SRNL-STI-2012-00290
Rev. 0

Treatability Study for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site

Brian Riha
Brian Looney
Jay Noonkester
Keith Hyde
Richard Walker

May 2012

Savannah River Nuclear Solutions, LLC
Savannah River Site
Aiken, SC, 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy

Contents

List of Figures

List of Tables

1. INTRODUCTION

Groundwater beneath T-Area, a former laboratory and semiworks operation at the Department of Energy (DOE) Savannah River Site (SRS), is contaminated by chlorinated solvents (cVOCs). Since the contamination was detected in the 1980s, the cVOCs at T-Area have been treated by a combination of soil vapor extraction and groundwater pump and treat. The site received approval to temporarily discontinue the active groundwater treatment and implement a treatability study of *enhanced attenuation* – an engineering and regulatory strategy that has recently been developed by DOE and the Interstate Technology and Regulatory Council (ITRC 2007). Enhanced attenuation uses active engineering solutions to alter the target site in such a way that the contaminant plume will passively stabilize and shrink and to document that the action will be effective, timely, and sustainable.

The paradigm recognizes that attenuation remedies are fundamentally based on a mass balance. Thus, long-term plume dynamics can be altered either by reducing the contaminant loading from the source or by increasing the rate of natural attenuation processes within all, or part of, the plume volume. The combination of technologies that emerged for T-Area included: 1) neat (pure) vegetable oil deployment in the deep vadose zone in the former source area, 2) emulsified vegetable oil deployment within the footprint of the groundwater plume, and 3) identification of attenuation mechanisms and rates for the distal portion of the plume. In the first part, neat oil spreads laterally forming a thin layer on the water table to intercept and reduce future cVOC loading (via partitioning) and reduce oxygen inputs (via biostimulation). In the second and third parts, emulsified oil forms active bioremediation reactor zones within the plume footprint to degrade existing groundwater contamination (via reductive dechlorination and/or cometabolism) and stimulates long-term attenuation capacity in the distal plume (via cometabolism). For T-Area, the enhanced attenuation development process proved to be a powerful tool in developing a strategy that provides a high degree of performance while minimizing adverse collateral impacts of the remediation (e.g., energy use and wetland damage) and minimizing life-cycle costs.

As depicted in Figure 1, Edible oil deployment results in the development of structured geochemical zones and serves to decrease chlorinated compound concentrations in two ways: 1) physical sequestration, which reduces effective aqueous concentration and mobility; and 2) stimulation of anaerobic, abiotic and cometabolic degradation processes. In the central deployment area, contaminant initially partitions into the added oil phase. Biodegradation of the added organic substrate depletes the aquifer of oxygen and other terminal electron acceptors and creates conditions conducive to anaerobic degradation processes. The organic substrate is fermented to produce hydrogen, which is used as an electron donor for anaerobic dechlorination by organisms such as *Dehalococcoides*. Daughter products leaving the central treatment zone are amenable to aerobic oxidation. Further, the organic compounds leaving the central deployment zone (e.g., methane and propane) stimulate and enhance down gradient aerobic cometabolism which degrades both daughter compounds and several parent cVOCs. Figure 1 depicts TCE concentration reduction processes (labeled in green) along with their corresponding breakdown products in a structured geochemical zone scenario.

A consortium of bacteria with the same net effect of *Dehalococcoides* may be present in the structured geochemical zones leading to the degradation of TCE and daughter products. Figure 2 shows a schematic of the documented cVOC degradation processes in both the anaerobic and aerobic structured geochemical zones. Specific aerobic and anaerobic bacteria and their degradation pathways are also listed in the diagram and have either been confirmed in the field or the laboratory. See references in the bibliography in Section 11.

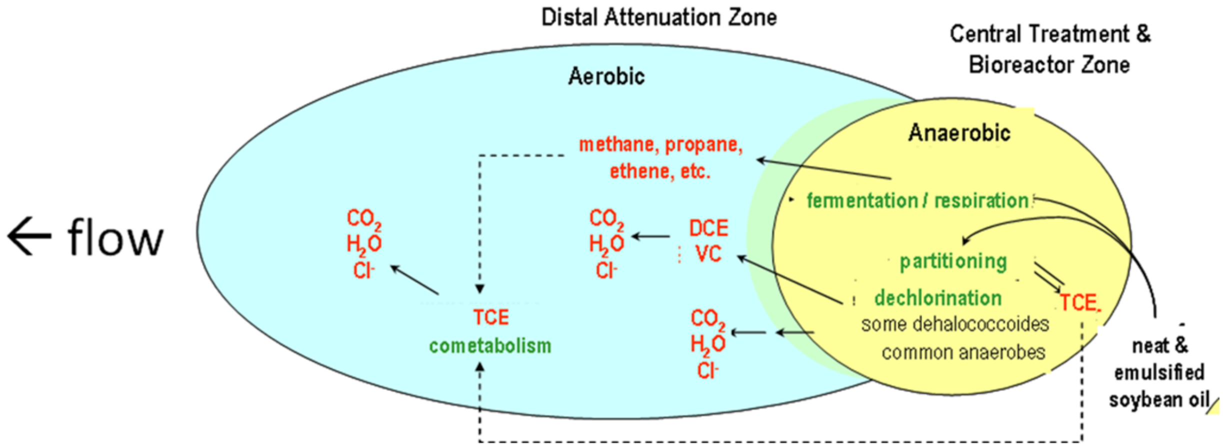

Figure 1 – Schematic of TCE Concentration Reduction Processes

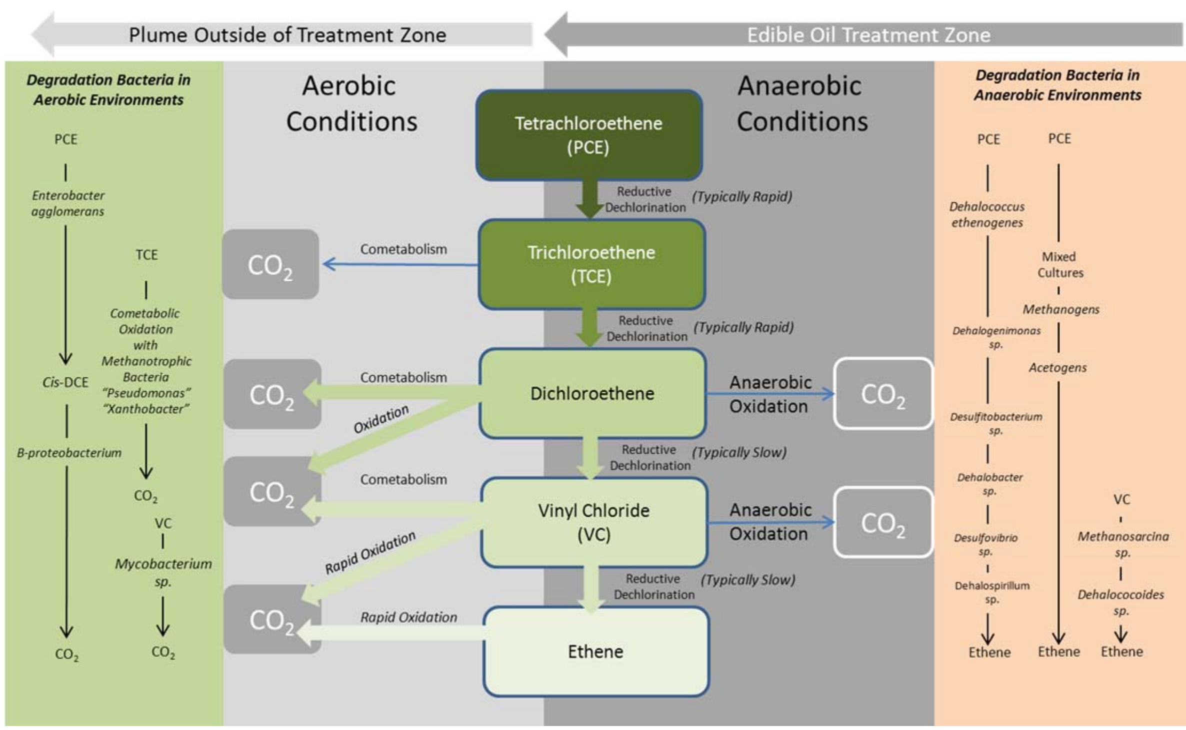

Figure 2 – cVOC Degradation Processes in Anaerobic and Aerobic Groundwater Plumes with Documented Bacteria

(Modified from Hazardous Substance Research Center (2005), and GeoMega (2005), Air Force Center for Environmental Excellence (2004); various literature sources for degradation bacteria. See Bibliography)

2. TEST GOALS

Analysis of the conditions in T-Area indicated oil and amendment emplacement along with moderate modifications to the groundwater geochemistry should provide appropriate conditions to change the source area aquifer to anaerobic and initiate reductive dechlorination of trichloroethylene (TCE). Other degradation processes, co-metabolic and abiotic, are also probable in the source area and distal portions of the plume. The overall objective of the testing is to assess the performance of the deployment strategy for long-term attenuation. The specific goals to meet this objective for full scale oil deployment are:

- Evaluate neat and emulsified oil distribution
- Assess the extent and rate of changes from aerobic to anaerobic
- Determine TCE degradation and degradation rates
- Assess degradation daughter products and their subsequent degradation
- Assess degradation pathways (reductive dechlorination, cometabolism, abiotic)
- Assess the recruitment of appropriate bacteria (i.e. fermentative, dechlorinating, and cometabolic) and sufficient amount of biomass
- Determine if additional means are needed to stimulate and/or maintain attenuation (e.g. geochemistry modifications, oil addition, nutrient addition, microbial inoculants, etc.)
- Assess the ability of the oil deployment to stabilize and shrink the groundwater plume and to provide a sustainable treatment to meet the cleanup levels of 5 µg/l TCE
- Determine long-term operation, maintenance and monitoring requirements.

3. DESIGN APPROACH

The design for this combined remedy to transition the remediation of cVOCs in the soil and groundwater of T-Area at the Savannah River Site to passive attenuation based remedy derives from two mechanisms, partitioning and degradation, combined with standard hydrology and engineering calculations. The current configuration of T-Area influenced the assumptions used in developing this design. Notably, the design used existing wells and piezometers for access. This required creative application of treatment reagents to exploit site features and characteristics such as existing well locations, water table and lithology to generate a deployment zone that has the correct geometry to intercept contaminants and effectively treat the groundwater plume.

The result of the design process was a two part deployment: 1) neat (pure) vegetable oil at the water table in the residual source area, and 2) emulsified vegetable oil (EOS™) in the core of the groundwater cVOC plume. The initial estimated distribution of neat and emulsified oil is shown in Figure 3. The full design and implementation plan are provided in the treatability study test plan (Riha and Looney 2007) and underground injection control (UIC) permit (WSRC 2007). Key deviations from the test plan are provided in the Field Implementation section.

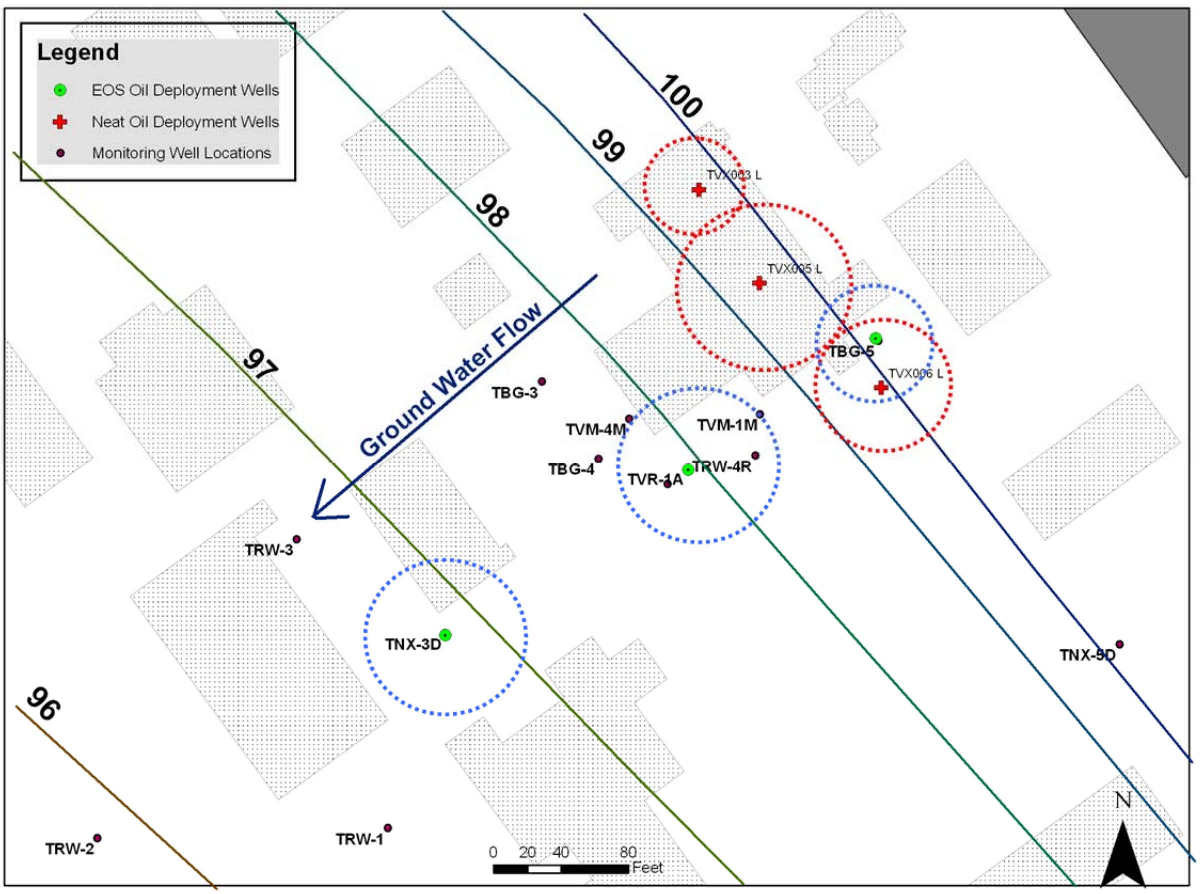

Figure 3 – Plan View Map of Oil Injection Wells and Estimated Initial Distribution

(EOS in blue and neat oil in red. Groundwater elevations as of January 2009)

4. FIELD IMPLEMENTATION

4.1 Emulsified Oil Deployment

The T-Area deployment operated in conjunction with a portable shallow tray air stripper to remove the cVOCs from the groundwater before re-injection. Water was extracted from a down gradient well, treated and re-injected in an up gradient well fitted with EOS and base metering systems. Contaminant mass removed by the air stripper was measured by sampling the air stripper inlet and outlet water stream and analyzing for cVOCs. Total TCE mass removed was 0.016 lbs. The shallow tray air stripper controlled the extraction pump and addition and mixing of reagents. Flexible hoses were used to transfer reagents and water. The air stripper and injection system are shown in Figure 4. In each injection well, the operation continued until the desired EOS was injected along with sufficient water to distribute the EOS throughout the targeted volume. A packer was placed in TRW-4R to maximize the injection or extraction in the upper portion of the screened interval. The progress of the deployment was monitored using periodic samples (contaminants, dissolved oxygen, ORP, total organic carbon (TOC), pH, alkalinity,) from available wells around the injection points.

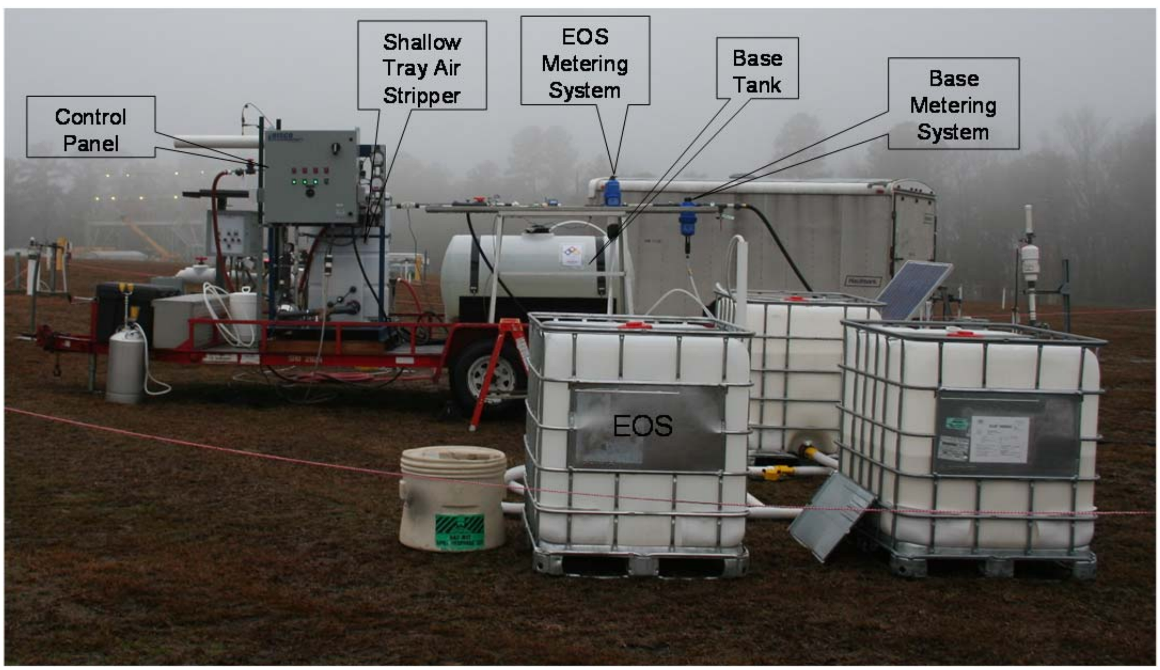

Figure 4 – Air Stripper, EOS and Base Injection System

The original design method of distributing the EOS with injection-extraction well pairs was not feasible in the field due to low well flow rates. The original design involved lowering the water table at the extraction well to guide the EOS from the injection well to the extraction well. For example, well TBG-5 began with an injection flow rate of about 3 gpm (gallon per minute) and dropped to about 1 gpm after the 50,000 gal of EOS and chase water were injected. A minimum of 5 gpm was needed to create the dipole distribution. EOS, water and base were injected by gravity feed. The decrease in flow could be attributed to lowering of permeability due to the oil injection and/or flocculation and clogging by clays from the addition of the base. An interlock sensor was used in each injection well to shut down the system to prevent overflow of the injection well.

As a result of the low flow rates, EOS was distributed radial outward from wells TBG-5, TRW-4R and TNX-3D. See Figure 3. These wells correspond with the flow path of the core of the dissolved plume. TRW-4R (average TCE concentration of 27 μg/l) was used as the extraction well for injection into TBG-5. TRW-3 (average TCE concentration of 3 μg/l) was used as the extraction well for injection into TRW-4R and TNX-3D. After treatment with the air stripper, TCE could not be detected in the injected water. Approximately 0.95 g/gal water of sodium bicarbonate ($NaHCO_3$) and 1.44 g/gal water of hydrous trisodium phosphate ($Na_3PO_4.12H_2O$) were added to the injected water as the pH buffer. The amount of EOS and chase water is provided in Table 1.

