Terra Systems INCORPORATED

# Case Study of pH Adjustment at a New Jersey Remediation Site

For many acidic aquifers, pH buffering will be required to bring the pH into a range of 6 to 8, which is favorable for reductive dechlorination. Various pH adjustment agents have been used including soluble materials like sodium or potassium bicarbonate, sodium carbonate, sodium hydroxide, calcium hydroxide (slaked lime) or less soluble materials like calcium carbonate, magnesium oxide, dolomitic hydrated lime, and limestone. Bicarbonates have the lowest pH for saturated solutions of these buffers, but also have the least buffering capacity and the potential for carbon dioxide production. Calcium carbonate or limestone is practically insoluble, but has an equilibrium pH of 9.4. The other soluble reagents including sodium hydroxide, sodium carbonate, and calcium hydroxide have higher pH equilibrium levels and could therefore overshoot the desired pH range. The less soluble buffers are more difficult to deliver and generally have high equilibrium pHs.

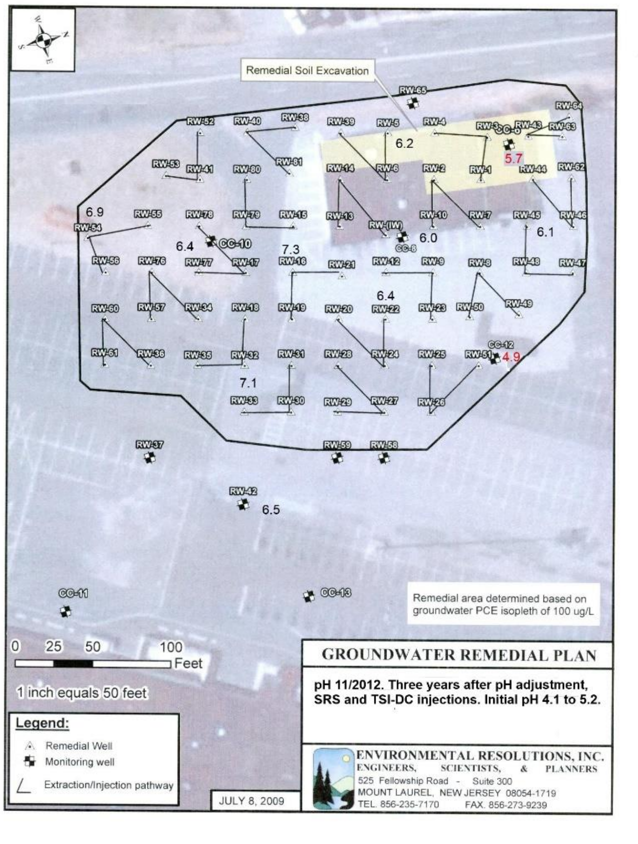
A treatability study was conducted for a site where chlorinated solvents and acids were co-disposed leading to acidic pH levels of 4.0 in the groundwater and 3.4 in the soil (50 g soil and 100 mL distilled water). Titrations to pH 8.0 were conducted with selected reagents for both soil and groundwater which lead to the following estimated quantities (lb) of the buffers per cubic yard of aquifer assuming 25% porosity: 13.8 sodium hydroxide, 15.5 dolomitic lime, 16.8 hydrated limestone, 105.8 magnesium oxide, 257 sodium bicarbonate, 3,832 calcium carbonate, and >6,394 pounds for pulverized limestone. The sodium hydroxide, dolomitic lime, and hydrated limestone, were possible reagents, but the requirements for magnesium oxide, sodium bicarbonate, and either of the limestone products were too high to be practical.

At a New Jersey site with somewhat less acidic groundwater (pH 4.8) and soil (pH 4.2 to 5.0 for 10 g soil in 50 mL distilled water), the buffer requirements to reach pH 8.0 were correspondingly less, ranging from 1.3 lbs per cubic yard aquifer (30% porosity) for sodium carbonate to 13.8 lb/yd$^3$ for sodium bicarbonate to 16.8 lb per cubic yard for calcium carbonate. Sodium carbonate was chosen as the buffering agent. A small field pilot demonstrated that the 68 kg pounds of sodium carbonate in 2,985 gallons groundwater could be used to raise the pH of the injection well above 6.0 with increased pH levels up to 6.1 m away after 2.5 months.

Full scale injections were conducted in May to June 2009 and September 2009 with 40,674 lbs of emulsified vegetable oil (EVO), 8,818 pounds sodium carbonate buffer, and 129,870 gallons groundwater with injection into 44 remediation wells within the 180 feet wide x 384 feet long x 25 ft thick treatment zone. The amendments were injected into two remediation wells while extracting from a nearby well. The pH of injection wells increased to >6.0 in all but one injection well after two months. Insufficient chase water was injected with the EVO and sodium carbonate to reach the 22 extraction wells. In September 2009 amendments including the SRS®-SD, sodium carbonate and sodium bicarbonate buffers, and the TSI-DC dechlorinating culture were injected into wells previously used for extraction.

Figure 1 shows the pH of the remedial and monitoring wells in September 2012, between 36 and 40 months after the SRS®-SD and buffer additions. The well sets used for the May-June injections are also shown.

**Figure 1. pH Results for Acidic New Jersey site in September 2012**




As part of our review of the acidic southern NJ November 2011, February, May, and November 2012 site data, Terra Systems Inc. (TSI) put together a summary of the well data (Table 1). TSI broke them down into favorable, mixed, or unfavorable conditions for pH, ORP, total organic carbon (TOC) and chlorinated ethenes (CE) and chlorinated methane (CM) biodegradation daughter products for the monitoring and remedial wells. Tetrachloroethene (PCE) is biodegraded to trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), vinyl chloride (VC), ethene, and ethane. Carbon tetrachloride (CT) is anaerobicaly reduced to chloroform (CF), dichloromethane (DCM), and chloromethane (CM). The average percent daughter products are shown in parenthesis. Terra Systems also calculated the first order exponential half-lives for PCE for each well.

