

The Remediation of Cr(VI) and Chloroethenes in Groundwater at Naval Air Station North Island, CA. Using Terra Systems Patented 60% SRS[®]-M EVO

Abstract. Bench and field pilot tests and full scale injections were conducted to assess a combined chemical/biological *in situ* approach for treating high concentrations of Cr(VI) and TCE in groundwater at Naval Air Station North Island, San Diego, CA. The approach involves using a novel formulation of emulsified vegetable oil (EVO) supplemented with a proprietary abiotic reductant (Terra Systems SRS[®]-M), combined with bioaugmentation using the SiREM KB-1 culture. In microcosm studies using site media, conventional EVO stimulated complete biological reduction of Cr(VI) over 75 to 102 days, but reductive dechlorination of TCE was not observed over 217 days except in one replicate where TCE was converted to cis-DCE. Bioaugmentation was required to achieve complete reductive dechlorination of TCE within 72 days. A pilot was conducted using two substrate delivery mechanisms: 1) liquid atomized injection and 2) direct push. With the liquid atomized injection process, the SRS[®]-M and KB-1[®] were effectively delivered 7.0 feet from the nearest injection point. With the direct push injections, a well 4.3 feet from the nearest injection well was greatly impacted by the SRS[®]-M and KB-1[®] injections, but not wells 5.2, 6.1, and 6.5 feet from the nearest injection points. Full scale implementation of the combined chemical/biological reduction process was conducted in 2012 with direct injection due to its lower cost. Hexavalent chromium reduction and reductive dechlorination of TCE was observed in many monitoring wells where TOC levels exceeded 10 mg/L.

Microcosm Studies. In bench studies using site media, conventional EVO stimulated complete biological reduction of Cr(VI) over 75 to 102 days. With the SRS[®]-M formulation, 67 mg/L of Cr(VI) was reduced to less than 0.06 mg/L within 1 day. Reductive dechlorination of TCE was not observed over 217 days except in one of three replicates with the conventional EVO where TCE was converted to cis-DCE.

Subsequent bioaugmentation with SiREM's KB-1 culture and re-amendment with EVO was required to achieve almost complete reductive dechlorination of TCE within 72 days. The combination of SRS[®]-M and KB-1 culture supported complete dechlorination to ethene in the one replicate in 35 days and partial dechlorination to cDCE, VC, and ethene in second replicate.

Field Activities. An ensuing field study was conducted to test the performance of the EVO/abiotic reductant formulation called SRS[®]-M from Terra Systems, Inc. and bioaugmentation with the KB-1[®] culture from SiREM using both a liquid atomized injection (LAI) process using nitrogen gas to atomize and move the EVO and traditional direct push injection using a Geoprobe. Almost complete dechlorination of the TCE to ethene and reduction of the hexavalent chromium was observed when the TOC levels were above 400 mg/L with increases in the *Dehalococcoides* (DHC) counts to more than 1E+05 gene copies per mL. Partial dechlorination and hexavalent chromium reduction was observed in many wells when the TOC was above 20 mg/L. With the LAI process, the SRS[®]-M and KB-1[®] were effectively delivered 7.0 feet from the nearest injection point with TOC increasing to a maximum of 2,660 mg/L, hexavalent chromium falling from 15.4 to <0.01 mg/L, total chromium from 15.4 to 0.4 mg/L, and 69 µM TCE reduced to 0.69 µM and the production of 15 µM ethene (Figure 1). There was some impact of the substrate on a well located 9.7 feet from the nearest injection point (Figure 2). The SRS[®]-M and KB-1[®] reached at least 12 feet, but had little impact on another well 11.2 feet or a well 20 feet from the nearest injection points.

