

**NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION
SCIENCE ADVISORY BOARD**

FINAL REPORT

Arsenic Mobilization Due to Pipeline Installation

January 6, 2020

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AND

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New Jersey Science Advisory Board
Water Quality and Quantity Standing Committee

“Arsenic Mobilization Due to Pipeline Installation”

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Charge Questions and Issue Statement (Provided by the NJDEP)

The following issue was assigned to the chair of the Water Quality and Quantity Standing Committee who referred it to Dr. Xiaoguang Meng to lead.

ISSUE	WORKING GROUP	DEP CONTACT
How could pipeline installation and operation affect groundwater quality in those areas of the Piedmont province with known arsenic issues? What data support this conclusion? What mitigation steps (e.g., construction practices) could be taken to minimize any impacts? What studies are needed to better answer this question?	X. Meng (chair) Bob Lippencott Rick Kropp Brian Buckley	Program Contact: WRM - Jeff Hoffman/Steve Spayd DSR Liaison: Nick Procopio (609-633-7713) nick.procopio@dep.nj.gov

Specific questions outlined by NJ Geologic and Water Survey:

1. Can disruption and exposure of arsenic-rich bedrock initiate the release and mobilization of arsenic in groundwater?
2. If so, how far can arsenic be expected to migrate from the disturbance area? What conditions will encourage or discourage migration?
3. If mobilization of arsenic occurs due to a bedrock disturbance, how long will the disturbed area release arsenic? What factors will slow or halt the release of arsenic?
4. As part of pipeline safety measures, can cathode protection measures spur arsenic release during operation?
5. If bedrock disturbances from pipeline construction initiates arsenic mobilization, would other subsurface disturbance (i.e. water or sewer main installation, road construction, installation of building foundations) be of equal concern?
6. What research studies can be recommended for short term and long-term investigations?
7. If a new pipeline will be installed in an arsenic-rich bedrock area with nearby private wells used for drinking water, what well monitoring program would be sufficient to protect public health? Specifically, if pre-pipeline construction and post-pipeline construction well monitoring were required, what distance from the pipeline would be adequate for inclusion of existing private wells or required monitoring wells, at what frequency should they be tested, what should they be tested for, and for how many years post-construction should the monitoring continue?

SHORT TERM ISSUE (3-6 months): How could pipeline installation and operation affect groundwater quality in those areas of the Piedmont province with known arsenic issues? What data support this conclusion? What steps (e.g., construction practices) could be taken to minimize any impacts? What studies are needed to better answer this question?

JUSTIFICATION: This is a question of significant public concern. Arsenic mobilization and migration in the Piedmont due to pipeline construction and operation has a number of unknowns. These unknowns are raising health and safety concerns.

INFORMATION NEEDED: What chemical processes associated with subsurface disturbance promote arsenic mobilization? If mobilized, how far might arsenic migrate in the subsurface? What subsurface conditions promote or hinder this migration?

SAB Response

Introduction

This report was prepared in response to the Charge Questions and Issue Statement noted above. The focus of this review is on conditions that may be created by disturbance of bedrock containing naturally elevated concentrations of arsenic, primarily as a result of natural gas pipeline construction. Other activities that may cause similar disturbance to bedrock are also addressed, along with the following considerations:

- Disturbance of saturated and unsaturated portions of bedrock may influence behavior of naturally-occurring arsenic in the subsurface.
- Unnatural saturated conditions and altered or preferential flow of groundwater in the subsurface may result from pipeline trenches and may impact fate and transport behavior of arsenic in localized areas.

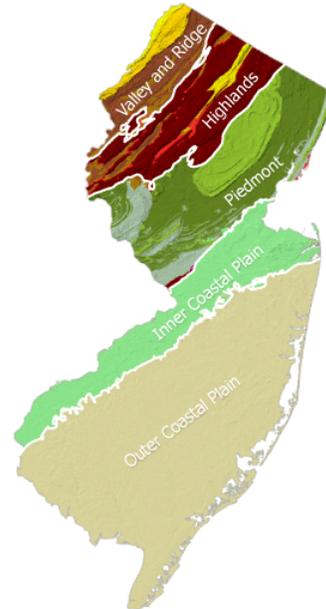
Background

In some areas of New Jersey, geologic formations including unconsolidated materials (overburden soil, parent material) and consolidated materials (bedrock) contain elevated levels of naturally-occurring arsenic. The fate and transport behavior of arsenic is a function of several factors, including the mineral form of arsenic, the natural geological formation, intrinsic surface area, hydrogeological characteristics (competence, connectivity), and the prevailing biogeochemical (e.g., pH, redox, TOC) conditions. Arsenic can become more or less soluble and, therefore, more or less mobile in groundwater due to changes in the subsurface biogeochemical conditions. Arsenic may also become mobilized due to physical disturbance of the bedrock formation.