Table 1 – Emulsified Oil Injection Volumes

Injection Well ID	Extraction Well ID	Injection Dates	Volume of EOS, gal	Volume of Chase Water, gal	Range of Injection Rates, gpm
TBG-5	TRW-4R	2/20/08-3/10/08	960	50,420	3.3-1.0
TRW-4R	TRW-3	3/17/08-3/26/08	1,250	92,405	7.2 (steady)
TNX-3D	TRW-3	3/27/08-4/19/08	1,250	76,277	6.3-1.8

4.2 Neat Oil Deployment

For neat oil deployment, pure soybean oil was used with 0.2% triethyl phosphate (TEP) as a phosphorous source. The oil was emplaced by gravity feed using deep vadose wells TVX-3L, TVX-5L and TVX-6L. The approximate location and dimensions of the neat oil deployment are based on the detailed characterization of the vadose zone to support the SVE operation. In this case, the amount of oil to be deployed was a straightforward geometric calculation (see Figure 3). The key deviation from the test plan was injection in well TVX-6L instead of TBG-5 to allow TBG-5 to be used as a monitoring well. The neat oil injected volumes and approximate flow rates are provided in Table 2 and oil injection into well TVX-5L is shown in Figure 5.

Table 2 – Neat Soybean Oil Injection Volumes

Injection Well ID	Injection Dates	Volume of Neat Soybean Oil, gal	Approximate Injection Rate, gpm
TVX-5L	4/7/08-4/9/08	1,500	1
TVX-3L	4/15/08-4/18/08	300	0.1
TVX-6L	4/24/08-4/25/08	900	0.6

Figure 5 – Neat Soybean Oil Injection in TVX-5L

4.3 Additional Emulsified Oil Deployment in TBG-4

Per agreement with the TNX Core Team and extension of UIC Permit #924, additional emulsified oil and amendments were injected into well TBG-4 due to an increase in concentration caused by dilute plume movement from the original emulsified oil deployment. Between 5/10/2010 and 5/20/2010 3,000 gal of water were extracted from well TBG-4 using a gas driven on demand pump. The well produced approximately 0.2 gpm and the water was stored in two 1,500 gal tanks. Between 5/25/2010 and 5/26/2010 110 gal of AquaBupH™ (EOS Remediation brand of emulsified soybean oil and buffer) and 55 gal of EOS™ (emulsified oil) was diluted 4:1 (water:amendment) and injected into the well by gravity feed followed by the 3,000 gal of extracted water to distribute the amendments. Injection rates by gravity feed were approximately 7 gpm. See Figure 6 for a picture of the injection/extraction setup for TBG-4.

Figure 6 – EOS and AquaBupH Injection/Extraction Setup for TBG-4

5. MONITORING

The goals, metrics and methods for monitoring the performance of the enhanced attenuation remedy are listed in Table 3. The sampling strategy was designed to optimize data collected to meet the study objectives, while minimizing analytical costs. Measurements are being made in a representative set of wells within the treatment zone and outside the treatment zone (for background information) and in representative down gradient wells (to evaluate the aerobic distal treatment zone). Samples were collected prior to injections and monthly after injections.

Table 3 – Strategy for Sampling and Analysis

Test Goal	Metric	Method
Evaluate neat oil distribution	Measure oil presence and thickness in existing wells	oil/water interface probe, bailing
Evaluate emulsified oil distribution	Measure oil presence and approximate concentration in the treated zone using existing wells	Visual identification in water samples. TOC analysis
Assess the extent and rate of change from aerobic to anaerobic	Measure temporal dissolved oxygen (DO) in existing wells	Field sensors and test kits
Determine TCE degradation and degradation rates	Measure temporal TCE and daughter product concentrations	SRNL modified method 5021 headspace analyses
	Measure TCE destruction	Stable C isotope enrichment analyses
Assess daughter products and their subsequent degradation	Measure temporal cVOC concentrations	SRNL modified method 5021 headspace analyses
Assess degradation pathways	dechlorination: measure cVOC daughter products	SRNL modified method 5021 headspace analyses
	cometabolism: measure activity dependent enzymes	Activity-dependent enzyme probes, North Wind Inc.; Stable C isotope ratios
	abiotic: TBD	Stable C isotope ratios
Assess the recruitment of appropriate bacteria and sufficient amount of biomass	Measure temporal type and abundance of the microbial community (fermentative, dechlorinating, and cometabolic)	Quantitative polymerase chain reaction (qPCR) by SRNL and/or commercial laboratory
Determine if additional means are needed to stimulate and/or maintain attenuation	Measure geochemistry and chemistry parameters for maintenance of appropriate attenuation conditions: DO, ORP, TOC, pH, alkalinity, ammonia, sulfate, phosphate, nitrate	Field sensors and test kits
	Measure co-metabolites: methane, propane, butane, ethene, ammonia (breakdown products of soybean oil)	Dissolved gas analysis by commercial lab

6. STATUS AND RESULTS

The initial field deployment of the amendments was initiated in February 2008 and completed in April 2008. Flow rates for diluted emulsion injection and groundwater extraction in the first well pair were below the design assumptions so radial injections were made in three wells along the flow path of the dissolved plume. Data collected from the twelve wells indicate that the injected fluids are being distributed in the subsurface as expected and the groundwater plume has decreased in size and concentration. TCE in the treatment zone decreased immediately after injections. This fast decrease in concentration resulted from partitioning and injection of treated (clean air-stripped) water but TCE concentrations have remained near or below 5 µg/l in this area. The data indicate that the buffer added to the injection (trisodium phosphate and bicarbonate) increased the pH from approximately 5 (typical for the Southeastern Coastal Plain) to approximately 6 within the treatment zone. Additional amendments were added to well TBG-4 in May 2010.

Full anaerobic conditions have been achieved throughout most of the treatment zone based low DO and ORP and elevated levels of methane that indicate strongly reducing conditions are present. Sulfate and nitrate have decreased as the anaerobic zones are established. Reductive daughter products (cis-DCE, vinyl chloride and ethene) have been observed in some wells indicating reductive dechlorination is occurring in parts of the treatment zone. Cometabolic degradation may be a dominant destruction mechanism in oxygenated zones. Methanotrophic (MOB) bacteria were present prior to deployment. MOB bacteria use methane as their primary food source and are capable of aerobically degrading TCE by cometabolism.

Table 4 provides a general discussion of the results of the metrics used to evaluate the treatment as related to the test goals for this treatability study for long-term attenuation of TCE at T-Area. The initial groundwater TCE concentration plume in 4Q07 is shown in Figure 7 and the concentration plume in 4Q09 and 4Q11 after the amendment injection shown in Figure 8 and Figure 9. The dashed blue line shows the original plume (>500 µg/l) in 4Q96. Comparison of these plume maps indicates that the primary impact of the treatment was the sharp decline in concentration throughout the former high concentration portion of the plume. Monitoring in wells TRW-1 and TRW-3 was begun June of 2009 as additional distal monitoring wells since it was impractical to install additional monitoring wells through the cap.

Overall, we estimate the groundwater is moving in the direction indicated in Figure 3. Based on the groundwater elevation contours, the velocity significantly decreases down gradient. During the four year study, the water levels have decreased approximately 4 ft in the up-gradient area and 2 ft in the down-gradient area. The engineered cap is controlling infiltration and velocities.

cVOC concentration and selected geochemistry parameter plots for the twelve monitored wells follow these figures with discussions for each well located in Table 5. In general, the data indicate significant progress toward the long term objectives for groundwater underlying T-Area. However, the current number and locations of available monitoring wells at this capped site limits the robustness of the data interpretation. Additional monitoring over time, as recommended below, will aid in developing a more definitive assessment of the performance and estimate of the time frame for achieving remedial objectives. The current conditions appear to be sustainable, however, additional oil injections may be necessary in the future near TRW-3 and TVM-1M.

Table 4 – Evaluation of T-Area Test Goals

Test Goal	Metric	Results
Evaluate neat oil distribution	Measure oil presence and thickness in existing wells	Neat oil has not been detected in any well except the injection wells at the time of this report.
Evaluate emulsified oil distribution	Measure oil presence and approximate concentration in the treated zone using existing wells	Elevated TOC has been measured in all wells at the time of this report. The carbon source is being distributed in the treatment zone with the advective groundwater flow. Increases in concentrations in TBG-4 indicate injections in TRW-4R moved contaminated water towards TBG-4 although groundwater mounding was not evident in TBG-4.
Assess the extent and rate of change from aerobic to anaerobic	Measure temporal dissolved oxygen (DO) in existing wells	DO has decreased in the treatment area and full anaerobic conditions exist in most of the main treatment area. DO is still decreasing in some areas Based on methane production, it is expected that full anaerobic conditions exist in most areas. Methane is close to solubility limits in some wells.
Determine TCE degradation and degradation rates	Measure temporal TCE and daughter product concentrations	TCE concentrations decreased immediately after injections likely due to partitioning and dilution. Concentrations have remained near or below 5 µg/l (ppb) throughout most of the treatment zone. Daughter products (cis-DCE, vinyl chloride and ethene) have been detected proving full reductive dechlorination. Traditionally calculated degradation rates at each well are not possible due to the immediate decrease in TCE concentrations. Total plume mass estimates were made over time to determine a rate constant for the total mass in the plume that resulted in a half-life of 1.4 years (see section 7.1.1). In addition, Mann Kendall and Linear Regression tests were conducted and are discussed section 7.1.2.
	Measure TCE destruction	Stable C isotope enrichment analysis is currently inconclusive because of the low TCE concentrations after deployment.
Assess daughter products and their subsequent degradation	Measure temporal cVOC concentrations	cis-DCE, vinyl chloride and ethene have been detected.

(continued on next page)

Table 4 – Evaluation of T-Area Test Goals (Continued)

Test Goal	Metric	Results
Assess degradation pathways	dechlorination: measure cVOC daughter products	Daughter products (cis-DCE, vinyl chloride and ethene) have been detected proving full reductive dechlorination.
	cometabolism: measure activity dependent enzymes	Methanogenic (MGN) and methanotrophic (MOB) bacteria were quite abundant prior to deployment (Riha, Looney et al. 2006). Activity dependent enzymes were detected in TRW-2 and show active although slow degradation in microcosm studies. The baseline half life of TCE is measured at 30.8 years. (Lee 2008). These rates should increase with the increased carbon and co-metabolite loading in the distal plume area that is now occurring.
	abiotic: TBD	Not addressed at the time of this report. Metrics have not been identified.
Assess the recruitment of appropriate bacteria and sufficient amount of biomass	Measure temporal type and abundance of the microbial community (fermentative, dechlorinating, and cometabolic)	Microbial analysis was conducted for each well and total biomass is below detection limits in the water samples. *Dehalococcoides* were therefore not detected. In dilute, low biomass systems, soil cores would likely provide detectable quantities. *Dehalococcoides* are likely present since this is the only documented pathway for these daughter products. A consortium of bacteria with same net effect of *Dehalococcoides* may be present in the structured geochemical zones leading to the degradation of TCE (refer to Figure 2).
Determine if additional means are needed to stimulate and/or maintain attenuation	Measure geochemistry and chemistry parameters for maintenance of appropriate attenuation conditions: DO, ORP, TOC, pH, alkalinity, ammonia, sulfate, phosphate, nitrate	The structured geochemical zones are continuing to mature with arrival of TOC and co-metabolites in the distal part of the plume. Additional amendments were added to TBG-4 to address an increase in concentration in this area. Based on the anaerobic conditions in the central treatment zone over four years, the treatment appears to sustain attenuation at this time. These parameters appear to still be equilibrating. Additional means to stimulate or maintain attenuation are not required currently, however TRW-3 and TVM-1M will be watched to determine if additional amendments are needed.
	Measure co-metabolites: methane, propane, butane, ethene, ammonia	Co-metabolites are increasing in concentration in the treatment zone. A significant amount of methane is being produced. Increases in methane and ammonia are evident in the distal monitoring wells at this time.

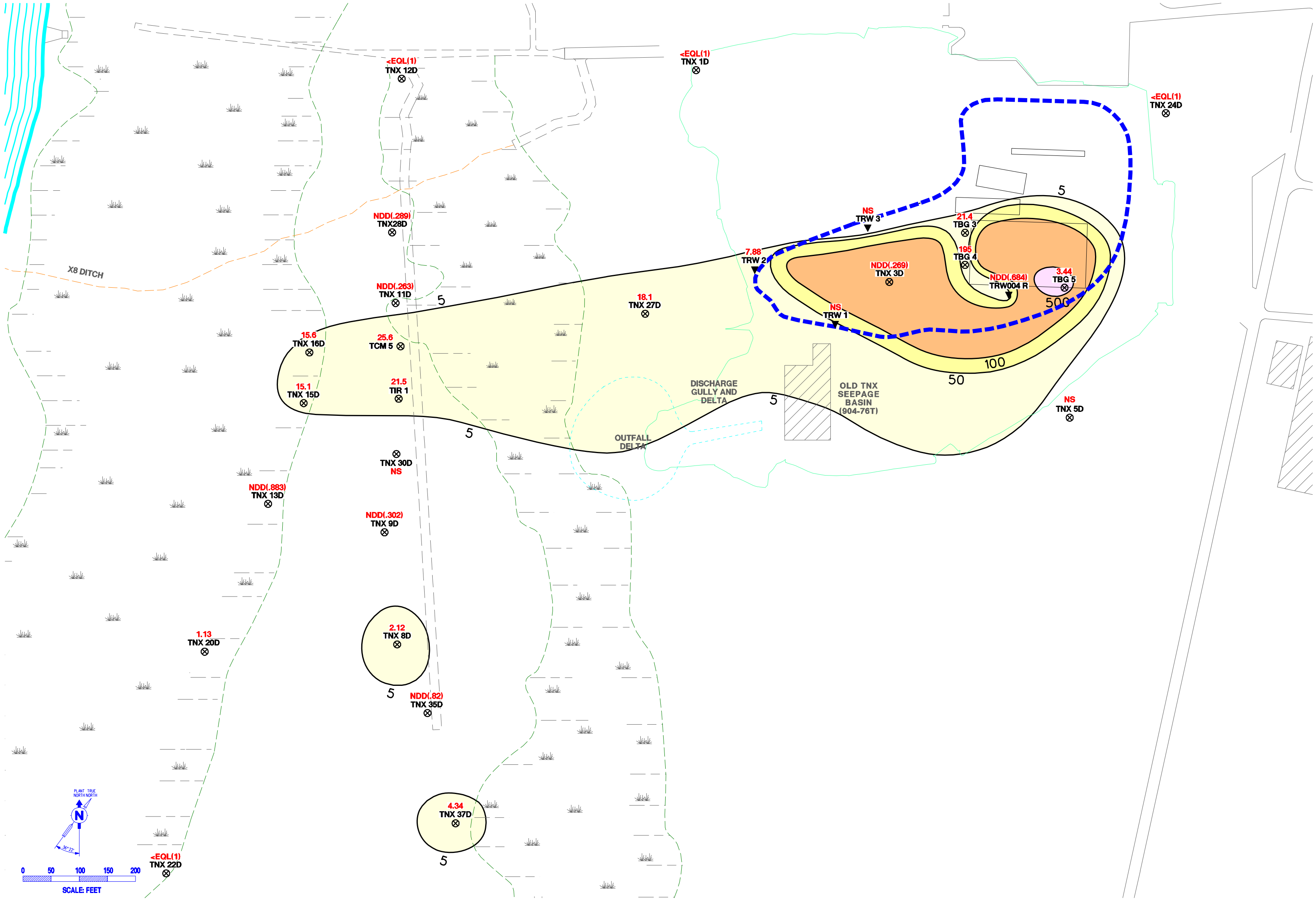

Figure 7 – TCE Concentration Plume Prior to Amendment Injections (4Q07)

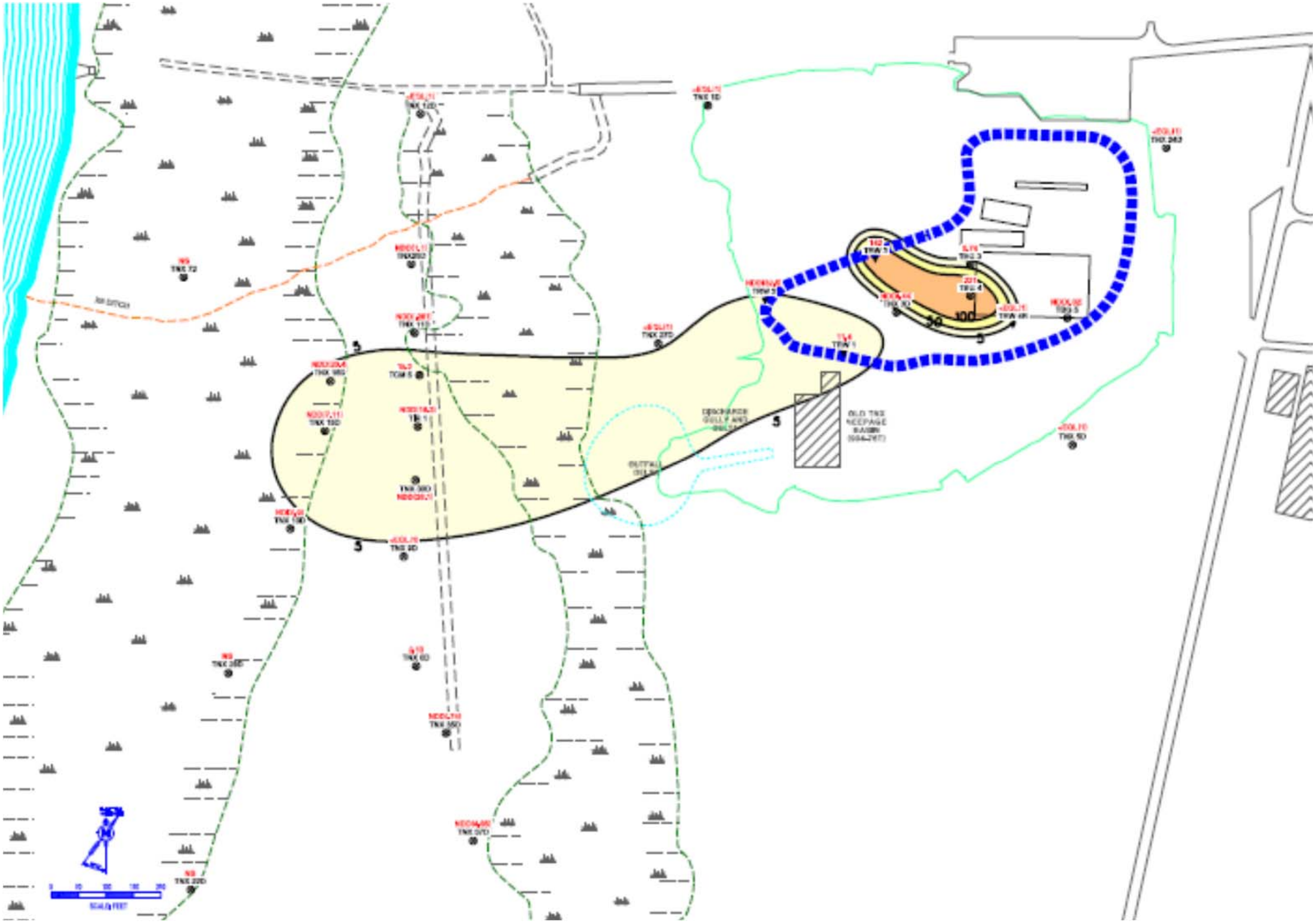

Figure 8 – TCE Concentration Plume after Amendment Injections (4Q09)

