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EXPLANATION OF SIGNIFICANT DIFFERENCES
PETERSON/PURITAN, INC. SUPERFUND SITE, OU-1

July 2013

Prepared by:

The United States Environmental Protection Agency

Region 1, New England

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DECLARATION FOR THE EXPLANATION OF SIGNIFICANT DIFFERENCES PETERSON/PURITAN, INC. SUPERFUND SITE, OU-1

SITE NAME AND LOCATION

Peterson/Puritan, Inc. Superfund Site, Cumberland and Lincoln, Rhode Island.

STATEMENT OF PURPOSE

The decision document sets forth the basis for EPA's determination to issue the attached Explanation of Significant Differences (ESD) for the Peterson/Puritan, Inc. Superfund Site (the Site), Operable Unit 1 (OU-1), located in Cumberland and Lincoln, Rhode Island. The State of Rhode Island has been consulted with during preparation of this ESD, and the State's comments have been incorporated into the ESD, as applicable.

STATUTORY BASIS FOR ISSUANCE OF THE ESD

Under Section 117(c) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. Section 9617(c), if the remedial action being undertaken at a site differs significantly from the Record of Decision (ROD) for that site, the EPA shall publish an explanation of significant differences between the remedial action being undertaken and the remedial action set forth in the ROD and the reasons such changes were made. The National Contingency Plan (NCP), 40 C.F.R. § 300.435(c)(2)(i), and Office of Solid Waste and Emergency Response (OSWER) Directive 9355.3-02 indicate that an ESD, rather than a ROD amendment, is appropriate where the adjustments being made to the ROD are significant but do not fundamentally alter the remedy with respect to scope, performance, or cost. EPA has determined that this ESD is properly issued because the adjustments to EPA's September 30, 1993 ROD for OU-1, as provided in this ESD, are significant but do not fundamentally alter the overall remedy for OU-1 with respect to scope, performance, or cost.

In accordance with Section 300.825(a) (2) of the NCP, this ESD will become part of the Administrative Record for the Site and will be available for public review at the EPA Region 1 Record Center in Boston, Massachusetts, the Cumberland Public Library and Lincoln Public Library in Rhode Island. A public notice, which summarizes the modifications to the remedy as set forth in the ESD shall be published in a local newspaper of general circulation following the signing of this ESD.

OVERVIEW OF THE ESD

Two aspects of the remedy selected by EPA in its ROD in 1993 will be modified by this ESD:

Cleanup Level for Arsenic -- After EPA issued the ROD for OU-1 in 1993, EPA revised the Maximum Contaminant Level (MCL) for arsenic under the Safe Drinking Water Act from 0.05 mg/L to 0.01 mg/L. Through this ESD, EPA incorporates this more stringent, currently promulgated standard as the cleanup standard for impacted groundwater within the ROD.

Augmentation of Enhanced Source Control Remedy for PAC Source Area with Monitored Natural Attenuation – In the ROD, EPA selected enhanced source control as the remedial approach for the PAC Source Area. The primary treatment method under this approach was the excavation and disposal of two leach fields and associated soils located in the PAC Source Area. According to the ROD, the leach field soils were a source of arsenic contamination and a source of carbon-rich materials causing groundwater contamination; the carbon source had the effect of making groundwater anaerobic, thus mobilizing naturally occurring arsenic from the overburden into groundwater. The excavation component of the remedy was enhanced with a secondary treatment method, an innovative in-situ oxidation treatment system, to stimulate aerobic conditions and help reduce the mobility of the arsenic in the groundwater from the leach field areas. Enhanced source control was chosen to limit the effect of the arsenic and carbon sources, and encourage the attenuation of dissolved arsenic from groundwater back to its adsorbed state in the overburden. Pursuant to a 1995 Consent Decree, certain Settling Defendants implemented these measures, including full excavation of physical evidence of the leach fields, operation of the oxidation system from 1997 to 2000, when the system was shut down due to the progressive, irrevocable degradation of the system under normal operation. After determining that replacement of the system would not accelerate the attenuation of remaining dissolved arsenic from groundwater, the system was decommissioned in 2004.

Arsenic levels in PAC Source Area groundwater have been reduced and continue to attenuate, but concentrations remain above cleanup levels at the present time. By this ESD, EPA is augmenting its remedial approach to the PAC Source Area to require monitored natural attenuation (MNA) in accordance with current EPA guidance to address the remaining arsenic concentrations in the PAC Source Area and achieve groundwater cleanup levels. MNA, currently the remedial component for the PAC Downgradient Area, will be included as a remedial component for the PAC Source Area.

This ESD formally incorporates these aforementioned changes into the CERCLA remedy. The State of Rhode Island has been consulted with during preparation of this ESD, and the State's comments have been incorporated into the ESD, as applicable.

DECLARATION

For the foregoing reasons, by my signature below, I approve the issuance of an Explanation of Significant Differences for Operable Unit 1 of the Peterson/Puritan, Inc. Superfund Site in Cumberland and Lincoln, Rhode Island, and the changes stated therein.

Date July 10, 2013

James T. Owens III, Director
Office of Site Remediation and Restoration
U.S. Environmental Protection Agency
Region 1 New England

EXPLANATION OF SIGNIFICANT DIFFERENCES
PETERSON/PURITAN, INC. SUPERFUND SITE, OU-1

I. INTRODUCTION

This document is an Explanation of Significant Differences (ESD) for the Record of Decision (ROD) for the Peterson/Puritan, Inc. Superfund Site (the Site), issued September 30, 1993 (EPA, 1993; Attachment 4). The ROD sets forth the selected remedy for the restoration of groundwater throughout Operable Unit 1 (OU-1) of the Site. Among other cleanup levels, the ROD sets forth a cleanup standard for arsenic in groundwater at .05 mg/L based on EPA's promulgated Maximum Contaminant Level (MCL) under the Safe Drinking Water Act at that time. Through this ESD, EPA incorporates into the ROD the more stringent MCL cleanup standard of .01 mg/L, which EPA promulgated in 2002.

