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LIMITED SOURCE REMOVAL WITH ETHYL-LACTATE BIOAGUMENTATION: A LOW-TECH APPROACH

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ABSTRACT: Groundwater contamination from tetrachloroethene (PCE) and daughter products, discovered at an electronic components manufacturing facility in west central Florida, had shown little change resulting from several years of operation of a groundwater extraction/treatment system. Analytical results from one monitoring well near the center of the dissolved plume were consistently in the concentration range that suggested the presence of residual non-aqueous phase liquid (NAPL), although none was ever encountered in the course of assessment sampling. Additionally, geochemical conditions were not optimal for reductive dechlorination, possibly due to operation of the groundwater extraction system.

To expedite the attainment of specific groundwater cleanup target levels (GCTLs), an interim remedial action plan was developed to meet the following objectives:

- Removal of the potential residual NAPL through excavation of a minimum quantity of soil in the vicinity of the "hot" well,
- Addition of an alternative substrate during backfilling to augment the existing conditions through a one-time substrate addition to provide a more reducing environment, without the installation of a substrate injection system, and
- To attain GCTLs through monitored natural attenuation within five years.

This paper presents the results of this interim remedial action, including comparison of groundwater contaminant concentration rates of change before and after the interim action, methods employed, overall project success, and relative costs associated with this approach.

INTRODUCTION

The study site occupies approximately nine acres in a developed portion of Hillsborough County, Florida. The surficial aquifer at the site consists of medium to dense poorly graded sand, ranging in thickness from seven to fourteen feet below land surface. The surficial aquifer is separated from the upper limestone aquifer by a confining layer consisting of clayey sand, sandy clay and clay that ranges in thickness from five to fifteen feet. Impact to groundwater does not extend to the limestone aquifer.

The active facility manufactures electronic components and, prior to 1986, discharged process wastewater and treated sanitary wastewater to an unlined percolation pond on-site. The percolation pond has since been closed in accordance with a closure permit issued by the Florida Department of Environmental Protection (FDEP). Groundwater was found to be contaminated with tetrachloroethene (PCE) and daughter products during sampling associated with closure of the percolation pond, and the area of impact appeared to be centered around a former concrete wastewater storage tank.

A groundwater extraction/treatment system was installed to address this contamination issue; however, concentrations of PCE, trichloroethene (TCE), cis-1,2-dichloroethene (DCE) and vinyl chloride (VC) had remained relatively constant over time in samples from several monitoring wells at the site despite several years of operation of this system. One well adjacent to the former wastewater storage tanks (TSM-10) consistently yielded concentrations of PCE approaching those suggesting the presence of residual dense non-aqueous phase liquid (DNAPL) (Cohen and Mercer, 1993).

Additional soil and groundwater sampling was conducted in November, 2001 from Geoprobe borings. Data from that sampling indicated an area of approximately 20 ft by 40 ft (800 square ft.) in plan elevation and an impacted depth of 16 feet below land surface (bls). The actual contamination in the soil exceeding 62-777 cleanup levels (leachability to groundwater) was limited to the zone immediately above (within two feet) of the clay layer, for a total volume of impacted soil estimated at approximately 740 cubic yards.

Although PCE and TCE can, under certain circumstances, be cometabolized under aerobic conditions, the initial step for most oxidation pathways of ethenes is through the insertion of an oxygen atom into a bond on the molecule. Due to the electrophilic nature of the oxygen insertion, other electrophilic substituents (e.g. chlorine) hinder the reaction. Higher numbers of chlorine substituents result in less likelihood for oxidation to occur (Vogel, 1994).

The development of reductive conditions is often limited by insufficient organic carbon to act as the electron donor for the reductive dechlorination reaction (Wiedemeier, et al., 1998). The addition of readily-degradable organic compounds can enhance this process.

Although daughter products of reductive dechlorination of PCE were present, geochemical conditions at the time of the pre-removal sampling were only marginally conducive to reductive dechlorination (elevated dissolved oxygen and elevated oxidation/reduction potential), possibly due to influence from the operation of the groundwater extraction system, and to less than ideal organic carbon content.

