Technical and Regulatory Challenges Resulting from Voc Matrix Diffusion in a Fractured Shale Bedrock Aquifer

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Abstract

During a RCRA Facility Investigation (RFI) at the Watervliet Arsenal, located in Watervliet, New York, groundwater contaminated with chlorinated volatile organic compounds (VOCs) was discovered within the bedrock adjacent to the downgradient site boundary. Rock core analytical data has shown that much of the VOC mass that initially migrated preferentially along the interconnected fracture network is now present as dissolved and sorbed mass in the low permeability shale bedrock due to diffusive mass transfer to the rock matrix. Based on groundwater and rock core data collected to date, it is anticipated that more than 99 percent of the VOC mass is present in the rock matrix. The presence of the VOCs in the bedrock matrix presents many technical and regulatory challenges when it comes to how to remediate the problem and how to define success. The only truly effective remediation technologies for the fractured bedrock aquifer are those that will treat the VOC mass in the rock matrix in addition to treating the VOCs in the groundwater. Failure to treat the VOC mass in the matrix will result in a continuous diffusive transfer of VOCs from the bedrock matrix into the groundwater over an extensive time period. In addition, it should be recognized that, although USEPA Maximum Contaminant Limits (MCLs) or equivalent state standards are always the ultimate objectives, it is unlikely that MCLs will ever be achieved by any remediation technology in matrix-dominated fractured bedrock environments. This leaves mass-based metrics (i.e., reduction of source mass and/or reduction in flux) as the only viable measures by which remedial programs in fractured bedrock should be evaluated and by which eventual site closure could be achieved. At the Watervliet Arsenal, mass-based metrics have been utilized to formulate an exit strategy for a corrective measure utilizing in-situ chemical oxidation with permanganate that is acceptable to both the regulatory community and the Arsenal. Use of this approach has allowed the Arsenal to move forward with a remedial program that is expected to reduce VOC mass in the rock matrix by more than 40 percent.

INTRODUCTION

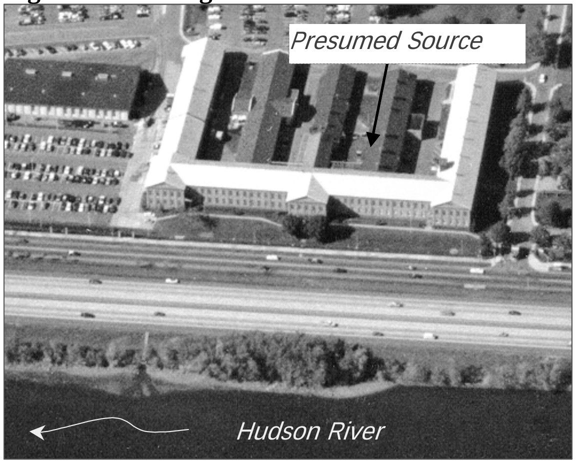
It is generally recognized that geologic complexities pose some of the greatest challenges to site characterization and remediation. Fractured rock sites are among the most complex because of their considerable geologic heterogeneity and the nature of fluid flow and contaminant transport through fractured media (USEPA, 2001). Until recently, the conventional view of fractured rock sites was that they are too complex to characterize and remediate. The most common remedial approach at fractured rock sites has been a containment strategy using groundwater extraction and treatment (USEPA, 2001). Recent work has shown that, in a dual porosity system such as fractured sedimentary rock, diffusive transport of contaminants present in fractures into the matrix porewater will result in the storage of the vast majority of contaminant mass in the rock matrix (Parker et al., 1994 & 1997). This concept has important implications in the characterization and remediation of fractured bedrock sites in that groundwater investigations need to focus on the rock matrix as well as the bedrock fractures. Likewise, treatment efficacy will depend almost entirely on the ability to treat the rock matrix, not just the fractures. This paper presents a case study describing the characterization of a fractured shale bedrock contaminated with chlorinated volatile organic compounds (VOCs) and the subsequent technical and regulatory challenges imposed by the presence of the VOCs in the bedrock matrix.

SITE BACKGROUND

The WVA is a 140-acre government-owned installation located in the City of Watervliet, New York, which is west of the Hudson River, and five miles north of the City of Albany. The WVA, a national registered historic landmark, is the oldest continuously operating cannon manufacturing facility in the United States. The WVA currently manufactures large caliber cannons. During a RCRA Facility Investigation (RFI), an area of groundwater contamination was discovered in the eastern portion of the WVA, adjacent to the site boundary and in front of Building 40 – a former manufacturing building now used primarily for office space. Groundwater contaminants include chlorinated volatile organic compounds (VOCs), predominantly tetrachloroethene (PCE) and cis-1,2-dichloroethene (DCE), with a lesser percentage of trichloroethene (TCE) and vinyl chloride. PCE has been detected at aqueous concentrations as high as 170 mg/L, suggesting the presence of dense non-aqueous phase liquid (DNAPL). VOCs are present in the bedrock groundwater from 20 feet to more than 150 feet below ground surface.

