

Final Report
Field Test of Biogeochemical Reductive
Dechlorination at
Dover Air Force Base Dover, Delaware



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1. INTRODUCTION

1.1. OBJECTIVE

This document is the final report for the field test of Biogeochemical Reductive Dechlorination (BiRD) performed in Target Area 1 at Dover Air Force Base (DAFB) in Dover Delaware. BiRD is a new technology being tested at DAFB for the treatment of chlorinated aliphatic hydrocarbons (CAHs). The approach facilitates reductive dechlorination of CAHs by mineral iron sulfides produced by engineered biogeochemical processes as further described below. Regular bioremediation by biostimulation was tested at an adjacent site using vegetable oil (VegOil) as the substrate. The primary objectives of this project were to:

- Test the efficacy of BiRD under field conditions;
- Obtain a better understanding and proficiency for BiRD by application;
- Compare the BiRD response against biostimulation.

One prior report, Progress Report 1, was issued (ESS, January 2004). Following the publication of that report a subsequent Aqueous and Mineralogical Bioremediation Assessment (AMIBA) was performed at the BiRD test site, several more aqueous monitoring events were performed, and laboratory batch studies were concluded. Based on these data this report:

- Provides summary information on the BiRD theory and its application at DAFB;
- Presents the mineralogical status of the test site before and after injection with respect to Fe and S minerals;
- Concludes the affects of BiRD on chlorinated solvent treatment;
- Gives the results of the laboratory batch study used to confirm BiRD at DAFB;
- Outlines recommendations for testing, improvement of the method, and application at DAFB in particular.

1.2. SITE DESCRIPTION AND HISTORY

Dover Air Force Base (DAFB) is located in Kent County, Delaware approximately 3.5 miles southeast of the City of Dover. DAFB owned and operated surface

impoundments that received hazardous waste from 1963 to 1984. This site is now known as Target Area 1 and is located southwest of the area known as Site Waste Pit 21 (WP21). Prior site investigations show that groundwater contains concentrations of chlorinated aliphatic hydrocarbons (CAHs) including PCE, TCE, cDCE, 1TCA, 1DCA, 2DCA, and 1DCE (Dames and Moore, 1999; Advanced Infrastructure Management Tech, 2002).

1.3. PREVIOUS VEGOIL TEST

ERD was tested using edible vegetable oil (VegOil) as the substrate at two test sites (Barriers 1 and 2) at Target Area 1 (Terra Systems, Inc., 2002). The VegOil cells are located approximately 200 feet south of the BiRD test site along 5th Street. Injection occurred in April 2000 and monitoring has been ongoing since. Barrier 1 consisted of 10 injection wells on 2.5' centers with down gradient monitoring wells beginning at the injectors. Injection at Barrier 1 consisted of 22 gallons of soybean vegetable oil/well. The oil was subsequently found to have "floated" to the top of the aquifer rather than being evenly dispersed. Therefore, a second injection consisting of 16.5 gallons of soybean oil/well emulsified with 5.5 gallons of lecithin was added in December 2000.

Barrier 2 consists of four injectors on 5 foot spacing and a series of monitoring wells down-flow gradient. For this injection array a total of 220 gallons of soybean oil, 22 gallons of lecithin, and 8,000 gallons of ground water were injected over 3 days.

1.4. REVIEW OF REMEDIATION TECHNOLOGIES

Treatment of chlorinated solvents has largely concentrated on two divergent technologies, bioremediation and chemical treatment. BiRD represents an intermediary treatment offering the potential of combining some of the beneficial attributes of both remediation end points.

Chemical Treatment

In-situ chemical treatment is usually performed by the addition of zero valence iron (Fe^0). Treatment is accomplished by abiotic oxidation of iron filings accompanied by the autoreduction and hydrogenation of the chlorinated solvent. Solid, zero valence iron chips must be directly emplaced in the path of the contaminant plume. This technology has the advantage of completely treating chlorinated solvents without the generation of chlorinated daughter products. The technology has the disadvantage that it is often very expensive and application can be difficult especially deep below the surface or in areas where access is encumbered with buildings, roads or other structures.

Bioremediation

Bioremediation via biostimulation requires the application of a labile organic to the aquifer system. Supplied organic may include molasses, vegetable oils, lactate or others which may be injected or solid substrate such as organic peat, mulch, or straw that can be directly emplaced in a permeable reactive barrier. The objective is to provide the organic electron donor to facilitate dechlorination by halo-respiring soil bacteria that utilize the CAH as an alternative electron acceptor. Common soil bacteria capable of using oxygen, nitrate and SO_4^{2-} as electron acceptors and methanogenic bacteria often directly compete with the dehalogens for the supplied organic. Respiratory dehalogenesis is typically stepwise resulting in daughter products of lower chloride content (e.g. TCE \rightarrow DCE \rightarrow VC \rightarrow ethylene/ethane). Some daughter products of partial reductive dechlorination are more toxic than the original parent chemical. Native soil bacteria capable of complete enzymatic reductive dechlorination are sometimes absent in sediment so treatment often stalls at DCE and/or VC. Therefore, complete dechlorination via ERD can require 1) bioaugmentation with bacteria that can completely reduce the CAH or 2) the migration of DCE to a less reduced subsurface environment where it can be selectively oxidized. Biostimulation may be expensive and ineffective and radically altering subsurface redox zones is often difficult to achieve.

Bioremediation has certain advantages including:

- It can be relatively inexpensive to apply;
- There are less depth limitations relative to chemical treatment;
- Application can be by trench or injection and surface treatment can facilitate many surface structures like roads and buildings.
- It is an ecofriendly biological process.

Bioremediation operates as a function of direct microbial respiration which can be summarized by the Monod equation as:

$$(1) \quad \frac{dc}{dt} = \frac{C^* \mu_{\max}}{C + k}$$

Where:

- dc/dt = Rate of substrate carbon utilization
C = Carbon substrate concentration

μ_{\max} = Maximum carbon substrate utilization rate
 k = Half saturation constant

Equation 1 is couched in terms of substrate carbon utilization, however, the rate of electron acceptor reduction, CAH compounds for chlororespiring bacteria, is directly proportional the rate of carbon utilization/oxidation. Therefore, increasing carbon mass results in increasing microbial respiration and faster CAH treatment up to a maximum limit (μ_{\max}). For conditions of high carbon concentrations the treatment rate becomes first order ($dc/dt = \mu_{\max}$). Therefore, the maximum CAH treatment rate should normally be found around the carbon substrate application point (near the injectors).

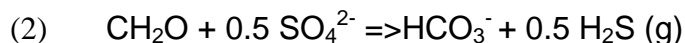
Biogeochemical Reductive Dechlorination (BiRD)

The BiRD approach can be divided into three steps including:

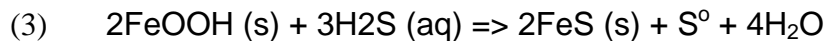
- Microbiological sulfate reduction,
- Geochemical mineral iron sulfide precipitation and
- Abiotic chemical reduction of CAH reductive dechlorination by reaction with iron sulfides.

As opposed to prior technologies, the approach is neither strictly biological nor chemical but employs aspects of both hence the term “biogeochemical”.

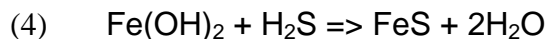
In the biological phase of BiRD, a soluble labile organic (e.g., lactate) is added to the aquifer with sufficient SO_4^{2-} to facilitate the desired end treatment parameters. These amendments are added to stimulate sulfate-reducing bacteria (SRBs). SRBs are ubiquitous in most subsurface environments so bioaugmentation is not required. Oxidation of the organic by SRBs initially produces hydrogen sulfide (H_2S) according to the reaction:



Most sediments contain high concentrations of available Fe^{3+} oxide/hydroxide minerals. Those minerals provide a strong chemical sink for H_2S forming iron sulfide minerals as, for example, with goethite:

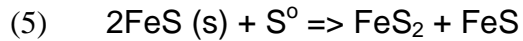


Alternatively, H_2S reaction with Fe(II) can be expressed as:



Minerals formed include amorphous FeS and mackinawite. These minerals form as a microfine mineral coating of high surface area. Equation 3 shows one sulfide in H_2S oxidized to elemental sulfur to facilitate the reduction of Fe^{3+} to Fe^{2+} to form mineral FeS. This reaction is almost instantaneous and reduces Fe^{3+}

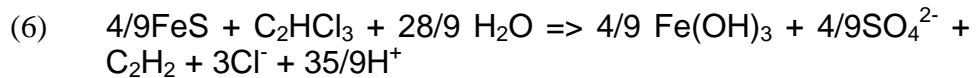
to Fe²⁺ abiotically. With time and under certain geochemical conditions FeS may be converted to FeS₂ as:



Therefore, Equations 2 - 4 show that 100% to 50% of the reduced SO₄²⁻ can precipitate as FeS with the remaining portion converted principally to S⁰ or FeS₂. FeS₂ is chemically stable and does not greatly benefit the BiRD process.

Generation of FeS via supplied organic and SO₄²⁻ in native sediments has been demonstrated under laboratory conditions by Kennedy and Everett (2001). FeS formation is rapid, typically beginning in just a few weeks, and can be sustained provided adequate sources of organic, SO₄²⁻, and Fe³⁺ are present. However, once formed, FeS can persist in the subsurface without ongoing SO₄²⁻ reduction.

FeS is a reduced, reactive mineral and has been shown to reductively dechlorinate many CAHs including TCE, PCE, PCA, TeCA, TCA, DCA, CT (Butler and Hayes, 1999 and 2000). Dechlorination via FeS oxidation is typically complete with no daughter products. Reaction half-lives are short, on the range of hours to days. Laboratory measured half-lives for TCE range from 19 to 41 days (Butler and Hayes, 1999; Terra Systems, 2002; and Kennedy and Everett, 2002). Although partial end products are possible, the complete oxidation of FeS by TCE would be expressed as:



The potential advantages to BiRD include:

- The added organic can be non-viscous and, thus, not reduce permeability or groundwater flux through the barrier;
- Subsurface mixing is not required;
- SO₄²⁻ reducing bacteria are ubiquitous in most aquifer environments so bioaugmentation is not necessary;
- FeS formation is rapid (weeks);
- Fast CAH treatment rates;
- Daughter products (i.e., DCE and VC) are not produced;
- Daughter products to DCE are treated.

BiRD treatment is independent of carbon substrate loading after FeS is formed, essentially independent of FeS concentration in a well mixed system, and follows first order kinetics. As such, CAH treatment begins at the edge of the reaction zone and continues at a uniform rate as the contaminant flows across the treatment area (Figure 1). Therefore, for a homogeneous aquifer with a relatively uniform circular distribution of FeS:

- About half the contaminant treatment possible will have occurred at the initial central injection point;
- Treatment will proceed down-flow gradient across the reaction zone with progressively lower CAH concentrations in more down gradient wells.

Therefore, theoretically the Dover test site, the injection point (ESM1) should represent the minimum observable treatment with maximum observable treatment at the most down flow gradient well (ESM5).

BiRD is a proprietary treatment technology developed and licensed by Earth Science Services, LLC. The approach includes the addition of a labile organic, sulfate source, possible iron amendment, and pH buffering as required. It may be applied by injection or by direct emplacement in a trench to form a permeable reactive barrier (PRB).

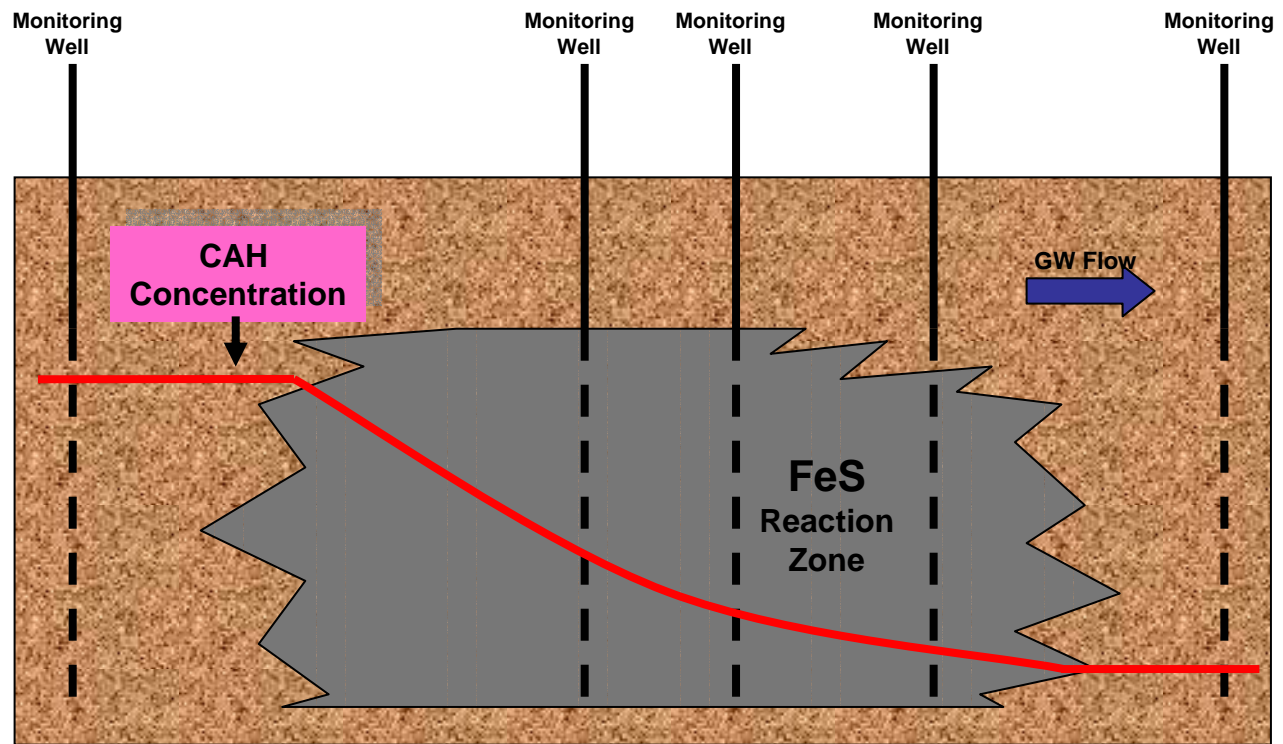


Figure 1. Conceptualized CAH treatment flowing through a FeS reaction zone.

2. BIRD IMPLEMENTATION

2.5. INJECTION SYSTEM INSTALLATION

The BiRD injection array is located immediately west of Building 616 (east of the open storage area) and mostly on the pavement of 5th Street in Target Area 1 of DAFB (Figures 2 and 3). The system was installed Aug. 18 – 22, 2003. The treatment array consists of five injection wells (ES11-ES15) and six monitoring wells (ESM1-ESM6). The injectors were positioned 10 feet apart and perpendicular to the groundwater flow at that time (Figure 4). The down-flow gradient distance for the monitoring wells (relative to the injection array) is 0, 3, 7, 12, and 18.5 feet. One background monitoring well (ESM6) was also drilled 27 feet up-flow gradient (northwest) of the injection array. One DAFB monitoring well, DM325D, is side gradient.

Monitoring wells were drilled to approximately 40 feet deep and were completed with 10-feet of 0.10-slot PVC well screen and 2-inch diameter casing to surface. The injection wells were drilled to approximately 42 feet and installed with 15 feet of 0.10-slot PVC well screen and 1.5-inch diameter casing to surface.

One 6-inch recovery well (ESR1) was drilled near the southwest corner of Building 616. This well was 40 feet deep and equipped with 30 feet of 0.20 slot PVC well screen and 6-inch casing. Although not tested for flow, ESR1 is high capacity, easily capable of producing 25 gpm.

All injection, monitoring, and production wells were completed with sand pack, bentonite pellets, and cement grout according to good engineering practices in accordance to the rules of the State of Delaware. All wells were appropriately pump developed. Purge water was containerized, treated at the DAFB water processing facilities and properly disposed.

2.6. AMENDMENT INJECTION

The injectate was prepared in two 500 gallon tanks using ground water pumped from ESR1. A total of 2,650 gallons injectate was added to each of the five injection wells. A total of 990 lbs Mg SO₄·7H₂O, 700 lbs Environlac 60 was added. Envirolac 60 is 40% Water and 60% Sodium (L) Lactate (NaC₃H₅O₃). Resulting concentrations SO₄²⁺ and lactate in the injection water are 3,500, and 3,000 mg/L, respectively. Injection occurred on August 27, 2003. Each well was injected individually at a rate of approximately 10 gpm.

2.7. SEDIMENT ANALYSES

As per the Scope of Work, sediment was sampled two times for AMIBA

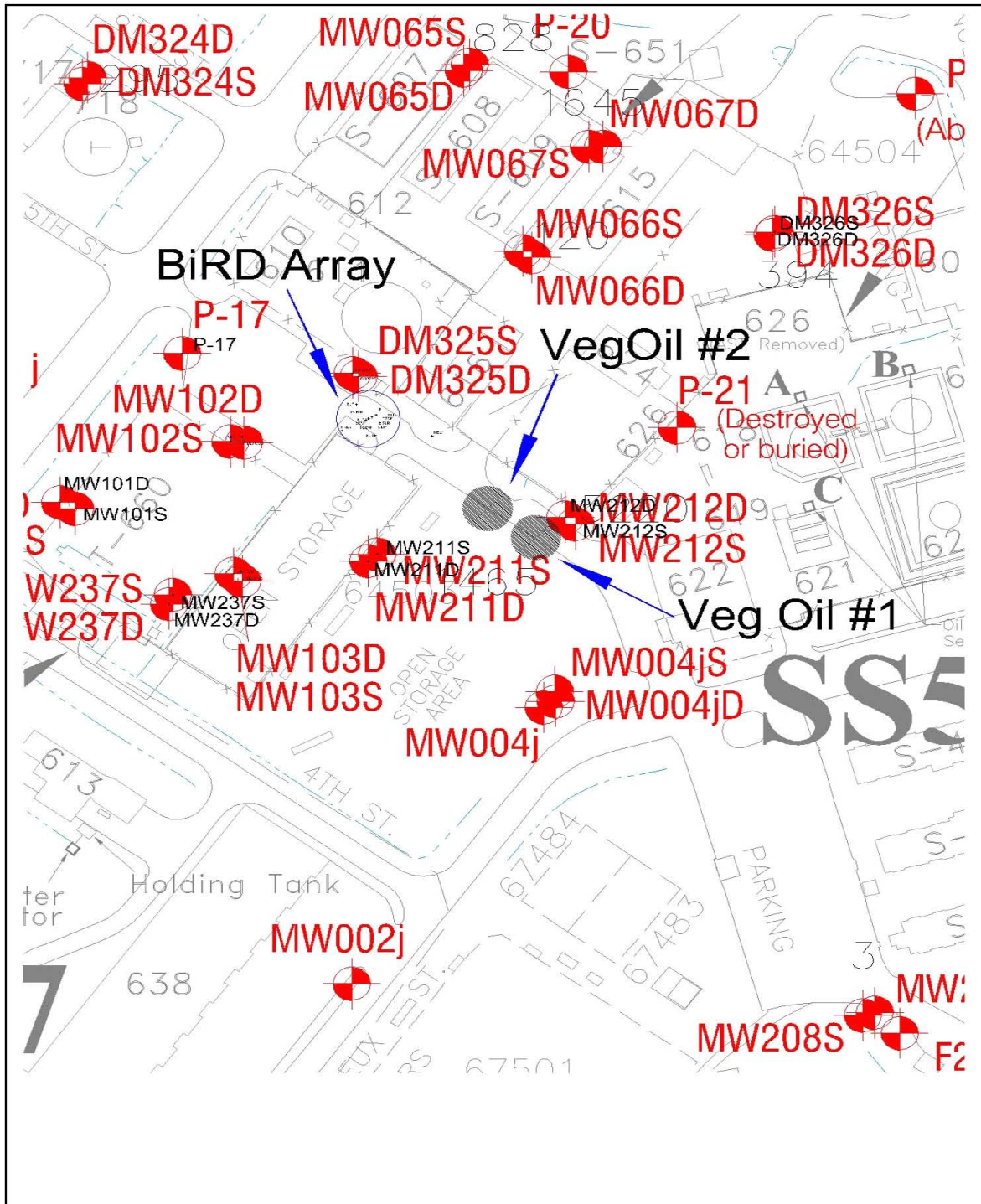


Figure 2. General site map showing the location of the BiRD and VegOil arrays.