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Figure 1. LIA Well 7' CE (μ M), Cr6+, Total Cr, and TOC (mg/L) from Nearest Injection Point

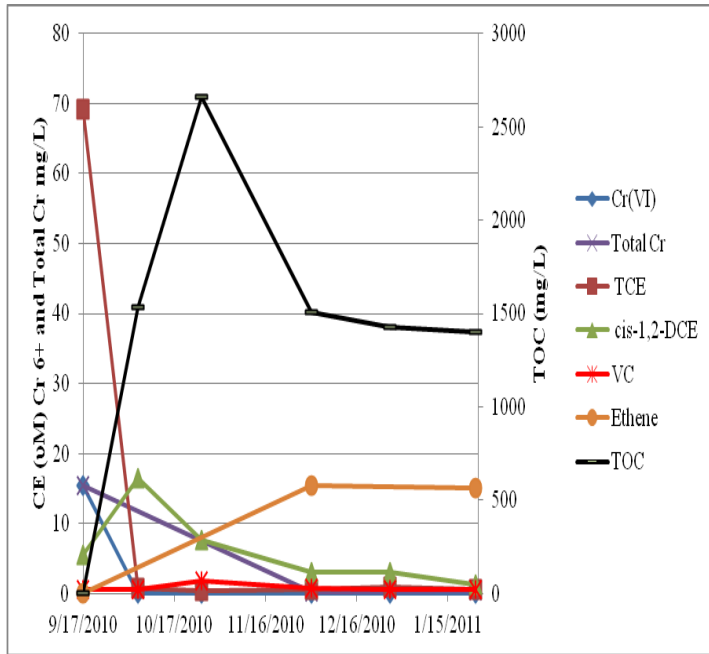


Figure 2. TOC Distribution with Distance from Injection Points Following LAI

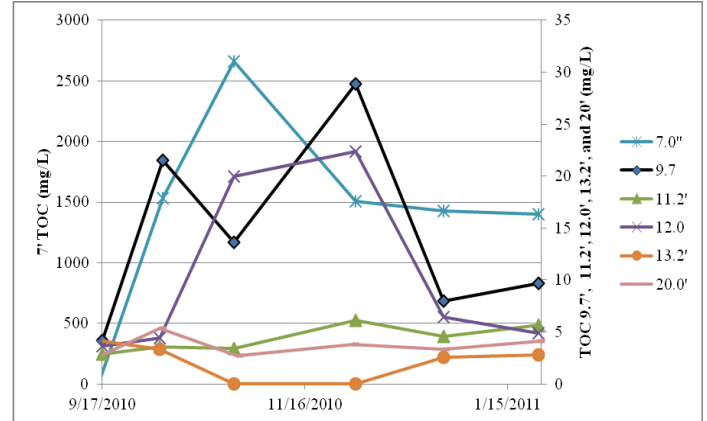
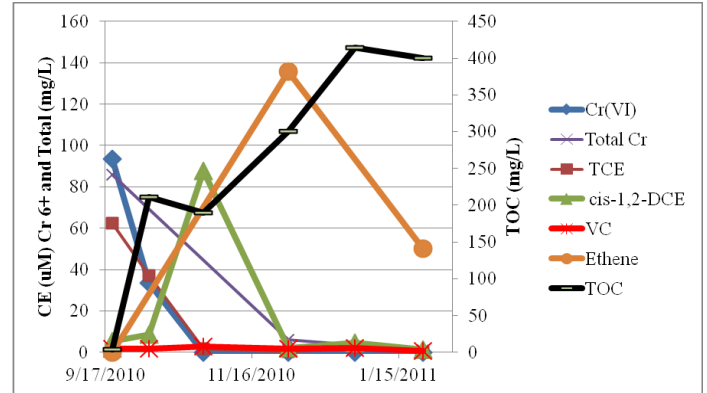


