

# REMEDICATION OF CHROMATE-CONTAMINATED GROUNDWATER USING ZERO-VALENT IRON: FIELD TEST AT USCG SUPPORT CENTER, ELIZABETH CITY, NORTH CAROLINA

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## Abstract

A field test was conducted near an old hard-chrome plating facility on the USCG Support Center near Elizabeth City, North Carolina to evaluate the in situ remediation of ground water contaminated by hexavalent chromium using a passive permeable reactive barrier composed of a zero-valent iron-sand-aquifer material mixture. The remedial effectiveness of this innovative in situ technology was monitored over a one year period. The success of this small-scale test has prompted a full-scale implementation of the technology at the site for late Spring, 1996.

Keywords: zero-valent iron, in situ reactive barrier walls, chromate, geochemical indicators

## BACKGROUND

The remediation of contaminated ground water using traditional pump-and-treat approaches has often been shown to be an extremely costly endeavor, and the results have been generally disappointing [1]. Innovative in situ treatment technologies are being proposed which take advantage of chemical or coupled biological-chemical reactions which are capable of transforming or degrading contaminants into non-toxic and/or immobilized chemical forms within a constructed permeable reactive barrier. Prior research has demonstrated the potential of using zero-valent iron to remediate chromate [2,3,4] and chlorinated organic compounds often found in ground water [5,6] in this manner. The use of this new technology will depend to a large extent on the persistence of the resulting geochemical changes induced by the base treatment metal and how these changes affect contaminant transformation and removal, changes in permeability in the reaction zone and within the aquifer.

In this paper we present results of a small-scale field test which was initiated in September, 1994, to evaluate the in situ remediation of ground water contaminated with hexavalent chromium using a permeable reactive barrier. The barrier was composed of an iron

metal-coarse sand-native aquifer solid mixture, and was installed using a staggered "fence" design through large hollow-stem augers. The objectives of the project were to evaluate the ability of the iron cylinders or "fence posts" to remove chromate from solution immediately downgradient and adjacent to the iron cylinders, evaluate the resultant changes in aqueous geochemistry induced by the presence of the zero-valent iron, and identify chemical, physical and biological processes which may affect long-term performance of such remedial technologies. In addition to chromium, chlorinated organic compounds (trichloroethylene [TCE], cis-dichloroethylene [c-DCE], and vinyl chloride) were also present in the portion of the plume treated by the "fence posts". While the test was not specifically designed to remediate the organic contaminants, their concentrations over time during the test were also monitored.

## **FIELD SITE**

The field site is located at the U.S. Coast Guard (USCG) Support Center near Elizabeth City, North Carolina, about 100 km south of Norfolk, Virginia and 60 km inland from the Outer Banks of North Carolina. The base is located on the southern bank of the Pasquotank River, about 5 km southeast of Elizabeth City. Hangar 79, which is only 60 m south of the river, housed a chrome plating facility which had been in use for more than 30 years and discharged acidic chromium wastes and associated solvents through a hole in the concrete floor. These wastes infiltrated the soils and the underlying aquifer immediately below the shop's foundation. Chromate concentrations in ground water range from non-detect to 12 mg/L. The center of mass is located near MW 31, at a depth of about 5 m, and about 25 m north of hangar 79 (Figure 1).

The site geology has been described in detail elsewhere [7], but essentially consists of typical Atlantic coastal plain sediments, characterized by complex and variable sequences of surficial sands, silts and clays. Ground-water flow velocity is extremely variable with depth, with a highly conductive layer at roughly 5 to 6 meters below ground surface. This layer coincides with the highest aqueous concentrations of chromium. The ground water table ranges from 1.5 to 2.0 m below ground surface.

## **MATERIALS & METHODS**

Two sources of iron were mixed and used in the field test. Low-grade steel waste stock, obtained from Ada Iron and Metal (AI&M, Ada, OK), was turned on a lathe (without use of cutting oils) using diamond bits to produce 200 L of turnings. The other iron material was obtained from Master Builder's Supply (MBS, Streetsboro, Ohio). The latter material was primarily in the 0.1 to 2 mm size range while the former was primarily in the 1 to 10 mm size range. The MBS iron exhibited greater total sulphur and carbon content than the AI&M iron. The aquifer material used was native to the site. A coarse, uniform, washed sand (3/16 x 10 mesh) was also added to the mixture for increased permeability within the iron cylinders. A summary of physical characterization data for the mixture is presented in Table 1. The four materials were

