Case Study: Longevity of Multiple Amendments used in Treatment of Chlorinated Solvents in Groundwater

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ABSTRACT:
In situ bioremediation is the prescribed remedy identified in the Record of Decision for a large chlorinated solvent plume at a New Jersey Superfund site. The acidic pH of the groundwater at this site has necessitated addition of sodium bicarbonate for pH adjustment, along with the electron donor that is added to promote reductive dechlorination of the primary contaminant TCE. A decision regarding the amount of bicarbonate to be added with the electron donor was made early in the treatment program, based upon a soil slurry pH neutralization test performed at bench scale. In situ reductive dechlorination treatment at the site has consisted principally of injection of electron donor and sodium bicarbonate in aqueous solution, followed by bioaugmentation solution injection after treated aquifer areas indicated water quality conditions suitable for *Dehalococcoides* species survival

A detailed analysis of amendment exhaustion indicators (pH, ORP, SC, TOC) at select groundwater monitoring points located in the target treatment area portion of this chlorinated solvent plume was conducted. The results of the analyses indicate that the bicarbonate is almost always exhausted before the electron donor. The trends in the bicarbonate indicator parameters pH and specific conductivity were developed to determine whether a mass balance analysis of bicarbonate could be used to approximate the time of exhaustion and need for amendment reapplication. The mass balance analysis considered the injected bicarbonate mass, proximity of monitoring point to injection locations, and consumption of bicarbonate for neutralization of the groundwater and aquifer matrix in the area between the injection and monitoring wells of interest.

INTRODUCTION

The in situ biodegradation of chlorinated solvents by enhanced reductive dechlorination (ERD) has been in practice for nearly two decades. Enhanced in situ biodegradation of chlorinated solvents is typically implemented by injecting one or more carbon sources into the impacted aquifer in some configuration to contain a plume at its downgradient end or to treat the plume body using injection points in a grid or barrier line configuration. Because this process is a biological in nature, the groundwater conditions for pH and redox must be within certain ranges for ERD to be successful. Therefore, an aquifer with acidic conditions may require pH adjustment.

The in situ treatment case presented herein describes the results of eight years of treatment of a large, dilute concentration plume, located at a Superfund site in New Jersey. The plume contains the primary contaminants trichloroethylene (TCE) and 1,1-dichloroethylene (DCE), which are present in aquifer that is acidic (pH less than 6.0 standard units [SU]). Over the eight year period of treatment to date, an electron donor and a pH neutralization agent have been injected in a consistent manner in order to prepare the aquifer for in situ ERD treatment.

BACKGROUND

Site Description. Groundwater contamination at this Superfund site originated from shallow surface or drain pipe discharges in 1980 at a building where circuit board manufacturing operations were occurring. The plume emanating from this source contains TCE and 1,1-DCE as the principal contaminants. The TCE is one of the original chemicals released at the site, while the 1,1-DCE presence is attributable to the abiotic degradation of the originally released 1,1,1-trichlorethane (TCA). At the time plume remediation began in 2010, the plume covered an area of 29 acres, and the leading edge of the plume extended 2,100 feet southeast and downgradient from the suspected point source (EPA 2005). Figure 1 depicts the TCE plume in mid-2011, just after the start of remedial activities in the fall of 2010.

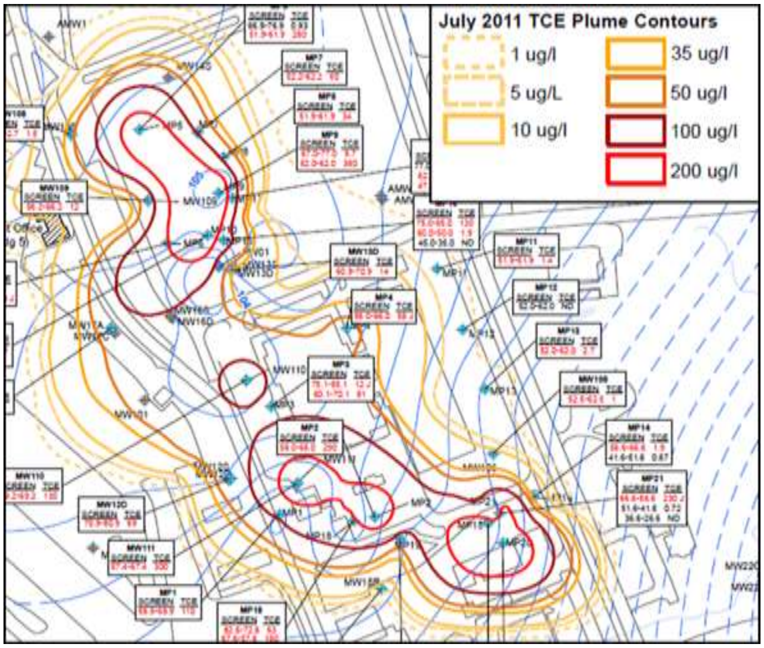


FIGURE 1. TCE plume extent at beginning of the in situ treatment process

The hydrogeology at the site consists of highly stratified sands, silts, and clays known as the Cohansey (upper) and Kirkwood (lower) formations, which sits on top of the Manasquan formation, being the uppermost aquitard at the site (Ecology and Environment 2007). The Manasquan aquitard lies at a depth of 100 to 150 feet below ground surface (bgs) at the site. The occurrence of fine sands, as well as the extent of silts and clays interbedded with the sand, increases with depth in the aquifer. The depth of the water table below the ground surface varies from approximately 40 feet bgs at the northwest portion of the site, to less than 5 feet bgs in the far southeastern portion of the plume. A depiction of the plume in cross-section is presented in Figure 2.

Plume Extent and Aquifer Conditions. The plume has three distinct lobes or areas of higher concentration of TCE, as depicted in Figure 1. These are referred to as Hot Spot #1, located in the northern area of the plume, Hot Spot #2, located in the central area of the plume, and Hot Spot #3, located in the south and southeastern area of the plume. The maximum concentration of TCE detected prior to remediation was approximately 600 micrograms per liter (µg/L), while the highest concentration of 1,1-DCE detected prior to remediation was less than 200 µg/L. The 1,1-DCE contamination distribution spatially mimics the TCE contamination across the site.

The baseline (undisturbed) condition of the groundwater at the site indicates pH levels in the range of 4 to 6 standard units (SU), aerobic dissolved oxygen (DO) levels in the range of 2 to 5 milligrams per liter (mg/L), and positive oxidation reduction potential

(ORP) levels, except in deeper portions of the aquifer where slightly negative ORP levels were more commonly observed. The aquifer pH is lower than the range of 6 to 8 SU considered necessary for effective ERD; values in the 5 to 6 SU range were most commonly observed. Additionally, the pH was also found to decrease to levels between 4 and 5 SU with greater depth in the Kirkwood-Cohansey formation. Therefore, the amendment mixture chosen for injection required a basic component to neutralize the pH upwards towards the appropriate range of 6 SU or above for ERD.

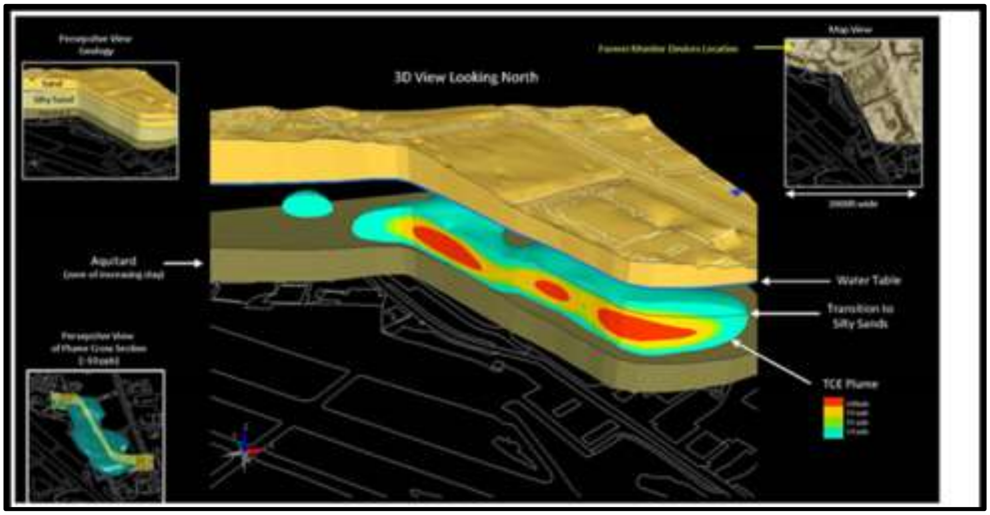


FIGURE 2. TCE plume three-dimensional view

MATERIALS AND METHODS

Amendment Injection. Emulsified vegetable oil (EVO) was chosen as the electron donor (carbon source) for implementation of ERD at the site, based upon favorable microcosm test results conducted during the remedy planning stage (SAIC 2010). Additionally, the groundwater quality data indicated a requirement for addition of a basic chemical to raise the aquifer pH, since the optimal range for reductive dechlorination bacteria activity is 6 to 8 SU, and the baseline groundwater is significantly acidic. Both carbonate and bicarbonate were considered for this neutralization of the groundwater pH. Bicarbonate was chosen as the most appropriate chemical for this task, after initial trials with both chemicals at the beginning of the first annual injection campaign indicated it was easier to work with. The final target concentrations of EVO and bicarbonate in the amendment injectate solution were 3.4 weight percent and 8.3 weight percent, respectively. These levels correspond to an amendment solution recipe of 4,000 lbs of bicarbonate and 200 gallons of EVO mixed with 5,800 gallons of water per each 10-foot injection well screen. The amount of bicarbonate finally selected for the amendment recipe was based upon a pre-treatment laboratory test for bicarbonate neutralization using a 50/50 wt% laboratory slurry mix prepared from soil and groundwater collected from the site. The results of this test are depicted in Figure 3, in which the two separate lines represent soil slurries prepared with upper aquifer (red symbol) and lower aquifer (green symbol) materials. This laboratory test indicated that a loading of at least 1 gram of bicarbonate per kilogram of aquifer matrix was needed to bring the aquifer pH up to a minimum of 6 SU, for the more acidic, deeper aquifer material encountered at the site (green symbol results). In the amendment delivery, effective sodium bicarbonate distribution was also indicated by specific conductivity (SC) increases, since the bicarbonate is ionic in nature.