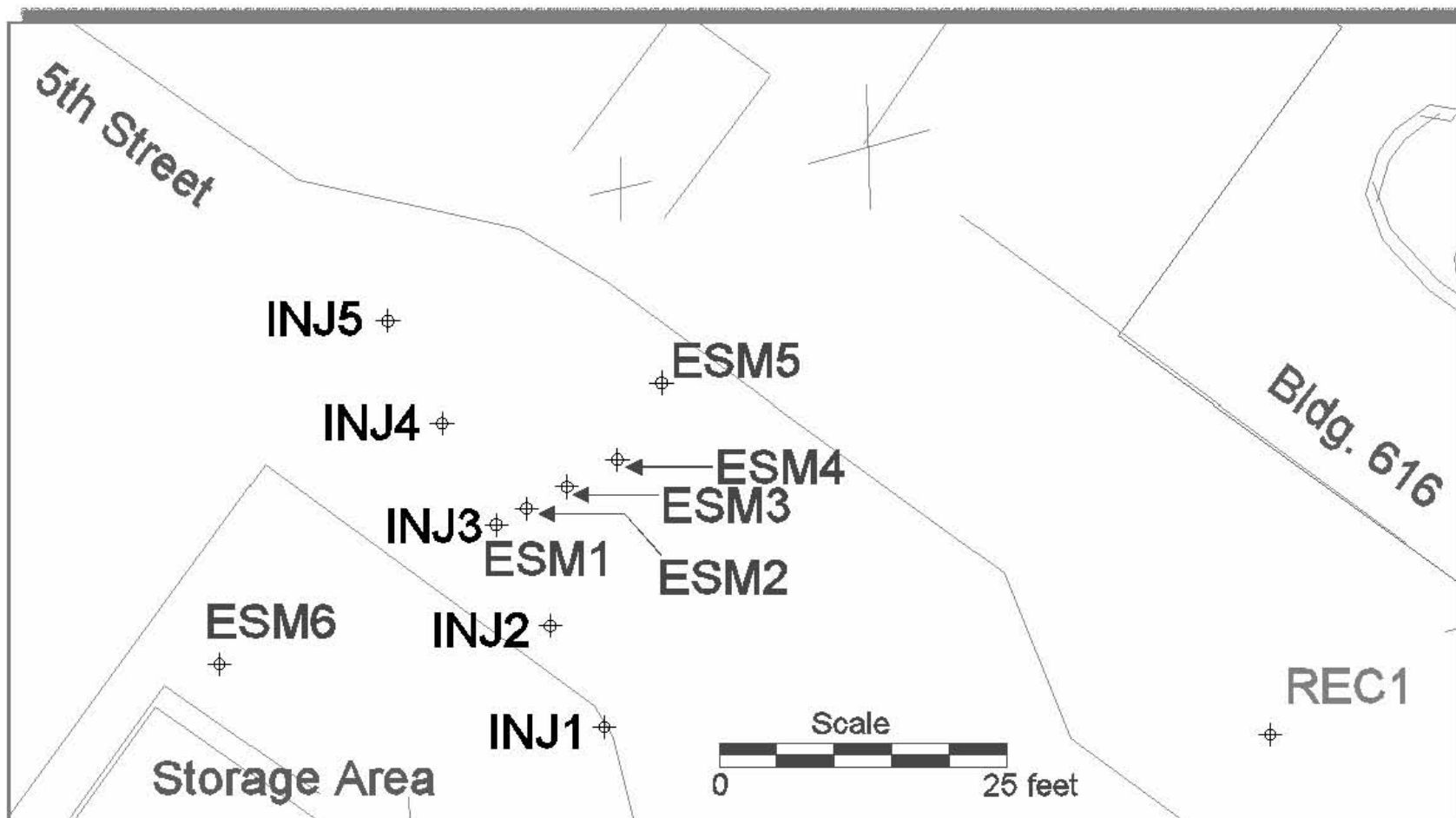


Figure 3. BiRD injection and monitoring array. A to A' is the line of section for the various profiles that follow.

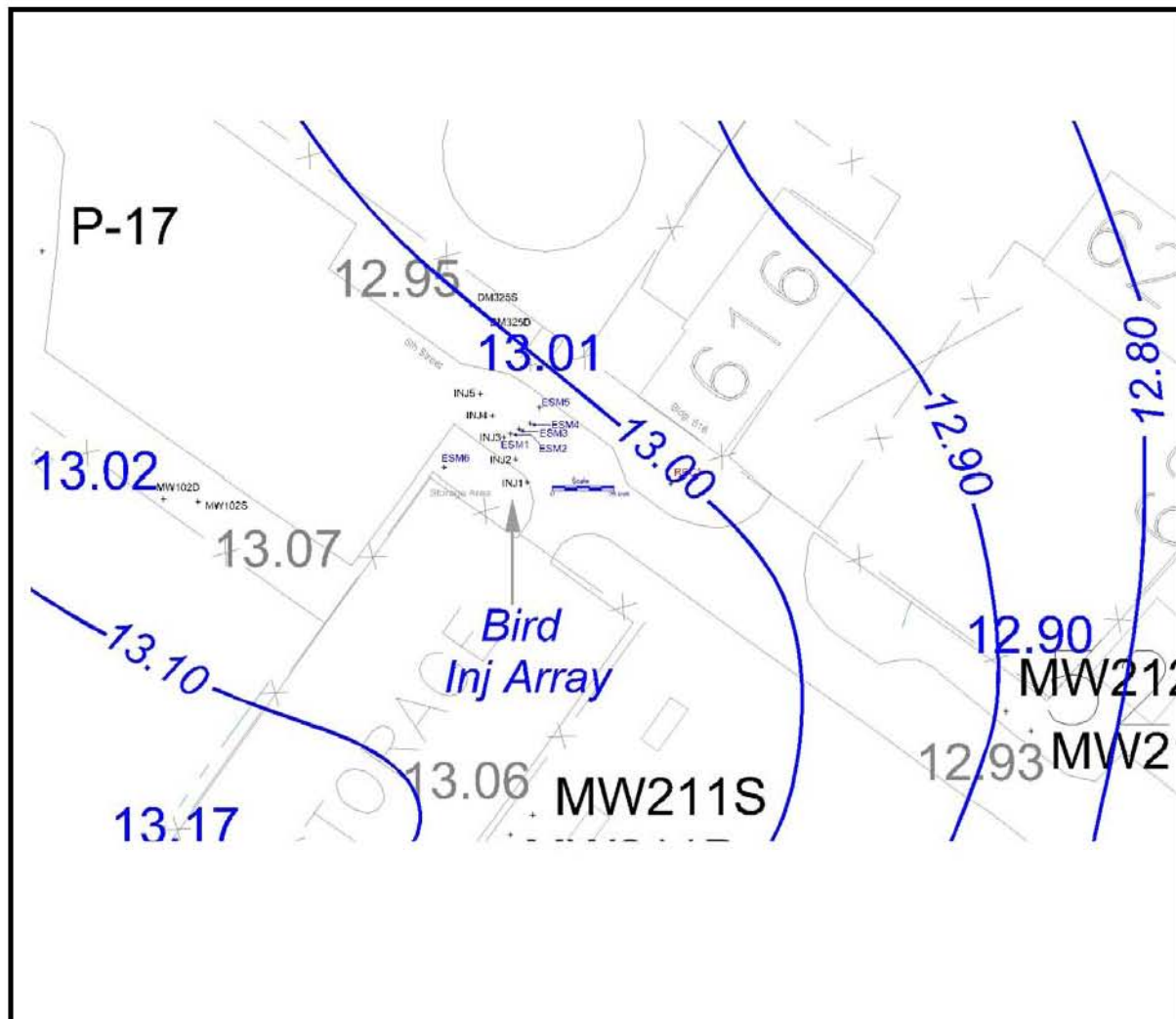


Figure 4. BiRD injection array relative to local ground water potentiometric surface (November 2003).

constituents, before the injection (August 2003) and eight months after the injection (April 2004).

For the initial sampling, all monitoring wells were full-hole cored from surface to total depth (0 – 40 feet). For the second sampling event, sediment was only cored beginning slightly above the injection screen elevation (~10 - 40 feet). Cores were inspected and the lithology described. Sediment was analyzed for weak acid extraction Fe^{2+} and Fe total, strong acid extraction Fe^{2+} and Fe^{3+} , FeS, and FeS_2 . Soil samples were collected at vertical increments of between 2.0 to 5.0 feet. Standard sampling and analyses methods were used as per the AMIBA protocol (Kennedy et al. 2000).

2.8. MICROCOSM METHODS

A microcosm batch test was performed to verify that biogeochemical reactions are responsible for CAH treatment as opposed to bioremediation. Sediment samples were obtained next to ESM1 from a depth of 38 to 40 feet. Upon retrieval, the core was immediately placed into a field portable anaerobic glove bag which had been quadruple purged with ultrapure N_2 gas. Approximately 10 g sediment was placed into serum tubes filling them to approximately 3/4 the bottle volume. Each bottle was sealed with a rubber stopper secured with an aluminum seal. The bottles were then removed from the glove bag, triple vacuum purged and refilled with N_2 gas in the field. Half the bottles were sterilized by irradiation to kill any chlororespiring bacteria which may have been present. Irradiation was selected as the sterilization technique because it does not adversely affect FeS mineral reactivity as does more traditional methods, such as autoclaving or chemical bactericide. Each bottle was then filled with 2500 $\mu\text{g/L}$ TCE in dionized water. Water in the microcosm had < 0.1 mg/L organic carbon removing the carbon source and further inhibiting any bioremediation from occurring. Sample bottles from both the killed and live systems were sacrificed in duplicate and periodically analyzed for TCE, cDCE, and VC.

2.9. AQUEOUS SAMPLING

Water from the monitoring wells was sampled before and immediately after injection then periodically (approximately each month) there after. Dissolved O_2 , pH and conductivity were measured in the field using probes inside a flow-through cell. Dissolved Fe^{2+} , Fe Total were also measured in the field using a Hach spectrophotometer. Water samples were collected from all monitoring wells for laboratory analyses of PCE, TCE, cDCE, and VC using (SW8260), total organic carbon (TOC), and SO_4^{2-} . Proper sample collection, preservation, and handling procedures were employed according to SW864.

3. RESULTS AND ANALYSES

3.10. *GROUND WATER FLOW*

As shown above, the injection and monitoring system was designed with the concept of ground water moving from northwest to southeast. ESM6 was designed as the up-gradient monitoring well with ESM1 to ESM5 being progressively down-gradient. Figure 5 shows the ground water gradient between ESM6 and ESM1 with respect to time. A positive gradient indicates flow from northwest to southeast but a negative gradient indicates flow moving in the opposite sense, from southeast to northwest relative to the line of section. As indicated, for the first 150 days after injection, ground water flow was in the designed direction (northwest to southeast). However, after that time the ground water direction rotated and reversed becoming east to west. There may be a correlation between the flow direction and ground water elevations which generally fell during the experiment (Figure 6) and/or pumping operations elsewhere on the base. The change in the ground water flow direction has a discernible affect on the observed CAH concentrations over the course of the experiment as shown below.

3.11. *LITHOLOGY*

The generalized lithologic column encountered was as follows:

- 0.0 - 11.0' Silt: Olive brown with 20% clay, dry
- 11.0 - 25.0' Sand: Pale brown or yellow laminated with white or light gray, medium to fine grained underlain by a few inches of discontinuous gravel.
- 25.0 - 38.0' Sand: Yellow brown, coarse or medium grained to fine grained with 5% pea gravel with occasional thin layers of clay and usually underlain by a thin layer of discontinuous gravel.
- 38.0 - 40.0' Clay: Strong brown, high plasticity

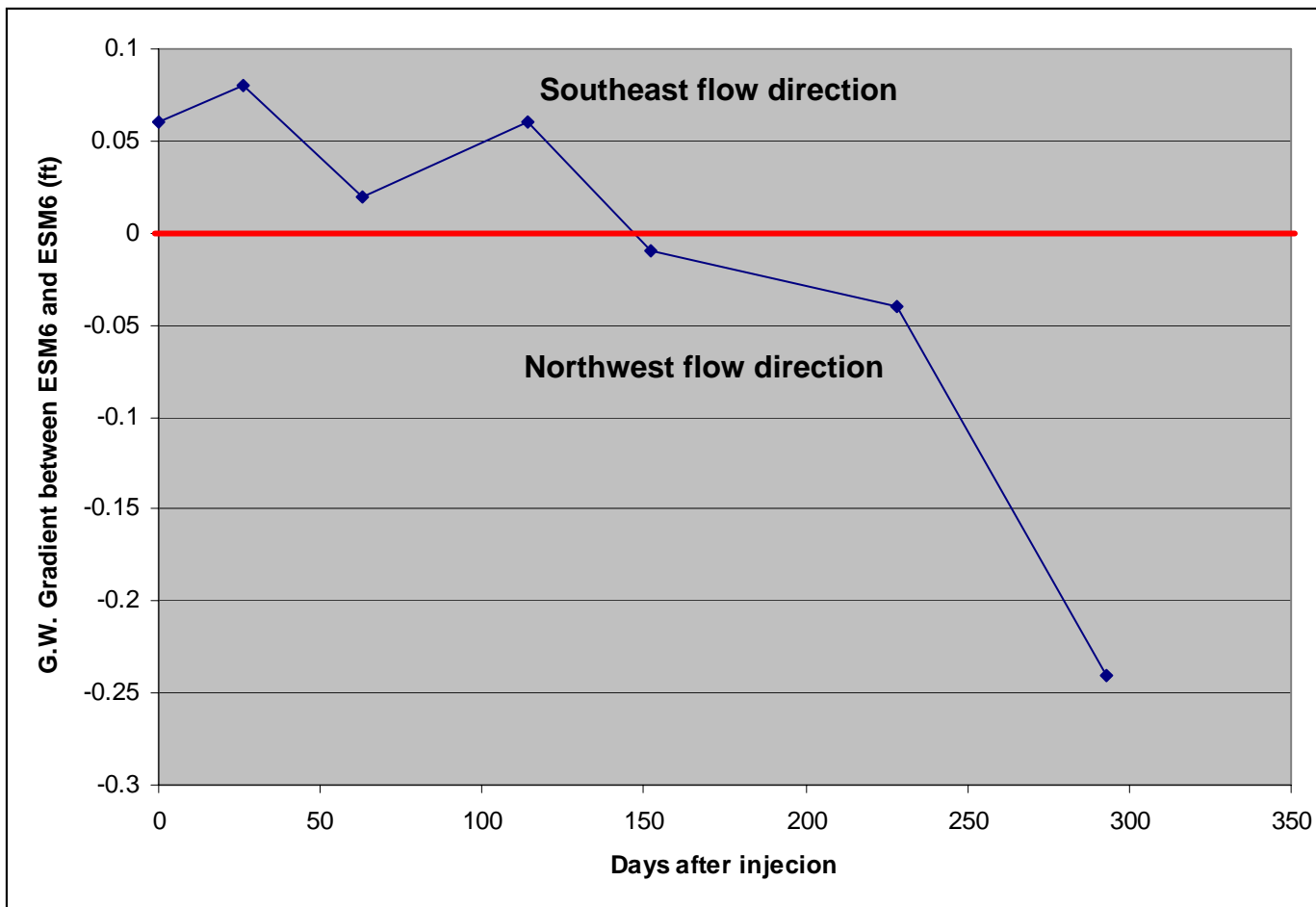


Figure 5. Ground water flow gradient between ESM6 and ESM1 with respect to time. A positive gradient indicates flow from ESM6 towards ESM1 (the injector) while negative indicates a reversal in ground water flow.

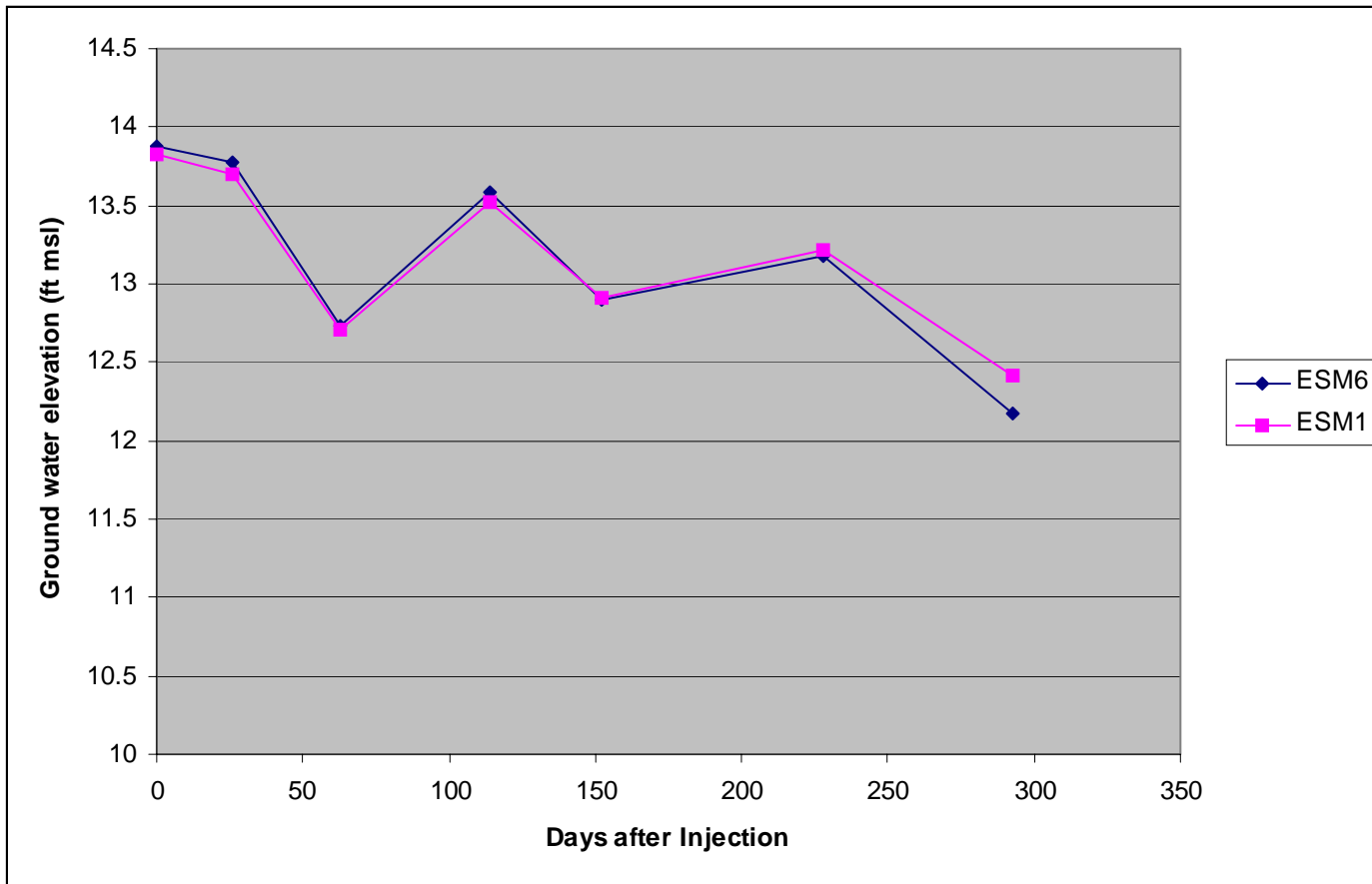


Figure 6. Ground water elevation (ft msl) for ESM1 and ESM6 with respect to time.

A structural geologic profile through the monitoring wells is shown on Figure 7. The observed lithology is consistent with fluvial (stream) deposition with classic coarsening downward sediment grain size. When complete, a fluvial channel depositional sequence consists of clays then silts underlain by sand grading with depth from fine to coarse grained with a layer of coarse gravel or cobbles in the base. However, such depositional sequences are often incomplete and successive channels cut into older ones making the final strata complex which is the case at DAFB. As shown below, lithology is important at this site as it controlled injectate dispersal which preferentially moved through the high permeability gravel immediately above clay layers.

There is a prominent color change in the sediment at approximately 20 - 25 feet below land surface (See Figure 8). Sediment above this level are light colored including pale brown, weak yellow, light grey or white laminated. Below that layer sediment is much darker in color consisting being rusty yellow or yellow brown. This abrupt color change is from naturally occurring iron leaching (gleying) and is not associated with any particular lithology. Iron has been chemically or biochemically dissolved from the shallow sediment layers and redeposited deeper in the aquifer. This affect can be caused by slightly acidic and/or slightly organic ground water percolating downward and may be mediated by soil bacteria.