In December 2001, an *Interim Measure Work Plan for Source Removal* was submitted to FDEP and received approval on January 24, 2002. This work plan described a process to remove a limited source area beneath and adjacent to the former concrete wastewater tanks, coupled with bioaugmentation with ethyl lactate to increase biological activity and create conditions favorable for reductive dechlorination to occur. Ethyl lactate was chosen by virtue of low cost, ease of degradation and ease of handling.

Source removal and bioaugmentation were completed during March 2002. Quarterly sampling following completion of the source removal/bioaugmentation to monitor the progress of the natural attenuation process (Monitored Natural Attenuation – MNA) was included in the work plan. A description of the removal action and subsequent sampling results are presented herein.

SOURCE REMOVAL AND BIOAUGMENTATION

One of the challenges to implementing this project was the location of the "hot spot" area, situated between two adjacent buildings to the east and west, and a subsurface sewer lift station directly to the north. Only the south side was accessible to heavy equipment. In addition, a decommissioned concrete wastewater tank was located directly above the impacted area, and required demolition before the source removal activities could proceed.

Due to the confining quarters, a coffer cell sheet-piling system was selected to shore the excavation. It was also decided for logistical purposes to split the source removal into two separate excavations phases, with individual coffer cell systems measuring 25 ft by 25 ft (625 sq. ft.) in plan dimension, to allow us to achieve the required depth of 16 feet without using internal bracing struts, making the working space more accessible to excavation equipment. The coffer cell design also minimized the flow of groundwater seepage into the excavation, allowing us enough time to maintain the depths required for implementing the bioaugmentation process.

Approximately 1,000 tons of impacted soil were excavated and transported off-site for disposal. When the control depth was achieved, the bioaugmentation process was initiated. The bioaugmentation process consisted of spreading ethyl lactate over each lift of the backfill. At an application rate of approximately one pound of ethyl lactate per square foot of backfill material placed under the normal ambient water table line (approximately 6 feet at the site).

Ethyl lactate was chosen for relatively high hydrogen yield capacity, and for cost considerations. Ethyl lactate normally sells for $1.60 to $2.00 per pound compared to other bioaugmentation agents that sell for as high as $8.00 to $10.00 per pound.

The application process involved pumping the ethyl lactate directly from the drums with hand application over each of the first ten backfill lifts (one foot each) using a 3/4-inch hose with and spay nozzle. Safety precautions used for handling the ethyl lactate including wearing gloves and eye protection, with adequate ventilation.

NATURAL ATTENUATION MONITORING

Six wells that lie generally along the axis of the groundwater plume were selected as monitoring points for the MNA evaluation (TSM-3R, TSM-6, TSM-7, TSM-10R, TSM-11 and TSM-16 – see Figure 1). All samples were collected using low-stress purging and sampling techniques as described in FDEP Standard Operating Procedure (SOP) #FS2200, and other associated and referenced SOPs. During the purging process, temperature, pH, specific conductance, dissolved oxygen, oxidation/reduction potential (ORP) and turbidity were monitored to determine when stable conditions had been achieved.

Samples were collected immediately following purge. One monitoring well (TSM-10R[1]) was sampled in duplicate. All samples were submitted to the contracted laboratory for analysis of volatile organic compounds, and for electron sources, alternative electron acceptors and degradation products by the methods listed in Table 1.

[1] Note: TSM-10 was destroyed during the removal action, and was replaced following backfilling operations. The replacement well, TSM-10R was installed in the same locations, and to the same completion specifications as the original well.