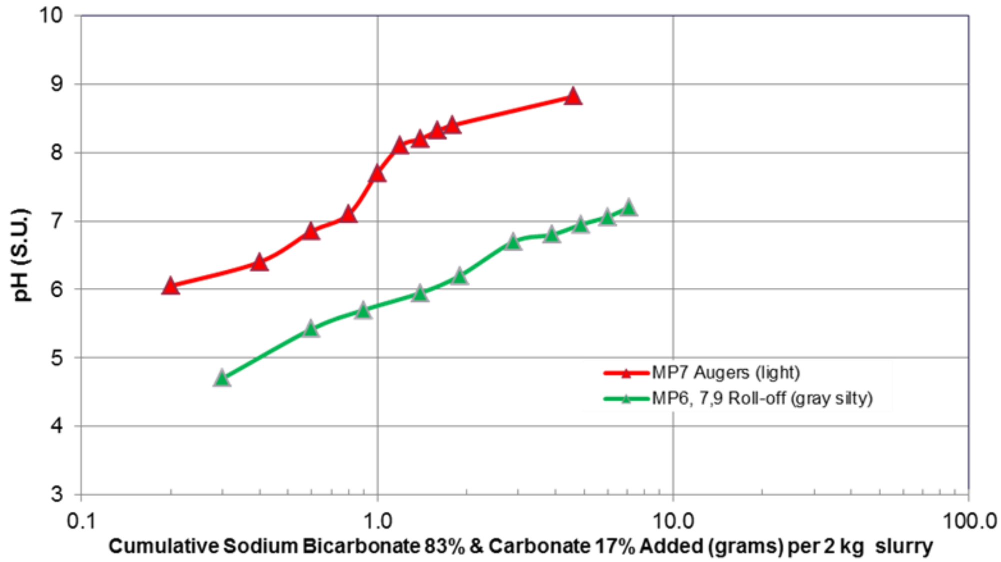


FIGURE 3. Bicarbonate/carbonate aquifer slurry neutralization test

The approach to plume treatment at the site was to treat high concentration areas of the plume first, with subsequent treatment effort directed at moderate to lower concentration areas. This treatment approach was continued until all areas of TCE contamination of 35 µg/L or greater was treated. After the initial amendment injection was completed in the three hot spot areas, subsequent treatment campaigns concentrated on plume areas indicating treatment resistance, contaminant rebound, or newly identified areas of TCE contamination discovered subsequent to the plume definition of the spring 2010 investigation. Table 1 presents the history of the annual amendment injection events at the site, which typically occurred each year in the late summer to mid-fall time frame. Semi-permanent injection wells (IWs) were used as the preferred method for amendment solution delivery to the aquifer for several reasons, including the ability to administer repeat injections without having a drilling or injection rig mobilized for each event. The IWs were located on a 40-foot square grid, and at this spacing, the 5,800 gallons of amendment injection per 10-foot screen was estimated to represent a 25 percent pore volume replacement when injected into the aquifer. Over the majority of the site, the plume thickness that required treatment was determined to be 25 to 45 feet, based upon data from push-boring investigative probes. Therefore, three 10-foot screens stacked vertically across the complete plume thickness were used as the injection well design to address the vertical plume extent. The injection locations across the entire site are depicted in Figure 4.

Data Analysis for Amendment Exhaustion. The bicarbonate amendment is considered exhausted when the pH decreases below 6.0 SU. This indication of exhaustion is commonly preceded by a fall in the SC to levels similar to background (approximately 0.2 milliSiemens per centimeter [mS/cm]). The electron donor is considered exhausted when the total organic carbon (TOC) level falls to within two to four times the background TOC concentration of approximately 2 mg/L. This exhaustion of TOC is commonly reflected with a rise in oxidation-reduction potential (ORP) above the level of -75 to -50 milliVolts (mV) necessary for reductive dechlorination. The amendment exhaustion analysis was performed by assessing the cumulative amount of bicarbonate injected into a localized aquifer area defined by a single IW and monitoring point (MP) pair. Three of these MP locations (identified in Figure 4) were analyzed in this manner. The analysis involved calculating the level of bicarbonate loading to the aquifer (grams of sodium bicarbonate per kilogram of aquifer material [gr SBC/kg soil]), based upon the volume of the localized area (see control volume schematic in Figure 5) and the amount of bicarbonate added with each amendment injection event. This loading value was then compared to groundwater quality levels and TCE degradation indicated for the localized area. Successful TCE treatment was consistently associated only with a sustained aquifer pH change to 6 SU or higher.

TABLE 1. Overview of Treatment Program

Program Year	Treatment Target	Number of Injection Locations (Wells)	Volume of Amendment Injected (gallons)
1 (2010)	100 ppb TCE isocontour	50	250,000
2 (2011)	100 ppb TCE isocontour	119	2,000,000
3 (2012)	50 ppb TCE isocontour	86	1,050,000
4 (2013)	35 ppb TCE isocontour	105	1,404,000
5 (2014)	Specific targets	36	560,000
6 (2015)	Specific targets	51	544,000
7 (2016)	Specific targets	8	101,000
9 (2018)	Specific targets	34	400,000

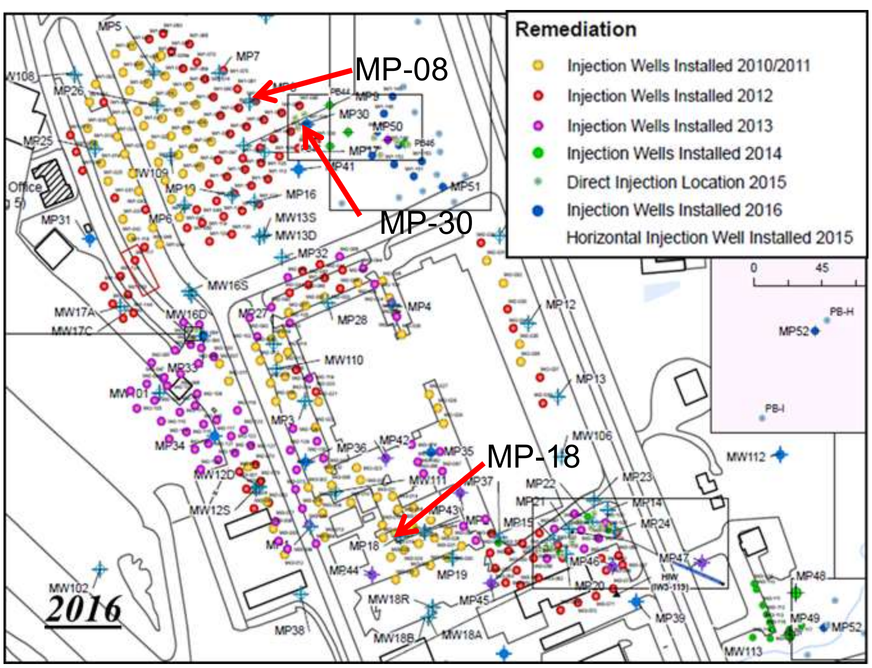


FIGURE 4. TCE plume injection well network and three injection locations of focused analysis