Prior to injection, sediment was orange or yellow brown in color at the level where wells were screened. This color indicated the abundant presence iron oxide mineral coating on grains of quartz sand or gravel. Post injection, there was a distinct change in sediment color which became medium to dark gray indicating the presence of black colored mineral FeS (Figure 9). Color was strongly altered in coarse sand/gravel interval immediately above the underlying confining clay layer.

3.12. MINERAL IRON DISTRIBUTION

Mineral Total Iron

Total iron (FeT) consists of both Fe(II) and Fe(III) mineral species. The strong acid laboratory extraction procedure used is aggressive and measures most of the bulk iron present in the sediment. FeT represents iron originally deposited in the sediment or arising from post depositional diagenetic processes. Charts of FeT and Fe(II) concentrations with respect to depth for the soil boring points are shown on Figures 10 with data in Appendix I.

A profile of FeT through line of section A to A' is shown on Figure 11. As described above, iron has been naturally leached from the upper part of the geologic section and redeposited deeper. The Fe leached boundary is marked by a color change which coincides with the 1,000 mg/Kg FeT concentration line. Above that boundary, FeT is low, generally between 250 and 500 mg/Kg. Below the leached boundary, FeT concentrations are very high, ranging from 2,000 to

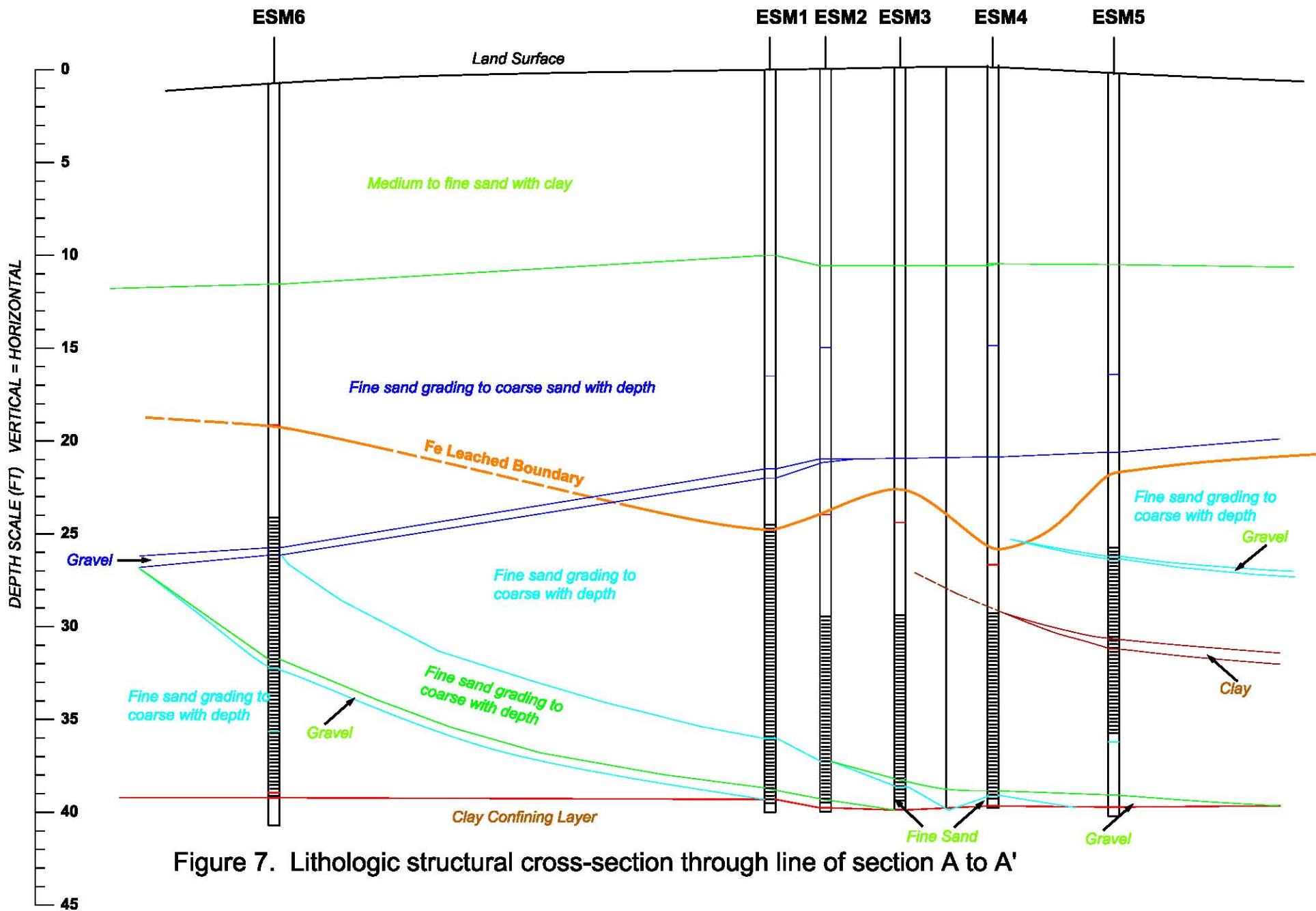


Figure 7. Lithologic structural cross-section through line of section A to A'

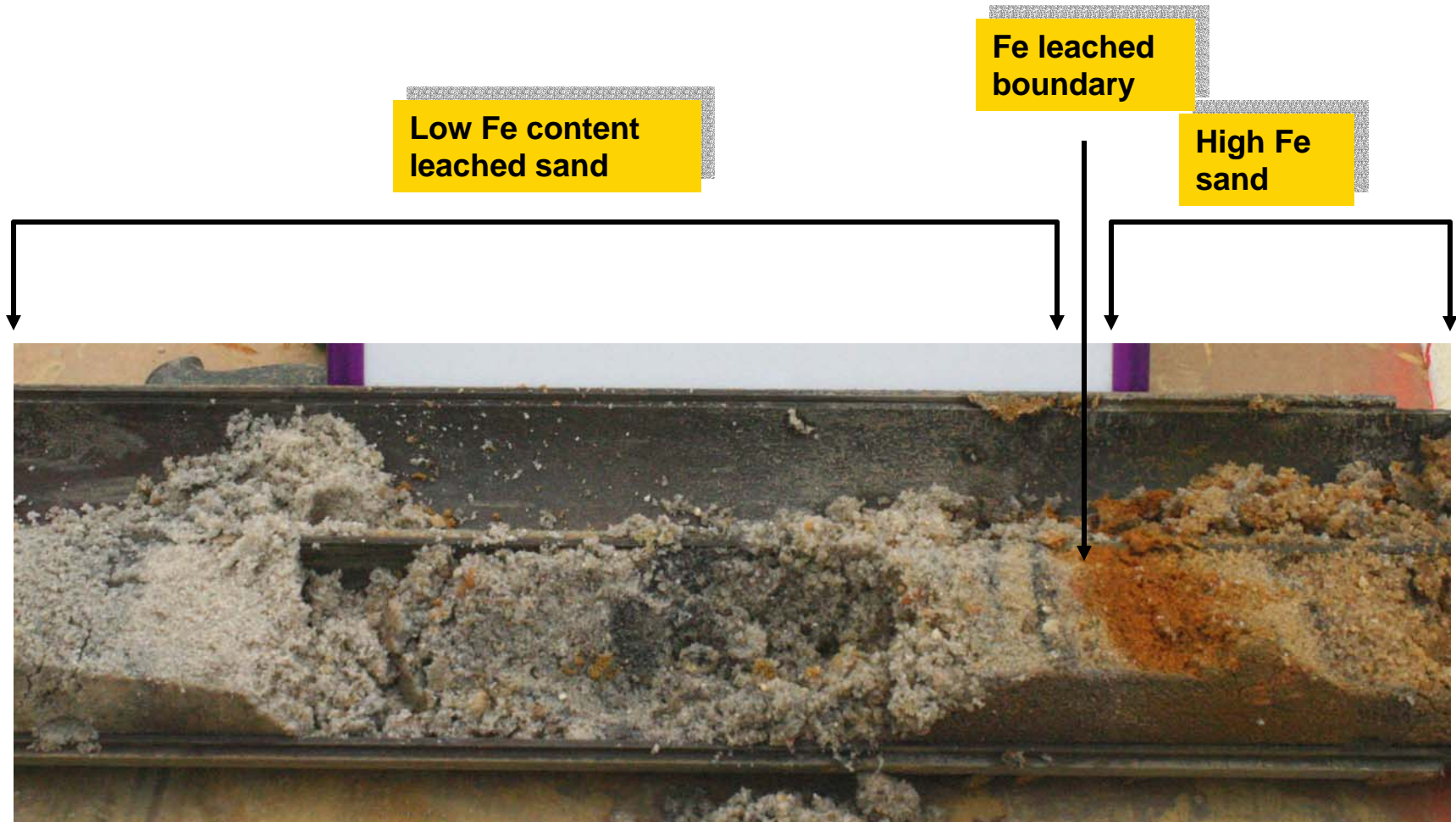


Figure 8. Example of sediment near the Fe leached boundary.

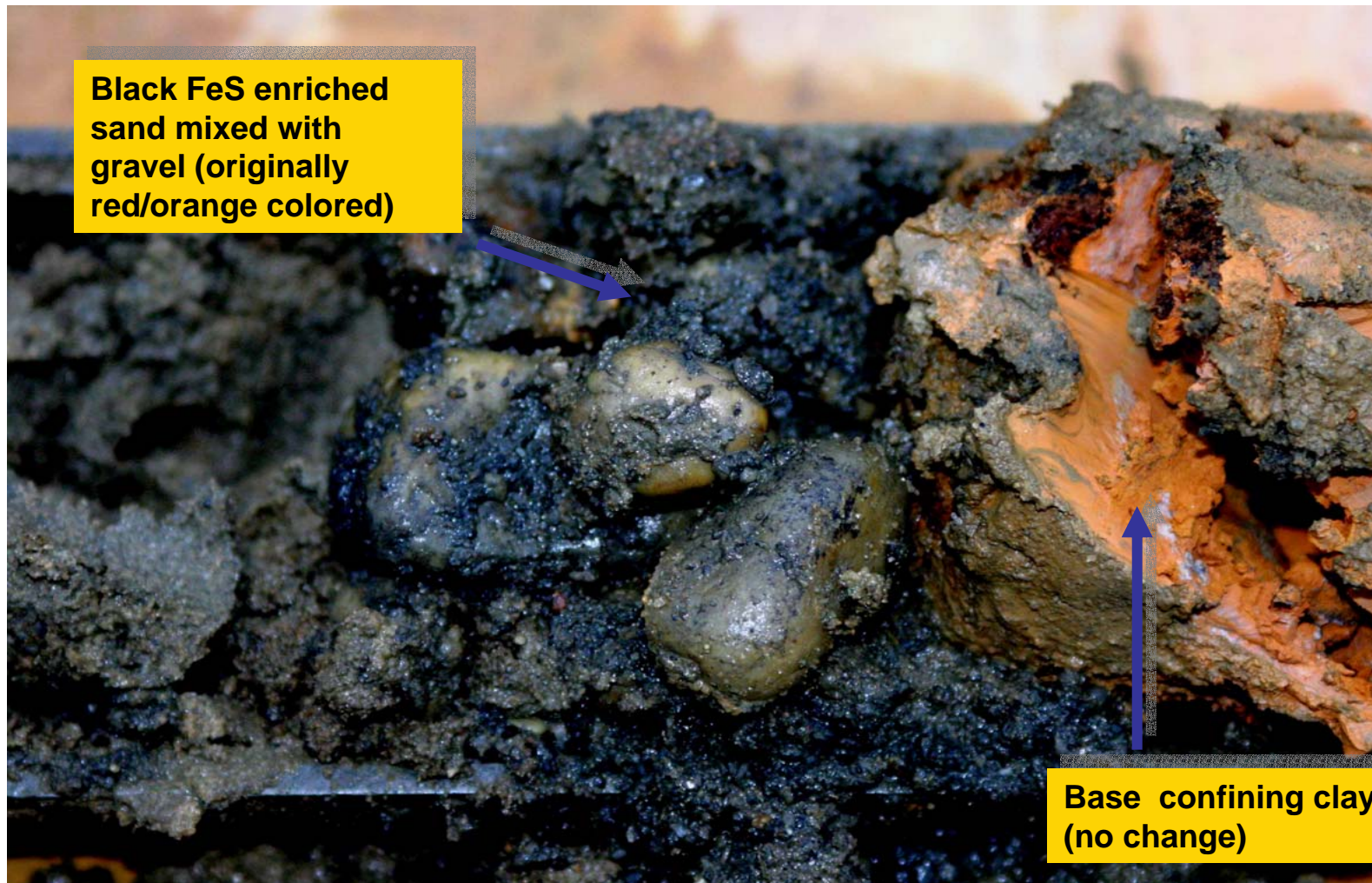


Figure 9. Example core of the gravel zone just above the underlying clay layer after injection. The black color is from mineral iron sulfide formation forming after injection. The original color was reddish orange similar to the clay layer shown.

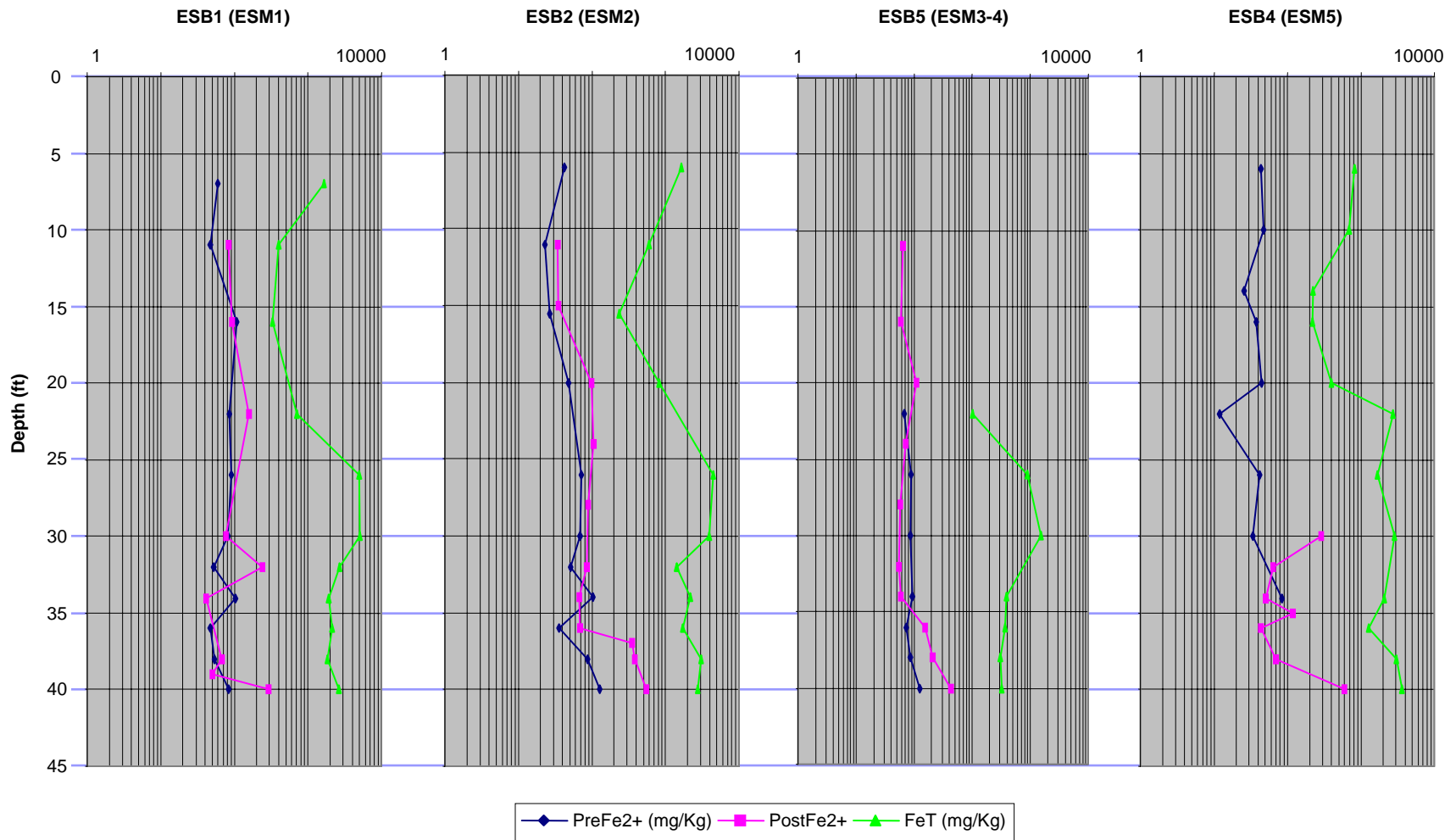


Figure 10. FeT and Fe2+ pre and post injection (mg/Kg)

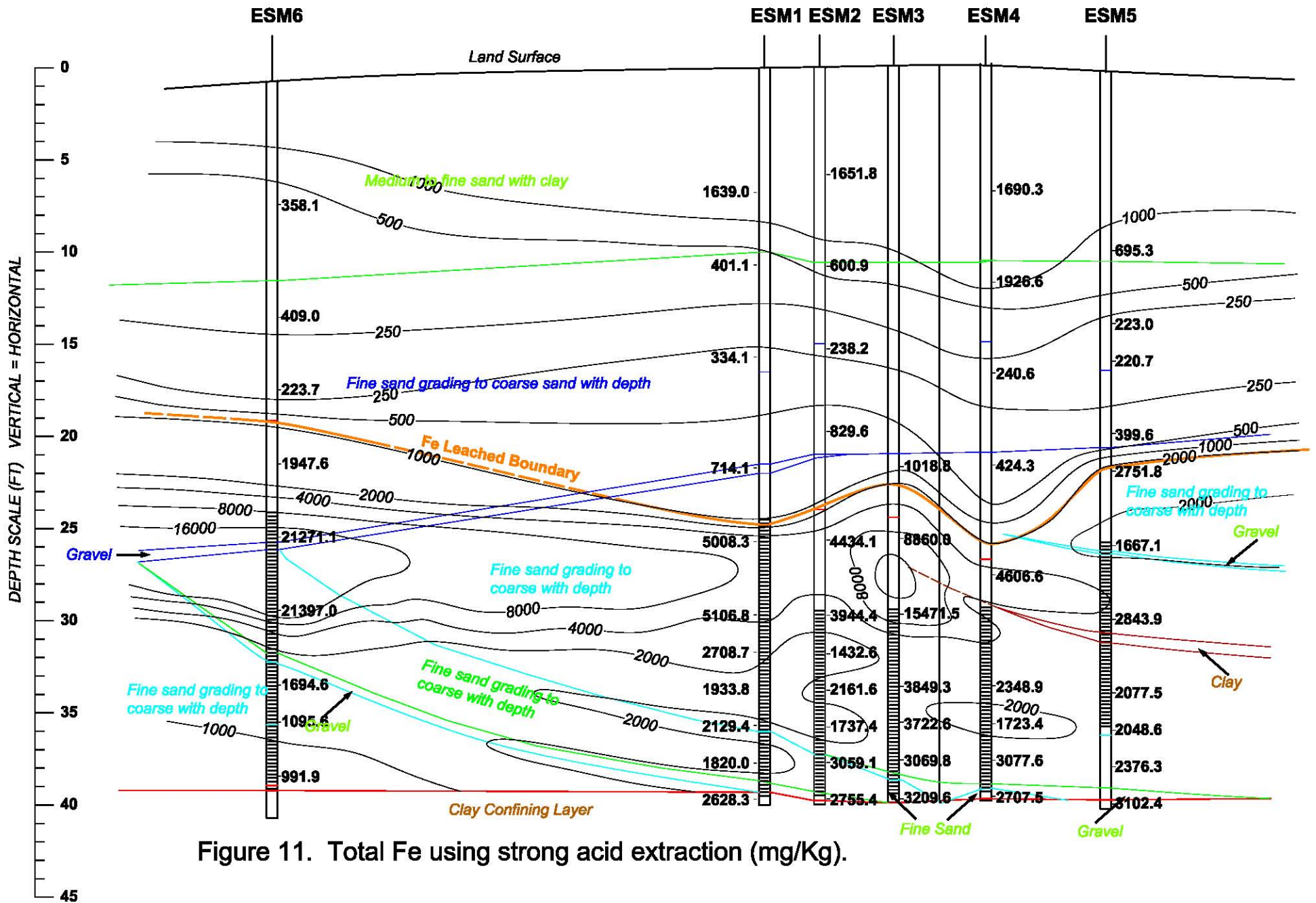


Figure 11. Total Fe using strong acid extraction (mg/Kg).