The original source of the chlorinated VOCs is likely a former degreasing unit located in the northwestern portion of Building 40 (**Figure 1**). It is estimated that the release(s) occurred more than thirty years before present. The Hudson River is located approximately 200 feet to the east of Building 40. Broadway Street and a six-land interstate highway (Interstate 787) are located between Building 40 and the Hudson River. The affected portion of the bedrock aquifer is not used as a source of potable water.

Figure 1: Building 40 at the WVA



PHYSICAL SETTING

Geology

The major overburden unit consists of brown or dark gray silty sand with angular gravel. Overburden thickness in the vicinity of Building 40 ranges from approximately ten feet below ground surface (bgs) to the west of the building, to approximately 19 feet bgs to the east of the building at the WVA property boundary. A thin layer of weathered shale bedrock, typically less than two or three feet thick, is present beneath the alluvium.

The bedrock underlying the site is black, medium-hard laminated shale, showing some characteristics of minor metamorphism. This shale has been identified as part of the Snake Hill Formation. The bedrock surface generally slopes to the east from an elevation of approximately 25 feet above mean sea level (amsl) to the west of Building 40 to an elevation of approximately 19 feet amsl at the WVA property boundary. The primary features identified in the bedrock in the Building 40 area during the various investigations include bedding planes, fractures, and mineral inclusions. Bedding planes dip to the east (median direction of 94 degrees) with a median dip of 54 degrees from horizontal. The strike of the bedding planes is north-south. Fractures are present along bedding planes and at angles to bedding. Fracture orientations range from sub-horizontal to nearly vertical. Veins of calcite and pyrite are commonly present along fracture and bedding planes, particularly at depths greater than 100 feet.

Hydrogeology

Groundwater flow in the vicinity of Building 40 is primarily controlled by the degree of fracturing within the bedrock aquifer. Based on Arsenal-wide groundwater elevations measured during multiple events, the predominant direction of groundwater in the Building 40 area is to the southeast towards the Hudson River. Hydraulic heads in the Building 40 area are upward. This is expected given the proximity of the building to the regional discharge boundary at the Hudson River. Extensive hydrogeologic characterization studies were performed in the bedrock aquifer in the Building 40 area. These investigations are discussed in detail in the following sections.

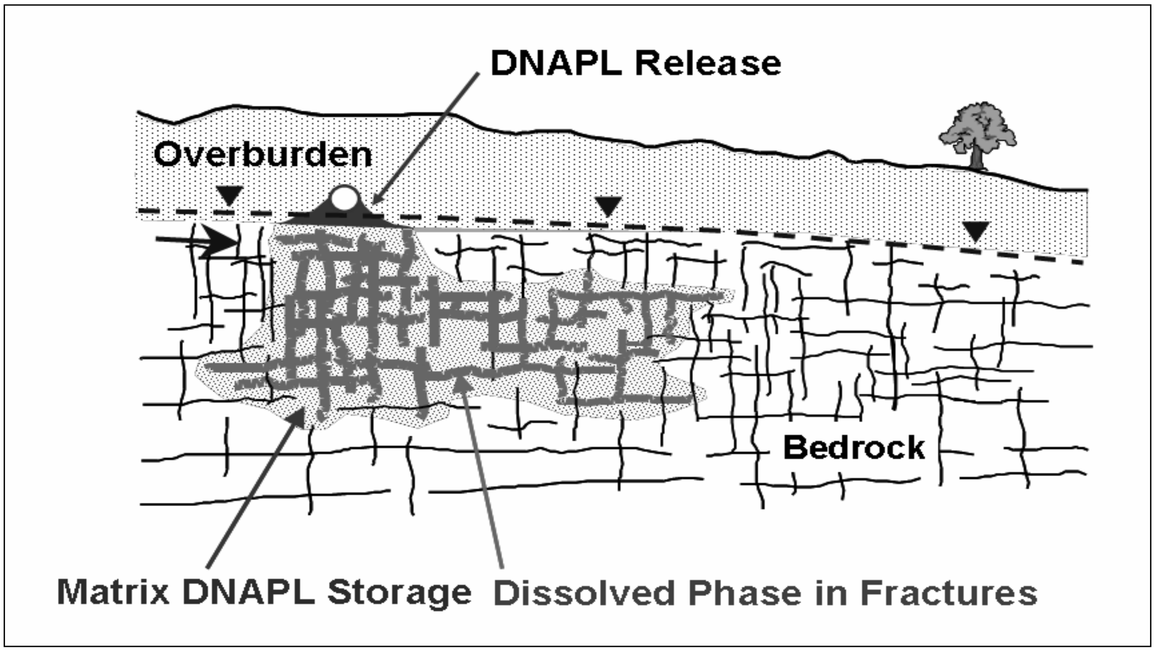
SITE CONCEPTUAL MODEL

The results of successive stages of site characterization have been compiled into an integrated site conceptual model (**see Figure 2**). This conceptualization is that VOCs are present in the bedrock aquifer in the Building 40 area. DNAPL, and dissolved-phase VOC concentrations indicating the potential presence of DNAPL, have been detected in the bedrock groundwater. Advective transport of the VOCs in the bedrock aquifer takes place through a well connected fracture network. The original source of the VOCs in the bedrock groundwater is presumed to be located in the northeastern portion of Building 40. Since significant VOC concentrations were not detected in the overburden soil in this area, it is possible that the release occurred through a subsurface storm sewer that was once connected to floor drains in this area of Building 40.

