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Remedial investigations of karst aquifers: a case study at former Marietta Air Force Station, Lancaster County, Pennsylvania

Marc Randrianarivelo[1] · Wanfang Zhou[2] · Michael Barsa[3]

Abstract A phased multi-disciplinary approach was used to investigate potential environmental impact on the overburden aquifer and karst (bedrock) aquifer from the historic use of a suspected fire training pit at the former Marietta Air Force Station in Lancaster County, Pennsylvania. Investigation techniques have included direct push technology, real-time sample analysis via use of a mobile laboratory, earth resistivity imaging/induced polarization, geophysical borehole logging, packer testing, installation of one multi-port well with five sampling ports set in the karst aquifer, installation of multiple conventional monitoring wells, and completion of multiple rounds of groundwater sampling and data analysis. Both the vertical and lateral extents of groundwater contamination by chlorinated volatile organic compounds were delineated in the overburden and karst aquifer. The pathway-focused human health risk assessment has indicated that groundwater remediation is required to meet the federal and state health standards for volatile organic compounds. Based on the hydrogeological conditions and the nature and extent of the delineated contamination, plumes in both the overburden and karst aquifers, chemical oxidation (in the karst aquifer), and enhanced bioremediation (in the overburden aquifer) have been selected as the preferred alternatives for groundwater remediation, with monitored natural attenuation included as a common component of both alternatives.

Keywords Karst aquifers · Groundwater contamination · Nature and extent · Fate and transport · Risk assessment

Introduction

Groundwater contamination in karst terranes is both persistent and widespread because approximately 20% of the earth's land surface is underlain by karst and karst aquifers are vulnerable to contamination. Karst has been considered the most difficult medium for remediation, especially when the contaminants are related to chlorinated volatile organic compounds (CVOCs) (National Research Council 1994; Malcolm Pirnie 2002; Deeb et al. 2011). Remedial investigation is an essential step toward groundwater restoration by characterizing the karst hydrogeologic conditions, defining the nature and extent of groundwater contamination, and assessing risks to human health and the environment. Knowledge of the fate and transport of contaminants in a karst setting is key to the development of a defensible conceptual site model that emphasizes pathways between the contaminated groundwater and receptors (USEPA 2002; Li et al. 2014; Newland 2015).

Figure 1 summarizes the fate and transport mechanisms in the context of a two-layer model consisting of the karst formation and the overlying soil. The surface of the bedrock is highly solutioned and exhibits a cutter and pinnacle surface with residuum and alluvium infilling between pinnacles. The water table is in the bedrock. Above the water table, the vadose zone is characterized by the

✉ Wanfang Zhou
wanfang.zhou@ertcorp.com; zhou_wanfang@yahoo.com

Marc Randrianarivelo
marc.randrianarivelo@usace.army.mil

Michael Barsa
michael.barsa@ertcorp.com

[1] Engineering Division, USACE Baltimore District, 10 South Howard Street, Baltimore, MD 21201, USA

[2] ERT, Inc, 2890 University Square, Suite 2A, Huntsville, AL 35816, USA

[3] ERT, Inc, 14401 Sweitzer Lane, Suite 300, Laurel, MD 20707, USA
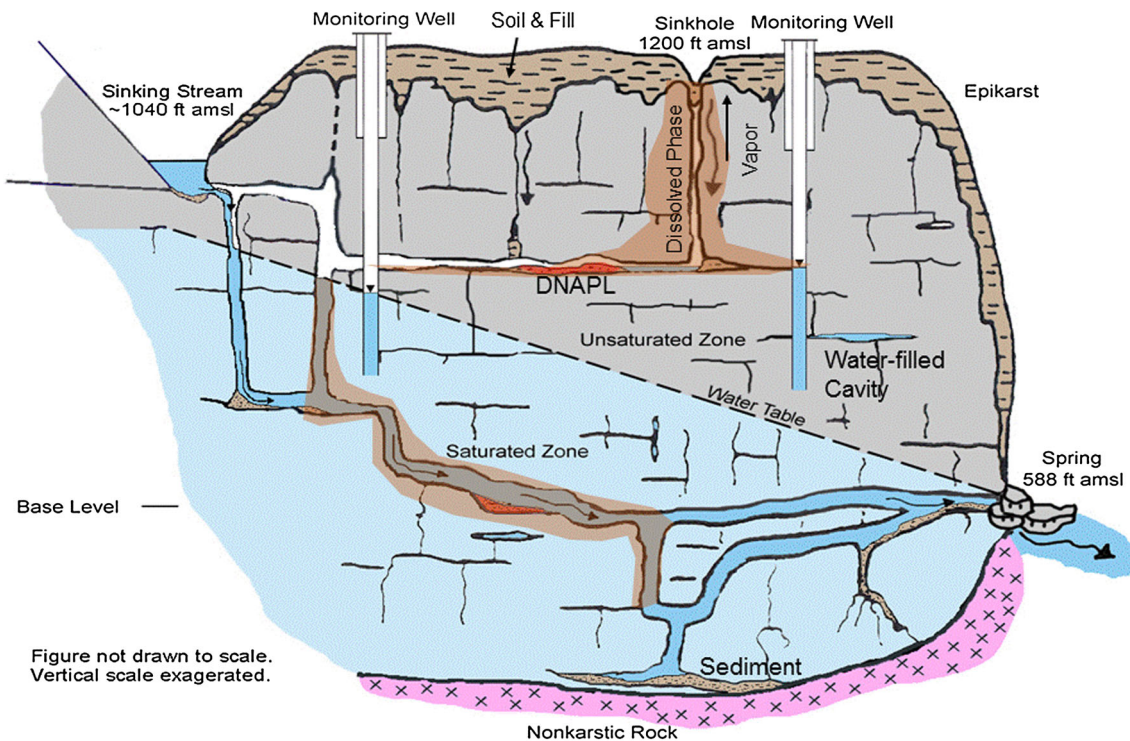
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Fig. 1 Generalized fate and transport processes of chlorinated hydrocarbons in a two-layer karst model

presence of both air and water in the pore spaces and is also termed the unsaturated zone. Below the water table, the geologic materials are shaded blue, indicating saturation of the primary matrix and secondary fracture and/or solution-enhanced porosity of bedrock in the saturated zone. Water-filled voids are present within the unsaturated zone and solution-enhanced cavities in the bedrock are partially filled with sediment. A release of CVOCs occurred at a sinkhole. Contaminants are present in non-aqueous, dissolved, sorbed, and vapor phases.

Dense non-aqueous phase liquid transport

CVOCs can be present as dense non-aqueous phase liquids (DNAPLs), which are, by definition, immiscible in water and exhibit a higher specific gravity than water. These DNAPLs include the halogenated solvents and any daughter products, e.g., trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-DCE), and vinyl chloride (VC). DNAPLs are not present in every contaminated site, and their presence is often inferred from empirical evidences. Factors affecting the transport of a DNAPL release are highly dependent on the geologic characteristics at the location of the release. DNAPL released at the sinkhole would seep vertically downward within the unsaturated zone. Separate phase liquid can also move horizontally depending on the vertical variation in water content of the soil and its texture and structure. As the DNAPL release

approaches the impermeable matrix rock, it begins to spread laterally and forms a zone of continuous DNAPL. Such an accumulation is commonly referred to as a "pool" or as a DNAPL accumulation zone (Zhou 2001).

The principal control over the lateral migration of DNAPL is the fracture network. The DNAPL can be directed deeper into the karstified aquifer via vertical fractures. Vertical movement of DNAPL in open voids is essentially unimpeded by capillary forces due to the size of the opening. The principal drivers of that downward transport are the DNAPL's greater specific gravity than the water that fills the voids and its immiscibility in water. By contrast, movement of DNAPL into and through granular residuum is strongly controlled by the size and geometry of pores and pore throats in that material (Kueper and McWhorter 1991). DNAPL accumulation zones in open voids may contain literal "pools" of separate phase liquid, while the DNAPL mass per unit volume of accumulation zones in residuum is capped by the porosity of the residuum itself.