In the ROD, EPA selected enhanced source control as the remedial approach for the PAC Source Area. The primary treatment method under this approach was the excavation and disposal of two leach fields and associated soils located in the PAC Source Area. According to the ROD, the leach field soils were a source of arsenic contamination and a source of carbon-rich materials causing groundwater contamination; the carbon source had the effect of making groundwater anaerobic, thus mobilizing naturally occurring arsenic from the overburden into groundwater. The excavation component of the remedy was enhanced with a secondary treatment method, an innovative in-situ oxidation treatment system, to stimulate aerobic conditions and help reduce the mobility of the arsenic in the groundwater from the leach field areas. Enhanced source control was chosen to limit the effect of the arsenic and carbon sources, and encourage the attenuation of dissolved arsenic from groundwater back to its adsorbed state in the overburden. Pursuant to a 1995 Consent Decree, certain Settling Defendants implemented these measures, including full excavation of physical evidence of the leach fields, operation of the oxidation system from 1997 to 2000, when the system was shut down due to the progressive, irrevocable degradation of the system under normal operation. After determining that replacement of the system would not accelerate the attenuation of remaining dissolved arsenic from groundwater, the system was decommissioned in 2004.

Arsenic levels in PAC Source Area groundwater has been reduced and continues to attenuate, but concentrations remain above cleanup levels at the present time. By this ESD, EPA is augmenting its remedial approach to the PAC Source Area to require monitored natural attenuation (MNA) in accordance with current EPA guidance (Wilson John T., 2011; EPA 2007b) to address the remaining arsenic concentrations in the PAC Source Area and achieve groundwater cleanup levels. An analysis of monitoring data collected over many years suggests that arsenic levels will attenuate within a reasonable period of time - 15-29 years - to achieve the designated cleanup standard of 0.01 mg/L for arsenic within the PAC Source Area.

A. Site Name & Location

Site Name: Peterson/Puritan, Inc. Superfund Site, Operable Unit 1

Site Location: Cumberland and Lincoln, Rhode Island

B. Lead & Support Agencies

Lead Agency: United States Environmental Protection Agency (EPA)

- *Contact: David J. Newton, EPA Remedial Project Manager (for the Peterson/Puritan, Inc. Site OU1), (617) 918-1243*
- *Contact: Gerardo Millán-Ramos, EPA Remedial Project Manager (lead author for this ESD), (617)918-1377*

Support Agency: Rhode Island Department of Environmental Management (RIDEM)

- *Contact: Paul Kulpa, RIDEM Project Manager, (401) 222-2797 x7148*

C. Legal Authority for ESD

This ESD is prepared in accordance with Section 117(c) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. 9617(c), and Section 300.435(c) of the National Oil and Hazardous Substances Pollution Contingency Plan (NCP), 40 C.F.R. 300.435(c)(2)(i), and documents a significant change to the remedy selected in the ROD for the Site. In accordance with Office of Solid Waste and Emergency Response (OSWER) Directive 9200.1-23P, EPA has determined that the changes to the remedial action as stated herein, significantly change but do not fundamentally alter the remedy selected in the ROD with respect to scope, performance, or cost.

D. Summary of Circumstances Necessitating this ESD

Section 121 of CERCLA and EPA regulations under the NCP at 40 CFR 300.400 require remedial actions to attain Applicable or Relevant and Appropriate Requirements (ARARs). Drinking water standards provide cleanup levels for current or potential sources of drinking water. Because Rhode Island is not a Comprehensive State Ground Water Protection Program (CSGWPP) state, federal groundwater cleanup standards apply. Rhode Island's standard (though not applicable) is GAA, which refers to those groundwater resources designated by RIDEM to be suitable for public drinking water use without treatment.

The ROD identified arsenic (among other OU-1 contaminants) as a Contaminant of Concern (COC) for groundwater and set forth a cleanup level of .05 mg/L based on EPA's promulgated MCL under the Safe Drinking Water Act at that time. In 2002, EPA promulgated an updated MCL of .01 mg/L for arsenic under the Safe Drinking Water Act. An ESD is necessary to formally incorporate this newly updated MCL as the cleanup standard for arsenic at OU-1.

EPA identified three COCs in the 1993 ROD for the PAC Source Area in OU-1: arsenic, acetone[1], and tetrachloroethene.[2] Groundwater data, on which the Risk Assessment and ROD

[1] Acetone has not been detected above the cleanup level in any JGWMP monitoring well since April 1998.

[2] Tetrachloroethene has not been detected in any portion of the PAC Source Area since the 1993 ROD and is now thought to have been erroneously reported in a single well during the latter stage of the remedial investigation of the Site.

were based, indicated that the average and reasonable maximum exposure carcinogenic risks associated with the potential future ingestion of groundwater were elevated (6×10^{-3} and 1×10^{-2} respectively) above EPA's acceptable risk range. Arsenic was the major contributor to the risk evaluated for the PAC Source Area, while these listed COCs also contributed to risk greater than one in a million, or otherwise achieved a hazard index greater than one.

Arsenic has been monitored at least annually, except in 2005 and 2006 when monitoring was not conducted, as part of a Joint Groundwater Monitoring Program (JGWMP) since 1995. Although arsenic concentrations continue to attenuate, at the present time arsenic levels generally remain above the 1993 ROD cleanup standard of 0.05 mg/L and well above the 2002 promulgated standard of 0.01 mg/L at a majority of the wells tested throughout the PAC Source Area. In wells sampled during the most recent monitoring event (April, 2012) arsenic concentrations ranged from 0.063 mg/L (non-detect) to 0.444 mg/L.