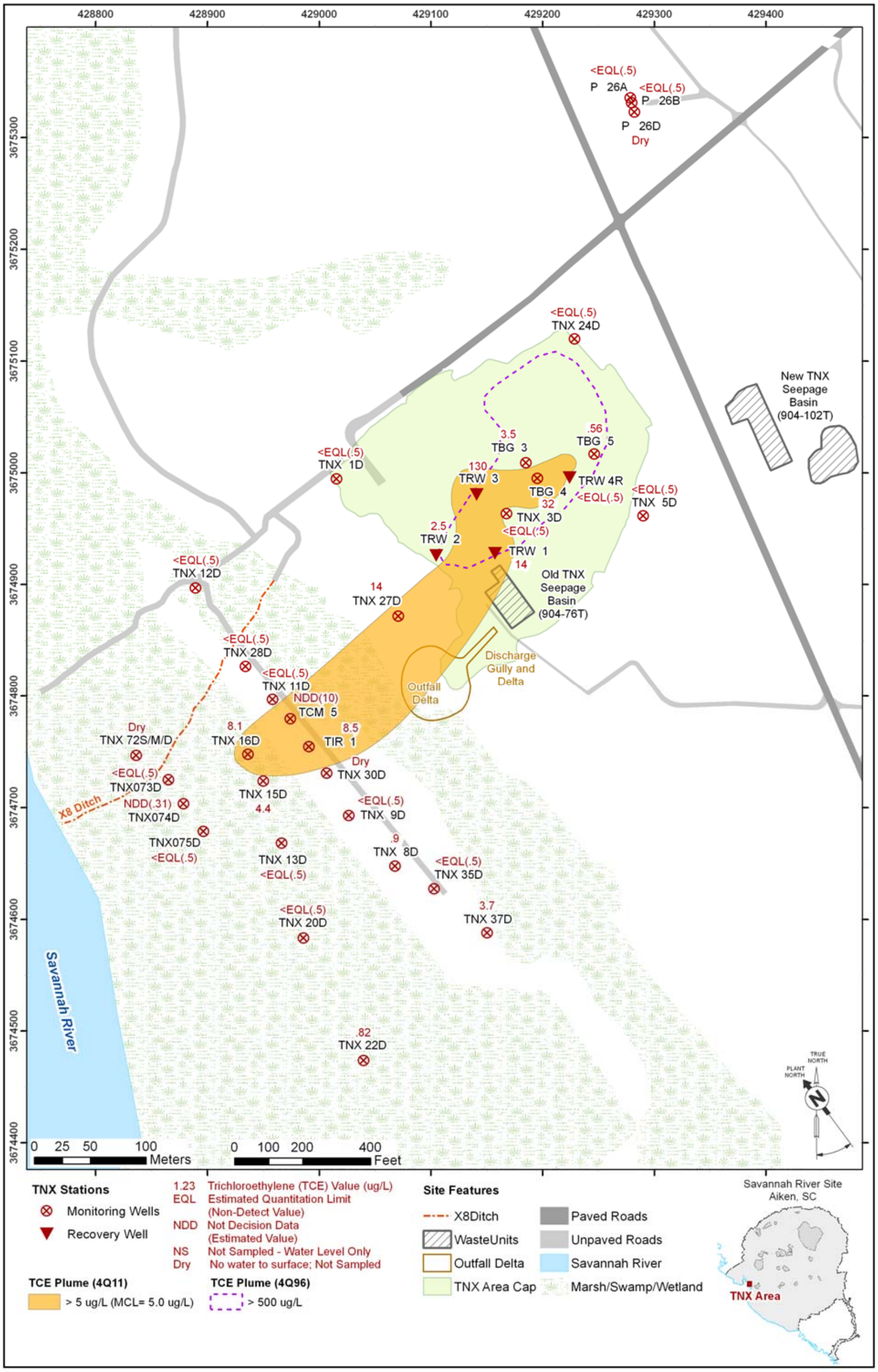

Figure 9 – TCE Concentration Plume after Amendment Injections (4Q11)

6.1 Individual Well Concentration Discussion and Plots

cVOCs and selected geochemical parameters are plotted for each of the twelve monitoring wells in Figure 10 through Figure 21. The wells are in order of groundwater flow (up-gradient to down-gradient). Note different scales and broken axes. The injection times are shown on each plot. In general, the black symbols should increase or remain elevated and the red and green symbols should decrease to support reductive dechlorination. Monitoring in wells TRW-1 and TRW-3 was begun June of 2009 as additional distal monitoring wells since it was impractical to install additional monitoring wells through the cap. Each well is discussed in Table 5.

Table 5 – Individual Well Discussion

Well	Discussion
TBG-5 Injection Well	TCE has decreased from approximately 600 µg/l to less than 5 µg/l . cis-DCE is increasing proving reductive dechlorination of TCE. Vinyl chloride (J value) and ethene have been detected. TOC has remained elevated. pH has increased from near 5 to 6 and is remaining stable. DO remains low and the increase indicated from 7/08 through 3/09 is likely a sampling artifact from drawing water down in the casing during sampling. Methane has remained elevated. Well production rate continued to decrease with time likely due to bio-fouling of the screen. An attempt to redevelop this well was not very successful. Low flow sampling (bladder pump) is now being used on this well and is providing representative samples.
TVM-1M Monitoring Well	This well was impacted briefly during the injection into TRW-4R. TCE concentrations remained around 5 µg/l after injections but are currently averaging around 100 µg/l and cis-DCE and ethene are present. TCE concentrations remain below pre-injection concentrations (~250 µg/l). Up-gradient injectants from TBG-5 appear to have started impacting this well around 9/09 based on increases of methane and TOC and a decrease in DO. Groundwater associated with this well will move into the treatment zone associated with injection well TRW-4R.
TRW-4R Injection Well	TCE has decreased from approximately 50 µg/l to less than 5 µg/l and cis-DCE and ethene are present. TOC was elevated and then decreased significantly but remains in the 3-5 mg/l range. pH has increased from near 5 to above 6. DO remains near 0 mg/l but the positive ORP does not indicate reducing conditions. Methane remains high. This well was a pump and treat well and sampling is being conducted from a 40 ft screen that likely impacts the analytical results.
TVR-1A Monitoring Well	TCE remained below 5 µg/l until higher concentration groundwater moved past the well from 12/08 to 1/09. TCE concentrations were sporadic and have remained below 5 µg/l for over a year. cis-DCE and ethene are present indicating reductive dechlorination. TOC was elevated and then decreased but remains around 20 mg/l. pH has increased from near 5 and remains around 6. DO remains around 0 mg/l and ORP is remaining low indicating reducing conditions. Methane was increasing and has remained relatively stable.
TVM-2M Monitoring Well	TCE has decreased from approximately 20 µg/l to around 0 µg/l. cis-DCE and ethene are present and there are periodic increases in TCE, cis-DCE and ethene. TOC has remained elevated. pH has increased from near 5 and remains between 6-6.5. DO remains near 0 mg/l and ORP is negative indicating reducing conditions. Methane is currently near or above solubility. This zone should provide reductive dechlorination and progression and growth of *Dehalococcoides* (DHC) however, little TCE (growth substrate) is present for growth.

(continued on next page)

Table 5 – Individual Well Discussion (continued)

Well	Discussion
TVM-4M Monitoring Well	TCE remains less than 5 µg/l. cis-DCE and ethene are present. This well does not appear to have been impacted directly by the oil injections but DO and ORP have decreased and methane is increasing indicating amendments are now impacting this area.
TBG-4 Monitoring Well then Injection Well	TCE increased from approximately 30 µg/l to approximately 300 µg/l and cis-DCE is present. Increases in concentrations in TBG-4 indicate injections in TRW-4R moved contaminated water towards TBG-4 although groundwater mounding was not evident in TBG-4. Additional emulsified oil and amendments were injected into this well in May 2010. After injections, TCE decreased from about 300 µg/l to an average of 20 µg/l . cis-DCE, vinyl chloride and ethene indicate full reductive dechlorination by DHC. However, DHC were not detected by qPCR analyses likely due to sample volume. The high DO and ORP immediately after injections are sampling artifacts and low flow sampling is now being employed. The high pH is an artifact of the solid buffer that likely remained in the sump and/or sand pack after the injections. The pH is lower in the formation around the well or the reductive dechlorination pathway would not be occurring at that high of a pH. Methane and TOC are increasing.
TBG-3 Monitoring Well	This well was not directly impacted by any of the injections. TCE has ranged between 0 and 35 µg/l but increased significantly to 160 µg/l during the 2/10 to 7/10 sampling events. This increase is directly correlated to a rise in the water table indicating contact with contaminants in the capillary fringe (smear zone). TCE fluctuations will likely continue to occur with fluctuations in the water table over time. This well has been impacted by the carbon addition from the neat soybean oil based on the increase in methane and TOC and indicates the structured geochemical zones continue to evolve as designed. The only practical way to treat contamination remaining in the smear zone is to allow it to be degraded once it moves into the groundwater.
TNX-3D Injection Well	TCE has decreased from approximately 20 µg/l to less than 5 µg/l and has remained below 5 µg/l . cis-DCE increased and decreased and ethene is present indicating reductive dechlorination. Low level VOCs were analyzed (December 2009) by a contract laboratory and 0.75 µg/l of vinyl chloride was measured. TOC has decreased but remains around 25 mg/l. pH has increased from near 5.5 and remains near 6. DO and ORP remain low. Methane remains elevated. Sampling of this well immediately after injections was delayed due to a delay in pump installation.
TRW-2 Distal Monitoring Well	TCE increased from approximately 10 µg/l to 100 µg/l and declined towards 5 µg/l. This increase may be due to rebound after shutting down the pump and treat system but does not correlate with groundwater levels. Up-gradient degradation processes may play a role in the concentration decrease. This well has now been impacted by the carbon addition based on the increase in methane and TOC and a decrease in DO and indicates the structured geochemical zones continue to evolve as designed.
TRW-1 Distal Monitoring Well	TCE is fluctuating and remained below 20 µg/l and is currently approaching 5 µg/l . The increase in 2011 could be attributed to dissolved plume movement during the injection into TBG-4 in May of 2010. This well has now been impacted by the carbon addition based on the increase in methane and TOC and indicates the structured geochemical zones continue to evolve as designed. This well was added as a distal monitoring well in June 2009 and was one of the pump and treat wells.

(continued on next page)

Table 5 – Individual Well Discussion (continued)

TRW-3 Distal Monitoring Well	TCE increased to approximately 200 µg/l, decreased to approximately 25 µg/l in 2010 and increased again to approximately 130 µg/l in 2011. TCE is declining in 1Q12. This increase may be due to rebound after shutting down the pump and treat system. The increase in 2011 could also be attributed to dissolved plume movement during the injection into TBG-4 in May of 2010. It is difficult to interpret if the water level fluctuations or up-gradient degradation process are the cause of the TCE concentration fluctuation. This well has now been impacted by the carbon addition based on the increase in TOC and methane. This well was added as a distal monitoring well in June 2009 and was one of the pump and treat wells.

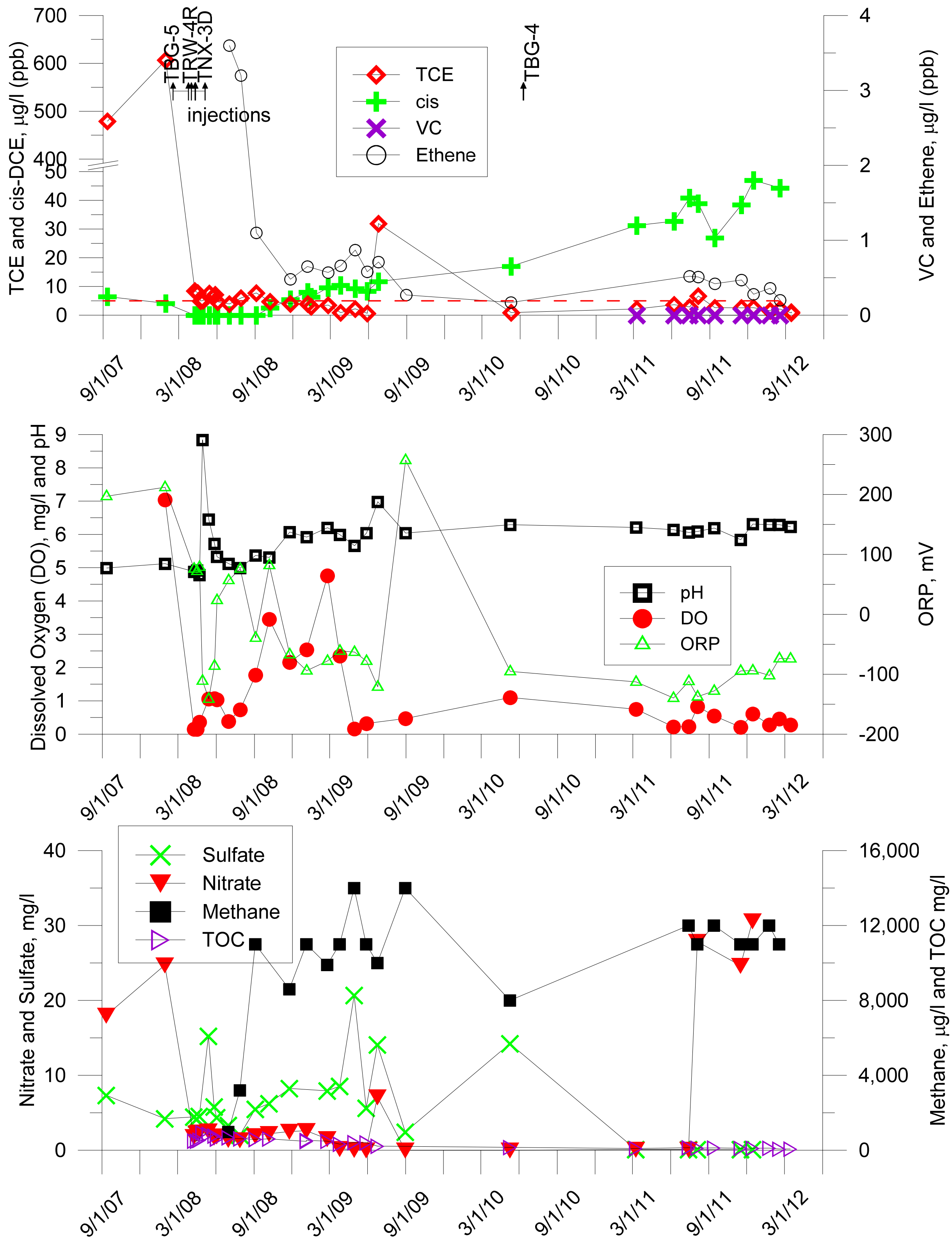

Figure 10 – Analytical Results for TBG-5 (Injection Well)

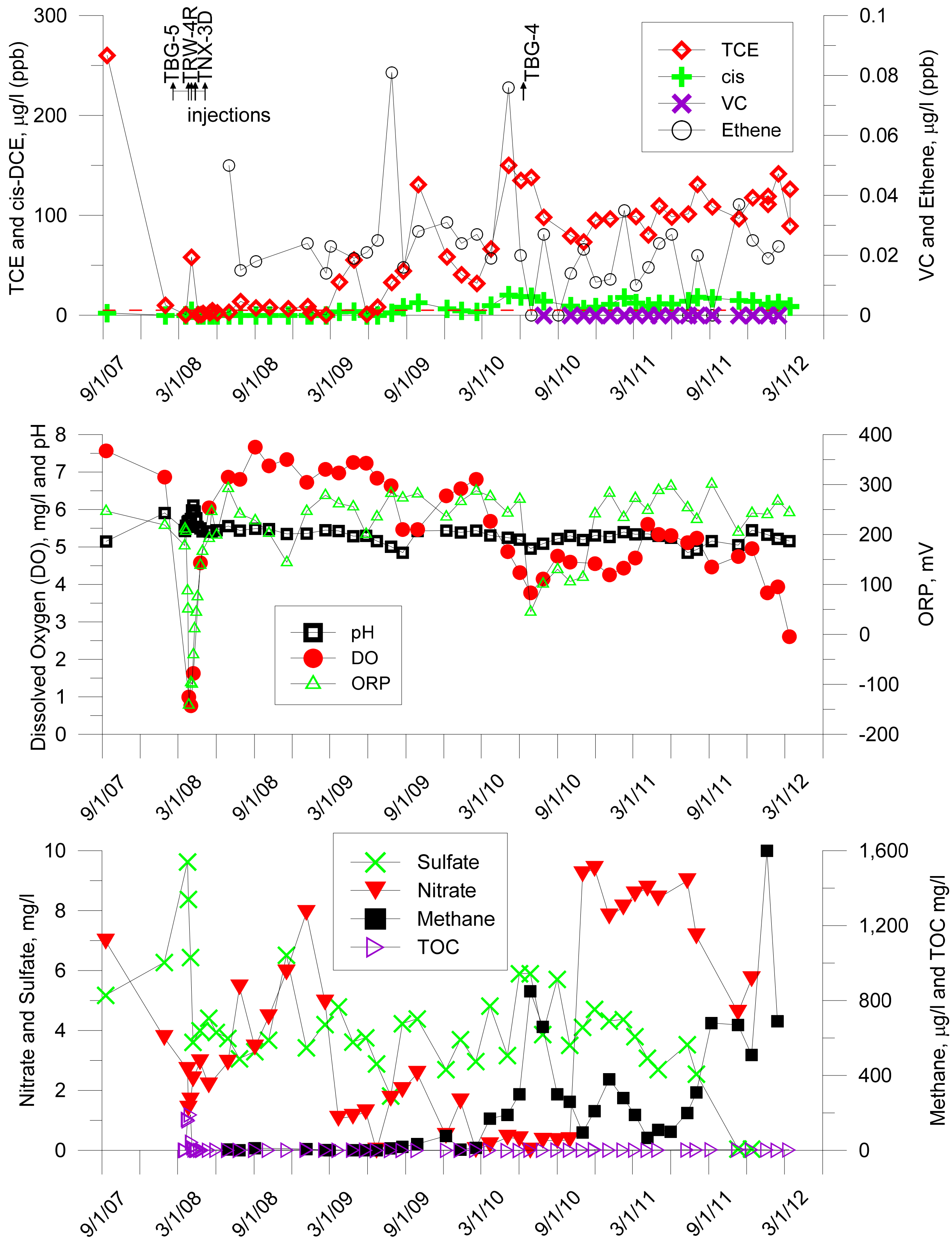

Figure 11 – Analytical Results for TVM-1M (Monitoring Well)