Although fractures provide the only pathway for advective transport of groundwater and VOCs through the bedrock aquifer, the ratio of the void space due to the presence of fractures to the bulk rock volume ("fracture porosity") is several orders of magnitude less than the matrix porosity of the rock itself – meaning that the capacity of the rock matrix to store VOCs is orders of magnitude greater than the storage capacity in the fractures. This matrix storage capacity creates a diffusive gradient by which VOCs present at high concentrations in the fractures can diffuse into the bedrock pore spaces. Thus, although DNAPL may still exist in some fractures, the majority of the DNAPL that was initially present in the fractures has likely dissipated due to dissolution and diffusive mass transfer to the rock matrix -- **causing nearly all the VOC mass to now reside in the rock matrix and not in the bedrock fractures**. Given the lack of any current surficial sources, it is presumed that the shale bedrock itself is the continuing source of the VOCs in the groundwater.

This site conceptualization indicates that the only truly effective remediation technologies for the fractured bedrock aquifer are those that will treat the VOC mass in the rock matrix in addition to treating the VOC mass in the fractures. Failure to treat the VOC mass in the matrix (i.e., the source area) will result in a continuous diffusive transfer of VOCs out of the bedrock into the groundwater in the fractures.

Figure 2. Site Conceptual Model



SITE CHARACTERIZATION SUMMARY

Site characterization activities in the Building 40 area were designed to provide the necessary information to confirm the conceptual model and to provide sufficient data for the analysis of corrective measures alternatives. This information included:

1. Horizontal and vertical extent of VOC contamination in the fractured bedrock groundwater and in the bedrock matrix.
2. Physical properties of the bedrock.
3. Location, size, and interconnectivity of bedrock fractures in the study area.
4. Transmissivity of the bedrock fractures and the associated VOC mass flux.

A summary of the site characterization techniques utilized for the project is provided in **Table 1**.

Table 1: Site Characterization Techniques

Characterization Technique	Purpose
Discrete Interval Packer Sampling	Delineate vertical and horizontal limits of VOC contamination in bedrock groundwater during drilling.
Rock Core Testing	Evaluate the degree of VOC matrix contamination and identify matrix diffusion parameters.
Geophysical Testing	Identify location and nature of bedrock fractures. Identify flow zones and evaluate transmissivity and hydraulic head.
Multi-level Monitoring Wells	Delineate vertical and horizontal limits of VOC contamination in the bedrock groundwater and monitor changes over time.

Discrete Interval Packer Sampling

Discrete interval packer sampling was conducted during drilling of monitoring wells to provide preliminary information on the degree of VOC groundwater contamination and the hydraulic properties of the bedrock aquifer. Information gathered during the sampling was used to determine monitoring well depths and to evaluate additional monitoring locations. Packer sampling was conducted at 20-foot intervals as each borehole was advanced into the bedrock. The isolated portion of each borehole was purged until three volumes had been removed. A groundwater sample was then collected for VOC analysis under a rapid turnaround time. Pumping rates and water levels in the isolated interval were monitored during purging to evaluate the relative hydraulic properties of each borehole interval. If an interval was pumped dry, the borehole was allowed to recharge, then pumped dry again, before groundwater samples were collected.

Rock Core Testing

Rock core testing was conducted to evaluate the physical properties of the rock matrix and the degree of VOC contamination in the matrix porewater. Continuous HQ-size bedrock cores were collected in five foot intervals from the competent bedrock surface to the final depth of the well from five monitoring well boreholes. These core samples were analyzed for physical properties and characterized for VOC matrix porewater contamination using techniques developed at the University of Waterloo (UW). Three types of samples were collected:

1. VOC samples, which were crushed and preserved in the field by placing in jars with methanol for extraction and later laboratory analysis;
2. Physical property samples, consisting of intact section of core that were analyzed for moisture content, porosity, bulk density, specific gravity, hydraulic conductivity, and organic carbon content; and
3. Matrix diffusion samples, consisting of intact sections of core designated for laboratory diffusion tests.

VOC samples were collected at fractures (i.e. one of the fracture faces) and bedding planes, at lithologic changes, and from matrix blocks between fractures. Sample lengths typically ranged from 0.1 to 0.4 feet of core, and averaged 0.2 feet. VOC samples were immediately wrapped in aluminum foil to minimize volatile losses, and were taken to an on-site field lab for crushing and processing. Prior to crushing, the outer rind of the core samples was chipped off to eliminate potential error from contact with the drilling fluids. Samples were then crushed with a hydraulic rock crusher using five stainless steel rock crushing cells, which typically allowed samples from one core run to be processed. Between samples, the cells were decontaminated using a four-part wash and rinse sequence. The crushed rock samples were then placed into sample jars containing a known amount of HPLC grade methanol (MeOH) to extract and preserve the VOC mass. Excluding duplicates, and using the total cored interval, the average sample spacing was about 1.2 feet.