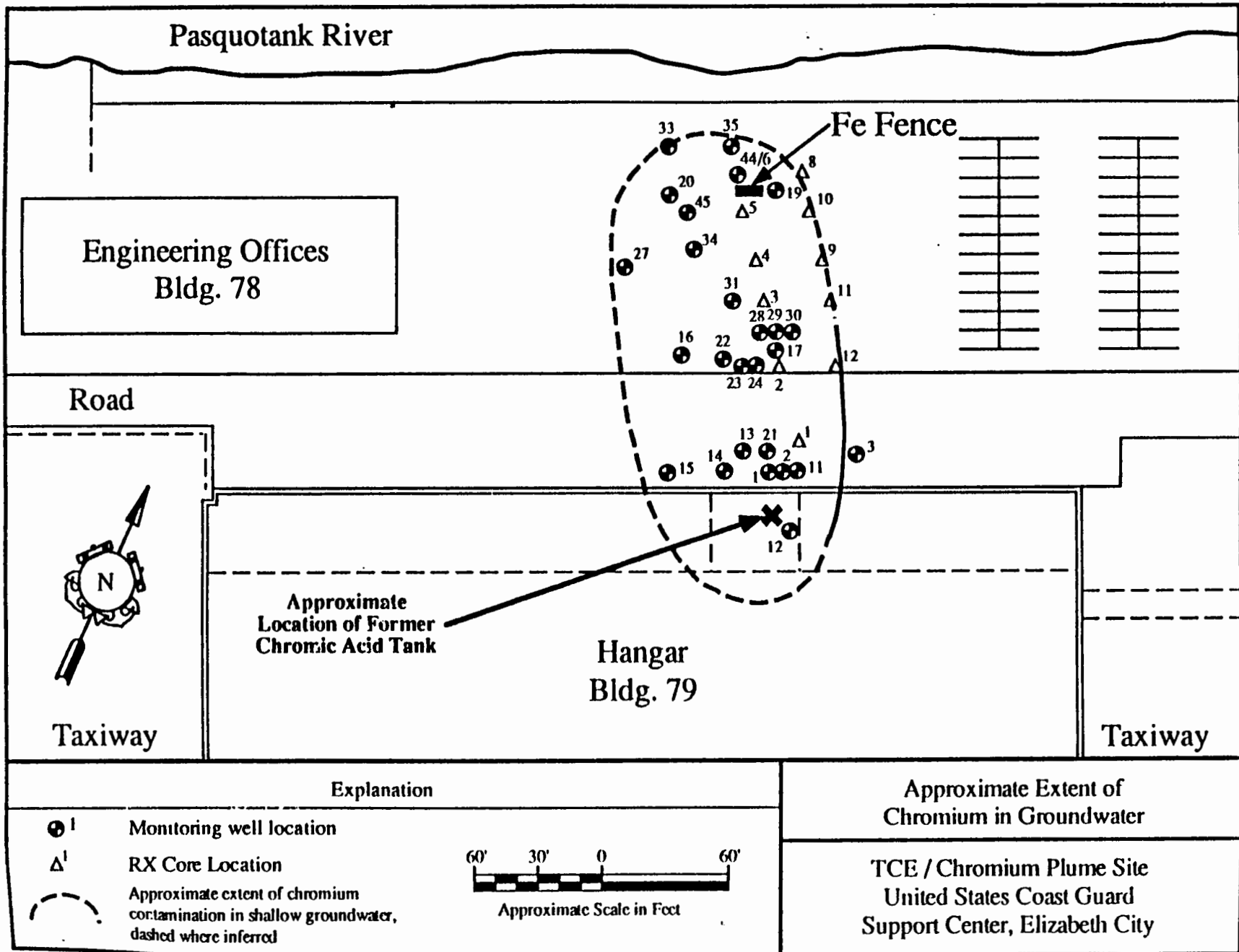


Figure 1. Site map, USCG site, Elizabeth City, North Carolina.

Table 1. Physical specifications for mixture used in the reactive barrier wall.

| Mixture Components | % Vol. | % Wt. | Particle Size (mm) | Surf. Area (m <sup>2</sup> /g) |
|--------------------|--------|-------|--------------------|--------------------------------|
| MBS Fe             | 25     | 29    | 0.2-4.0            | 1.1                            |
| Al&M Fe            | 25     | 33    | 1-15               | 1.4                            |
| E.C.Aquifer        | 25     | 19    | <0.1               | 5.8                            |
| Gravel-Sand        | 25     | 19    | 1-4                | <1                             |

mixed in equal volumes on-site and poured through 16 cm i.d. hollow stem augers. The estimated diameter of the emplaced cylinders was 20 cm and they were installed from 3 to 8 m below ground surface. A total of 21 such cylinders were installed in three rows as indicated in Figure 2.

Twenty-four monitoring wells were installed within the approximately 5.5 m<sup>2</sup> treatment zone, in addition to four up-gradient reference wells and one downgradient well. Most are 1.9 cm i.d. polyvinylchloride (PVC) wells with 30 or 45 cm long screens which are completed between 4.2 and 6.0 m below ground surface. One is a 10.2 cm i.d. PVC well with 150 cm screen completed 5.5 m below ground surface and another is a 5.1 cm i.d. PVC well with 300 cm screen completed 7.3 m below ground surface. Monitoring before and after "fence" installation was conducted for the following water quality parameters: pH, oxidation-reduction potential, dissolved oxygen, alkalinity, Cr(VI), ferrous iron, total iron, total sulfide, trichloroethylene (TCE), cis-dichloroethylene (c-DCE), vinyl chloride, and major cations and anions. In addition to the permanent well sampling points, temporary sampling points were utilized to increase the spatial resolution of the data. These were obtained using a Geoprobe® and peristaltic pump. Tracer tests to evaluate ground water flow velocity through the "fence" were performed prior to and following installation. Bromide was used as a conservative tracer. Solids were also recovered and analyzed using electron microprobe and scanning electron microscopy with energy dispersive X-ray analysis.

## RESULTS & DISCUSSION

Figures 3-7 show the changes in aqueous concentration of some of the monitored constituents over time for wells GMP1-2 and 1-3 (upgradient reference wells), F5, F7, and F9, following initial "fence" emplacement September 13-16, 1994. Initial conditions are indicated by the June, 1994 sampling data. Well screen depth intervals are listed in Table 2. The upgradient reference wells (GMP1-2, 1-3) indicate that TCE concentrations decreased over time from 300-400 ug/L to about 40 ug/L in GMP 1-2 and to less than 10 ug/L in the deeper well, GMP 1-3.