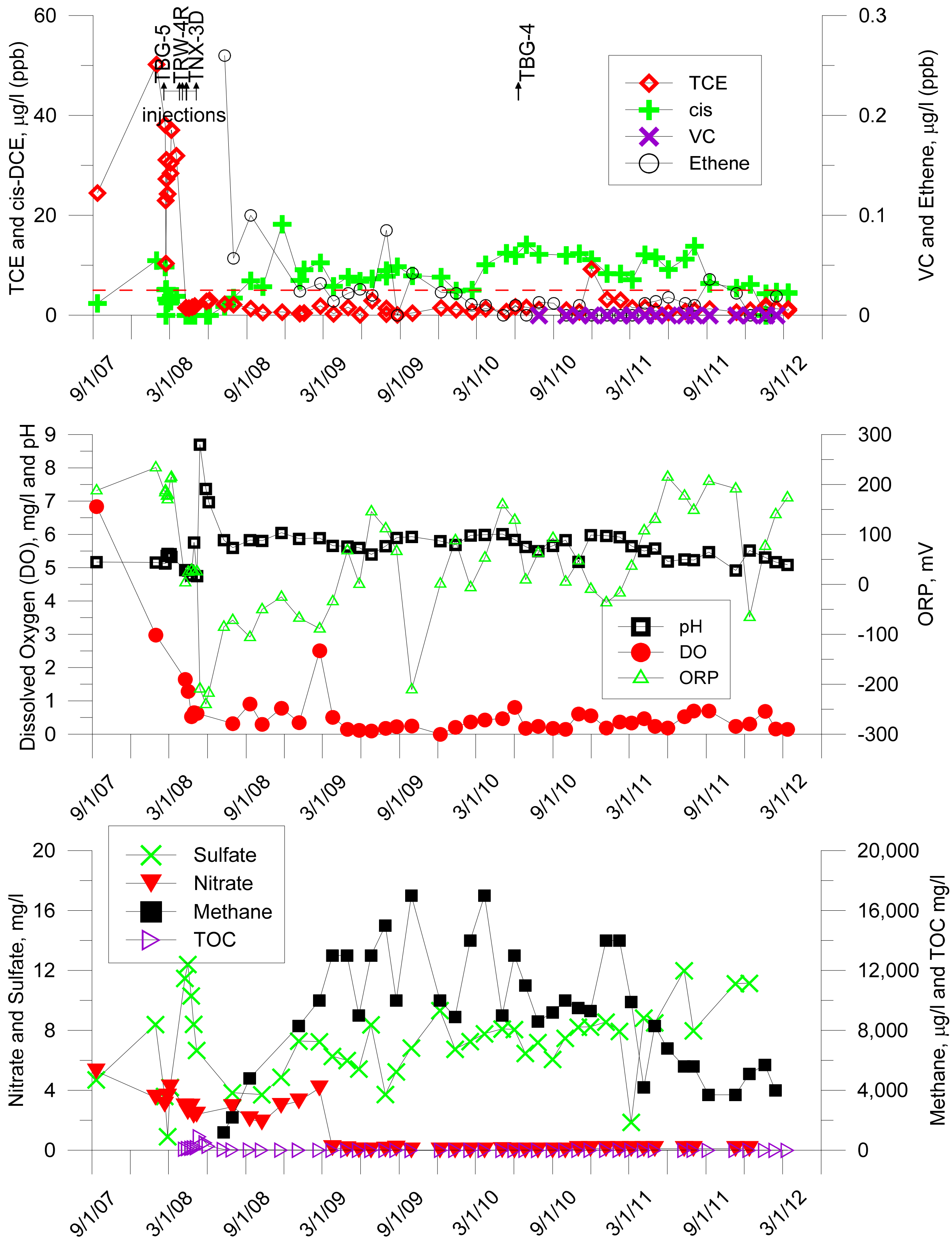

Figure 12 – Analytical Results for TRW-4R (Injection Well)

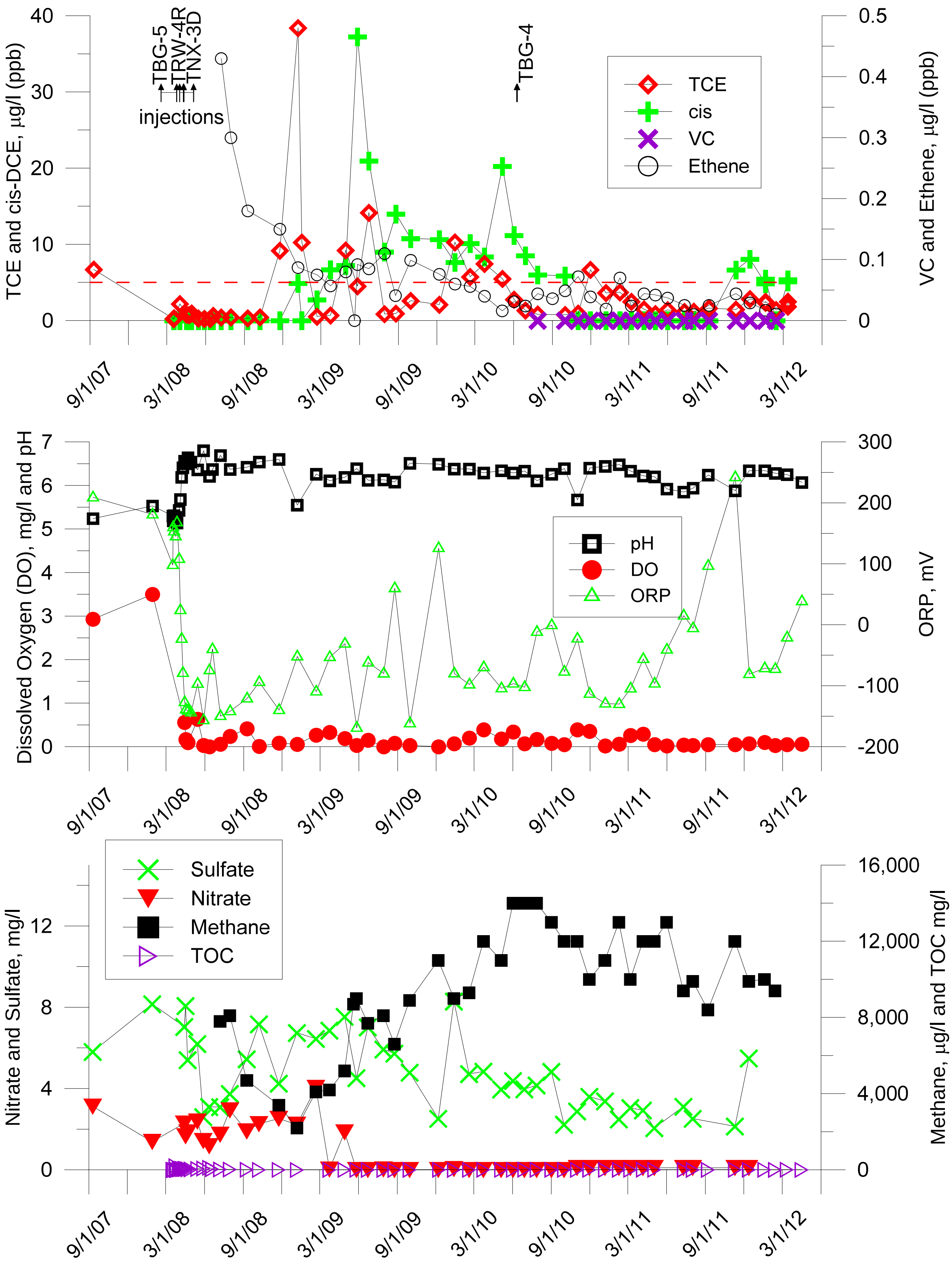

Figure 13 – Analytical Results for TVR-1A (Monitoring Well)

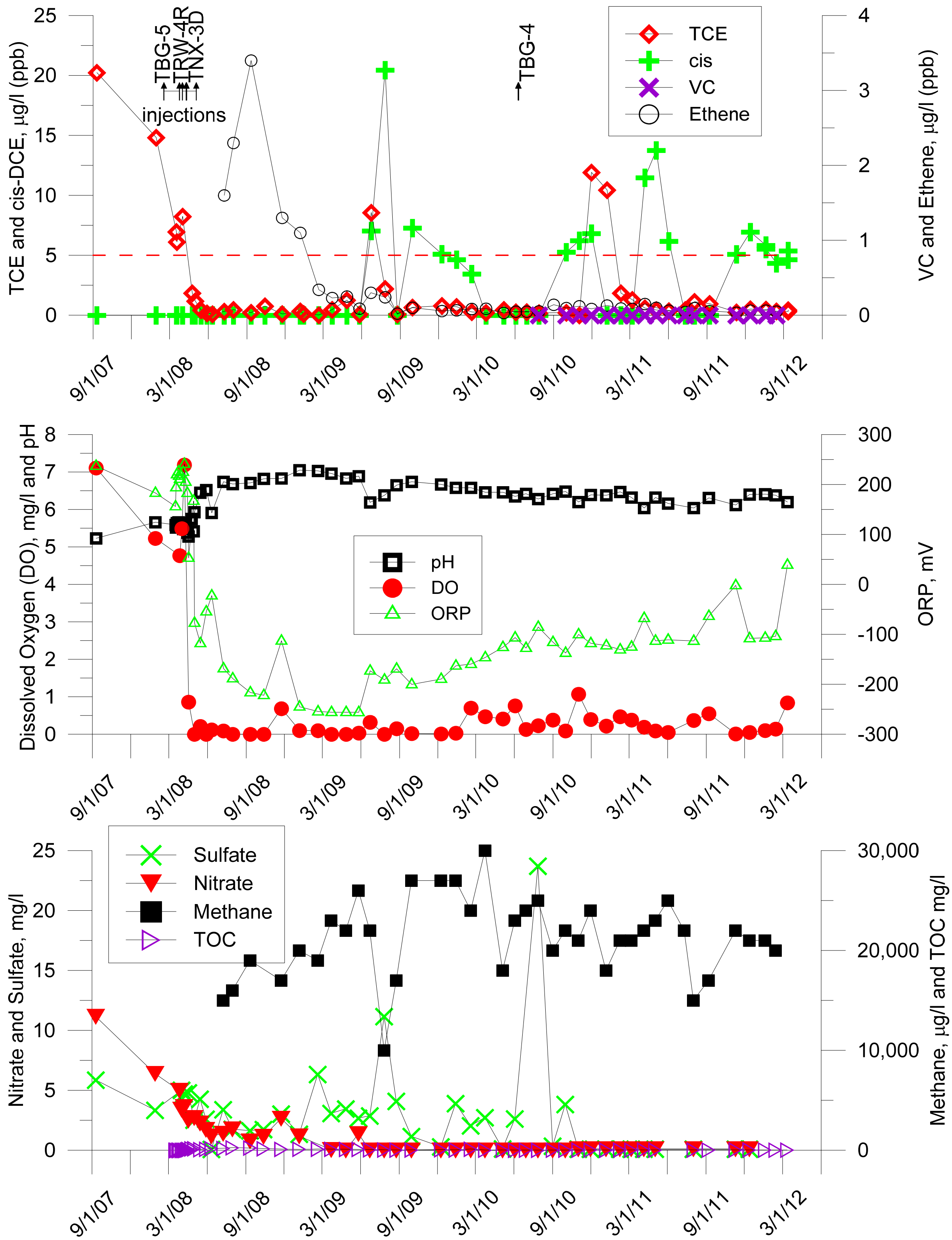

Figure 14 – Analytical Results for TVM-2M (Monitoring Well)

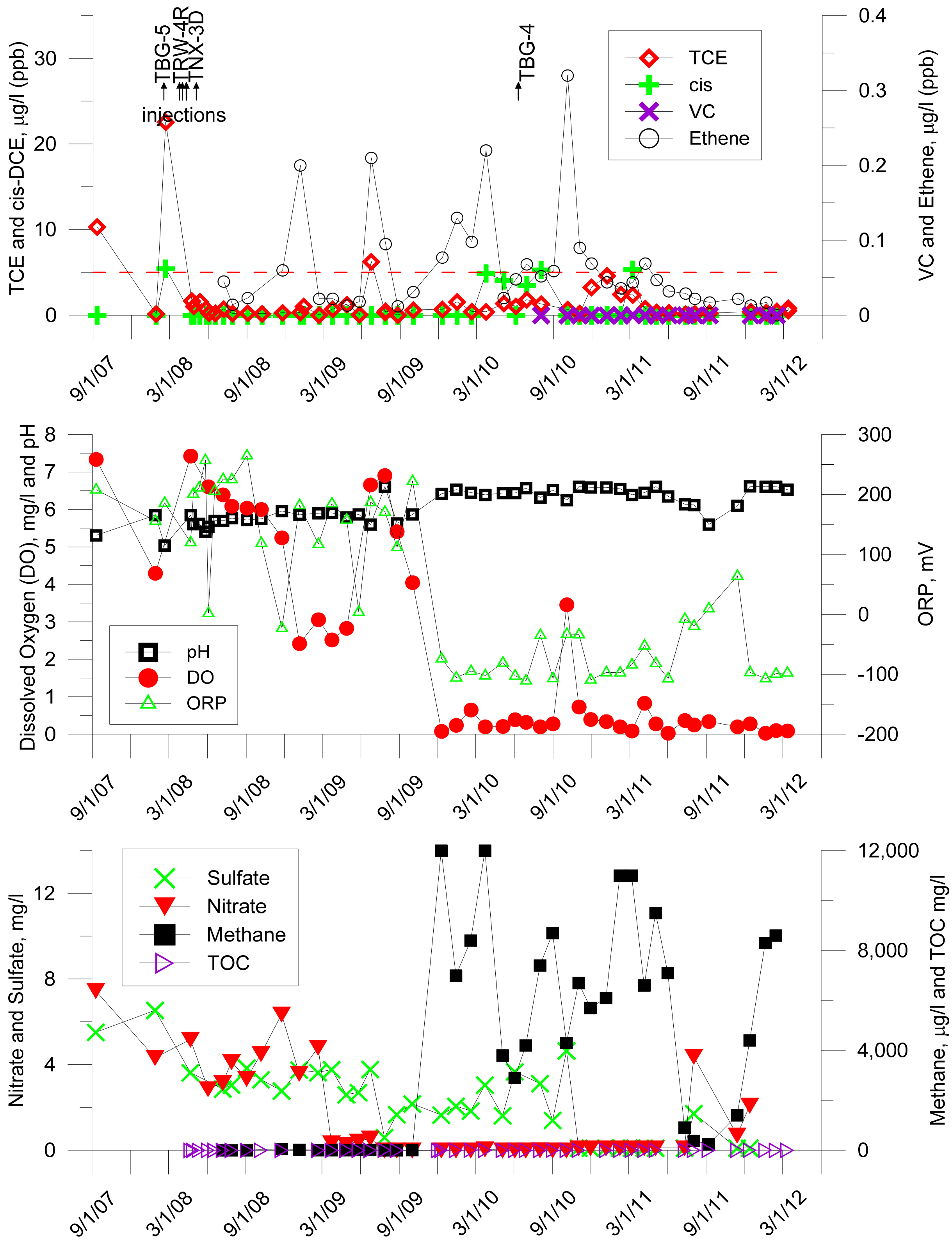

Figure 15 – Analytical Results for TVM-4M (Monitoring Well)

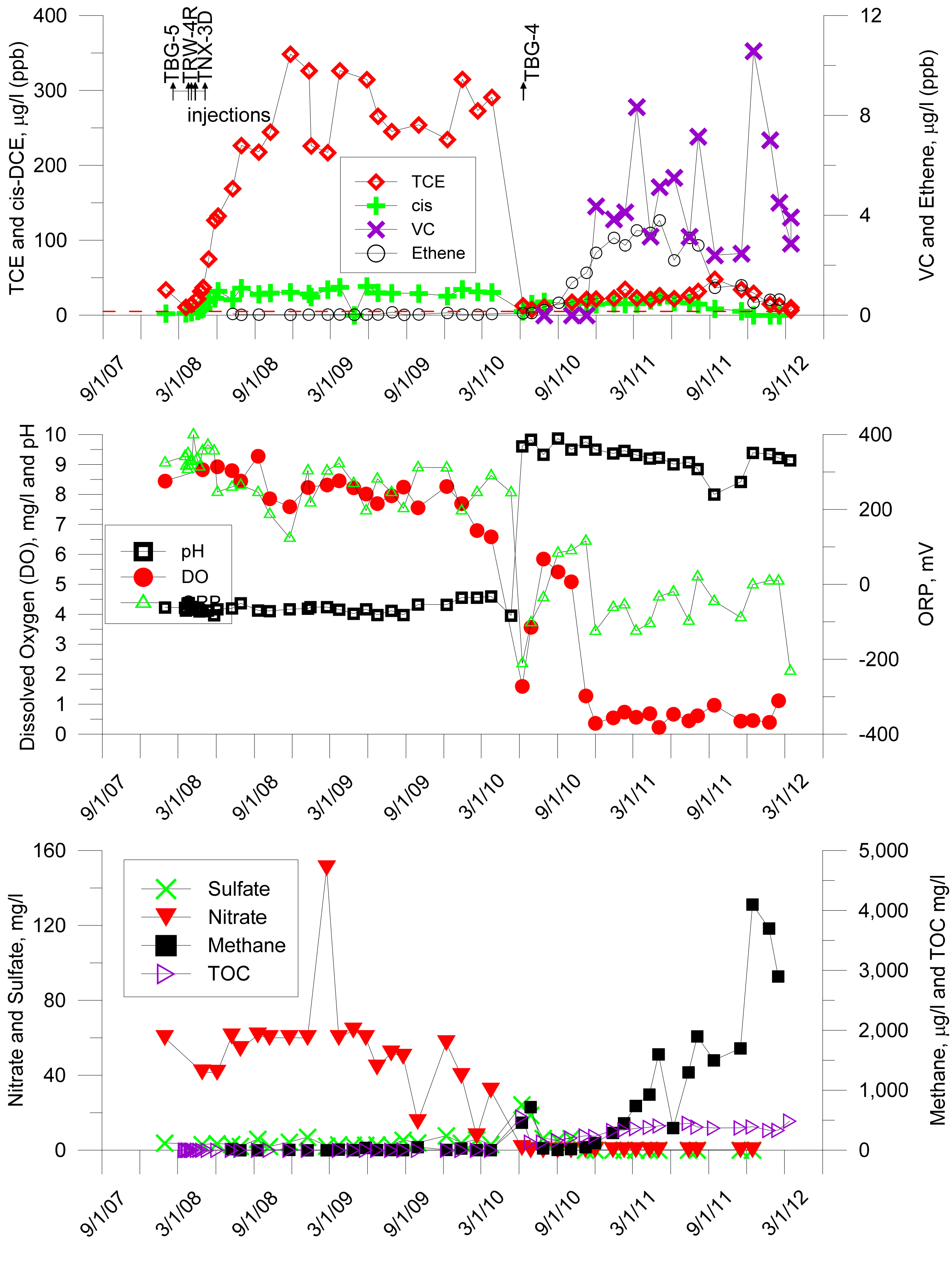

Figure 16 – Analytical Results for TBG-4 (Monitoring Well/Injection Well)

