Back

FIELD TESTING OF NANOSCALE ZERO-VALENT IRON PARTICLE TECHNOLOGY FOR IN-SITU GROUNDWATER TREATMENT

Robert Glazier[1], Florin Gheorghiu[2], Lindsey Walata[3],
Ramesh Venkatakrishnan[2], and Wei-xian Zhang[4]

1) Golder Associates Inc., 1630 Heritage Landing, Suite 103, St. Charles, MO 63303
rglazier@golder.com, / Tel: (636) 936-1554

2) Golder Associates Inc., 1951 Old Cuthbert Road, Cherry Hill, New Jersey 08034
ramesh@golder.com, florin@golder.com, / Tel: (856) 616-8166

2) GlaxoSmithKline, lw11065@gsk.com, / Tel: (919) 483-4640

3) Lehigh University wez3@Lehigh.EDU / Tel: (610) 758-5318

Abstract

This pilot test has been carried out as part of a RCRA Corrective Measure Study (CMS) at a facility located in Research Triangle Park, North Carolina. The study area is located in the Durham subbasin of the Deep River Triassic Basin and is underlain by interbedded siltstone and sandstone sequences. Groundwater underlying portions of the site has been impacted by historical industrial activities conducted by previous owners; groundwater contaminants consist mainly of chlorinated volatile organic compounds. Bimetallic nanoscale particles (BNP) consists of nanoscale particles of zero-valent iron (Fe^0) with a trace coating of palladium. The rapid destruction of a wide range of recalcitrant contaminants is based on a surface-catalyzed redox process where the contaminant serves as an electron acceptor and BNP as the electron donor and can be accomplished either in situ or ex situ (Wei-xian Zhang, 1997, 1999, 2000). This study presents the field demonstration of the BNP effectiveness to treat in-situ chlorinated volatile organic compounds (VOCs) in a complex fractured bedrock aquifer setting. During the pilot test, 11 kilograms of BNP mixed in a water-based slurry were injected into the shallow bedrock groundwater suspected to contain dense non-aqueous phase liquids (DNAPLs). The results of the test indicated rapid treatment of chlorinated VOCs 20 feet to 40 feet around the injection well. In addition, the oxidation-reduction potential (ORP) and dissolved oxygen (DO) values have decreased and persisted for more than six months at very low levels of -750 millivolts and less than 0.001 milligrams per liter, respectively, indicating favorable conditions for reductive dechlorination. Interpretation of pre- and post-test data on the in-situ microbiological community in the test area indicate changes in ORP and DO that might stimulate anaerobic bacteria known to degrade chlorinated solvents. Redox-induced mobilization of naturally occurring inorganics from the aquifer solids was not detected. Treatment efficiencies closely correlate with predictions from bench scale tests, suggesting that very little reagent interacted with non-target constituents within the aquifer matrix.

Introduction

This paper presents the results of a field pilot test that used bimetallic nanoscale particles (BNP) to provide in-situ treatment of chlorinated solvents in groundwater. The field demonstration included the installation of an injection well and additional monitoring wells, hydrogeologic testing of the test area wells, baseline sampling of the monitoring well network prior to the BNP slurry injection, and post-injection monitoring. In-Situ, Inc. Troll 9000 multi parameter dataloggers were used throughout the test to record changes in oxidation reduction potential (ORP), dissolved oxygen (DO), pH, specific conductance (SC), temperature, and groundwater elevation.

Geology

The test site is located in the Durham sub-basin of the Deep River Basin in the Piedmont Physiographic Province of North Carolina. The Deep River Basin is one of many Mesozoic Rift Basins that occur along the eastern seaboard of North America (Froehlich and Robinson, 1988, Bain and Harvey, 1977). The basin lower Mesozoic rocks lie unconformably on Precambrian and Paleozoic crystalline rocks, and locally on Paleozoic sedimentary rocks (Hoffman and Gallagher, 1991). In North Carolina, the rocks in the Triassic Basin consist of cyclical interbedded shale, sandstone, and siltstone, all typically red, reddish brown, or maroon but locally gray or black. The Durham sub-also includes conglomerate, dolomite, lacustrine black mudstone, and coal beds. In many places, diabase dikes and sills have been intruded in the sedimentary rocks. In the Durham sub-basin the bedding orientation on a mesoscale is generally homoclinal towards basin-bounding normal faults (i.e., to the east or the southeast towards the Jonesboro (border) fault).

