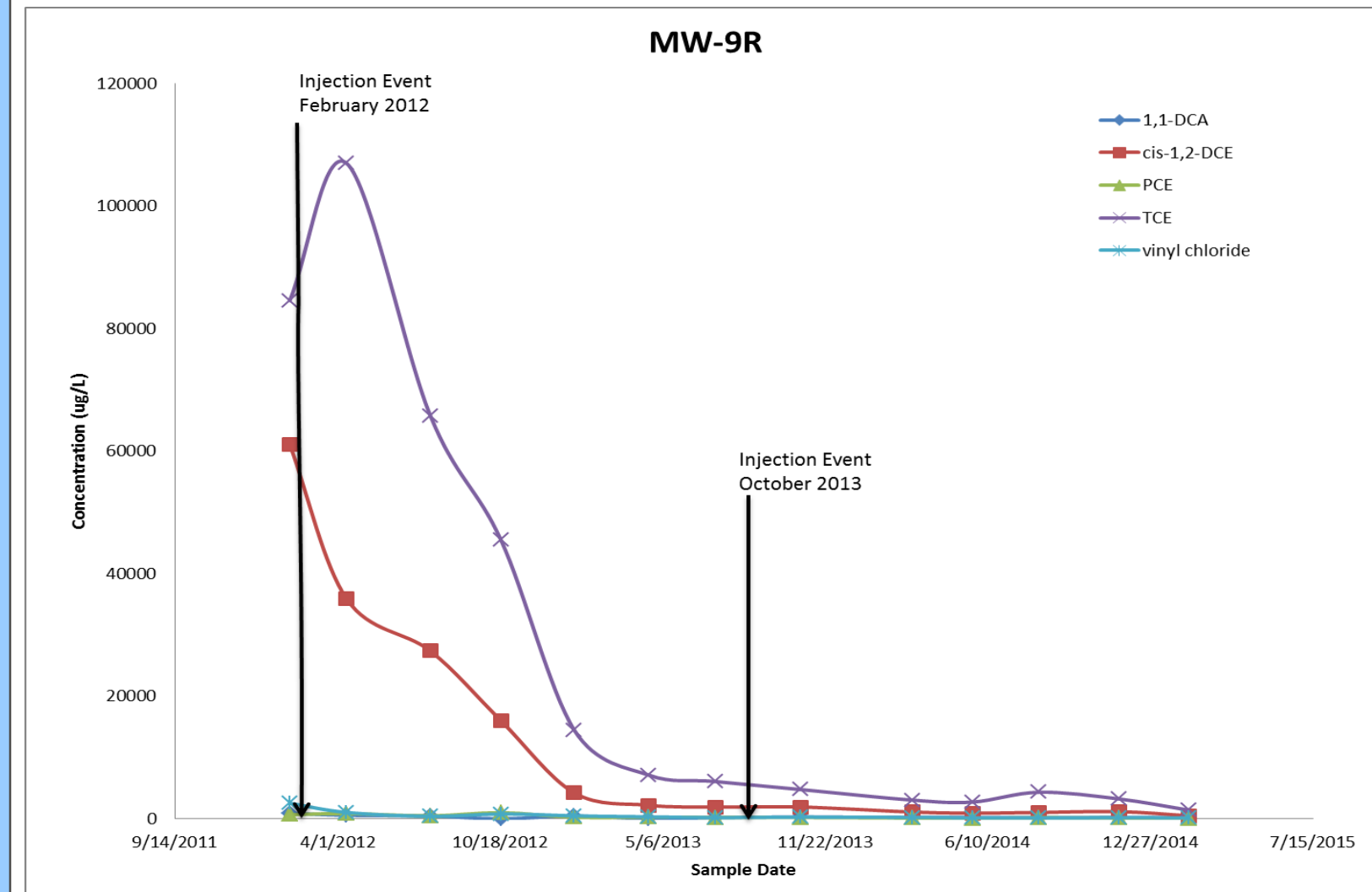
Results



Well ID	Date	pH (S.U.)	DO (mg/L)	ORP (mV)	Conductivity (mS/cm)
MW-9R	02/02/2012	10.54	1.80	-210.6	7.617
	04/12/2012	12.72	0.30	-300.9	8.905
	07/24/2012	12.00	0.10	-196.2	9.079
	10/19/2012	11.59	0.80	-369.4	7.479
	01/16/2013	10.89	1.10	-348.3	14.150
	04/19/2013	10.54	0.40	-17.5	6.023
	07/12/2013	11.88	0.27	-331.5	6.635
	10/23/2013	12.00	0.14	-199.4	7.189
	03/19/2014	12.07	0.68	-124.0	5.725
	05/22/2014	12.11	0.79	-60.5	5.939
	08/14/2014	11.65	0.40	-225.7	5.420
	11/19/2014	11.73	0.58	-226.4	5.801
	02/12/2015	12.35	0.70	-234.2	5.317

Well ID	Date	Methane	Ethane	Ethene	Sulfate	Dissolved Iron	Total Iron	Acetylene
MW-9R	02/02/2012	147	11.4	179	1,340,000	<100	1,970	NA
	04/12/2012	198	20.9	170	1,380,000	148	4,630	NA
	07/24/2012	138	48.6	408	1,810,000	142	8,440	NA
	10/19/2012	2,820	74.0	510	1,350,000	<100	2,730	NA
	01/16/2013	5,420	67.4	395	1,360,000	327	1,880	NA
	04/19/2013	9,300	96.0	417	926,000	<100	1,560	210
	07/12/2013	5,750	<10	253	1,430,000	208	523	210
	10/23/2013	5,640	84.5	669	1,410,000	71.3	303	91.0
	03/19/2014	9,790	154	628	1,380,000	262	1,050	76.0
	05/22/2014	7,680	<10	476	1,300,000	246	1,220	45.0
	08/14/2014	5,730	107	510	589	487	6,520	140.0
	11/19/2014	8,320	195	888	1,570,000	326	1,960	160.0
	02/12/2015	6,310	152	837	1,150,000	<100	139	23.0

Well ID	Date	02/2012	04/2012	07/2012	10/2012	01/2013	04/2013	07/2013	10/2013	03/2014	05/2014	11/2014	02/2015
MW-9R	PCE	678	841	487	1,000	255	254	233	219	119	86.3	129	72.6
	TCE	84,600	107,000	65,800	45,500	14,500	7,120	6,080	4,770	3,060	2,730	3,240	1,420
	cis-1,2-DCE	61,100	35,900	27,400	16,000	4,240	2,210	1,920	1,920	1,110	915	1,170	500
	Vinyl Chloride	2,550	1,040	403	794	478	324	201	275	221	146	179	153
	1,1-DCA	896	582	450	<500	471	<50	194	294	230	205	205	158



Conclusions

PCE, TCE, cis-1,2-DCE and vinyl chloride have overall decreased by 89%, 98%, 99% and 94% respectively since the baseline sampling event of February 2012.

1,1-DCA concentration has overall decreased by 82%, while the parent compound 1,1,1-TCA is currently measuring below its respective laboratory detection limit.