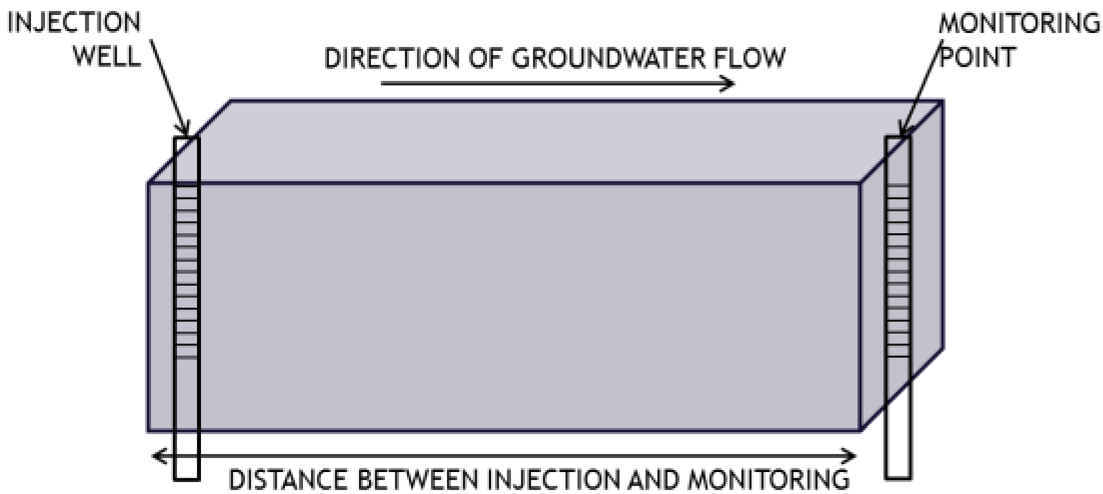


FIGURE 5. Control volume analysis for bicarbonate consumption

RESULTS AND DISCUSSION

Cumulative Bicarbonate Loading Correlation with Solvent Treatment. The first bicarbonate loading analysis was conducted at monitoring point MP-08B. The closest up gradient injection well was located 40 feet from this monitoring point, where amendment injections were conducted in fall of 2012 and 2015. The groundwater conditions and contaminant concentrations versus time at MP-08B are depicted in Figure 6. The injection of amendment in the fall of 2012 was the first event in the immediate vicinity of this monitoring point. This amendment produced the desired response of decreased ORP and increased SC, however these changes were not sustained for more than a couple of months. At the same time, the TCE and 1,1-DCE levels declined to nearly non-detect levels after this first amendment injection event, however, contaminant rebound subsequently occurred in 2014. The second injection event in 2015 finally resulted in more sustained negative ORP levels, and concomitant decline in TCE, followed by appearance of TCE daughters cis-1,2-DCE and VC in 2016 and later. The summary of the bicarbonate analysis, presented in Table 2, indicates a cumulative loading value of approximately 4 gr SBC/kg soil was obtained only after the second injection event.

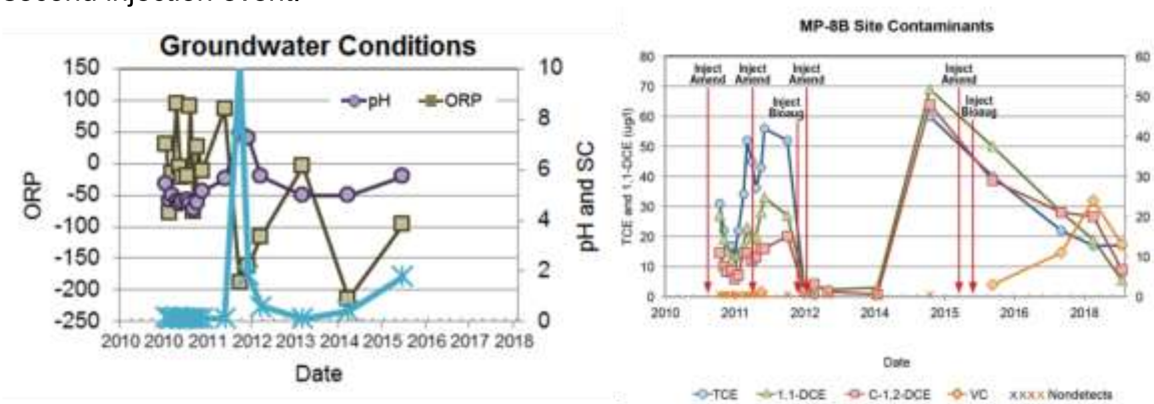


FIGURE 6. Groundwater conditions over time at Hot Spot #1 well MP-08

TABLE 2. Results of Sodium Bicarbonate Consumption Analysis

MP well	Distance [IW→MP] (ft)	Pre-treat pH (SU)	Date injections	Cumulative gr SBC/ kg soil	Date effective treatment
MP-08	40	4.5	9/2012	2.05	2013-Rbnd
			9/2015	4.1	2016
MP-18	15	6.5	9/2011	5.4	2012
MP-30	60	4.5	9/2012	1.35	2013 minimal
			9/2014	2.7	Insufficient data
			9/2015	4.1	2016

The second bicarbonate loading analysis was conducted at monitoring point MP-18B. The closest up gradient injection well was located a mere 15 feet from this monitoring point, and amendment injection was only conducted in fall of 2011. The groundwater conditions and contaminant concentrations versus time at MP-18B are depicted in Figure 7. This amendment injection produced a sustained response of decreased ORP lasting 5 years, increased SC lasting 3 to 4 years, and increased pH lasting 5 to 6 years. The TCE and daughter contaminant decreases reflect this very strong aquifer response towards ERD-conducive conditions, with no substantial rebound evident until 2015-2016. The only lasting rebound to date is cis-1,2-DCE, which has occurred since the amendment appears completely exhausted as of 2016 or 2017. The summary of the bicarbonate analysis, presented in Table 2, indicates a cumulative loading value of approximately 5.4 gr SBC/kg soil was obtained with the first injection event.

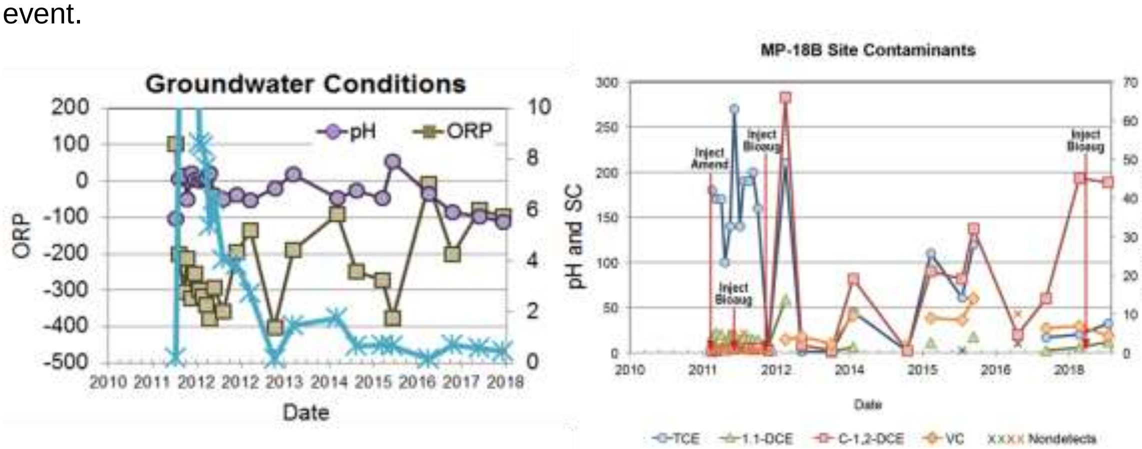


FIGURE 7. Groundwater conditions over time at Hot Spot #3 well MP-18

The third bicarbonate loading analysis was conducted at monitoring point MP-30B. The closest up gradient injection well was located 60 feet from this monitoring point, where amendment injections were conducted in fall of 2012, 2014, and 2015. The groundwater conditions and contaminant concentrations versus time at MP-30B are depicted in Figure 8. The injection of amendment in the fall of 2012 was the first event in the immediate vicinity of this monitoring point. The first amendment injection produced only a very brief and highly muted response in the groundwater conditions of pH, SC, and ORP. Only with the second injection event of 2014 did the groundwater conditions for pH, SC, and ORP change to levels conducive to ERD treatment, and these conditions were sustained for a longer duration with the 2015 injection event. Only after this third event did the TCE and 1,1-DCE levels decline, followed by a significant increase in the TCE daughter products cis-1,2-DCE, and with time, also VC. The summary of the bicarbonate analysis, presented in Table 2, indicates a cumulative loading value of approximately 4 gr SBC/kg soil was obtained only after the third injection event.

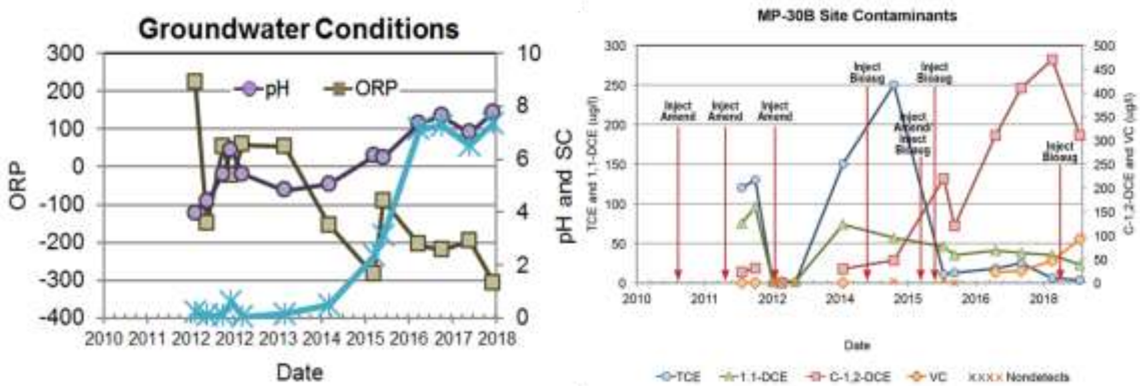


FIGURE 8. Groundwater conditions over time at Hot Spot #1 well MP-30

CONCLUSIONS

The bicarbonate loading analysis for three spatially separated locations within the plume indicates that a cumulative loading of approximately 4 to 5 grams sodium bicarbonate per kilogram of soil aquifer matrix is required before a sustained aquifer pH change occurs, which leads to sustained biodegradation of the primary contaminant TCE. Persistence varied with the level of effectiveness of amendment distribution at the respective monitoring point. Generally, for areas where good distribution was achieved, the electron donor was found to persist for 18 months to three years, while the bicarbonate was found to persist for a slightly shorter time period, on average.