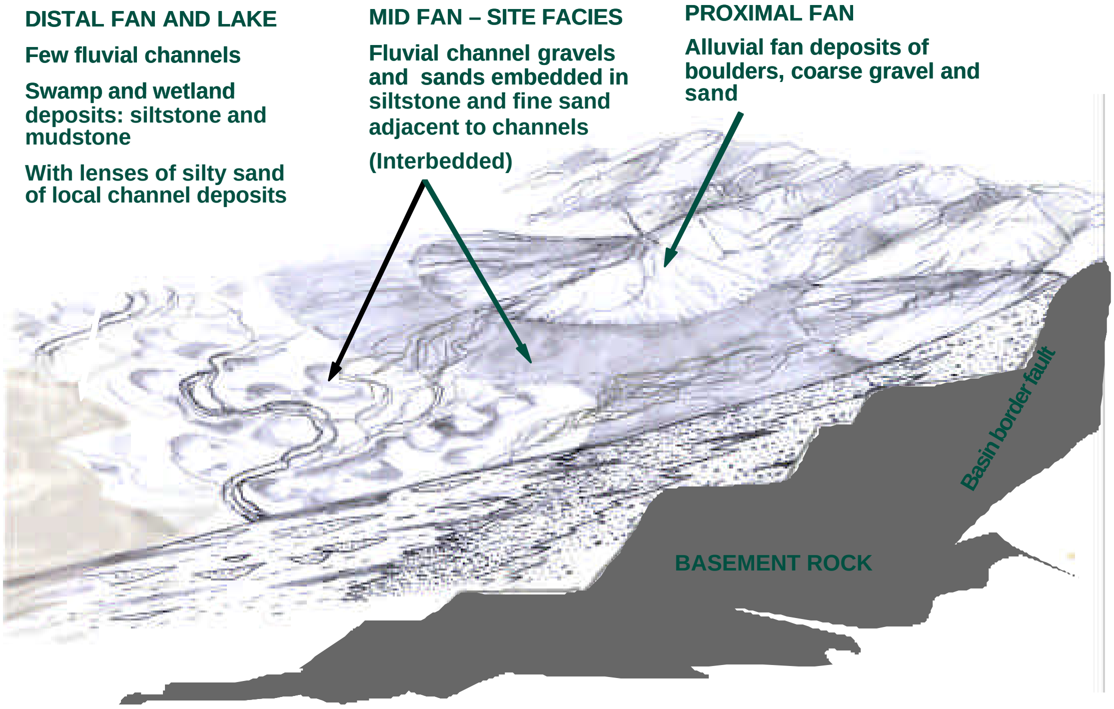


Figure 1: Facies Association of Typical Half Graben Basin.

The cyclical packages at the site are illustrated in Figure 1 in a conceptual interpretation of the facies associations in a typical half graben depositional environment. At the regional scale, similar facies associations have been assigned to the “Lithofacies Association II” (see Hoffman and Gallagher, 1991, pp. 10 through 16) consisting of siltstone grading downward and interbedded with sandstones.

