



**FOSTER WHEELER ENVIRONMENTAL CORPORATION**

November 19, 1998  
File #: 1284-0009-98-0452

Commanding Officer  
Northern Division  
Naval Facilities Engineering Command  
10 Industrial Highway, Mail Stop #82  
Lester, PA 19113  
Attn: Code 402A (T. Gibison)

**SUBJECT: US NAVY NORTHERN DIVISION  
REMEDIAL ACTION CONTRACT (RAC)  
CONTRACT NO. N62472-94-D-0398  
DELIVERY ORDER NO. 0009 - NAVAL AIR WARFARE CENTER,  
TRENTON, NEW JERSEY  
REVISED POST-REMEDICATION LETTER REPORT  
ZERO VALENT IRON PILOT STUDY**

Dear Mr. Gibison:

Foster Wheeler Environmental Corporation (FWENC) is pleased to provide you with this revised Post-Remediation Report associated with the zero valent iron pilot study at the Naval Air Warfare Center (NAWC) located in Trenton, New Jersey. This Post-Remediation Report has been prepared in accordance with the requirements of the above-referenced Delivery Order. All work was performed in accordance with the approved letter-workplan dated January 27, 1997.

**CONSTRUCTION**

Mobilization of FWENC personnel and site equipment had already occurred since there were other ongoing tasks being performed at the site. On January 27, 1997, a low shear air driven bladder pump, along with the necessary controller and discharge tubing, was installed in well MW36BR near the bottom of the well within the open interval. The well is approximately 136 feet deep. Associated PVC piping was connected into the building. The piping was elevated above the ground using supports and heat traced to avoid freezing during the winter months. A 180-gallon drum of iron filings was staged inside the treatment building that contained approximately 85 gallons of iron filings. Influent piping from the well to the drum had a sample tap for influent sample collection and an in-line sight glass to check for free phase TCE. Effluent piping from the drum also had a sample tap for effluent sample collection. The effluent was piped into the influent line from well 15BR which runs into the groundwater treatment system. The attached figure shows the pilot system configuration. A discussion of the iron filings technology is provided in the attached report by Envirometal Technology, Inc.

## OPERATION AND MAINTENANCE

From May 13, 1997 to September 9, 1997, the pump in monitor well MW36BR was operated between 0.05 and 0.2 gpm as continuously as possible. The groundwater treatment system operator was also operating the pilot plant. In order to determine the effectiveness of the pilot plant, influent and effluent samples were collected and analyzed using the on-site gas chromatography (GC) unit as well as by an independent analytical laboratory. Influent and effluent samples were collected 2 to 3 times week for GC analysis and monthly for laboratory analysis.

On site analysis of the pilot study was conducted utilizing a SRI Instruments' 8610B portable gas chromatograph. The instrument was calibrated for four compounds, vinyl chloride, cis-1,2-dichloroethene, trans-1,2-dichloroethene and trichloroethylene. A purge and trap method was employed, using a 10 ml aliquot of sample. A mid-range standard (50 ppb) was prepared daily from stock solutions of each compound and analyzed at start-up along with an air blank and water blank. Duplicate samples were analyzed every 20 samples. A copy of the Standard Operating Procedure is provided attached.

Based on the analytical results from the study, it was decided to utilize an iron filings technology consultant, Envirometal Technology, Inc. (ETI), as a FWENC subcontractor. Upon ETI's recommendation and the Navy's concurrence, it was decided that nickel-plated iron filings were to be used in place of the existing iron filings. A discussion of the iron filings variation is provided in the attached report by ETI. The pilot study operated at the same flow rate from monitor well MW36BR with the nickel-plated iron filings from November 18, 1997 to March 4, 1998. Sampling and analysis was performed with the same frequency as described above.

The Navy directed FWENC to increase the flow rate in order to determine if breakthrough of the nickel-plated iron filings had occurred and to see if decreasing the retention time in the filings container would affect the removal efficiency. The influent was switched from monitor well MW36BR to extraction well 15BR in order to accommodate the increased flow. Well 15BR was operated with the following schedule:

- 0.1 gpm from April 20, 1998 to June 5, 1998
- 0.2 gpm from June 5, 1998 to June 11, 1998
- 0.5 gpm from June 11, 1998 to July 1, 1998
- 1.0 gpm from July 1, 1998 to July 13, 1998

Sampling and analysis was performed with the same frequency as described above.

A summary of analytical data generated from the on-site GC is provided attached. Further, provided attached is ETI's technology description.



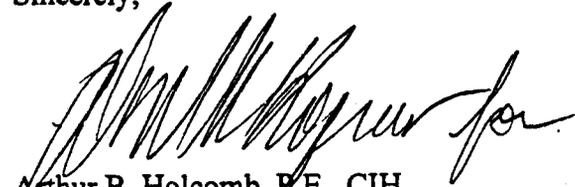
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## CONCLUSIONS

The original iron filings did not prove very efficient in removal of the volatile organic compounds found in the groundwater influent. However, the nickel-plated iron filings were effective in removal of the groundwater contaminants. Further, with the increased flow, removal efficiency was reduced but breakthrough did not occur as indicated by the reduced flow afterwards with increased removal efficiency. For a more detailed conclusion and in-depth discussion on utilization of the nickel-plated iron filings, please refer to the attached ETI report.

Please call me or the Delivery Order Manager, Dan Kopcow, if you should have any questions or comments regarding this Report.