In general, construction activities expose new surfaces, creating more availability for arsenic mobilization; while also introducing oxidative conditions, temporarily changing previous weakly reductive conditions. Overall, oxidative conditions favor demobilization of arsenic. In the long term (once everything is buried), a greater reductive stressor may be introduced by the presence of a pipeline, and arsenic is more likely to be mobilized with time. While the oxidation and reduction potential (ORP) is the primary driver of arsenic mobilization, conditions such as Fe concentration, pH, cathodic shielding and organic carbon are important factors in driving the reductive or oxidative conditions that have the potential to influence changes in arsenic fate and transport characteristics.

NJ Physiographic Provinces

Passaic and Lockatong formations are within the Piedmont physiographic province (a.k.a., Newark Basin).



General Statement

The pipeline installation usually involves a work area that can vary in width from 90 feet to 125 feet and a depth of 3.5 to 6 feet. However, pipeline trenching activities in some areas may extend deeper and disturb consolidated materials (bedrock) or exposure of fresh rock surfaces. In some areas of New Jersey, bedrock formations contain elevated levels of naturally-occurring arsenic. While arsenic is associated with pyrite minerals, such as arsenopyrite (FeAsS) and FeS_2 , in the Lockatong formation of the Newark Basin, it is adsorbed by iron oxides, such as hematite, in the Passaic formation of the Newark Basin.

Generalized Example Trench Cross-Section



The mobility of arsenic in the environment is mainly affected by the ORP, which controls the redox reactions of arsenic-bearing minerals. The disturbance can temporarily expose the bedrock to the air and introduce oxygen into the trench backfill. The addition of oxygen via exposure to the atmosphere can cause oxidation of arsenic-bearing pyrite minerals when present and release arsenic from those minerals. However, the oxidative release of arsenic may not last long after pipeline construction is completed. Potential leakage of natural gas (hydrocarbon compounds) from the pipeline and generation of H_2 by the cathodic shield will tend to stimulate biological activity, which generally decreases the ORP and can potentially result in reductive dissolution of iron oxide minerals and long-term mobilization of arsenic.

The effects of the trenching activity on arsenic mobility may not be limited to within the trench, as changes in ORP and arsenic mobility may extend for some distance in the groundwater hydraulically downgradient of the pipeline. The distance of the pipeline impacts on the arsenic mobility and migration is likely to be affected by the co-occurrence of many factors, such as arsenic concentration, mineralogy, and iron mineral concentration; crosslink flow caused by fractures, faults and bedding planes, etc.; the existence, amount and duration of any natural gas leaked; amount of H_2 generated; local biogeochemical conditions; and the oxidation and adsorption capacity of the materials downstream of the pipeline.

Specific questions outlined by NJ Geologic and Water Survey:

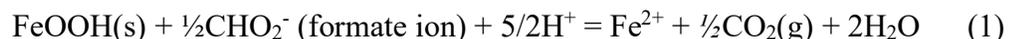
1. Can disruption and exposure of arsenic-rich bedrock initiate the release and mobilization of arsenic in groundwater?

Responses

Where bedrock is shallow, or where pipeline excavations are deep, bedrock may be disturbed. In these areas, trenching activities may result in fracturing of arsenic-bearing rock formations. Arsenic release rate from the freshly exposed rock surface should be higher than from the original rocks due to the high content of arsenic on the fresh rock surface.

The mobilization of arsenic in rocks and sediments is affected by ORP, pH, the concentrations of co-existing ions and organic carbon, and biological activities. The sediments can act as both sources and sinks for As, depending on the redox conditions in the aquifer. The Passaic formation in the Newark basin contains iron oxide minerals with adsorbed arsenate. It is reported that reductive dissolution of arsenic-containing iron oxide minerals is the main mechanism of arsenic release from sediments into groundwater in Bangladesh and the Central Yangtze River Basin in China (Nickson et al., 1998; Zheng et al., 2004; Schaefer et al., 2017). Serfes et al. (2005, 2010) reported that wells with high As concentration generally have low dissolved oxygen concentrations in bedrock aquifers in the Newark Basin in New Jersey. A spatial association between high As in groundwater and black shale is also observed.