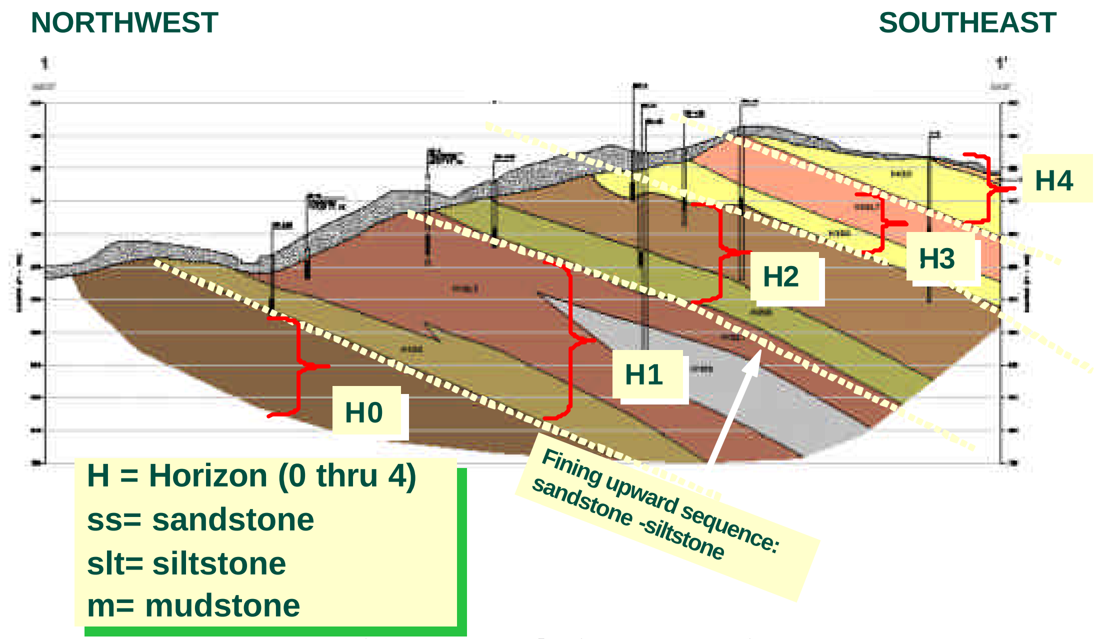


Figure 2 – Geologic Cross Section

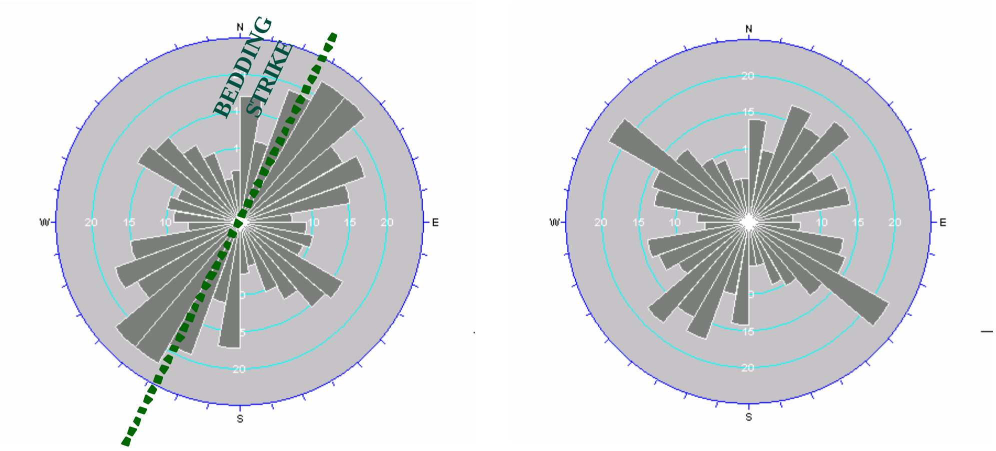
The sandstones form fining-upward sequences and are often cross-laminated with scour bottom to channels. The sandstones are typically lenticular with variable continuity. The siltstones display a wide variety of sedimentary structures and are often thinly bedded to laminated.

The site is located on a topographic high (approximately 380 feet mean sea level - MSL). The surface water drainage is radial from the topographic high and no perennial streams have been noted in the vicinity of the site. The topographic high forms a northeast-southwest trending ridge that parallels the regional strike of the bedrock strata.

The geologic units at the site include a surficial geologic unit and a bedrock unit. The surficial geologic unit at the site consists of a variably thick mantle of native residual soils and fill materials. The native residual soils consist of tan to brown sandy silt, silty clays, and fine sandy silts and clays. The fill materials encountered at the site are heterogeneous in nature and include sandy materials with variable amounts of construction debris, wood fragments, etc.

The bedrock unit has been subdivided in horizons that include sandstone and siltstone packages. Using a site-specific nomenclature (Figure 2), bedrock horizons have been numbered H0 (stratigraphically the oldest investigated horizon) through H4 (stratigraphically the youngest investigated horizon). Each horizon includes a sandstone package at the base, and a siltstone package at the top, indicating a fining upward sequence that is also recognized at the regional scale (Hoffman and Gallagher, 1991). Siltstone and sandstone dominated facies/bedrock packages are identified with the abbreviation “SLT” and “SS,” respectively (e.g., H2SLT would be assigned to horizon number 2 dominated by siltstone). The bedrock horizon H1 includes a discontinuous layer of mudstone (H1MS). Much of the contamination occurs in the intermediate age H3SS and H3SLT horizons. At some of the stratigraphic breaks paleosols have been observed. Diabase intrusions are present in the southern part of the site outside of the area of BNP test.

The most frequently observed discontinuities are the bedding planes. The bedrock beds dip gently (less than 15 degrees) to the southeast and bedrock strike ranges from about North 10 degrees East to about North 20 degrees East. Younger stratigraphic horizons occur in the eastern part of the site (i.e., beneath the BNP test area) and older stratigraphic horizons outcrop in the western and northwestern portions of the site. However, dip and strike deviations as a result of the cross-bedded stratification are common. Other discontinuities of the rock mass are represented by higher angle fractures. The high angle fractures are relatively common in the Durham sub-basin (see Bain and Harvey, 1977; and Hoffman and Gallagher, 1991). These discontinuities display preferred orientations that are in general parallel with either bedrock strike (strike-joints), and bedrock dip (dip-joints) or form conjugate fracture sets.



A) **B)**

Figure 3 – High Angle Fracture Data: A) Stream Alignments; B) Televiewer Data

The steep fracture orientations were estimated based on the regional drainage pattern and topography as well as optical and sonic televiewer logs obtained from an extensive subsurface investigation program conducted at the site (Figure 3). Strike joints trend northeast-southwest, and dip joints trend northwest-southeast, and these preferred trends dominate on rose diagram plots. In addition, moderately well developed northerly-trending and easterly-trending sets are also present.

Hydrogeology

The groundwater flow at the site is radial away from a hydraulic divide that parallels the bedrock strike-controlled topographic ridge. The horizontal hydraulic gradient values range from 0.02 to 0.2 feet/foot with the steepest gradients along the northwest flank of the ridge. Vertical hydraulic gradients are in general downward and groundwater from the overburden and upper weathered bedrock recharges deeper groundwater within the bedrock. The vertical hydraulic gradients range from 0.03 feet/foot to 0.5 feet/foot (Venkatakrishnan and others, 2003).