REFERENCES

Ecology and Environment, Inc., 2007, Predesign Investigation Report, Monitor Devices Site, Wall Township, Monmouth County, New Jersey. October 2007.

EPA, 2005. Record of Decision, Monitor Devices, Inc. / Intercircuits, Inc. Site, Operable Unit One-Groundwater, Wall Township, Monmouth County, New Jersey. United States Environmental Protection Agency, New Jersey. September 2005.

SAIC, 2010. Remedial Action Work Plan, Monitor Devices, Inc. / Intercircuits, Inc. Superfund Site, Wall Township, Monmouth County, New Jersey. Revision 5, December 2010.

Case Study: Longevity of Multiple Amendments Used in Treatment of Chlorinated Solvents in Groundwater

Fifth International Symposium on Bioremediation and Sustainable Environmental Technologies

Presented by: Matt Alexander

April 16, 2019

leidos ENGINEERING

Problem Statement

- In situ treatment of solvent plume (TCE and 1,1-DCE) at Superfund site in NJ, using biological reductive dechlorination (RDC) technique
- Low pH of surficial groundwater aquifer requires pH adjustment to optimal conditions for RDC

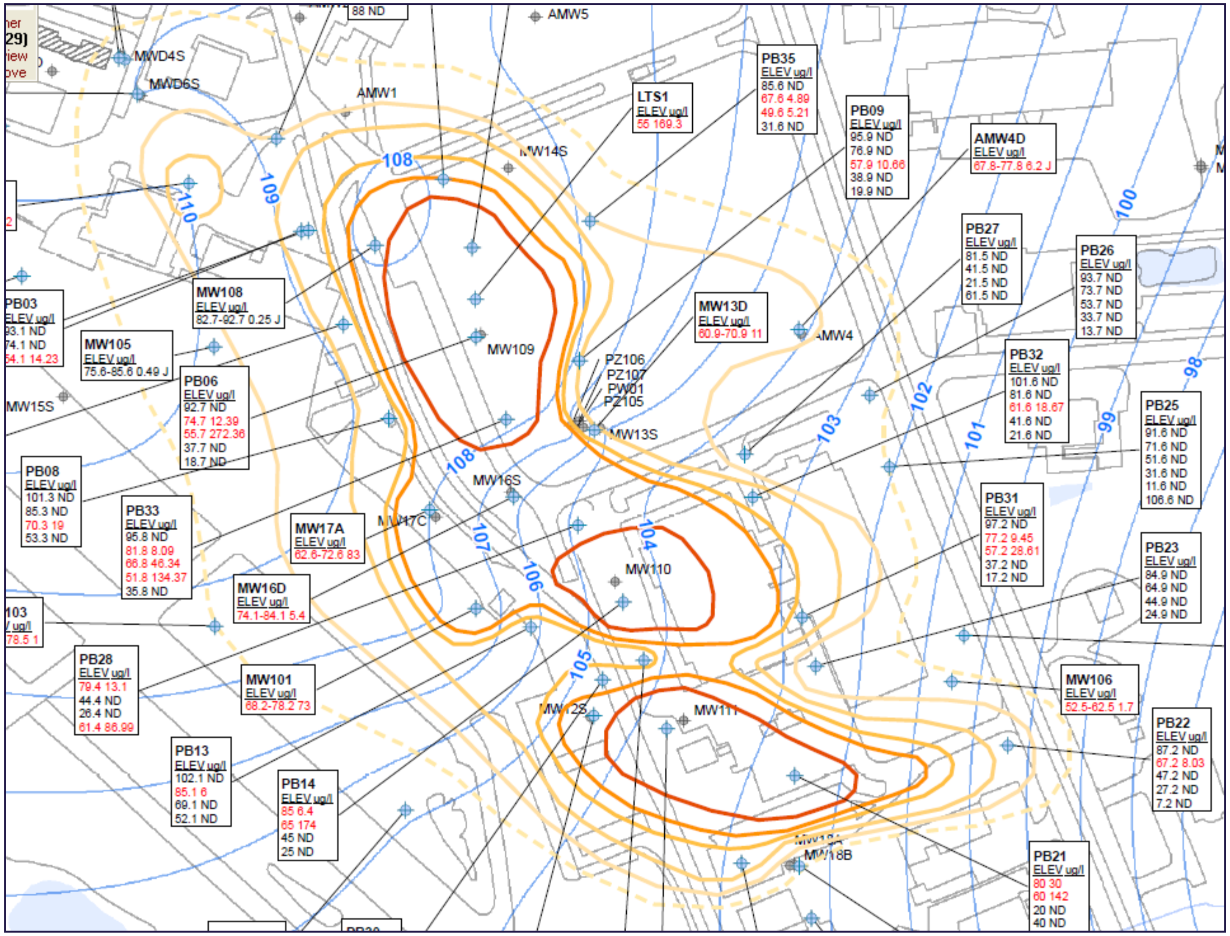
Objective

- Quantify amendment efficacy in situ through monitoring, to establish GW conditions when amendment re-application may be needed

Overview

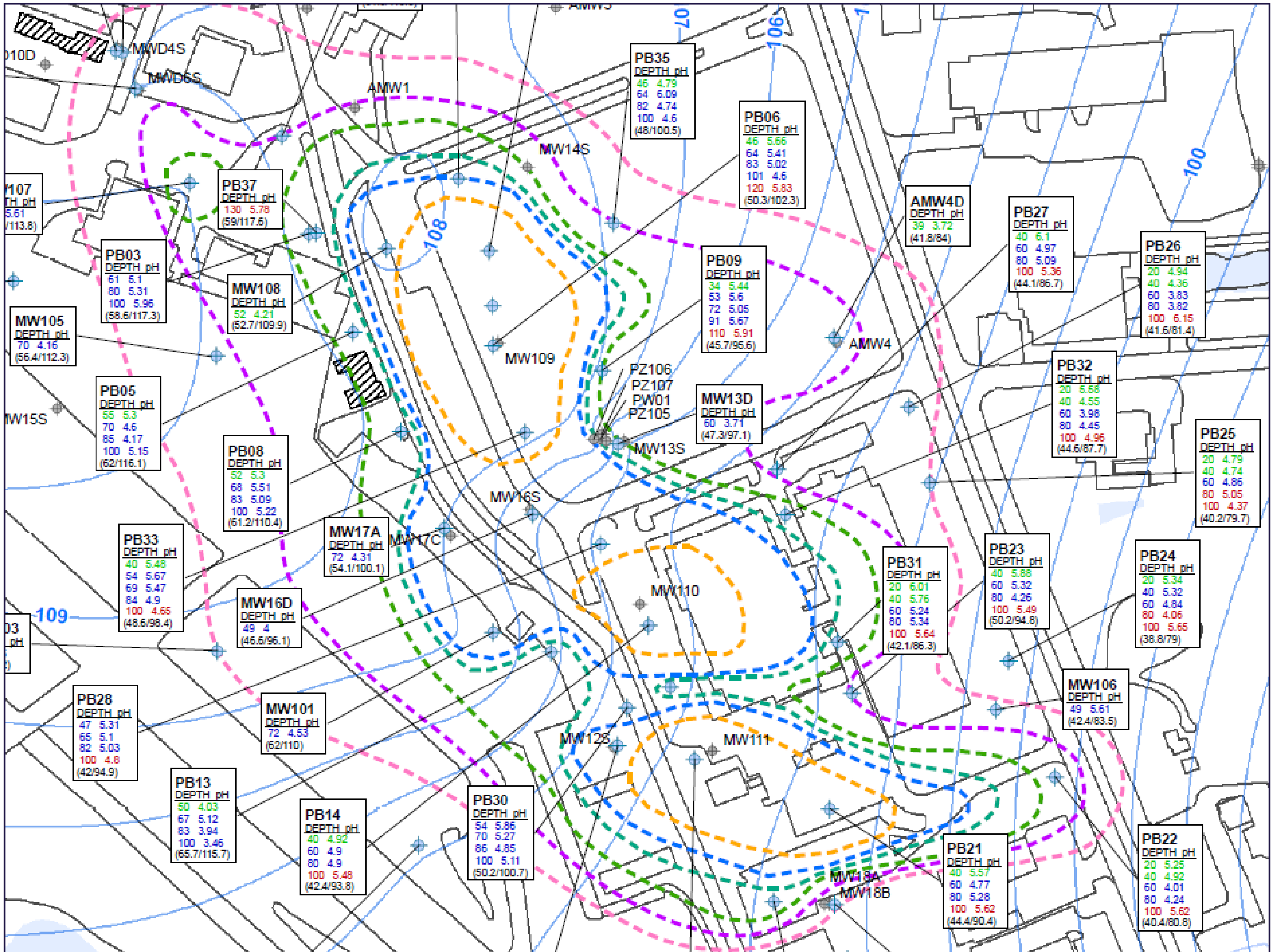
- > Site Background
- > Treatment Description
- > Achieving In situ Conditions for Treatment
- > Summary and Conclusions