The reduction of the minerals in groundwater is coupled with oxidation of organic matter and is mediated by iron-reducing bacteria. Equation 1 is a general reduction reaction for iron (oxy)hydroxides and formate ion represents organic compounds in groundwater (Nickson et al. 1998). The reduction reaction will result in an increase in the pH and bicarbonate concentration.



A study on arsenic in New Jersey Coastal Plain Streams, Sediments, and Shallow Groundwater found that the inputs of dissolved organic carbon (DOC) stimulated microbial growth, decreased ORP, and mobilized arsenic beneath the streambeds (Barringer et al. 2014). In addition, sampling of streambed pore waters in the Passaic formation in the Newark basin showed higher concentrations of arsenic in the streams with low dissolved oxygen content in contrast to those with high dissolved oxygen content, indicating that the arsenic is more mobile under low-dissolved-oxygen conditions (Mumford et al., 2014).

The cathodic shield that is used for protection of the pipeline from corrosion may generate H₂ in the water surrounding the pipeline. There may be leakage of natural gas (methane, ethane, propane) and other hydrocarbon compounds from the pipeline. McKain et al. (2015) estimated that the leakage rate to the atmosphere from all downstream components of the natural gas system, including transmission, distribution, and end use, was 2.7± 0.6% in the Boston urban region. The hydrocarbon compounds and H₂ may enhance microbial growth

and activity, which will deplete the dissolved oxygen in water and result in reductive dissolution of the iron oxide minerals and release of arsenic (Cozzarelli et al, 2015, Ziegler et al, 2015).

Arsenic is associated with pyrite minerals, such as FeS₂ and arsenopyrite (FeAsS), in the Lockatong formation of the Newark Basin, and also in black beds of the Passaic Formation. The trench activities will expose the arsenic-bearing rocks and sediments to the air. Numerous studies on oxidative release of arsenic from arsenopyrite have been conducted (Corkhill and Vaughan, 2009; Ramirez-Aldaba, et al., 2016; Deng et al., 2018). The results indicated that the release of arsenic from minerals caused by chemical oxidation was very slow (Equation 2). The presence of sulfur-oxidizing and/or iron-oxidizing bacteria significantly increased the rates of arsenic release. The oxidation reaction will decrease the water pH.



Laboratory incubation experiments indicated that arsenic could be released from arsenopyrite and black shale samples from the Newark Basin (Lockatong formation) under sulfate-reducing conditions due to sulfide-arsenide exchange (Zhu et al. 2008).

Arsenate adsorption by iron oxides and hydroxides increases with decreasing pH from 10 to 5, while arsenite adsorption increases when pH increases from 5 to 9 (Figure 1). It is reported that high As concentration is related to high pH in groundwater in the Newark Basin in New Jersey (Serfes et al. 2005, 2010), Eastern New England (Ayotte et al., 2003) and Pennsylvania (Senior and Sloto, 2006; Gross and Low 2012). The impact of pipeline installation on water pH is unknown. The effect likely is variable depending upon whether sulfide minerals or organic matter oxidation predominates in the various geological materials after the disturbance associated with pipeline installation.

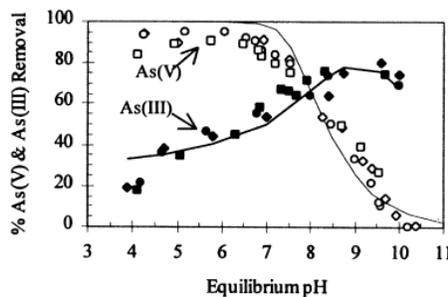


Figure 1. Adsorption of arsenate (AsO₄³⁻) and arsenite (AsO₃³⁻) by Fe(OH)₃ precipitates, Meng et al. (2000).

Phosphate and silicate compete with arsenate and arsenite for the adsorption sites on iron oxide surfaces, which increases the mobility of arsenic in groundwater (Meng et al. 2000, 2002). While bicarbonate reduces the adsorption of arsenite on the mineral surface, it has little effect on arsenate adsorption. There are no related research results available for

predicting the effects of the pipeline installation on concentrations of phosphate, silicate, and bicarbonate.