## 1.0 Conclusions and Recommendations

The SRS®-SD, sodium carbonate, and bioaugmentation culture injections have created pH neutral conditions in all six remedial wells within the treatment zone and in three of the monitoring wells (CC-6, CC-8 and CC-10) monitored in November 2011 to November 2012. The pH has increased in four of the five monitoring wells. Reducing conditions were observed in all six of the remedial wells and four of the monitoring wells (CC-6, CC-8, CC-10, and RW-42). TOC levels are currently below optimal in the remedial wells RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 and monitoring wells CC-6, CC-8, CC-10, CC-12, and RW-42. There is evidence for reductive dechlorination of the chlorinated ethenes and chlorinated methanes in many of the monitoring and remedial wells. Monitoring wells CC-6, CC-8, and CC-10 are showing partial conversion of PCE to TCE, cDCE, and/or VC and CT to CF and DCM. Well CC-10 has detectable levels of ethene and ethane. CT has been converted to CF and DCM in monitoring wells CC-6, CC-10, and CC-12. Carbon tetrachloride was not detected in any of the remedial wells in November 2012 or monitoring well CC-6. Treated groundwater from the remedial wells has continued to move with the groundwater flow and impacted monitoring well CC-8. First order exponential half-lives of 400 days or less for PCE were found in remedial wells RW-5, RW-16, RW-22, and RW-32. *Dehalococcoides* counts above 1,000 cells/mL were found in remedial wells RW-5, RW-22, and RW-54, and CC-6.

PCE concentrations are declining in all of the monitoring wells. However, well CC-8 still has the highest concentrations of PCE. Dechlorination of PCE to cDCE was observed for this well when TOC levels were elevated between 11.9 and 4.6 mg/L from February 2011 to May 2012. Less cDCE is being produced now that the TOC levels are below 5 mg/L. Targeted injections into RW-10, RW-IW, RW-9, and RW-12 should promote dechlorination in CC-8.

**Table 1. Monitoring and Remedial Wells Classification November 2011 to November 2012**

| Well | pH | ORP | TOC (mg/L) | CE Biodegradation Products (% Total CE) | PCE Half-Life (Days) | CM Biodegradation Products (% Total CM) |
|---|---|---|---|---|---|---|
| CC-6 | 5.7-6.2 | -53 to 87 | 2.5-3.1 | TCE, cDCE, VC (30.9-52.5) | 1,575 | CF (100) |
| CC-8 | 5.1-6.2 | -8 to 108 | 2.0-44.1 | TCE, cDCE, VC (6.7-53.2) | 3,915 | CF (25.1-42.0) |
| CC-10 | 5.3-6.4 | -41 to 27 | 2.0-3.7 | TCE, cDCE, VC, Ethene, Ethane (26.9-53.5) | 410 | CF (48.0-70.4) |
| CC-12 | 4.7-5.0 | 89 to 209 | 1.1-1.2 | TCE (0-0.4) | 1359 | CF (0-14.7) |
| RW-5 | 6.1-6.5 | -135 to -9 | 10-24.3 | TCE, cDCE, VC, Ethene (51.4-97.0) | 363 | No chloromethanes |
| RW-16 | 6.6-7.3 | -149 to -84 | 8.8-17.5 | TCE, cDCE, VC, Ethene (95.1-99.1) | 172 | No chloromethanes |
| RW-22 | 6.4-6.7 | -96 to -20 | 11.4-25.1 | TCE, cDCE, VC, Ethene (53.2-99.8) | 281 | No chloromethanes |
| RW-32 | 6.6-7.1 | -100 to -55 | 8.7-31.8 | TCE, cDCE, VC, Ethene (68.9- 99.2) | 200 | No chloromethanes |
| RW-42 | 4.8–6.5 | -268 to 115 | 1.3-9.8 | PCE only | 1540 | CT only 2/12-11/12, no chloromethanes 8/11-11/11 |
| RW-45 | 6.1-6.7 | -24 to -124 | 5.8-14.7 | TCE, cDCE, VC (26.1-65.9) | 423 | MC only 11/11, no chloromethanes 2/12 to 11/12 |
| RW-54 | 6.5-7.0 | -115 to -59 | 3.5-33.7 | TCE, cDCE, VC, Ethene (99.2-99.98) | 198 | No chloromethanes |

| | |
|---|---|
| Green | Favorable |
| White | Mixed |
| Red | Unfavorable |

Based upon the following factors, TSI would recommend injection of additional substrate, buffer, or bioaugmentation culture:

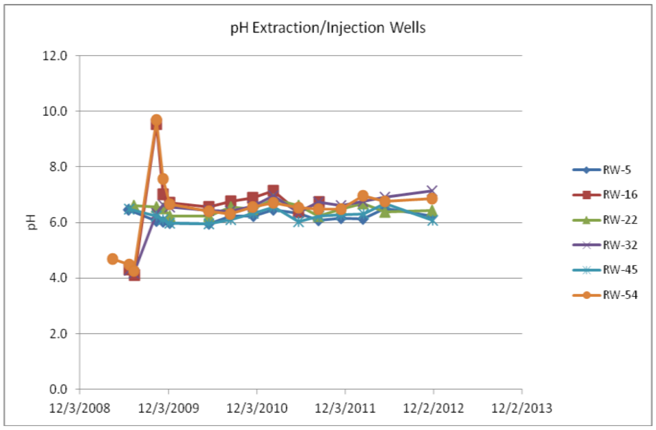
- TOC levels below optimal in RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 and monitoring wells CC-6, CC-8, CC-10, CC-12, and RW-42.
- Changes in electron acceptors between November 2011 and November 2012 consistent with the substrate being consumed and the groundwater becoming less anaerobic
- pH below 6.0 in wells CC=6 and CC-12 in the latest round of samples in November 2012
- drops in the numbers of *Dehalococcoides* in remedial wells RW-32 and RW-54

TSI would also recommend measuring the field parameters in as many of the remedial wells as possible to see if favorable conditions still exist in those wells.

## 2.0 pH AND ORP

**2.1 Injection/Extraction Wells.** In the November 2011 to November 2012 samples, the pH favorable (between 6 and 8) in remedial wells RW-5, RW-16, RW-22. RW-32, RW-45, and RW-54 (Figure 2).