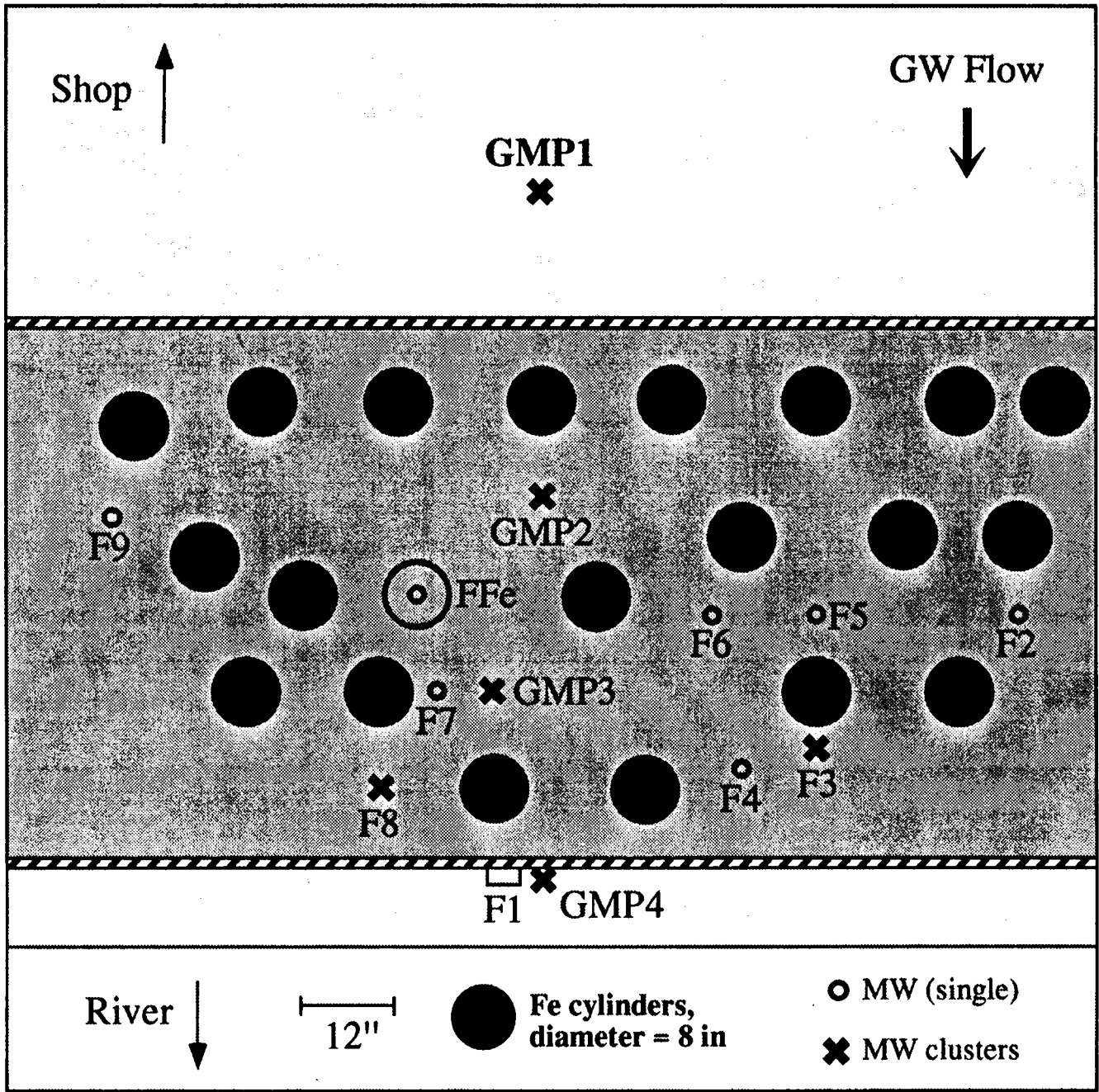


Figure 2. Iron fence plan view showing locations of iron cylinders in staggered "fence" array.

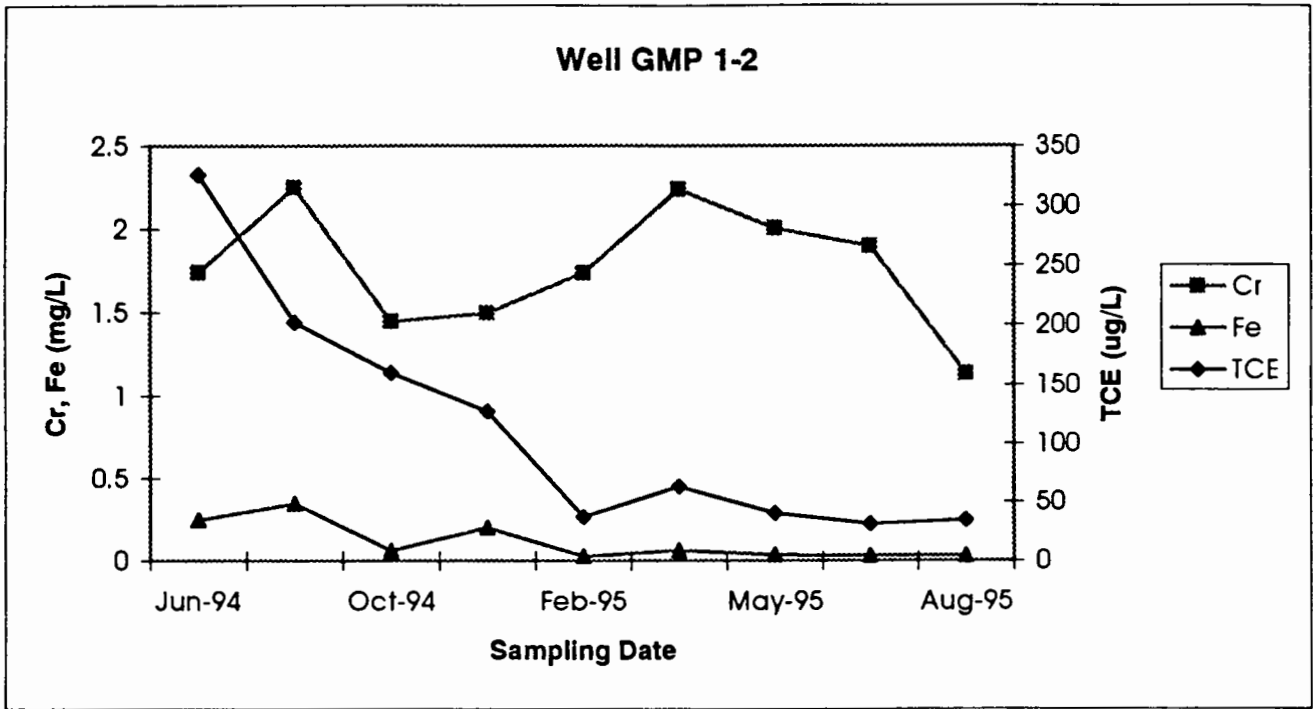


Figure 3. Well GMP 1-2 - changes in total chromium, total iron and TCE over time.