The hydraulic conductivity of fill material used to backfill excavated pipeline trenches will likely be higher than the surrounding undisturbed bedrock and soils. In this way, pipeline corridors can be expected to exhibit preferential flow of soil water and perched water infiltrating from surface runoff and precipitation to groundwater from, in and around pipeline trenches. In some areas along pipeline corridors, excavation trenches may cut through one or more stratigraphic units that contain aquifers or fractures that connect to local aquifers. This combination of conditions represents a potential to cause mixing of water infiltrating the pipeline backfill material to groundwater in distant or isolated aquifers, which may affect As mobility. For example, physical conditions as noted above may result in influx of water migrating preferentially via a pipeline trench that causes changes in the ORP, pH, and other chemical properties of the aquifer groundwater. If the ORP increases in the aquifer containing sulfide minerals as the result of the preferential flow, it may increase oxidative release of arsenic from certain As-rich minerals, if present. Reductive release of arsenic from iron oxide minerals may happen if the ORP decreases due the preferential flow. Of course, the potential for this example to occur is dependent on the biogeochemical properties of the aquifer material in addition to the coexistence of several of the above variables that are subject to local conditions.

2. If so, how far can arsenic be expected to migrate from the disturbance area? What conditions will encourage or discourage migration?

Responses

Potential arsenic migration distances and rates will vary locally as ground water moves through the network of interconnecting fractures, bedding planes, and joints of the Newark Basin. Herman (2010) concluded that stratigraphic bedding is the major control of groundwater storage and movement in the basin. The ground-water system consists of beds with relatively high transmissivity separated by beds with relatively low transmissivity that form a leaky, multi-aquifer system (Sloto and Schreffler, 1994). Local water-bearing zones and well yields have been characterized by numerous studies for the Newark Basin, (Sloto and Schreffler, 1994, Lewis-Brown and Jacobsen, 1995; Carleton et al, 1999; Herman, 2010) with major differences in hydraulic conductivity reported. The aquifers of the Passaic Formation (red beds) and the Stockton Formation have been shown to produce the highest flows and high-capacity yields (Herman, 2010; Sloto, 1994). Arsenic migration rates from the disturbance area will greatly vary depending on the local geology, fracture density, fracture connectivity to major water-bearing zones, and geochemical conditions. It may be impossible to determine exact migration distances and rates from the expansive pipeline disturbance area due to these factors.

The duration of the increased arsenic release in the disturbed area and the distance of arsenic migration from the disturbance area are also affected by many factors, such as the stability of the arsenic-bearing rocks and sediments in the disturbed and surrounding areas, sustainable

inputs of reductants (organic compounds and/or H₂) or oxygen in the areas, arsenic adsorption capacity of the sediments downgradient of the disturbed area, and redox- and pH-buffer capacities of the sediments.

Recent batch experiments by Serfes et al. (2016) have shown that the increased arsenic release from the iron oxide minerals in the backfilled trench should not last long in the presence of oxygen because the minerals are stable under oxic conditions. However, if there are sustained inputs of reductive materials, such as hydrocarbon compounds leaked from the pipeline and/or H₂ generated by the cathodic shield, the enhanced biological growth will decrease the ORP and subsequently result in continuous reductive dissolution of the minerals and release of the adsorbed arsenic. The anoxic water in the trench will migrate and cause the reductive release of arsenic in the surrounding area. Arsenic migration rates through the trench and nearby fractures will ultimately be controlled by the geochemical conditions (primarily redox condition) of the aquifer and sorption processes (Ziegler, et al. (2017a).

The pyrite minerals can be continuously oxidized as long as they are exposed to oxygen, forming soluble arsenite and ferrous ions. However, if there is sufficient oxygen and insufficient reductants, ferrous ions and arsenite can be oxidized to ferric ions and arsenate. Then, ferric hydroxide precipitates will be formed and arsenate will be adsorbed by the precipitates in the backfilled trench. If there is sustained input of oxygen, the surrounding area will be gradually converted from anoxic to oxic conditions.

Ziegler, et al. (2017b) investigated the mobilization of arsenic in a groundwater aquifer caused by spilled crude oil. A crude oil pipeline ruptured near Bemidji, MN, releasing 10,700 barrels of crude oil to a shallow unconfined aquifer in 1979, creating a plume of dissolved hydrocarbons in groundwater. Over the 35-year period, the leading edge of the dissolved arsenic and Fe plume migrated about 130 m downgradient of the contaminated site (Cozzarelli et al., 2016).

3. If mobilization of arsenic occurs due to a bedrock disturbance, how long will the disturbed area release arsenic? What factors will slow or halt the release of arsenic?