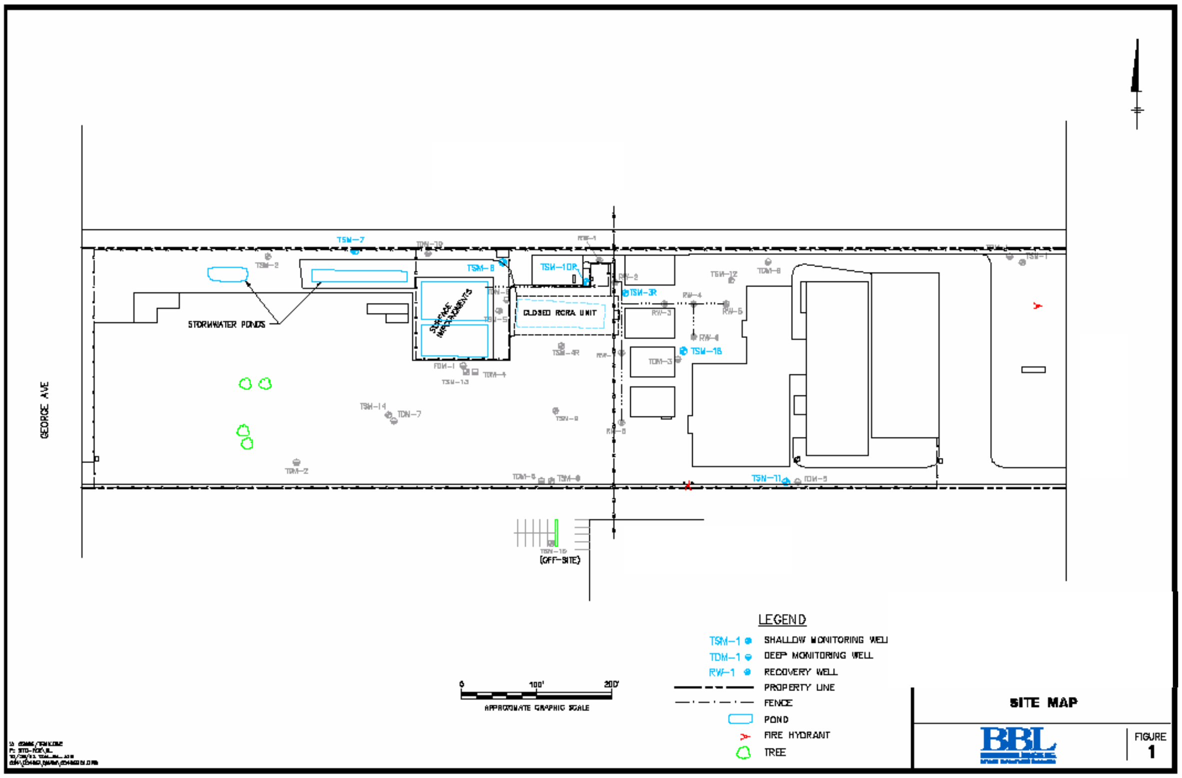


TABLE 1. Analysis methods used for samples.

Selected Analyte	Analytical Method VOCs & EPA Method 8021
Nitrate	EPA 353.2
Sulfate	EPA 375.4
Alkalinity	EPA 310.1
Chloride	EPA 325.3
Sulfide	EPA 376.2
Ferrous Iron	SM 3500
Total Organic Carbon	EPA 415.1
Methane	SOP AR30
Ethane	SOP AR30
Ethene	SOP AR30
Carbon Dioxide	SOP AR30

PCE concentration in TMW-10/10R declined dramatically during the first quarter of monitoring (15,000 ug/l to non-detectable concentrations), exhibited a slight (and expected) rebound, and appears to have begun to decline with the third quarterly sampling (Figure 2). Currently, no samples from wells at the site contain PCE at concentrations above Table V, Chapter 62-777 Natural Attenuation Default Concentrations (NADC).

TCE concentrations have exhibited a similar pattern with time to that of PCE; however, the sample from TSM-3R is currently the only sample with TCE concentrations above MCLs. The concentration of TCE in the sample from TSM-3R is, again, below the NADC (Figure 3).