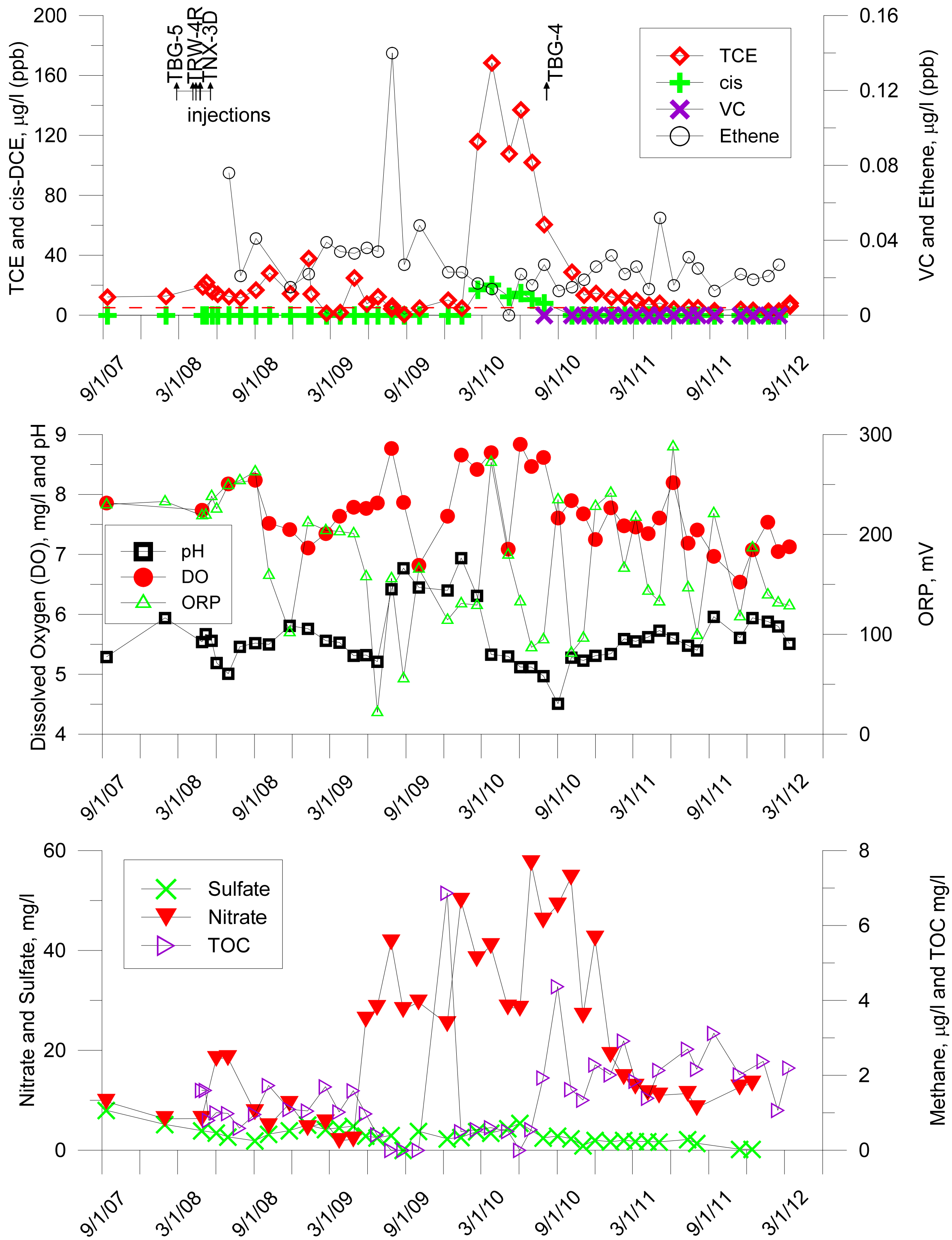

Figure 17 – Analytical Results for TBG-3 (Monitoring Well - Background)

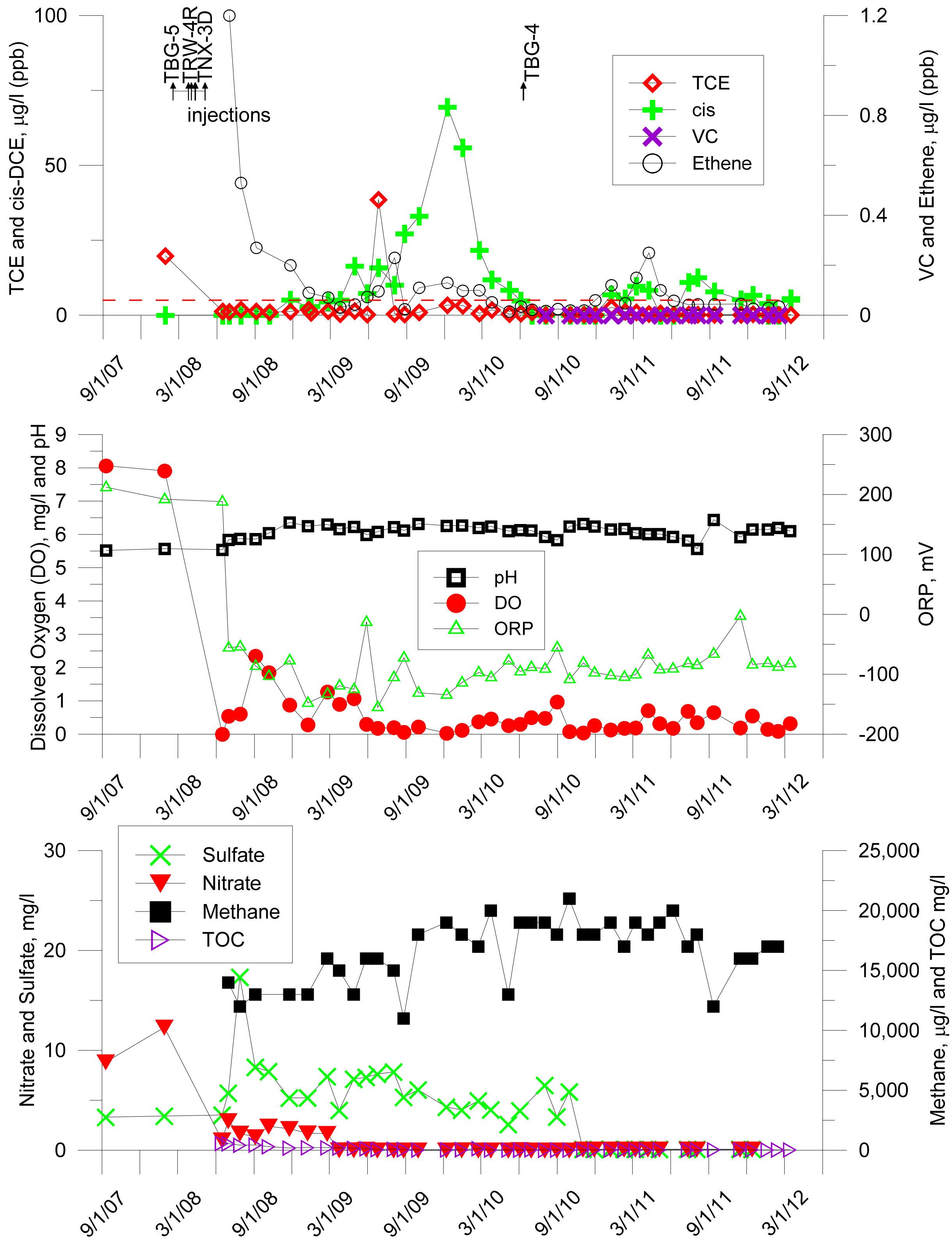

Figure 18 – Analytical Results for TNX-3D (Injection Well)

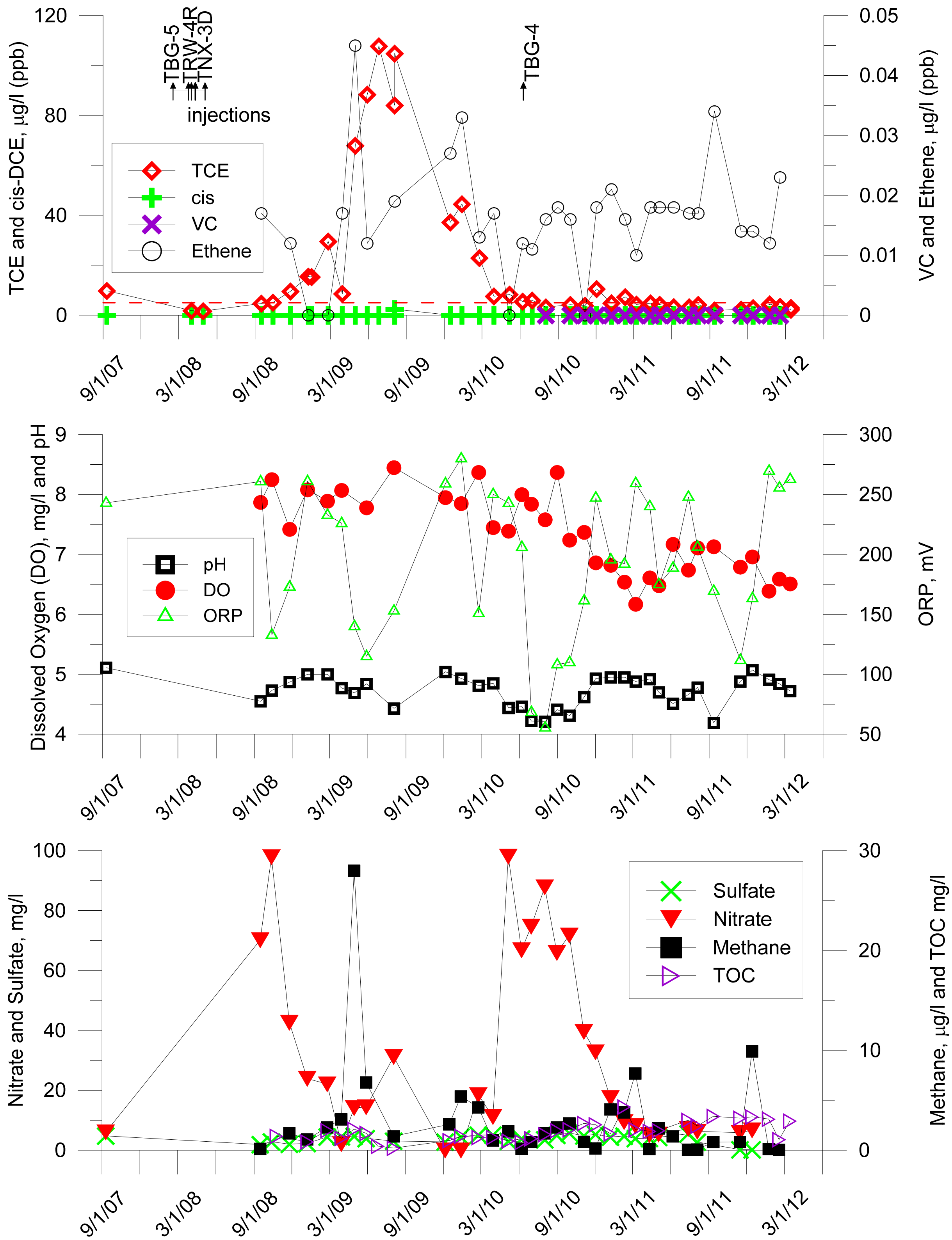

Figure 19 – Analytical Results for TRW-2 (Distal Monitoring Well)

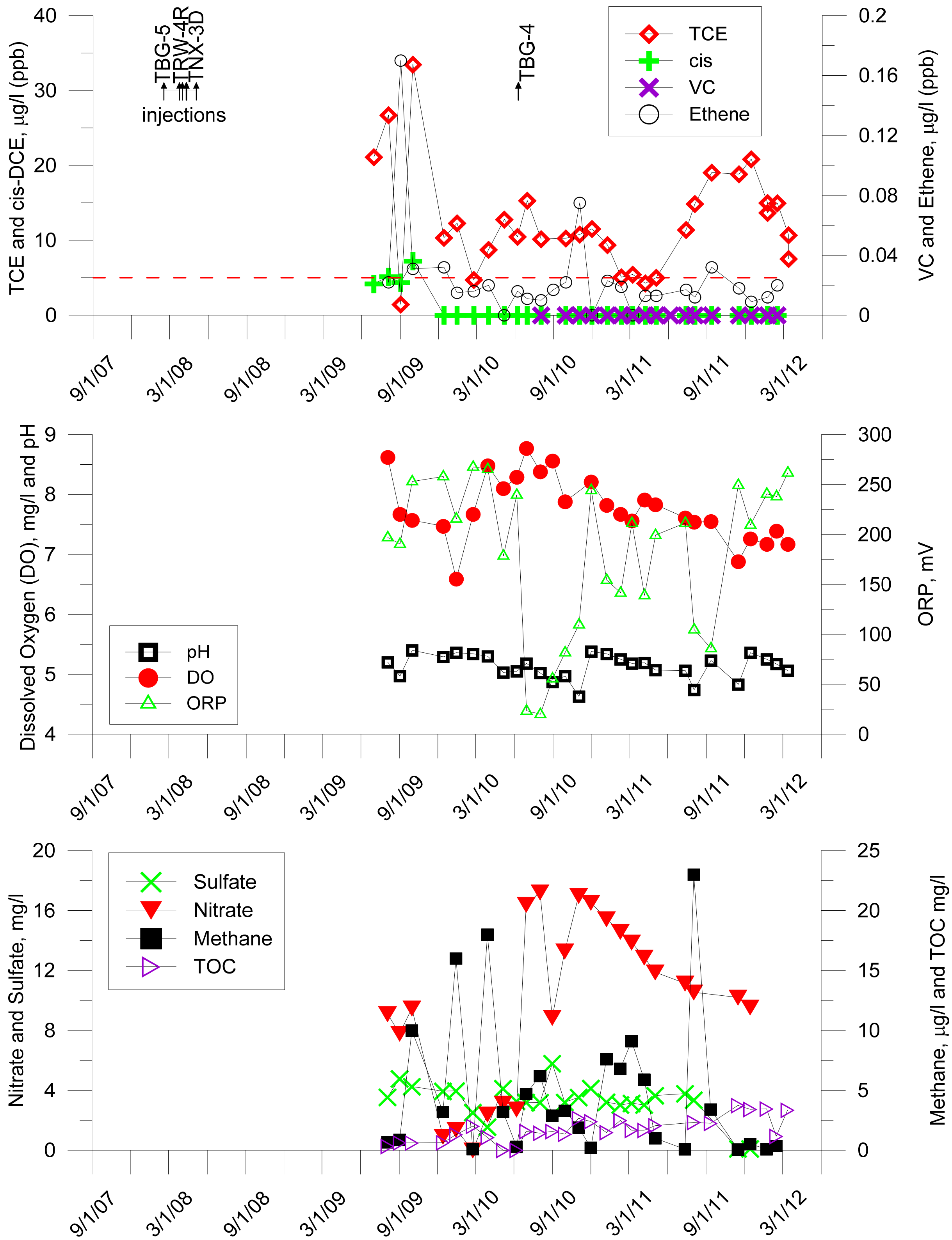

Figure 20 – Analytical Results for TRW-1 (Distal Monitoring Well)

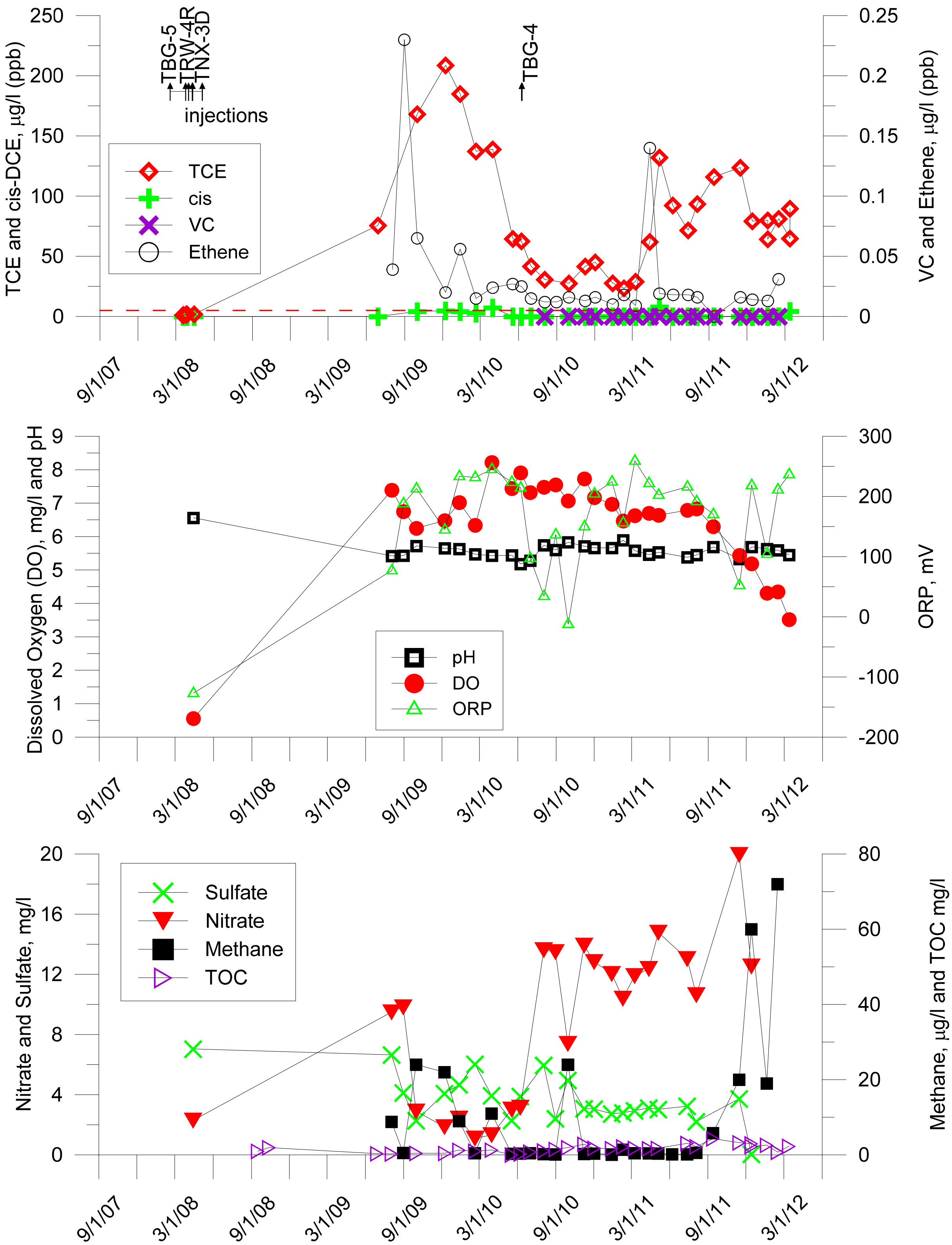

Figure 21 – Analytical Results for TRW-3 (Distal Monitoring Well)

7. ATTENUATION MECHNISMS AND EFFECTIVENESS

The overall effectiveness of the edible oil treatment will be discussed in terms the lines of evidence similar to those needed to evaluate the potential efficacy of monitored natural attenuation (MNA) as a potential corrective measure. The authors believe this will be the most appropriate means to evaluate the remediation using edible oils at T-Area and to determine if any contingency measures are needed in the future.