In addition, five representative rock core samples were collected and sent to Golder Associates Ltd. (Golder) of Mississauga, Ontario, Canada for analysis of physical and hydrogeologic parameters. Matrix diffusion tests were also performed on the rock cores to evaluate the rock matrix diffusion coefficient for the bedrock in the Building 40 area. The average hydraulic conductivity of the shale bedrock matrix is approximately $1\text{x}10^{-7}$ feet per day (ft/d) indicating that, as expected, advective groundwater transport in the bedrock is entirely controlled by fractures. The average porosity of the shale is approximately 2.3 percent, as compared to a typical range of five percent to 25 percent for sedimentary rocks (shale and sandstone). This low porosity is likely a result of the low-grade metamorphism to which the rock has been exposed. The average matrix diffusion coefficient (D) of the shale was $7.5\text{x}10^{-7}$ cm^2/second.

Laboratory rock matrix VOC analyses were conducted after allowing sufficient time for the VOCs to completely extract into the methanol (approximately six weeks). An aliquot of methanol was injected directly into a gas chromatograph (GC) for separation and quantification using a microelectron capture detector (μ−ECD). The list of analytes quantified included TCE, PCE and the DCE isomers. The direct, on-column injection of methanol onto the gas chromatograph was tailored by UW for analysis of PCE, TCE and relevant breakdown products so that the resulting detection limits were very low (<0.1 ug/L in MeOH for TCE and PCE, and <10 ug/L in MeOH for the DCE isomers). These were converted to equivalent pore water concentrations using bulk density, porosity and sorption estimates, as well as rock sample and MeOH masses.

Geophysical Analysis

The United States Geological Survey (USGS) performed several geophysical tests during the installation and completion of the monitoring wells installed during the site characterization activities. Characterization techniques utilized by the USGS are summarized in **Table 2**. Detailed methods for the geophysical investigations performed by the USGS at the Building 40 area are discussed in a USGS Open File Report (Williams and Paillet, 2002).

Table 2: Geophysical Techniques

Characterization Technique	Purpose	Results Summary
Borehole-wall image logs (acoustic and optical televiewer)	Delineate distribution and orientation of fractures	79 fractures identified in 500 feet open hole in 8 wells and coreholes
Fluid and flowmeter logs (heat pulse flowmeter, electromagnetic flowmeter. Integrated analysis with borehole-wall image logs.	Distribution of fracture-flow zones intersected by the monitoring wells and coreholes.	14 flow zones consisting of one to several fractures were detected in the approximately 500 feet of open hole in the 8 wells and coreholes
Flowmeter model analysis (see Paillet, 2000)	Determine transmissivity and hydraulic head of flow zones	Calculated transmissivities and ambient hydraulic heads for identified flow zones.
Cross-hole flow tests (see Paillet, 1998)	Hydraulic connections between flow zones	Identified a major fracture feature oriented in north-south direction

The results of the USGS survey indicated the presence of numerous fracture features. In addition to these features, several other crosscutting fractures were identified. While the imaging data clearly showed the fractures present in each borehole, those data do not indicate the degree of interconnection of the fractures of if the fractures are transmissive. In order to address those data gaps, the USGS completed intra-and inter-borehole flowmeter and fluid temperature/resistivity testing. Each of these tests were completed under ambient and short-term injection or pumping conditions. During the injection/pumping conditions the flow rates varied from 1 to 6 gallons per minute. The results of the inter-borehole testing indicated the presence of approximately 14 transmissive flow zones, which consisted of single or very closely spaced sets of fractures. A major north-south trending fracture flow system was also identified during the testing. The transmissivity values calculated ranged from 0.1 to more than 250 square feet per day.