Figure 2.
PCE Concentration vs Time

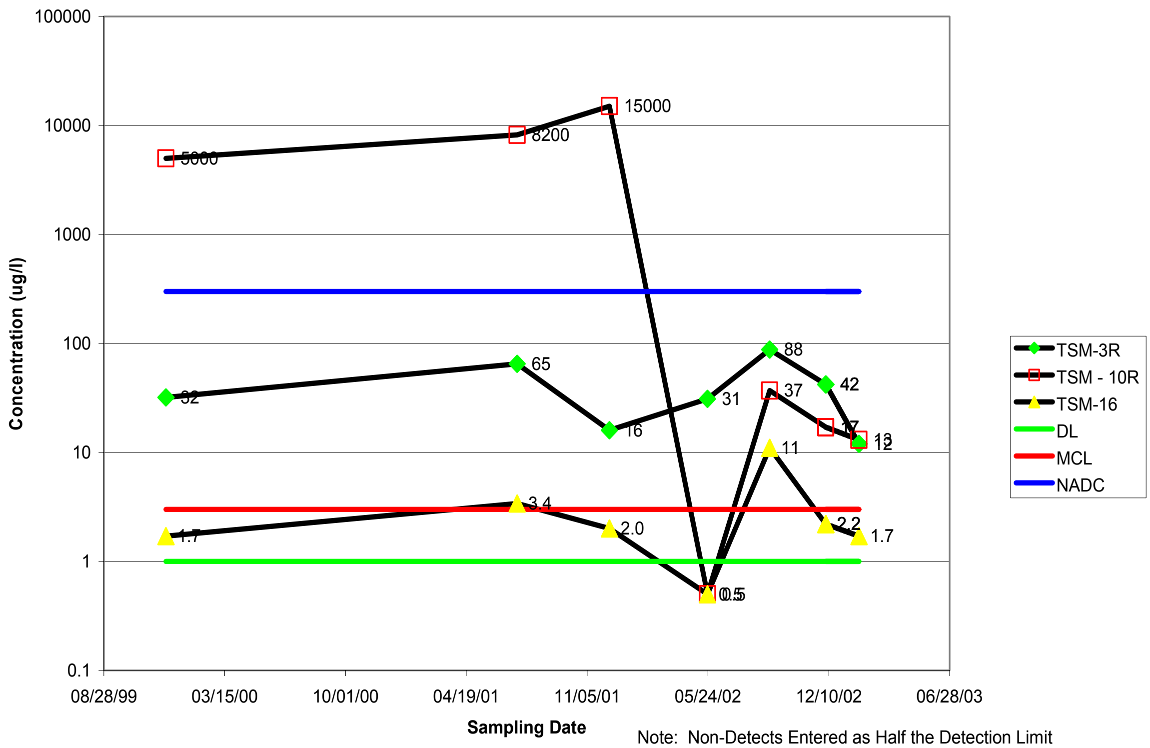
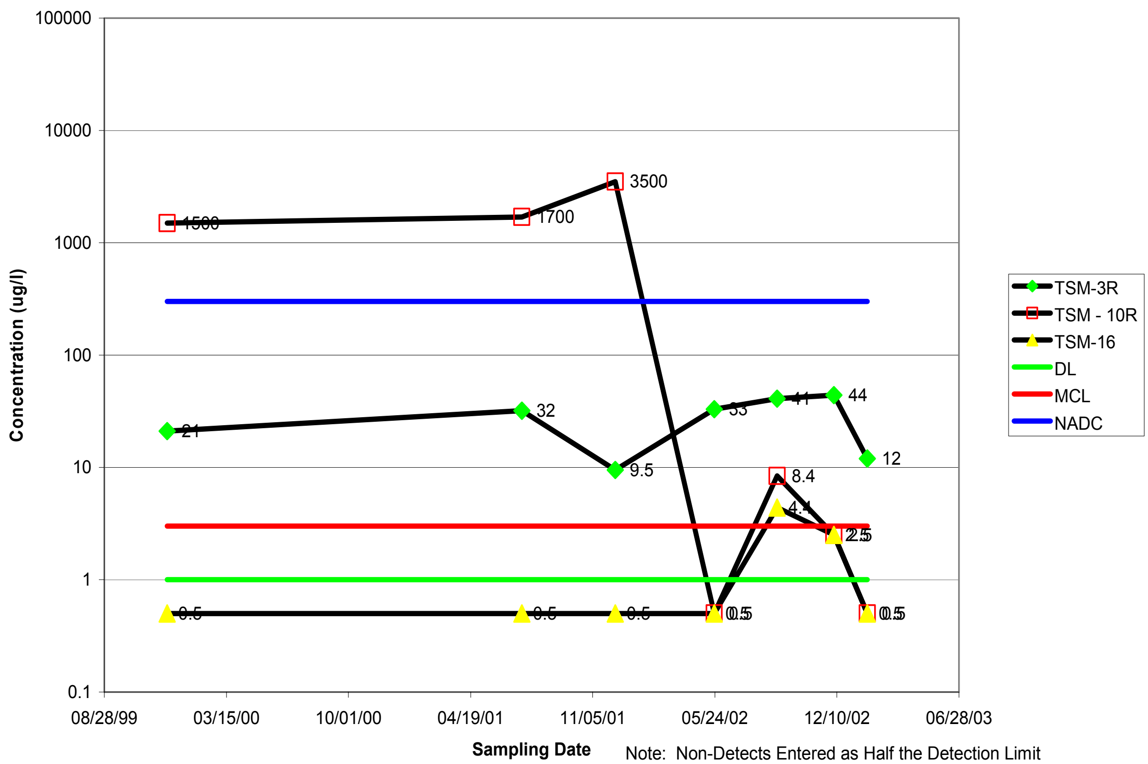