First Line of Evidence: Historical groundwater data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time and the presence of daughter products at appropriate monitoring points. This typically includes graphical techniques using the contaminant monitoring data and statistical tests such as the Mann-Kendall test.

Second Line of Evidence: Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. Example analytes include competing electron acceptors (e.g., oxygen, sulfate and nitrate), helpful electron donors (e.g., hydrocarbons and hydrogen), and diagnostic indicators/byproducts (e.g., methane and iron). Other destruction mechanisms such as cometabolism, anaerobic and aerobic oxidation, abiotic degradation and the like are not fully addressed in the typical interpretation of data collected to support the second line of evidence.

Third Line of Evidence: Other information such as data from field or microcosm studies which directly demonstrate or quantify the occurrence of a particular natural attenuation process and ability to degrade contaminants of concern.

7.1 First Line of Evidence: Mass and Concentration Trends

7.1.1 Time/Mass Plot

An estimate of total mass in the plume was assessed based on plume dimensions and average concentrations during five time periods. Time period 4Q07 is immediately prior to the edible oil injections. The estimate assumed TCE contamination to a depth of 20 ft in the aquifer and a porosity of 0.3. Table 6 provides the areas measured from plume maps and the corresponding estimated total mass. The estimated mass in the plume has decreased by approximately 90% from 2.73 kg in 4Q07 prior to the treatment to 0.27 kg in 4Q11.

A mass over time rate constant (k_{mass}) was derived as the slope of the natural log of mass versus time. This rate constant provides information on the potential plume lifetime. The k_{mass} in units of time^{-1} is simply a first order decay constant and it allows projection of the mass in the plume. The k_{mass} is representative of both attenuation processes (e.g., abiotic or biological degradation) and, in some cases, an exhausted or depleted source. The k_{mass} can be used to estimate the time required to reach a remediation goal (method adapted from (Newell, Rifai et al. 2002)).

Based on this analysis, $k_{mass} = -1.38 \times 10^{-3}$ day^{-1} with a half-life of 1.4 years (Figure 22). Although the authors concede this is an estimate and longer term monitoring is warranted, we estimate TCE concentrations throughout the plume will be below 5 µg/l within 7 to 10 years.

Table 6 – Contoured Areas used to Calculate Mass from Plume Maps

Date	Area (ft^2) 5 µg/l	Area (ft^2) 50 µg/l	Area (ft^2) 100 µg/l	Area (ft^2) 500 µg/l	TCE Mass (kg)
9Q07	316,262	37,512	72,826	2,637	2.733
4Q08	28,693	7,208	4,958	NA	0.662
2Q10	402,129	31,837	NA	NA	0.667
4Q10	289,151	NA	NA	NA	0.422
4Q11	81,627	NA	NA	NA	0.265

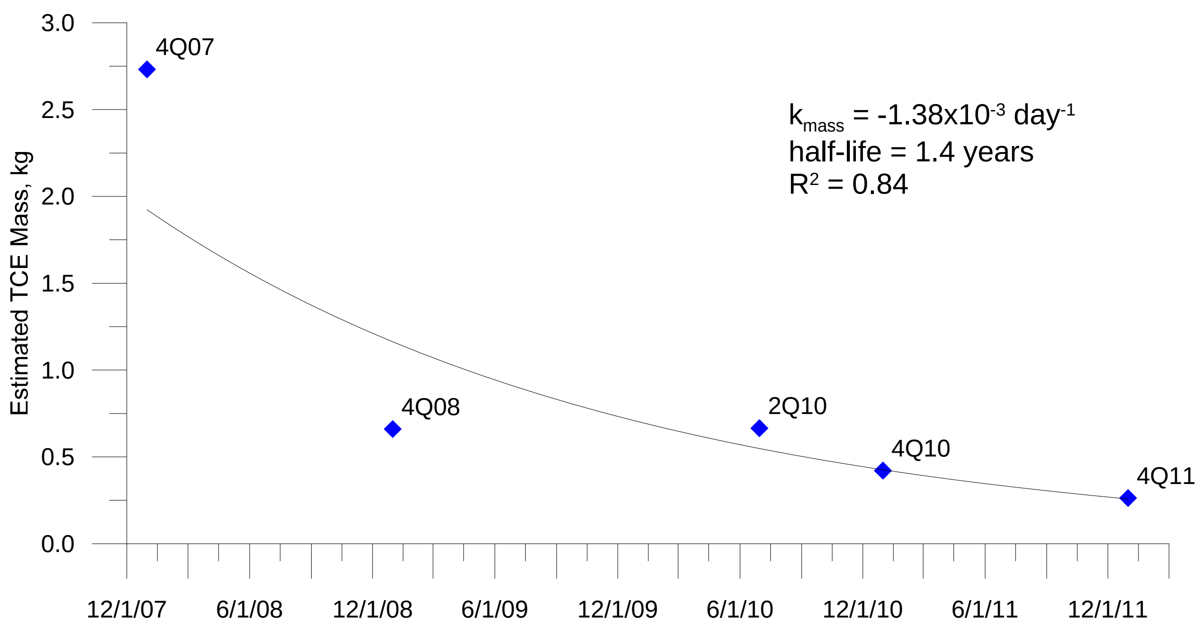

Figure 22 – Estimated TCE Plume Mass Reduction and Rate

7.1.2 Individual Well Statistical Tests

Mann Kendall (MK) and linear regression (LR) statistical testing were completed on analytical data since the shutdown of the pump and treat system in late 2007. Statistical tests were conducted using the software program MONITORING AND REMEDIATION OPTIMIZATION SYSTEMS (MAROS) (http://www.gsi-net.com/en/software/free-software/maros.html). Data collected and analyzed by SRNL included a limited number of wells (12) on the cap at T-Area and included monthly results for TCE with dates from 9/10/2007 to 1/24/2012). In addition, biannual data collected by SRS Area Closure Projects (ACP) for all wells were also statistically evaluated for TCE with dates from 5/19/2008 to 12/5/2011. Summary outputs from the statistical analysis are provided in Appendix A. For each data set, there is a summary report of the two statistical tests including the average concentration over the time period and a more detailed report for the Mann Kendall and linear regression tests that provide a confidence in the trend. The SRNL reports are titled "TNX SRNL" and the ACP reports are titled "TNX ERDMS".

Table 7 provides a summary of the trend analysis from 36 wells. The table includes the authors' interpreted 'trend' from the MAROS analysis, the 4Q07 and 4Q11 TCE concentration, the average and median TCE concentrations and the percent change in concentration from 4Q07 to 4Q11. Approximately 56% of the wells are decreasing (D) or probably decreasing (PD) and 19% had no detection and 14% are stable (S) or have no trend (NT). Approximately 11% (4) of the wells indicate increasing (I) trends however 3 of these wells are currently less than 5 µg/l . Although the statistics indicate TRW-3 has NT or is S, it is the only well indicating a significant increase in concentration. In 4Q11 approximately 75% of the wells were less than 5 µg/l compared to approximately 30% in 4Q07.

The concentration trend analyses are shown graphically on a map in Figure 23 that better illustrates the statistical trends with color coding to identify wells with greater or less than 5 µg/l TCE. The furthest down-gradient wells are all less than 1 µg/l and the majority of the wells just down-gradient of the cap are decreasing and less than 5 µg/l . The actual TCE concentration changes between 4Q07 and 4Q11 are displayed and contoured on a map in Figure 24. The greatest changes are evident in the up-gradient anaerobic treatment areas as would be expected since anaerobic degradation is a much faster biological process and the distal aerobic zones are still developing for cometabolism and other degradation processes. The up-gradient area also corresponds to the main source area of the plume and began with much higher concentrations.

Overall, the Mann Kendall and linear regression analyses can be deceiving for such a varied dataset that includes anaerobic and aerobic treatment zones and data that varies over orders of magnitude. This is particularly true for low concentration values and those with trace (TR) detects that can increase the noise in the data. Based on the combined statistical analysis, the areas in the vicinity of wells TRW-3 and TVM-1M warrant watching over time to determine if additional amendments are needed in these areas.

Summary – First Line of Evidence: Mass and Concentration Trends

The mass and concentration trends and statistical analysis show a decrease in plume strength and size. The time and mass estimation indicates a decrease in TCE mass of approximately 90% (2.73 kg to 0.27 kg) from 4Q07 to 4Q11 with a plume half-life of 1.4 years. TCE concentrations are expected to be below 5 µg/l within 7 to 10 years.

The statistical analyses indicate a primarily shrinking plume. In 4Q11 approximately 75% of the wells were less than 5 µg/l compared to approximately 30% in 4Q07. Based on the combined statistical analysis, the areas in the vicinity of wells TRW-3 and TVM-1M warrant watching over time to determine if additional amendments are needed in these areas.

Table 7 – Summary of Statistical Trend Analyses

Well ID	Trend	4Q07 TCE µg/l	4Q11 TCE µg/l	Difference µg/l	Average µg/l	Median µg/l	% Change
TBG 3	PD	12.7	2.6	-10.1	25	12	-79.5%
TBG 4	D	33.9	15.2	-18.7	120	36	-55.2%
TBG 5	D	735	0.56	-734.44	41	4	-99.9%
TCM 5	PD	37.2	10	-27.2	14	13	-73.1%
TIR 1L	D	4.36	0.41	-3.95	1.1	0.96	-90.6%
TIR 1M	D	13.5	5.6	-7.9	9.6	10	-58.5%
TIR 1U	D	15.5	8.5	-7	19	20	-45.2%
TNX 1D	D	0	0	0	0.34	0.25	N/A
TNX 3D	D	84.4	0.64	-83.76	2.4	0.27	-99.2%
TNX 8D	D	7.64	0.9	-6.74	1.6	1.5	-88.2%
TNX 9D	S	0.38	0	-0.38	0.29	0.25	-100.0%
TNX 11D	PD	1.87	0	-1.87	0.39	0.37	-100.0%
TNX 12D	ND	0	0	0	0	0	N/A
TNX 13D	PD	0	0	0	0.97	0.76	N/A
TNX 15D	PD	14	4.4	-9.6	11	10	-68.6%
TNX 16D	PD	11.2	8.1	-3.1	15	15	-27.7%
TNX 20D	D	2.71	0	-2.71	0.87	0.94	-100.0%
TNX 22D	PI	0.34	0.82	0.48	0.59	0.71	141.2%
TNX 24D	ND	0	0	0	0	0	N/A
TNX 27D	NT	40.1	14	-26.1	6.5	2.7	-65.1%
TNX 28D	NT	0	0	0	1.4	0.54	N/A
TNX 35D	D	3.44	0	-3.44	0.64	0.71	-100.0%
TNX 37D	PD	5.61	3.7	-1.91	4.2	4.4	-34.0%
TNX 72D	ND	0	0				N/A
TNX 72M	ND	N/S	N/S				N/A
TNX073D	ND	N/S	0				N/A
TNX074D	TR	N/S	0.31				N/A
TNX075D	ND	N/S	0				N/A
TRW 1	S	16.2	14	-2.2	9.6	8.6	-13.6%
TRW 2	D	5.21	2.5	-2.71	16	3.8	-52.0%
TRW 3	NT S	0.36	130	129.64	67	55	36011.1%
TRW 4R	D	20.6	0	-20.6	3.1	1.3	-100.0%
TVM 1M	I	260	119	-141	61	57	-54.2%
TVM 2M	D	20.2	0.5	-19.7	2.1	0.45	-97.5%
TVM 4M	I?	10.3	0.3	-10	1.2	0.54	-97.1%
TVR 1A	I?	6.7	2.4	-4.3	3.6	1.4	-64.2%

Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Sample (N/S); Not Applicable (N/A) - Not Applicable; No Detectable Concentration (ND) Trace - J value (TR)

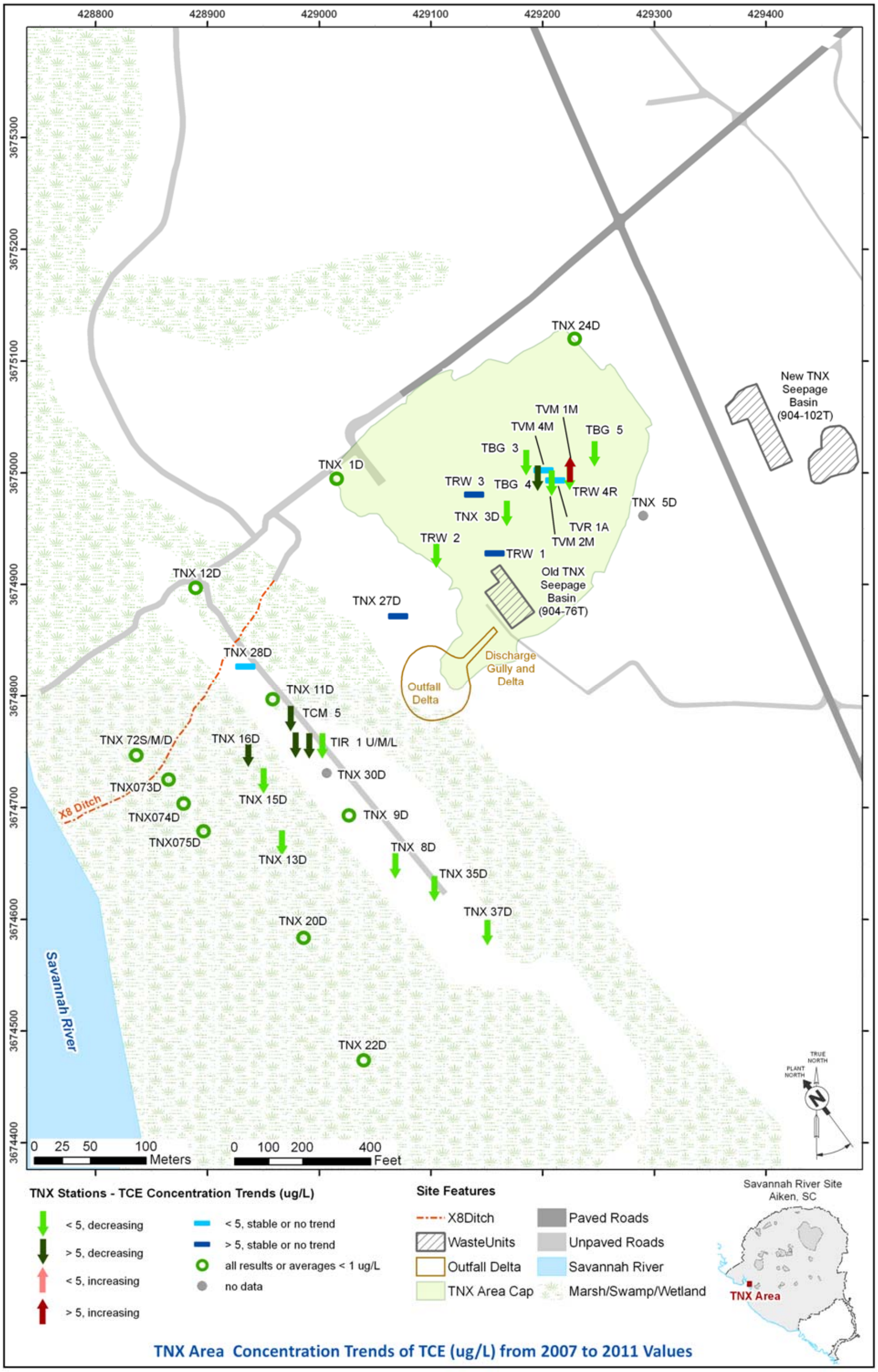

Figure 23 – Graphical Trends of TCE Concentration between 4Q07 to 4Q11

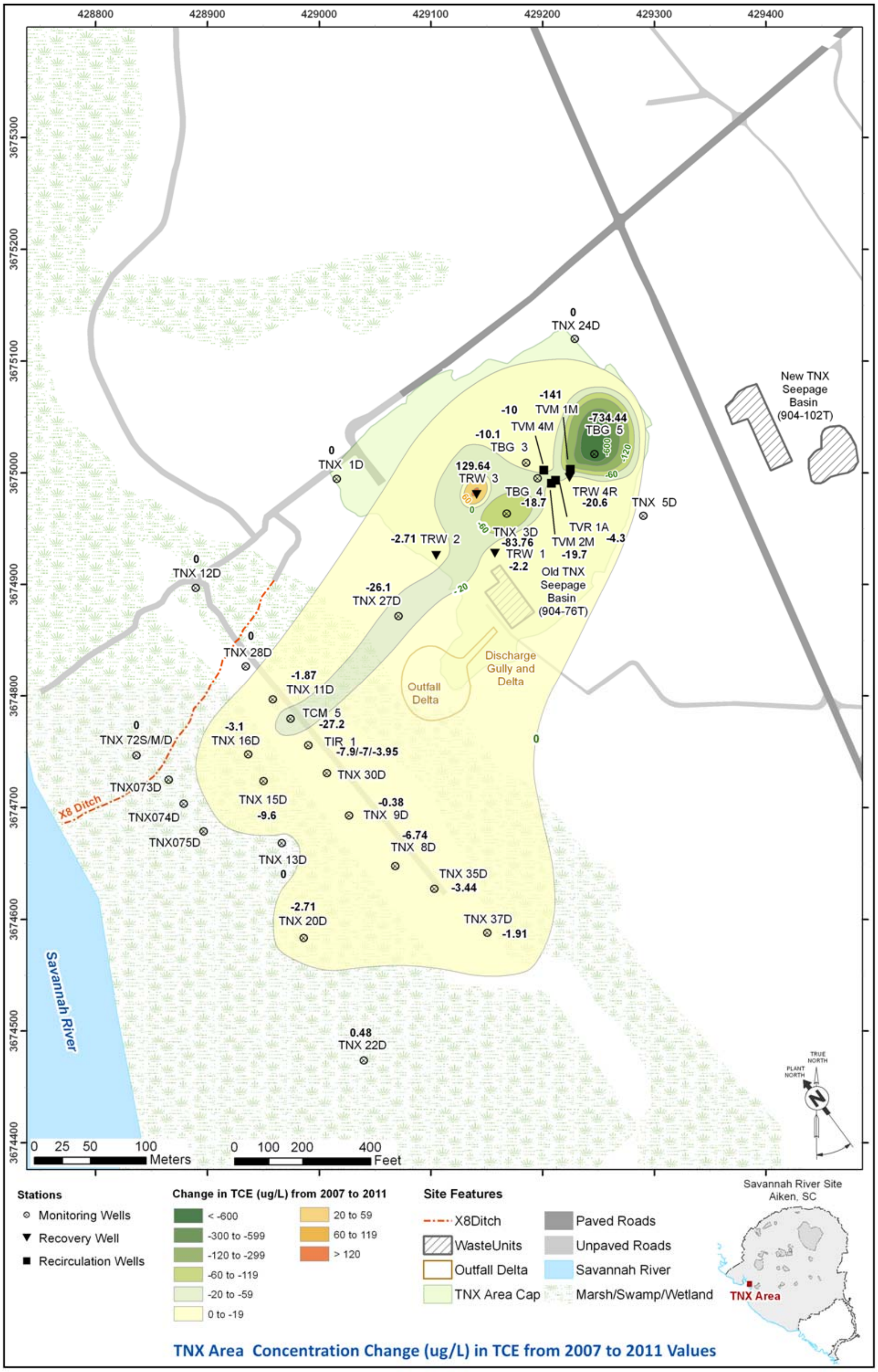

Figure 24 – Change in TCE Concentration between 4Q07 to 4Q11

7.2 Second Line of Evidence: Geochemical Footprint

Geochemical data indicate the presence of conditions conducive to reductive dechlorination and distal plume aerobic zone cometabolism and oxidation.