Site and TCE Plume Map 2010



1,1-DCE is also a principal site contaminant, having originated from released 1,1,1-TCA

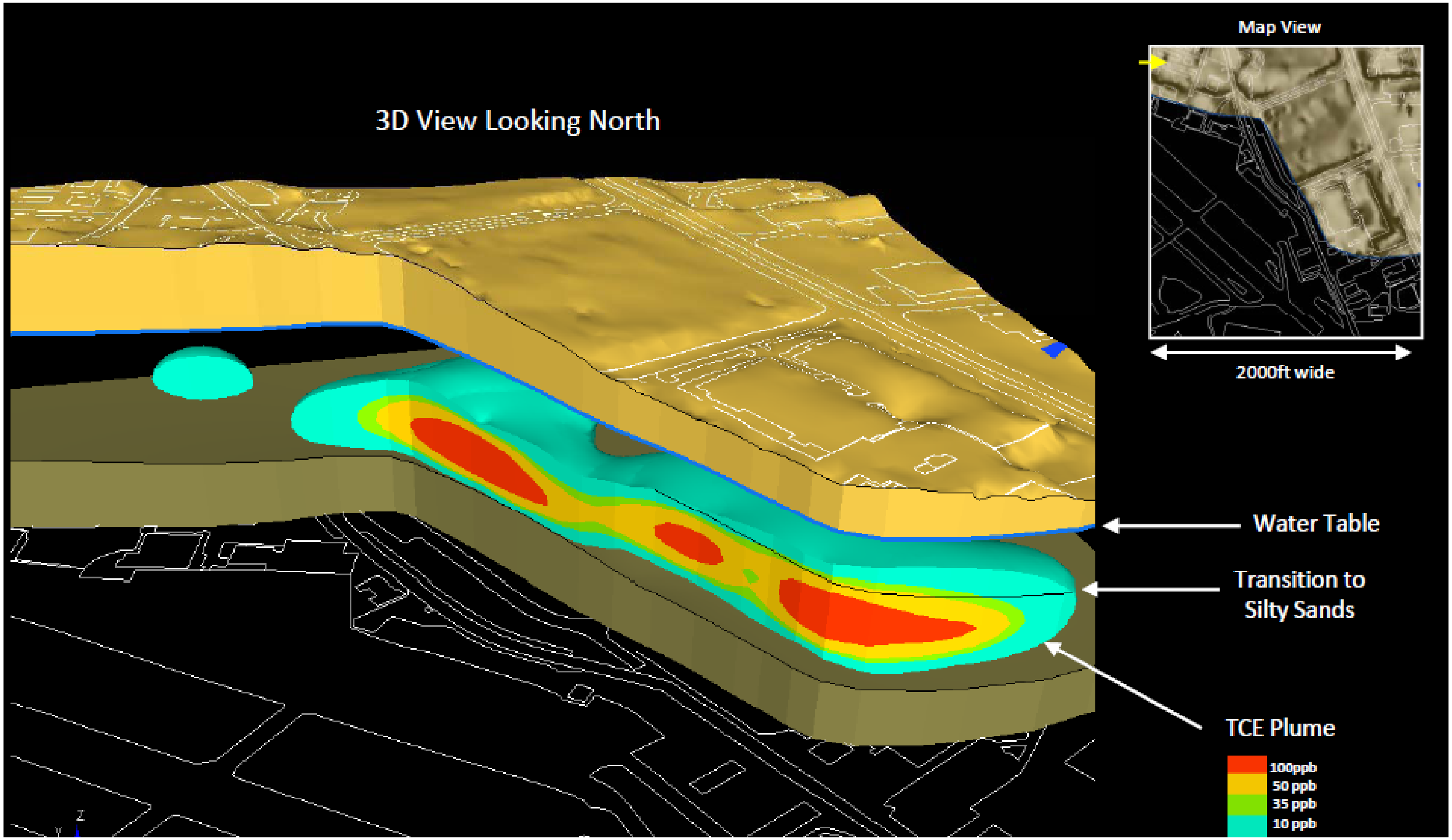
Aquifer pH Baseline Sampling 2010



Site Hydrogeology

> Upper surficial aquifer:
> Medium to coarse sands—Cohansey formation
> Sands with alternating and discontinuous layers of silt and clay—Kirkwood formation
> Kirkwood-Cohansey is 100-150 ft thick at site
> Clayey sand and clayey silt—Manasquan formation, serves as regional aquitard

Site Cross-section



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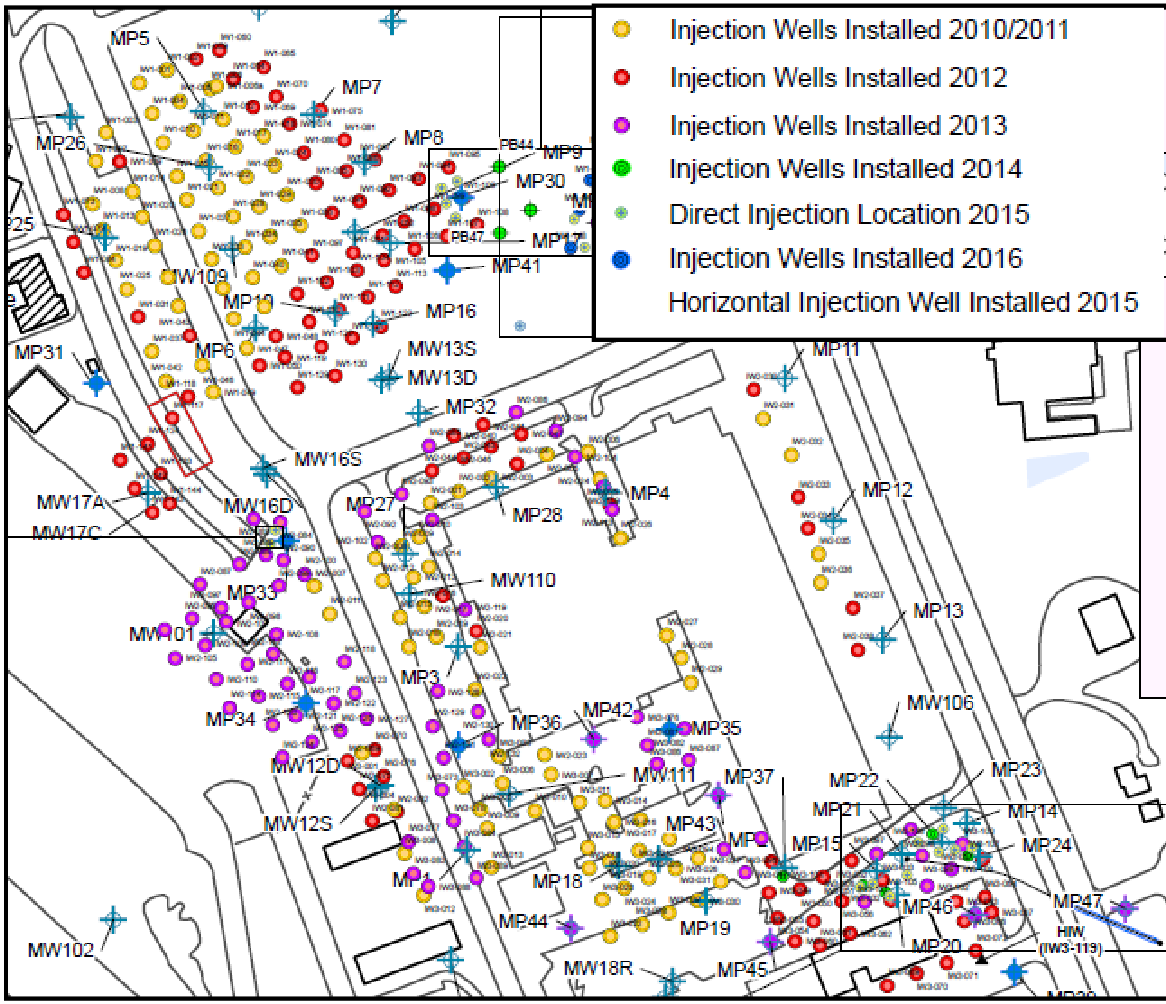
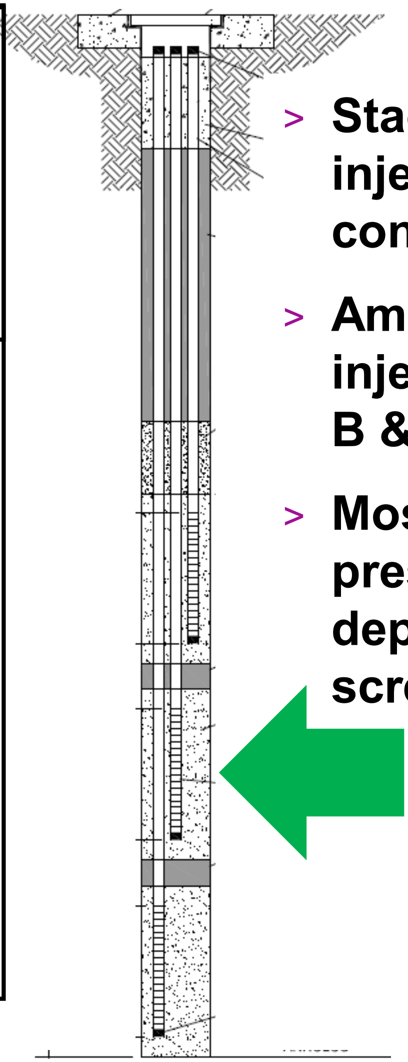
In situ Treatment for 100 ppb Hot Spot Areas