While arsenic can come from human-made products, it also occurs naturally in rocks and soil, and is found widely in the environment (EPA, 2007a). Naturally occurring arsenic within unconsolidated aquifer material is common in Rhode Island, and is expected to be most prevalent where there are deposits of arsenopyritic (FeAsS) minerals. This occurrence has been observed in the Site's overburden substrates and it is expected to be in nearby bedrock. Arsenic can be mobilized from these deposits into a dissolved form through natural processes such as weathering or through anthropogenically induced changes to pH or oxidation-reduction conditions. In particular, if aquifer chemistry becomes anaerobic or reduced in oxygen, arsenic that was partitioned onto the aquifer matrix can be released to the groundwater.

Natural microbial activity, like that associated with the degradation of the organic waste, such as the organic materials placed in the PAC leach fields, (along with potentially other anthropogenic activities/sources affecting local groundwater), can cause groundwater to become anaerobic or reduced in oxygen for extended periods of time. (EPA, 2007a). The anaerobic or reduced oxygen conditions in the aquifer, in turn, can cause the mobilization of arsenic to groundwater over roughly the same period, giving rise to elevated arsenic concentrations in the aquifer for an extended period of time.

The remedy selected in the ROD required the design, installation and operation of an innovative in-situ oxidation treatment system of the soils to reduce the mobility of the arsenic from the leach field area in the PAC Source Area. Certain Settling Defendants operated the oxidation treatment system for three years between 1997 and 2000, but then shut the system down, with the concurrence of EPA, due to progressive, irreversible degradation of the gas transfer modules under normal operation. After determining that replacement of the system would not accelerate the attenuation of remaining dissolved arsenic from groundwater, the system was decommissioned in 2004.

Since the shutdown and decommissioning of the oxidation treatment system, EPA and certain Settling Defendants have continued to monitor arsenic levels in the entire PAC Remediation Area. At EPA's request, certain Settling Defendants submitted an analysis of long-term monitoring data under current EPA Guidance for MNA, which indicates that MNA is an appropriate remedial component to use in addressing remaining arsenic concentrations above the

cleanup level in the PAC Source Area. EPA is issuing this ESD to formally document the inclusion of this remedial component for the PAC Source Area.

This ESD and supporting documentation will become part of the Administrative Record for the Site. The ESD, supporting documentation for the ESD, and the Administrative Record are available to the public at the following locations and may be reviewed at the times listed:

U.S. Environmental Protection Agency
Records Center
1 Congress Street
Boston, MA 02114
(617) 918-1440

Business Hours

Monday-Friday: 9:00 am - 5:00 pm; (closed first Friday of every month and federal holidays)

RI Department of Environmental Management
235 Promenade Street
Providence, RI 02908
(401) 222-2797 Ext. 7307

Business Hours

Monday-Friday: 8:30 am - 4:00 pm

Repositories

Cumberland Public Library
1464 Diamond Hill Road
Cumberland, RI 02864
401-333-2552

Business Hours

Monday -Thursday: 9:00 am – 8:00 pm
Friday: 9:00 am – 5:00 pm
Saturday: 9:00 am – 1:00 pm

Lincoln Public Library
145 Old River Road
Lincoln, RI 02865
401-333-2422

Monday -Thursday: 9:00 am – 8:00 pm
Friday and Saturday: 9:00 am – 5:00 pm

II. SUMMARY OF SITE HISTORY, CONTAMINATION PROBLEMS AND THE SELECTED REMEDY

A. Site History and Contamination Problems

The Site encompasses over two miles of mixed industrial/residential property in the towns of Cumberland and Lincoln, Rhode Island. The Site is situated in the north-central portion of

Rhode Island along the Blackstone River and includes a portion of the Blackstone River Valley National Heritage Corridor between the Ashton Dam to the north, and the Pratt Dam to the south along the river's course. To address the various environmental issues efficiently, the Site is broken into subareas defined as Operable Units (OUs). There are currently two OUs: OU-1 (Primary Source Area), and OU-2 (J. M. Mills Landfill and the associated parcels south of OU-1), and there remains a third area under consideration known as the "potential" OU-3 area (Mackland Farm/Kelly House, north of OU-1). Please see Figure 1 in Attachment 3. OU-1 also includes the Lincoln Quinnville Well Field. The Lincoln Quinnville Well Field was used by the Town of Lincoln as a municipal water supply until 1979 when it was closed by the Rhode Island Department of Health due to the presence of chlorinated volatile organic compounds (CVOCs) in the water. EPA included the Site on the Superfund National Priorities List on September 8, 1983.

Groundwater generally flows towards the Blackstone River in the southwest direction on the Cumberland side and to the east from the Lincoln side of the river. Please see Figure 2 for a general depiction of groundwater flow within the proposed MNA Compliance Zone. For further information about the Site's geology, please see the Third Five-Year Review Report (EPA 2012).

Land uses surrounding the PAC Remediation Area include a mixture of industrial, commercial, residential, and recreational uses. The properties to the north include the former Owens Corning property (now an industrial condominium) and an undeveloped parcel referred to as the "Triangular Parcel." The area to the east (along Mendon Road) is mixed commercial/residential. The area to the immediate south (i.e., the CCL Custom Manufacturing, Inc. (CCL) Remediation Area) is predominantly industrial with some recreational uses across Martin St. The area to the west is recreational (in and along the Blackstone River) and residential across the river. The area immediately to the north and west is predominantly residential property. Drinking water is provided by the municipality, and there are no known residential wells currently operating as a drinking water supply in the Blackstone Valley Aquifer in the vicinity of OU-1.