Another DNAPL transport mode unique to karst aquifers is the bulk transport of DNAPL in water flowing at high velocities through open voids (Loop and White 2001). Bulk transport can occur in open (sediment free) portions of solution cavities during elevated flow conditions when water flows over a DNAPL pool and entrains droplets of free product. Likewise, open-channel flow may entrain sediment particles together with DNAPL that may be present due to DNAPL penetration into the porous residuum or sediments that occupy the bottom of the channel.

Aqueous phase transport

Once a DNAPL release has reached equilibrium in the subsurface such that, with the exception of entrainment in high-velocity open-channel flow, separate phase transport is no longer relevant, the mass of DNAPL is gradually diminished by two mechanisms: dissolution in pore water in the vadose zone and groundwater in the saturated zone and evaporation to soil vapor in the vadose zone. Dissolution of the DNAPL in pore water and groundwater will create an aqueous (dissolved) phase of the CVOC that typically will extend along the entire DNAPL migration pathway(s). In the area directly impacted by a DNAPL release, aqueous concentrations near the interface of water and DNAPL will approach the solubility of the CVOCs (Zhou et al. 1997).

Once DNAPL has come into contact with pore water and gravitational water in the vadose zone and with groundwater in the saturated zone, the dissolved phase of the CVOCs develops by direct dissolution from the DNAPL. Essentially, there are three principal mechanisms for aqueous phase transport of dissolved contaminants: advective transport, dispersion, and diffusion.

Aqueous phase advective transport

Aqueous phase advective transport is the process that generates a plume of dissolved CVOCs extending from the source area to the point of discharge to surface water or an extraction well. At any given location beneath the site there are two natural sources of water. These are recharge derived from infiltration of precipitation at the ground surface and upgradient groundwater flow. Within the vadose zone, infiltration moves downward as gravitational pore water drains freely to the water table. In a DNAPL source zone, this gravitational water can dissolve soluble compounds directly from separate phase liquid associated with a DNAPL source in the vadose zone and transport that dissolved mass downward into the saturated zone. Upgradient groundwater flow entering a given area can either be clean if it has not already been impacted by a source or it can contain dissolved CVOCs either from contacting an upgradient DNAPL source in the saturated zone or as a result of mixing with contaminated recharge also at some upgradient location. Recharge into the aquifer at the site not only provides the driving force for the groundwater flow and advective transport of the contaminants, but also dilutes the concentration of the contaminants over time, especially after the source removal. As shown in Fig. 1, there is also potential for vertical advection of groundwater downward into and through the very permeable fractured and solution-enhanced zones in the carbonate bedrock.

Aqueous phase dispersion

Hydrodynamic dispersion describes the process of horizontal and vertical aqueous mixing of a solute being advected resulting in a blended zone between adjacent aqueous solutions or the displacement of aqueous solutions. Many studies indicate that longitudinal dispersivity is scale dependent. Anderson (1984) and Fetter (1999) show a graph originally published by Lallemand-Barres and Peaudecerf indicating that field-scale longitudinal dispervity is about one tenth of the characteristics length scale. Neuman (1990) extended the work of Lallemand-Barres and Peaudecerf and derived a universal scaling rule. Neuman related longitudinal dispersivity to scales of investigation within a variety of porous media under diverse conditions of groundwater flow and solute transport. Gelhar et al. (1992) published several scatter diagrams, similar to those of Neuman (1990), comparing longitudinal dispersivity to observation scale. At a given scale, the longitudinal dispersivity values ranged across 2–3 orders of magnitude. Gelhar et al. (1992) also point out that vertical dispersivities are typically an order of magnitude smaller than transverse dispersivities and that transverse dispersivities are typically an order of magnitude less than longitudinal dispersivities.

Aqueous phase diffusion

In addition to horizontal and vertical groundwater flow, dissolved CVOCs can be transported by aqueous diffusion into groundwater contained in pores bounded by individual soil particles in the residuum and into the matrix porosity of the bedrock in response to a chemical concentration gradient. This can occur in both the DNAPL source area and the plume emanating from it. Studies of DNAPL fate at the University of Waterloo (Plett 2006; Kennel 2008) have shown that DNAPL held in bedrock fractures by capillary forces may, depending on the characteristics of the surrounding rock matrix, diffuse over time into the pore water contained in the rock. This process, otherwise termed as "matrix diffusion", can result in the complete elimination of the separate phase liquid from individual fractures. Where this occurs, the mass of CVOCs previously present as DNAPL in the fractures is then present as aqueous phase, high concentration dissolved CVOC in pore water within the rock matrix adjacent to the fracture. Since many DNAPL releases have remained unremediated for several decades, there can be substantial transfer of mass from the separate phase to the aqueous phase by aqueous diffusion, with the latter becoming the repository of a significant percentage of the mass originally released to the environment.

At any given DNAPL site, it is difficult to approximate the mass of DNAPL that has been released to the environment. It is especially difficult to assess the extent to which matrix diffusion has diminished the percentage of the mass remaining as separate phase liquid. What is certain is that once separate phase DNAPL comes into contact with a geologic medium that exhibits interconnected pores containing clean pore water, a chemical concentration gradient exists that will result in the diffusion of mass from the dissolving DNAPL into the adjacent pore water.

Within the plume area generated by advective transport in fractures and solution conduits, matrix diffusion will also occur in response to the substantial chemical gradient between the open conduits in the carbonate aquifer, within which advective transport of dissolved CVOCs preferentially occurs, to the adjacent solid rock, residuum or sediment, all of which typically exhibit lower hydraulic conductivity than the open fractures and, therefore, do not represent the principal pathways for plume migration. As a result, groundwater flowing in fractures and containing dissolved CVOCs is in direct contact with groundwater contained in pores of the adjacent rock matrix, residuum, and sediment, thus creating a chemical diffusion gradient from the water in the fracture to the water in these pores.

In contrast with the high concentrations expected to be produced in the matrix pore water in the source area, the concentrations in pore water adjacent to fractures conveying dissolved CVOCs away from the source area will typically diminish with distance from the source area as the concentrations in the plume diminish downgradient. If the concentrations of CVOCs in fracture flow decline for any reason, such as dilution or inception of groundwater remediation, there will be a reversal of the diffusion gradients from the rock matrix back out to the fracture flow.

Vapor phase transport processes

The development of the vapor phase results from two mechanisms: direct evaporation of CVOCs from residual DNAPL in the vadose zone and volatilization of CVOCs from groundwater at the water table (USEPA 2015). Evaporation from residual DNAPL in the vadose zone is controlled by the vapor pressure of each individual compound. In the immediate vicinity of the DNAPL source, this process should produce vapor phase concentrations that are near each substance's saturation concentration in air. By contrast, volatilization of VOCs from the water table will be controlled by the concentration of each compound in the groundwater and its Henry's Law constant. In general, direct evaporation from residual DNAPL will be expected to produce higher vapor phase concentrations than volatilization from groundwater. This is due in

large part to the relatively low solubility of these substances in groundwater.

Once in the vapor phase, the principal transport mechanism is vapor diffusion. Transport by this means will occur primarily in response to the chemical concentration gradient between comparatively high vapor concentrations in the soil air versus negligible concentrations of these substances in atmospheric air. Vapor diffusion will, therefore, be primarily upwards to the ground surface from DNAPL source zones in the vadose zone and dissolved CVOCs at the water table. The result is diffusive losses of VOC mass to the atmosphere.