**Figure 2. pH in Remedial Wells**




Strongly reducing conditions of -9 mV or less were found in remedial wells RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 in November 2011 to November 2012 (Figure 3). TOC levels in the remedial wells sampled in November 2012 ranged from 3.2 mg/L in RW-32 to 13.6 mg/L in RW-22. None of the remedial wells had TOC above the 25 mg/L target in November 2012.

**2.2 Monitoring Wells.** Of the five monitoring wells (CC-6, CC-8, CC-10, CC-12, and RW-42) that were sampled in November 2011 to November 2012, wells CC-6 and CC-10 generally had neutral pHs (Figure 4) with slightly acidic conditions found in CC-8 and acidic conditions of 4.7 to 5.0 in CC-12. Well RW-42 had pHs ranging from 4.8 in November 2011 to 6.5 in November 2012. Mildly oxidizing to slightly reducing conditions were observed in wells CC-6, C-8, and CC-10 (Figure 5). The pH has come up in wells CC-6, CC-8, and CC-10 to between 5.1 and 6.4, but was below optimal for anaerobic bioremediation in well CC-6 in November 2012. TOC levels were 7.5 mg/L or below in well CC-6, CC-8, CC-10, CC-12, and RW-42. TOC levels had increased to above the background levels in monitoring well CC-8 (11.9 to 60.5 mg/L), but was only 4.6 mg/L in May 2012.

**Figure 3. ORP in Remediation Wells**

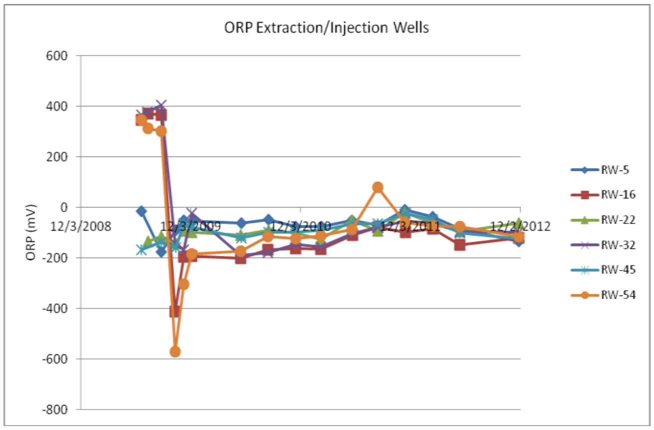


**Figure 4. pH in Monitoring Wells**

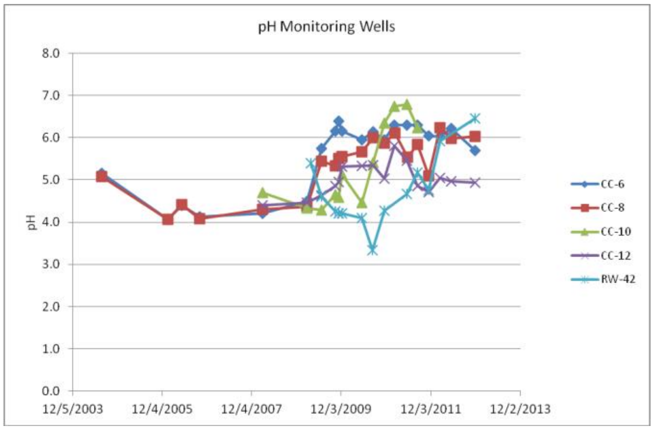
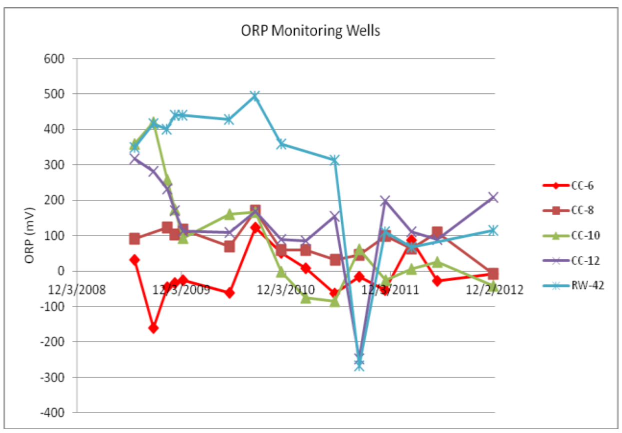



**Figure 5. ORP in Monitoring Wells**

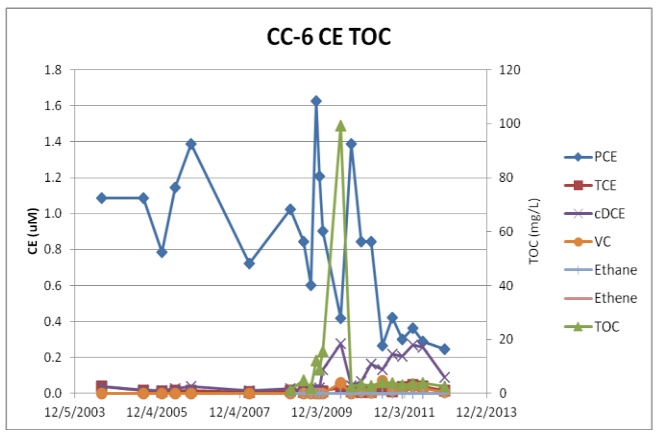



## 3.0 EVIDENCE FOR DECHLORINATION

**3.1 Chlorinated Ethenes.** VOC samples were collected for the monitoring wells (CC-6, CC-8, CC-10, CC-12, and RW-42) and selected extraction/injection wells (RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54) over time. TSI have converted the data to micromolar units by dividing by the molecular weight so that one micromole of tetrachloroethene (PCE) is equivalent to one micromole of trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), vinyl chloride (VC), and ethene or ethane. TSI have also prepared micromolar graphs for the chloromethanes: carbon tetrachloride (CT), chloroform (CF), dichloromethane (DCM), chloromethane (CM), and methane. Methane is produced by biodegradation of many compounds and thus may not be representative of the final biodegradation product of the chloromethanes.