21,000 mg/Kg. Concentrations of FeT are very adequate for long-term FeS development.

Mineral Fe(II)

As above, the Fe(II) analyses described here utilize a strong acid extraction process representing an assay of total Fe(II) present in the bulk matrix of the sediment. However, Fe(III) can be microbially and biogeochemically converted to Fe(II) in response to BiRD stimulation. Pre- and post injection Fe(II) concentrations are plotted against depth for each soil boring point as shown on Figure 10.

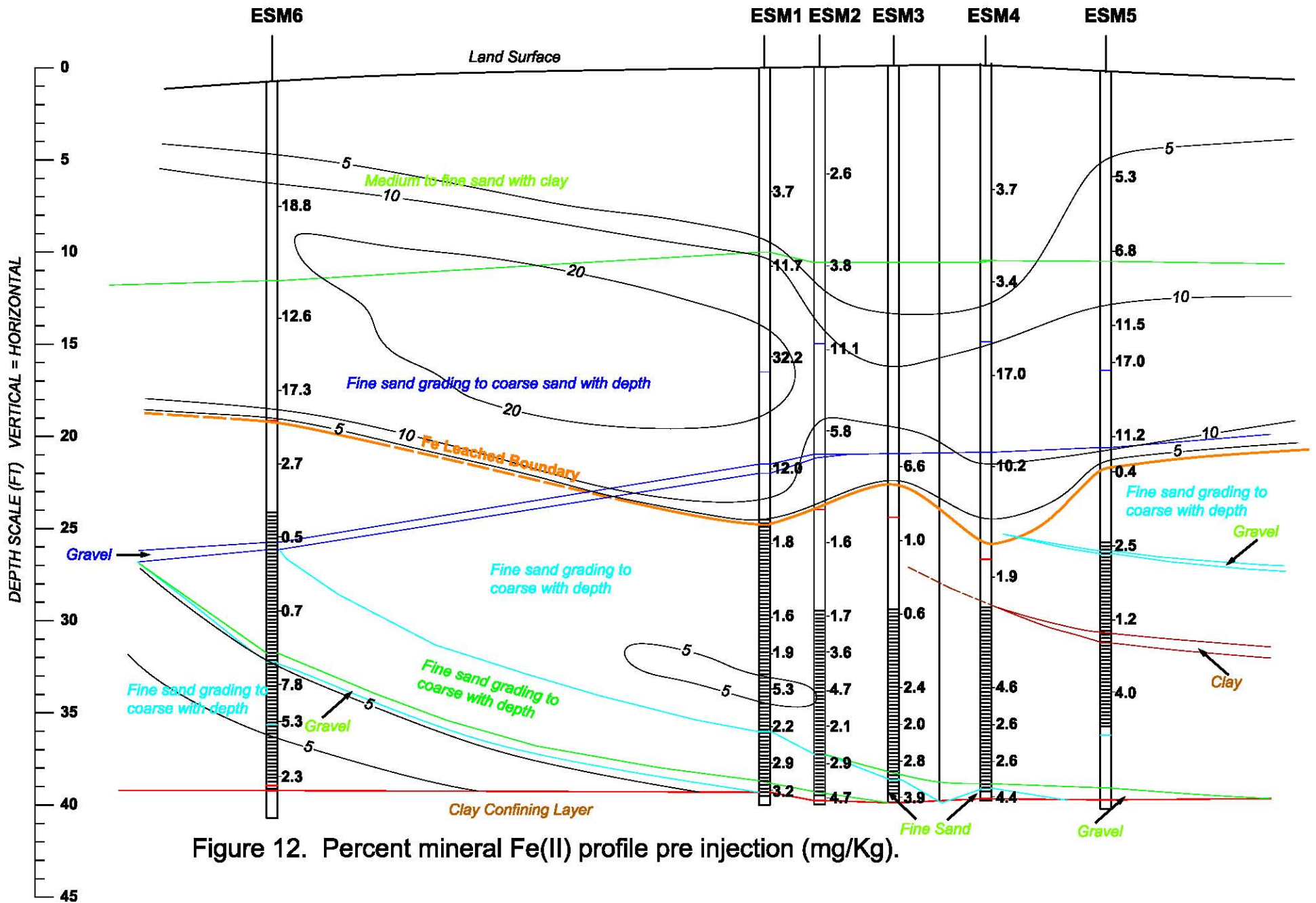
The percentage of Fe(II)/FeT before injection is represented in profile through line of Section A to A' on Figure 12. Prior to injection, the concentration of Fe(II) was quite low throughout the vertical geologic section from surface to the total drilled interval. Fe(II) typically ranged from about 25 to 100 mg/Kg. The percentage of Fe(II)/FeT above the Fe leached boundary is slightly higher (5 to 20%) but is very low, typically only 5% below that boundary.

Post injection, the concentration of Fe(II) above the well screens, where sampled, was about the same as before injection (Figure 13). However, significant mineral Fe(II) was formed in response to the treatment test via direct biological or indirect biogeochemical Fe(III) reduction processes. Post injection Fe(II) concentrations up to 592 mg/Kg were observed. As shown on Figure 13, Fe(II) developed principally in the bottom of the geologic profile above the lower confining clay layer. However, the percentage of Fe(II) only increased from a preinjection concentration of 5% to approximately 15% post injection; about a 10% change overall. Fe(III) mass was not greatly reduced during the course of this experiment. These data suggests that sufficient naturally occurring Fe mass exists in the sediment to support long-term BiRD treatment with much higher concentrations of injectate if desired.

3.13. MINERAL IRON SULFIDES

Pre- and post injection FeS and FeS₂ concentrations with respect to depth for the bore holes are shown graphically on Figure 14 with data in Appendix I. Prior to injection, insignificant concentrations of FeS were present in the aquifer sediment. Pre-injection FeS was insignificant (~1.5 mg/Kg). FeS concentrations increased significantly after injection in all borings attaining a maximum of 174 mg/Kg at ESM2. Vertically, concentrations of FeS generally increased with depth attaining maximum values between at between 35 and 40 feet deep.

Post injection FeS concentrations are shown in profile along Line of Section A to A' on Figure 15. FeS developed higher in the sediment section at the point of injection but is concentrated more near the base of the sand layer away from that point. This figure shows the pronounced affects that lithology/permeability had on the distribution of the injectate which subsequently dictated FeS development.



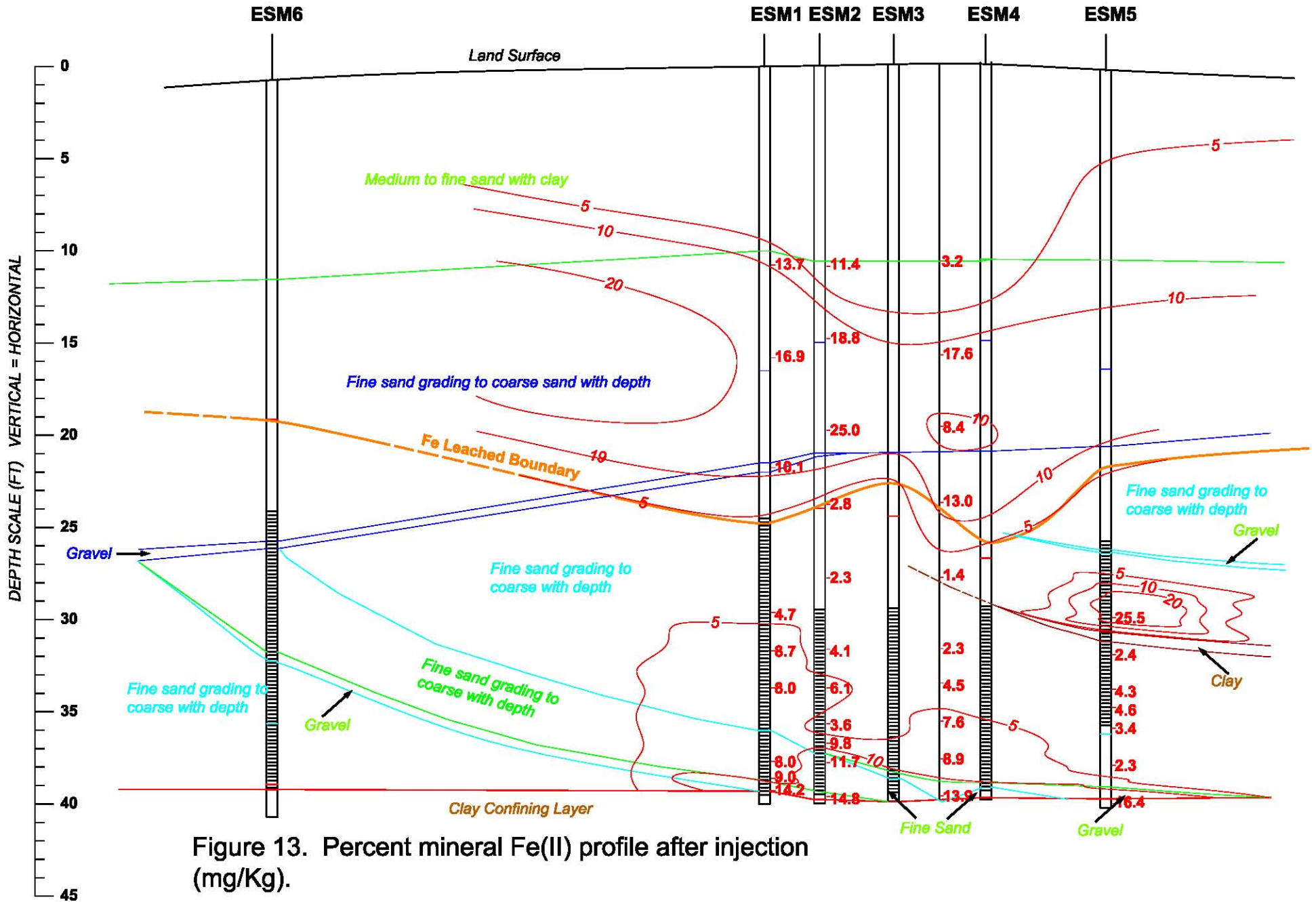


Figure 13. Percent mineral Fe(II) profile after injection (mg/Kg).

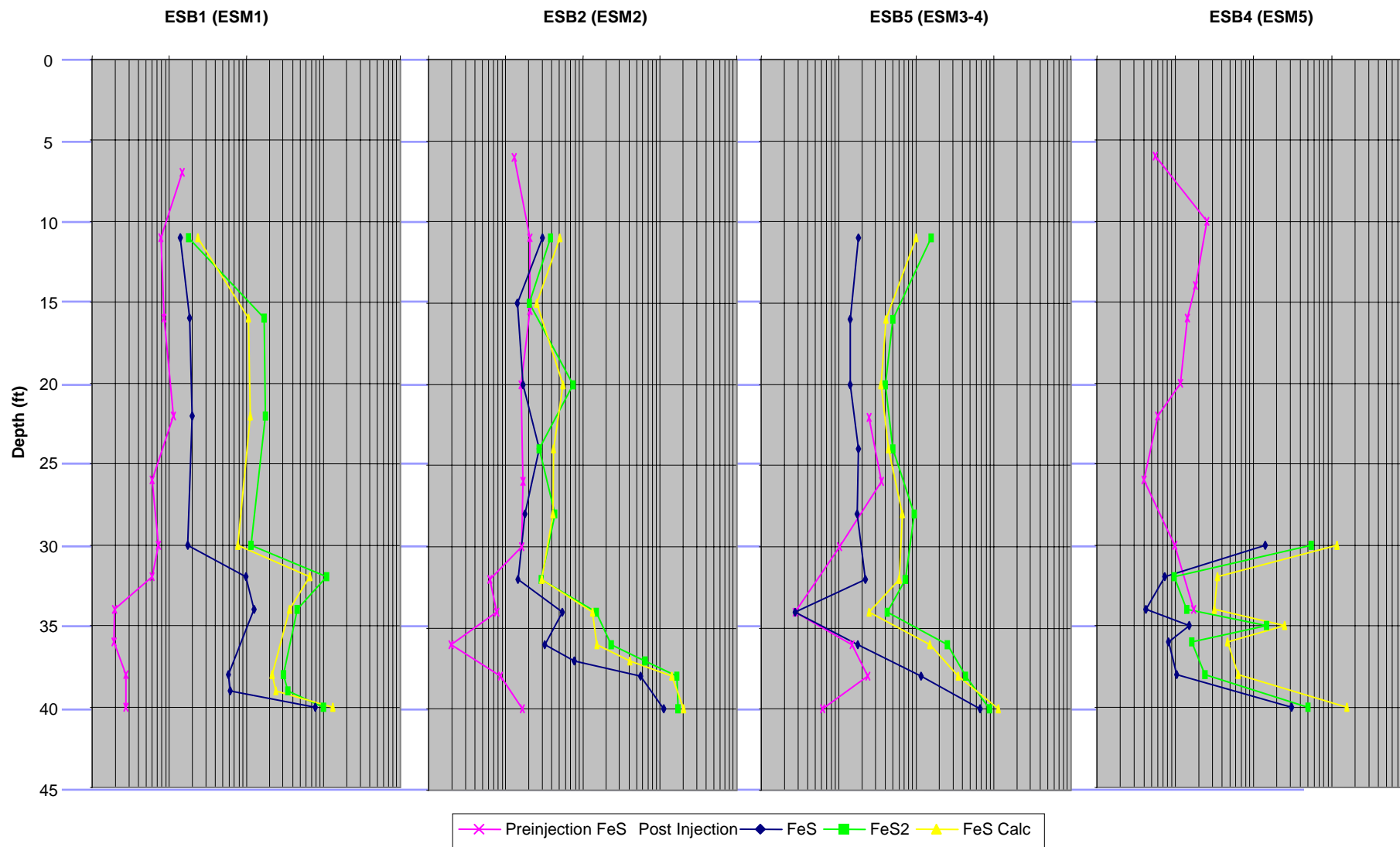


Figure 14. Iron sulfide concentrations showing pre injection FeS and all other values being post injection.

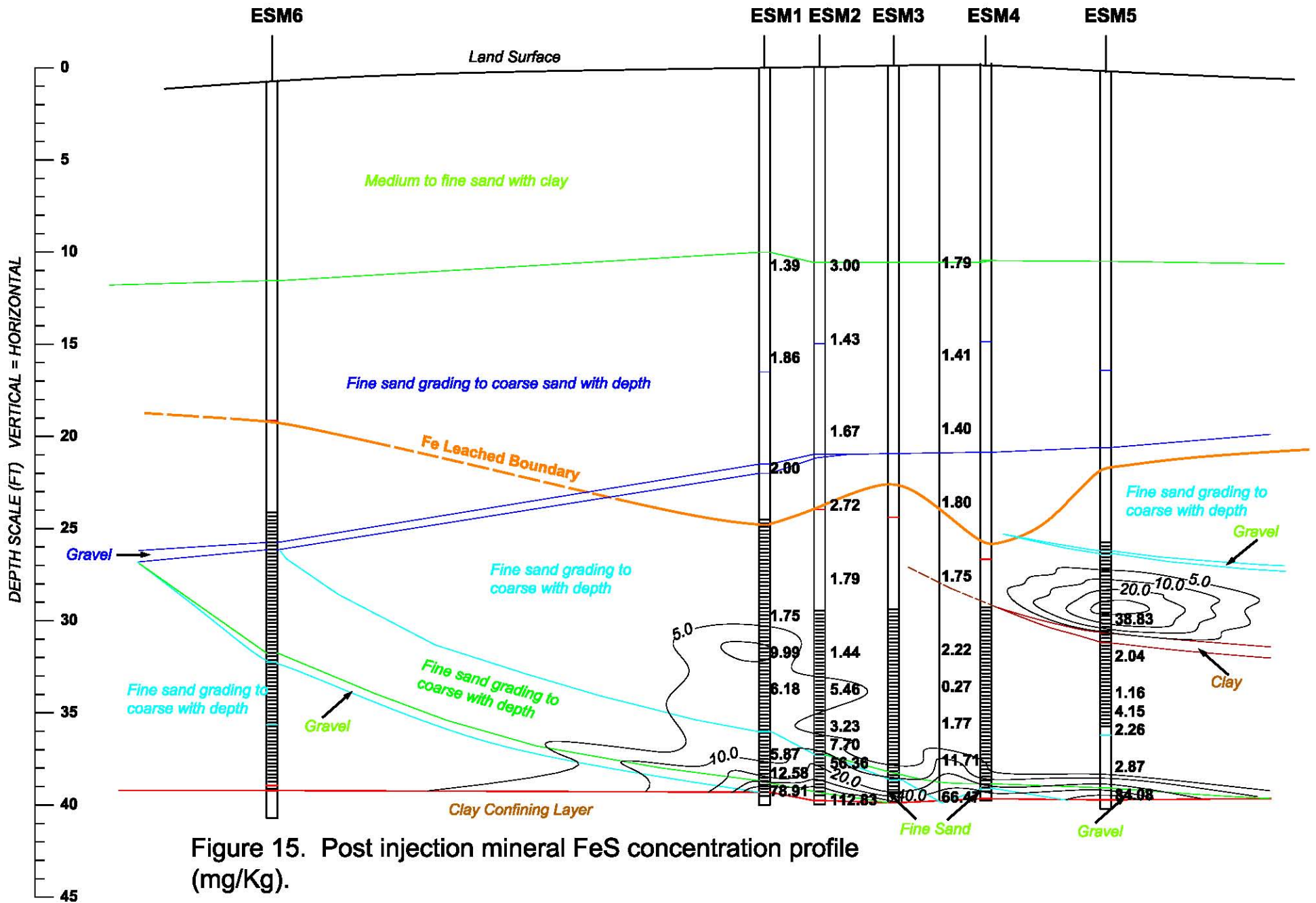


Figure 15. Post injection mineral FeS concentration profile (mg/Kg).

The entire sand section is quite permeable; however; much of the injectate moved along the base of the section in the highly permeable gravel just above the underlying confining clay. Injectate distribution was not uniformly emplaced across the height of the targeted treatment zone and was concentrated near the base. As a result, the injectate was emplaced/flowed over a vertically narrower but aerially wider than anticipated area.

Most FeS was found near the base of the sand and lower clay confining layer boundary. However, good concentrations of FeS were found much higher in ESM5 at about 30 feet. As is shown on Figure 7, there is coarse sand bound by a thin underlying clay at that depth which represents a small channel sequence. This channel sand is evidently oblique to the monitoring well array, essentially connecting ESM5 to the injectors. Evidently, injectate was preferentially conducted to ESM5 via this upper channel sand layer resulting in more FeS development and faster treatment for this well as is shown below.

FeS₂ distribution mirrors that of FeS in profile but extends slightly higher in the sediment section and is more concentrated (Figure 16). The ratio of FeS to FeS₂ is slightly lower than the theoretical relationship. Based on Equations 2 to 4, the ratio of S from FeS vs. FeS₂ should range from .5 to 1; typically .5 to .66 in an Fe(III) rich environment. Higher concentrations of FeS were probably present in the aquifer but have been lost due to 1) in-situ auto-oxidation and 2) oxidation during sample collection; both were almost certainly a factor. However, FeS₂ is chemically stable unlike FeS which can be easily oxidized. In-situ FeS concentrations can be partially corrected based on measured FeS₂ concentrations using:

$$(7) \quad S_{calc} = S_1 + \frac{S_2}{2}$$

Where:

S_{calc} = Calculated minimum S from FeS

S_1 = S⁻ from FeS

S_2 = S⁻ from FeS₂

Equation 6 is based on the stoichiometry derived from Equation 4. In-situ FeS concentrations approached 206 mg/Kg (Figures 14).