Response

If the disturbed bedrocks are stable under the chemical conditions in the backfill, such as iron oxide minerals in unsaturated backfill and in the presence of oxygen, the relatively high arsenic release rate from the freshly exposed rock surface may decrease to a release rate similar to that of the old mineral surface in a short period of time. However, if the minerals are not stable under the chemical conditions, such as iron oxides under anoxic condition and pyrite minerals under oxic conditions, they will be gradually weathered and arsenic will be continuously released. ORP is the most important parameter affecting the stability of the minerals. High organic matter content, leakage of natural gas, and H₂ generated by the cathodic shield may enhance biological growth, deplete oxygen, and decrease the ORP, leading to continuous release of arsenic.

4. As part of pipeline safety measures, can cathode protection measures spur arsenic release during operation?

Response

The cathodic shield that is used for protection of the pipeline from corrosion may generate H₂ in the water surrounding the pipeline. It is reported that autotrophic bacteria can utilize H₂ to reduce vanadium(V) (Zhang et al. 2018), perchlorate (Yu et al. 2007) and nitrate (Su et al. 2017). The autotrophic reactions should also result in reductive dissolution of iron oxide minerals and subsequent release of arsenic from them. However, no related papers and reports have been found.

5. If bedrock disturbances from pipeline construction initiates arsenic mobilization, would other subsurface disturbance (i.e. water or sewer main installation, road construction, installation of building foundations) be of equal concern?

Response

Bedrock is not always disturbed by construction, whether pipeline installation or other forms of construction. However, concerns regarding arsenic mobilization associated with pipeline construction may apply to bedrock disturbances from activities other than pipeline construction under certain conditions.

Mobilization of naturally-occurring arsenic could result from construction activities that represent disturbance to certain bedrock formations enriched with arsenic, if those activities cause bedrock disturbance similar to pipeline construction activities. Water or sewer utilities share similar characteristics in that they can tend to be linear construction projects that involved buried pipelines. Thus, these types of projects are more likely to share some of the same risks for potential disturbance to bedrock as pipeline construction projects. Some water utilities require installation to deeper depths due to sloping to facilitate gravity drainage. Examples are storm water and wastewater utility lines. Based on experience with existing utilities throughout New Jersey, leakage in and out of buried storm water and sewer utility lines can be expected. These utilities typically contain natural and anthropogenic organic substances that may leak into surrounding bedrock fractures, potentially affecting the biogeochemical conditions (redox, pH, etc.) and mobility of arsenic in certain bedrock formations. The likelihood for construction of these types of utilities to cause disturbance during installation is greater than other utilities, such as electrical conduits or drinking water utilities. The latter often require comparatively minimal depths for thermal insulation and typically operate under pressure. Therefore, new drinking water service utilities generally are not installed more than 4 or 5 feet below the ground surface as they do not require maintaining a downward pitch, as do other water utilities noted above. However, where construction of any utilities requires disturbance of bedrock that contains high concentrations of naturally occurring arsenic and water-bearing zones, the potential for mobilization of

arsenic due to bedrock disturbance is expected to be similar to pipeline construction within bedrock with similar conditions.

Road construction and installation of building foundations may be of equal concern relative to pipeline construction regarding arsenic mobilization due to disturbance of arsenic-rich bedrock formations. However, this is expected to be much more limited because construction of roadways and building foundations is often limited to shallow depths. During these types of construction projects, any bedrock disturbance generally occurs near the surface, and the disturbance generally does not extend deep enough vertically to intersect water-bearing units in the bedrock formation. Developments that occupy larger areas and/or require deeper excavations into saturated, arsenic-enrich bedrock are of greater general concern. New road construction that requires installation of tunnels, road cuts through outcrops, or installation of deep caissons may be uncommon, limited exceptions. In these circumstances, the potential for mobilization of arsenic bedrock disturbance is expected to be limited.