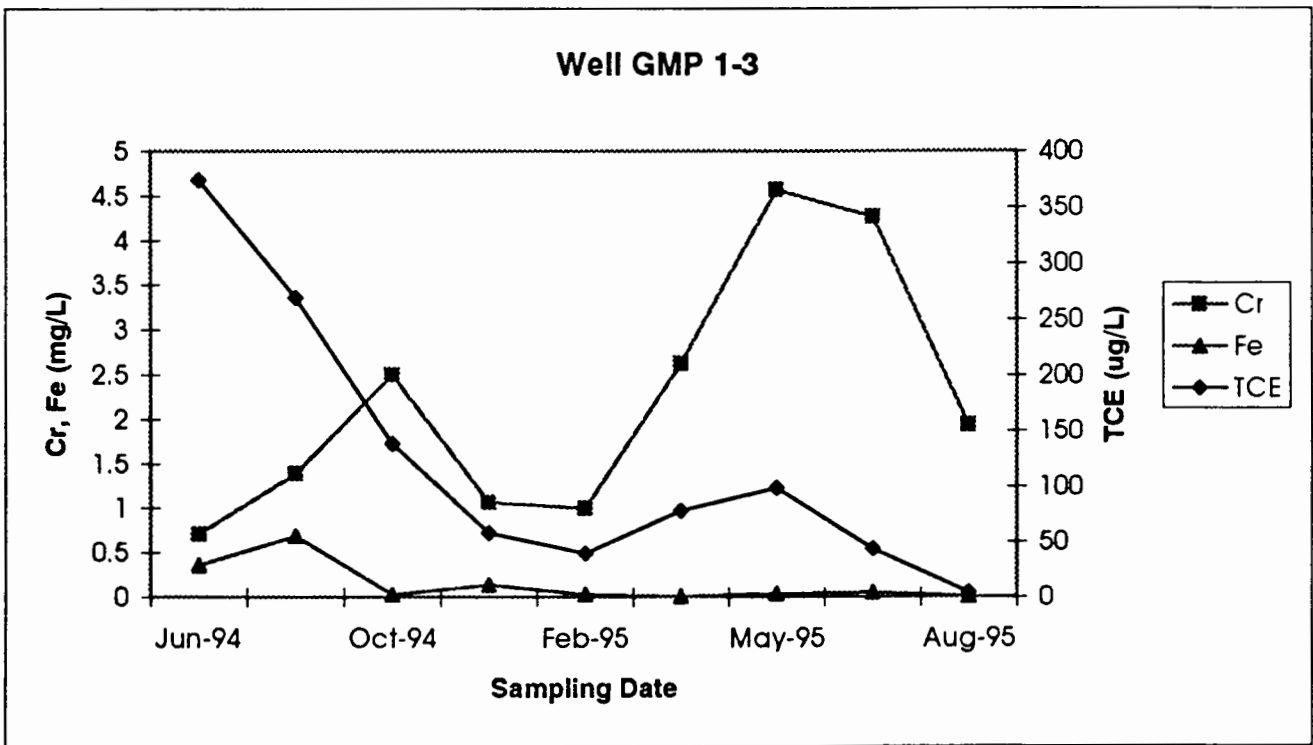


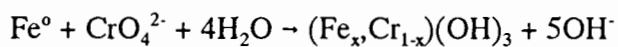
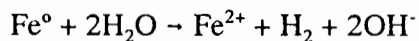
Figure 4. Well GMP 1-3 - changes in total chromium, total iron, and TCE over time.

Table 2. Screen interval depth of the monitoring wells in the iron fence area.

| Well   | Screen Interval Depth (m) |
|--------|---------------------------|
| F5     | 5.1-5.5                   |
| F7     | 4.8-5.2                   |
| F9     | 4.7-5.1                   |
| GMP1-2 | 4.9-5.2                   |
| GMP1-3 | 5.4-5.7                   |

This was consistent with other well data at the site over this time period indicating that the chlorinated organics plume had sunk to lower depths and contracted on the east side of the site. Chromium concentrations are relatively stable and range from 1 to 5 mg/L depending upon depth. All iron detected was colloidal; there was no detectable ferrous iron. Well F5 is located in a “gap” where no iron is intercepted by ground water and thus little change is observed in chromium concentrations over time. There is no increase in iron concentration and TCE concentrations decline similar to those changes observed in GMP 1-2 and 1-3. Wells F7 and F9 were located immediately behind iron cylinders. In both cases, chromium concentrations immediately declined to less than 0.01 mg/L, iron increased substantially, and TCE concentrations initially declined more rapidly than observed in the upgradient wells and to about 10 ug/L.

Changes in geochemistry over this same time period for these same (F series) wells was also monitored. Variation in effectiveness of contaminant removal from the aqueous phase is directly correlated with changes in geochemistry and position of monitoring points relative to the iron cylinders. A summary of the monitoring results for the period September, 1994 thru June, 1995 is presented in Table 3. Wells located within or downgradient of the "fence posts" (treated zones, Table 3) show reduction of chromate to below detection limits (<0.01 mg/L), greater than 70% reduction of TCE, and reduction of vinyl chloride to less than 2 ug/L. In these treated zones, ferrous iron is present, Eh is reduced, pH is elevated, dissolved oxygen is consumed, and sulfides are detected in both the aqueous and solid phases. Figure 8 shows changes in geochemical parameters over time in well F7, which is representative of the “treated” areas. These geochemical changes are identical to prior laboratory observations by Powell et al. [2] and are consistent with the following reactions:



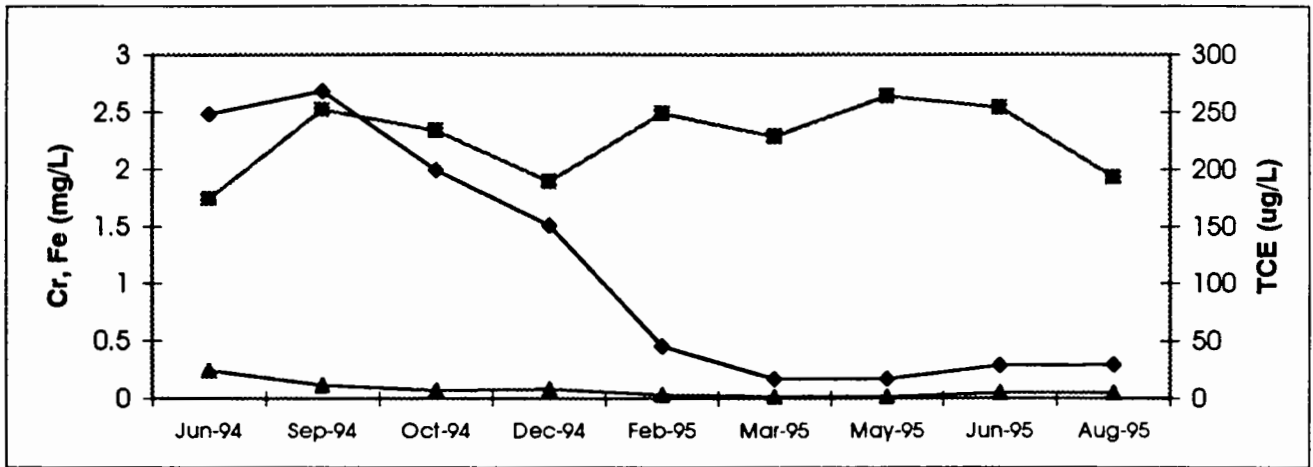


Figure 5. Well F5 - changes in total chromium, total iron, and TCE over time.

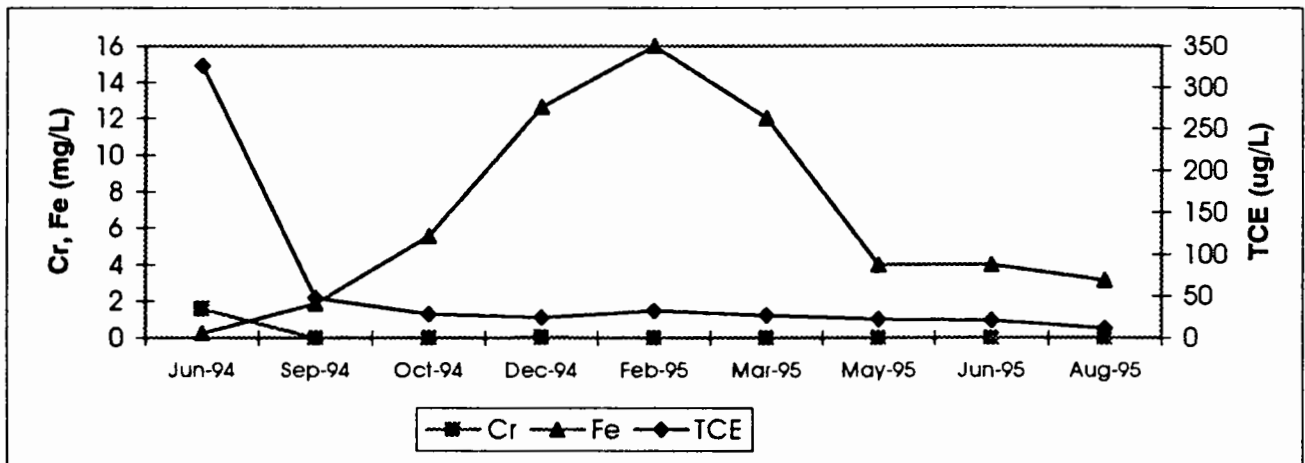


Figure 6. Well F7 - changes in total chromium, total iron, and TCE over time.

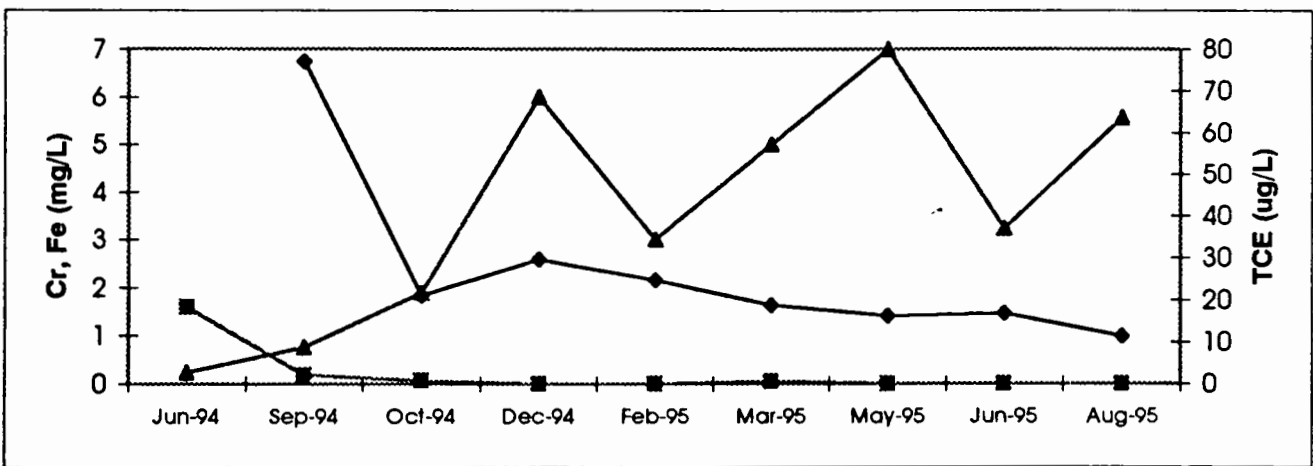


Figure 7. Well F9 - changes in total chromium, total iron, and TCE over time.