The distribution of the injectate was not uniform and flowed to the base of the aquifer in a transmissive gravel layer just above the lower confining clay layer and in at least one other channel feature. Despite this problem, significant

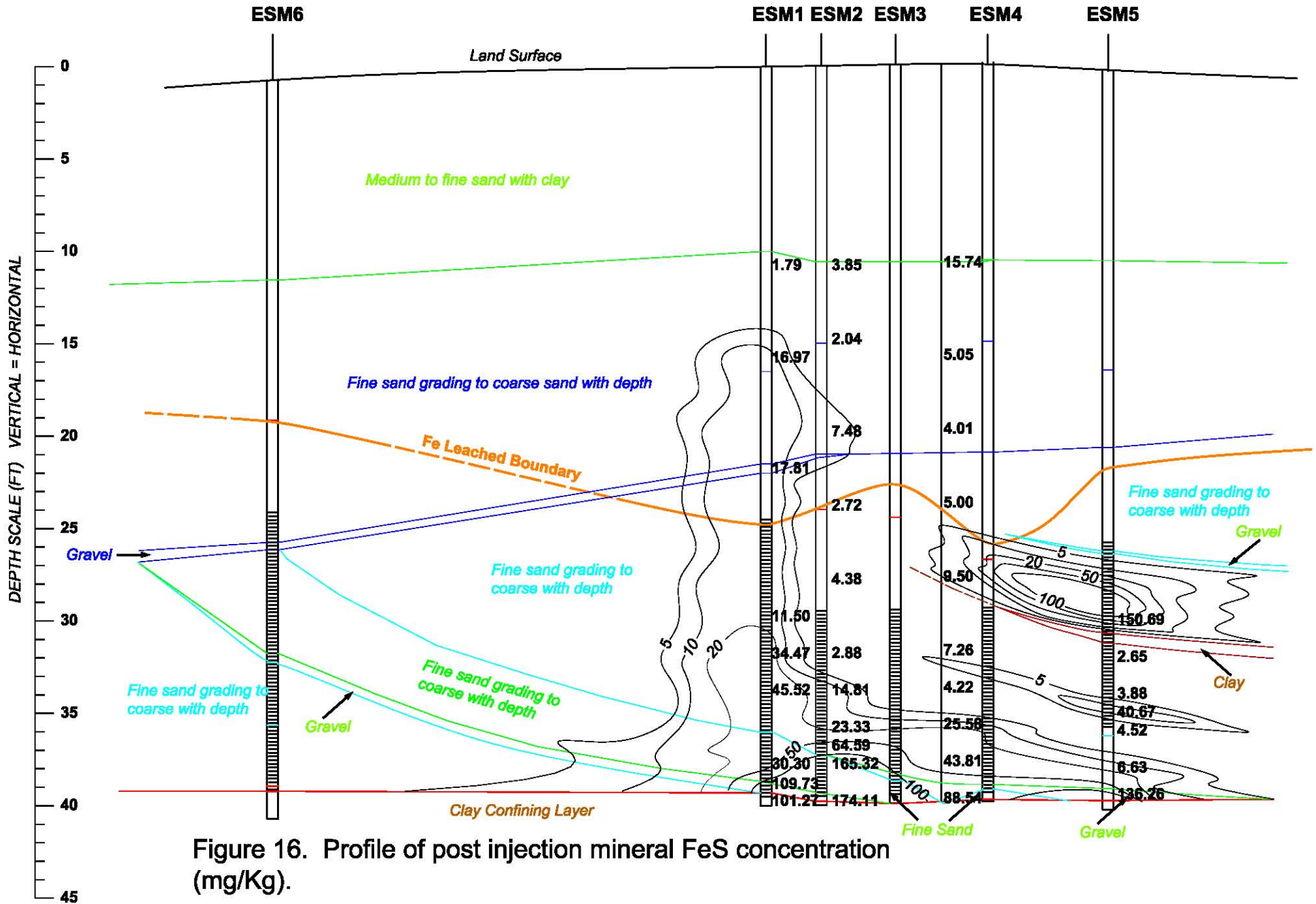


Figure 16. Profile of post injection mineral FeS concentration (mg/Kg).

concentrations of FeS developed as a result of the injection test. FeS developed in the permeable layers of the aquifer which are probably also pervasive pathways for contaminant migration.

3.14. OBSERVED AQUEOUS REACTIONS

Charts of TCE, cDCE, VC, TOC, and SO_4^{2-} with respect to time for the monitoring wells are shown on Figures 17 to 22 and in tabular form in Appendix I. Note that separate scales are used for TCE and DCE concentrations.

Injectate

Injectate concentrations were initially high immediately after injection at ESM1 but decreased rapidly due to mass transport and biological consumption. Initial maximum TOC concentrations were 1191 mg/L. Detectable TOC concentrations migrated as far down gradient as ESM4 (12 feet from the injection point). TOC wasn't observed in either of the peripheral wells (ESM5 or ESM6) but, based on FeS development lactate must have advanced to ESM5 at some time. Lactate was essentially consumed 150 days after injection.

Maximum measured SO_4^{2-} was 3987 mg/L immediately after injection. SO_4^{2-} migrated to the end of the monitoring array to ESM5. SO_4^{2-} above background concentrations was not detected in ESM6 until the final sampling event, reflecting the change in ground water flow direction. Although high concentrations of SO_4^{2-} were injected, no well had concentrations above the drinking water standard (250 mg/L) at the end of the experiment. Based on the injectate design all SO_4^{2-} should have been consumed by microbial respiration. These data indicate that a slightly higher lactate to sulfate ratio should be used to account for substrate competition by non-sulfate respiring bacteria.

CAH Response

Significant decreases in both DCE and TCE concentrations were observed in ESM1 and ESM2 during the first 228 days of the test but stabilized after that time. The observed initial decrease in CAH concentration occurred as the FeS zone developed and expanded away from the injection point. Concentrations stabilized when the FeS reaction zone expanded to its maximum up-flow gradient extent. Because ESM1 and ESM2 are near the center of the injection array they should be the least impacted by any change in ground water flow direction. CAH contact with the FeS reaction zone should be about the same irrespective of ground water flow. Stabilized CAH values at the end of the test infer that active BiRD treatment was still ongoing at steady state.

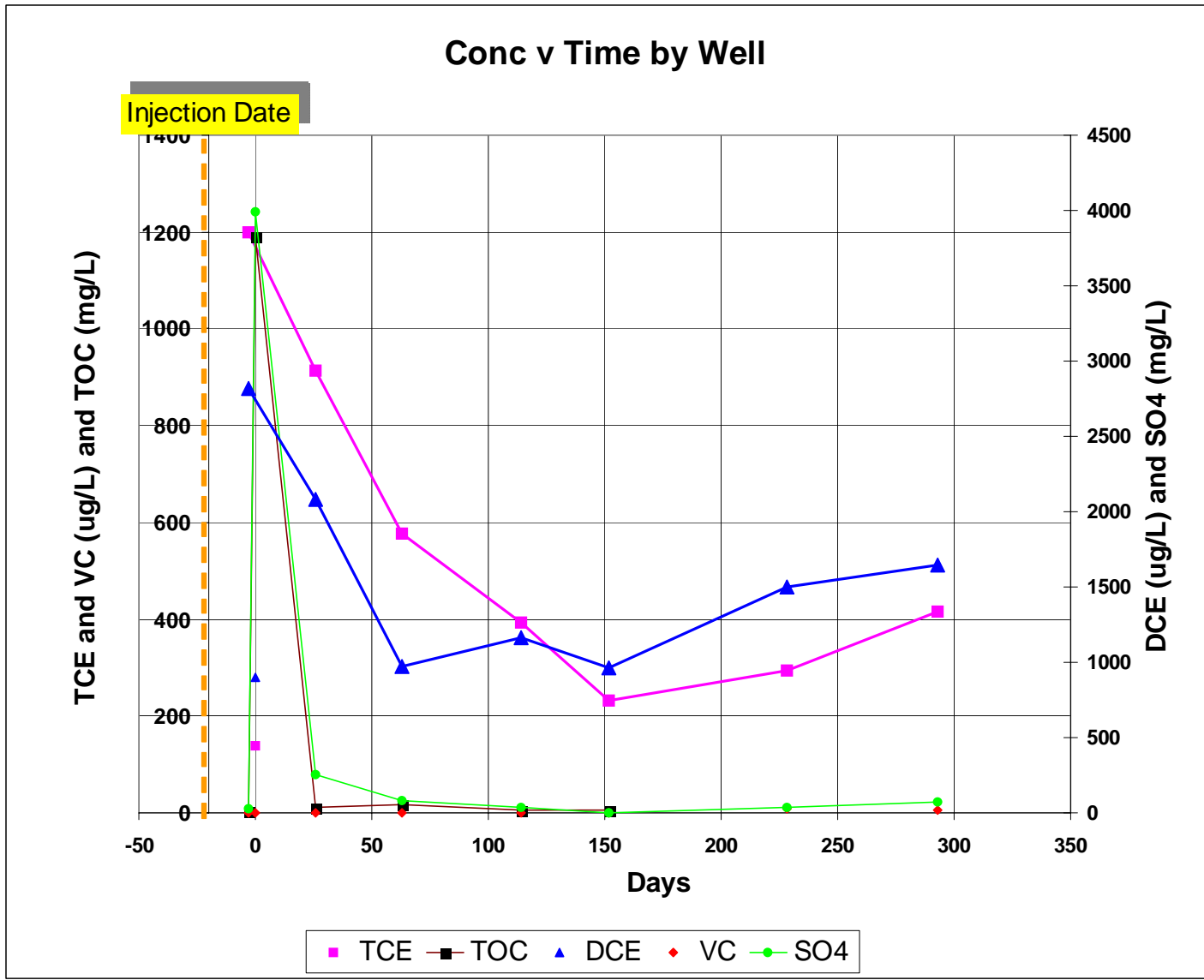


Figure 17. ESM1 aqueous CAH and injectate concentrations with respect to time.

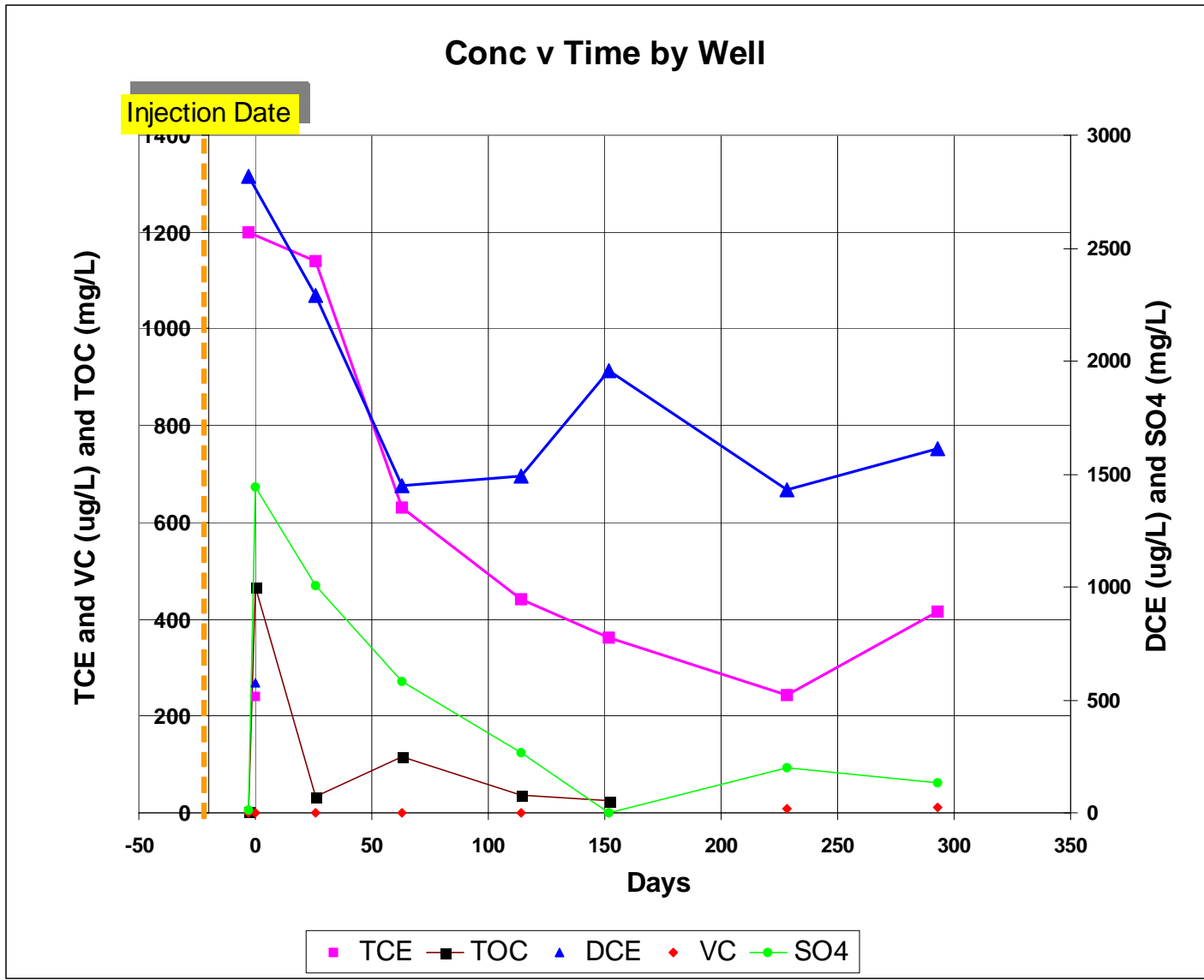


Figure 18. ESM2 aqueous CAH and injectate concentrations with respect to time.

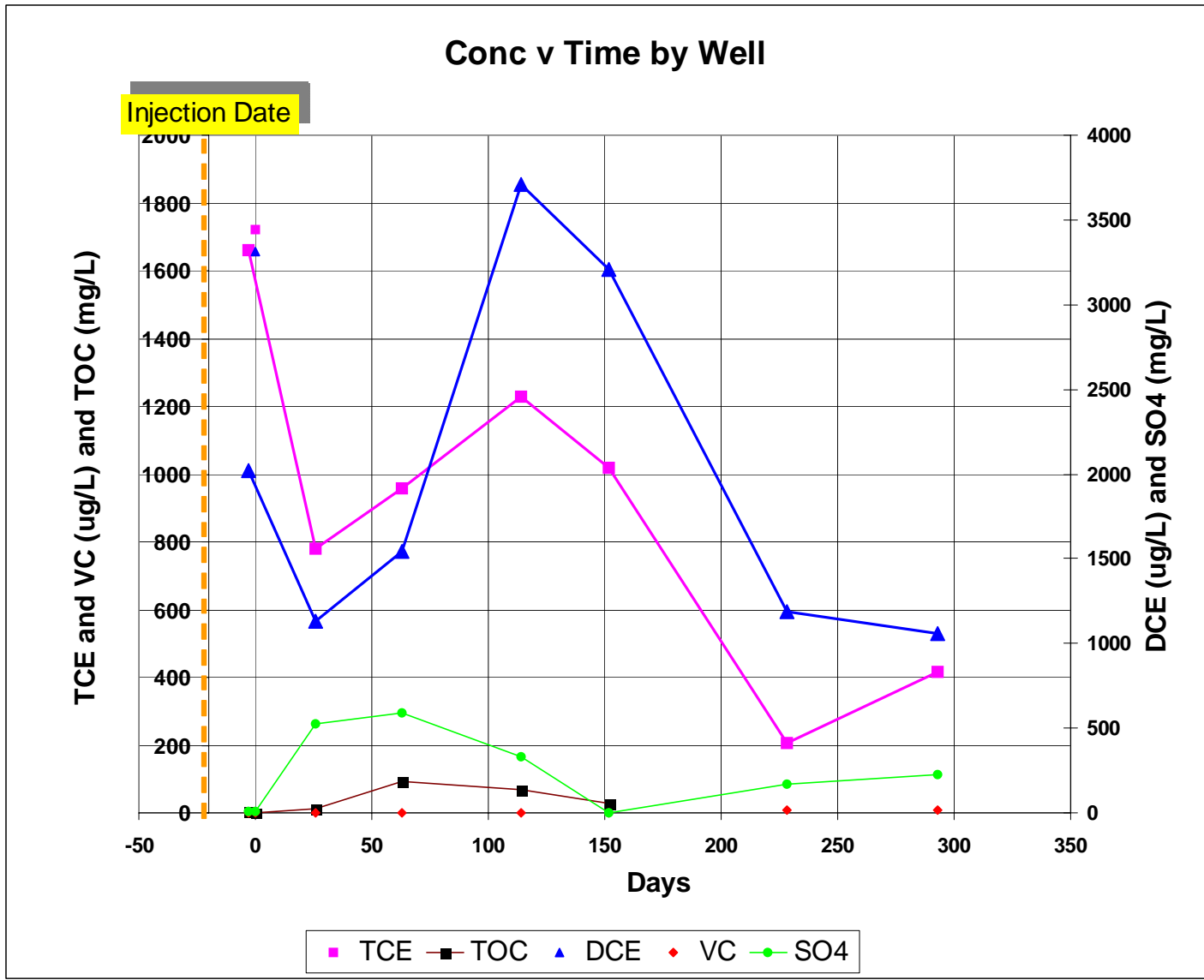


Figure 19. ESM3 aqueous CAH and injectate concentrations with respect to time.

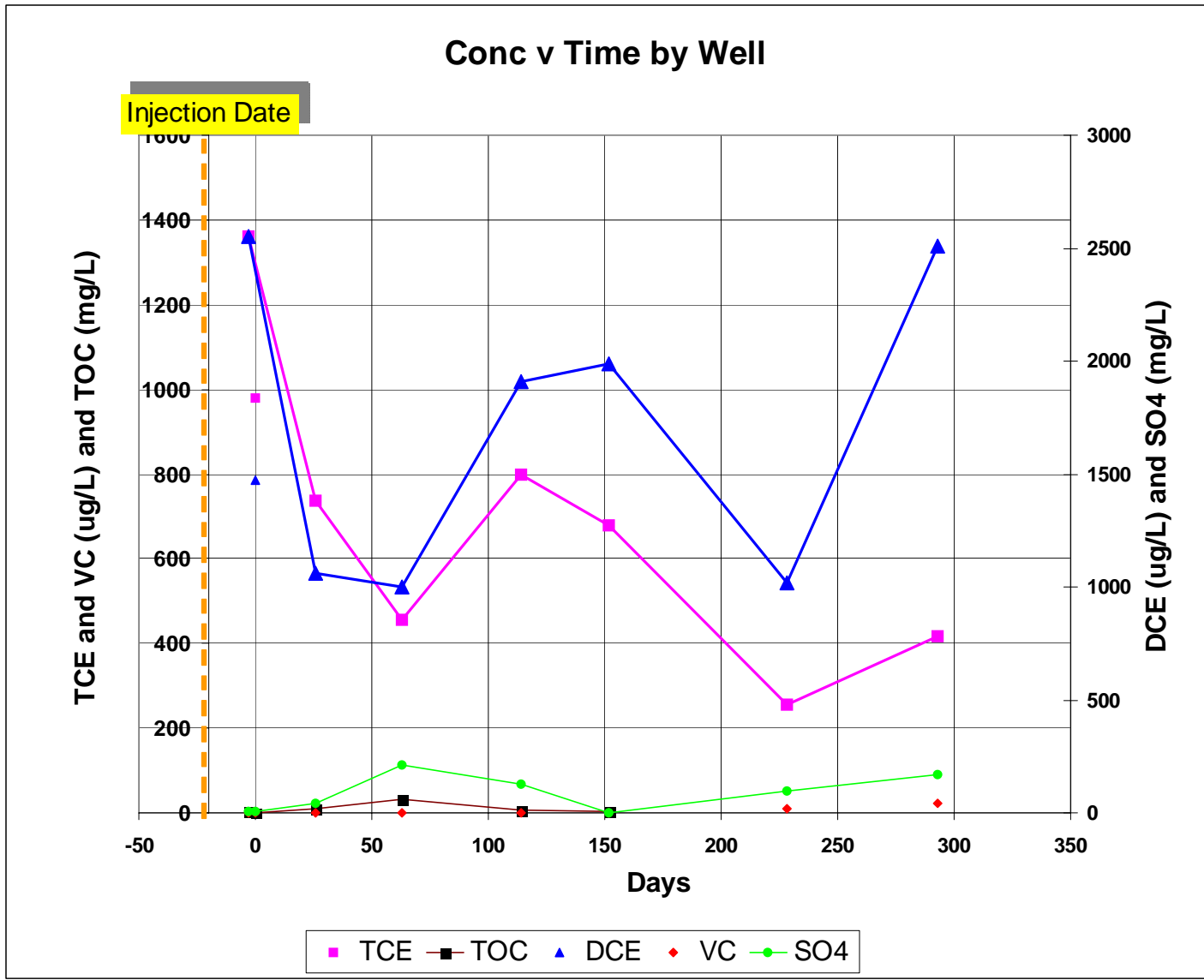


Figure 20. ESM4 aqueous CAH and injectate concentrations with respect to time.