Sincerely,



Arthur B. Holcomb, P.E., CIH  
Program Manager

cc: Jeff Dale, NAWC  
Ed Boyle, Northdiv  
Bill Lewendowski, NAWC  
Dan Kopcow, FWENC  
Don Vogen, FWENC



# FOSTER WHEELER ENVIRONMENTAL CORPORATION

Naval Air Warfare Center, Trenton NJ

Weekly Field Data Summary

Iron Filings Pilot Study

Nickel Enhanced Iron

Field GC and Laboratory Results

Sample Date	Sample ID	Sample Location	Vinyl Chloride	Vinyl Chloride	cis-1,2 DCE	cis-1,2 DCE	trans-1,2 DCE	trans-1,2 DCE	Trichloroethene	Trichloroethene
			(ug/L)		(ug/L)		(ug/L)		(ug/L)	
			Field	Lab	Field	Lab	Field	Lab	Field	Lab
6/17/97	01IPS06179701	System Influent	34	D	8000	1,200	20	D	135,800	32,000
6/17/97	02IPS06179701	System Effluent	36	D	16000	2,400	39	D	44,800	6,200
7/29/97	01IPS07299701	System Influent	49	D	7500	4,000	26	D	145,700	140,000
7/29/97	02IPS07299701	System Effluent	59	D	12700	8,100	23	D	108,000	93,000
1/6/98	01IPS01069801	System Influent	51	D	58,000	13,000	24	D	237,500	120,000
1/6/98	02IPS01069801	System Effluent	ND	ND	ND	ND	ND	ND	4	11
2/24/98	01IPS02249801	System Influent	101	< 2000	40,300	17,800	66	< 400	230,300	179,000
2/24/98	02IPS02249801	System Effluent	7	< 10	3	< 2	5	< 2	42	23
4/30/98	01IPS04309801	System Influent	7100	6040	57,100	23,500	134	45	13,500	6,970
4/30/98	02IPS04309801	System Effluent	77	392	782	2,670	15	< 50	23	< 50
5/15/98	01IPS05159801	System Influent	4800	4100	37,000	24,900	97	59	8,800	4,230
5/15/98	02IPS05159801	System Effluent	126	226	637	1,560	12	< 5	20	6
5/20/98	01IPS05209801	System Influent	3280	6450	28400	23,500	100	68	7,090	6,150
5/20/98	02IPS05209801	System Effluent	107	< 10	16	8	9	< 2	30	15
6/18/98	01IPS06189801	System Influent	4,400	4,630	27,700	25,000	125	34	7,700	4,460
6/18/98	02IPS06189801	System Effluent	3,500	3,870	15,300	27,400	95	23	1,800	1,480

**Notes:** D- Not detected at a reporting limit of 20000 ppb for Vinyl Chloride and 10000 ppb for trans-1,2-DCE. In addition, Toluene was detected in the laboratory analysis of the influent sample at 6500 ppb. ug/L - Micrograms per Liter, or parts per billion, ppb.

**SRI 8610B Gas Chromatograph  
With Peak Simple/ Peak 2 Software  
Standard Operating Procedures (SOP)**

**I. INTRODUCTION**

This SOP has been designed for use of the SRI 8610B Gas Chromatograph with Peak Simple Software currently in operation at the NAWC, Trenton, NJ Groundwater Treatment Facility. Prior to operation of this analytical instrument, the user should be familiar with the general chromatographic process, as well as the basic features of the SRI 8610 instrument.

**II. BASIC STARTUP PROCEDURES**

Please follow these procedures in the given order. The location and description of all the instrument controls located on the front panel of the GC can be found in the front GC operations manual

1. Turn carrier gas pressure up at the dual head pressure regulator located on the Helium cylinder by turning the knob in a clockwise direction. Set the pressure to 50 psi, it must be greater than 45 psi.
2. Turn on GC main power switch, located on the left side panel, behind purge and trap apparatus. If this does not supply power to the GC check to see that the surge protector located on the wall behind the GC is in the on position.
3. Turn on PID lamp. Set the PID lamp current to 100mA. The PID lamp current adjustment knob is located on top right of the main body of instrument. The red lid must be lifted to reach this knob. Set the top Temperature/Voltage display knob (knob #9) to PID lamp current. Be sure the meter function select switch is in the up position (knob # 17). Turn the PID lamp current knob in a clockwise direction until the PID is lit (the PID will glow purple when lit). Then adjust the knob until the current displayed on the LCD (location 10) is 100mA. The base of the PID lamp should be cleaned periodically (see footnotes).
4. Turn on computer.
5. To get into Peak Simple from the c:\prompt:  
(If the computer is at the A:\ prompt, type C: then enter.)  
  
Type cd\PKSMPL, then press enter.  
  
At the C:\PKSMPL\ prompt, type PEAK2, then press enter.
6. Now load the DEFAULT.CON file from the C drive.  
  
Go to CONTROLS/LOAD  
  
Scroll to and double click on C:

Highlight the DEFAULT.CON file and click on OK.

A red box will appear that states, "EPAP%T.EVT file is not found" click on OK.

7. Set the computer to save chromatograms on the A drive. Go to CHROMATOGRAM/SAVE, scroll down to A: and double click, then click on abort.

8. Check to see that the TEMPERATURE and EVENT programs are loaded.

Go to CONTROL/CHANNEL.

Click on the TEMP box under Channel 1 - Master Channel.

If the temperature program is loaded, click on abort. If it is not loaded, click on FILE/LOAD.

Next double click on the C Drive.

Highlight the EPAP&T.TEM file by double clicking on it. Click OK. Check to make sure the Channel 1 event file is loaded by clicking on CHANNEL 1/EVENTS, if there is data listed on the screen the file is loaded. If the Channel 1 event file is not loaded, click on FILE/LOAD. Next double click on C:, highlight file EPAP&T.EVT and click OK.

9. You now should be ready to start. The instrument should be warmed up for 1/2 hour, pass this time by running an air blank.

Remove the tube from the purge and trap if one has been left on and replace it with a clean dry tube.

Hit the space bar on the computer keyboard to begin the run.

Two chromatograph screens will display, Channel Two at the top for the PID, and Channel Three at the bottom for the DELCD. Red letters will display RUNNING and the min. will be running. The program is set to begin displaying the chromatogram baseline after 5 minutes.

The first file number of the day must be entered manually, throughout the rest of the day the computer will automatically save the file to the next highest file number. To enter the initial file number go to ANALYSIS/PRINT/PRINT CHROMATOGRAM and enter the appropriate file number according to the last file number recorded in the logbook.

10. After a successful air blank run a water blank.

Water blank is simply 10 mLs of the spring water.

11. While the water blank is running, prepare the daily standard, 25 ppb of the four compounds of interest:

Vinyl Chloride  
trans 1,2 - DCE  
cis 1,2 DCE  
TCE

Into 10 mLs of clean water, add 10  $\mu$ L of each compound (taken from the 25 ppm stock STD solutions kept in the refrigerator in 4 mL screw cap vials.)

Use the 100  $\mu$ L syringe for the transfer. Be sure to decontaminate the syringe with methanol after each transfer. Keep the stopper in the test tube between additions and until it is ready to be loaded on the purge and trap. Do not place on instrument until the analytical run in process has completed the sparging/bake out event at ~ 13 minutes.