There has been some conversion of PCE to cDCE and VC in monitoring well CC-6 (Figure 6) soon after the SRS®-SD injections. The PCE first order half-life was relatively slow, 1,575 days. TOC levels were elevated up to 99 mg/L in May 2010, but declined to 2.5 mg/L in November 2012. The pH has been in a favorable range in well CC-6 since October 2009, except for a decrease to 5.7 in November 2012. However, less extensive dechlorination has been observed since August 2010 when the TOC levels fell below 10 mg/L.

**Figure 6. Chlorinated Ethene Biodegradation and TOC Levels in Monitoring Well CC-6**




Monitoring wells CC-8 and CC-10 were moderately acidic to slightly acidic and under mildly reducing to oxidizing conditions. Increasing dechlorination of PCE to cDCE had been observed in well CC-8 (Figure 7) as TOC levels increased until August 2011; cDCE concentrations have since fallen and PCE levels have rebounded after the TOC was depleted. The PCE half-life in well CC-8 was 3,915 days. There is more evidence for reductive dechlorination of the chlorinated ethenes in monitoring well CC-10 (Figure 8) as the pH was more neutral (5.3-6.4) and ORP slightly reducing to oxidizing (-41 to 27 mV) in November 2011 to November 2012. The first order half-life for PCE in CC-10 was a moderate 410 days. Ethene and ethane were generated in well CC-10. Well CC-12 has seen only slightly elevated TOC levels and little dechlorination (Figure 9) with a first order degradation rate of 1,359 days. Well RW-42 is downgradient of the treatment zone and has lower concentrations of PCE (6.5 to 31 µg/L in 2009). PCE concentrations have decreased in RW-42 with a first order degradation half-life of 1,540 days (Figure 10). TOC levels reached 16.4 mg/L in November 2010, but have been below 9.8 mg/L since then.

**Figure 7. Chlorinated Ethene Biodegradation and TOC Levels in Monitoring Well CC-8**

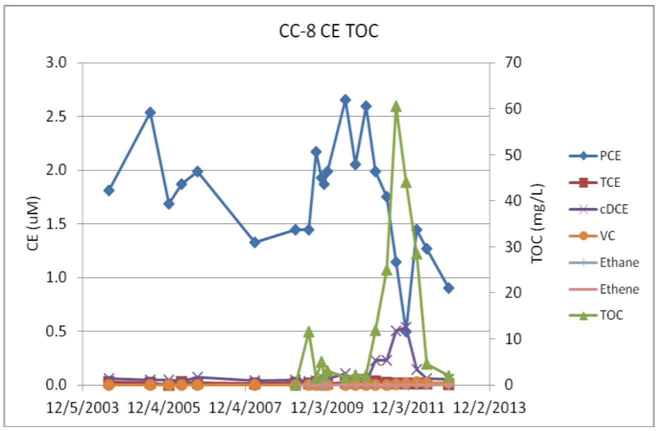



**Figure 8. Chlorinated Ethene Biodegradation and TOC Levels in Monitoring Well CC-10**

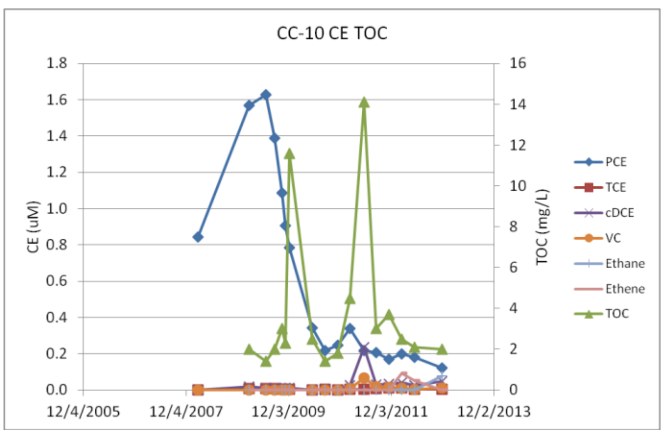



**Figure 9. Chlorinated Ethene Biodegradation and TOC Levels in Monitoring Well CC-12**

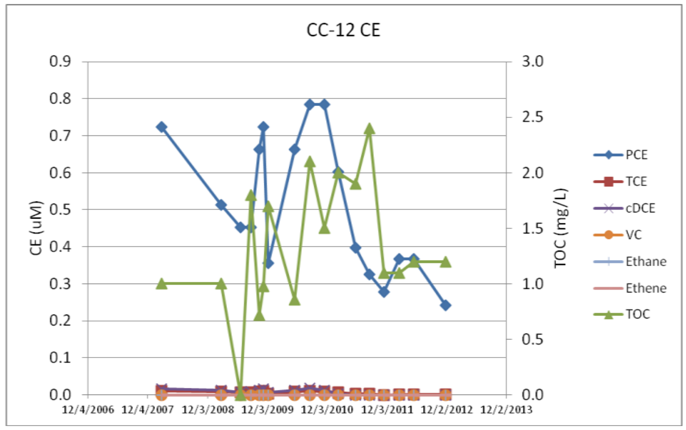
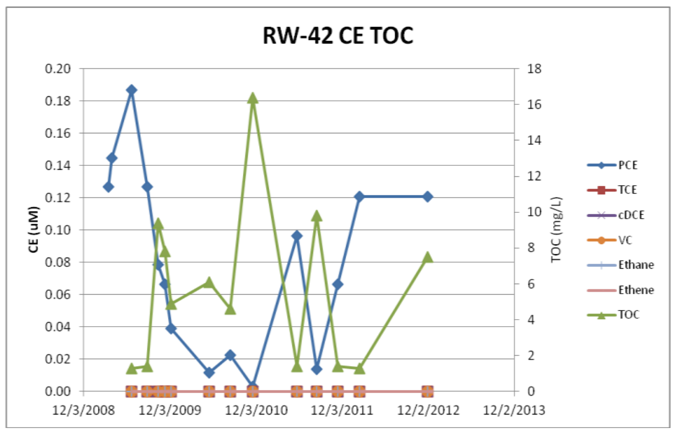



**Figure 10. Chlorinated Ethene Biodegradation and TOC Levels in Monitoring Well RW-42**




There is more evidence for reductive dechlorination of the chlorinated ethenes occurring in remedial wells RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 (Figures 11, 12, 13, 14, 15, and 16). PCE degradation half-lives for these wells ranged from 92 (RW-32) to 300 (RW-45) days. Daughter products including TCE, cDCE, and VC account for between 58 and 98% of the total chlorinated ethenes in these six remedial wells monitored in February to August 2011. VC has been generated in RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54. Ethene and ethane were observed in RW-22 in October and November 2009 reaching up to 68% of the total chlorinated ethenes. Ethene and ethane have not been detected since that time in any of the remedial wells (possibly due to the high dilution used for the methane analyses).