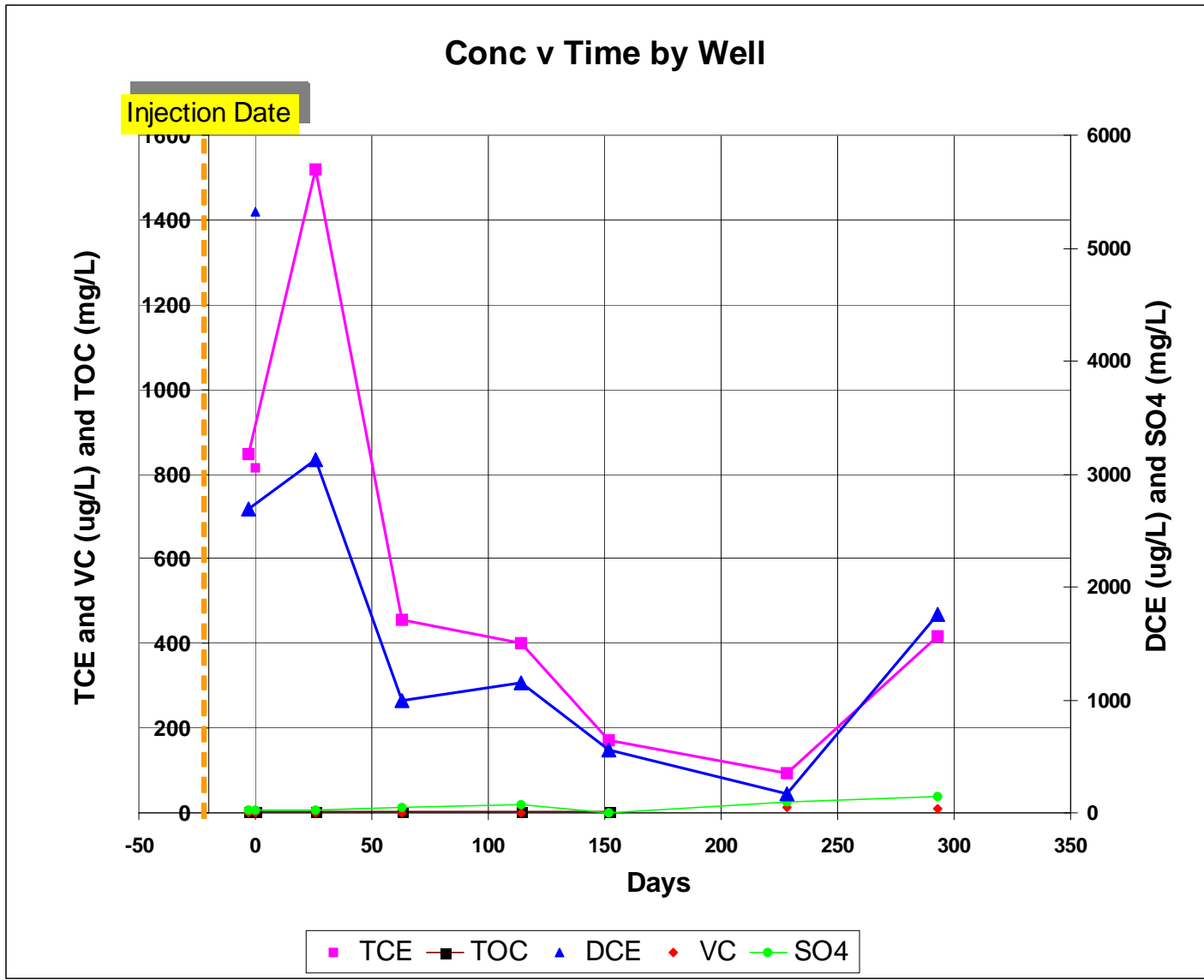


Figure 21. ESM5 aqueous CAH and injectate concentrations with respect to time.

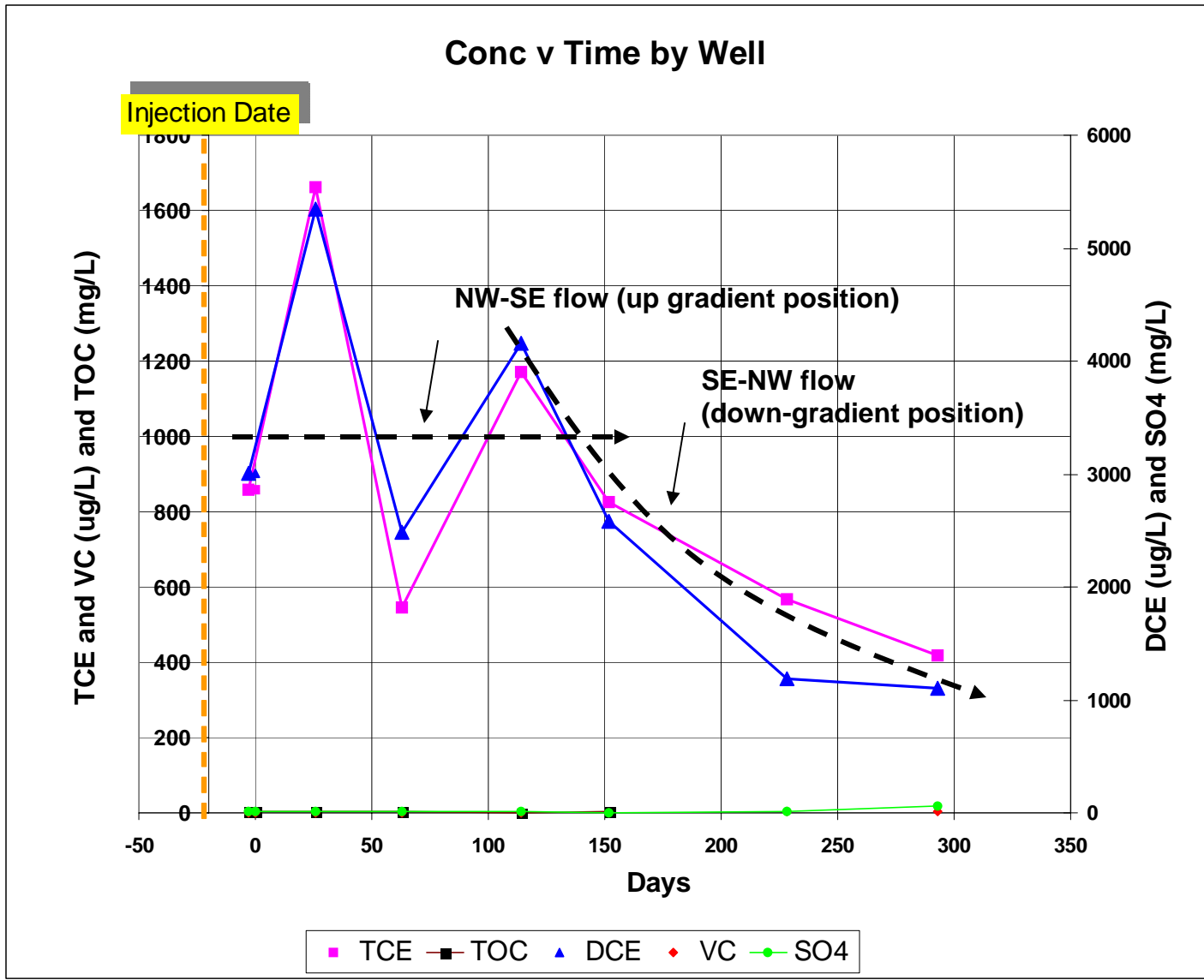


Figure 22. ESM6 aqueous CAH and injectate concentrations with respect to time.

ESM5 experienced the greatest TCE and DCE declines during the entire test. That observation is consistent because ESM5 was the most down-gradient observation point and CAH receives greater treatment as it passes through a larger FeS treatment zone. TCE concentrations decreased substantially in this well from initial concentrations of over 1500 ug/L to 93 ug/L at 228 days and DCE from 5320 ug/L to 167 ug/L. CAH concentrations even further down-flow gradient from ESM5 were probably lower than observed.

Although ESM5 was the most down-gradient monitoring point, after the ground water flow reversed, it became the most up-gradient observation point. So, late in the test, CAH arriving at ESM5 received the least contact with the FeS reactive zone and the least amount of treatment. This was probably the reason that CAH concentrations slightly increased at ESM5 for the last observation point.

As described above, ESM5 is connected to the injection array via a conductive channel sand at about 30 feet. Therefore, the BiRD affect was observable in ESM5 faster than ESM3 and ESM4 which were a little hydraulically isolated from the injection point though closer to it. However, by the end of the test, ESM3 and ESM4 showed substantial reductions in TCE ultimately decreasing from 1720 to 207 ug/L and 979 to 255 ug/L respectively. Though variable, DCE decreased considerably in ESM3 from over 3,000 ug/L to 1060 ug/L. DCE decreased slightly in ESM4 from 3,000 ug/L to 1020 ug/L after 229 days but rebounded to near its original concentrations at the end of the test. The reason for that rebound is unclear but may be due to the ground water reversal.

ESM6 was originally designed as the up-gradient background monitoring well to be used as a control point. CAH concentrations, though variable, showed no discernable decrease for the first 150 days while the ground water flow was towards the east. During this time, wells in the reaction zone showed rapid declines in CAH. Therefore, ESM6 provided the necessary control for the test demonstrating that changes in CAH concentrations in the reaction zone were in response to treatment. However, after about 150 days, the ground water flow direction began to reverse. At that time, ESM6 became the most down-gradient well in the observation array receiving ground water which had passed through the BiRD treatment zone. Concentrations of both TCE and DCE began to drop at ESM6 from a maximum of 1660 ug/L to 417 ug/L for TCE and 5340 ug/L to 1100 ug/L for DCE. Concentrations were still decreasing for ESM6 at the end of the observation period.

PCE concentrations for all monitoring wells are shown on Figure 23. PCE was extremely responsive to BiRD treatment decreasing from ~200 ug/L to ~10 ug/L. PCE concentrations remained consistently low through the end of the test.

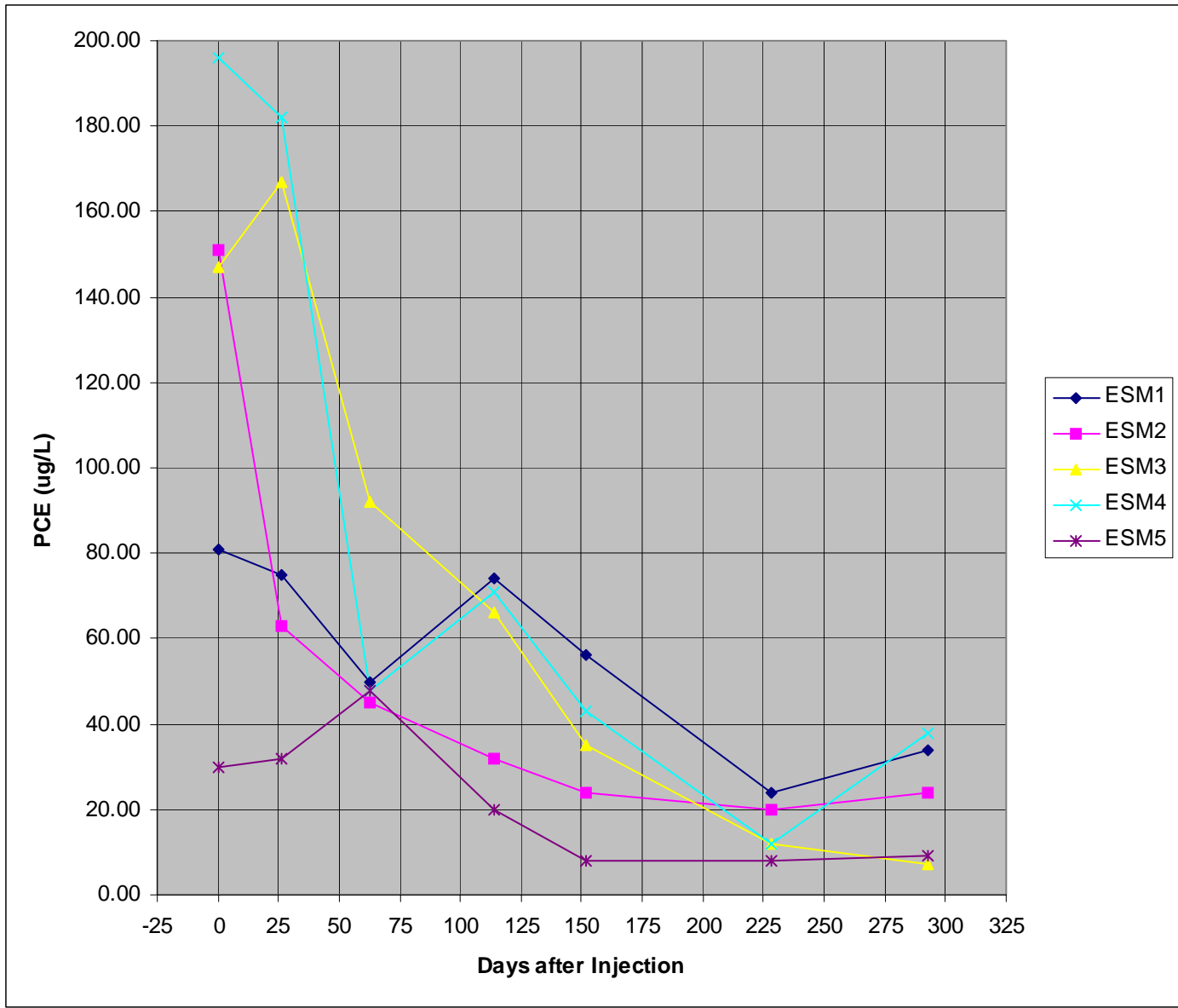


Figure 23. PCE concentrations for monitoring wells ESM1 to ESM5 (ug/L)

Demonstrating CAH remediation vs. distance is difficult to do because of changing ground water flow directions. The January 2004 sample date was selected because the FeS reaction had developed to the maximum and the affects of changing ground water flux across the reaction zone had nominal affect on concentrations. Figure 24 shows CAH concentrations with respect to distance beginning at the original up-gradient monitoring well (ESM6) to the original down-gradient well ESM5. TCE and DCE decrease along the original flow path and no daughter products, including VC were formed. Incidentally, the original injection wells were also sampled in January, 2004 and relative to that array, the ground water flow was from ESM5 to ESM1 though probably oblique to the general flow direction (Figure 25). PCE, TCE, and DCE decrease along this line of section and no daughter products, including VC were formed.

As described above, there were considerable decreases in PCE, TCE, and DCE during the test. TCE was treated without the generation of DCE as a daughter product. VC was present in all monitoring wells prior to injection at concentrations ranging from 10 to 87 ug/L. There was no significant change in VC concentrations over the course of the test. Final concentrations of VC ranged from 12ug/L to 40 ug/L. VC was neither treated nor produced by BiRD.

3.15. COMPARISON WITH VEGOIL TEST

Comparisons between the behavior of the BiRD test and Barrier 2 of the VegOil test have been made to examine the potential differences between the two treatment approaches. Similar monitoring wells are compared based on their position to their respective injection arrays. For this comparison, the most up-gradient and down-gradient monitoring points were selected for equivalent time periods. ESM1 is compared with AA-112 which were both at the point of injection and ESM5 is compared to AA-114 as the most down-flow gradient points.

To compare the behavior between the VegOil and BiRD sites the initial concentrations for TCE and cDCE were normalized to 1.0 (Figures 26 and 27). The highest starting concentration for stabilized post injection was selected as the initial value (41 days after injection for the VegOil data). As indicated on the figures, the starting concentrations for TCE and DCE at the BiRD site were equal to or several times greater than that of the VegOil site.

TCE was comparably removed from both the bioremediation and BiRD sites. Treatment response was slightly faster for BiRD and slightly more TCE was removal occurred in the up-gradient position wells. However, the most striking difference between the two treatment techniques is in the generation of daughter products. Although TCE was removed by bioremediation, equivalent concentrations of cDCE were generated and persisted in the aquifer. For BiRD both TCE and DCE were treated. The bioremediation test site also generated significant quantities of VC which were not produced using BiRD.

Well ID	Dist.	TCE	DCE	VC
ESM6	-27	824	2580	10
ESM1	0	231	967	5
ESM2	3	362	1960	7
ESM3	7	1020	3210	13
ESM4	12	678	1990	7
ESM5	18.5	170	561	3

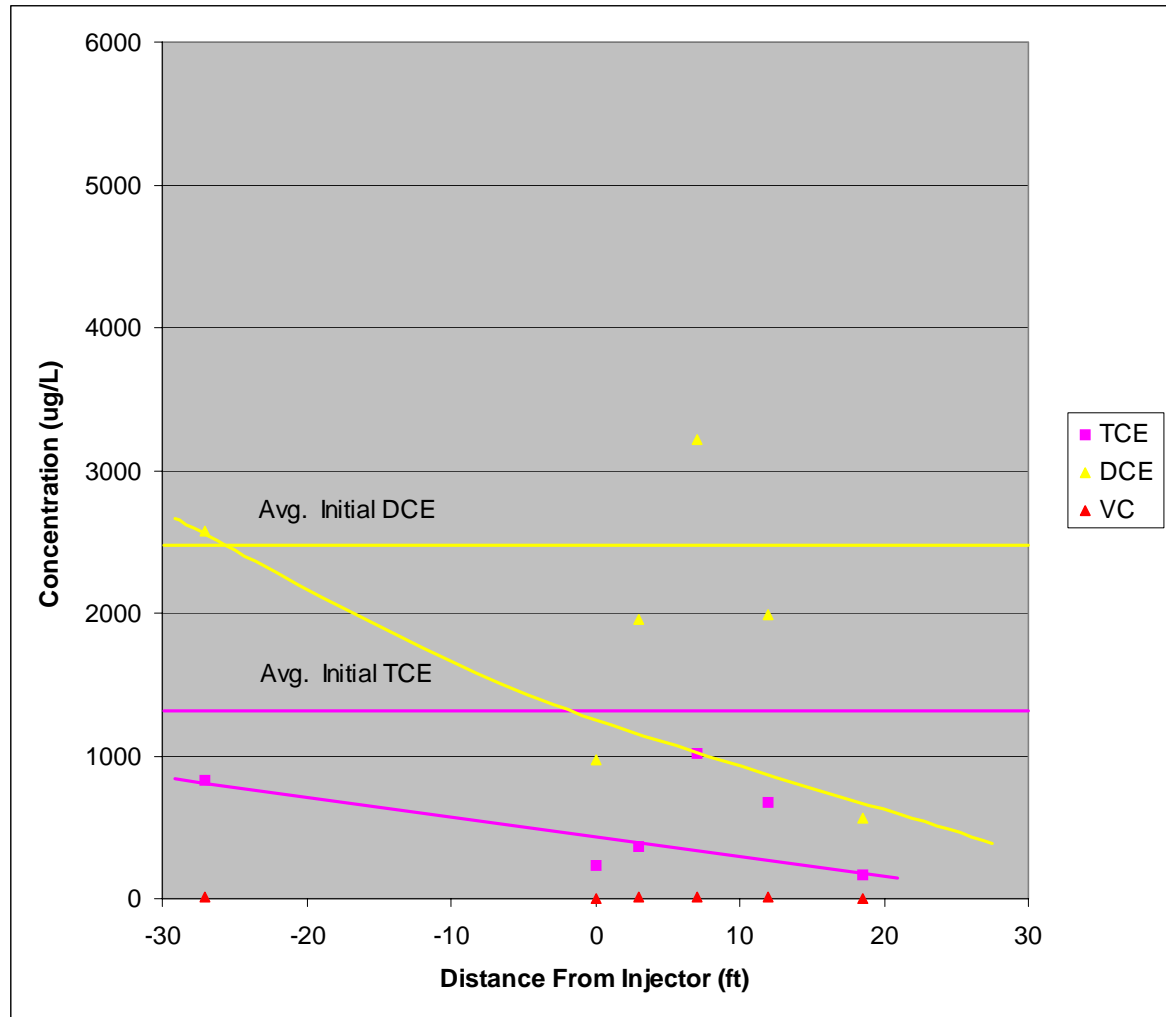


Figure 24. CAH concentrations with respect to distance for January 2004 through the monitoring wells.