OU-1 is comprised of two areas: the CCL Remediation Area (comprised of the CCL Source Area and CCL Downgradient Area), and the Pacific Anchor Chemical Corporation (PAC) Remediation Area (comprised of the PAC Source Area and PAC Downgradient Area. (Attachment 3 – Figure 1). The CCL Remediation Area, which includes the former CCL facility (previously known as the Site's namesake, the Peterson/Puritan, Inc. facility), is a source of volatile organic contamination.

The PAC Source Area - of greatest pertinence to this ESD - includes the property containing the former PAC facility. At this facility, PAC manufactured specialty chemical materials for use in detergents, cosmetics, agricultural, food, and general industrial chemicals. Beginning in the 1950s, the PAC facility was owned and operated by a series of chemical companies. In sequence, the owner/operators have been Universal Chemical Company, Lonza Inc., Trimont Chemicals, and Pacific Anchor Chemical Corporation. Manufacturing operations were discontinued in 2002 and currently the property is owned by Berkeley Acquisition Corporation, which leases the space to several small commercial/industrial operations.

The PAC Downgradient Area includes the property formerly owned and operated by Supervalu Operations, Inc. (as a supermarket warehouse), and is currently owned and operated by Berkeley Acquisition Corporation, which leases the space to several small commercial enterprises.

Information obtained from PAC indicates that there were three leach fields located at the PAC facility, which were in use at various times. The two main leach fields, designated as #1 and #2 in the ROD, were installed in approximately 1973 and used until 1985. The third leach field, designated as Leach field #3, is known to have been in use in 1972, and may have been installed as early as 1962, but further investigations concluded that it was a dry well with no significant contribution as a contaminant source. An important source of contamination at the PAC facility was the discharge of VOCs, primarily acetone and isopropanol, to on-site septic systems and leach fields.

The ROD states that groundwater arsenic contamination stems in part from discharge of arsenic-contaminated wastewater and dissolution of native aquifer minerals. The ROD also states that carbon-rich materials in the leach fields have the effect of creating anaerobic groundwater conditions, which mobilize naturally occurring arsenic into a dissolved state in the groundwater.

B. Response History

From 1981 through 1986, Peterson/Puritan, Inc. investigated the contamination in OU-1 and submitted its findings to EPA in two technical reports. These reports were not formally accepted as Remedial Investigation/Feasibility Study (RI/FS) reports pursuant to the NCP, but were used as supporting data in the development of subsequent studies. In September 1983, EPA listed the Site on the National Priority List (NPL).

In 1986, EPA decided to conduct the Remedial Investigation/Feasibility Study (RI/FS), and initiated field efforts in January 1987. On May 29, 1987, Peterson/Puritan, Inc. signed an Administrative Order on Consent to perform an RI/FS for the entire Site study area. In 1990, EPA divided the Site study area into the above-described OUs to promote resource efficiency in a phased approach. Consequently, a second, more focused phase of study commenced at OU-1. This study (ABB, 1993a; ABB, 1993b) included an FS that presented remedial alternatives for the CCL and PAC Remediation Areas of OU-1.

On September 30, 1993, EPA issued the OU-1 ROD, which addressed both the CCL Remediation Area and the PAC Remediation Area. On December 18, 1995, a Consent Decree (CD) between EPA and certain Settling Defendants for the performance of the remedy selected in the ROD was entered by the U.S. District Court for the District of Rhode Island. Pursuant to the CD, remedial activities in the PAC Source Area were performed by the PAC Source Area Settling Defendants, namely Lonza, Inc., and Pacific Anchor Chemical Company.

During the period between EPA's issuance of the ROD in 1993 and EPA's First Five-Year Review Report in 2002, certain Settling Defendants excavated Leach field #1 and Leach field #2 in the PAC Source Area as a primary source control measure to prevent leaching of compounds from contaminated soils into the groundwater and eliminate a source of oxidizable carbon in the aquifer (EPA, 2002). In the area north of the PAC facility, near Leach field #1, certain Settling Defendants installed an asphalt cap on soils outside of the excavation area that may have

contained additional carbon-rich materials to minimize recharge and consequent leaching of residual carbon from the vadose zone to the groundwater.

To supplement the excavation source control measure, certain Settling Defendants also installed a secondary treatment method - an innovative in-situ oxidation treatment system within the excavation area at former Leach field #1 to help reduce the mobility of arsenic in groundwater by trying to reverse the anaerobic oxygen reduced state of the groundwater (ENSR, 2000a). This oxidation system was comprised of gas transfer module used to super-oxygenate potable water that was then pumped into an infiltration gallery placed within the former leach field. In March 2000, certain Settling Defendants shut down the oxidation system upon EPA's concurrence, due to the progressive, irrevocable degradation of the gas transfer modules over the course of the system's three year operation. After determining that replacement of the system would not accelerate the attenuation of remaining dissolved arsenic from groundwater, the system was decommissioned in 2004. Around the time the oxidation treatment system was shut down, certain Settling Defendants evaluated alternative systems for enhanced source control, including in-situ soil heating, in-situ soil stabilization/solidification and in-situ chemical oxidation (ENSR, 2000b); no alternative, however, was found to be a reliable, practical and effective option for reducing arsenic concentrations in the PAC Source Area.

Pursuant to the CD and Remedial Design/Remedial Action (RD/RA) Statement of Work (SOW), EPA and the Settling Defendants created a Joint Groundwater Monitoring Program (JGWMP) in 1995 (ABB/ENSR, 1995) to monitor the groundwater quality at the Site, including the PAC Remediation Area. Between October 1995 and April 2012, twenty-three rounds of groundwater sampling were conducted at the PAC Remediation Area under the JGWMP.