**Figure 11. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-5**

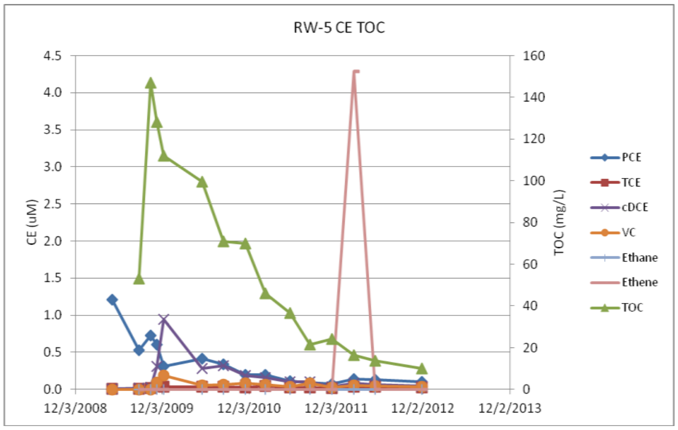



**Figure 12. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-16**

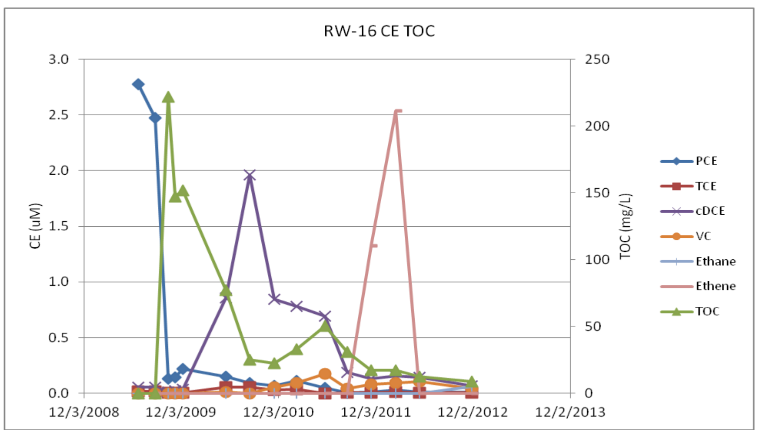



**Figure 13. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-22**

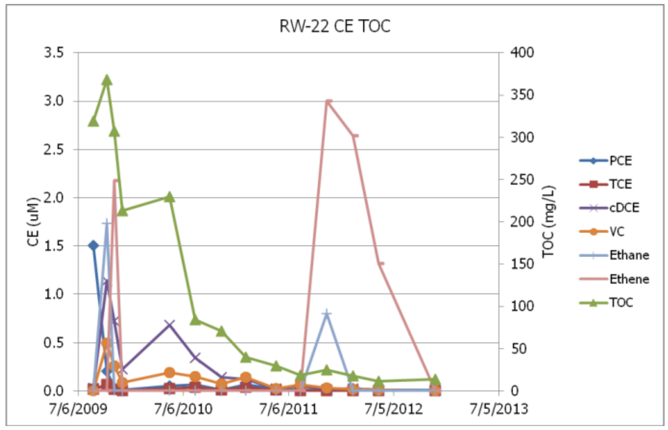



**Figure 14. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-32**

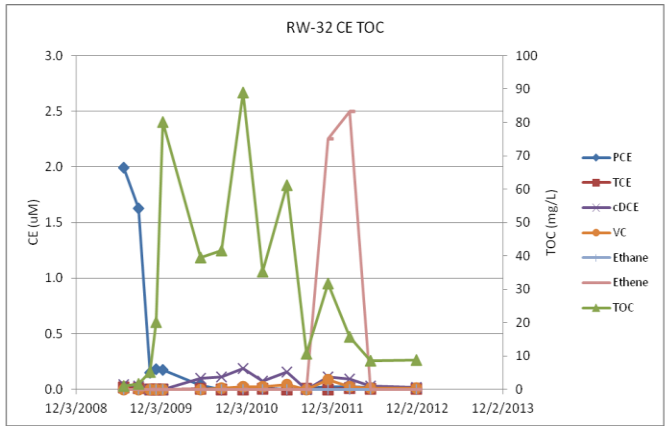



**Figure 15. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-45**

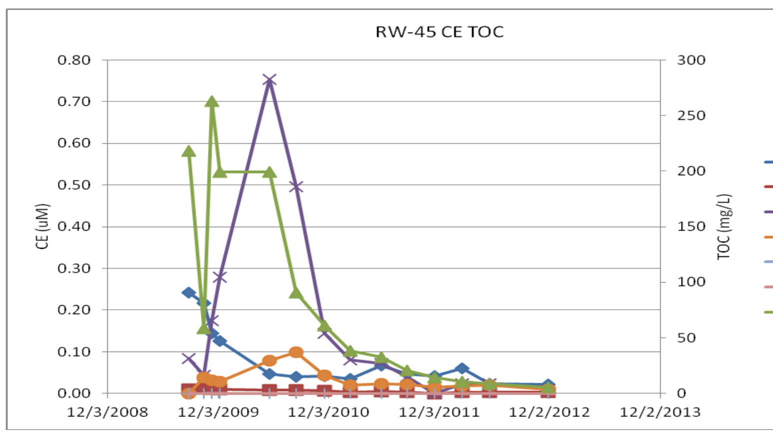
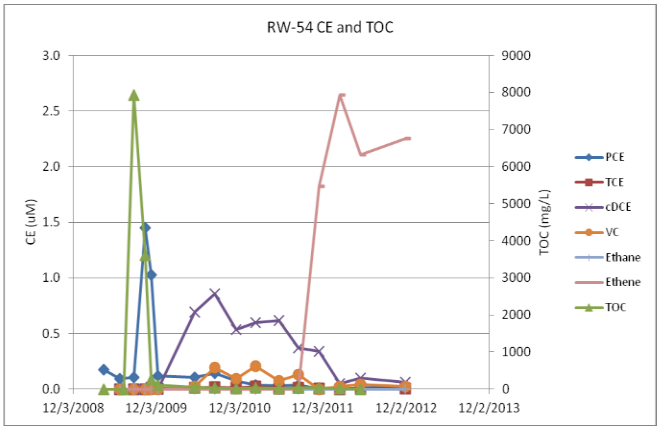


**Figure 16. Chloroethene Biodegradation and TOC Levels in Remedial Well RW-54**




**3.2 Chlorinated Methanes.** The chlorinated methanes are undergoing reductive dechlorination in well CC-6 with the complete removal of CT and the production of CF and DCM (Figure 17). CF, the first daughter products from carbon tetrachloride, represented 100% of the total chlorinated methanes in November 2011 to November 2012. Monitoring well CC-8 is showing limited transformation of CT to CF (Figure 18). There was also evidence for substantial reductive dechlorination of the chloromethanes in monitoring well CC-10 (Figure 19) with the sporadic production of MC and CM. Monitoring well CC-12 is also showing limited transformation of CT to CF (Figure 20). The downgradient monitoring well RW-42 had no detectable CT in 5 out of the last 8 monitoring events (Figure 21) and has had no detectable chloromethane degradation products. There is also evidence for reductive dechlorination of the chlorinated methanes occurring in remedial wells RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 (Figures 22, 23, 24, 25, 26, and 27). No CT or daughter products has been found in remedial wells RW-5, RW-16, RW-22, RW-32, RW-42, RW-45, and RW-54 since 5/2011.