STOCK STD solutions should be remade if the results of the daily standard are excessively poor. (Concentrations are < 50% or if retention times are out).

Transfer the entire contents of the amber ampoule (1 mL of 100 ppm std.) into 3 mLs of methanol into the 4 mL screw cap vials. Use the 250  $\mu$ L syringe. Make one stock standard for each compound. Once again decontaminate the syringe with methanol after each transfer. Be very careful to transfer all the standard without spillage, use gloves during preparation.

Once this has been completed you have a 25 ppm STOCK STANDARD SOLUTION in Methanol.

Note: These stock standards are prepared separately, one 4 mL vial is prepared for each compound.

12. After the daily 25 ppb STD has been run and results are acceptable (somewhere between 10-31 ppb and all compounds have been identified) you are ready to run samples. Samples should be refrigerated until they are analyzed, but brought to room temperature prior to the actual analysis. If you are going to run samples that are expected to have low concentrations, it is recommended to run a water blank first. If possible, run the samples from least contaminated to most contaminated. For example if there are samples from locations 10, 08, 07, and 01, run the sample from location 10 first and 01 last. Run a water blank between two samples any time the possibility of carry over needs to be eliminated.
13. Check the actual temperatures of trap 1 and trap 2 between samples (knob 9). Do not start the next analytical run until this temperature lowers to approximately 40-45°C. Be consistent. This is important because the trap needs to be cool while it is desorbing onto the column. Also remember not to load the next sample too early, there is a post run event that purges and heats the trap and the sample will be lost.

14. Run one duplicate sample for every 20 samples collected. Be sure to collect two vials of sample if you plan to run a duplicate analysis. Do not take a second aliquot of sample from the same vial.
15. Dilutions should be run if the sample exceeds the calibration range. Note the highest area of the largest standard in the calibration file for that compound. This may occur on samples collected from the influent port, location 01. Take two vials from this location regularly. It can always be used as a duplicate if it doesn't need to be diluted. Dilutions, however, do not count as duplicates.
16. The pressure of the He tank should be lowered at the end of each day after the GC has been shut off. Turn the dual pressure regulator back several revolutions, but not all the way down. It is critical to the longevity of the GC that the He pressure never reach 0 psi.
15. Turn the PID lamp off before turning off the GC.

### III. FOOTNOTES:

1. To clean the PID lamp, slide electricity supply coil off the lamp. Be sure the PID lamp is off, otherwise a electric shock will result. Gently lift the PID retaining clip and slide the lamp toward the right side of the GC. Moisten a Q-tip with water and coat with Bon Ami. Clean the flat piece of glass at the bottom PID as well as the metal contact ring around the bottom of the PID. Remove any remaining residue with a soft dry cloth. Paper towels are not recommended for this task. When reinstalling the PID be sure that its glass bottom is centered with the white ferrule on the GC. If these two are not centered the sample will leak out and no contaminants will be detected by the ELCD. If the PID lamp is always cleaned in the morning before start-up the problem would be detected as soon as the daily standard is analyzed and no contaminants are detected.



envirometal  
technologies  
inc.

## Memorandum

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**To:** Dan Kopcow, Foster Wheeler Environmental Corporation

**From:** Stephanie O'Hannesin, EnviroMetal Technologies Inc.  
Robert Focht, EnviroMetal Technologies Inc.  
Robert Gillham, Department of Earth Sciences, University of Waterloo

**Date:** 4 November 1998

**Re:** Discussion of Results for the Enhanced Iron Pilot Study at the Naval Air Warfare Center, Trenton, New Jersey - 31377.10

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EnviroMetal Technologies Inc. (ETI) has reviewed the data collected during the enhanced iron pilot study at the Naval Air Warfare Center (NAWC), Trenton, New Jersey. This memorandum discusses ETI's interpretation of the pilot study results.

### INTRODUCTION

As a consequence of the significant limitations of pump-and-treat systems, *in-situ* permeable reactive barriers have been identified as an innovative alternative for groundwater remediation (Gillham, 1996). The concept involves the construction of a permeable wall or barrier containing appropriate reactive materials across the path of a contaminant plume. As the contaminated groundwater passes through the wall, the contaminants are removed through chemical or physical processes. Configurations of *in-situ* treatment systems have been evaluated for various site-specific conditions. Advantages of *in-situ* reactive barriers include:

- long-term passive treatment
- low operation and maintenance costs
- absence of waste materials requiring treatment or disposal
- absence of invasive surface structures and equipment
- conservation of groundwater resources

Several types of materials have been suggested for use in *in-situ* treatment zones. The most advanced stage of application has been achieved with systems using zero-valent iron to

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42 Arrow Road  
Guelph, Ontario  
Canada N1K 1S6  
Tel: (519) 824-0432  
Fax: (519) 763-2378

degrade halogenated organic compounds. Under highly reducing conditions and in the presence of metallic iron surfaces, many dissolved chlorinated organic compounds in groundwater degrade to non-toxic products such as ethene, ethane, and chloride (Gillham and O'Hannesin, 1994). The process is abiotic reductive dehalogenation, with the metal serving to lower the solution redox potential (Eh) and as the electron source in the reaction. Using iron as the reactive metal, reaction half-lives (the time required to degrade one half of the original contaminant mass) are commonly several orders of magnitude lower than those measured under natural conditions. The technology is highly effective for the remediation of contaminated groundwater because of the high rates of degradation, the iron is relatively inexpensive, the process requires no external energy supply, and because most compounds are degraded with production of few, if any, hazardous (chlorinated) organic by-products.

The process is abiotic reductive dechlorination, and involves two redox couples; oxidation of iron coupled with reduction of water and oxidation of iron coupled with reduction of the organic compound. That is:



and



Though the connection between the two redox couples has not been confirmed, (1) may provide the hydrogen necessary for hydrogenation of the hydrocarbon in (2). Furthermore, from (1), atomic hydrogen forms hydrogen gas, leaving  $\text{OH}^-$  in solution. The  $\text{OH}^-$  commonly results in an increase in pH. In (2), the iron serves as a source of electrons for dechlorination of the hydrocarbon (R-Cl). The products are chloride in solution ( $\text{Cl}^-$ ) and the hydrogenated hydrocarbon (R-H).  $\text{Fe}^{2+}$  is a product of both redox couples. Because  $\text{Fe}^{2+}$  has a relatively low solubility, at neutral pH it will precipitate as siderite ( $\text{FeCO}_3$ ) and at elevated pH (as a result of  $\text{OH}^-$ ), will precipitate primarily as iron hydroxide (in the pH range of about 9-10).