Multi-level Monitoring Wells

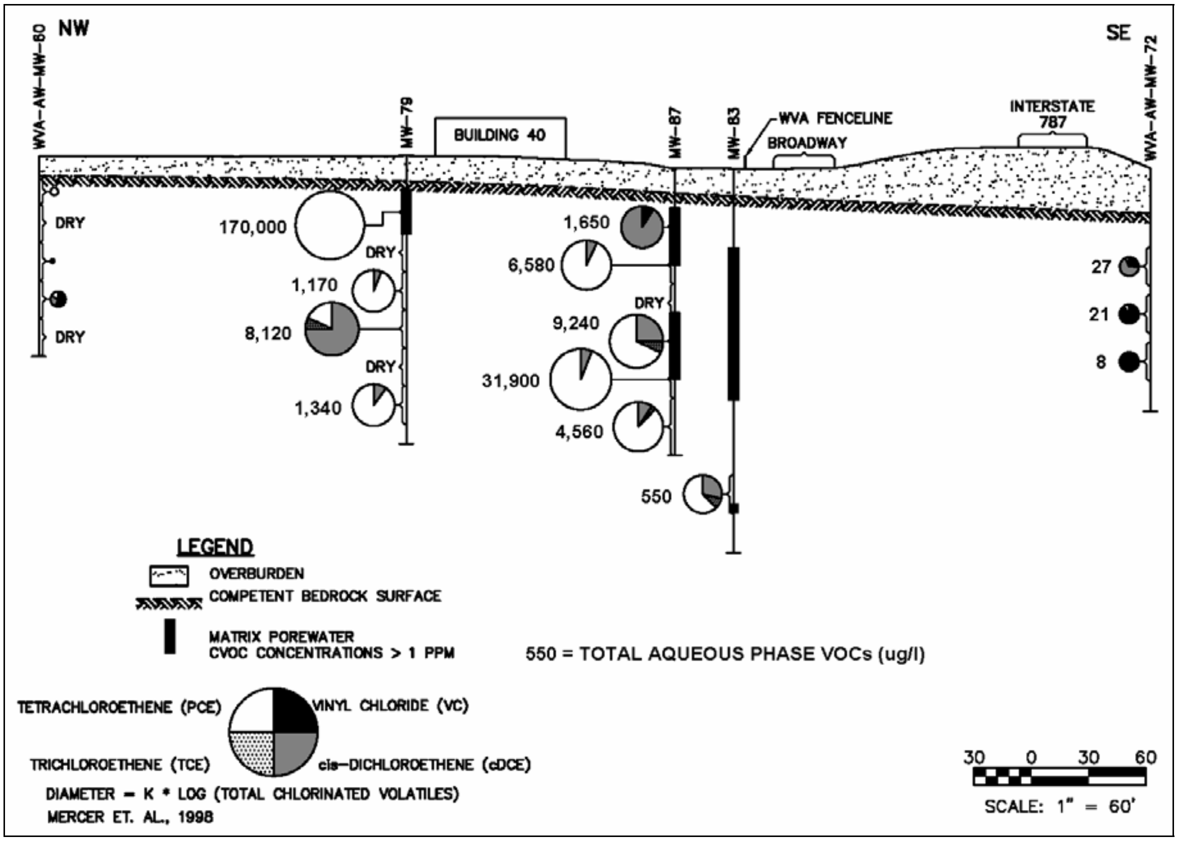
Nine monitoring wells were completed with multi-level monitoring systems to allow for the evaluation of VOC concentrations in groundwater with depth. These multi-level systems were also used to evaluate fracture interconnectivity and hydraulic head distribution during subsequent testing. Multi-level monitoring well placement was based on the results of the discrete interval packer testing and the USGS geophysical analysis. Seven of the wells were completed with Westbay MP38 Multi-Level Sampling Systems. The remaining two wells were equipped with the Solinst Continuous Multi-Channel Tubing (CMT$^{®}$) System.

SITE CHARACTERIZATION RESULTS

Groundwater

Figure 3 presents VOC concentrations in bedrock groundwater and in the bedrock matrix along the predominant flow direction of northwest to southeast. The data used to construct this figure was obtained from rock core analysis, multi-level monitoring well sampling results, packer testing results, and long-term monitoring results. As shown on these figures, the distribution of VOCs in the bedrock groundwater indicates a source in the northwestern portion of the building. This is supported by the fact that PCE was detected at a concentration of 170 milligrams per liter (mg/l) in the 21 to 41 foot bgs interval in monitoring well MW-79. This concentration is 85 percent of the aqueous solubility of PCE of 200 mg/l. The presence of PCE at this concentration near the bedrock surface indicates that monitoring well MW-79 is closer to the source than the wells to the east of Building 40. The rock matrix testing results also support this conclusion.

Figure 3: VOC Concentrations in Bedrock Groundwater and Matrix



The results of the rock core VOC analysis conducted by the University of Waterloo show that several rock core samples contained PCE at equivalent porewater concentrations approaching solubility. Figure 3 also includes information derived from rock core VOC analysis conducted by the University of Waterloo during monitoring well installation. These data indicate that, although elevated VOC concentrations were detected in groundwater samples collected below this depth, the majority of the VOC mass present in the subsurface is present in the 20 to 100 foot bgs interval. Representative rock core VOC profile from two of the boreholes in the central portion of the site are shown on **Figures 4 and 5**.