**Figure 17. Chloromethane Biodegradation and TOC Levels in Monitoring Well CC-6**

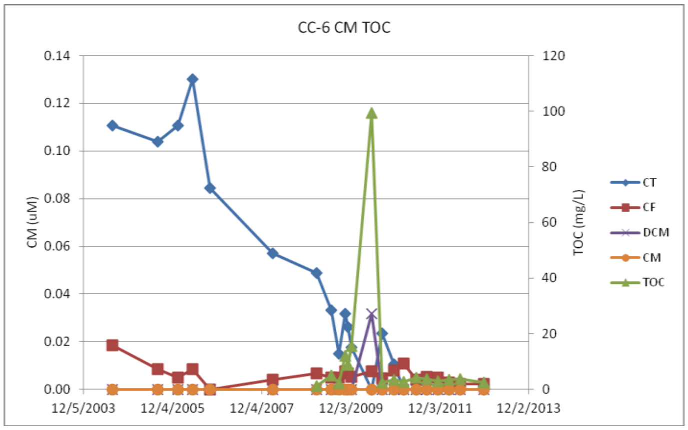



**Figure 18. Chloromethane Biodegradation and TOC Levels in Monitoring Well CC-8**

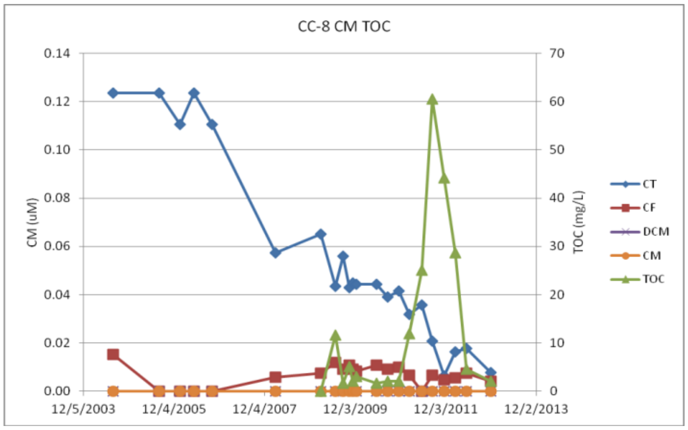



**Figure 19. Chloromethane Biodegradation and TOC Levels in Monitoring Well CC-10**

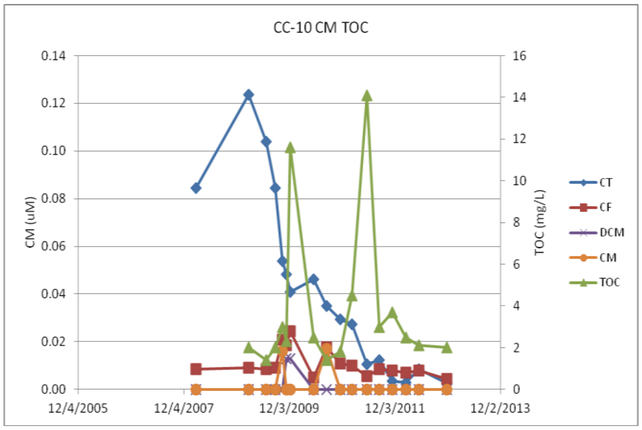



**Figure 20. Chloromethane Biodegradation and TOC Levels in Monitoring Well CC-12**

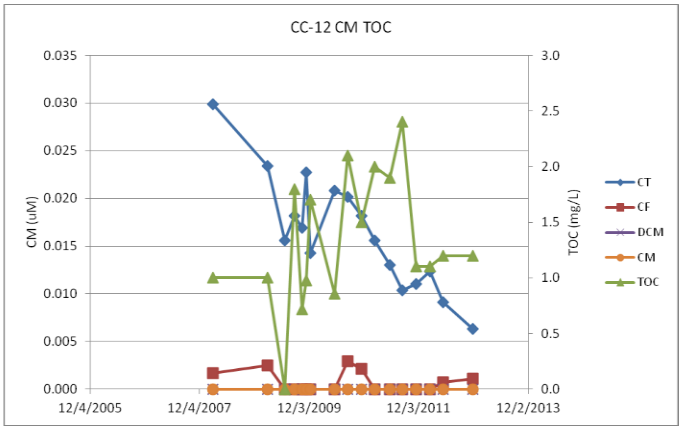



**Figure 21. Chloromethane Biodegradation and TOC Levels in Monitoring Well RW-42**

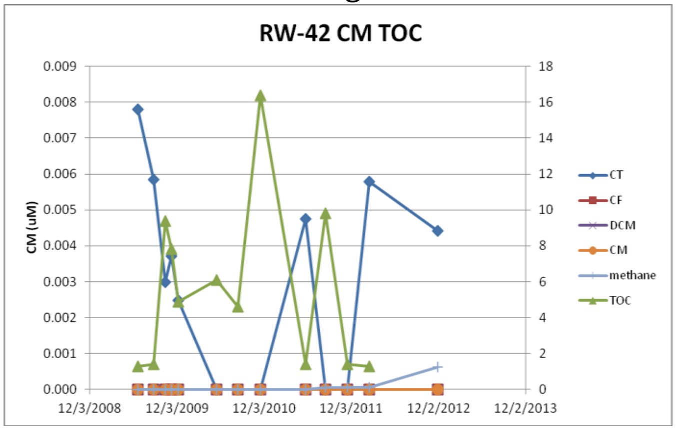



**Figure 22. Chloromethane Biodegradation and TOC Levels in Remedial Well RW-5**

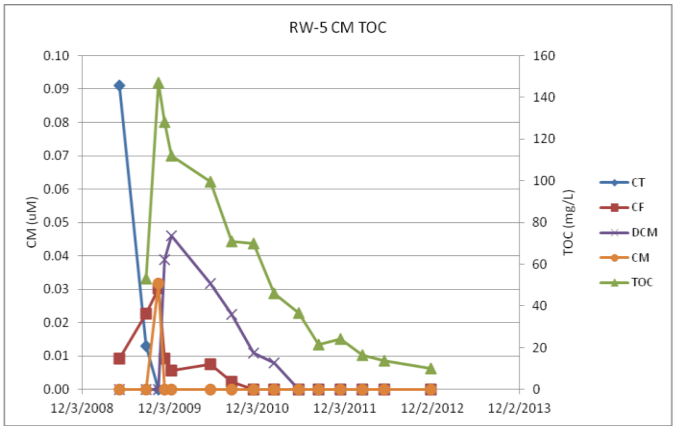



**Figure 23. Chloromethane Biodegradation and TOC Levels in Remedial Well RW-16**

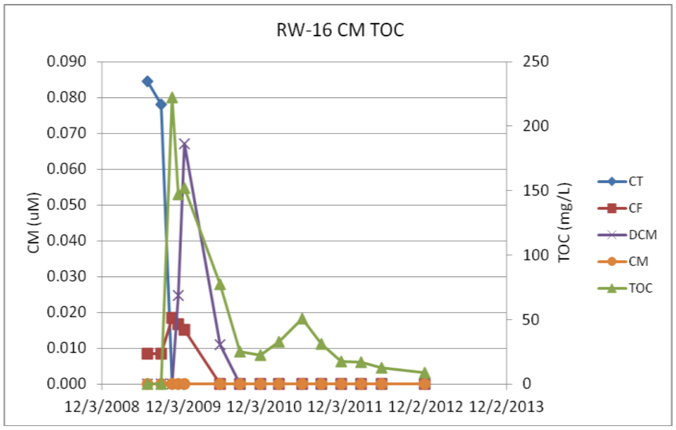



**Figure 24. Chloromethane Biodegradation and TOC Levels in Remedial Well RW-22**

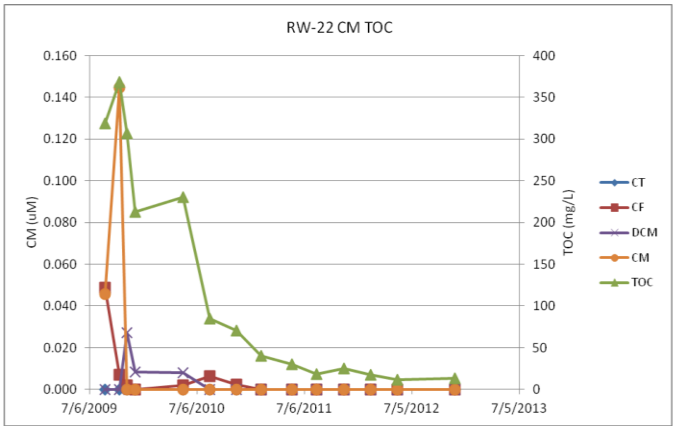



**Figure 25. Chloromethane Biodegradation and TOC Levels in Monitoring Well RW-32**

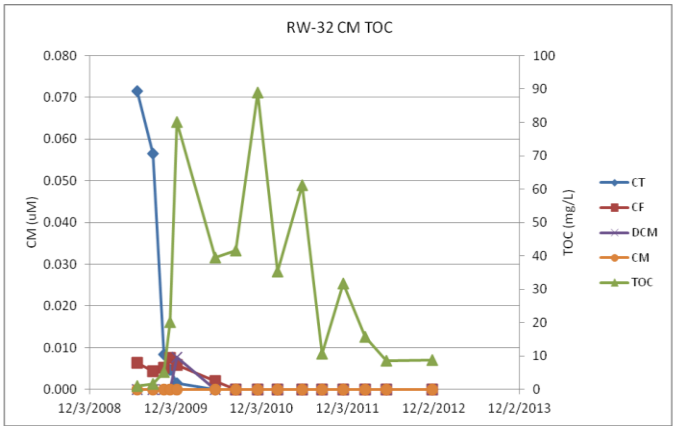



**Figure 26. Chloromethane Biodegradation and TOC Levels in Monitoring Well RW-45**

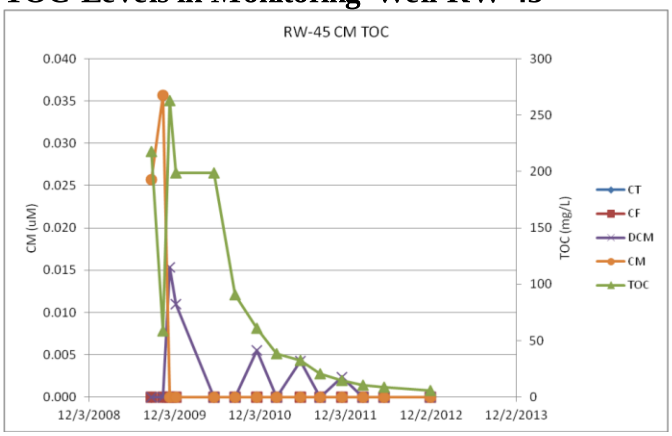
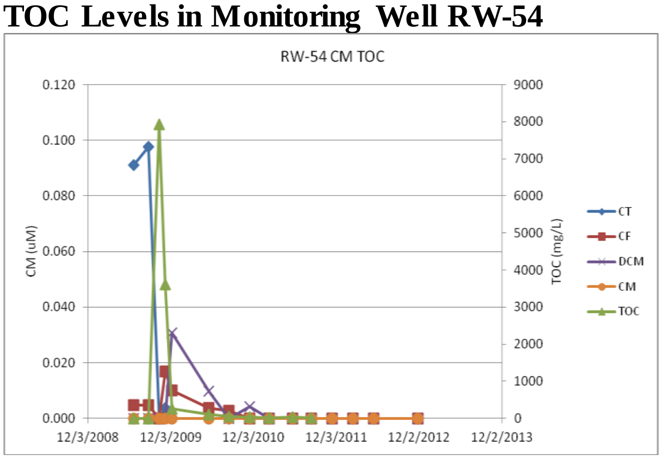



**Figure 27. Chloromethane Biodegradation and TOC Levels in Monitoring Well RW-54**



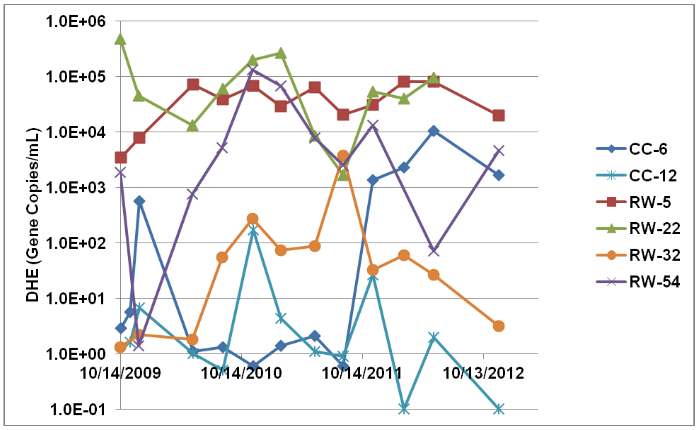