In addition to vapor diffusion, vapor transport may occur as a result of advection. This mechanism may occur across the concrete slab of buildings over a source or plume in response to a difference in air pressure across the slab. Advective transport of vapors may also result from "barometric pumping,", whereby changes in atmospheric pressure result in a pressure gradient from the soil air to the atmospheric air resulting in the movement of some volume of the soil air containing CVOC vapors as opposed to just the molecules of VOCs as is the case for diffusion.

Reductive dechlorination of organic compounds

Under reducing anaerobic conditions, the principal chlorinated solvents found in the groundwater at the site can undergo biotic reductive degradation and be transformed into less chlorinated compounds. These reactions are mediated by natural bacteria. In most aquifers, the rate of each transformation step slows as reductive dechlorination proceeds so that the concentrations of the later transformation products including *cis*-DCE or VC can appear to increase relative to the concentrations of the parent solvents. In some cases, the increase in the relative concentrations of the transformation products occurs with increasing distance from the source zone and may occur also with increasing time at a given location as biogeochemical conditions may become more favorable with time.

Most frequently, these transformations occur in source areas where the CVOCs were co-disposed with other organic compounds such as petroleum products. The biotic degradation of these other substances typically creates the sulfate-reducing or methanogenic geochemical conditions necessary for reductive dechlorination of CVOCs to occur. However, once the assemblage of parent compounds and daughter products is transported away from the source area, frequently the conditions within the plume area are no longer conducive to reductive dechlorination and the transformation process ceases. Progressive changes in the ratio of the parent compounds to the daughter products do

not continue to occur with increasing distance downgradient.

The reduction of organic compounds is the result of electron transfers between a donor and an acceptor, which occurs within an aerobic reducing environment. These chemical reactions are generally defined as biologically mediated redox reactions (USEPA 1998) and are typically facilitated by naturally occurring microorganism populations. Microbial degradation is most effective on low to moderate organic constituent concentrations (Environmental Security Technology Certification Program 2011). Normally, microorganism populations capable of effectively degrading organic compounds flourish in a pH range of between 5 and 9 (USEPA 1998). Carbon dioxide is a byproduct of the oxidation of organic compounds, which produces carbonic acid in groundwater, effectively reducing the groundwater pH. The oxygenation potential of a groundwater environment is considered the redox potential, and in aerobic environments the redox potential is typically above 50 mV and a DO concentration of greater than 0.8 mg/L.

Microbial degradation of organic compounds typically results in an aerobic environment transforming into an anaerobic environment as electron acceptors are systematically depleted. With the introduction of organic compounds, oxygen favored by microbial populations is depleted. Upon transitioning to an anaerobic environment, microbial populations begin to sequentially utilize other components for respiration including nitrate, manganese oxide, ferrous oxide, and sulfate.

Typical organic compound plumes exhibit aerobic degradation along the outer limits of the plume and anaerobic degradation within the center of the plume. It is not uncommon for contaminant plumes to have differing zones of reduction that are supported by specific components. Anaerobic degradation may be assisted by the occurrence compounds such as ferrous iron and manganese oxide.

Natural attenuation is generally confirmed via a series of evidence supporting the overall degradation process. Primary evidence for natural attenuation is evaluated by the accumulation of historical analytical data. Geochemical data can be used as a secondary form of evidence to support natural attenuation. Geochemical data include groundwater quality parameters such as redox, pH, and dissolved oxygen. A pH level between 5 and 9 is considered to be favorable for supporting aerobic degradation of organic compounds. Anaerobic bacteria cannot typically survive if the dissolved oxygen is above 0.5 mg/L.

Other fate processes that result in the loss of CVOCs include degradation, temporary storage by sorption, or transformation in both the saturated and unsaturated zones.

Secondary sourcing

Several of the processes discussed above are reversible (Zhou 2001). These include the following:

- aqueous diffusion into pore water within the carbonate rock matrix, the residuum, and the sediments that partially or completely fill voids in the carbonate rock both in DNAPL source areas and CVOC plume areas;
- partitioning from soil vapor or DNAPL to pore water in the vadose zone; and.
- sorption onto the organic carbon fraction of formation solids and metal oxide coatings in both the saturated and unsaturated zone.

All of these processes effectively work to store mass in the solid phase of the soil and bedrock. The extent to which any of these processes stores mass and maintains that mass in storage relies on either the continuing presence of DNAPL as a primary source of aqueous and vapor contamination or simply the presence of groundwater with concentrations of the constituents as high or higher than those that originally determined the levels of sorbed and diffused mass. Once groundwater concentrations have declined appreciably, these processes will be reversed, at which point the associated fate and transport mechanisms are termed reverse diffusion and desorption.

As groundwater and soil vapor concentrations continue to decline, the processes of desorption and reverse diffusion will return previously stored mass to the flowing groundwater in the saturated zone and gravitational water in the vadose zone. Because this mass is stored in the solid phase and available to re-enter the aqueous phase, it constitutes a secondary source of contamination to groundwater that may retard the rate at which groundwater concentrations can decline over time. As such, these processes are typically the cause of the tailing effect often observed in groundwater monitoring data at CVOC remediation sites.

A case study is presented in this paper to illustrate that understanding of these fate and transport processes help determine the most appropriate technical approaches for remedial investigations in karst settings.

Hydrogeologic setting of the former Marietta Air Force Station

The former Marietta Air Force Station, located topographically above the north bank of the Susquehanna River, approximately 20 miles southeast of Harrisburg, Pennsylvania, consists of 387 acres just west of the Borough of Marietta in Lancaster County (Fig. 2). The area is

bounded to the north by Pennsylvania Route 441, to the south by railroad tracks running parallel to the Susquehanna River, to the west by an unnamed stream, and to the east by the Borough of Marietta. The predominant current and foreseen future land use is industrial. Surrounding land use is a mix of industrial, agricultural, and residential. The topography is relatively flat, sloping gently to the south, with elevations at approximately 290 feet above mean sea level (msl). The base flow water surface of the Susquehanna River is approximately 240 feet above msl.

Geologically, the area is underlain by the alluvial overburden deposits, which consist of interbedded layers of clays, silts, sands and gravels, and Antietam, Vintage, and Ledger Formations of the Cambrian system (Berg and Christine 1981). The Antietam Formation is predominately light-gray quartzitic sandstone with calcareous cement. The Vintage and Ledger Formations are composed of gray dolomite, with the Ledger being typically coarser-grained than the Vintage. The Vintage Formation is known locally to be host to well-developed karst features, in the form of caves and sinkholes. Groundwater at the site exists within the overburden and dolomite bedrock, including the karst features. Groundwater flows along surface topography toward the Susquehanna River.

CVOCs, primarily trichloroethene (TCE), *cis*-1,2-dichloroethylene (*cis*-DCE), and vinyl chloride (VC), have been detected in groundwater at concentrations above the respective US Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCL) and Pennsylvania Department of Environmental Protection (PADEP) Act 2 Medium-Specific Concentration (MSC) for Used Residential Aquifers (with total dissolved solids [TDS] of less than 2500

milligrams per liter [mg/L]). The respective USEPA MCLs/PADEP MSCs for TCE, *cis*-DCE, and VC are 5, 70, and 2 micrograms per liter (µg/L) (PADEP 2002, 2011). Additionally, lead has also been detected in site groundwater in concentrations above the USEPA MCL (15 µg/L) and/or PADEP MSC (5 µg/L). The contamination source area has been determined to be associated with a suspected fire training pit (SFTP) area in the northeastern portion of the site (USACE 2005; Foothill Engineering Consultants Inc. 2000; Langan 2006). Figure 2 shows the site location and layout, as well as the location of the suspected fire training pit and groundwater monitoring wells that have been installed throughout the course of the remedial investigation to investigate potential impacts to the groundwater within the overburden aquifer and karst aquifer from operations involving the SFTP. Historically, fire training pits were constructed as shallow depressions in the ground and either unlined or utilized a thin layer of clay as a liner. For training purposes, these pits were filled with water, fuel, and/or waste (such as chlorinated solvents) and then ignited. Installation personnel would then extinguish the fire as a practice exercise.