Shallow groundwater flow at the site is controlled by topography (Figure 4), dominated by the northeast-southwest-oriented ridge that parallels the regional strike of the bedrock. The shallow groundwater flow in the overburden is locally influenced by site infrastructure, man-made drainage features, and backfill areas providing preferential groundwater migration pathways.

The bedrock groundwater flow is influenced by bedrock discontinuities (Figure 4). The bedrock beneath the site consists of a weathered (transition) zone that grades downward into a sequence dominated by interbedded siltstones and sandstones that are laterally traceable. Together, the fracture system allows for groundwater flow along bedding planes and vertical hydraulic connection between strata through the steeper-dipping joint planes. The up-dip extensions of the bedding planes provide for down-dip drainage of groundwater into deeper portions of the bedrock.

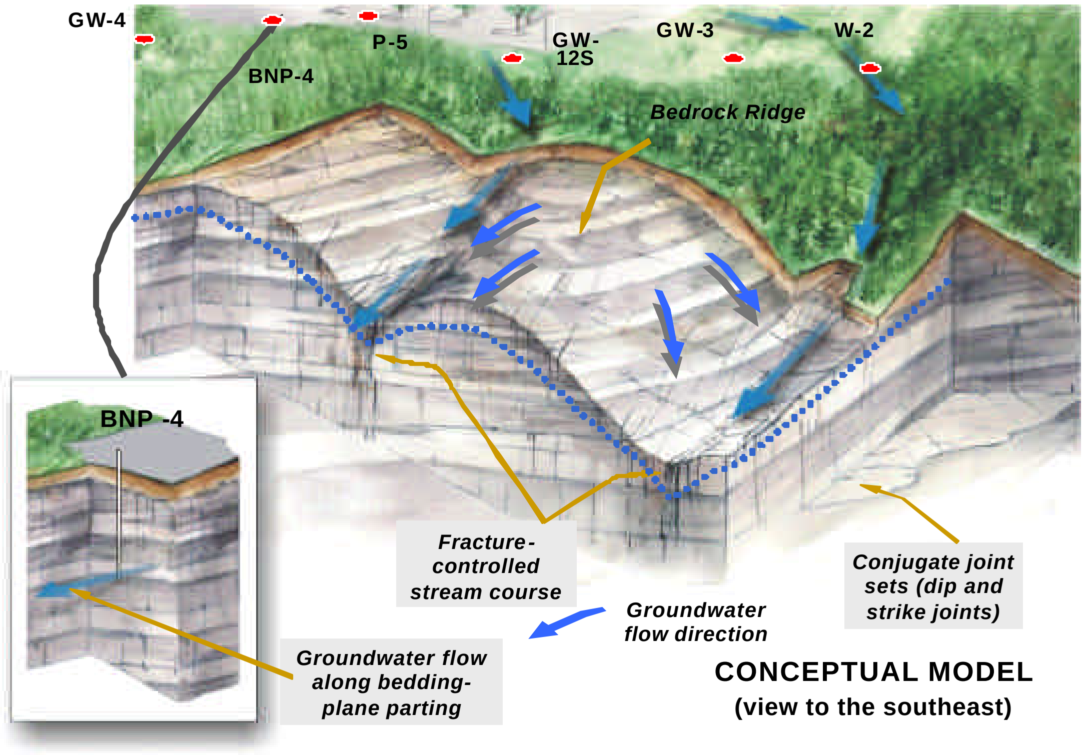


Figure 4 – Conceptual Geologic and Hydrogeologic Model

Within the deeper bedrock, the groundwater flows through rock discontinuities including bedding plane partings and to a lesser extent through the rock matrix. The hydrogeologic tests indicated typical fracture flow behavior and none of the pumping tests conducted at the site indicated a typical dual porosity behavior. The groundwater flow is anisotropic showing higher groundwater velocities and implicitly higher groundwater fluxes along the bedding planes, and lower groundwater velocities/fluxes perpendicular to the bedding planes. This is more pronounced with depth since the fracture frequency of low angle discontinuities decreases with depth. As a result, although the vertical hydraulic gradients at the site are consistently downward, the downward groundwater flux is much lower in deeper bedrock compared to shallow bedrock. The dominance of shallow groundwater flow at the site is consistent with the higher concentrations of VOCs detected by the shallow monitoring well network compared to the deeper wells.