**3.3 Competing Electron Acceptors**
Microorganisms use the most energetically favorable electron acceptors in the following order: dissolved oxygen, nitrate, sulfate, ferric iron (reducing it to the ferrous form), and finally reducing carbon dioxide to methane. Nitrate is decreasing in all of the monitoring wells with the highest concentration remaining in RW-42. Sulfate concentrations are decreasing in monitoring wells CC-6 and CC-10. Increasing concentrations of ferrous iron (up to 69 mg/L), have been observed in CC-6, CC-8, and CC-10. Methane concentrations are also increasing in CC-6, CC-8, CC-10, and CC-12.

In the remedial wells within the treatment area, nitrate has been completely consumed except in RW-54. Sulfate levels are decreasing, although there has been a rebound in 2011-2012 in RW-5, RW-16, RW-22, and RW-45. Increased concentrations of ferrous iron have been noted in all remedial wells, but ferrous iron concentrations have dropped from peak levels in May 2011 all of the remedial wells. Methane concentrations have increased from low □g/L levels to as much as 23,000 □g/L in all of the remedial wells except RW-54. Methane concentrations have dropped in wells RW-5, RW-16, RW-22, RW-32, and RW-45 since May 2011.

**2.4 *Dehalococcoides* Counts.** Figure 28 presents the *Dehalococcoides mccartyi* (DHE) microbial counts from the remedial wells. DHE counts have increased in well CC-6 from 2.9 cells/mL in October 2009 to a maximum of 10,400 cells/mL in May 2012, but then fell to 1,660 in November 2012 even though dechlorination to cDCE and VC was observed. Monitoring well CC-12 has had low DHE counts of 173 cells/mL or less. DHE counts increased from 3,470 cells/mL to a maximum of 81,600 cells/mL in RW-5 and remained elevated through November 2012. The DHE counts in RW-22 have ranged from 480,000 cells/mL in October 2009 to a low of 1,660 cells/mL in August 2011, but have increased to 96,200 cells/mL in May 2012. Counts of DHE increased in RW-32 from the 1.3

cells/mL detected in October 2009 to 3,750 cells/mL in August 2011, but have been lower since then. In RW-54, the DHE counts increased from 1,860 to a maximum of 132,000 cells/mL in November 2010 before decreasing to 4,640 cells/mL in November 2012. A count of 1,000 DHE cells/mL is generally required for ethene production. Wells CC-6, RW-5, RW-22, and RW-54 had counts greater than this level in November 2012.

**Figure 28. *Dehalococcoides mccartyi* Microbial Counts**




## 4.0 CONCLUSIONS

Conditions have become less favorable for reductive dechlorination in the last sampling event as TOC levels were all below 10 mg/L and the extent of dechlorination fell in wells CC-6, CC-8, RW-5, RW-16, RW-22, RW-32, RW-45, and RW-54 from earlier sampling events.

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