Previous investigations led to contaminated soils in the suspected fire training pit being removed in 2006; however, contamination was also determined to exist within the groundwater. The dimensions of the suspected fire training pit were found to be approximately 55 feet long by 45 feet wide by 14 feet deep (Langan 2006). The objectives of the remedial investigation were to determine the hydrogeologic properties of the aquifers, delineate the lateral and vertical extent of groundwater contamination, understand the fate and transport of the primary contaminants, and evaluate human health risks.
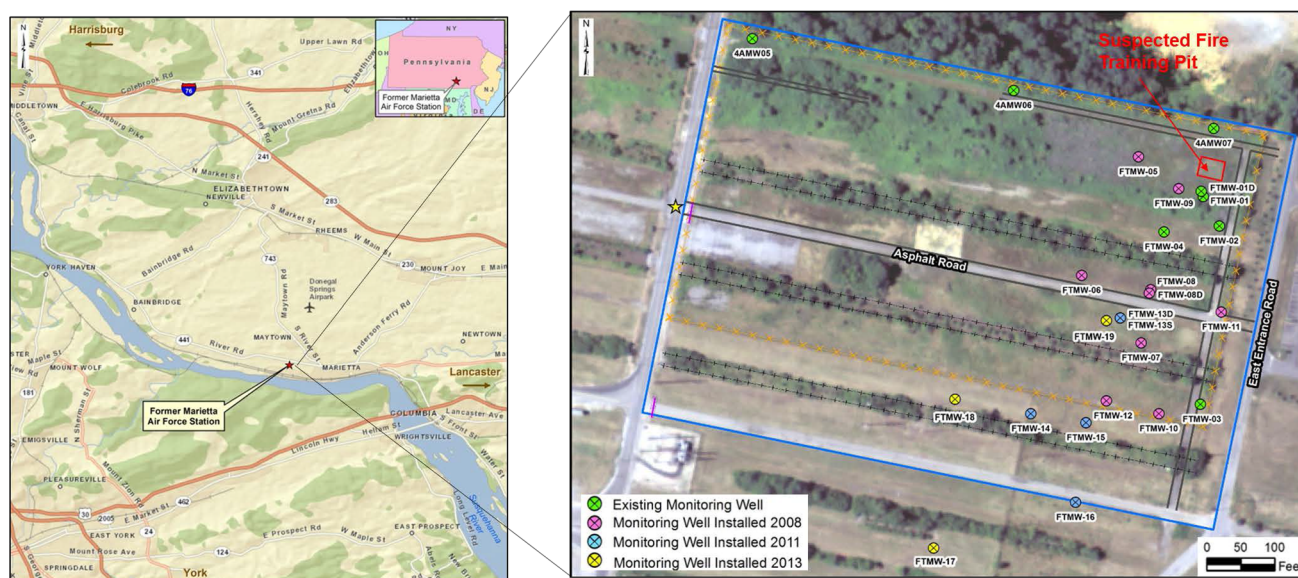

Fig. 2 Site location and layout

Investigation approach

Because of the presence of karst-type lithologies beneath the site, data requirements for the hydrogeologic characterization were expected to be more intensive and difficult to obtain than those for aquifers in most other types of hydrogeologic settings (Teutsch and Sauter 1991). Karst is defined by an unusual landscape developed on rocks that are predominantly weathered and eroded by being dissolved, rather than being worn away by rivers, waves, or glaciers. The presence of karst usually is indicated by the occurrence of distinctive physiographic features that develop as a result of the dissolution of soluble bedrock such as limestone or dolomite. In well-developed karst, these physiographic features may include sinkholes, sinking streams, caves, and springs. The hydrologic characteristics associated with the presence of karst also are distinctive and generally include (1) internal drainage of surface runoff through sinkholes; (2) underground diversion or partial subsurface piracy of surface streams (sinking streams and losing streams); (3) three-zone vertical structure consisting of overburden, epikarst, and bedrock (Williams 1983); (4) triple-porosity (pores, fractures, and conduits) karst aquifer; and (5) discharge of subsurface water from conduits by way of one or more large perennial springs. Karst aquifers are heterogeneous and have hydraulic properties that are scale dependent and temporally variable.

Wherever karst features are present, it is necessary to anticipate the presence of a flow system that cannot be completely characterized using conventional hydrogeologic methods such as potentiometric mapping, hydraulic tests of observation wells, or by numerical modeling (Cherry et al. 2007). The acquisition of these data typically requires a phased and multi-disciplinary study approach that includes using more specialized investigation methods such as water-tracing tests, digital geophysical mapping, packer testing, and multi-level groundwater monitoring (ERT 2015). Figure 3 shows the various multi-disciplinary techniques used in the technical approach of each phase of the remedial investigation of the site.

Hydrogeological characterization

Irregular bedrock surface

Figure 4 shows a two-layer hydrogeological cross-section from north to south. Overburden materials have been observed to be composed of silt and clay. Some overburden materials likely have formed as a result of the weathering of residual material from carbonate bedrock. The depth to bedrock has been observed to vary dramatically over a short distance, ranging from 13 to 129 feet below ground surface (bgs) (approximately 280–160 feet amsl). FTMW-15 and FTMW-1D appear to be located at bedrock cutters with overburden greater than 100 feet in thickness. These features may be buried in sinkholes that were entrenched into the surrounding bedrock in the geological past. The bedrock elevation at FTMW-12, approximately 60 feet north of FTMW-15, is 116 feet higher than that at FTMW-15, resulting in a steep slope of 2–1. These bedrock lows create direct contacts laterally between the bedrock formation and the overburden. A cavity filled with mud and silt was encountered at FTMW-16 from 59 to 61.5 feet bgs. Approximately, five drums of mud were generated while drilling through this cavity. Competent rock was observed as being present above the cavity (43 feet). Low water productivity was exhibited within this 43 feet of competent rock. At FTMW-10, bedrock was encountered twice with a 9 feet sand and silt layer between 26 and 35 feet bgs. This sand and silt layer may be interpreted as being in a solution void. At FTMW-19, which was ultimately constructed as a 5-port well, voids were encountered, with clay and sand fill, between 78 and 79 feet bgs.