The degradation pathway depends upon the compound being degraded. For the chlorinated ethenes, the compounds present in groundwater at NAWC Trenton, New Jersey site, two pathways have been identified. The first is sequential degradation by which tetrachloroethene (PCE) degrades to trichloroethene (TCE), to the dichloroethene (DCE) isomers, to vinyl chloride (VC) and ultimately to ethene. In the second pathway, PCE or TCE are transformed to chloroacetylene which transforms rapidly to chloride and ethene.

At concentrations in the range normally encountered in contaminated groundwater (a few micrograms per litre to a few tens of milligrams per litre), the reaction is generally considered to be pseudo first order with respect to the contaminant concentration. As a result, the rate of degradation can be represented by a half life. As a useful "rule of thumb", a decline in concentration of three orders of magnitude (1000 to 1 µg/L for example) requires 10 half lives. For commercial-grade granular iron materials, half lives for TCE are generally within the range of about 30 to 60 minutes.

Since 1994 over thirty-three permeable treatment walls containing granular iron have been installed to remediate volatile organic compounds (VOCs). There are currently 19 *in-situ* full-scale systems and several smaller *in-situ* and above-ground pilot-scale systems, removing VOCs (mainly chlorinated ethenes) from groundwater. Further discussion of the reaction processes and implementation criteria are given in Gavaskar et al., 1998 and ITRC, 1997.

While degradation rates using granular iron are substantial, and practical for *in-situ* applications, higher rates could be beneficial in broadening the scope of application of the technology. In particular, higher degradation rates could extend the scope of application to high-flow above-ground treatment systems. Various researchers have shown that the plating of a small amount of a more noble metal onto the iron surface can result in a substantial increase in degradation rates (Sweeny and Fischer, 1973; Grittini et. al., 1995 and Maftikian et.al., 1995 for example). Much of the recent research has studied palladium as the second metal; however, as a consequence of lower cost, studies at the University of Waterloo have focused on the use of nickel-plated iron (Odziemkowski et al., 1998). Typically, as reported in Gillham et.al. (1997), reaction rates for Ni-Fe materials increase by about a factor of ten relative to Fe<sup>0</sup>. As an example, a reduction in half life from 30 minutes to about 3 minutes was reported for TCE, using a Ni-Fe material containing about 0.3% Ni.

Though the use of bimetals for accelerating the degradation of chlorinated organic compounds is an active topic of research at many institutions, there is a very limited amount of published information available. Mechanisms, degradation pathways and long-term performance are therefore topics of speculations rather than scientific knowledge.

Work at the University of Waterloo, which remains largely unpublished, has shown that Ni-Fe materials generally increase degradation rates by a factor of ten or more for a wide range of VOCs.

It is generally assumed that the reaction is similar in many ways to the reactions with iron. That is, reduction of the organic occurs by direct electron transfer at the metal surface (or at the surface of oxyhydroxide coatings). For the chlorinated ethenes, the class of compounds that have received the greatest attention, the product distribution differs from that observed for iron. In particular, with the Ni-Fe material, there appears to be little or no production of the DCE isomers or VC from the degradation of PCE or TCE, suggesting that the chloroacetylene pathway is strongly preferred. In addition, ethane is the primary final product, indicating an environment sufficiently reducing to break the double bond of ethene.

There is considerable speculation concerning the enhancement caused by the second metal (Ni in our case). It is widely accepted that the second metal acts as a catalyst, and is not consumed by the degradation process. A promising, but not fully developed, hypothesis is that the enhancement is a consequence of galvanic coupling between the iron and the second (more noble) metal.

Reactions between iron and chlorinated VOCs are stoichiometric and non-catalytic and thus the issue regarding long-term performance concerns the persistence of the iron metal and possible effects of surface coatings on the electron transfer process. Because the reactions with Ni-Fe are clearly catalytic, there is an additional concern regarding reductions in the catalyzing effect over time. Currently there is conflicting evidence with the results of some tests indicating no apparent loss of activity over time, while others suggest significant declines in reaction rates. Sulphide is a widely recognized catalyst "poison", and indeed there is evidence to suggest that sulphide in solution will reduce the activity of bimetal materials. There is also evidence that nitrate will compete with chlorinated compounds (reducing the VOC degradation rates) and that bicarbonate may also serve as a passivating "poisoning" agent.

As in the case of iron, the reaction kinetics appear to be pseudo-first order up to a few tens of milligrams per litre of VOC. At higher concentrations the kinetic order is unclear. It is thought however, that as in the case of iron, at high concentrations the rate will be determined by the capacity of the metal, rather than by the concentration of the organic. This would result in zero-order kinetic behaviour.

Though early laboratory tests showed the Ni-Fe bimetal to perform effectively and consistently, the initial field trial, as reported in Gillham et. al. (1997) gave inconsistent results. These inconsistencies were subsequently attributed to the commercial process used for producing large quantities of the Ni-Fe material. The Ni-Fe material provided for the NAWC test was from a second (and improved) commercial plating process. It has not been

confirmed however, that this material could give results consistent with small amounts of Ni-Fe produced in the laboratory. Efforts are continuing to improve the commercial plating process, and to evaluate possible issues concerning the long-term performance of the catalyst.

## OPERATION OF PILOT-SCALE REACTOR

The pilot-scale reactor was installed and operated by Foster Wheeler Environmental Corporation at the NAWC. The reactor consisted of a cylindrical vessel; with flow upward through approximately 85 gal of the reactive material. Sample ports were located in both the influent and effluent lines to the vessel. Groundwater was supplied from monitoring well MW36BR, which contained high VOC concentrations, at a flow rate of about 0.05 gallons per minute (gpm). Assuming a porosity of 40% gives a pore volume (total volume of void space within the reactive material) of 34 gal. Thus, at a flow rate of 0.05 gpm, and assuming uniform flow, the residence time within the reactive material would be 11 hours. After 14 weeks of operation, the influent water was supplied from monitoring well MW15BR. This well could provide larger volumes of groundwater but had slightly lower VOC concentrations. Several pore volumes were passed through the vessel at each of several flow rates including 0.05, 0.1, 0.2, 0.5 and 1 gpm. The influent was then supplied from well MW36BR and the flow rate reduced to about 0.05 to 0.1 gpm to provide long-term cleanup of the high concentration groundwater. More detailed information of the operation of the reactor is contained in Foster Wheeler's 2 September 1998 letter to the Commanding Officer, Naval Facilities Engineering Command.