Figure 4: MW-87 Rock Core Profile

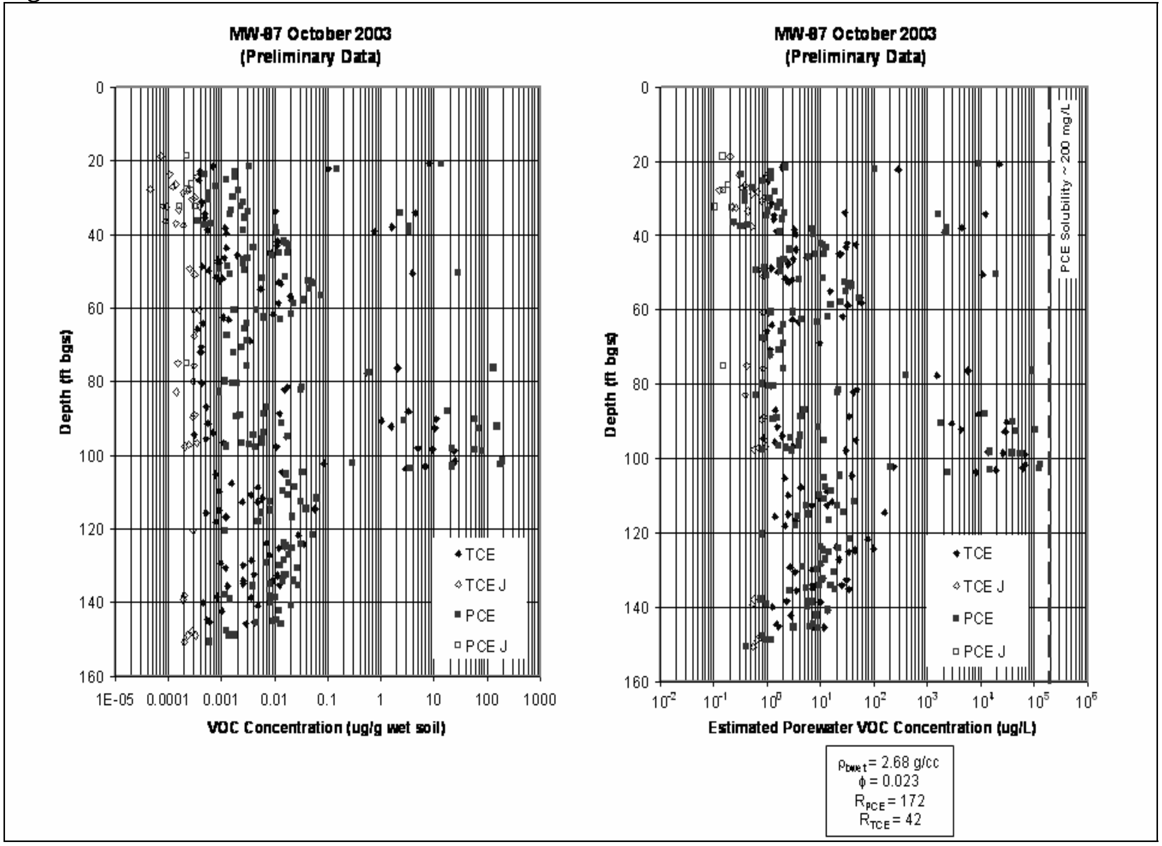
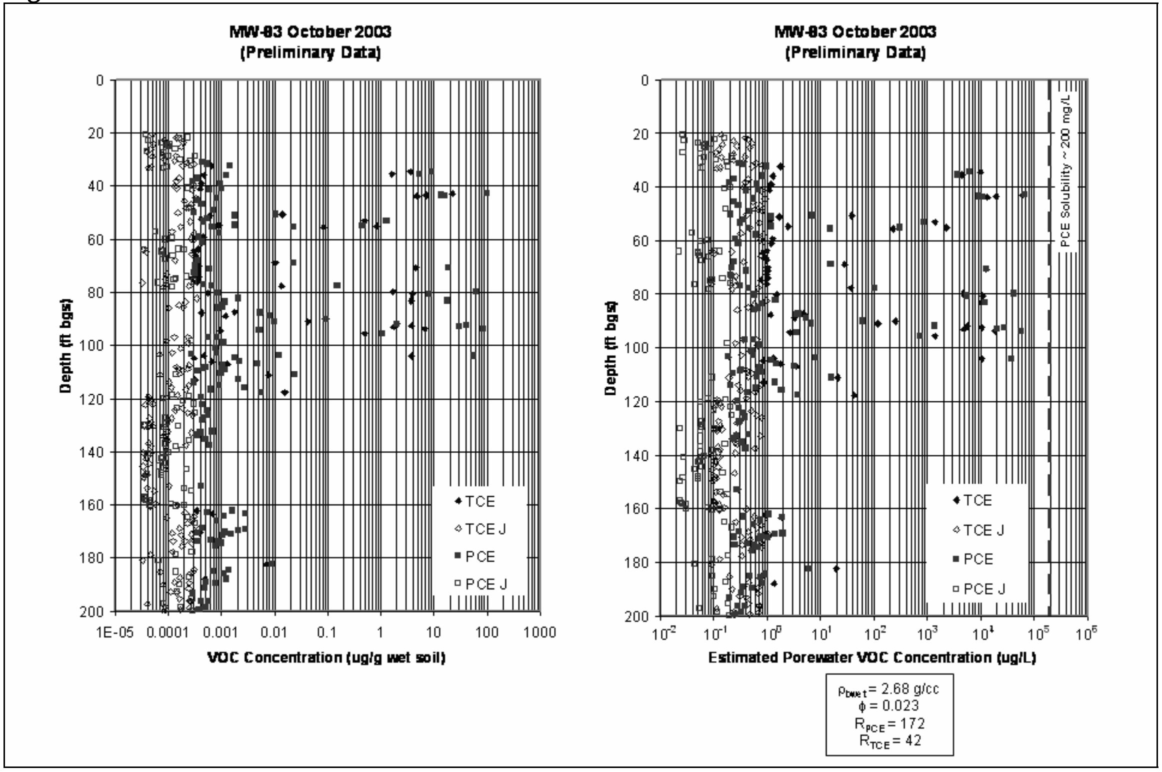


Figure 5: MW-83 Rock Core Profile



The characterization data support the conceptual model in that, although groundwater concentrations approaching solubility were detected in the bedrock fracture network, DNAPL was not present in any of the fractures intersected by the monitoring well borehole. At the same time, bedrock matrix porewater concentrations at and/or approaching solubility were detected in rock core samples collected in the same boreholes. Since the storage capacity of the rock matrix is orders of magnitude greater than that of the bedrock fractures, these data confirm that the majority of the VOC mass is entrained in the rock matrix.