Unstable boreholes

An unstable borehole was encountered at bedrock well FTMW-14. Rounded 0.5–2-in. quartz and dolomite cobbles were observed during the borehole advancement. These rounded gravels and cobbles together with evidence of a productive zone also observed at FTMW-14 suggest that FTMW-14 is likely located in a groundwater preferential flow path. Discrete fracture zones were observed at FTMW-13. Borehole logging at this well indicates irregular borehole walls and water flow occurred through three discrete fracture zones from 19 to 31 feet bgs, 31 to 52 feet bgs, and 52 to 71 feet bgs. The packer test data suggest that pumping at one zone caused drawdowns at other zones. Another unstable borehole was encountered at bedrock well FTMW-19. As the borehole was being advanced, the 5-in. casing had to be pushed in the borehole into 90 feet bgs to avoid falling fragments of fractured dolomite between 75 and 85 feet bgs. Borehole logging conducted at FTMW-19 indicated irregular borehole walls and groundwater flow occurring through five discrete fracture zones from 96.4 to 106.4 feet bgs, 124.9 to 130.9 feet bgs, 137.9 to 143.9 feet bgs, 188.9 to 193.9 feet bgs, and 226.9 to 231.9 feet bgs (these discrete fracture zones would guide placement of ports during construction of the multi-port well). The fractures at different zones appeared to be hydraulically connected.
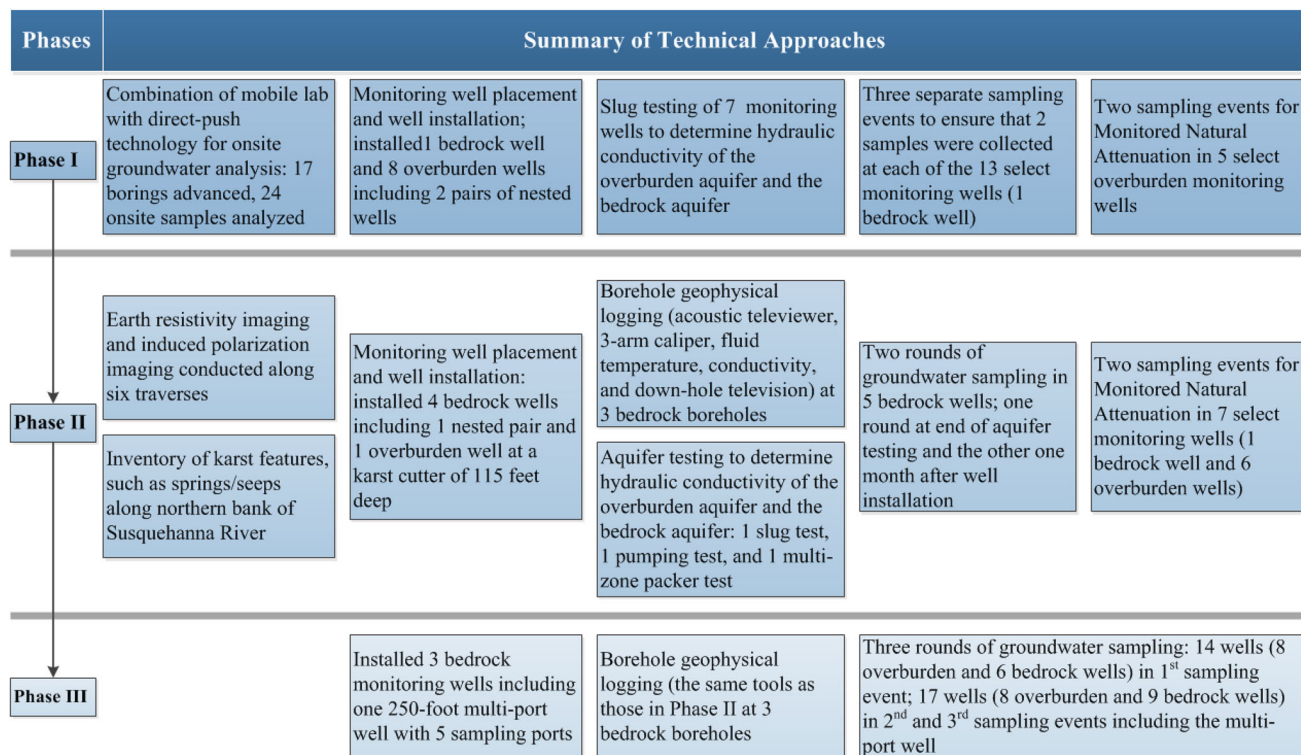
Phases	Summary of Technical Approaches				
Phase I	Combination of mobile lab with direct-push technology for onsite groundwater analysis: 17 borings advanced, 24 onsite samples analyzed	Monitoring well placement and well installation; installed1 bedrock well and 8 overburden wells including 2 pairs of nested wells	Slug testing of 7 monitoring wells to determine hydraulic conductivity of the overburden aquifer and the bedrock aquifer	Three separate sampling events to ensure that 2 samples were collected at each of the 13 select monitoring wells (1 bedrock well)	Two sampling events for Monitored Natural Attenuation in 5 select overburden monitoring wells
Phase II	Earth resistivity imaging and induced polarization imaging conducted along six traverses / Inventory of karst features, such as springs/seeps along northern bank of Susquehanna River	Monitoring well placement and well installation: installed 4 bedrock wells including 1 nested pair and 1 overburden well at a karst cutter of 115 feet deep	Borehole geophysical logging (acoustic televiewer, 3-arm caliper, fluid temperature, conductivity, and down-hole television) at 3 bedrock boreholes / Aquifer testing to determine hydraulic conductivity of the overburden aquifer and the bedrock aquifer: 1 slug test, 1 pumping test, and 1 multi-zone packer test	Two rounds of groundwater sampling in 5 bedrock wells; one round at end of aquifer testing and the other one month after well installation	Two sampling events for Monitored Natural Attenuation in 7 select monitoring wells (1 bedrock well and 6 overburden wells)
Phase III		Installed 3 bedrock monitoring wells including one 250-foot multi-port well with 5 sampling ports	Borehole geophysical logging (the same tools as those in Phase II at 3 bedrock boreholes	Three rounds of groundwater sampling: 14 wells (8 overburden and 6 bedrock wells) in 1st sampling event; 17 wells (8 overburden and 9 bedrock wells) in 2nd and 3rd sampling events including the multi-port well	

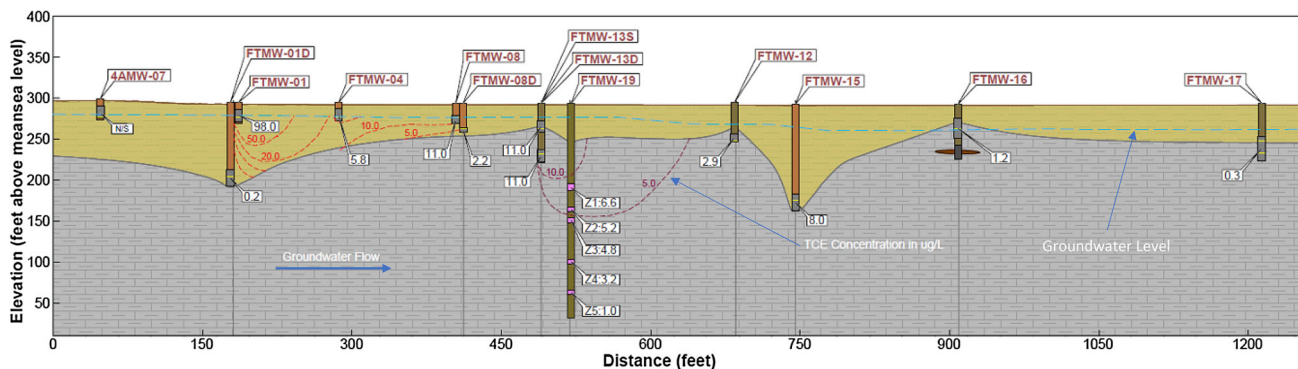Fig. 3 Summary of technical approaches used in the multiple-phased remedial investigation

Fig. 4 Two-layer hydrogeological cross section (data collected in November 2013)

Large variation in aquifer properties

The specific capacity of the karst aquifer was found to vary from 0.24 to 18.55 gallons per minute per foot. FTMW-16 has been shown to exhibit the lowest specific capacity, while FTMW-14 has been shown to exhibit the highest specific capacity. At FTMW-13, the top zone has been shown to exhibit the highest specific capacity, while the middle zone has the lowest capacity. Comparing the recovery percentage after purging at the five zones of FTMW-19, the top zone exhibits the highest specific capacity, and the bottom zone exhibits the lowest specific capacity.

The calculated hydraulic conductivity varies over three orders of magnitude with an average of 17.43 feet/day. The formation intercepted by FTMW-16 has very low hydraulic conductivity even though a clay-filled cavity was encountered. The borehole could not produce enough water for a meaningful packer test. The calculated hydraulic conductivity is 0.09 feet/day, which may be greater than the actual value. At FTMW-14, however, it was determined that either a paleochannel or a conduit may be present. The formation was found to be highly conductive with a calculated hydraulic conductivity of 79.9 feet/day. The hydraulic conductivity values at FTMW-13 indicate that the formation is heterogeneous in the vertical profile. The

top zone was found to be the most conductive zone, while the middle zone was found to be the least conductive zone. Purging data at the five zones of FTMW-19 were shown to exhibit a similar trend with the greatest hydraulic conductivity at the top zone, and hydraulic conductivity decreasing with depth.