## DATA EVALUATIONS

Based on extensive experience with iron, and more limited experience with Ni-Fe, degradation data are generally interpreted within the context of a first-order kinetic model. That is, the first order decay equation is fitted to concentration versus time data. In the present case, only influent and effluent concentration values are available. This raises several difficulties with respect to data interpretation.

1. If the effluent concentration is below detection, then the first order model can not be applied and the degradation rate (half-life) can not be calculated.
2. Relatively small changes in the influent or effluent concentration can cause significant differences in the calculated half life. This is particularly important in the present case where the effluent concentration is many orders of magnitude lower than the influent.

3. The influent shows large and rapid variations in concentration and thus the effluent concentration may not represent the response to the influent concentration measured at the same time.
4. Production of DCE isomers or VC as a consequence of TCE degradation, is commonly the case. This can not be detected from only influent and effluent samples and thus estimates of half lives for these compounds will be too high and highly uncertain.
5. At the high concentrations encountered, there is some concern that zero-order kinetics may be more appropriate than first order, and that there may in fact be a transition from zero-to first-order along the length of the reactor. With only influent and effluent concentrations, there is no opportunity to evaluate this concern.
6. There is some evidence to indicate that passivation of the Ni-Fe material may proceed as a slowly moving front initiated at the influent end. Without sampling ports within the interior of the reactor, there is no opportunity to evaluate this possibility.
7. Maintaining constant flow rates over long periods of time can be difficult. Calculated degradation rates are, of course, very sensitive to residence time and thus flow rate. That is, uncertainty of 50% in flow rate will result in a 50% uncertainty in degradation rate. Thus undetected variations in flow rate could contribute to the variations in calculated degradation rates.

In the absence of additional data, half lives were calculated by fitting the first order decay equations to the influent and effluent concentrations. In cases where the effluent concentration was below detection, no half life was calculated.

## DISCUSSION OF RESULTS

### Behavior of VOCs

Influent and effluent VOC data and flow rates were provided by Foster Wheeler. The flow rate was converted to residence time in the drum assuming a total volume of 85 gallon and a porosity of 0.4. Given the residence time and the influent and effluent VOC concentrations, apparent half-lives were estimated using a two-point regression. In addition, because only influent and effluent concentrations were measured, some VOCs may have been both produced and degraded within the reactor (e.g. cDCE from TCE), resulting in further

uncertainty in the degradation half-lives for these compounds. Influent and effluent VOC concentrations and half-lives are listed in Table 1 for the three test periods.

This discussion will be limited primarily to the period in which Ni-Fe was used as the reactive material (after 11/21/97); however, brief comments will be made on the initial period when  $\text{Fe}^0$  was used. In particular, half-lives for TCE through not calculated precisely, were approximately 3 to 6 hr. This is considerably longer than normally encountered in laboratory tests (about 0.5 hr) and is probably a consequence of the very high influent concentrations and lower groundwater temperature. In addition, the effluent concentrations for the DCE isomers and VC were frequently higher than the influent concentrations. This is consistent with the high influent TCE concentration and the conversion of a small percentage of TCE to the less chlorinated hydrocarbons.

As indicated in the graphs included in the Foster Wheeler report, the performance of the reactor was greatly improved through replacement of the  $\text{Fe}^0$  material with the Ni-Fe material on the twenty first of November, 1997. During the initial period of the Ni-Fe test (Test 1), the influent TCE concentration (well MW36BR) ranged from 17,100 to 244,600  $\mu\text{g/L}$ , while effluent values ranged from 4 to 101  $\mu\text{g/L}$ . During this period the calculated half life values ranged from 0.41 to 6.1 hr. Calculated half life values for all paired influent and effluent values are included in Table 1. For the reasons indicated previously, it is our view that little weight should be given to an individual value and the averages or trends are more relevant to representative. For the initial test period (Test 1), there is no apparent trend in half life, and the average value was 1.9 hr. This is lower by a factor of about 3 than that estimated for the  $\text{Fe}^0$ , the performance and improvement is less than generally observed in the laboratory using laboratory-prepared Ni-Fe materials (half life of 0.05 hr and ten-fold improvement over  $\text{Fe}^0$ ). It is our strong expectation that the lower-than-expected improvement is a consequence of the high influent concentration, though the fact that the reaction may not be first-order and the quality of the commercially plated Ni-Fe material could also be contributing factors.

As shown in the graphs of the Foster Wheeler report, during Test 1 the concentrations of the DCE isomers and VC in the effluent were very low and consistently lower than the influent values (in contrast to the results when only  $\text{Fe}^0$  was used). This is consistent with the higher reaction rates of Ni-Fe, as well as the lower conversion of TCE to the less chlorinated hydrocarbons as commonly observed for the Ni-Fe material. Though half lives for the DCE isomers and VC are included in Table 1 of this report, because of the simultaneous formation and degradation that undoubtedly occurred within the reactor, little credibility can be given to these values.

For Test 2, the water was withdrawn from MW15BR, and there was a step-wise increase in flow rate from 0.05 to 1 gpm. During this test, the influent TCE concentration ranged from 5,200 to 16,500 µg/L and effluent values and effluent values ranged from 9 to 4,400 µg/L. Because of the short period of record for individual flow rates, it is difficult to relate a particular reaction rate with a particular flow rate. Nevertheless, it is apparent (Table 1), that the effluent concentrations increase with increasing flow rate. Clearly flow rates in excess of 0.2 gpm exceed the capacity of the reactor to effectively treat the groundwater. Within the variability of the numbers, there is no apparent trend in half life with velocity. It should be noted, however, that at the lower influent TCE concentration, the average half life was 0.57, a factor of almost four shorter than observed in Test 1 (high concentration influent) and a factor of about 10 shorter than estimated for the Fe<sup>0</sup> portion of the test.