CAH Data

Sample ID	Dist	PCE	TCE	DCE	VC
ESI5	0	84	606	2840	13
ESI4	10	22	437	3880	13
ESI3 (ESM1)	20	35	1020	3210	13
ESI2	30	25	101	860	5
ESI1	40	11	45	156	2

Water level data

Well	Elev	DTW	Elev
ESI1	23.1	10.19	12.89
ESI2	23.3	10.41	12.90
ESI3 (ESM1)	23.4	10.46	12.91
ESI4	23.3	10.42	12.92
ESI5	23.2	10.33	12.90

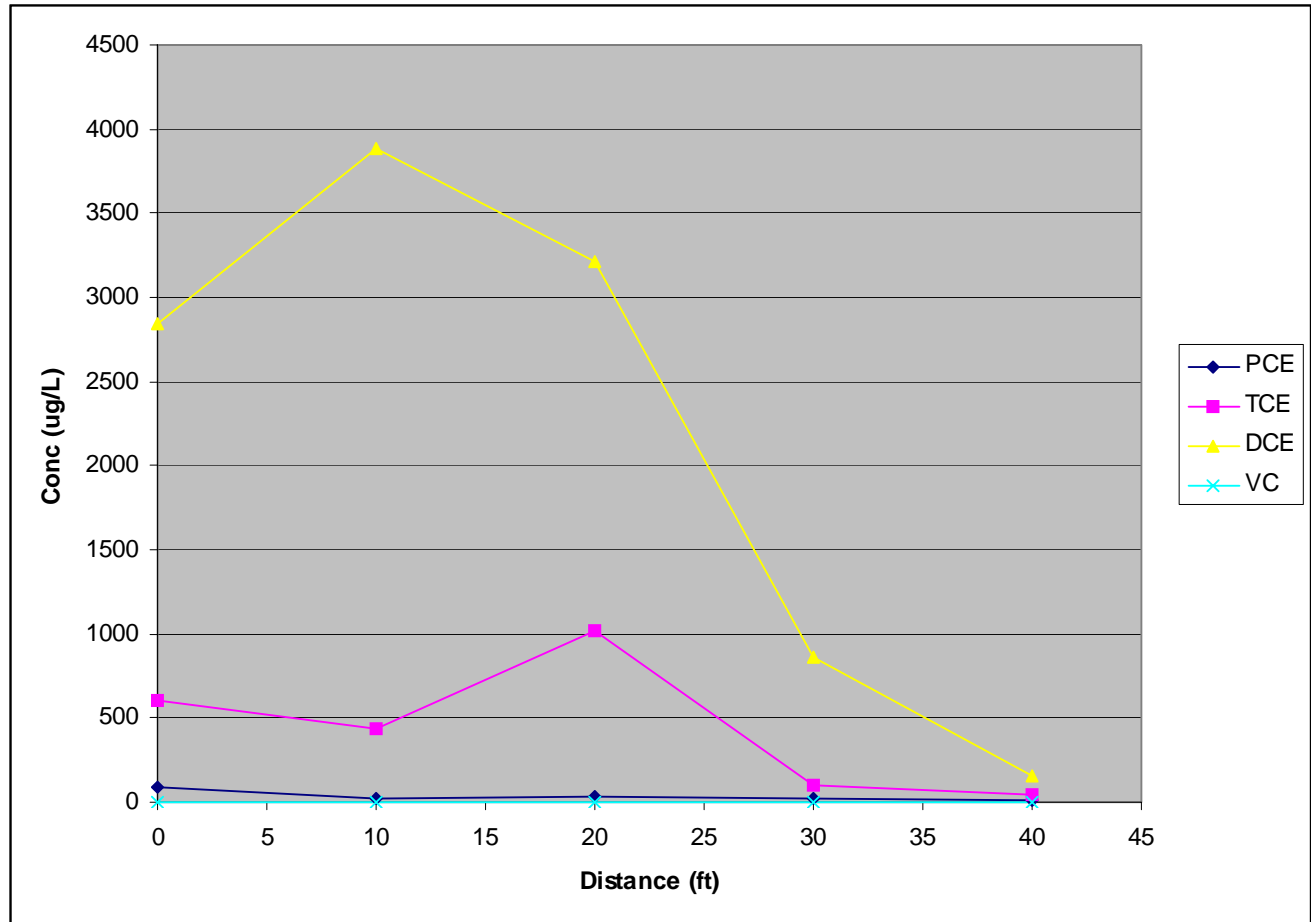


Figure 25. CAH concentration vs. distance from up-gradient to down-gradient along the injection wells for January 2004.

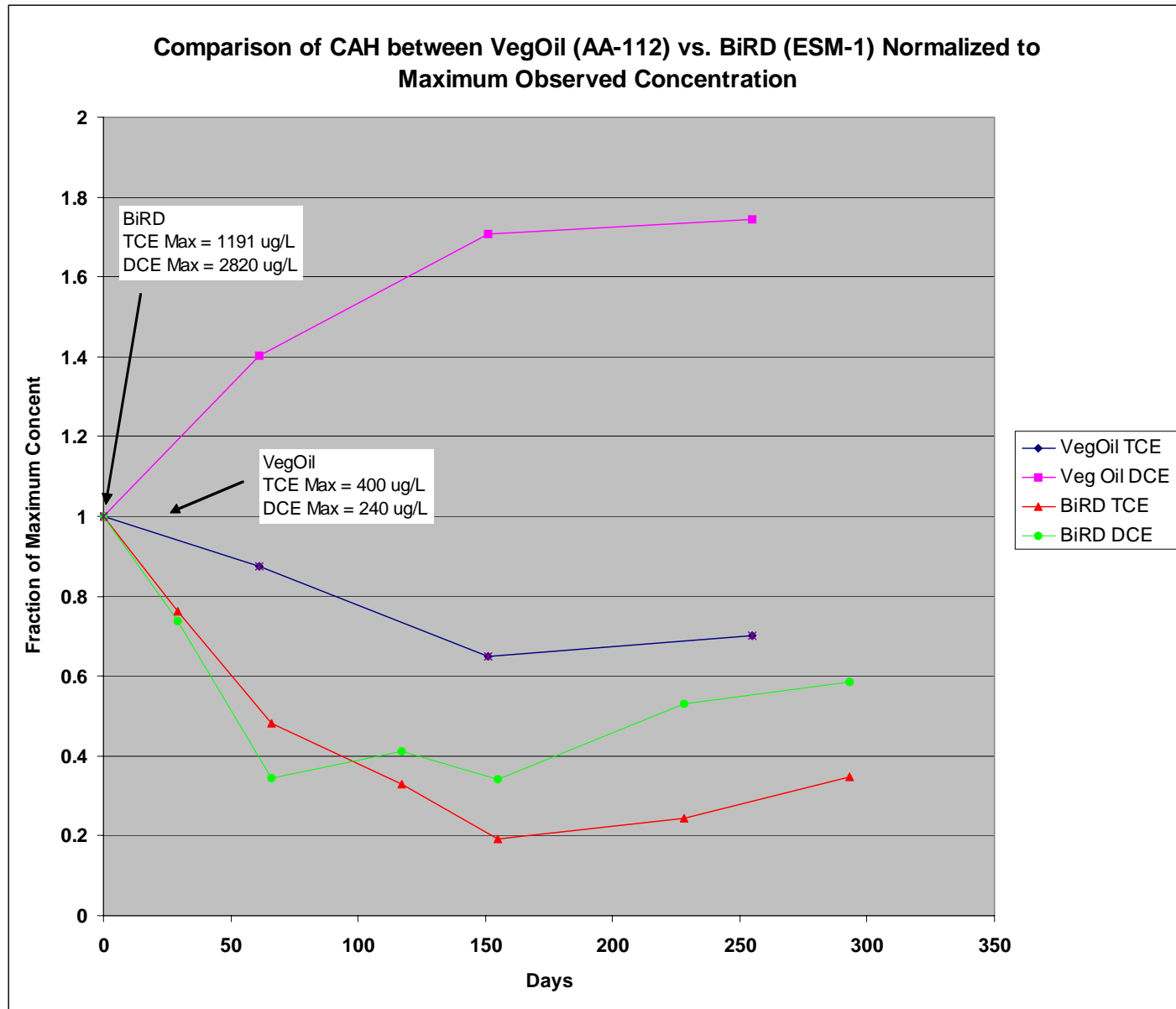


Figure 26. Comparison of TCE and DCE concentrations for the BiRD and bioremediation sites for the most up-gradient monitoring points. Data were normalized to 1.0.

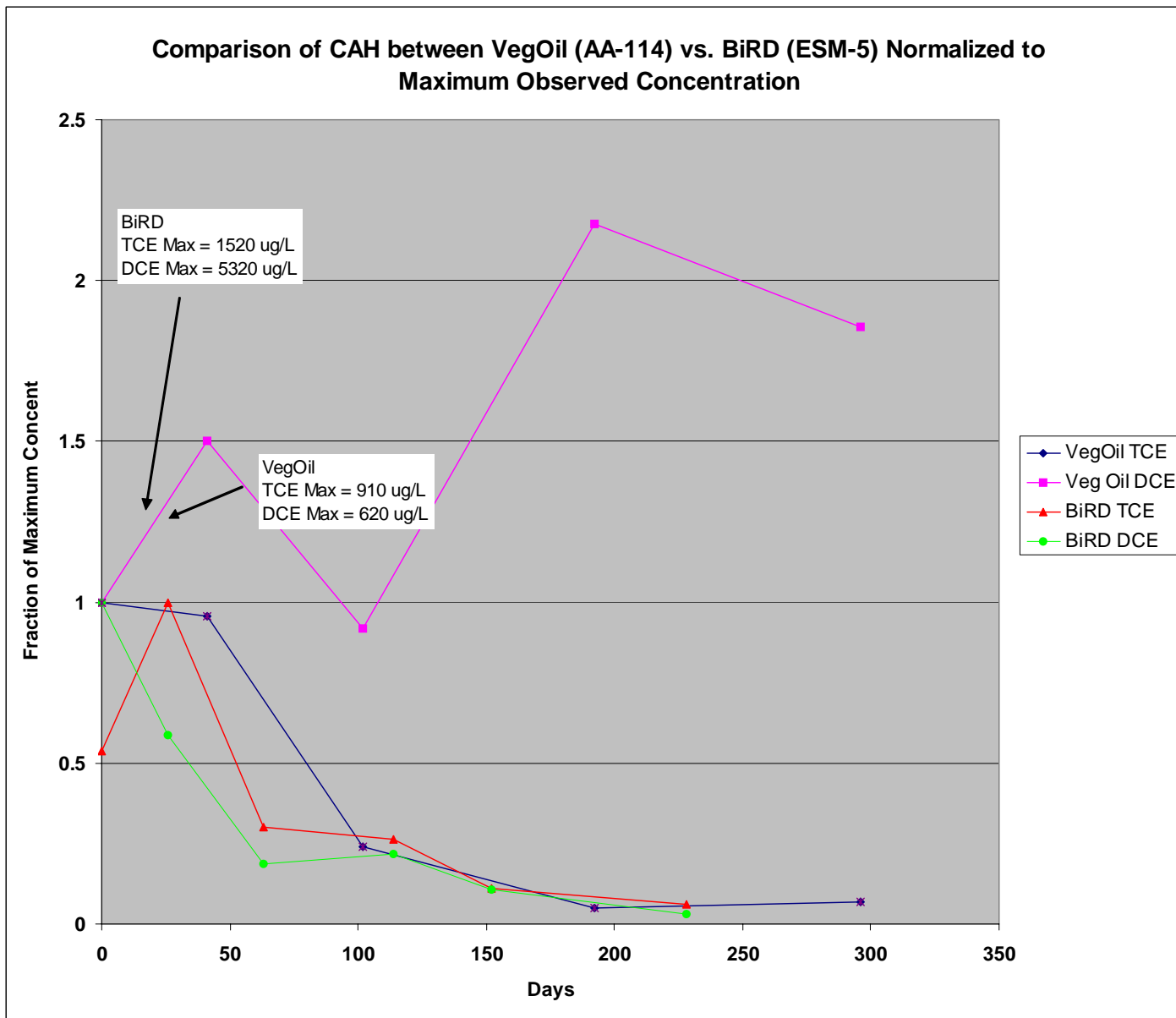


Figure 27. Comparison of TCE and DCE concentrations for the BiRD and bioremediation sites for the most down-gradient monitoring points. Data were normalized to 1.0.

3.16. *MICROCOSM ANALYSES*

The results of the microcosm test are presented on Figure 28. Sediment from the sample depth was determined to have 129 mg/Kg FeS. Both the killed and live systems showed strong TCE removal with no significant difference between the two systems. TCE is removed from the live and killed systems equally indicating that the “abiotic” pathway from biogeochemical reductive dechlorination is actually responsible for treatment rather than bioremediation. No DCE was produced by either system.

Least squares fit for the microcosm decline curves were fit assuming a first order kinetic model. TCE half life at the end of the microcosm experiment (day = 76) was 31 d^{-1} and 27 d^{-1} for the killed and live systems respectively averaging 29 d^{-1} . However, the apparent half life of TCE was faster during the early part of the test from 0 to 27 days with the killed = 20 d^{-1} and live = 24 d^{-1} averaging 22 d^{-1} .

Days	Killed		Live	
	TCE (mg/L)	DCE (mg/L)	TCE (mg/L)	DCE (mg/L)
1	2.2350	0.0000	2.0500	0.0174
3	2.3850	0.0012	2.3700	0.0000
6	1.4150	0.0024	1.9450	0.0000
14	1.2500	0.0000	1.2250	0.0000
27	0.9880	0.0126	1.1100	0.0013
31	1.0700	0.0000	0.8530	0.0014
76	0.4980	0.0058	0.3715	0.0022

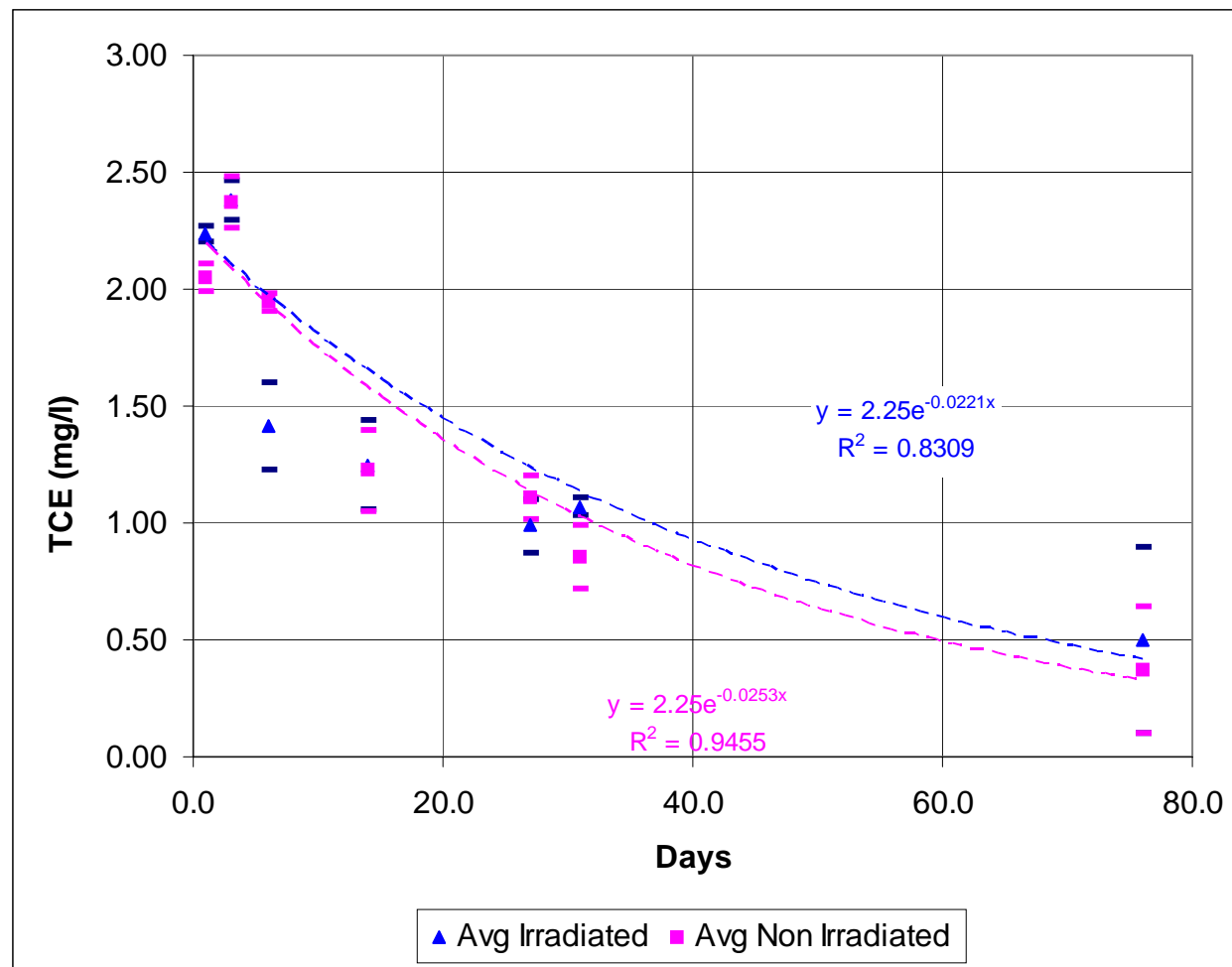


Figure 28. TCE concentrations for the live and killed microcosms. Table values are the average of duplicate values.

4. CONCLUSIONS

Biogeochemical Reductive Dechlorination was successfully tested at the Target Area 1 site at Dover Air Force Base. Much information was gained concerning the application and optimization of this treatment technology. DAFB was a good test site because the ground water had very low naturally occurring concentrations of SO_4^{2-} and bioremediation via vegetable oil injection had been tested nearby. Therefore, BiRD does not occur naturally and a direct comparison between biostimulation and BiRD could be made.

The native sediment consisted predominantly of sand grading to gravel with depth above a confining clay layer at 40 feet. Below 25 feet the native sand was rich in Fe containing up to 21,000 mg/Kg which could easily support for formation of FeS. Only 10% of the Fe was utilized during the test so Fe is not limiting to the BiRD process even if much higher concentrations of reagent are used.

The injection of SO_4^{2-} and lactate resulted in the generation of significant quantities of FeS via biogeochemical processes. Prior to injection FeS concentrations were minor (<1 mg/Kg). After injection, quantities of FeS formed up to 174 mg/Kg. Due to permeability anisotropy, injectate preferentially flowed through a thin gravel layer just above the lower confining clay where the majority of the FeS developed. Therefore, the actual treatment zone was shorter but covered a wider area than originally expected. Based on the strong CAH treatment response, FeS evidently formed along the same pervasive pathways of contaminant flow.

FeS_2 distribution mirrored that of FeS. Slightly higher FeS_2 was observed than normally would be expected. FeS_2 mass suggests that FeS was present at higher concentrations in the aquifer than was actually measured. Loss of FeS was probably due to in-situ oxidation and/or loss due to oxidation during sampling.

After injection the maximum concentrations of SO_4^{2-} and TOC were 1191 mg/L and 3987 mg/L respectively. During the course of the test, 293 days, injectate concentrations decreased to minimum levels. Sulfate was above its original background concentration (~14 mg/L) but well below the drinking water standard (250 mg/L). Further sulfate consumption is expected with time.

Treatment response was almost immediate in the two most up gradient (ESM1 and ESM2) and the most down gradient (ESM5) monitoring wells. Due to reservoir anisotropy, the treatment response was slightly delayed in the intermediate wells (ESM3 and ESM4). All monitoring wells eventually showed significant treatment response for PCE, TCE, and DCE. VC, which was present prior to injection at concentrations between 10 to 87 ug/L, was neither treated nor generated during the test.

For individual wells, CAH concentrations decreased with respect to time rapidly during the first half of the experiment while the FeS reaction zone was developing and expanding but stabilized when steady state conditions occurred. Water flowing to the most down-gradient well, ESM5, passed across a larger treatment zone and showed the greatest response. Up-gradient concentrations of TCE at ~1500 ug/L decreased to 93 ug/L across the treatment zone and DCE decreased from ~3000 ug/L to 167 ug/L. PCE concentrations decreased from ~200 ug/L to ~10 ug/L. Depending on the extent of the treatment zone, further reductions in CAH would occur down-flow gradient. Treatment rebound was not observed during the course of the experiment. Daughter products were including VC were not generated.

BiRD treated TCE about the same as the bioremediation test site, possibly occurring slightly faster and to a slightly greater degree. However, biostimulation resulted in generation of large quantities of DCE and VC. For the most part, bioremediation merely transformed TCE to DCE which accumulated in the aquifer. BiRD not only didn't generate DCE, the approach substantially treated DCE entering into the reaction zone from up gradient resulting in complete CAH treatment rather than transforming one contaminant type to another.