Groundwater flow

Data collected at the site indicate that there is hydraulic connection between the overburden and the bedrock formations. Confined and unconfined conditions coexist in both the overburden aquifer and the karst aquifer. No hydrological barriers were observed at any of the boreholes that may function to separate the groundwater flow in the overburden and the bedrock formation. The groundwater levels measured in both overburden and bedrock wells show a relatively uniform gradient across the site, indicating good hydraulic connection between overburden and bedrock. The average groundwater table gradient is approximately 0.015, flowing southward to the Susquehanna River. Because of the pinnacle-and-cutter bedrock surface, the hydraulic connection is expected to be significantly enhanced at bedrock lows.

Vertical gradients at the site have been determined by measuring groundwater levels in paired or clustered wells that are open to different depths. Well pairs at the site [FTMW-01 (shallow), FTMW-01D (deep), FTMW-08 (shallow), FTMW-08D (deep), FTMW-13S (shallow), and FTMW-13D (deep)] were utilized to measure the vertical gradient. Vertical hydraulic gradients are present in both overburden wells and bedrock wells. Hydraulic heads measured at FTMW-01 and FTMW-01D were found to demonstrate consistently higher groundwater elevations at FTMW-01. The hydraulic head measurements recorded at FTMW-08 and FTMW-08D, a separate pair of overburden monitoring wells, were found to not exhibit a similar consistency as in FTMW-01 and FTMW-01D. The hydraulic head measured in October 2008 and December 2008 indicated that the groundwater table at FTMW-08 was lower than the groundwater table at FTMW-08D, which provided indication of an upward flow. Hydraulic head measured after 2008 demonstrated that the groundwater table at FTMW-08 was higher than the groundwater table at FTMW-08D, which provided indication of a downward flow.

Alternatively, at the nested bedrock wells FTMW-13S and FTMW-13D, the hydraulic head measured in 2012 and 2013 indicated that the groundwater table at FTMW-13S is lower than the groundwater table at FTMW-13D, which provided indication of an upward flow. Data suggest that the downward flow pattern is the dominant flow pattern in the groundwater at the northern part of the site. At the center of the site, the flow may either be downward or upward. This downward flow may have facilitated the transport of the constituents of potential concerns (COPCs) to deeper portions of the overburden and laterally to the bedrock formation.

At FTMW-19, the groundwater elevation level of five zones measured in October 2013 and November 2013 indicated that the groundwater table was highest in Zone 1 and gradually decreased to the lowest levels in Zone 5. This change in hydraulic head at FTMW-19 is also indicative of a downward groundwater flow.

As groundwater flows towards the Susquehanna River, the upward flow becomes dominant at the southern part of the site. This variation in vertical gradient suggests that the Susquehanna River is the discharge point of groundwater at the site. However, no springs or seeps were observed during a field reconnaissance effort conducted along the northern bank of the Susquehanna River.

Extent of contamination

The extent of contamination is associated with the COPCs (TCE, *cis*-DCE, and VC), as determined from sampling events. While the extents of *cis*-DCE and VC were determined as part of the remedial investigation, only the extent of TCE is discussed in this paper based on the most recent data collected in November 2013. Figures 5 and 6 show the lateral extent of TCE plume in the overburden and bedrock, respectively.

Extent of contamination in the overburden

As shown in Fig. 5, two higher concentration zones within the overall TCE plume were observed to be present in the overburden aquifer. The larger zone has an elongated shape with the highest concentration being 98 micrograms/liter (µg/L) at FTMW-01 in the vicinity of the former SFTP (the suspected contaminant source area). This zone was observed to have a limited extent in the northwest–southeast direction, approximately 100 feet between FTMW-06 and FTMW-10. The smaller zone was found to be located around FTMW-15; the presence of this zone may indicate interaction between contaminants and exchanges between the karst aquifer and overburden aquifer at the location of the cutter.

The great variation of the overburden thickness was found to result in a wide range of depths in monitoring intervals. The vertical extent could not be defined by a single continuous contour line. Figure 3 shows the vertical profile of the TCE distribution. The deepest monitoring interval in the overburden is at FTMW-15 from 108 to 118 feet bgs. The fact that TCE was detected in a
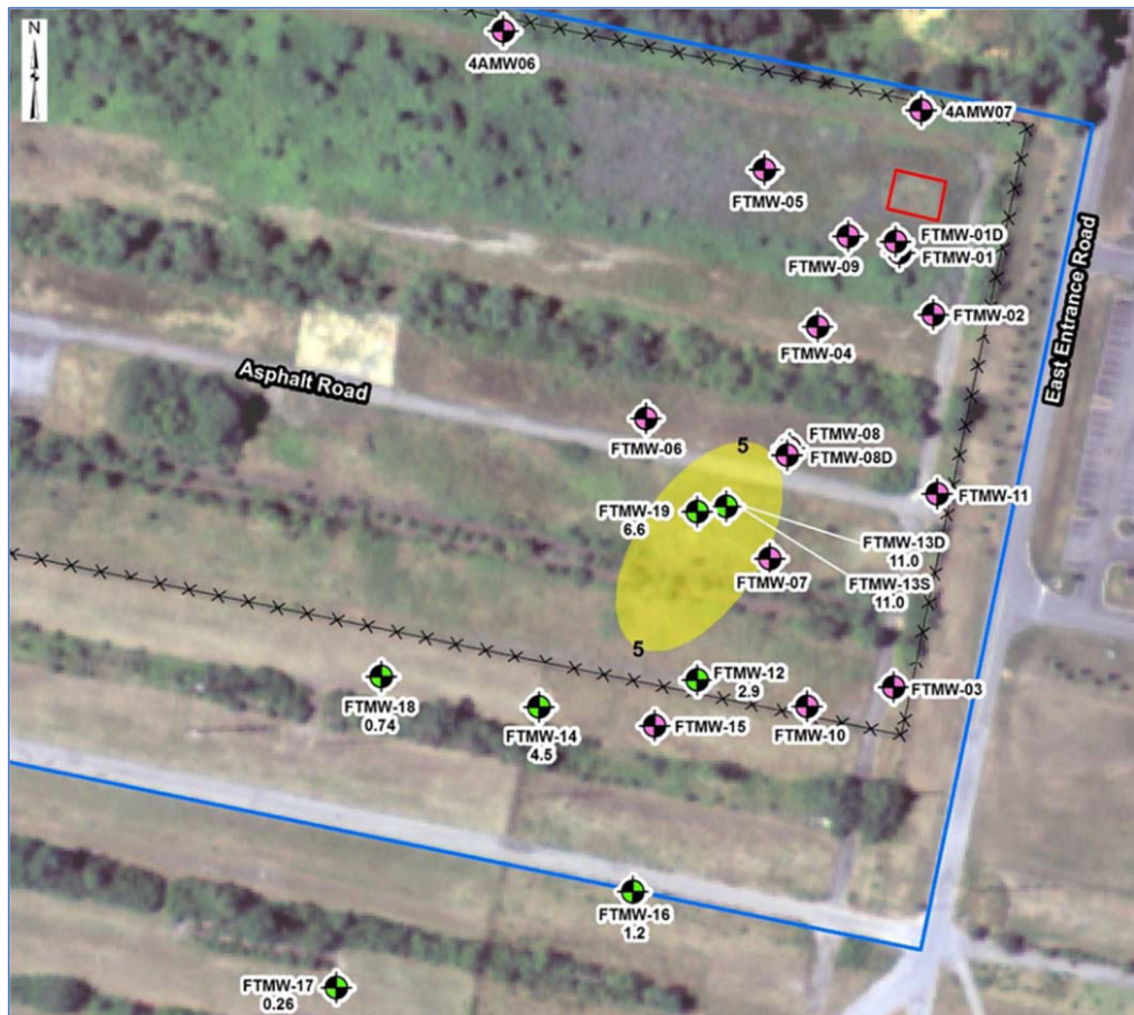
Fig. 5 Lateral extent of TCE plume in overburden (samples collected in November 2013)

concentration of 8 µg/L suggests that the vertical extent of TCE contamination at FTMW-15 represents the vertical extent of the entire overburden aquifer, and that the total depth is deeper than 118 feet bgs, most likely to the top of bedrock.