The hydrogeological properties of the subsurface materials have been determined by conducting slug testing of a network of 48 groundwater monitoring wells and the completion of 6 pump-in tests and 4 short-term pump-out tests. The hydrogeologic test results indicated the following:

- The overburden materials showed hydraulic conductivity ranges from 10^{-6} cm/s to 10^{-4} cm/s. The hydraulic conductivity of the native overburden materials is in general lower than the hydraulic conductivity of fill materials;

- The overburden-bedrock interface showed low hydraulic conductivity values in the range of 10^{-6} cm/s to low 10^{-5} cm/s;

- The upper bedrock horizons (i.e., H4SS, H3SS, and H3SLT) show low hydraulic conductivity values generally in the range of 10^{-6} cm/s to low 10^{-5} cm/s;

- The intermediate bedrock horizons (i.e., H2SLT and H2SS) show the most variable results. There are local low hydraulic conductivity values of 10^{-7} cm/s and frequent occurrences of relatively higher hydraulic conductivity values ranging from 10^{-5} cm/s to low 10^{-3} cm/s. In general, there is a decrease of hydraulic conductivity with depth for all the geologic units and at depth, these units show very low hydraulic conductivity values in the order of 10^{-7} cm/s; and,

- The lower bedrock horizons (i.e., H1SLT, H1MS, H1SS, and H0SLT) consistently show low hydraulic conductivity values in the range of 10^{-7} cm/s to mid 10^{-5} cm/s.

Groundwater flow velocities at the site are variable as a result of typical bedrock heterogeneities (hydraulic conductivity and effective porosity). The effective porosity of the bedrock materials is expected to be low. The results of the BNP pilot tests allowed the estimation of the bedrock effective porosity. The results indicate an effective porosity value of about 2.5 percent (between BNP-4 and GW-4). These estimate was calculated from pumping tests conducted in the BNP pilot test area and include changes in hydraulic gradients (I), BNP slurry arrival times (t) based on changes in ORP monitored with electronic In-Situ, Inc. Troll 9000 dataloggers. The effective porosity (n) that closely matches travel time (t) was estimated using Darcy's formula ($V = KI/n$) for the distance (D) between the injection well and monitoring wells (D = t V; V = KI/n, where n is the parameter to be estimated; see Venkatakrishnan and others, 2003).

Results of the BNP Treatability Test

The results of the field-scale treatability pilot test agree favorably with those of previously-published laboratory tests (Wang and Zhang, 1997; Lien and Zhang, 1999; Xu and Zhang, 2000; Lien and Zhang, 2001) as well as a prior BNP field pilot test conducted at another site (Elliot and Zhang, 2001). The test well location is shown in Figure 5 and a northeast-southwest oriented cross section through the test area is presented in Figure 6.