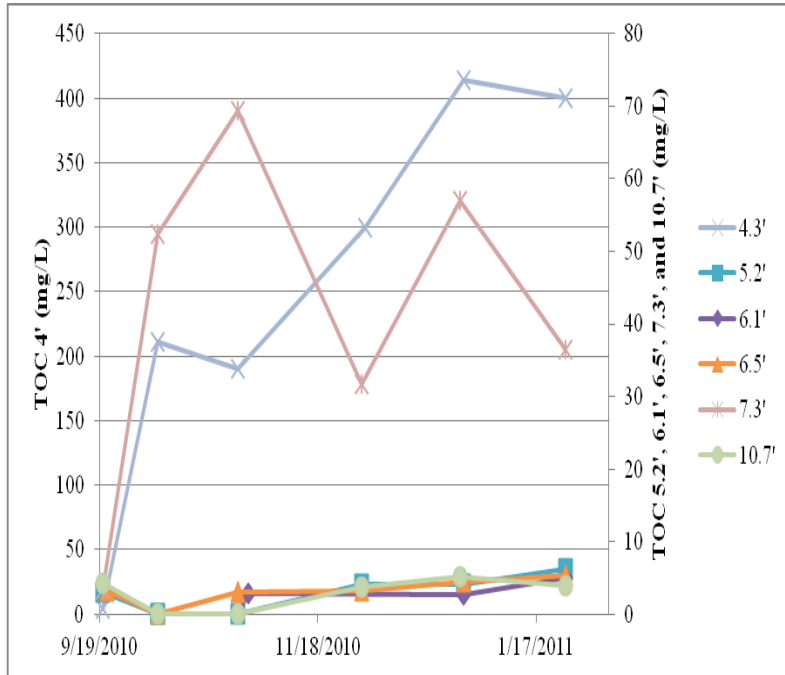
Figure 3. DP Well 4.3' CE (μ M), Cr6+, Total Cr, and TOC (mg/L) from Nearest Injection Point



With the direct push injections, a well 4.3 feet from the nearest injection well was greatly impacted by the SRS[®]-M and KB-1[®] injections with TOC as high as 414 mg/L, hexavalent chromium concentrations falling from 93.3 to <0.01 mg/L, total chromium from 85.8 to 0.9 mg/L, TCE decreasing from 62 to 0.040 μ M, ethene increasing to 136 μ M, and DHC counts increasing from 6.2E1 to 2.7E6 cells/mL (Figure 3). Although wells 5.2 6.1, and 6.5 feet respectively from the nearest injection points showed little change in the TOC concentrations or reductions in the TCE or Cr(VI) concentrations, another monitoring well located 7.3 feet from the nearest injection point did show limited impact (Figure 4).

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Figure 4. TOC Distribution with Distance from Injection Points Following Direct Push



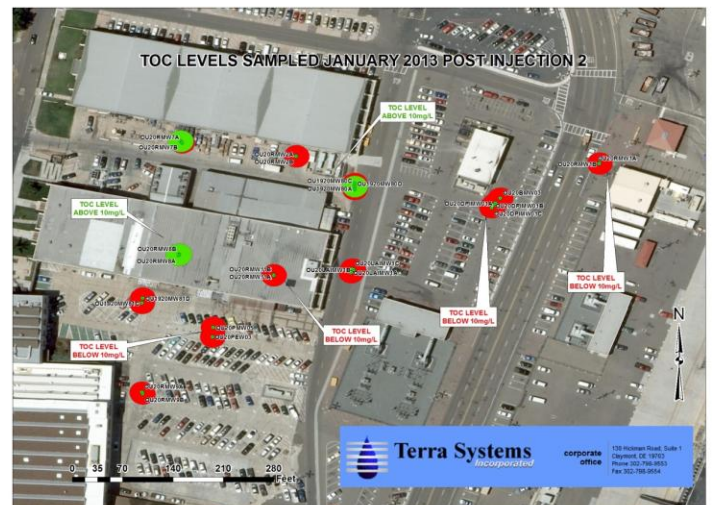
Full Scale. Full scale implementation of the combined chemical/biological reduction process was conducted in 2012 with direct injection due to its lower cost than LAI. Diluted SRS[®]-M and KB-1[®] were injected into approximately 330 locations throughout the approximately 450 x 460 foot treatment zone. Hexavalent chromium reduction and reductive dechlorination of TCE was observed in many monitoring wells where TOC levels exceeded 10 mg/L. Other wells not impacted by the SRS[®]-M and KB-1[®] injections showed little change in the hexavalent chromium and TCE levels.