As shown in Fig. 6, the vertical extent of the contamination plume was also evaluated by comparing the laboratory results from two pairs of monitoring wells, namely FTMW-01/FTMW-01D and FTMW-08/FTMW-08D. FTMW-01 was screened at a level above 22.8 feet bgs, while FTMW-01D was screened between 79.6 and 99.6 feet bgs. The concentration of TCE was found to be significantly lower at FTMW-01D than that at FTMW-01, indicating a significant decrease in contamination at depth. The TCE data from November 2013 at FTMW-08 and FTMW-08D, however, do not necessarily agree with the findings at FTMW-01 and FTMW-01D. FTMW-08 was screened from 13 to 23 feet bgs, while FTMW-08D was screened from 28 to 33 feet bgs. In general, the

concentrations of TCE decrease from FTMW-08 to FTMW-08D, while the concentrations of *cis*-DCE and VC increase. Therefore, it could be surmised that vertical contamination extended beyond the bottom of FTMW-08D to the top of the bedrock formation.

Extent of contamination in the bedrock formation

The November 2013 laboratory results for samples at FTMW-13D and FTMW-13S show the same TCE concentration of 11 µg/L at both depths. Zone 1 of FTMW-19 showed a TCE concentration of 6.6 µg/L. These data were the only observed concentrations of TCE in November 2013 above screening criteria for TCE in the karst aquifer. Laterally, the TCE plume in the karst aquifer was determined to extend in an oval shape approximately 100 feet from the FTMW-13S/FTMW-13D area southwest, along the pattern of groundwater flow, towards FTMW-14 and FTMW-18. The lateral extent of the TCE plume was

Fig. 6 Lateral extent of TCE plume in bedrock (samples collected in November 2013)

determined to be bounded by observed concentrations in sentinel wells that fell below the screening criteria of 5 µg/L. The observed TCE concentration at FTMW-14 was 4.5 µg/L, and the observed TCE concentration at FTMW-18 was 0.74 µg/L. To the southeast, the observed TCE concentration at FTMW-12 was 2.9 µg/L, and the observed TCE concentration at FTMW-16 was 1.2 µg/L.

The vertical extent of TCE contamination in the bedrock is then represented by the lowest concentration observed in any port of FTMW-19. Zone 2 of FTMW-19 had an observed TCE concentration of 5.2 µg/L (slightly above screening criteria), compared to Zone 3, which had an observed TCE concentration of 4.8 µg/L (below screening criteria). The vertical extent of contamination in the karst aquifer is between the terminus of Zone 2 in FTMW-19 at a depth of 130.9 feet bgs and the top of Zone 3 at depth of 137.9 feet bgs. Graphical representation of the vertical extent of the TCE plume is depicted in Fig. 4.

Pathway focused risk assessment

Figure 7 presents a summary of the human health risk assessment (HHRA) results. The HHRA evaluated potential cumulative risks for the resident (adult and child), construction worker, and commercial worker exposure to groundwater. The resident (adult and child) and the commercial worker were evaluated for ingestion of, dermal contact with, and inhalation of VOCs in groundwater. Noncarcinogenic hazards for the resident child, resident adult, and commercial worker are above 1.0. cis-DCE, TCE, and VC were found to have chemical-specific hazard quotients (HQs) greater than 1. In addition, the liver, kidney, and immunological system were found to have all hazard indices (HIs) greater than 1. Incremental lifetime carcinogenic risks for the resident (adult and child combined) and the commercial worker were found to be above the USEPA and PADEP upper end of the risk threshold of 10^{-6}–10^{-4}.

Source	Pathway	Receptor	Risk Assessment	
			Carcinogenic Risks	**Non-carcinogenic Risks**
Groundwater in overburden and bedrock; COPCs –TCE VC, cis-DCE, lead	☐ Ingestion ☐ Dermal Contact ☐ Inhalation ☐ Cumulative	Child, Resident	$= 1.3 \times 10^{-3}$ $= 1.8 \times 10^{-4}$ $= $ n/a $= 1.5 \times 10^{-3}$	$= 25$ $= 5.4$ $= $ n/a $= 30$
	☐ Ingestion ☐ Dermal Contact ☐ Inhalation ☐ Cumulative	Adult, Resident	$= 8.0 \times 10^{-4}$ $= 1.2 \times 10^{-4}$ $= 2.3 \times 10^{-4}$ $= 1.2 \times 10^{-3}$	$= 11$ $= 2.3$ $= 23$ $= 36$
	☐ Ingestion ☐ Dermal Contact ☐ Inhalation ☐ Total Risk Across All Media and All Exposure Routes ☐ Total Risk Across Groundwater ☐ Total Hazard Index Across All Media and All Exposure Routes (Child) ☐ Total Hazard Index Across All Media and All Exposure Routes (Adult)	Adult and Child Combined	$= 2.1 \times 10^{-3}$ $= 3.0 \times 10^{-4}$ $= 2.3 \times 10^{-4}$ $= 2.6 \times 10^{-3}$ $= 3 \times 10^{-3}$ $= $ n/a $= $ n/a	$= $ n/a $= $ n/a $= $ n/a $= $ n/a $= $ n/a $= 30$ $= 36$
	☐ Ingestion ☐ Dermal Contact ☐ Inhalation ☐ Cumulative	Construction Worker	$= 7.0 \times 10^{-8}$ $= 3.0 \times 10^{-7}$ $= 1.0 \times 10^{-13}$ $= 1.0 \times 10^{-6}$	$= 0.04$ $= 0.2$ $= 0.000006$ $= 0.2$
	☐ Ingestion ☐ Dermal Contact ☐ Inhalation ☐ Cumulative	Commercial Worker	$= 2.4 \times 10^{-4}$ $= 6.6 \times 10^{-6}$ $= $ n/a $= 2.4 \times 10^{-4}$	$= 3.8$ $= 0.2$ $= $ n/a $= 4$

Fig. 7 Summary of pathway-focused risk assessment

TCE and VC were found to have carcinogenic risks above 10^{-4}. Therefore, concerns were determined to exist for use of groundwater as a tap water source. In addition, the resident adult was evaluated for potential concerns for VOC vapor intrusion from groundwater to indoor air. Based on the USEPA Johnson and Ettinger model (USEPA 2004) and vapor intrusion screening levels (USEPA 2015), volatilization of COPCs in groundwater into site buildings may be a potential concern. TCE was found to have a non-cancer HQ greater than 1 as well.

The construction worker was evaluated for incidental ingestion of, dermal contact with, and inhalation of VOCs from groundwater while in a trench. Results for the construction worker exposure to groundwater are below the risk thresholds set forth by USEPA and PADEP. Lead in groundwater was evaluated through the use of the Integrated Exposure Uptake Biokinetic (IEUBK) model (USEPA 2002). Calculations from the modeling concluded that lead in groundwater does not constitute a health concern.

Cost-effective remediation approach

Aquifer remediation is warranted at sites where risks exceed the acceptable levels. The objectives of aquifer remediation are to (1) prevent exposure to groundwater contamination in concentrations above acceptable risk levels (health protection); (2) prevent or minimize further migration of the contaminant plume (plume containment); (3) prevent or minimize further migration of contaminants from source materials to groundwater (source control); and (4) return the groundwater to its expected beneficial use, wherever practicable (aquifer restoration).