TECHNICAL CHALLENGES

Until recently, the conventional view of fractured rock sites was that they are too complex to remediate. As such the most common remedial approach at fractured rock sites has been a containment strategy using groundwater extraction and treatment and/or monitored natural attenuation (USEPA, 2001). However, the presence of the VOCs in the bedrock matrix presents many technical and regulatory challenges when it comes to how to remediate the problem and how to define success. The only truly effective remediation technologies for the fractured bedrock aquifer are those that will treat the VOC mass in the rock matrix in addition to treating the VOCs in the groundwater.

Data collected during the site characterization showed that natural attenuation of the VOCs in the bedrock groundwater via reductive dechlorination is ongoing. However, natural attenuation, by itself, has not significantly reduced the concentration of VOCs in the bedrock groundwater or the mass of VOCs in the bedrock matrix. This is due to the fact that, based on rock core analytical data, little attenuation is occurring in the bedrock shale matrix. As such, VOCs are continually being added to the bedrock groundwater from the shale matrix (via a reverse diffusion gradient) as quickly as they are removed from the groundwater by natural attenuative processes. While these processes have served to reduce the mass and extent of VOCs in the bedrock groundwater to some degree, the rate at which they currently occur is extremely slow and would not result in a measurable decrease in contaminant mass or groundwater concentrations in the foreseeable future (i.e., greater than 100 years).

Similar to monitored natural attenuation, the use of containment technologies, while they would result in a reduction in groundwater VOC concentrations in the treatment area, would do little to reduce VOC mass in the shale bedrock matrix. As such, groundwater concentrations would be expected to rebound to near their pre-remediation concentrations upon shut down of the containment remedy since VOC source concentrations in the shale bedrock aquifer would be relatively unaffected by extraction of the groundwater. A recent USEPA study of 28 sites at which groundwater containment remedies have been implemented found that, while 21 of 25 sites have met plume containment goals, only 2 of 28 sites have met their aquifer restoration goals (USEPA, 1999). These data indicate that, while containment remedies are viable remedies to eliminate potential exposure pathways, they are not effective source treatment technologies and are not suitable at sites where the source of the contamination, in this case, the bedrock matrix, has not been treated.

The need to treat the rock matrix left in-situ chemical oxidation as the only potentially applicable technology for the remediation of the site. The primary advantages of in-situ chemical oxidation technologies are their relatively low cost and short treatment times. However, the use of fast-reacting chemical oxidants, such as hydrogen peroxide, at the site, would have an effect similar to that of groundwater extraction: removal of VOCs from the bedrock fractures, but little treatment of the VOC mass in shale bedrock matrix source. However, the use of permanganate as an oxidant was considered to be potentially applicable to the site for the following reasons:

- Permanganate is chemically stable in the subsurface and has been shown to remain active in the subsurface for months after injection.
- Since unreacted potassium permanganate in solution is relatively stable, it can diffuse into media with low permeabilities (i.e., porous rock) over time, destroying VOC mass in the matrix.
- Application of excess permanganate will allow for diffusion of permanganate into the matrix at the same time as contamination is diffusing out of the matrix (i.e., the reactants will be moving towards each other) speeding the treatment of VOC in the rock matrix.

IN-SITU CHEMICAL OXIDATION PILOT STUDY

A pilot study (Pilot Study) was conducted in the Building 40 area to evaluate the degree to which the VOCs in the bedrock groundwater and, more importantly, the bedrock matrix, could be treated using potassium permanganate (KMnO4). The objectives of the pilot study were as follows:

- Evaluate whether potassium permanganate could be effectively delivered and distributed through the bedrock treatment area;
- Confirm that VOCs in the bedrock groundwater could be oxidized by the permanganate;
- Assess the persistence of the permanganate in the subsurface; and
- Estimate the degree and rate of diffusion of permanganate into the shale bedrock matrix.

A summary of the Pilot Study is provided below.

Permanganate Distribution and VOC Destruction

Single-point injections of potassium permanganate in the affected area resulted in distribution of permanganate both laterally and vertically throughout the bedrock aquifer in the Pilot Study area. These data indicate that the fracture network in the affected area is well connected and that distribution of permanganate is possible through a limited number of injection points. VOC concentrations in the bedrock groundwater were dramatically reduced in monitoring zones where permanganate was present. Based on rebound monitoring conducted after the completion of injections, permanganate residence time in the fractures was approximately two to three months (using the 2.5 percent solution of KMnO4 injected during the pilot study).

Permanganate Matrix Invasion

Laboratory testing was conducted to measure the rate of permanganate invasion into the shale bedrock. This was accomplished by submerging rock core samples in $KMnO_4$ solution for a period of time during which diffusion into the core would take place. Preliminary analysis indicates that the permanganate has successfully invaded the shale bedrock matrix, but that the invasion distances into the shale during the six month test period were less than 100 microns. Based on the data, it is expected that further invasion will occur over time.