The fact that the capacity of the reactor was exceeded at the high flow rates is further reflected in the effluent concentrations for the DCE isomers and VC. In particular, at the highest flow rate, the effluent concentration for VC was about 4,000 µg/L. For the reasons given previously, we attach little credibility to the half lives given in Table 1 for the DCE isomers and VC.

Test 3 used the same groundwater (MW36BR) and a similar flow rate (0.05 to 0.1 gpm) as in Test 1. The influent concentrations were generally similar to Test 1, ranging from 75,500 to 109,500 µg/L and the effluent values ranged from 19 to 6,400 µg/L. The average half life over Test 3 of 1.4 hr was similar to, though somewhat lower than calculated for Test 1 (1.9 hr). Thus, with respect to TCE, the performance of the reactor in Test 3 was similar to that in Test 1. It should be noted however that the effluent concentrations of the DCE isomers and VC in Test 3, though generally low, are higher than in Test 1. This may reflect early evidence of a decrease in the catalytic effect of the Ni.

### **Behaviour of Inorganic Parameters**

Samples for analysis of major inorganic parameters were collected at the end of Test 1, while the influent water was continuing to be withdrawn from MW36BR, and on two occasions during Test 2 when the influent was from MW15BR. The results are included in Table 2.

It should first be noted that the inorganic characteristics of the two source wells were very similar. Total iron is an exception, at 6.7 mg/L in MW36BR and 3.6 and 1.5 mg/L in the two samples representing MW15BR. For most parameters, the influent and effluent concentrations were very similar. This appears to be the case for the major cations including calcium, magnesium, sodium and metals including chromium, copper, zinc and mercury.

There was a significant change in total iron, from values of about 5 mg/L in the influent to 78 mg/L in the case of Test 1 and 32 and 24 mg/L in the case of Test 2. The increase iron in solution is a consequence of the corrosion reactions given previously in equations (1) and (2). While the decrease in alkalinity (Table 2) suggests that some iron may be precipitating as siderite, the low pH (6.3) indicates that iron hydroxides are not precipitating. As a consequence, much of the iron released to solution through the corrosion reactions is remaining in solution. Though the data is not entirely consistent, there is an indication of increasing manganese concentration, probably as a consequence of leaching from the iron.

The nickel concentration increased from non-detectable in the influent to values ranging from 0.007 to 0.031 mg/L in the effluent. Though thermodynamically Ni plated on  $\text{Fe}^0$  should not leach, clearly a very small amount is being released to solution. Further, the results suggest that lower flow rates result in higher concentrations. Though measurable, the concentrations are well below the US EPA 1992, MCL of 0.1 mg/L.

Chloride increased from 50 to 57 mg/L, clearly as a result of the dechlorination reaction. No nitrate was detected in the influent or effluent, and the decline in sulphate suggests that sulphate reduction may have been occurring within the reactor. As indicated previously, the decline in alkalinity was most probably a consequence of precipitation with iron.

In general, the changes in inorganic parameters decrease with increasing flow rate. Furthermore, the only change of environmental significance appears to be the increase in total iron.

## SUMMARY

The Ni-Fe material proved to be much more effective in degrading the VOCs in the site water than iron alone. Furthermore, the reactor performed consistently over the ten-month period of the test.

Reaction rates were lower (longer half lives) than generally observed in laboratory tests. There is some evidence that this could be a consequence of the very high influent concentrations, but could also be a result of the quality of the commercially plated material or the fact that under the conditions of the test, the reaction is not first order.

With the exception of total iron, there was little change in the inorganic properties of the water. In some applications, removal of dissolved iron from the effluent could be required.

From the data available, there is no reasonable means of predicting the performance life of the reactor. Continued monitoring, with particular attention to the effluent concentrations of the DCE isomers and VC, would be desirable.

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**Table 2: Inorganic Data from the Ni-Fe Canister**

	Ni-Fe Reactor Influent			Ni-Fe Reactor Effluent			Detection Limits
	189.4 <sup>a</sup>	315.8 <sup>b</sup>	739.9 <sup>b</sup>	189.4 <sup>a</sup>	315.8 <sup>b</sup>	739.9 <sup>b</sup>	mg/L
<b>Pore Volumes</b>							
<b>Cations (mg/L)</b>							
Barium	0.32	--	--	0.589	--	--	0.01
Calcium	34	56	55	53	54	55	0.10
Iron, Total	6.7	3.6	1.5	78	32	24	0.01
Magnesium	14.7	20	18.9	17	19	19	0.05
Manganese	0.089	0.431	0.403	1.63	0.668	0.411	0.005
Sodium	13	14	19	14	14	19	0.5
Nickel	nd**	nd*	nd	0.031**	0.011*	0.007	0.005/ 0.01*/0.02**
Chromium	0.014*	nd	nd	0.016*	nd	nd	0.005/0.01*
Copper	0.012*	nd	nd	0.038*	nd	nd	0.005/0.01*
Zinc	nd	nd	0.092	nd	0.010	0.073	0.005
Mercury	0.0006	nd	nd	0.0011	nd	nd	0.0005
Silica	28	26	12	0.823	nd	13	0.10
<b>Anions (mg/L)</b>							
Chloride	----	----	51	---	----	57	1.0
Nitrate	nd	nd	Nd	nd	nd	nd	0.03
Sulphate	17.4	20	20	6.95	16.5	12	1.0
Alkalinity (mg/L HCO <sub>3</sub> )	128	180	182	44	136	172	1.0
pH	7.10	---	---	6.3	---	---	---

Influent MW36BR

Influent MW15BR

## ZERO VALENT IRON PILOT STUDY AT NAWC TRENTON

### PURPOSE

This paper documents the work undertaken at Naval Air Warfare Center Trenton for an ex-situ Zero Valent Iron Filings Pilot Study.