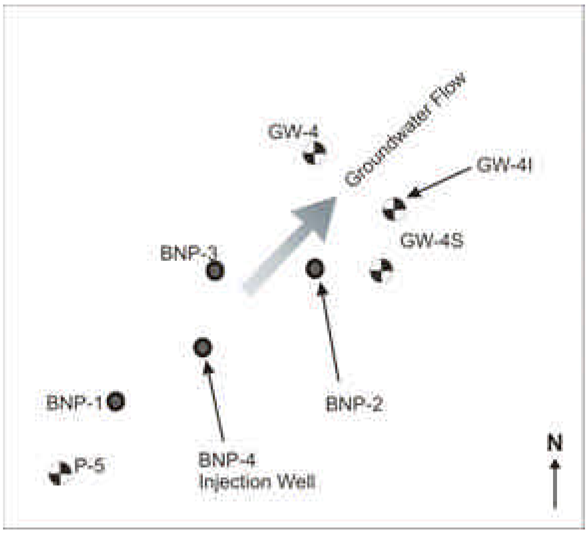


Figure 5 – BNP Test Area Map

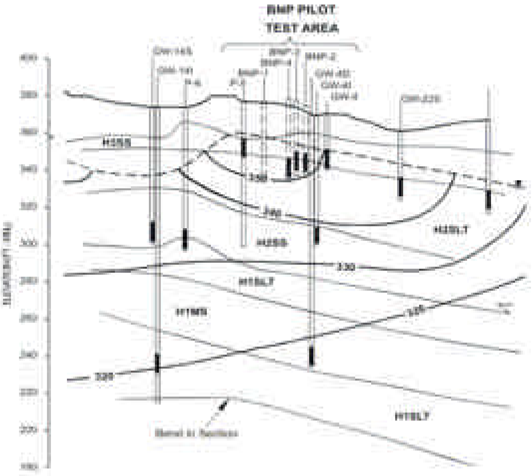


Figure 6 – BNP Test Area Cross Section

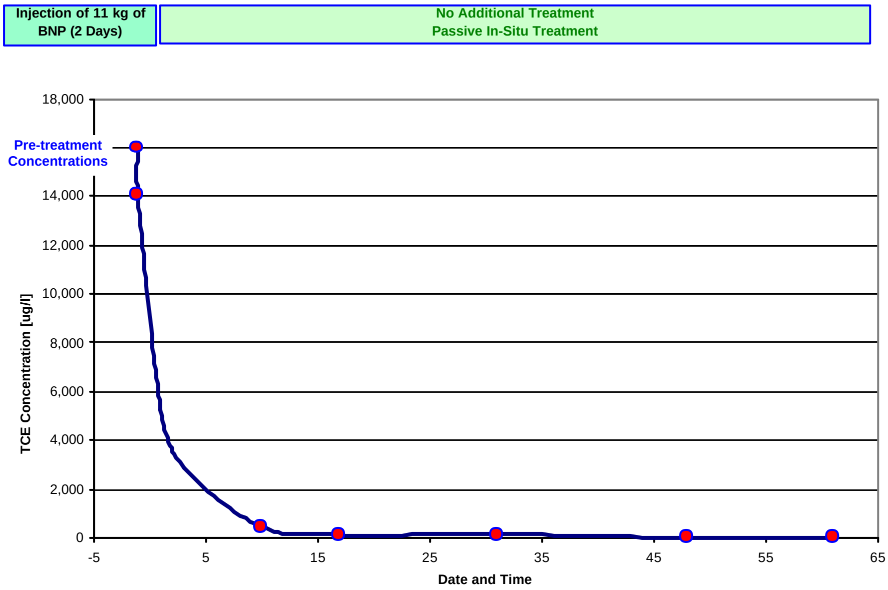


Figure 7 - Trichloroethene (TCE) Concentration Reduction in BNP-4

Following is a summary of the test findings. TCE reductions are illustrated in Figures 7 through 10.

- ***VOC Treatment***

  Over 90 percent reduction in the pre-injection baseline concentration of approximately 32,000 ug/L of total chlorinated VOCs, most of which is TCE and cis-1,2-DCE, was achieved within several days, and lasted for over two months, in the injection well BNP-4. In addition, the concentration of 1,2-dichloroethane (1,2-DCA) as well as benzene, toluene, ethylbenzene, and xylenes [BTEX] also declined. It appears that treatment of these compounds did occur because the concentrations remained lower than the pre-injection baseline samples in excess of two months after injection.

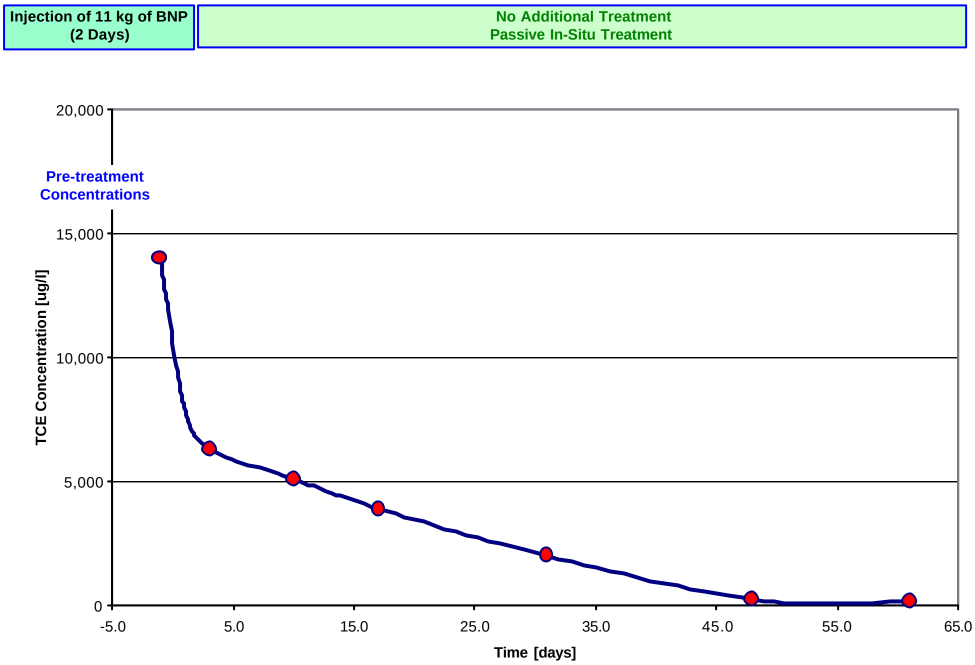


Figure 8 – TCE Concentration Reduction in BNP-3

The pre-injection baseline redox conditions in most of the test area were indicative of iron-reducing conditions (e.g., ORP measurements of approximately +50 mV to -100 mV) and were lowered to methanogenic conditions with measured in-situ redox potentials of approximately -700 mV in the injection well BNP-4 and -500 mV in the nearby monitoring wells. Monitoring for potential mobilization of redox-sensitive metals including manganese, barium, and arsenic was conducted. No increased concentrations of these constituents were detected after BNP injection. The lower redox potentials persisted for at least 28 weeks in the injection well and observation wells BNP-3 and BNP-2, located 20 feet and 40 feet downgradient of the injection well BNP-4, respectively.

- ***Radius of Influence***

  The radius of influence of the injection, as measured by VOC concentration reduction, was at least 20 feet around the injection well as shown by the concentration reductions at BNP-3. However, the treatment radius is somewhat larger because some concentration reductions were observed at BNP-2 and GW-4 (see Figures 9 and 10) located 40 feet and 63 feet, respectively, downgradient of injection well BNP-4 (see Figures 5 and 6).