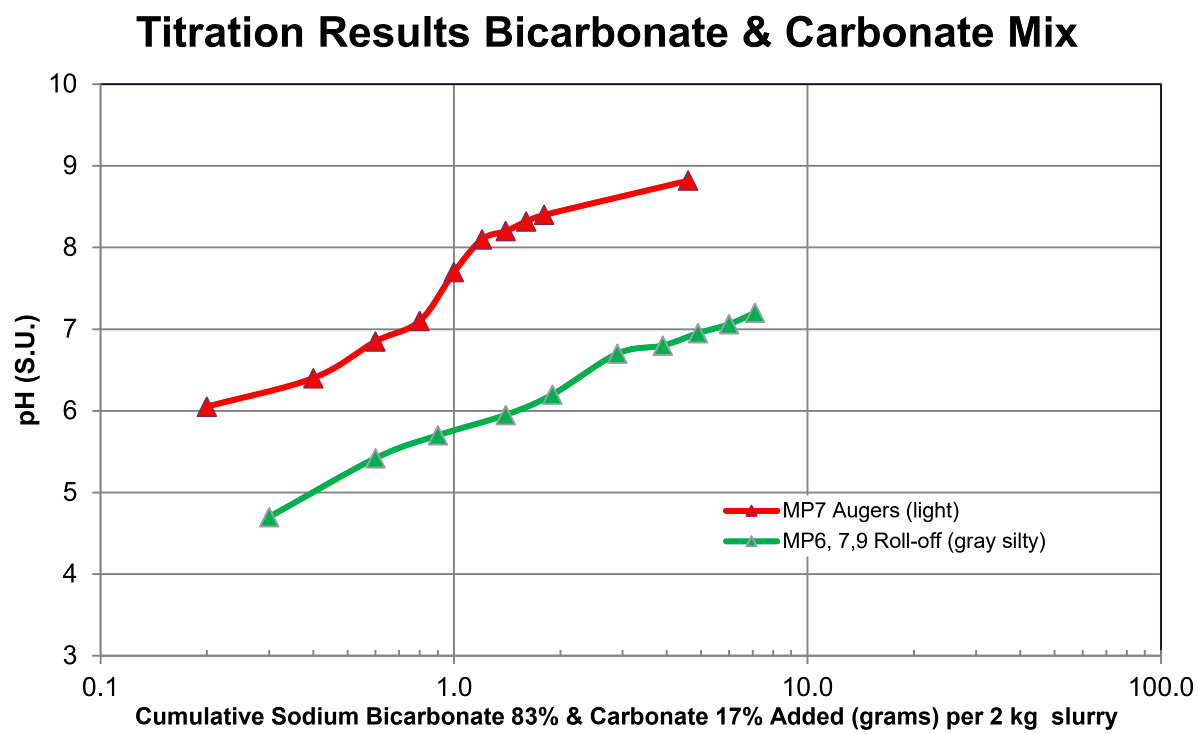
- Stacked injection well construction
- Amendment injected to A, B & C screens
- Most all TCE present at depth of B screen

Neutralization Requirements

- Considered Neutralization--
  - Sodium Hydroxide—strong base, hazardous chemical, likely overshoot of target aquifer pH
  - Sodium Carbonate—moderately weak base, equilibrium pH ~11, possible overshoot of target aquifer pH
  - Sodium Bicarbonate--weaker base, equilibrium pH ~8.5, low possibility to overshoot target aquifer pH

- Conclusion: Lab test neutralization demand using sodium carbonate, bicarbonate, and carbonate/bicarbonate mix

Neutralization Requirements—lab titration test



- Red data represents upper aquifer material, less acidic (A)
- Green data represents lower aquifer material, more acidic (B & C)
- Basis of 2 kg due to soil slurry 1 kg soil & 1 kg groundwater

Amendment Components and Formulation

- Emulsified vegetable oil (EVO) as carbon source to drive biological reductive dechlorination
- Buffering agent (e.g. sodium bicarbonate) to increase pH of aquifer to optimal pH range (6.5 – 8.5) for reductive dechlorination
- Detailed amendment formulation injected per 10-ft IW screen
  - 1,000 lbs veg oil (emulsified) [EVO]
  - 4,000 lbs sodium bicarbonate [SBC]
  - 5,800 gallons water
  - SBC is 8.3 wt%, near solubility limit

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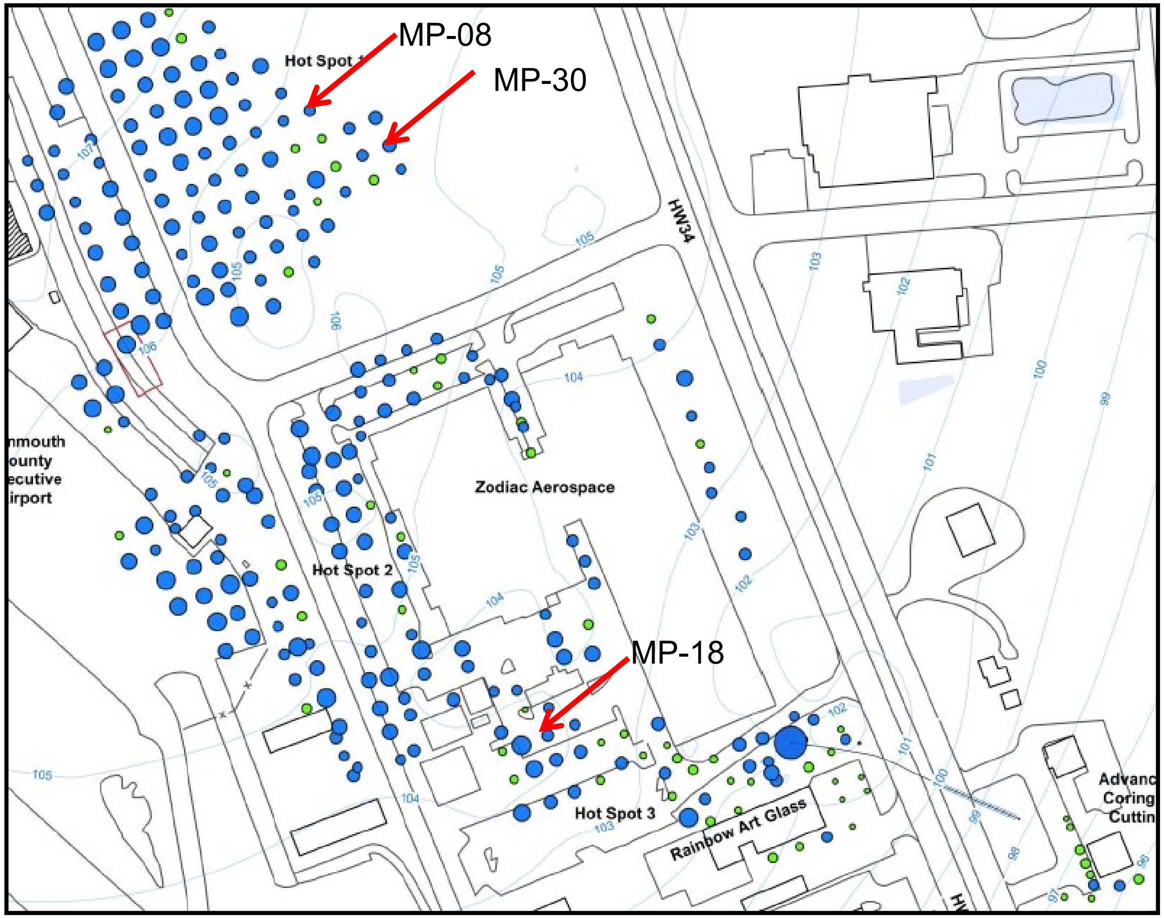
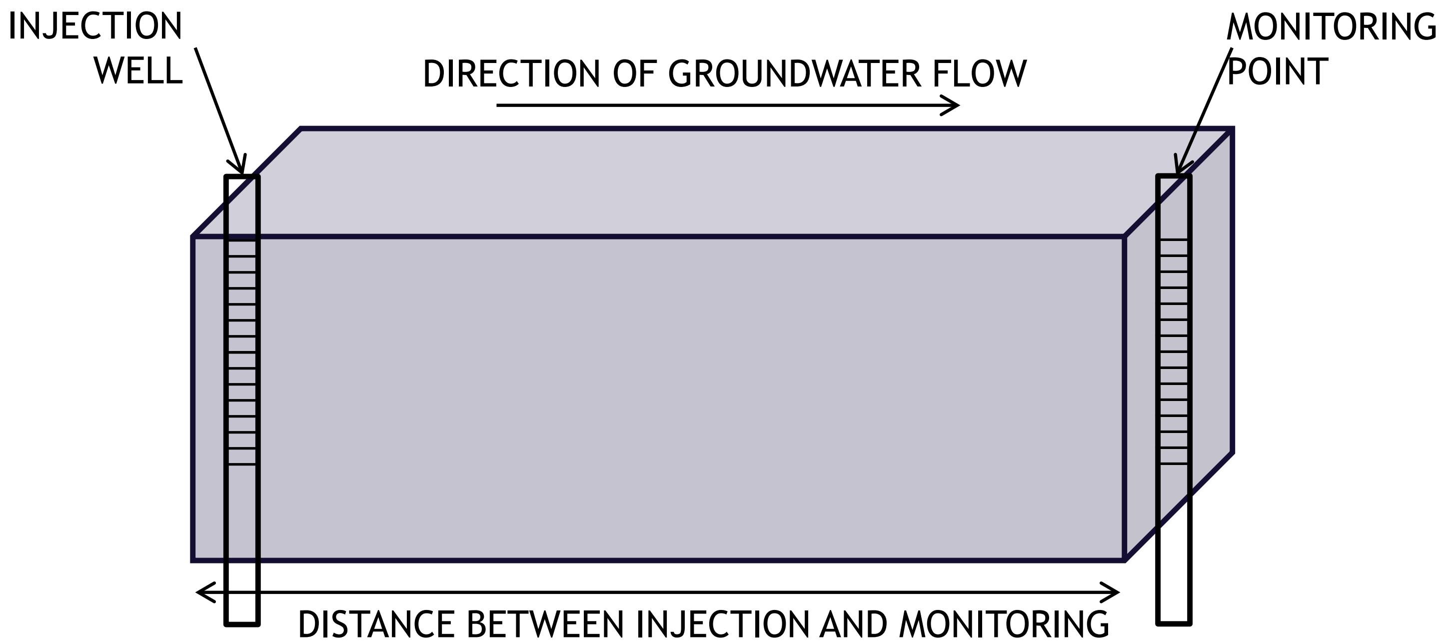
Analysis of Aquifer Volume Treated by Amendment Injection