Figure 8 shows the general decision framework of selecting the most appropriate remediation methods in karst aquifers. In general, source materials represent the highest concentration of contaminants in the environment. Remedies aimed at removing these materials from subsurface environments generally offer the greatest value in terms of amount of contaminant addressed per unit of expenditure. As a consequence, source control measures

may be a cost-effective step in most groundwater restoration programs. Pathway elimination is another useful approach for groundwater remediation in karst. Although using an alternative water supply source does not address the contaminated groundwater, it eliminates the receptors' exposure to the groundwater. Treating impacted groundwater is probably the most researched topic and many technologies are available for karst aquifers. Selection of the most appropriate methods must take site-specific conditions into consideration because each karst aquifer is unique. Technical impracticability is considered only as a last resort. A regulatory waiver can be granted only when other options have been evaluated and proved to be impractical. Of the four remediation options, managing impacted groundwater was determined to be the strategy most applicable to the former Marietta Air Force Station site.

Figure 9 presents specific techniques for each remediation option and their challenges. Technologies in the

category of managing impacted groundwater include pump and treat, permeable reactive barrier, enhanced chemical oxidation and/or bioremediation, and monitoring of natural attenuation.

Table 1 presents a summary of the primary active groundwater remediation techniques used at 71 karst CERCLA sites with records of decision in files (Lipson and White 2014; http://www.epa.gov/superfunds/sites/rods). The most commonly used techniques consist of monitored natural attenuation, pump and treat, and/or in situ treatment. Based on the hydrogeological conditions and the delineated extents of COPCs in the overburden and karst bedrock formations, chemical oxidation in the karst aquifer and enhanced bioremediation in the overburden aquifer are considered to be viable alternatives for the groundwater remediation at the Marietta site, with monitored natural attenuation and land use control as shared components of both techniques.
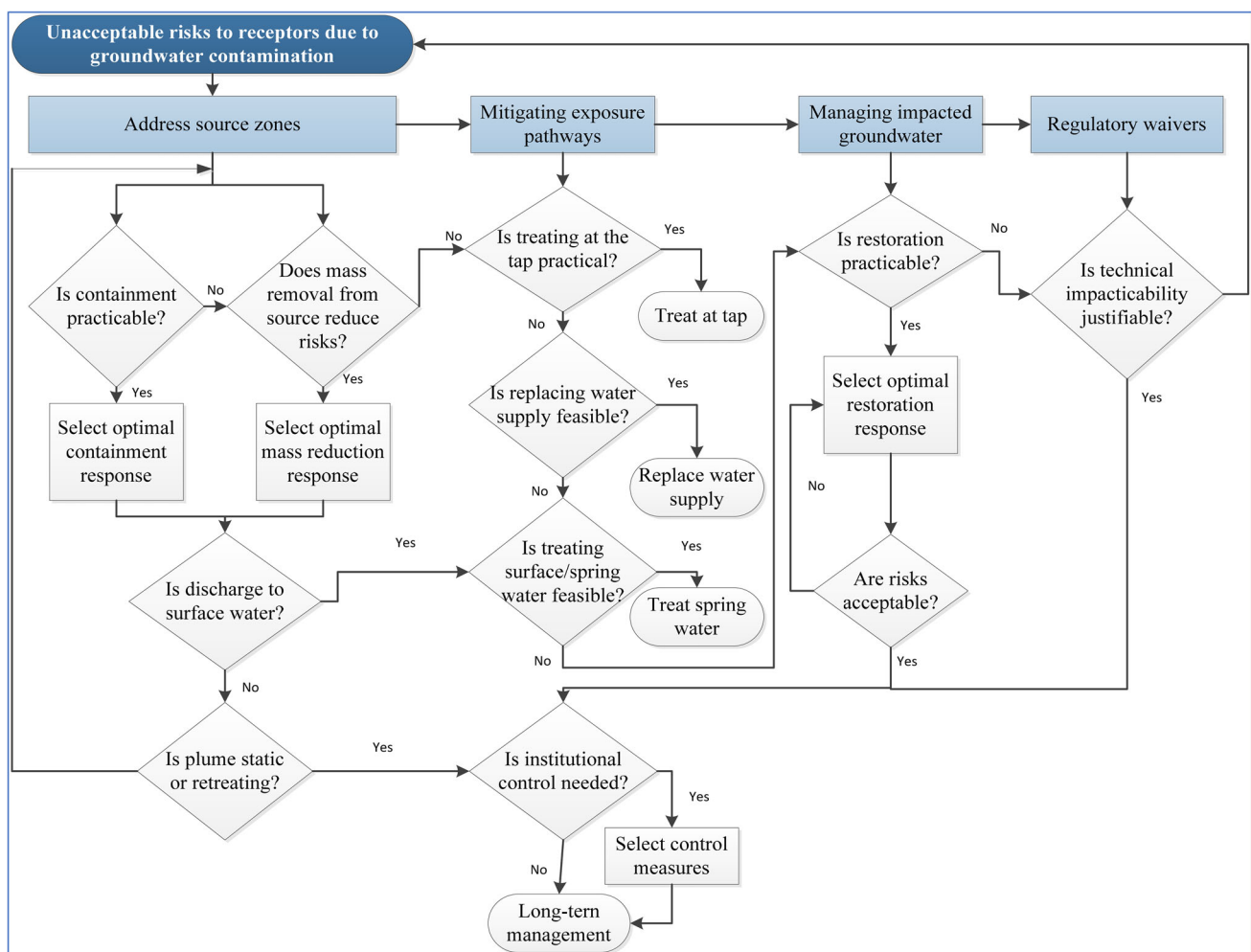
Fig. 8 General decision framework for addressing contaminated groundwater in karst aquifers

Fig. 9 Karst aquifer remediation strategies and their challenges

Table 1 Active groundwater remediation techniques at CERCLA sites with record of decision (http://www.epa.gov/superfunds/sites/rods/index.htm)

Remediation techniques	Number of sites	Percentage (%)
Groundwater extraction and treatment	17	24
Hydraulic containment	2	3
Vertical barrier wall/Groundwater diversion trench	2	3
Compression/Jet grouting to seal karst features	1	1
In situ groundwater treatment	13	18
Permeable reactive barrier	2	3
Evapotranspiration/phytoremediation	2	3
NAPL collection/removal	2	3
Monitored natural attenuation	20	28
No active groundwater remediation	10	14
Total	71	100

Conclusions

Groundwater exists in both the overburden and the underlying bedrock formation. The overburden is composed of silt and clay with a wide range in thickness from 13 to 129 feet. The bedrock is composed of carbonate rock characterized by irregular bedrock surface, water-filled or clay-filled voids and discrete fracture zones. Large variation in specific capacity and hydraulic conductivity, coexistence of confined and unconfined conditions, preferential flow pathways, and connected fractures have been observed within the karst aquifer.

Karst features have complicated the determination of both the vertical and lateral extents of contamination plumes. Through a phased approach that involved multidisciplinary techniques, both the vertical and lateral extents of groundwater contamination in the overburden and karst bedrock formations have been successfully delineated.

The HHRA has evaluated potential cumulative risks for the resident (adult and child), construction worker, and

commercial worker exposure to contaminated groundwater. Based on results of the HHRA, there are concerns for use of groundwater as a potential future tap water source. Volatilization of COPCs in groundwater into site buildings may be a potential concern. Results for the construction worker exposure to groundwater are below the risk thresholds set forth by USEPA and PADEP. Lead in groundwater was evaluated through the use of the IEUBK model; the model has calculated that lead in groundwater is not a health concern. Unacceptable health risks have necessitated groundwater remediation.

Based on the delineated extents of COPCs in the overburden and bedrock formations, chemical oxidation in the karst aquifer and enhanced bioremediation in the overburden aquifer are viable alternatives for groundwater remediation, with monitored natural attenuation and land use control as shared components of both techniques.

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