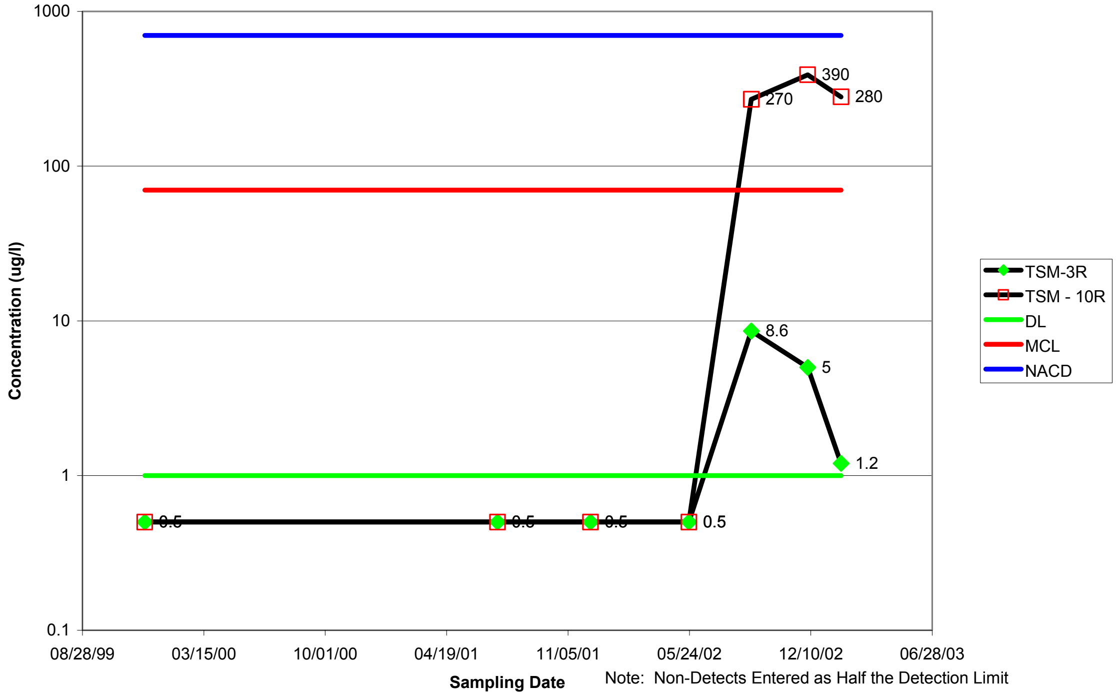
Figure 3.
TCE Concentration vs Time



Prior to the removal action and bioaugmentation, cis-1,2-DCE and VC had not been detected in samples collected from either TSM-10/10R or TSM-3, the “source area” wells. During the second and third quarterly samplings, DCE and VC were detected in the samples from TSM-10R and TSM-3R, while VC was detected in the sample from TSM-10R. Low concentrations of VC were also detected in the second quarterly sample from TSM-6, downgradient from the source area (Figures 4 and 5).