### BACKGROUND/DEVELOPMENT

The Navy was interested in providing treatment for the high levels of Trichloroethylene (TCE) detected in monitoring well MW-36 BR. Historic contaminant levels in the well were 750-8,900 ppm, sometimes above the theoretical solubility. Treating this water would provide additional mass removal to supplement the existing interim action pumping of well 15BR. The New Jersey Department of Environmental Protection and US Environmental Protection Agency suggested using some of the more contaminated wells for "hot spot" pumping and treatment. An opportunity presented itself for a pilot study at this site. First, there was additional hydraulic capacity at the interim plant (until the final action was selected). The most contaminated well was adjacent to the treatment building, making a short term hook-up relatively simple. The Ground Water treatment Plant (GWTP) also had a full time operator and an in-house Gas Chromatograph that could be used to verify effectiveness of the pilot system. Also, the confidence the regulators have with the Navy allowed the pilot project to be implemented with limited documentation. If successful, a less expensive and more effective treatment method for highly contaminated ground water could be proven for use in the final remedy.

Northdiv and the Naval Facilities Engineering Service Center (NFESC) performed a literature search during 1996 for developing technologies that could treat ground water with the contaminant levels of well 36 BR. The most promising method was Zero Valent Iron Treatment; which was showing success in lab scale testing performed by the University of Waterloo. Through a licensing agreement at NFESC, Northdiv obtained and reviewed copies of about fifty relevant journal articles on zero valent iron treatment. A simple design was scaled up from the published data and it was estimated that one 55 gallon drum full of iron filings would provide one gpm of treatment capacity (from 100 ppm to 100 ppb), which would be suitable for treating MW-36BR water for discharge to the existing GWTP. With all of the economies mentioned, the first phase of the pilot study estimated to cost less than \$25,000.

### PHASE 1

Northdiv tasked Foster Wheeler Environmental Corporation (FWEC) to implement the pilot test as designed via their subcontractor Ground Water Technologies. Foster Wheeler performed a search for iron filings, and obtained some from the Coast Guard who was installing a subsurface zero valent iron treatment wall in North Carolina. The iron was shipped to Trenton and placed in a treatment vessel during February of 1997. An air driven bladder pump was installed in MW-36BR and the well was piped above grade into the building.

After reviewing a few weeks of operational data at 1.0 gpm, it appeared that the pilot plant was not removing the TCE as anticipated. The flow rate was lowered as much as possible (0.05 gpm or lower) to further evaluate performance. After a few months of operational data (May through August 1997), the Navy examined the results. It was again observed that the system was not removing as much TCE as expected (see Figure 1), and Dichloroethylene (DCE) was actually increasing in the effluent. Also, a steady flow rate was difficult to control at the low rates attempted. The problem stemmed from the fact that pump lift was limited to 20 feet, which was equivalent to 4 feet of drawdown in the well and 16 feet of lift to the plant. A drought contributed additional lowering of the water table. Influent TCE concentrations from MW-36BR were 70-155 ppm. The design was re-evaluated in light of more recent information regarding the differing properties of the field grade iron versus the "lab grade" iron. The Navy determined that the unit was undersized for the type of iron it contained, and therefore could at best expect 10% treatment.

The Navy met with FWEC to discuss options. In the intervening years between concept and implementation, the zero valent treatment technology had reached field implementation stage (versus lab scale tests). There was at least one company that offered ex-situ treatment vessels and consulting services for just this type of project.

Envirometal Technologies was published in the EPA Superfund Innovative Technologies Evaluation (SITE) Program for a project in Wayne New Jersey utilizing an ex-situ iron reactor. Envirometal was subcontracted to evaluate the existing system and offer suggestions. Envirometal Technologies visited the site on July 10, 1997; and reviewed the system. As it turns out, Envirometal also was providing consulting services for the Coast Guard project in North Carolina. This gave them detailed information on the iron used in both projects. They utilized software models to predict vessel size and performance with site specific water quality parameters. Envirometal Technologies confirmed the system was working as predicted given that it was undersized. Also, the increase in DCE should be expected because the dechlorination process is partially sequential. Envirometal Technologies provided a cost estimate for a properly sized 1-gpm unit, a 20 gpm unit, and an option to utilize the site for a field test of developmental Nickel-plated iron. That field test could be in parallel with a field scale study at the EPA SITE Project in Wayne New Jersey.

## PHASE 2

The Navy chose to fund the Nickel-plated iron project as Phase 2, with restart after the nickel plated iron was manufactured and delivered. The iron was obtained from Envirometal who had it custom made for the Wayne, NJ project. The cost was \$2,500-3000 per ton. The total cost of Phase 2 was estimated to be less than \$25,000. Delivery of the iron occurred late in November of 1997. The pilot system was restarted around December 1, 1997. As Table 1 and Figure 1 show, the treatment efficiency of the system was greatly improved. For the months of December and January, the nickel enhanced iron removed over 99% of the influent TCE. Over 200 pore volumes of water were treated in the reactor at a flow rate of 0.05 gpm. The reactor often had effluent concentrations at or near the detection limits. In order to better determine the half life of TCE and its breakdown products in the enhanced iron reactor, the flow rate is being increased to obtain more data points with less retention time. Other information being evaluated is the formation of precipitates on the surface of the iron, and the concentrations of metals before and after treatment. The Navy extended the Phase 2 work through June 1998 in order to obtain the additional information on reaction rates and precipitate formation. The information obtained is also being compared with the system in Wayne, New Jersey.

The pilot study was discontinued in March and April 1998 to allow final modifications to the ground water treatment plant. The number of operational extraction wells, and the system flow rate were increased to provide the final remedy for the site. In late April, the system was restarted at the higher flow rates. The Navy is keeping the pilot study in place to evaluate long term performance of the reactor vessel after June 1998. As functioning, the system continues to remove contaminant mass from the aquifer. The life of the iron is currently projected to be a number of years. The continued operation of this system will allow the private sector to gain long term information on benefits and limitations involved with zero valent iron systems.

## CONCLUSIONS

This was a successful pilot scale test of nickel enhanced zero valent iron reactor. Contaminant mass was removed from the aquifer and destroyed by the treatment process. An emerging technology was shown to effectively treat highly contaminated ground water. It was also a successful demonstration where the field performance of conventional zero valent iron matched the software prediction; even if the unit was undersized.

Recent ground water modeling results indicate the extraction system already constructed can capture the entire plume and does not need further expansion. The zero valent iron reactor will be kept in place as long as it functions to remove contamination from the aquifer.

For additional information contact:

Jeff Dale code 1822

Naval Facilities Engineering Command, Northern Division

10 Industrial Highway MS 82

Lester PA 19113.