On March 29, 2011, upon EPA's recommendation, Lonza submitted an Evaluation of Arsenic and TOC "Decay" in the PAC Source Area (AECOM, 2011). The document updated a previous, simpler analysis submitted to EPA in 2001 (ENSR 2001a). Per EPA's request, Lonza submitted a further revised Monitored Natural Attenuation Assessment for the PAC Source Area of the Peterson-Puritan Superfund Site on April 24, 2012 (MNA Assessment). The MNA Assessment included updated information from the 2011 round of sampling under the JGWMP (AECOM, 2012), and more distinctly addressed the relevant requirements within EPA guidance. The MNA Assessment indicates that MNA in the PAC Source Area is an appropriate remedial component, consistent with the four-tiered framework defined in the 2007 MNA Guidance for inorganics because: (1) data demonstrate that the arsenic plume is either static or shrinking; (2) an apparent rate and mechanism for attenuation has been determined, including an estimated timeframe for attenuation to meet the arsenic MCL cleanup standard for OU-1; (3) the capacity and stability of attenuation has been determined; and (4) MNA can be conducted under a monitoring plan. (USEPA, 2007a; USEPA, 2007b).

C. Summary of Selected Remedy

The ROD describes distinct components of the remedy for OU-1 for each remediation area. For the PAC Remediation Area the following remedial components were selected:

- Excavation, disposal and reconstruction of the leach fields,

- In-situ oxidation treatment of the PAC Source Area groundwater,
- Natural attenuation of the PAC Downgradient Area ground water,
- Institutional controls throughout the PAC Remediation Area,
- Focused investigation of the PAC Downgradient Area, and
- Environmental monitoring.

All of these remedies have been implemented as described above, except the deed restrictions on the four parcels in the PAC Downgradient Area, which are in progress. Also it should be noted that the oxidation treatment system was shut down in 2000 and decommissioned in 2004. Environmental monitoring of the entire PAC Remediation Area is ongoing.

III. DESCRIPTION OF SIGNIFICANT DIFFERENCES

Two aspects of the remedy selected by EPA in the ROD will be modified by this ESD:

A. More Stringent Cleanup Level for Arsenic

The ROD sets forth the selected remedy for the restoration of groundwater in OU-1. Among other cleanup levels, the ROD sets forth a cleanup standard for arsenic in groundwater at 0.05 mg/L based on EPA's promulgated MCL under the Safe Drinking Water Act at that time.

In 1996, the Safe Drinking Water Act was amended and required EPA to review drinking water standards for arsenic and propose a new MCL. Through proper rulemaking, EPA changed the MCL for arsenic in drinking water from 0.05 mg/L to 0.01 mg/L. Through this ESD, EPA incorporates this more stringent, currently promulgated standard as the cleanup level for impacted groundwater within EPA's OU-1 ROD.

The change in the arsenic cleanup level affects only the performance time line, not the protectiveness of the remedy. Institutional Controls in the form of deed restrictions, which restrict land owners' rights to withdraw and use groundwater, are completed for the properties within the PAC Source Area. (Property owners within the PAC Source area use municipal water supplies.) These deed restrictions will help ensure that the remedy will remain protective in the short term within the PAC Source Area until the remedy is complete.

B. Augmentation of Enhanced Source Control for PAC Source Area with MNA

In the ROD, EPA selected enhanced source control as the remedial approach for the PAC Source Area. The primary treatment method under this approach was the excavation and disposal of two leach fields and associated soils located in the PAC Source Area. According to the ROD, the leach field soils were a source of arsenic contamination and a source of carbon-rich materials causing groundwater contamination; the carbon source had the effect of making groundwater anaerobic, thus mobilizing naturally occurring arsenic in bedrock and soils into groundwater. The excavation component of the remedy was enhanced with a secondary treatment method, an innovative in-situ oxidation treatment system, to help reduce the mobility of the arsenic in the

groundwater from the leach field areas. Enhanced source control was chosen to limit the effect of the arsenic contamination and carbon-rich materials, and encourage the attenuation of dissolved arsenic from groundwater back to its adsorbed state in overburden soils.

Arsenic levels in PAC Source Area groundwater have been reduced and continue to attenuate, but concentrations remain above cleanup levels at the present time. By this ESD, EPA is augmenting its remedial approach to the PAC Source Area to require monitored natural attenuation (MNA) in accordance with current EPA guidance to address the remaining arsenic concentrations in the PAC Source Area and achieve groundwater cleanup levels. MNA, currently the remedial component for the PAC Downgradient Area, will be included as a remedial component for the PAC Source Area.

1. Rationale

Pursuant to a 1995 Consent Decree, certain Settling Defendants implemented the selected remedy in the PAC Source Area, including full excavation of physical evidence of the leach fields, and operation of the oxidation system from 1997 to 2000, when the system was shut down due to the progressive, irrevocable degradation of the system under normal operation. After determining that replacement of the system would not accelerate the attenuation of remaining dissolved arsenic from groundwater, the system was decommissioned in 2004. According to EPA's First Five-Year Review Report, the oxidation treatment system was researched and recommended by certain Settling Defendants as an acceptable alternative and was considered by EPA to be an innovative technology in the treatment of arsenic concentrations in groundwater. EPA chose the oxidation treatment system as an enhancement of the primary treatment method, excavation source control, which has been fully implemented.