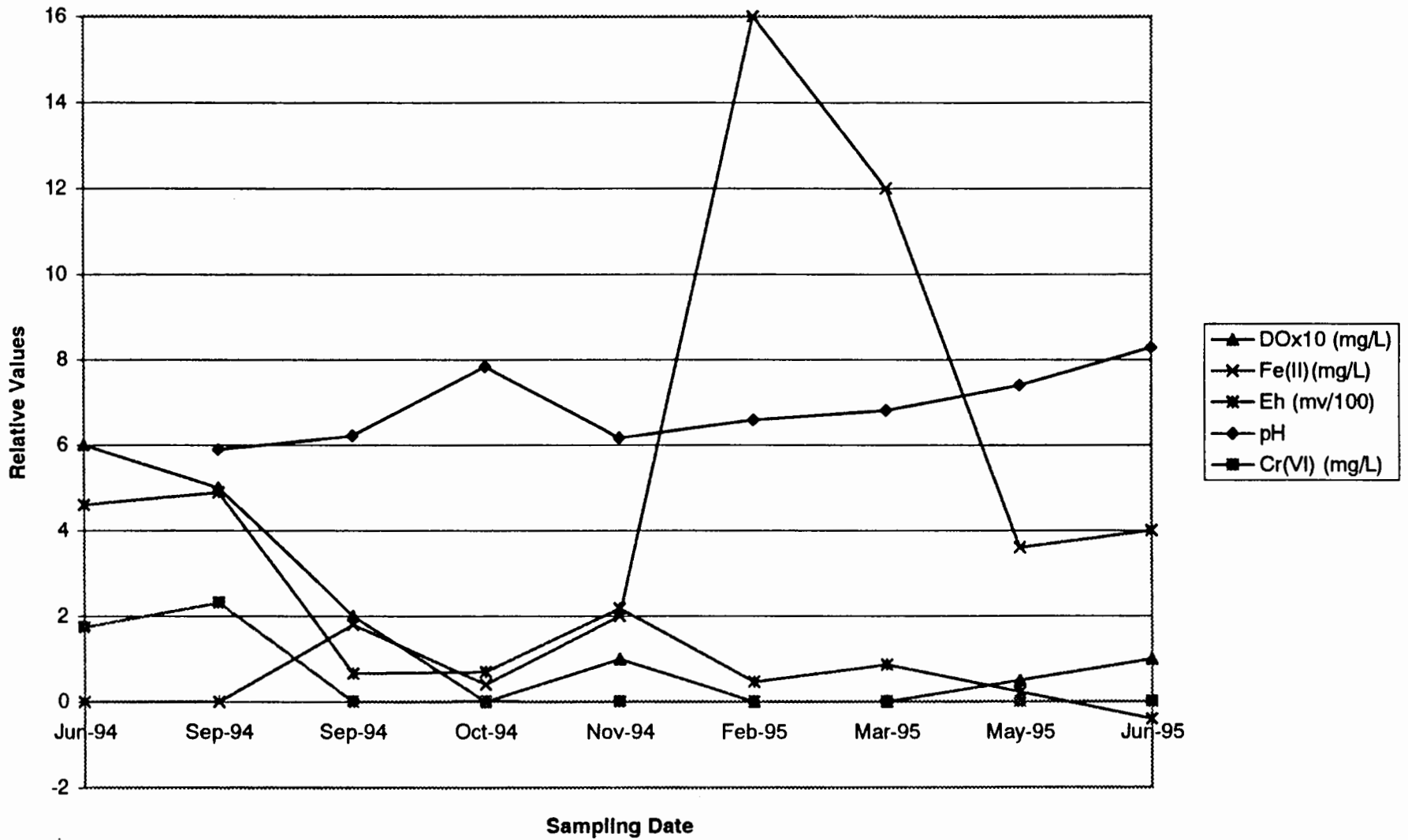


Figure 8. Well F7 - geochemical parameter changes over time.

Table 3. Summary of geochemical monitoring parameters for iron "fence" area.

|                          | Untreated Zones | Treated Zones   |
|--------------------------|-----------------|-----------------|
| Cr(VI)                   | 1-3 mg/L        | <0.01 mg/L      |
| Fe(II)                   | 0               | 2-20 mg/L       |
| Eh                       | >400 mV         | -100 to +200 mV |
| pH                       | 5.6-6.1         | >7.5            |
| DO                       | >0.6 mg/L       | <0.1 mg/L       |
| Sulfides                 | absent          | present         |
| dissolved H <sub>2</sub> | <10 nMol        | >1000 nMol      |

Some wells (e.g. F6) show only minor reduction in contaminant level concentrations (untreated zones, Table 3), and other geochemical parameters are essentially unchanged. These wells are located in "gaps" where ground water does not intercept the "fence posts" or where emplacement was poor in terms of continuous vertical coverage of the 3 to 7 meter depth interval. The latter has been verified through extensive coring from September 1994 through August, 1995.

Passive sampling techniques are also being employed to evaluate the potential mobilization of colloidal constituents downgradient of the iron cylinders. Appreciable quantities of colloidal particles were observed (> 400 NTU's) during the March, May, and June, 1995 sampling trips; however, this phenomena existed elsewhere on site and may solely be due to a water main break which introduced millions of gallons of low ionic strength water into the aquifer mobilizing indigenous colloids. This input of "clean" water may also explain the depression of the TCE concentrations observed in F5 and GMP 1-2 after December of 1994. The most ubiquitous particles detected from passive sampling of a number of wells include silica and kaolinite and range in size from 0.2 to several microns. Iron sulfides have been detected in well F7, primarily as coatings on mineral surfaces.