Phone 610-595-0567 x120

jmdale@efdnorth.navfac.navy.mil

Figure 1

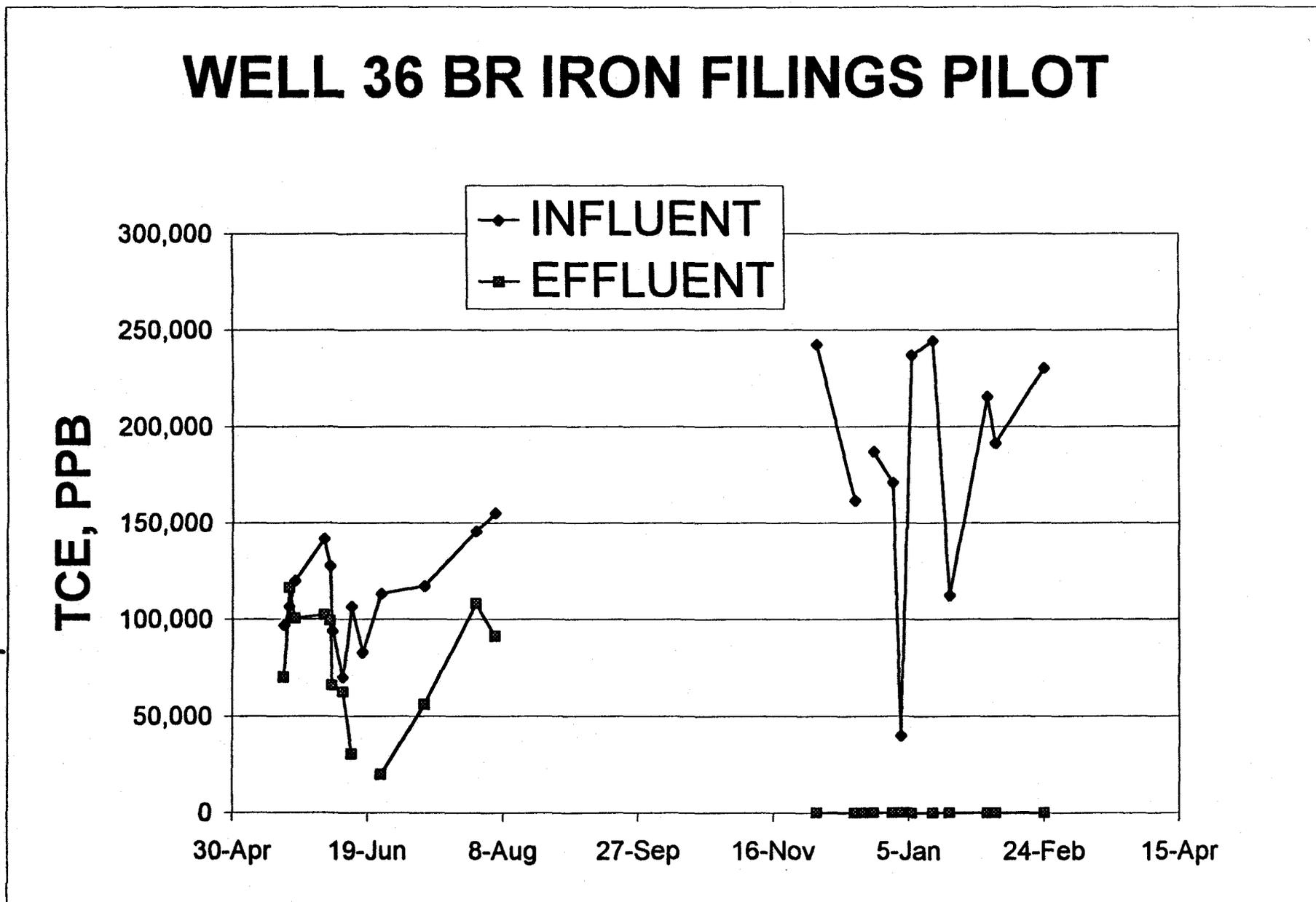


Figure 3

WELL 36 BR AND ZERO VALENT IRON PILOT PLANT TCE DATA

DATE	INFLUENT ppb from 36 BR	EFFLUENT ppb	SOURCE	
11/18/93	750,000		IT	
3/10/95	300,000		EA	
3/15/95	310,000		EA	
3/16/95	1,200,000		EA	
3/17/95	1,300,000		EA	
3/18/95	4,000,000		EA	
3/19/95	350,000		EA	
3/24/95	3,900,000		EA	
3/31/95	4,100,000		EA	
4/5/95	310,000		EA	
6/8/95	8,900,000		EA	
9/14/95	500,000		EA	
12/6/95	320,000		EA	Percent effective
5/19/97	96,842	70,051	FIELD GC	28
5/21/97	106,555	116,490	FIELD GC	-9
5/23/97	119,977	100,523	FIELD GC	16
6/3/97	141,600	102,300	FIELD GC	28
6/5/97	127,800	99,300	FIELD GC	22
6/6/97	93,900	65,900	FIELD GC	30
6/10/97	70,100	62,500	FIELD GC	11
6/13/97	106,700	30,500	FIELD GC	71
6/17/97	83,000		EA/USGS	
6/24/97	113,300	19,900	FIELD GC	82
7/10/97	117,400	56,000	FIELD GC	52
7/29/97	145,700	108,000	FIELD GC	26
8/5/97	155,000	91,300	FIELD GC	41
8/8/97			FOR GRAPH US	
12/2/97	242500	25	FIELD GC	99.9897
12/16/97	161600	20	FIELD GC	99.9876
12/19/97		17	FIELD GC	
12/23/97	187000	16		
12/30/97	171000	14	FIELD GC	99.9918
1/2/98	40000	15	FIELD GC	99.9625
1/6/98	237000	4	FIELD GC	99.9983
1/14/98	244600	73	FIELD GC	99.9702
1/20/98	112500	9	FIELD GC	99.9920
2/3/98	215600	8	FIELD GC	99.9963
2/6/98	191300	35	FIELD GC	99.9817
2/24/98	230300	42	FIELD GC	99.9818

NOTES

All results are for Trichloroethylene in parts per billion PPB  
 Well 36BR data is from well itself or influent to Iron Filings Pilot Plant  
 Effluent data is only available during operation of Iron Filings Pilot Plant  
 Sample from 6-17-97 was collected by EA/USGS and sent to EA Lab.