BiRD was verified as the treatment pathway in batch microcosm. Both live and killed microcosms containing FeS bearing sediment from the site treated TCE at the same rate without generating DCE. The half life for TCE treatment was fast, averaging between 22 to 29 d⁻¹.

Due to the fast microbial response and high native Fe concentrations, much higher concentrations of SO₄²⁻ and organic could have been applied at this site. The data suggest that a slightly higher organic: SO₄²⁻ ratio should be used to facilitate more complete SO₄²⁻ consumption. Additionally, a basic pH should have been used in the injectate. Adjusting pH to at least 9.0 could significantly increase FeS reaction kinetics inducing faster CAH treatment rates. Increasing the width of the treatment zone will result in greater overall treatment.

This field test suggests that BiRD should be very beneficial in the in-situ treatment of PCE, TCE, and DCE, at Dover AFB. The technology is effective, easy to apply, and the amendments are inexpensive. The data obtained here can be used for design purposes and the process can easily be up-scaled for general ground water remediation on a larger basis.

5. ACKNOWLEDGMENTS

We gratefully acknowledge the funding of this demonstration project by the Air Force Center for Environmental Excellence (AFCEE). Additionally, aqueous organic analyses data were kindly provided by the Dover National Environmental Technology Test Site laboratory.

The field demonstration for the technology described in this report was conducted at the Dover National Environmental Technology Test Site (NETTS), established and managed on behalf of the U.S. Department of Defense Strategic Environmental Research and Development Program (SERDP). The demonstration complied with prescribed NETTS protocols and guidelines for quality assurance, health and safety, technical completeness, and regulatory compliance. Support provided by the NETTS facilities and test location manager and staff are gratefully acknowledged. For further information on NETTS locations or SERDP, contact Andrea Leeson at 703-696-2118, or Scott Dockum at 703-326-7808, or visit the SERDP web site at www.serdp.org.

6. REFERENCES

- Advanced Infrastructure Management Technologies and URGS Group, Inc. 2002. Target Area 1 semi-annual monitoring report May 2002 sampling event Dover Air Force Base, Delaware.
- Butler, E. C., and K. F. Hayes, 1999. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide, *Environmental Science Technology*, 33:2021-2027.
- Butler, E. C., and K. F. Hayes, 2000. Kinetics of the transformation of halogenated aliphatic compounds by iron sulfide, *Environ. Sci. Technol.*, 34:422-429.
- Dames and Moore, 1999. Site WP21 Semi-annual compliance monitoring report, May 1999 Sampling Event.
- Everett and Kennedy, 2002. TCE dechlorination via reaction with microbially generated mineral FeS at the SS-17 VegOil test site, Rowan University, Glassboro, NJ, in progress.
- Earth Science Services (ESS), 2004. Progress report 1: Field test of biogeochemical reductive dechlorination at Dover Air Force Base Dover, Delaware, AFCEE Internal Report.
- Kennedy L.G., J.W. Everett, 2001. Microbial degradation of simulated landfill leachate: Solid iron/sulfur interactions, *Applied Environmental Research*, Vol 5/2, pp 103-116
- Kennedy, L.G., J.W. Everett, and J. Gonzales, 2000. Technical protocol for natural attenuation assessments using solid and aqueous electron acceptors; Air Force Center for Environmental Excellence, San Antonio, TX, In Review.
- Terra Systems, 2002. Technology application of low cost emplacement of insoluble organic substrate for enhanced in-situ reductive dechlorination of halogenated aliphatic hydrocarbons: Dover Air Force Base, Dover, Delaware: Draft interim report

Appendix I

Date	Location	(ft)	FeS (mg/Kg)	FeS2 (mg/Kg)
9/29/2003	ESM1	7	1.47	3.12
9/29/2003	ESM1	11	0.79	5.30
9/29/2003	ESM1	16	0.86	3.88
9/29/2003	ESM1	22	1.14	6.47
9/29/2003	ESM1	26	0.60	1.99
9/29/2003	ESM1	30	0.73	1.98
9/29/2003	ESM1	32	0.60	1.00
9/29/2003	ESM1	34	0.20	0.78
9/29/2003	ESM1	36	0.19	1.61
9/29/2003	ESM1	38	0.27	0.80
9/29/2003	ESM1	40	0.27	1.06
9/22/2003	ESM2	6	1.28	2.56
9/22/2003	ESM2	11	2.06	3.36
9/22/2003	ESM2	15.5	2.07	2.07
9/22/2003	ESM2	20	1.60	1.00
9/22/2003	ESM2	26	1.67	1.88
9/22/2003	ESM2	30	1.63	1.15
9/22/2003	ESM2	32	0.62	1.45
9/22/2003	ESM2	34	0.77	1.16
9/22/2003	ESM2	36	0.20	1.37
9/22/2003	ESM2	38	0.86	3.44
9/22/2003	ESM2	40	1.64	1.23
9/15/2003	ESM3	22	2.47	4.94
9/15/2003	ESM3	26	3.59	3.99
9/15/2003	ESM3	30	1.02	3.27
9/15/2003	ESM3	34	0.27	3.52
9/15/2003	ESM3	36	1.49	2.14
9/15/2003	ESM3	38	2.37	2.56
9/15/2003	ESM3	40	0.62	2.27
9/8/2003	ESM4	7	1.32	1.69
9/8/2003	ESM4	12	1.56	12.88
9/8/2003	ESM4	17	1.19	1.59
9/8/2003	ESM4	22	1.01	1.42
9/8/2003	ESM4	28	1.39	1.97
9/8/2003	ESM4	34	0.00	1.21
9/8/2003	ESM4	36	0.20	1.02
9/8/2003	ESM4	38	1.25	2.09
9/8/2003	ESM4	40	0.86	1.94

Preinjection iron sulfides

8/26/2003	ESM5	6	0.56	1.67
8/26/2003	ESM5	10	2.55	4.11
8/26/2003	ESM5	14	1.83	1.62
8/26/2003	ESM5	16	1.43	2.25
8/26/2003	ESM5	20	1.17	3.71
8/26/2003	ESM5	22	0.60	3.19
8/26/2003	ESM5	26	0.40	0.60
8/26/2003	ESM5	30	0.99	1.19
8/26/2003	ESM5	34	1.74	1.75
8/25/2003	ESM6	7	0.71	3.36
8/25/2003	ESM6	13	1.34	1.15
8/25/2003	ESM6	17	1.42	1.83
8/25/2003	ESM6	21	1.01	1.81
8/25/2003	ESM6	25	1.02	2.44
8/25/2003	ESM6	29	0.81	2.02
8/25/2003	ESM6	33	0.00	3.27
8/25/2003	ESM6	35	3.33	3.77
8/25/2003	ESM6	38	2.87	2.17

Preinjection iron sulfides

Date	Location	(ft)	FeS (mg/Kg)	FeS2 (mg/Kg)	Theoretic al FeS
5/25/2004	ESB1	11	1.39	1.79	2.36
5/25/2004	ESB1	16	1.86	16.97	10.66
5/25/2004	ESB1	22	2.00	17.81	11.24
5/25/2004	ESB1	30	1.75	11.50	7.73
5/25/2004	ESB1	32	9.99	109.73	66.85
5/25/2004	ESB1	34	12.58	45.52	36.42
5/25/2004	ESB1	38	5.87	30.30	21.67
5/25/2004	ESB1	39	6.18	34.47	24.14
5/25/2004	ESB1	40	78.91	101.27	133.52
5/25/2004	ESB2	11	3.00	3.85	5.07
5/25/2004	ESB2	15	1.43	2.04	2.53
5/25/2004	ESB2	20	1.67	7.48	5.57
5/25/2004	ESB2	24	2.72	2.72	4.21
5/25/2004	ESB2	28	1.79	4.38	4.10
5/25/2004	ESB2	32	1.44	2.88	2.97
5/25/2004	ESB2	34	5.46	14.81	13.25
5/25/2004	ESB2	36	3.23	23.33	15.36
5/25/2004	ESB2	37	7.70	64.59	41.23
5/27/2004	ESB2	38	56.36	165.32	143.29
5/30/2004	ESB2	40	112.83	174.11	206.03
6/3/2004	ESB3	16	1.01	6.86	4.57
6/4/2004	ESB3	20	1.69	3.81	3.71
6/5/2004	ESB3	24	1.87	12.23	8.23
6/6/2004	ESB3	28	1.59	4.18	3.80
6/7/2004	ESB3	32	1.62	3.84	3.65
6/8/2004	ESB3	34	1.59	3.38	3.38
6/9/2004	ESB3	36	0.79	4.93	3.35
6/10/2004	ESB3	38	1.78	13.66	8.88
6/11/2004	ESB3	40	58.63	133.84	129.42
6/17/2004	ESB4	30	38.83	150.69	117.69
6/14/2004	ESB4	32	2.04	2.65	3.47
6/15/2004	ESB4	34	1.16	3.88	3.20
6/20/2004	ESB4	35	4.15	40.67	25.23
6/21/2004	ESB4	36	2.26	4.52	4.65
6/22/2004	ESB4	38	2.87	6.63	6.38
6/23/2004	ESB4	40	84.08	136.26	156.89
6/26/2004	ESB5	11	1.79	15.74	9.96
6/27/2004	ESB5	16	1.41	5.05	4.06
6/28/2004	ESB5	20	1.40	4.01	3.51
6/29/2004	ESB5	24	1.80	5.00	4.43
6/30/2004	ESB5	28	1.75	9.50	6.70
7/1/2004	ESB5	32	2.22	7.26	6.02
7/2/2004	ESB5	34	0.27	4.22	2.46
7/3/2004	ESB5	36	1.77	25.58	15.01
7/4/2004	ESB5	38	11.71	43.81	34.65
7/5/2004	ESB5	40	66.47	88.54	114.15

Post injection iron sulfides

Date	Bottle/ Exp.	(ft)	Fe 2+ mg/kg	Fe T mg/Kg	%Fe2+	Date	Bottle/ Exp.	(ft)	Fe 2+ mg/kg	Fe T mg/Kg	%Fe2+
9/29/2003	ESM1	7	60.1	1639.0	3.7	9/8/2003	ESM4	7	62.4	1690.3	3.7
9/29/2003	ESM1	11	46.8	401.1	11.7	9/8/2003	ESM4	12	66.2	1926.6	3.4
9/29/2003	ESM1	16	107.7	334.1	32.2	9/8/2003	ESM4	17	40.9	240.6	17.0
9/29/2003	ESM1	22	85.6	714.1	12.0	9/8/2003	ESM4	22	43.1	424.3	10.2
9/29/2003	ESM1	26	91.3	5008.3	1.8	9/8/2003	ESM4	28	88.6	4606.6	1.9
9/29/2003	ESM1	30	81.0	5106.8	1.6	9/8/2003	ESM4	34	107.5	2348.9	4.6
9/29/2003	ESM1	32	52.1	2708.7	1.9	9/8/2003	ESM4	36	44.2	1723.4	2.6
9/29/2003	ESM1	34	102.5	1933.8	5.3	9/8/2003	ESM4	38	79.8	3077.6	2.6
9/29/2003	ESM1	36	47.2	2129.4	2.2	9/8/2003	ESM4	40	119.8	2707.5	4.4
9/29/2003	ESM1	38	53.6	1820.0	2.9	8/26/2003	ESM5	6	43.5	813.8	5.3
9/29/2003	ESM1	40	83.0	2628.3	3.2	8/26/2003	ESM5	10	47.1	695.3	6.8
9/22/2003	ESM2	6	42.6	1651.8	2.6	8/26/2003	ESM5	14	25.6	223.0	11.5
9/22/2003	ESM2	11	23.1	600.9	3.8	8/26/2003	ESM5	16	37.6	220.7	17.0
9/22/2003	ESM2	15.5	26.5	238.2	11.1	8/26/2003	ESM5	20	44.6	399.6	11.2
9/22/2003	ESM2	20	48.0	829.6	5.8	8/26/2003	ESM5	22	11.9	2751.8	0.4
9/22/2003	ESM2	26	72.7	4434.1	1.6	8/26/2003	ESM5	26	41.6	1667.1	2.5
9/22/2003	ESM2	30	68.6	3944.4	1.7	8/26/2003	ESM5	30	34.0	2843.9	1.2
9/22/2003	ESM2	32	51.1	1432.6	3.6	8/26/2003	ESM5	34	83.9	2077.5	4.0
9/22/2003	ESM2	34	102.4	2161.6	4.7	8/25/2003	ESM6	7	67.3	358.1	18.8
9/22/2003	ESM2	36	36.1	1737.4	2.1	8/25/2003	ESM6	13	51.3	409.0	12.6
9/22/2003	ESM2	38	87.3	3059.1	2.9	8/25/2003	ESM6	17	38.7	223.7	17.3
9/22/2003	ESM2	40	128.1	2755.4	4.7	8/25/2003	ESM6	21	53.4	1947.6	2.7
9/15/2003	ESM3	22	67.1	1018.8	6.6	8/25/2003	ESM6	25	116.2	21271.1	0.5
9/15/2003	ESM3	26	88.4	8860.0	1.0	8/25/2003	ESM6	29	151.3	21397.0	0.7
9/15/2003	ESM3	30	87.1	15471.5	0.6	8/25/2003	ESM6	33	131.6	1694.6	7.8
9/15/2003	ESM3	34	92.1	3849.3	2.4	8/25/2003	ESM6	35	58.0	1095.6	5.3
9/15/2003	ESM3	36	72.6	3722.6	2.0	8/25/2003	ESM6	38	22.4	991.9	2.3
9/15/2003	ESM3	38	85.1	3069.8	2.8						
9/15/2003	ESM3	40	125.1	3209.6	3.9						

Fe concentrations pre-injection.

Date	Bottle/ Exp.	(ft)	Fe 2+ mg/kg	Fe T mg/Kg	%Fe2+	Date	Bottle/ Exp.	(ft)	Fe 2+ mg/kg	Fe T mg/Kg	%Fe2+
5/25/2004	ESB1	11	82.9	607.2	13.7	5/25/2004	ESB4	30	288.8	1133.9	25.5
5/25/2004	ESB1	16	93.6	554.3	16.9	5/25/2004	ESB4	32	63.8	2625.5	2.4
5/25/2004	ESB1	22	158.1	1571.9	10.1	5/25/2004	ESB4	34	50.3	1164.3	4.3
5/25/2004	ESB1	30	77.3	1629.7	4.7	5/25/2004	ESB4	35	118.9	2602.7	4.6
5/25/2004	ESB1	32	240.4	2759.3	8.7	5/25/2004	ESB4	36	43.6	1276.3	3.4
5/25/2004	ESB1	34	41.3	517.6	8.0	5/25/2004	ESB4	38	69.7	3039.4	2.3
5/25/2004	ESB1	38	68.3	858.1	8.0	5/25/2004	ESB4	40	592.6	3610.4	16.4
5/25/2004	ESB1	39	50.6	560.3	9.0	5/25/2004	ESB5	11	63.7	1964.1	3.2
5/25/2004	ESB1	40	292.7	2057.8	14.2	5/25/2004	ESB5	16	58.8	333.2	17.6
5/25/2004	ESB2	11	34.5	302.6	11.4	5/25/2004	ESB5	20	108.1	1287.4	8.4
5/25/2004	ESB2	15	35.0	186.8	18.8	5/25/2004	ESB5	24	70.5	541.4	13.0
5/25/2004	ESB2	20	98.5	394.0	25.0	5/25/2004	ESB5	28	58.1	4016.5	1.4
5/25/2004	ESB2	24	106.1	3770.5	2.8	5/25/2004	ESB5	32	54.1	2358.6	2.3
5/25/2004	ESB2	28	89.6	3978.3	2.3	5/25/2004	ESB5	34	59.1	1302.8	4.5
5/25/2004	ESB2	32	85.1	2091.2	4.1	5/25/2004	ESB5	36	156.6	2048.6	7.6
5/25/2004	ESB2	34	68.1	1113.9	6.1	5/25/2004	ESB5	38	211.4	2376.3	8.9
5/25/2004	ESB2	36	69.0	1909.8	3.6	5/25/2004	ESB5	40	432.8	3102.4	13.9
5/25/2004	ESB2	37	353.1	3598.7	9.8						
5/25/2004	ESB2	38	381.6	3269.5	11.7						
5/25/2004	ESB2	40	544.5	3685.9	14.8						
5/25/2004	ESB3	16	53.7	932.3	5.8						
5/25/2004	ESB3	20	67.7	482.4	14.0						
5/25/2004	ESB3	24	116.5	4138.3	2.8						
5/25/2004	ESB3	28	61.1	1707.1	3.6						
5/25/2004	ESB3	32	69.7	2893.9	2.4						
5/25/2004	ESB3	34	67.6	1626.0	4.2						
5/25/2004	ESB3	36	50.6	1441.2	3.5						
5/25/2004	ESB3	38	128.1	2700.5	4.7						
5/25/2004	ESB3	40	436.1	4389.2	9.9						

Fe concentrations post-injection.

Active Well for Graphs: ESM1

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	81	859	3007	0.03	3.3	24.205
8/28/2003	0	81	138	899	0.09	1191	3987.44
9/24/2003	26.00	75	914	2080	0.24	10.8	253.41
10/31/2003	63.00	50	577	972	0	16.53	84.2044
12/22/2003	114.00	74	394	1160	0	4.701	38.9992
1/30/2004	152.00	56	231	967	0	7.031	
4/16/2004	228.00	24	294	1500	30		34.6
6/21/2004	293.00	34	417	1650	19		70.48

Active Well for Graphs: ESM2

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	90.17	859	3007	0.02	2.3	11.46
8/28/2003	0	151	240	576	0.04	466.6	1445.05
9/24/2003	26.00	63	1140	2290	0.18	34.03	1006.1
10/31/2003	63.00	45	632	1450	0	115.7	584.7363
12/22/2003	114.00	32	442	1490	0	35.82	264.7945
1/30/2004	152.00	24	362	1960	0	26.82	
4/16/2004	228.00	20	243	1430	21		198.33
6/21/2004	293.00	24	417	1610	25		130.61

Aqueous Data: PCE, TCE, DCE, VC (ug/L), TOC and SO4 (mg/L)

Active Well for Graphs: ESM3

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	90.27	859	3007	0.1	2.6	10.3
8/28/2003	0	147	1720	3310	0.06	0	5.605
9/24/2003	26.00	167	779	1130	0.02	10.76	521.44
10/31/2003	63.00	92	957	1540	0	91.665	587.5669
12/22/2003	114.00	66	1230	3710	0	70.49	330.6229
1/30/2004	152.00	35	1020	3210	0	28.81	
4/16/2004	228.00	12	207	1190	19		173.62
6/21/2004	293.00	7	417	1060	15		226.86

Active Well for Graphs: ESM4

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	81.77	859	3007	0.03	2.2	4.66
8/28/2003	0	196	979	1470	0.02	0	4.14
9/24/2003	26.00	182	738	1060	0.01	8.119	42.995
10/31/2003	63.00	48	455	1000	0	31.56	210.1261
12/22/2003	114.00	71	797	1910	0	5.417	128.6497
1/30/2004	152.00	43	678	1990	0	4.623	
4/16/2004	228.00	12	255	1020	19		96.58
6/21/2004	293.00	38	417	2510	40		168.14

Aqueous Data: PCE, TCE, DCE, VC (ug/L), TOC and SO4 (mg/L)

Active Well for Graphs: ESM5

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	30	859	3007	0.22	2.6	26.35
8/28/2003	0	30	815	5320	0.3	2.167	20.39
9/24/2003	26.00	32	1520	3130	0.15	2.122	26.76
10/31/2003	63.00	48	455	1000	0	1.955	43.2525
12/22/2003	114.00	20	402	1150	0	2.061	70.88835
1/30/2004	152.00	8	170	561	0	2.911	
4/16/2004	228.00	8	93	167	44		92.57
6/21/2004	293.00	9	417	1760	31		140.83

Active Well for Graphs: ESM6

Date	Days	PCE	TCE	DCE 1, 2	VC	TOC	SO4
8/25/2003	-3.00	0	859	3007	0	2.6	10.25
8/28/2003	0	117	859	3007	0.05	2.315	14.57
9/24/2003	26.00	87	1660	5340	0.29	2.27	9.24
10/31/2003	63.00	35	545	2480	0	3.013	13.6088
12/22/2003	114.00	67	1170	4160	0	1.736	8.6661
1/30/2004	152.00	36	824	2580	0	2.467	
4/16/2004	228.00	26	567	1190	15		13.36
6/21/2004	293.00	23	417	1100	12		61.71

Aqueous Data: PCE, TCE, DCE, VC (ug/L), TOC and SO4 (mg/L)