Hydraulic conductivity estimations for two different locations near the iron "fence" site are shown in Figure 9. While considerable variation in hydraulic conductivity exists both vertically and areally at the site, there is a consistent high permeability zone from about 5 to 6 m below ground surface. Tracer test data collected before and after "fence" installation shows increased groundwater flow velocity through the "fence" area (Figure 10). Post-installation velocities were approximately 0.3 and 0.5 m/day at the 4.7-5.0 m (GMP 2-1) and 5.2-5.5 m (GMP 2-2) depth intervals, respectively, compared with pre-installation velocities of 0.1 and 0.2 m/day at the same locations. While some increase may be due to the emplacement of the more conductive iron

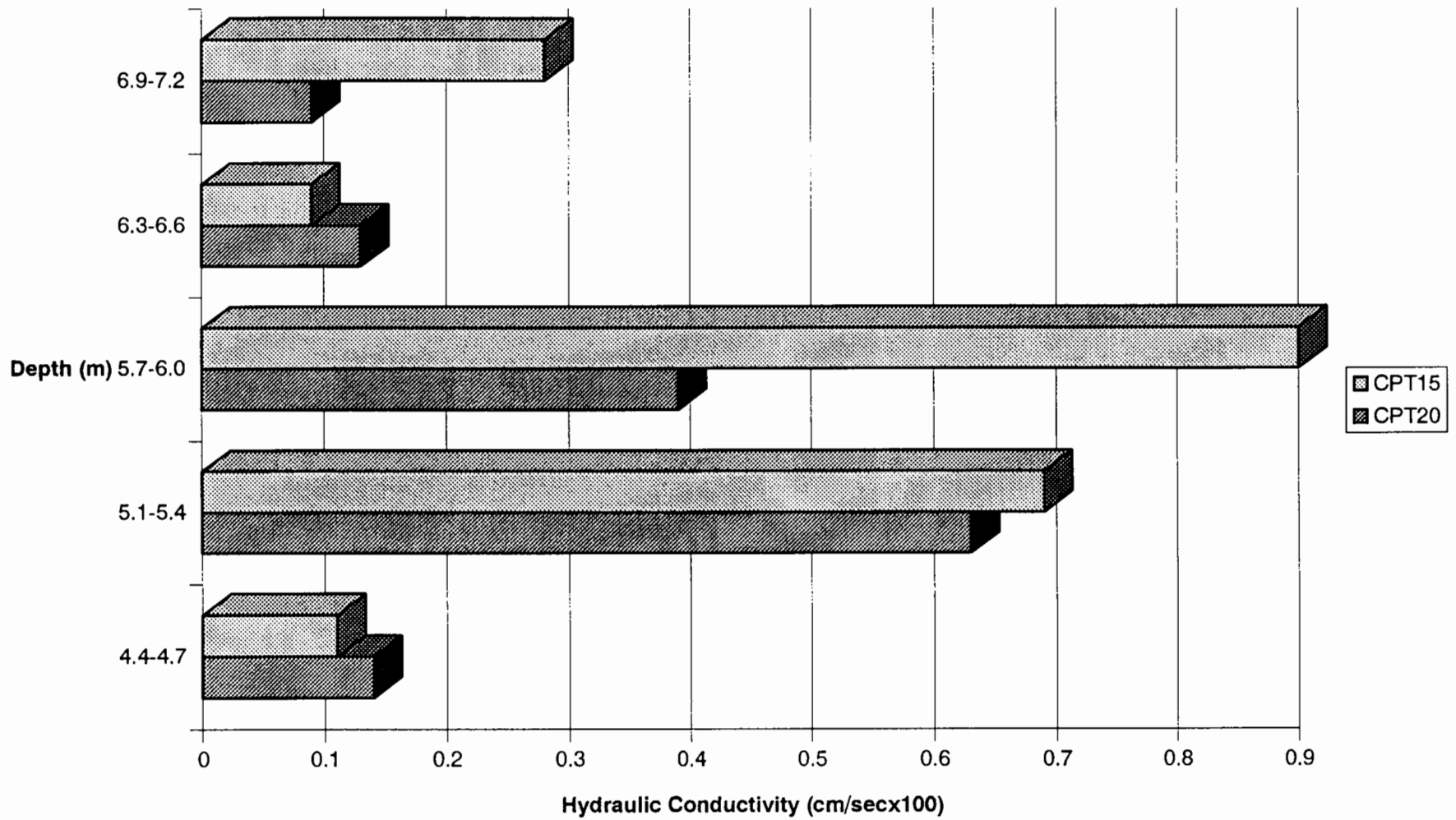


Figure 9. Hydraulic conductivity variation with depth near the iron fence pilot test.