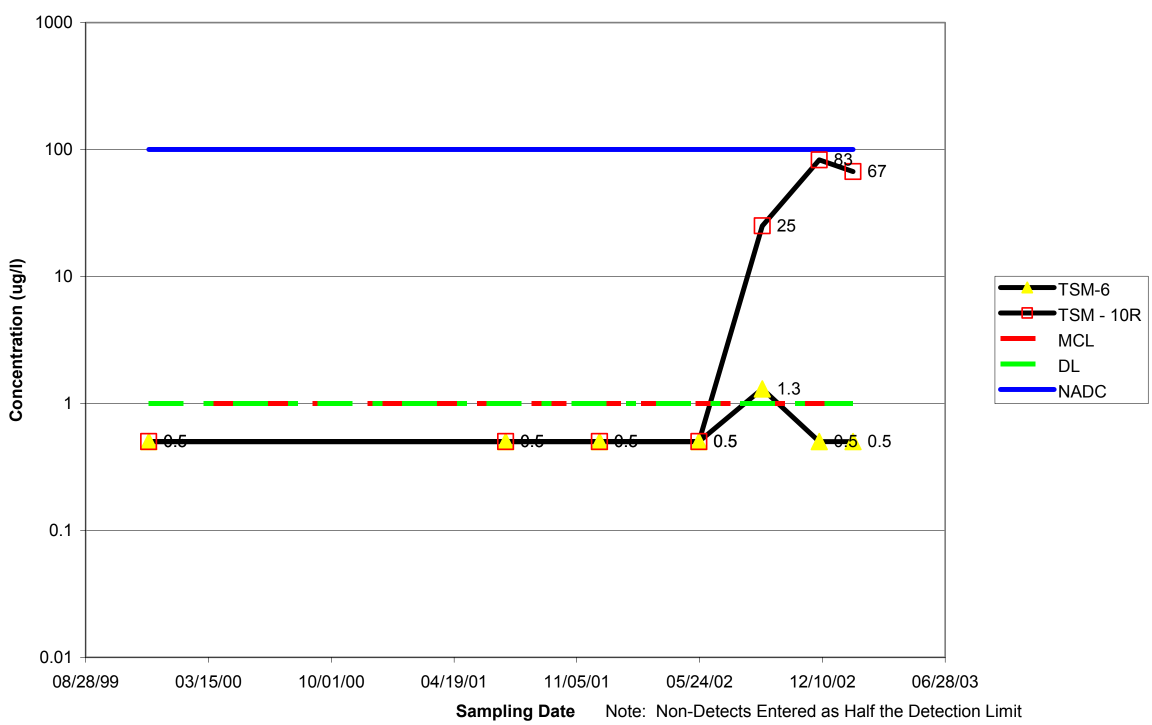
The occurrence of these degradation products are an indication that the reductive dechlorination process are beginning to occur in the former source area, and they are possibly resulting from the degradation of PCE and TCE as they begin to migrate back into the excavated area from surrounding groundwater.

Figure 4.
cis-1,2-DCE Concentration vs Time



Note: Non-Detects Entered as Half the Detection Limit

Figure 5.
Vinyl Chloride Concentration vs Time



Note: Non-Detects Entered as Half the Detection Limit

Sulfate reducing and methanogenic conditions are also becoming evident at the site (Figures 6, 7 and 8), lending further support to the onset of conditions that will facilitate reductive dechlorination.