6. What research studies can be recommended for short term and long-term investigations?

Response

- a) Short- and long-term release of arsenic from fresh rock surfaces (NJGWS Question 1): Representative bedrocks and soils can be obtained from the proposed pipeline areas. A portion of the rock samples can be crushed to create fresh surface. The release rates of arsenic from the old and fresh rock surfaces will be determined. Arsenic and iron contents and their oxidation states on the rock surfaces before and after the tests will be characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX), X-ray diffraction (XRD), extended X-ray absorption fine structure spectroscopy (EXAFS), and Fourier transform infrared spectroscopy (FTIR). The experimental conditions and parameters include DOC, DO, open/closed systems, oxic, anoxic, pH, and microorganisms.
- b) Cathodic effects on arsenic release (NJGWS Question 4): Bench-scale cathodic systems can be set up in saturated minerals or soil to simulate a pipeline in the saturated backfill. Control systems without the cathode and with different content of soil organic matter will also be tested under the same conditions. The pH, DO, ORP, As, and Fe in the soil solution will be monitored over 6-12 months.
- c) Factors that could slow or halt the release of arsenic (NJGWS Question 3): Research can be conducted to investigate what kinds of materials can be added into the backfill to reduce the effects of the pipeline and increase the stability of arsenic.
- d) Review of existing well arsenic data (NJGWS Questions 2 & 7): A review of the existing data on arsenic concentration in the wells along the existing natural gas pipelines can be performed to evaluate if arsenic concentrations in wells near the pipelines are higher than in the wells far from the pipeline.

7. If a new pipeline will be installed in an arsenic-rich bedrock area with nearby private wells used for drinking water, what well monitoring program would be sufficient to protect public health? Specifically, if pre-pipeline construction and post-pipeline construction well monitoring were required, what distance from the pipeline would be adequate for inclusion of existing private wells or required monitoring wells, at what frequency should they be tested, what should they be tested for, and for how many years post-construction should the monitoring continue?

Response

The distance of arsenic migration is affected by the hydraulic conductivity, hydraulic gradient, bedrock fracture flow patterns, and adsorption capacity of the aquifer materials around the pipeline trench and in the groundwater system. It has been documented that arsenic concentrations can vary seasonally, related to geochemical variability seen with seasonal changes in groundwater levels, recharge rates and pumping effects (Buckwalter and Moore, 2007; Savarimuthu, et al. 2006; Ayotte et al, 2015, Levitt et al, 2019). Therefore, it is important to define the temporal arsenic variability in domestic wells both pre- and post-pipeline installation.

If groundwater monitoring is implemented, water samples should be collected from existing domestic wells located within a few hundred meters of the pipeline for measurement of As(V), As(III), DO, ORP, TOC, Fe, and SO_4^{2-} . Groundwater monitoring programs should consider collection of pre-construction (i.e., baseline) samples and post-construction samples in accordance with statistical-based sampling plan design in accordance with existing NJDEP and USEPA groundwater sampling guidance (e.g., NJDEP 2012; USEPA 2009). For example, sample collection every three months to determine baseline levels for one year to two years (e.g., 4 to 8 quarterly pre-installation sample rounds) and 8 or more post installation sampling rounds (e.g., 8 quarterly post-installation sample rounds) to provide statistically valid data sets for comparative trend evaluation. If the data show minimal variability over this time duration, limiting the sampling frequency may be warranted. For example, consider reduction of sampling to twice a year, once during the wet season (January-June) and once during the dry season (July-December) as demonstrated by Ayotte et al, 2015 and Levitt et al, 2019.

If monitoring wells are installed, they should be placed within a short distance hydraulically downgradient of the proposed pipeline (i.e., pre-installation) to establish baseline levels of the parameters noted above. Water samples should be collected from monitoring wells at frequencies and timeframes, and data evaluation should be performed, following similar protocols to those described above for domestic wells.

Summary

Arsenic is naturally occurring in some New Jersey bedrock formations that contain potable ground water resources. Disturbance of bedrock during certain types of construction projects (including pipeline installation) has the potential to cause conditions that allow release of more mobilized forms of arsenic in local groundwater from the bedrock. As noted above in this report,

the behavior of arsenic in the subsurface environment is dependent on several variable factors such as oxidation reduction potential, pH, concentration of arsenic in bedrock, depth to groundwater, fracture connectivity within the bedrock, etc. While portions of some construction projects such as pipeline installation and other construction that result in disturbance of bedrock may contribute to the release of naturally-occurring arsenic, a co-occurrence of several factors is necessary to create the conditions to cause increased mobilization of arsenic in groundwater. The physical activity of disturbing the bedrock creates exposure of fresh surfaces and larger surface area representing conditions that may facilitate arsenic mobilization that are likely to be localized and short-term, as the subsurface returns to pre-construction conditions after excavations are closed. Longer-term, arsenic impacts covering larger areas are somewhat limited and less likely as the necessary conditions depend on the co-occurrence of several biogeochemical and hydrogeologic factors in association with disturbances in areas of arsenic-enriched bedrock. Additional evaluation is recommended including testing various rock types, cathodic system impacts to redox, backfill amendments, and details to support monitoring programs.

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