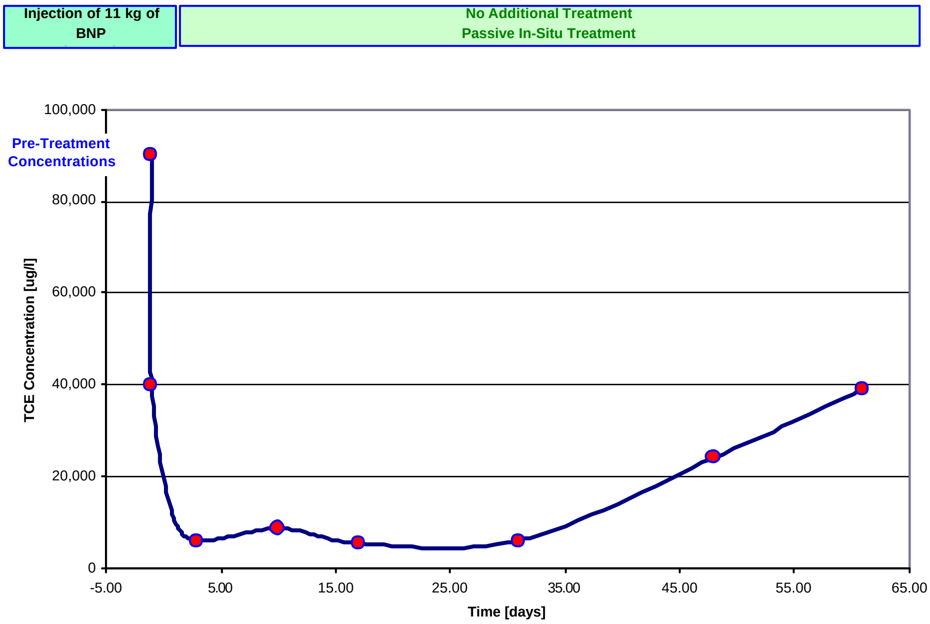


Figure 9 – TCE Concentration Reduction in BNP-2

- ***BNP Treatment Duration***

  Monitoring results confirm VOC concentration rebound that begins to appear in the Day 61 data for the injection well BNP-4. ORP and pH data are available through week 28 from the in-situ dataloggers. It appears that the effective treatment lifetime for the particles in the test area is approximately two to three months based on current conditions in this area and the particle composition that was used during the pilot study, although the ORP remained lower than pre-injection conditions for at least six months. It is possible that particle lifetimes would be greater for repeat injections because the initial injection will have already lowered the ORP.

- ***Microbiological Determinations***

  Microbiological testing of groundwater samples from the pilot test monitoring wells indicates that injection of BNP has had little affect on the total biomass and community structure. It appears that BNP injection temporarily decreased the proportion of Gram negative bacteria (a.k.a. Proteobacteria) within the microbial community at BNP-4. It appears that injection of BNP does not preclude follow-up use of bioremediation at the site. Traces of *Dehalococcoides ethanogenes* were detected only in a deep monitoring well (i.e., GW-4I) where chloroform was not present.

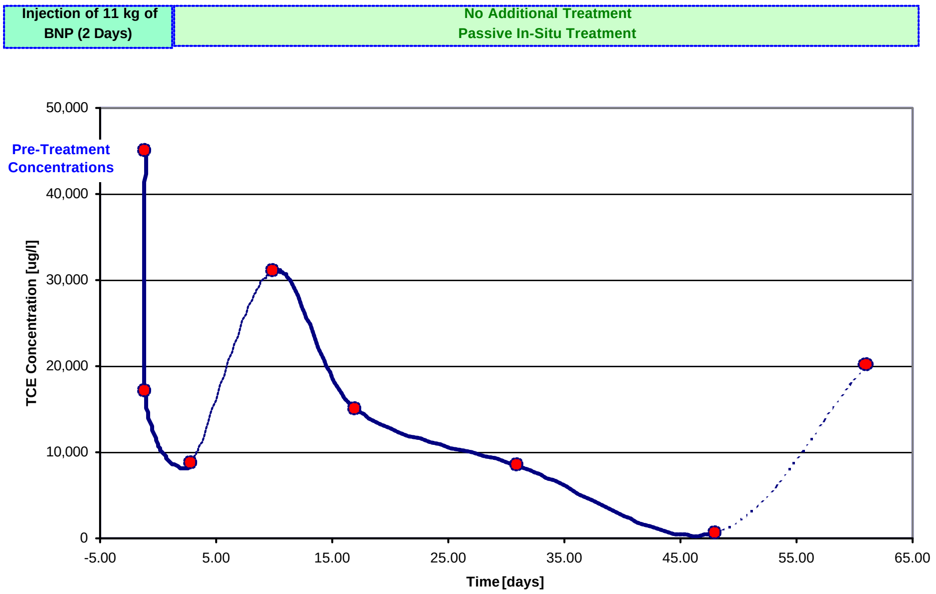


Figure 10 – TCE Concentration Reduction in GW-4

Summary

In summary, the following results were observed during the BNP pilot test conducted at the site:

- Rapid decrease in chlorinated ethene concentrations at injection well BNP-4 with over 90 percent reduction of total chlorinated VOC concentration;
- Maintenance of chlorinated VOC treatment efficiency in excess of two months;
- Maintenance of extremely low ORP conditions (methanogenic) for over 6 months; and,
- No mobilization of redox-sensitive metals.