7.2.1 Reducing conditions:

Reductive dechlorination of TCE generally requires conditions reducing enough to promote methanogenesis (anaerobic respiration). Measurements that may indicate redox conditions include oxidation-reduction potential (ORP), dissolved oxygen, dissolved iron, nitrate, ammonia, sulfate and hydrogen.

- ORP: Low ORP is being maintained in the anaerobic treatment zones
- Dissolved Oxygen: Low dissolved oxygen is being maintained in the anaerobic treatment zones
- Methane: Methane has reached saturation levels in some wells in the anaerobic treatment zone
- Dissolved iron: High dissolved iron concentrations are indicative of reducing conditions at pH values of 5 to 8. Within this pH range, ferrous iron is far more soluble than ferric iron. Dissolved iron has been measured up to 200 mg/l in the anaerobic treatment zones.
- Ammonia: Under strongly reducing conditions, microbial reactions will convert nitrate to ammonia. Ammonia has been measured up to 150 mg/l and nitrate has declined in the anaerobic treatment zones.
- Sulfate: The presence of dissolved sulfate in groundwater may inhibit reductive dechlorination of solvents. Sulfate has been reduced in the anaerobic treatment zones
- Hydrogen: sampling for hydrogen was not conducted
- Oder and orange colored water (dissolved iron) from wells in the anaerobic treatment zone is indicative of reducing conditions

7.2.2 Cometabolism conditions:

The literature clearly shows the ability of aerobic cometabolism to remediate low solvent concentrations (< 1 mg/l TCE) in groundwater to non-toxic end products (CO_2 and Cl^-). Cometabolic bioremediation relies on a primary substrate (electron donor) dissolved oxygen (electron acceptor), nutrients and the appropriate microorganisms. Cometabolic organisms for TCE destruction use other growth substrates (TOC, methane, propane, butane, ethene, ammonia, etc.) to produce enzymes capable of degrading TCE to the end product CO_2 (Arp, Yeager et al. 2001).

- TOC, methane and ammonia are increasing in the down-gradient aerobic zones
- Dissolved oxygen is decreasing slightly in the down-gradient zones but is not expected to decrease below levels to support cometabolism

Summary – Second Line of Evidence: Geochemical Footprint

The geochemical conditions are currently favorable to sustain the anaerobic reductive dechlorination zones and aerobic degradations zones as described in Figure 1and Figure 2. Reducing conditions are evident by methanogenesis conditions including low ORP, DO, sulfate and nitrate and higher methane, iron and ammonia. TOC, methane and ammonia are increasing in the distal aerobic treatment zone to support cometabolism.

7.3 Third Line of Evidence: Demonstration of Attenuation Processes

The third line of evidence uses data from field or microcosm studies which directly demonstrate or quantify the occurrence of a particular attenuation process and/or the ability to degrade contaminants of concern.

7.3.1 Reductive Dechlorination

The results indicate that TCE reductive dechlorination is occurring. The pathway for this mechanism includes the degradation of TCE to intermediates dichloroethene (DCE), vinyl chloride, and ethene. This microbial activity requires strongly anaerobic conditions and the presence of microorganisms possessing reductive dechlorination capability. If the correct microorganisms (*Dehalococcoides*) were not present, the degradation would be expected to stall at cis-DCE, however vinyl chloride and ethene are both present in the anaerobic zones. A consortium of bacteria with same net effect of *Dehalococcoides* may also be present in the structured geochemical zones leading to the degradation of TCE (refer to Figure 2).

7.3.2 Cometabolism

Co-metabolism is occurring. Activity dependent enzymes were detected in TRW-2 and show active although slow degradation in microcosm studies. The baseline half-life of TCE is measured at 30.8 years. (Lee, 2008). Methanogenic (MGN) and methanotrophic (MOB) bacteria were quite abundant prior to deployment (Riha, Looney et al. 2006). These rates should increase with the increased carbon and co-metabolite loading in the distal plume area that is now occurring.

7.3.3 Flux Reduction

Groundwater flow has significantly decreased in the heart of the plume since the installation of the cap (Figure 25). This reduces the down-gradient flux and provides longer residence times for degradation in the structured geochemical treatment zones.

Summary – Third Line of Evidence: Demonstration of Attenuation Processes

Three attenuation mechanisms have been documented. Reductive dechlorination is occurring in the anaerobic treatment zones based on the TCE daughter products cis-DCE, vinyl chloride and ethene. Cometabolism is likely occurring in the distal aerobic treatment zone based on activity dependent enzyme testing and the presence of methanotrophic bacteria. The TCE contaminant flux has been reduced down-gradient due to the installation of the cap and reduced infiltration. This allows a longer residence time for the contaminants in the anaerobic and aerobic treatment zones.

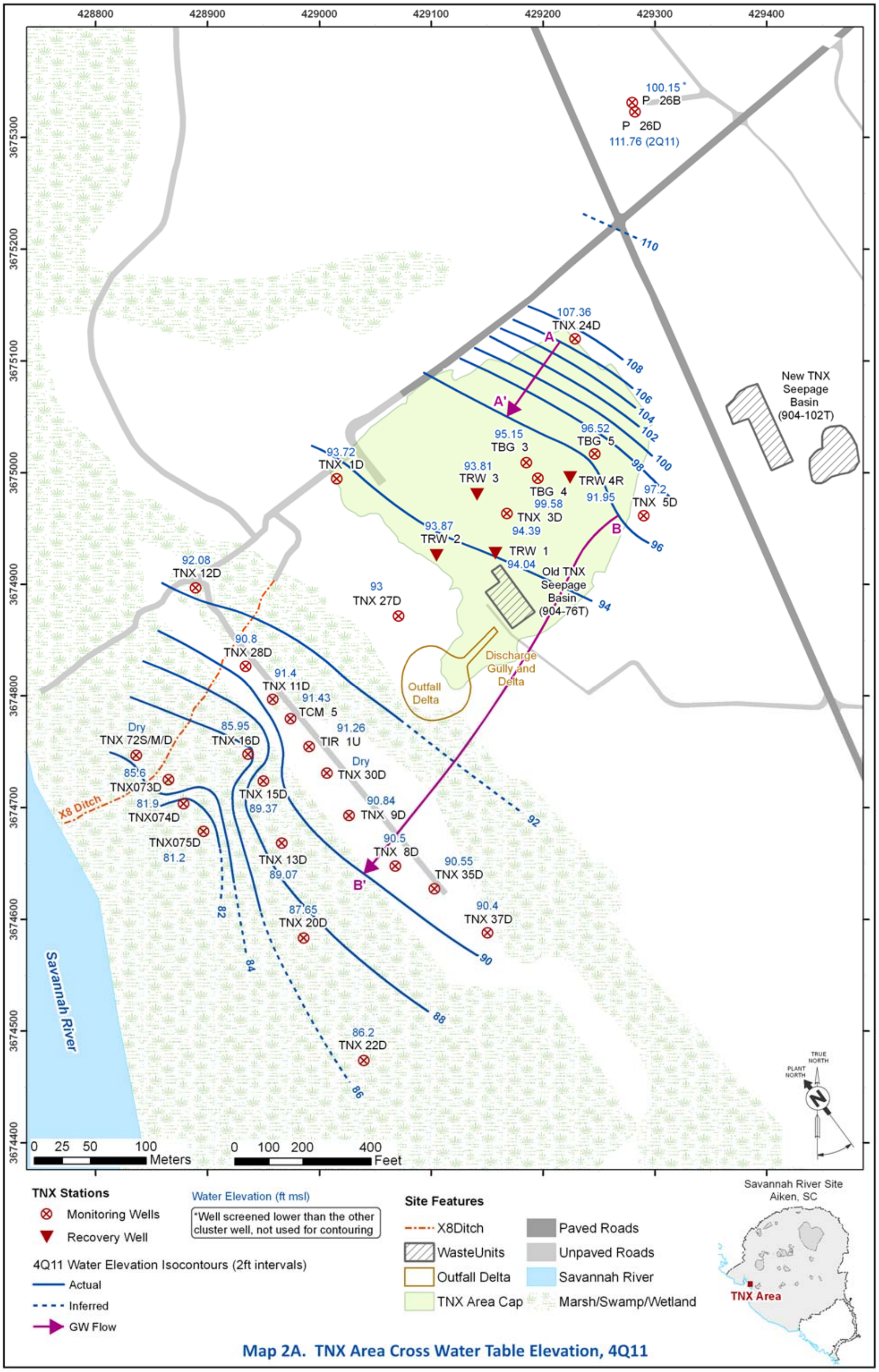

Figure 25 – 4Q11 Water Table Elevation

8. SUMMARY

The basis of the enhanced attenuation paradigm is to implement up-front active engineering solutions that alter the target site in such a way that the contaminant plume will passively stabilize and shrink and to document that the action will be effective, timely, and sustainable. The paradigm encourages combining remedial technologies so that each is matched to the target conditions and contaminant concentrations throughout the life of the site (until achieving regulatory goals). The combination of technologies that emerged for the treatability study for the remediation of T-Area included: 1) neat (pure) vegetable oil deployment in the deep vadose zone in the former source area, 2) emulsified vegetable oil deployment within the footprint of the groundwater plume, and 3) stimulation and documentation of aerobic attenuation for the distal portion of the plume. The following list summarizes the results from the first 4 years of the T-Area treatability study:

1. The dissolved TCE plume has decreased in size and mass – a measure of success in the enhanced attenuation and monitored natural attenuation paradigms:
    a. The estimated mass in the plume has decreased by approximately 90% from 2.73 kg in 4Q07 prior to the treatment to 0.27 kg in 4Q11
    b. The half-life of TCE in the plume is calculated to be 1.4 years
    c. Statistical tests indicate the TCE concentrations in the majority of the wells are decreasing
    d. It is estimated that TCE concentrations throughout the plume will be below 5 μg/l within 7-10 years
2. The central zone biogeochemistry is continuing to develop and appears sustainable to support reductive dechlorination and cometabolism of TCE,
3. Reductive dechlorination is evident based on daughter products and ethene,
4. Cometabolites (e.g. methane, ammonia, TOC) are being generated and distributed to stimulate aerobic attenuation in the distal plume zone,
5. There may be some isolated higher concentration areas (TRW-3 and TVM-1M) that may warrant further treatments.
6. Water table fluctuations may cause significant variability in concentrations in some wells,
7. The limited number and locations of available monitoring wells likely bias interpretations of the data.

Based on these results, the edible oil treatment is an appropriate and viable technology to complete the T-Area TCE remediation in a reasonable timeframe.

9. PATH FORWARD

The proposed path forward is to continue monitoring to focus on attenuation sustainability. The authors believe the treatment zones will continue to develop and that the edible oil addition and development of the structured geochemical zones is the appropriate remedy for the TCE contamination at T-Area.

The dissolved contaminants are easily treated at this time and would demonstrate the near complete degradation of the plume as part of the study. The following tasks are proposed.

1. Continue monitoring,
2. Revisit the lines of evidence as needed to determine if additional amendments are needed,
3. Observe TRW-3 and TVM-1M to determine if additional amendments are needed in these areas,
4. Perform analyses of geochemical parameters and dissolved gases in the down-gradient wells (wetland area) to evaluate attenuation mechanisms, and
5. After conditions stabilize, repeat enzyme activity probes for cometabolic organisms and perform a rate study to quantify enhancement at TRW-2.

10. REFERENCES

Arp, D. J., C. M. Yeager, et al. (2001). "Molecular and cellular fundamentals of aerobic cometabolism of trichloroethylene." Biodegradation 12: 81-103.

ITRC (2007). A Decision Flowchart for the Use of Monitored Natural Attenuation and Enhanced Attenuation at Sites with Chlorinated Organic Plumes, Interstate Technology and Regulatory Council, Enhanced Attenuation Chlorinated Organics Team.

Lee, M. H. (2008). Enzyme Activity Probe Microcosm Study: T-Area. Idaho Falls, ID, North Wind, Inc.

Newell, C. J., H. S. Rifai, et al. (2002). Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation. Ada, OK, U. S. Environmental Protection Agency.

Riha, B. D. and B. B. Looney (2007). Treatability Study Work Plan for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site. Aiken, SC, Savannah River National Laboratory.

Riha, B. D., B. B. Looney, et al. (2006). Studies to Support Deployment of Edible Oils as the Final cVOC Remediation in T-Area: Summary Report. Aiken, SC, Savannah River National Laboratory.

WSRC (2007). Underground Injection Control Permit Application for Edible Oil Deployment for Enhanced cVOC Attenuation at the SRS T-Area OU (U). Aiken, SC, Westinghouse Savannah River Company.

11. BIBLOGRAPHY

Brigmon, RL. (2001). Methanotrophic Bacteria: Use in Bioremediation. WSRC-MS-2001-00058, Savannah River Site, Aiken SC.

Chappell, F. (1998). Effect of Contaminant Concentration on Aerobic Microbial Mineralization of DCE and VC in Stream-Bed Sediments, Environmental Science and Technology, Vol 32, No. 5,

Chartrand, MMG, Waller A, Mattes TE, Elsner M, Lacrampe-Couloume G, Gossett JM, Edwards EA, Sherwood Lollar B, (2005). Carbon Isotopic fractionation during aerobic vinyl chloride degradation. Environ. Sci. Technol. 39 (4), 1064-1070.

Coleman NV, Matts TE, Gossett JM, Spain JC, (2002) Biodegradation of cis-dichloroethane as a sole carbon source by B-proteobacterium. Appl. Environ. Microbiol. 68:2726-2730.

DiStefano TD, Gossett JM, Zinder SH, (1991). Reductive dechlorination of high concentrations of tetrachloroethane to ethane by an anaerobic enrichment culture in the absence of methanogenesis. Appl. Environ. Microbiol. 57:2287-2292.

Doohyun R, Shim H, Canada K, Barbieri P, and Wood T, (2000). Aerobic degradation of tetrachloroethylene by toluene-o-xylene monooxygenase of Pseudomonas stutzeri OX1. Nature Biotechnology. Vol 18, 775-778.

Freedman DL, Gossett JM, (1989). Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55:2144-2151.

Gostern A, and Edwards E, (2006). A 1,1,1-Trichloroethane-Degrading Anaerobic Mixed Microbial Culture Enhances Biotransformation of Mixtures of Chlorinated Ethenes and Ethanes. Appl. Environ. Microbiol. 72(12):7849-7856.

Hanada et al. (1998). Phylogenetic Analysis of Trichloroethylene-Degrading Bacteria Newly Isolated from Soil Polluted with this Contaminant. Vol 86, No. 6, 539-544 September 1998. Journal of Fermentation and Bioengineering

Hartman S, de Bont JAM, Tramper J, Luyben K, (1985). Bacterial degradation of vinyl chloride. Biotechnol. Letters. 7:383-388.

Heimann AC, Batstone DJ, Jakobsen R, (2006). Methanosarcina spp. Drive Vinyl Chloride Dechlorination via Interspecies Hydrogen Transfer. Appl. Environ. Microbiol. 72(4):2942-2949.

Little CD, Palumbo AV, Herbes SE, Lidstrom ME, Tyndall RL, and Gilmer PJ, (1988). Trichloroethylene Biodegradation by Methane-Oxidizing Bacterium. Appl. Environ. Microbiol. 54:951-956.

Loffler FE, Sun Q, Li J, Tiedje JM, (2000). 16S rRNA gene-based detection of tetrachloroethene-dechlorinating Desulfuromonas and Dehalococcoides species. Appl. Environ. Microbiol. 66:1369-1374.

Maymo-Gatell X, Chien YT, Gossett JM, Zinder SH (1997). Isolation of a bacterium that reductively dechlorinates tetrachloroethane to ethane. Sci. 276:1568-1571.

Maymo-Gatell X, Tandoi V, Gossett JM, Zinder SH, (1995). Characterization of an H2-utilizing enrichment culture that reductively dechlorinates tetrachloroethane to Vinyl chloride and ethane in the absence of methanogenesis and acteogenesis. Appl. Environ. Microbiol. 61:3928-3933.

Nonaka H, Keresztes G, Shinoda Y, Ikenaga Y, Abe M, Naito K, Inatomi K, Furukawa K, Inui M, And Yukawa H, (2006). Complete Genome Sequence of the Dehalorespiring Bacterium Desulfitobacterium halfniense Y51, and Comparison with Dehalococcoides ethenogenes 195. Jour. Bacteriology, 188(4):2262-2274.

Olaniran A, Pillay D, Pillay B, (2004). Chloroethenes contaminants in the environment: Still a cause of concern. African Jour. Biotech. Vol 3 (12), pp 675-682.

Roberts P, Semprini L, Hopkins GD, Grbic-Galic D, McCarty PL, and Reinhard M, (1989). In-situ aquifer restoration of chlorinated aliphatics by methanotropic bacteria. EPA/600/2-89/033, USEPA, Washington DC.

Rosner et al. (1997). In vitro studies on reductive vinyl chloride dehalogenation by an anaerobic mixed culture. Appl Environ Microbiol 63:4139–4144

Schnoor (1997). Design of Phytoremediation at Contaminated Sites. Groundwater Remediation and Technologies Analyses Center, Presentations: Advances in Innovative Groundwater Remediation Technologies. Philadelphia, PA. July 31, 1997.