Figure 5 depicts the TOC distribution in January 2013 following the SRS-M injections in the spring of 2012. TOC levels above 10 mg/L (shown in green) were only observed in wells RMW-8A, LAIMW1B, DPIMW1A, and MW-80C. The TOC distribution was not as great as desired. Where the TOC levels reached greater than 10 mg/L, there was strong evidence for reductive dechlorination and hexavalent chromium reduction. In

well LAI-MW-01B shown in Figure 6, little change was observed between September 2009 and December 2011 when the TOC levels remained below 5.0 mg/L. After the substrate injections in the spring of 2012, the TOC levels increased to 33 mg/L and TCE levels fell from 1,100 µg/L (8.4 µM) to a low 34 µg/L (0.26 µM) with increases in ethene up to 8.9 µM and decreases in hexavalent chromium from 3.3 mg/L to non-detect. Ethene accounts for 78% of the total chlorinated ethenes in July 2013. In contrast, well RMW-1A shown in Figure 7, the TOC increased only to 8.1 mg/L and there was no reductions in the TCE or hexavalent chromium levels or increases in cDCE, VC, or ethene levels.

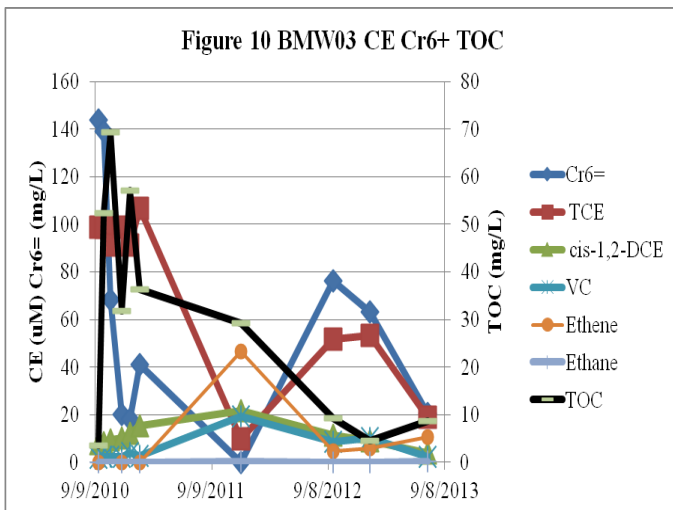
Figure 8 depicts the hexavalent chromium distribution in January 2013 following the SRS[®]-M injections in the spring of 2012. Hexavalent chromium levels below 2 mg/L (shown in green) were detected in wells MW-81D, MW-80A, MW-80C, MW-80D, LAIMW1A, LAIMW1B, LAIMW1C, PEW-03, MW-11A, RWM-7A, RMW-7B, RMW-8A, RMW-9A, and RMW-9B.

Figure 5. TOC Distribution in January 2013 Following SRS[®]-M Injections in Spring 2012



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Figure 10 shows the TCE and daughter products, hexavalent chromium, and TOC in well BNW03 which was impacted by the SRS[®]-M injection in September 2010 pilot. TOC levels increased to 69 mg/L, but had fallen to below 10 mg/L by September 2012. The hexavalent chromium concentrations had increased from 0.01 mg/L in December 2011 to 76 mg/L in September 2012. The concentrations of TCE increased from 1.3 to 6.8 mg/L, cis-DCE decreased 2.1 to 1.1 mg/L, VC decreased from 1.2 to 0.54 mg/L, and ethene decreased from 1.3 to 0.13 mg/L over this period. The substrate was effective in promoting reducing conditions for between 445 and 735 days, but then TCE and hexavalent chromium rebounded after the substrate was depleted.



In conclusion, where the combination of SRS[®]-M and bioaugmentation with KB-1 was adequately distributed, it was effective in reducing high concentrations of hexavalent chromium and promoting reductive dechlorination of high concentrations of TCE. For example in well LAI-MW-01B, there was a decrease from 23 mg/L hexavalent chromium to non-detect and TCE was reduced from 7.7 to 0.034 mg/L with increases in VC and ethene.