References

Bain, George L., and Bruce W. Harvey, 1977. "Field Guide to the Geology of the Durham Triassic Basin," Carolina Geological Society, Fortieth Anniversary Meeting.

Chapelle, F.H., 2001. Groundwater Microbiology and Geochemistry, (Second Edition), John Wiley, New York, New York, 477p.

Elliot, D.W., and W.-x. Zhang, 2001. "Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment," Environmental Science and Technology, Vol. 35, pp. 4922-4926.

Froelich, A.J., and G.P. Robinson, Jr., 1988. "Studies of the Early Mesozoic Basins of the Eastern United States," U.S. Geological Survey Bulletin 1776.

Glazier, R.E., Venkatakrishnan, R., Gheorghiu, F., Lindsey Walata, Nash, R., Zhang, W.X., 2003. "Nanotechnology Takes Root," Civil Engineering, May 2003, pp.64-69.

Hoffman, C.W., and P.E. Gallagher, 1991. "Geology of the Southeast Durham and Southwest Durham 7.5 Minute Quadrangles, North Carolina," North Carolina Geological Survey, Bulletin 92.

INTERPRET/2 Scientific Software Intercomp, Inc., 1994. Petroleum Workbench Well test Analysis –Interpret/2 User Manual, 1994.

Lien, H.-L., and W.X. Zhang, 1999. "Transformation of Chlorinated Methanes by Nanoscale Iron Particles," Journal of Environmental Engineering, Vol. 125, pp. 1042-1047.

Lien, H.-L., and W.X. Zhang, 2001. "Nanoscale Iron Particles for Complete Reduction of Chlorinated Ethenes," Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 191, pp. 97-105.

Venkatakrishnan R., Gheorghiu F., Glazier R.E., Elsea J., Lindsey Walata, and Zhang W.X. "Multi-Parameter Monitoring of Nanoscale Particle Injection in Triassic Basin Bedrock, North Carolina," Petroleum Hydrocarbons and Organic Chemical in Ground Water, API and NGWA Conference, Costa Mesa, CA, August 2003.

Wang, C.B. and W.-x. Zhang, 1997. "Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs," Environmental Science and Technology, Vol. 31, pp. 2154-2156.

Wilkin, R.T., Puls, R.W., and G. W. Sewell, 2002. "Long-Term Performance of Permeable Reactive Barriers Using Zero-Valent Iron: An Evaluation at Two Sites." EPA/600/S-02/001, March 2002.

Xu, Y. and W.-x. Zhang, 2000. "Subcolloidal Fe/Ag Particles for Reductive Dehalogenation of Chlorinated Benzenes," Industrial Engineering and Chemical Research, Vol. 39, pp. 2238-2244.

Biographical Sketches

Mr. Glazier is an Associate in Golder Associates and is responsible for development and implementation of project strategy, as well as groundwater geochemistry and environmental chemistry evaluations, for remediation projects under CERCLA, RCRA, State, and Voluntary Corrective Action programs. He has a broad perspective of regulatory approaches to site remediation through project work throughout North America, and is also well-versed in risk assessment, indoor air pathway evaluations.

Mr. Gheorghiu is a Principal in Golder Associates, and directs numerous environmental projects requiring numerical groundwater flow and solute transport modeling, particularly supporting in-situ remedial systems. He was the Project Director for design and implementation of a large bedrock remedial system at Modern Landfill that received the Year 2000 Outstanding Groundwater Remediation Project Award from NGWA.

Lindsey Walata is an Environmental Engineer at GlaxoSmithKline. Her primary responsibilities include direction of RCRA corrective actions activities. Ms. Walata is a registered professional geologist in North Carolina and has extensive experience with environmental investigations and evaluations.

Dr. Venkatakrishnan is a Principal in Golder Associates. As practice leader in the firm he directs geologic and hydrogeologic aspects of site investigation at mine developments, subsurface exploration for civil, geotechnical and environmental investigations. He serves as a peer reviewer for geologic and hydrogeologic projects in the Golder's northeast region.

Dr. Zhang is an Associate Professor of Civil and Environmental Engineering at Lehigh University. Dr. Zhang is the leading expert on the manufacture, treatment mechanics, and use of the BNP technology and has led successful field demonstrations of BNP treatment of chlorinated VOCs at an industrial site in Trenton, New Jersey. Dr. Zhang is also working on a part-time basis with Golder Associates Inc.