Significant amounts of data have been collected under the JGWMP since 1995. Data from the monitoring indicate that (1) biodegradation of organic carbon is occurring; (2) natural attenuation is occurring; and (3) arsenic concentrations in the groundwater at the PAC Source Area do not currently pose a threat to human health or the environment because no one in the vicinity of the PAC Source Area is drinking the groundwater and Institutional Controls in the form of deed restrictions limiting its use, are effectively in place within the PAC Source Area. (AECOM 2012). Please see the MNA Assessment (2012) and the MNA Evaluation (2011) in Attachment 2.

The MNA Assessment makes use of the vast JGWMP dataset to support the use of MNA as a remedial component within the PAC Source Area. The MNA Assessment indicates that MNA in the PAC Source Area is consistent with the four-tiered framework defined in the 2007 MNA Guidance for inorganics. First, the data generally demonstrate that the arsenic plume is either static or shrinking. Second, a rate and mechanism for attenuation has been determined. Organic carbon, which creates anaerobic/reduced oxygen conditions, thus liberating arsenic from subsurface soils, is naturally attenuating, and over time liberated arsenic will precipitate out of its dissolved state. Based on data trends, this natural attenuation process is expected to achieve the MCL cleanup standard within 15 – 29 years in the PAC Source Area. Third, the capacity and stability of the PAC Source Area for continued attenuation to achieve the arsenic MCL cleanup standard is apparent. Fourth, as described in greater detail below, MNA can be conducted under

an enhanced and updated version of the JGWMP, complete with a contingency plan in the case of MNA failure.

As part of EPA's Third Five Year Review (EPA 2012), the United States Army Corps of Engineers (USACE) independently evaluated the data used to support the MNA Assessment. The USACE concluded that the data support a finding of natural attenuation of arsenic in the PAC Source Area. The data show trends fitting the conceptual model in which dissolved arsenic will remain stable or decrease as the reducing conditions found in the aquifer within the Site become ameliorated (*i.e.*, organic carbon concentrations leached from past leach field use diminishes, while groundwater flowing into and throughout the Site maintains adequate dissolved oxygen levels). See Section 6.6.3.3. of EPA 2012.

2. MNA Plan

As described above, OU-1 has been monitored at least annually, except in 2005 and 2006, since 1995 under the JGWMP. Under this modified remedy, EPA will use and build upon the current JGWMP to support MNA within the PAC Source Area. Figure 2 in Attachment 3 shows the current JGWMP network of monitoring wells in OU-1 within the vicinity of the PAC Source and Downgradient Areas. It also shows the boundaries of what will constitute an MNA Compliance Zone. MNA Compliance Zone boundaries were established by connecting the wells at the periphery of the current JGWMP network for the PAC Remediation Area. The current wells within this Zone, and any newly required monitoring wells, will be used to monitor the progress of the MNA remedy.

A revised JGWMP for the PAC Remediation Area will include several groundwater monitoring parameters that will serve to assess arsenic attenuation patterns in the future. The annual groundwater monitoring parameters, will include TOC, arsenic (including speciation per EPA guidance 2007b), ferrous iron (Fe+2), total iron, dissolved oxygen, pH, and oxidation-reduction potential (ORP). Sampling conducted in 2011, included the annual parameters noted above, plus dissolved methane, sulfate, nitrate, manganese, alkalinity, and carbon dioxide, which provide additional information on the redox state of the aquifer (EPA, 2012). All of the above-listed parameters are recommended for continued measurement of MNA at wells within the MNA Compliance Zone. The parameter list and sampling frequency will be further refined and incorporated into a revised JGWMP for the Site.

In addition to the above-listed JGWMP parameters, the revised JGWMP shall also include, at a minimum, a detailed description of what constitutes the triggers for re-evaluation of the adequacy of the MNA (*e.g.*, upward trends in arsenic and TOC concentrations in groundwater, and/or a decrease in the groundwater's dissolved oxygen). Furthermore, it is critical that such triggers include changes in groundwater chemistry that may lead to re-mobilization of attenuated arsenic. Examples of such changes are increases in the concentration of phosphate along with changes in pH, and/or increases in the concentration of dissolved iron or sulfate. Many of the identified parameter fluctuations may occur prior to changes in soluble arsenic, thus they can provide an early warning of MNA failure (EPA 2007b).

At each five-year review, the progress of the MNA remedy for arsenic shall be consistently evaluated throughout the PAC Remediation Area. Thus, PAC Remediation Area wells shall be

statistically evaluated according to EPA guidance (Wilson, 2011) to ensure that: (1) the MNA remedy continues to effectively reduce arsenic concentrations and (2) the time to cleanup for arsenic at the PAC Remediation Area wells does not increase appreciably from current expectations.

If, after a reasonable period of time, monitoring data indicate that the time for natural attenuation to achieve the MCL cleanup standard throughout the MNA Compliance Zone may exceed the 15 – 29 year estimated cleanup time frame, EPA may require additional response actions, as necessary, to achieve cleanup standards.

C. SUPPORT AGENCY COMMENTS

RIDEM participated with EPA in developing the changes to the selected remedy described herein and was consulted during the preparation of this ESD. The State's comments have been incorporated into the ESD, as applicable.

D. STATUTORY DETERMINATIONS

In accordance with Section 121 of CERCLA, EPA, in consultation with RIDEM, has determined that the modified remedy remains protective of human health and the environment, complies with all Federal and State requirements that are applicable or relevant and appropriate to this remedial action, meets the remedial action objectives specified in the ROD, and is cost-effective.

E. PUBLIC PARTICIPATION COMPLIANCE

In accordance with Section 117(d) of CERCLA and Section 300.825(a) of the NCP, this ESD and supporting documentation shall become part of the Administrative Record for the Site, which is available for public review at the locations, and times listed in Section I (E) above. A public notice, which summarizes the modifications to the remedy as set forth in the ESD shall be published in a local newspaper of general circulation following the signing of this ESD.