Scholz-Muramatsu H, Neumann A, Mebmer M, Moore E, Diekert G, (1995). Isolation and characterization of Dehalospirillium multivorans gen. nov. sp. Nov., a tetrachloroethane-utilizing, strictly anaerobic bacterium. Arch. Microbiol. 163:48-56.

Sharma PK, McCarty PL, (1996). Isolation and characterization of a facultatively aerobic bacterium, that reductively dehalogenates tetrachloroethane to cis-1, 2-dichloroethene. Appl. Environ. Microbiol. 62:761-765

Verce MF, Gunsch CK, Danko AS, Freedman DL, (2002). Cometabolism of cis-1,2-dichloroethane by aerobic cultures grown on vinyl chloride as the primary substrate. Environ. Sci. Technol. 36:2171-2177.

Wilson JT, Wilson BH, (1995). Biotransformation of trichloroethylene in soil. Appl. Environ. Microbiol. 49:242-243.

Yan J, Rash BA, Rainey FA, Moe WM, (2009). Isolation of novel bacteria within the Chloroflexi capable of reductive dechlorination of 1,2,3-trichloropropane. Environ. Microbiol. 11(4):833-843.

MAROS Statistical Trend Analysis Summary

Project: TNX SRNL 2008

Location: SRS

User Name: Brian Riha

State: South Carolina

Time Period: 9/10/2007 **to** 1/24/2012

Consolidation Period: No Time Consolidation

Consolidation Type: Median

Duplicate Consolidation: Average

ND Values: 1/2 Detection Limit

J Flag Values : Actual Value

Well	Source/ Tail	Number of Samples	Number of Detects	Average Conc. (mg/L)	Median Conc. (mg/L)	All Samples "ND" ?	Mann-Kendall Trend	Linear Regression Trend
TRICHLOROETHYLENE (TCE)								
TBG-03	S	45	45	2.5E-02	1.2E-02	No	D	NT
TBG-04	S	44	44	1.2E-01	3.6E-02	No	D	D
TBG-05	S	30	30	4.1E-02	4.0E-03	No	D	D
TNX-03D	S	40	40	2.3E-03	7.4E-04	No	D	D
TRW-01	T	27	27	1.2E-02	1.1E-02	No	NT	NT
TRW-02	T	37	37	1.8E-02	5.5E-03	No	D	D
TRW-03	T	25	25	8.6E-02	7.2E-02	No	S	S
TRW-04R	S	46	46	3.1E-03	1.3E-03	No	D	PD
TVM-01M	S	46	46	6.1E-02	5.7E-02	No	I	I
TVM-02M	S	46	42	2.1E-03	4.5E-04	No	D	NT
TVM-04M	S	46	43	1.2E-03	5.4E-04	No	I	NT
TVR-01A	S	46	46	3.6E-03	1.4E-03	No	I	I

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A); Not Applicable (N/A) - Due to insufficient Data (< 4 sampling events); No Detectable Concentration (NDC)

The Number of Samples and Number of Detects shown above are post-consolidation values.

MAROS Mann-Kendall Statistics Summary

Project: TNX SRNL 2008 **User Name:** Brian Riha

Location: SRS **State:** South Carolina

Time Period: 9/10/2007 **to** 1/24/2012
Consolidation Period: No Time Consolidation
Consolidation Type: Median
Duplicate Consolidation: Average
ND Values: 1/2 Detection Limit
J Flag Values : Actual Value

Well	Source/ Tail	Number of Samples	Number of Detects	Coefficient of Variation	Mann-Kendall Statistic	Confidence in Trend	All Samples "ND" ?	Concentration Trend
TRICHLOROETHYLENE (TCE)								
TBG-03	S	45	45	1.53	-258	100.0%	No	D
TBG-04	S	44	44	0.98	-102	100.0%	No	D
TBG-05	S	30	30	3.36	-249	100.0%	No	D
TNX-03D	S	40	40	2.85	-328	100.0%	No	D
TRW-01	T	27	27	0.59	5	53.3%	No	NT
TRW-02	T	37	37	1.54	-236	99.9%	No	D
TRW-03	T	25	25	0.61	-38	80.4%	No	S
TRW-04R	S	46	46	2.61	-161	100.0%	No	D
TVM-01M	S	46	46	0.93	577	100.0%	No	I
TVM-02M	S	46	42	2.06	-39	100.0%	No	D
TVM-04M	S	46	43	1.57	8	100.0%	No	I
TVR-01A	S	46	46	1.70	211	100.0%	No	I

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A)- Due to insufficient Data (< 4 sampling events); Source/Tail (S/T)

The Number of Samples and Number of Detects shown above are post-consolidation values.

MAROS Linear Regression Statistics Summary

Project: TNX SRNL 2008 **User Name:** Brian Riha

Location: SRS **State:** South Carolina

Time Period: 9/10/2007 **to** 1/24/2012
Consolidation Period: No Time Consolidation
Consolidation Type: Median
Duplicate Consolidation: Average
ND Values: 1/2 Detection Limit
J Flag Values : Actual Value

Well	Source/ Tail	Average Conc (mg/L)	Median Conc (mg/L)	Standard Deviation	All Samples "ND" ?	Ln Slope	Coefficient of Variation	Confidence in Trend	Concentration Trend
TRICHLOROETHYLENE (TCE)									
TBG-03	S	2.5E-02	1.2E-02	3.9E-02	No	-4.4E-04	1.53	85.5%	NT
TBG-04	S	1.2E-01	3.6E-02	1.2E-01	No	-1.2E-03	0.98	99.7%	D
TBG-05	S	4.1E-02	4.0E-03	1.4E-01	No	-1.3E-03	3.36	99.4%	D
TNX-03D	S	2.3E-03	7.4E-04	6.6E-03	No	-1.8E-03	2.85	100.0%	D
TRW-01	T	1.2E-02	1.1E-02	7.3E-03	No	7.1E-05	0.59	55.9%	NT
TRW-02	T	1.8E-02	5.5E-03	2.8E-02	No	-1.0E-03	1.54	98.8%	D
TRW-03	T	8.6E-02	7.2E-02	5.3E-02	No	-4.7E-04	0.61	81.9%	S
TRW-04R	S	3.1E-03	1.3E-03	8.0E-03	No	-5.1E-04	2.61	92.1%	PD
TVM-01M	S	6.1E-02	5.7E-02	5.7E-02	No	2.6E-03	0.93	100.0%	I
TVM-02M	S	2.1E-03	4.5E-04	4.3E-03	No	-2.9E-04	2.06	72.3%	NT
TVM-04M	S	1.2E-03	5.4E-04	1.8E-03	No	-1.7E-05	1.57	51.7%	NT
TVR-01A	S	3.6E-03	1.4E-03	6.2E-03	No	6.7E-04	1.70	95.2%	I

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Non-detect (ND); Not Applicable (N/A) - Due to insufficient Data (< 4 sampling events); COV = Coefficient of Variation

MAROS Statistical Trend Analysis Summary

Project: TNX ERDMS 2006

User Name: Brian Riha

Location: SRS

State: South Carolina

Time Period: 1/1/2008 **to** 12/5/2011

Consolidation Period: No Time Consolidation

Consolidation Type: Median

Duplicate Consolidation: Average

ND Values: 1/2 Detection Limit

J Flag Values : Actual Value

Well	Source/ Tail	Number of Samples	Number of Detects	Average Conc. (mg/L)	Median Conc. (mg/L)	All Samples "ND" ?	Mann-Kendall Trend	Linear Regression Trend
TRICHLOROETHYLENE (TCE)								
TBG 3	S	8	8	2.1E-02	6.0E-03	No	PD	NT
TBG 4	S	9	9	1.1E-01	7.8E-02	No	S	D
TBG 5	S	8	8	1.2E-03	6.6E-04	No	PD	D
TCM 5	T	8	8	1.4E-02	1.3E-02	No	S	PD
TIR 1L	T	8	8	1.1E-03	9.6E-04	No	D	D
TIR 1M	T	8	8	9.6E-03	1.0E-02	No	D	D
TIR 1U	T	8	8	1.9E-02	2.0E-02	No	D	D
TNX 1D	T	8	1	3.4E-04	2.5E-04	No	S	D
TNX 3D	S	11	7	2.4E-03	2.7E-04	No	PD	PD
TNX 8D	T	8	8	1.6E-03	1.5E-03	No	D	D
TNX 9D	T	8	1	2.9E-04	2.5E-04	No	S	S
TNX 11D	T	8	7	3.9E-04	3.7E-04	No	PD	PD
TNX 12D	T	8	0	3.1E-04	2.5E-04	Yes	ND	ND
TNX 13D	T	8	7	9.7E-04	7.6E-04	No	PD	PD
TNX 15D	T	8	8	1.1E-02	1.0E-02	No	PD	D
TNX 16D	T	8	8	1.5E-02	1.5E-02	No	PD	D
TNX 20D	T	7	6	8.7E-04	9.4E-04	No	D	D
TNX 22D	T	7	5	5.9E-04	7.1E-04	No	PI	I
TNX 24D	T	8	0	3.1E-04	2.5E-04	Yes	ND	ND
TNX 27D	T	8	7	6.5E-03	2.7E-03	No	NT	NT
TNX 28D	T	8	6	1.4E-03	5.4E-04	No	NT	NT
TNX 30D	T	1	1	2.8E-02	2.8E-02	No	N/A	N/A
TNX 35D	T	8	7	6.4E-04	7.1E-04	No	D	D
TNX 37D	T	8	8	4.2E-03	4.4E-03	No	S	PD
TNX 72D	T	3	0	2.5E-04	2.5E-04	Yes	ND	ND
TNX 72M	T	2	0	2.5E-04	2.5E-04	Yes	ND	ND
TNX073D	T	1	0	2.5E-04	2.5E-04	Yes	ND	ND
TNX074D	T	1	1	3.1E-04	3.1E-04	No	N/A	N/A
TNX075D	T	1	0	2.5E-04	2.5E-04	Yes	ND	ND
TRW 1	T	7	7	9.6E-03	8.6E-03	No	S	S
TRW 2	T	9	9	1.6E-02	3.8E-03	No	PD	NT
TRW 3	T	8	8	6.7E-02	5.5E-02	No	NT	I
TRW 4R	S	8	4	4.9E-04	3.3E-04	No	S	S

MAROS Statistical Trend Analysis Summary

Well	Source/ Tail	Number of Samples	Number of Detects	Average Conc. (mg/L)	Median Conc. (mg/L)	All Samples "ND" ?	Mann-Kendall Trend	Linear Regression Trend
TRICHLOROETHYLENE (TCE)								

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A); Not Applicable (N/A) - Due to insufficient Data (< 4 sampling events); No Detectable Concentration (NDC)

The Number of Samples and Number of Detects shown above are post-consolidation values.

MAROS Mann-Kendall Statistics Summary

Project: TNX ERDMS 2006 **User Name:** Brian Riha

Location: SRS **State:** South Carolina

Time Period: 1/1/2008 **to** 12/5/2011
Consolidation Period: No Time Consolidation
Consolidation Type: Median
Duplicate Consolidation: Average
ND Values: 1/2 Detection Limit
J Flag Values : Actual Value

Well	Source/ Tail	Number of Samples	Number of Detects	Coefficient of Variation	Mann-Kendall Statistic	Confidence in Trend	All Samples "ND" ?	Concentration Trend
TRICHLOROETHYLENE (TCE)								
TBG 3	S	8	8	1.75	-12	91.1%	No	PD
TBG 4	S	9	9	0.83	-12	87.0%	No	S
TBG 5	S	8	8	0.91	-14	94.6%	No	PD
TCM 5	T	8	8	0.38	-7	76.4%	No	S
TIR 1L	T	8	8	0.62	-20	99.3%	No	D
TIR 1M	T	8	8	0.39	-16	96.9%	No	D
TIR 1U	T	8	8	0.31	-19	98.9%	No	D
TNX 1D	T	8	1	0.36	-11	88.7%	No	S
TNX 3D	S	11	7	2.42	-18	90.5%	No	PD
TNX 8D	T	8	8	0.42	-20	99.3%	No	D
TNX 9D	T	8	1	0.30	-5	68.3%	No	S
TNX 11D	T	8	7	0.31	-14	94.6%	No	PD
TNX 12D	T	8	0	0.37	-6	72.6%	Yes	ND
TNX 13D	T	8	7	0.80	-12	91.1%	No	PD
TNX 15D	T	8	8	0.45	-14	94.6%	No	PD
TNX 16D	T	8	8	0.33	-14	94.6%	No	PD
TNX 20D	T	7	6	0.56	-15	98.5%	No	D
TNX 22D	T	7	5	0.44	11	93.2%	No	PI
TNX 24D	T	8	0	0.37	-6	72.6%	Yes	ND
TNX 27D	T	8	7	1.06	-4	64.0%	No	NT
TNX 28D	T	8	6	1.25	1	50.0%	No	NT
TNX 30D	T	1	1	0.00	0	0.0%	No	N/A
TNX 35D	T	8	7	0.28	-18	98.4%	No	D
TNX 37D	T	8	8	0.17	-7	76.4%	No	S
TNX 72D	T	3	0	0.00	0	0.0%	Yes	ND
TNX 72M	T	2	0	0.00	0	0.0%	Yes	ND
TNX073D	T	1	0	0.00	0	0.0%	Yes	ND
TNX074D	T	1	1	0.00	0	0.0%	No	N/A
TNX075D	T	1	0	0.00	0	0.0%	Yes	ND
TRW 1	T	7	7	0.50	-7	80.9%	No	S
TRW 2	T	9	9	1.72	-16	94.0%	No	PD
TRW 3	T	8	8	0.74	6	72.6%	No	NT
TRW 4R	S	8	4	0.78	-11	88.7%	No	S

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Not Applicable (N/A)- Due to insufficient Data (< 4 sampling events); Source/Tail (S/T)

The Number of Samples and Number of Detects shown above are post-consolidation values.

MAROS Linear Regression Statistics Summary

Project: TNX ERDMS 2006

User Name: Brian Riha

Location: SRS

State: South Carolina

Time Period: 1/1/2008 **to** 12/5/2011

Consolidation Period: No Time Consolidation

Consolidation Type: Median

Duplicate Consolidation: Average

ND Values: 1/2 Detection Limit

J Flag Values : Actual Value

Well	Source/ Tail	Average Conc (mg/L)	Median Conc (mg/L)	Standard Deviation	All Samples "ND" ?	Ln Slope	Coefficient of Variation	Confidence in Trend	Concentration Trend
TRICHLOROETHYLENE (TCE)									
TBG 3	S	2.1E-02	6.0E-03	3.6E-02	No	-1.1E-03	1.75	82.0%	NT
TBG 4	S	1.1E-01	7.8E-02	9.1E-02	No	-2.6E-03	0.83	99.9%	D
TBG 5	S	1.2E-03	6.6E-04	1.1E-03	No	-1.5E-03	0.91	97.1%	D
TCM 5	T	1.4E-02	1.3E-02	5.3E-03	No	-4.0E-04	0.38	90.7%	PD
TIR 1L	T	1.1E-03	9.6E-04	7.0E-04	No	-1.2E-03	0.62	99.5%	D
TIR 1M	T	9.6E-03	1.0E-02	3.7E-03	No	-7.3E-04	0.39	98.6%	D
TIR 1U	T	1.9E-02	2.0E-02	5.7E-03	No	-6.7E-04	0.31	99.4%	D
TNX 1D	T	3.4E-04	2.5E-04	1.2E-04	No	-5.5E-04	0.36	97.6%	D
TNX 3D	S	2.4E-03	2.7E-04	5.9E-03	No	-1.6E-03	2.42	93.8%	PD
TNX 8D	T	1.6E-03	1.5E-03	6.6E-04	No	-8.8E-04	0.42	99.8%	D
TNX 9D	T	2.9E-04	2.5E-04	8.8E-05	No	-1.0E-04	0.30	66.9%	S
TNX 11D	T	3.9E-04	3.7E-04	1.2E-04	No	-4.1E-04	0.31	94.3%	PD
TNX 12D	T	3.1E-04	2.5E-04	1.2E-04	Yes	-2.7E-04	0.37	81.8%	ND
TNX 13D	T	9.7E-04	7.6E-04	7.7E-04	No	-1.0E-03	0.80	92.9%	PD
TNX 15D	T	1.1E-02	1.0E-02	5.0E-03	No	-7.9E-04	0.45	97.5%	D
TNX 16D	T	1.5E-02	1.5E-02	4.9E-03	No	-5.7E-04	0.33	97.7%	D
TNX 20D	T	8.7E-04	9.4E-04	4.9E-04	No	-1.2E-03	0.56	99.0%	D
TNX 22D	T	5.9E-04	7.1E-04	2.6E-04	No	9.4E-04	0.44	98.6%	I
TNX 24D	T	3.1E-04	2.5E-04	1.2E-04	Yes	-2.6E-04	0.37	81.5%	ND
TNX 27D	T	6.5E-03	2.7E-03	6.9E-03	No	-6.7E-04	1.06	70.7%	NT
TNX 28D	T	1.4E-03	5.4E-04	1.8E-03	No	7.8E-04	1.25	75.2%	NT
TNX 30D	T	2.8E-02	2.8E-02	0.0E+00	No	0.0E+00	0.00	0.0%	N/A
TNX 35D	T	6.4E-04	7.1E-04	1.8E-04	No	-6.3E-04	0.28	98.1%	D
TNX 37D	T	4.2E-03	4.4E-03	7.0E-04	No	-2.4E-04	0.17	94.4%	PD
TNX 72D	T	2.5E-04	2.5E-04	0.0E+00	Yes	0.0E+00	0.00	0.0%	ND
TNX 72M	T	2.5E-04	2.5E-04	0.0E+00	Yes	0.0E+00	0.00	0.0%	ND
TNX073D	T	2.5E-04	2.5E-04	0.0E+00	Yes	0.0E+00	0.00	0.0%	ND
TNX074D	T	3.1E-04	3.1E-04	0.0E+00	No	0.0E+00	0.00	0.0%	N/A
TNX075D	T	2.5E-04	2.5E-04	0.0E+00	Yes	0.0E+00	0.00	0.0%	ND
TRW 1	T	9.6E-03	8.6E-03	4.8E-03	No	-7.5E-04	0.50	83.0%	S
TRW 2	T	1.6E-02	3.8E-03	2.8E-02	No	-1.2E-03	1.72	84.7%	NT
TRW 3	T	6.7E-02	5.5E-02	5.0E-02	No	2.0E-03	0.74	95.7%	I
TRW 4R	S	4.9E-04	3.3E-04	3.9E-04	No	-4.7E-04	0.78	75.2%	S

Note: Increasing (I); Probably Increasing (PI); Stable (S); Probably Decreasing (PD); Decreasing (D); No Trend (NT); Non-detect (ND); Not Applicable (N/A) - Due to insufficient Data (< 4 sampling events); COV = Coefficient of Variation