- Locations selected for analysis:
  - Injection rate > 1 gpm;
  - Full target volume of 5,800 gallons readily achieved;
  - No apparent injection hindrance due to lithology

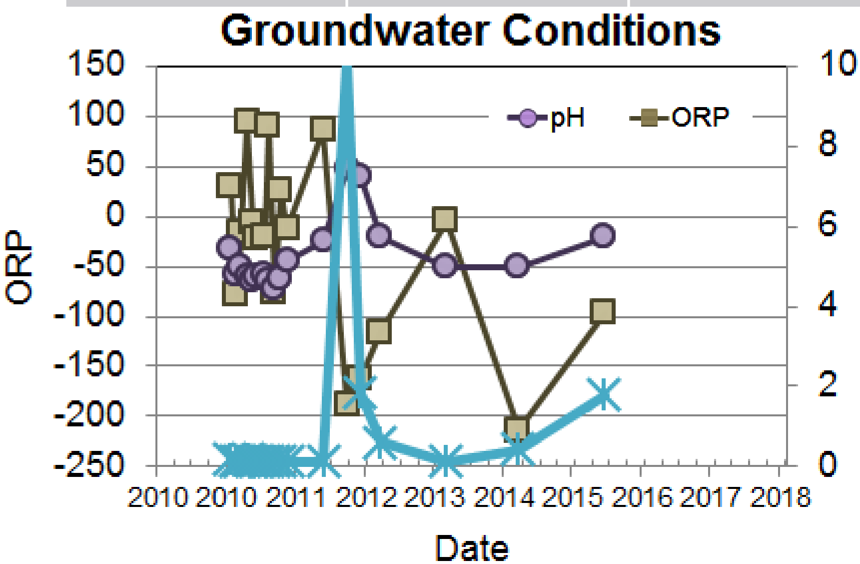
Analysis of Aquifer Volume Treated by Amendment Injection

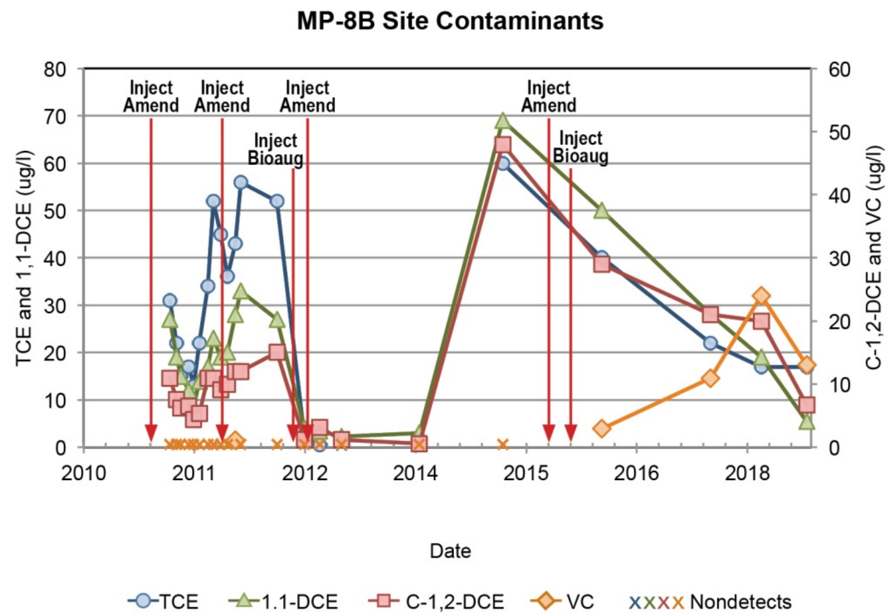


- Control volume dimensions for analysis:
  - Width = 30 ft (IW spacing 40 ft on square grid
  - Height = 15 ft (10-ft screen plus ½ distance to next screen above & below
  - Length = distance varies in each case (see below)

Analysis of Aquifer Volume Treated by Amendment Injection

MP well	Distance [IW→MP] (ft)	Pre-treat pH (SU)	Date injections	Cumulative gr SBC/ kg soil	Date effective treatment
MP-08	40	4.5	9/2012	2.05	2013-Rbnd
			9/2015	4.1	2016

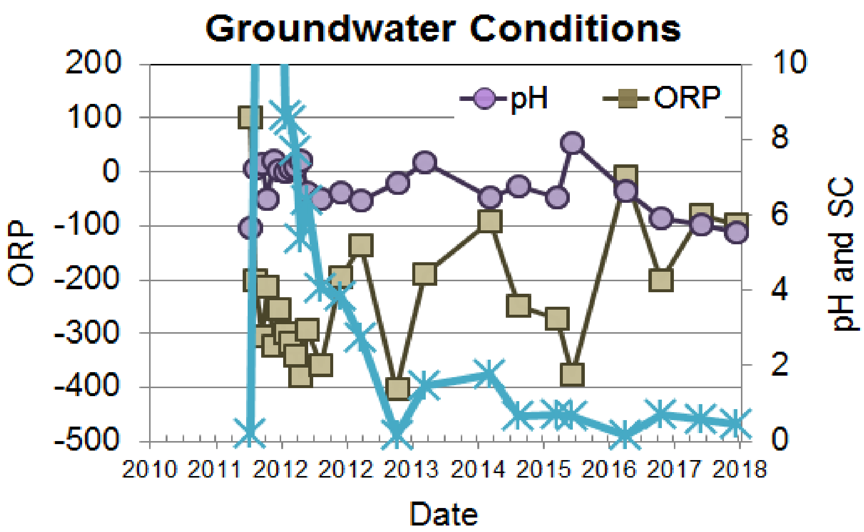


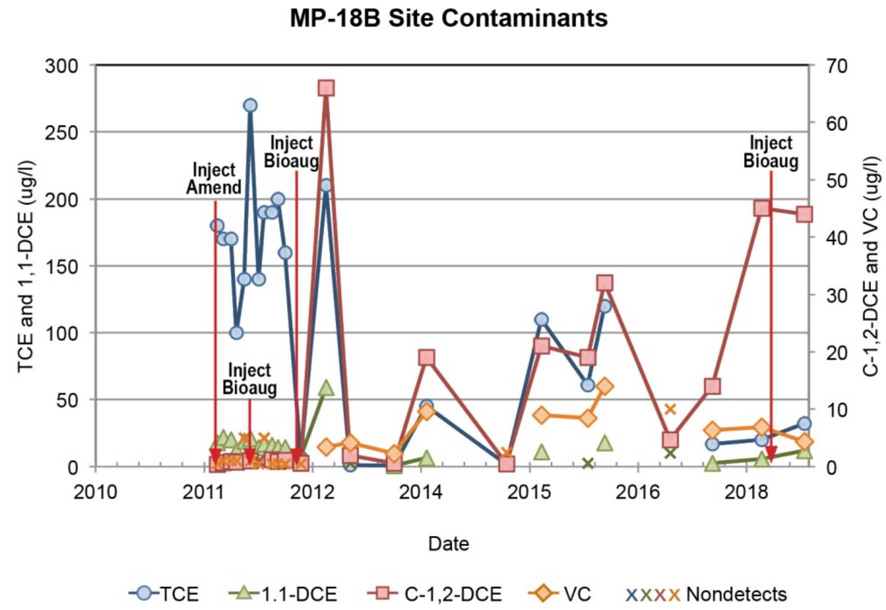


- Initial treatment in 2012, w/ rebound
- Injection 2015 re-set GW conditions, led to lasting treatment