F. APPROVAL OF EXPLANATION OF SIGNIFICANT DIFFERENCES

So approved:

July 10, 2013

James T. Owens III, Director
Office of Site Remediation and Restoration

Date

ATTACHMENT 1

REFERENCES

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ATTACHMENT 2

MNA ASSESSMENT (2012) AND MNA EVALUATION (2011), SUBMITTED BY LONZA, INC.

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April 24, 2012

Mr. Larry Brill
Branch Chief, OSRR Branch I
United States Environmental Protection Agency – Region I
5 Post Office Square - Suite 100
Boston, MA 02109-3912

Subject: Monitored Natural Attenuation Assessment for PAC Source Area of the Peterson-Puritan Superfund Site
Peterson/Puritan, Inc. Superfund Site, OU1
Cumberland and Lincoln, Rhode Island

Dear Mr. Brill,

The United States Environmental Protection Agency (USEPA) has requested that Lonza update the evaluation submitted on March 29, 2011 concerning the Prediction of MNA Effectiveness at the PAC Source Area of the Peterson-Puritan Superfund Site to Support Potential Remedy of Monitored Natural Attenuation (MNA) to include the most recent sampling results from April 2011 and to address relevant elements from the 1999 and 2007 USEPA MNA Guidance.

The attached report responds to USEPA's request. The body of the report considers the four tiers of evidence defined by USEPA's 2007 MNA Guidance for inorganic compounds. Lonza's 2011 data assessment is updated with the most recently available data to support Tier II of the guidance. The updated data analysis is provided as an appendix to the report and is generally consistent with Lonza's findings in 2011.

The report concludes that implementation of MNA in the PAC Source Area is an appropriate remedy as it is consistent with the four-tiered framework defined in the 2007 MNA Guidance for inorganics (USEPA, 2007a; USEPA, 2007b) as follows:

- The PAC Source Area has been characterized and it has been demonstrated that arsenic concentrations are generally stable or decreasing (Tier I);
- The apparent rate and mechanism of attenuation have been demonstrated (Tier II);
- The capacity of the aquifer to continue and sustain attenuation has been shown (Tier III); and
- A monitoring plan, along with triggers for reevaluation, has been developed (Tier IV).

We look forward to discussing this assessment and working with USEPA to implement an MNA remedy for the PAC Source Area. Please call us if you have any questions or comments on the attached document.

Yours sincerely,

Mark Gerath
Technical Director

Carolyn K. Scott
Senior Project Manager

cc: Mike Jasinski, USEPA
David Newton, USEPA
Ruthann Sherman, USEPA
John Hultgren, USEPA
David Freeman, Paul Hastings LLP
Paul Sieracki, Lonza Inc.
Project File

Monitored Natural Attenuation Assessment for PAC Source Area of the Peterson-Puritan Superfund Site

Summary

This assessment updates the March 27, 2011 Assessment of Arsenic and Total Organic Carbon (TOC) "Decay" in the PAC Source Area at the Peterson/Puritan Superfund Site in Cumberland, RI (AECOM, 2011c). For the 2011 assessment, temporal trends in organic carbon and arsenic were evaluated in data collected over 15 years in several monitoring wells to evaluate the potential for natural processes to affect Monitored Natural Attenuation (MNA) of arsenic concentrations elevated above the Maximum Contaminant Level (MCL) in groundwater in the PAC Source Area. This update includes the most recent sampling results from April 2011 (Joint Groundwater Monitoring Program [JGWMP] Round 22). This report also evaluates the available site-related data and information in the context of the relevant elements of the 1999 and 2007 United Stated Environmental Protection Agency (USEPA) guidance to demonstrate consistency of the MNA remedy for the PAC Source Area at the Peterson/Puritan Superfund Site with that guidance (USEPA, 1999; USEPA, 2007a; USEPA, 2007b).

The 1999 USEPA guidance states that MNA may, under certain conditions, effectively reduce dissolved concentrations in groundwater.

> "*Natural attenuation processes are typically occurring at all sites, but to varying degrees of effectiveness depending on the types and concentrations of contaminants present and the physical, chemical, and biological characteristics of the soil and groundwater. Natural attenuation processes may reduce the potential risk posed by site contaminants in three ways:*
>
> > *(1) Transformation of contaminant(s) to a less toxic form through destructive processes such as biodegradation or abiotic transformations;*
> > *(2) Reduction of contaminant concentrations whereby potential exposure levels may be reduced; and*
> > *(3) Reduction of contaminant mobility and bioavailability through sorption onto the soil or rock matrix.*
>
> *Where conditions are favorable, natural attenuation processes may reduce contaminant mass or concentration at sufficiently rapid rates to be integrated into a site's soil or groundwater remedy*" (USEPA, 1999).

As shown below under the criteria set out in the USEPA MNA guidance for inorganics (USEPA, 2007a), MNA is occurring at the PAC Source Area. The geochemical processes occurring in the PAC Source Area are reducing arsenic concentrations in the groundwater through mechanisms that are well understood and within reasonable timeframes, indicating the appropriateness of an MNA remedy for the PAC Source Area.

Background

On September 30, 1993, USEPA documented the arsenic cleanup remedy in a Record of Decision (ROD) (USEPA, 1993). The remedial actions selected for the PAC Source Area were excavation and removal of contaminated soils from leachfields in the PAC Source Area (ENSR, 1997); in-situ oxidation treatment in the form of an Oxidant Delivery System (ODS) to reduce the mobility of the arsenic in groundwater migrating from the leachfields in the PAC Source Area; institutional controls; and environmental monitoring. These remedies have been implemented, with the environmental monitoring ongoing. Based on data collected in the PAC Source Area, it has been determined that: (a) the operation of the ODS had only a localized and transient effect on arsenic levels in the aquifer; (b) biodegradation of organic carbon is occurring irrespective of ODS operation; (c) natural attenuation is occurring in the absence of ODS operation; (d) arsenic concentrations in the groundwater at the PAC Source Area did not and do not currently pose a threat to human health or the environment and are not likely to pose such a threat in the future; and (e) operation of the ODS was not a cost-effective method for arsenic remediation at the PAC Source Area (AECOM, 2011b).