# GMP 2

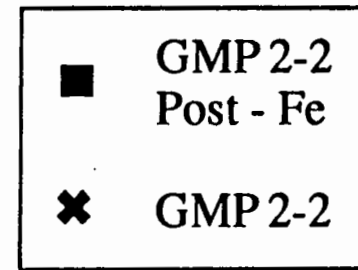
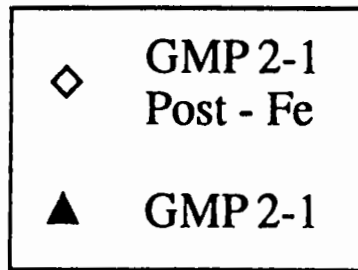
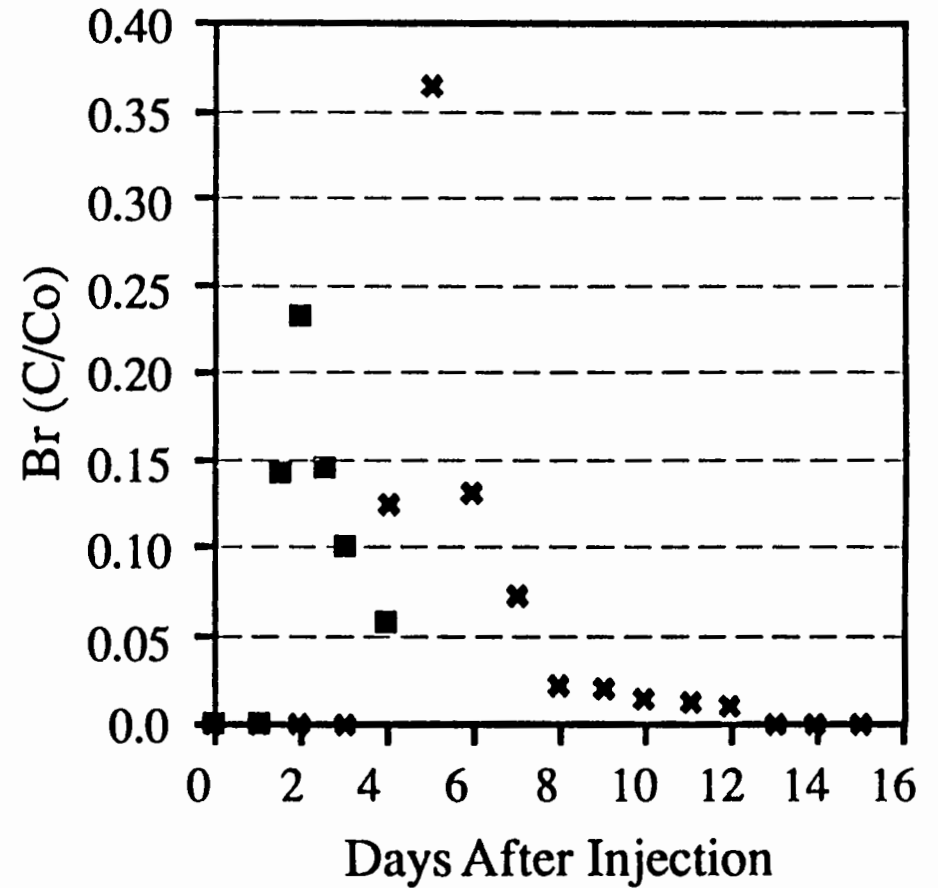
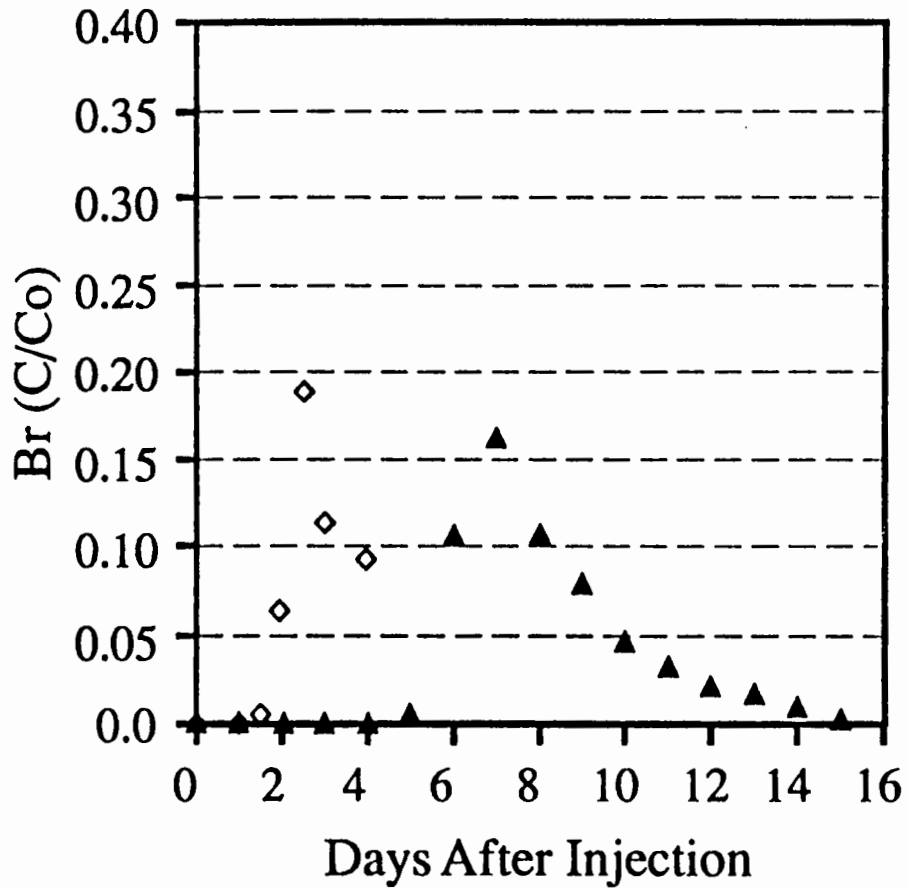


Figure 10. Tracer test results for iron "fence" before and 7 months following iron installation.

mixture, most has been attributed to increased velocity due to temporal variations associated with greater rainfall in the winter and early spring months. There has been no indication of decreased permeability in the iron cylinders since emplacement.

## **SUMMARY**

A range of redox zones exist from low Eh within the cylinders to higher Eh downgradient of the cylinders. In addition to an increase in pH, decrease in oxidation-reduction potential, consumption of dissolved oxygen and increase in alkalinity, there is the generation of detectable sulfides and appreciable ferrous iron in the ground water. Sulfides are not detected in the ground water beyond 0.3 m downgradient from an iron cylinder and ferrous iron persists only for about 1 m downgradient. Likely phases which may form from the iron corrosion and natural water-sediment interaction are metal sulfides, siderite and iron oxyhydroxides. Iron sulfides and a mixed iron-chromium oxide or hydroxide phase have been observed, siderite has not.

Field and laboratory results indicate almost instantaneous removal of chromium from the aqueous phase, and chemical extraction together with surface analytical techniques confirm that this is through reduction and precipitation reactions forming a very insoluble mixed chromium-iron hydroxide phase. Field geochemical changes observed as a result of iron mixture emplacement in the aquifer are consistent with those observed in the laboratory experiments. The removal or reduction in chlorinated organics aqueous concentrations are variable and in the order TCE >> vinyl chloride > c-DCE.

Improvement in chlorinated organics remediation will be addressed in the Phase II study in cooperation with the University of Waterloo. This project will implement a full-scale permeable reactive barrier wall at the site to treat both the chromate and chlorinated solvent plumes which overlap in the aquifer. Current plans are for a continuous trench design composed of one type of iron which intersects the leading edge of the plumes approximately where the current iron "fence" test is located, but is 45 m long, installed to a depth of 8 m and about 0.6 m wide.

## **Acknowledgments**

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## Notice

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement may be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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**TECHNICAL REPORT DATA**

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