Analysis of Aquifer Volume Treated by Amendment Injection

MP well	Distance [IW→MP] (ft)	Pre-treat pH (SU)	Date injections	gr SBC/ kg soil	Date effective treatment
MP-18	15	6.5	9/2011	5.4	2012

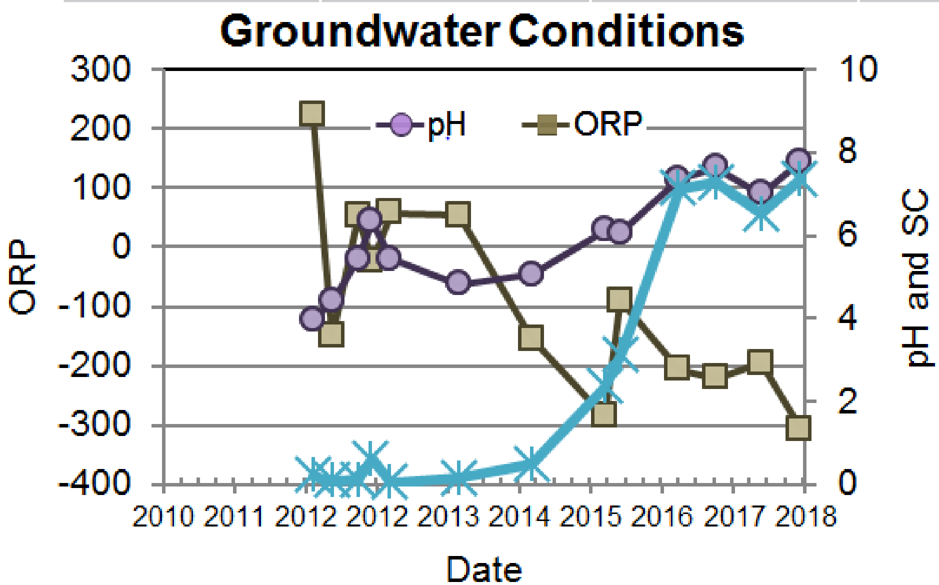


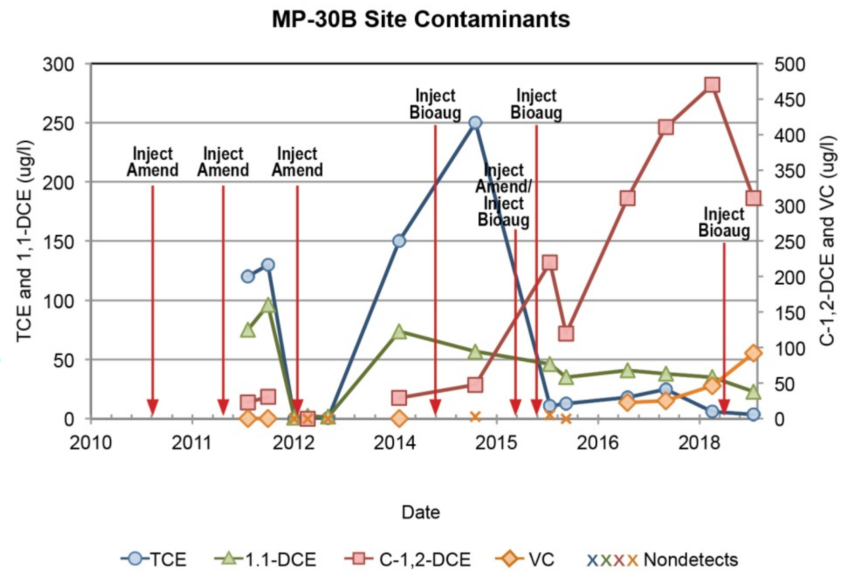


- Initial treatment in 2011, w/ rebound
- 2011 amendments persisted to 2016
- Moderate rebound cis-DCE, may require re-treatment

Analysis of Aquifer Volume Treated by Amendment Injection

MP well	Distance [IW→MP] (ft)	Pre-treat pH (SU)	Date injections	Cumulative gr SBC/ kg soil	Date effective treatment
MP-30	60	4.5	9/2012	1.35	2013 minimal
			9/2014	2.7	Insufficient data
			9/2015	4.1	2016





- Initial treatment in 2012, minimal treat effect
- Two more injections required to improve GW conditions, for lasting treatment

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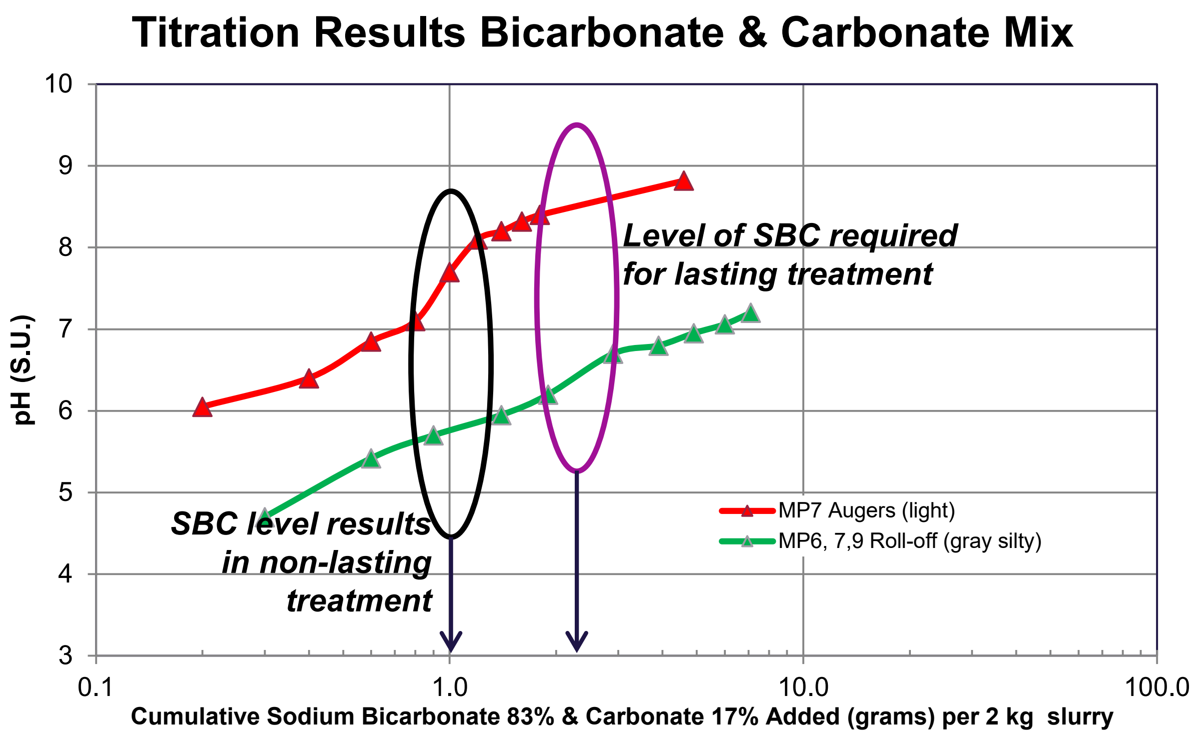
Summary of well treatments presented

MP Well	Distance [IW→MP] (ft)	No. amendment injections	Years to effective treatment after 1st injection	Cumulative SBC (gr SBC/kg soil)
MP-08	40	2	4	4.1
MP-18	15	1	1	5.4
MP-30	60	3	4	4.1

Neutralization level required for lasting treatment



Lower level of SBC application results in incomplete treatment (typically rebound)

Effective In Situ Treatment at Site

- Treatment requires
  - EVO as electron donor to promote reductive dechlorination
  - SBC to increase aquifer pH to minimum 6.0 SU
  - Bioaugment (*Dehalococcoides* species)—not discussed here
- Field monitoring data indicates treatment does not occur unless pH ~6.0 SU or greater, even if TOC and ORP are sufficient
- At least 4.0 gr SBC / kg aquifer soil is needed to raise pH adequate for treatment. This provides for lasting pH of 6.0 or greater.

Acronyms

- DCE 1,1-dichloroethylene
- EVO emulsified vegetable oil
- ft feet
- GW groundwater
- gr grams
- IW injection well
- kg kilograms
- MCL maximum contaminant level
- MP monitoring point
- ORP oxidation reduction potential
- pH (-) log of aqueous hydrogen ion concentration
- RDC reductive dechlorination
- SBC sodium bicarbonate
- SC specific conductivity
- SU standard units for pH
- TCE trichloroethylene
- TCA trichloroethane
- VC vinyl chloride

Thank You

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