Figure 6. Sulfate vs Time

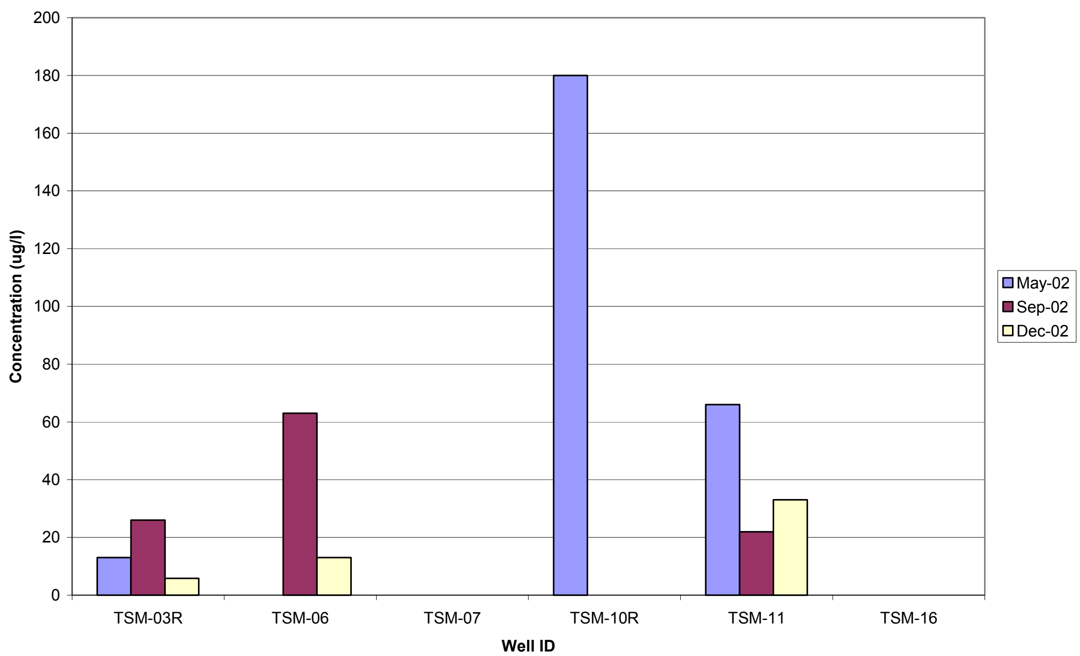


Figure 7. Sulfide vs Time

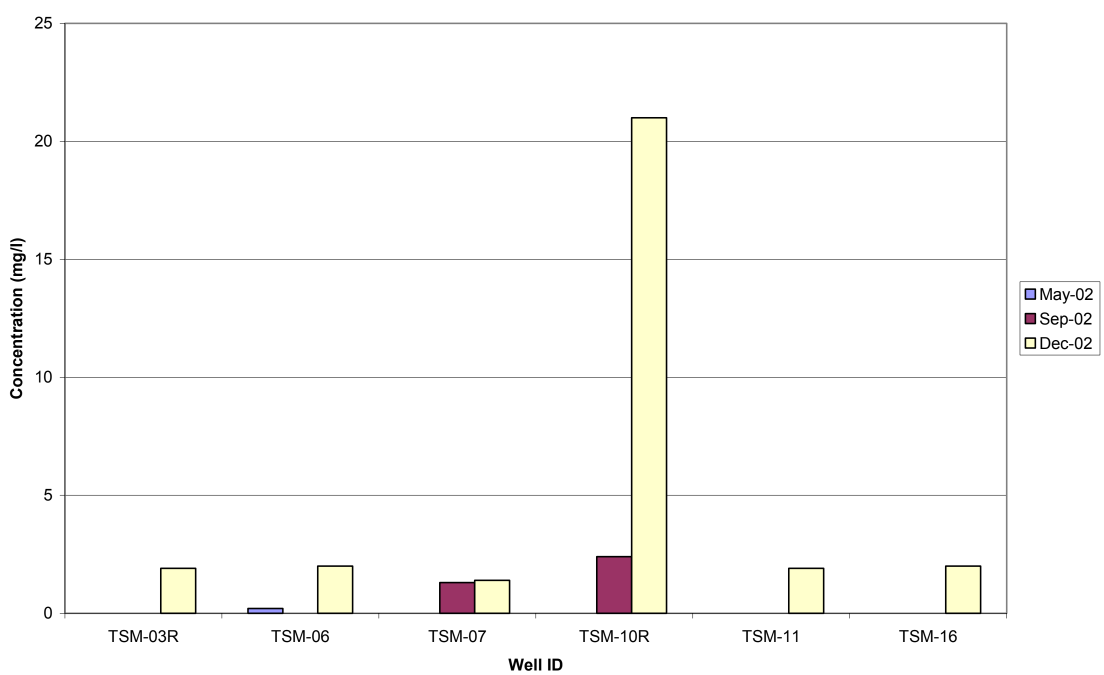
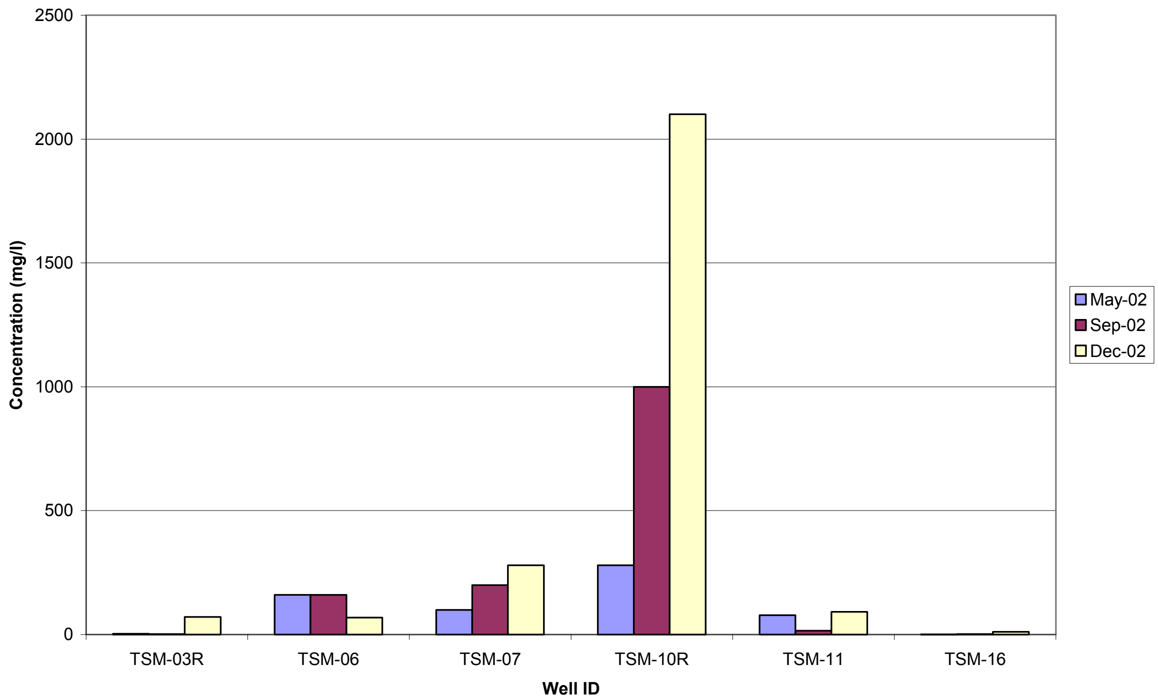


Figure 8. Methane vs Time



CONCLUSIONS AND FUTURE CONSIDERATIONS

Early data indicate that the shift to reductive conditions required for the dechlorination of PCE and TCE are beginning to manifest at the site. When evaluated using the scoring protocol provided in BIOCHLOR (USEPA, 2000), oxidation/reduction potential and state of alternate electron acceptors, low dissolved oxygen, the presence of degradation products, and current total organic carbon conditions resulting from the ethyl lactate augmentation indicate strong evidence for ongoing natural attenuation, and the likelihood that this process can ultimately reduce contaminant concentrations to levels below GCTLs. This trend will continue to be monitored, and the need for additional substrate addition will be evaluated as the system progresses.

One consideration is the increasing presence of cis-1,2-DCE and vinyl chloride in samples from the source area wells. This trend will also continue to be monitored in these wells, as well as additional wells at the site. These analytes, in particular vinyl chloride, are more conducive to attack through oxidative processes. At a time when the parent material has been degraded to concentrations below GCTLs, the need for additional substrates to facilitate degradation of these products, either in the source or as a barrier to downgradient migration, will be evaluated.

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Wiedemeier, et al. 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. USEPA Publication EPA/600/R-98/128.