Conclusions

The results of the in-situ chemical oxidation pilot study support the following conclusions:

1. Permanganate can be distributed both vertically and horizontally throughout the treatment area using a small number of injection points.
2. Permanganate reduced the concentration of VOCs in the bedrock groundwater and was able to diffuse into the bedrock matrix.

REGULATORY CHALLENGES

The site characterization showed the majority of the VOC mass in the bedrock aquifer in the vicinity of Building 40 is entrained in the shale bedrock matrix pore spaces – not in the bedrock fractures. This confirmed the conceptual model and proved that remediation of the site will require treatment of the rock matrix. The characterization also showed that the bedrock fracture network is interconnected and that the majority of the groundwater flow is present in a north-south trending fracture complex. The pilot study demonstrated that KMnO4 can be distributed both vertically and horizontally throughout the treatment area using a small number of injection points.

However, it has been recognized by all involved parties that, although USEPA Maximum Contaminant Limits (MCLs) or equivalent state standards are the ultimate objective, it is unlikely that MCLs will be achieved in a reasonable timeframe by any remediation technology in a matrix-dominated fractured bedrock environment such as that at Building 40 of the Watervliet Arsenal. For example, removal of more than 90 percent of the contaminant source mass, if possible, would likely still result in the exceedance of MCLs at the boundary monitoring wells. This leaves mass-based metrics (i.e., reduction of source mass and/or reduction in flux) as the only viable measures by which a remedial program in fractured bedrock could be evaluated. The concept of mass-based metrics is being debated throughout the environmental community. Unfortunately, at present, most state regulatory are still constrained by concentration-based standards that must be used as the ultimate remedial goals.

Although state groundwater standards are still the required corrective action objectives, at the Watervliet Arsenal, mass-based metrics have been incorporated into a performance strategy for a full-scale corrective measure utilizing in-situ chemical oxidation with permanganate that is acceptable to both the regulatory community and the Arsenal. The full-scale corrective measure focuses on source remediation through the treatment of the shale bedrock matrix as well as treatment of the VOCs in the bedrock groundwater. The corrective measure involves the injection of sodium permanganate ($NaMnO4$) into the bedrock aquifer using a phased injection process. Injection of the permanganate will be performed for a period of five years, after which five years of groundwater monitoring will be conducted to evaluate long-term groundwater concentrations and the degree to which natural attenuation further decreases groundwater concentrations. Between injections, permanganate will be allowed to passively enter the system via the placement of solid permanganate pellets into the injection wells.

Groundwater monitoring will be the tool for measuring the performance criteria. A compliance monitoring array consisting of six bedrock monitoring wells located along the eastern WVA property boundary will be installed and completed with a three-zone, multi-level monitoring system. Achievement of the corrective action performance criteria will be based on sampling results from the 18 monitoring zones within the six property boundary monitoring wells. Mass-based metrics that will be utilized during include integrated mass flux testing to evaluate mass flux under known flow conditions over the entire affected area, and property boundary mass flux monitoring utilizing multi-level monitoring wells.

Integrated Mass Flux Testing

Integrated mass flux testing will be conducted to evaluate permanganate treatment efficacy with respect to mass destruction. The testing will consist of two pumping tests in one of the injection wells located adjacent to the eastern side of Building 40. One test will be conducted prior to the first sodium permanganate injection event. The remaining test will be conducted at the end of the treatment period, after the permanganate has dissipated from the boundary monitoring wells. Each test will consist of a 24-hour limited-flow pumping test designed to extract water from the treatment area to evaluate contaminant flux under known conditions (i.e., constant pumping rate). Each test will be conducted until hydraulic heads in the treatment area have stabilized (if greater than 24 hours); however, based on previous experience, it is expected that stabilization of hydraulic heads will occur well before the end of the 24-hour test period. Time-series VOC sampling will be conducted during each test to evaluate integrated (average) contaminant concentrations in the treatment area. Results of the two tests will be used to evaluate permanganate treatment efficacy through the comparison of integrated mass flux values derived from the test analyses.

Property Boundary Monitoring

The property boundary monitoring will focus the remedial metrics on the zone within each boundary well that transmits the greatest VOC mass flux across the property boundary. This is desired since, although less transmissive zones may contain relatively higher aqueous concentrations of VOCs, the VOC mass flux from these zones is insignificant compared to the flux in the more transmissive zones that may contain somewhat lower aqueous VOC concentrations. Mass flux in the lower flux zones will also be monitored during remedial activities to track overall remedial efficacy.

CONCLUSIONS

The use of mass-based metrics in a remedial strategy has allowed the Watervliet Arsenal to proceed with a remedial measure that focuses on source removal rather than merely containment or monitoring. Based on laboratory testing and preliminary numerical modeling, it is estimated that implementation of these measures will remove more than 40 percent of the VOC mass present in the bedrock matrix. It is expected that removal of this source material will result in a "win-win" situation for the Arsenal, the regulatory community, and the environment through eventual site closure after post-remedial monitored natural attenuation.

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