As documented in the first Five-Year Review, "*Further understanding of aquifer geochemistry, upgradient water quality, and residual carbon at the PAC Source Area has changed significantly since remedy selection and design*" (USEPA, 2002). These changes have affected the expected efficacy of the remediation and remediation time estimates for arsenic in the PAC Source Area. The ROD states that groundwater arsenic contamination stems from discharge of arsenic-contaminated wastewater and dissolution of native aquifer minerals. Information collected since the ROD was issued indicates that arsenic groundwater contamination is solely attributable to dissolution of aquifer minerals, and the detection of arsenic in wastewater was an artifact of an inferior analytical method that yielded unreliable data and false positive analytical results (ENSR, 2001).

In addition, "*Since preparation of the ROD in 1993, considerable knowledge has been gained on the occurrence and transport of arsenic in groundwater. For example, the book "Arsenic in Ground Water" (Welch and Stollenwerk 2003) provides useful information that was not available in 1993. Information in this book and related studies in New England (Stollenwerk and Colman 2004) indicate that arsenic can be widely distributed in groundwater systems and tends to persist for a very long time after it dissolves in groundwater" (USEPA, 2007c).*

The geochemistry describing mobilization of arsenic from aquifer sediments is better understood than at the time of remedy selection. Biodegradation of organic carbon leads to consumption of oxygen, as well as other terminal electron acceptors, and reduced aquifer conditions. Dissolution of iron hydroxides in reduced aquifers liberates arsenic, which is naturally associated with iron hydroxide minerals. Furthermore, sources of organic carbon, which create reducing conditions in the aquifer, are now known (or suspected) to exist in numerous locations (e.g., release of hydrocarbons at the LukOil site to the east of the PAC Source Area [AECOM, 2011a; AECOM, 2011b]).

Based upon discussions with USEPA, including a technical call with USEPA's expert in arsenic dynamics, Dr. Robert Ford, on October 8, 2010 and calls between USEPA and Settling Defendants' attorneys on February 23, 2011 and March 3, 2011, the site conditions appear to support an application for MNA as the remedy for arsenic.

Implementation of MNA

USEPA guidance (USEPA, 2007a; USEPA, 2007b) provides a four-tiered framework by which to evaluate site data in a step-wise process to show that MNA is a viable remedy for the site. The four tiers include the following objectives:

- Demonstration, through site characterization, that the plume is static or shrinking (Tier I);
- Determination of the apparent rate and mechanism of attenuation (Tier II);
- Determination of the system capacity and stability of attenuation (Tier III); and
- Establishment of a monitoring plan (Tier IV).

Support for implementation of MNA in the PAC Source Area is presented below within the four-tiered framework. The re-assessed rates of arsenic attenuation (i.e., the update to AECOM, 2011c) are provided as part of the Tier II assessment.

Tier I

Under this tier of data assessment, USEPA (2007a) asks that the site characterization data be used to evaluate whether the plume is static or shrinking. The objective under Tier I is "*to eliminate sites where site characterization indicates that the groundwater plume is continuing to expand in aerial or vertical extent*" and "*demonstrate active contaminant removal from ground water*" (USEPA, 2007a).

Site characterization data for the PAC Source Area has been collected since the early 1990s. Numerous soil and groundwater samples have been analyzed as part of the Remedial Investigation, excavation of the PAC Source Area leachfields, 22 rounds of JGWMP groundwater monitoring, and groundwater

monitoring associated with the three years of ODS operation. Data from these investigations and monitoring are provided in a variety of reports, including the Remedial Investigation Report (ABB-ES, 1993), Remedial Action Report (ENSR, 1998a), MNA Report (ENSR, 2000a), JGWMP Report (ENSR, 2000c) and annual JGWMP submittals, and are summarized in the Settling Defendants' Five Year Review Reports (ENSR, 2001; ENSR, 2007; AECOM, 2011b). The extensive and lengthy data record indicates that the arsenic plume is not expanding, that arsenic concentrations at most wells have declined, and that the concentrations in some wells have declined to below the MCL.

Groundwater flow as measured during the JGWMP shows consistent results between rounds and has been modeled by USEPA's contractor. The general direction of groundwater flow is southwest across the PAC Source Area towards the Blackstone River followed by a more southerly trend in the PAC Downgradient Area. Figures depicting groundwater flow at the site may be found in the JGWMP reports described above.

Demonstration of stable or declining arsenic concentrations is provided through the data collected as part of the JGWMP, established in 1995 to meet the requirement for environmental monitoring specified in the ROD. To date, 22 rounds of groundwater sampling (between October 1995 and April 2011) have been conducted for the PAC Source Area for constituents as specified in the ROD and Remedial Design/Remedial Action Statement of Work. This ongoing effort has included parameters appropriate for evaluating the presence and fate of arsenic in groundwater. Initially, isopropyl alcohol and acetone, potential sources of organic carbon, were included as analytes in the JGWMP; however, these constituents are not currently monitored as they have not been detected in groundwater for many years.

Current JGWMP groundwater monitoring parameters will serve to assess arsenic attenuation patterns in the future. The annual groundwater monitoring parameters (as described under the Tier IV discussion, below) include TOC, arsenic, iron (Fe) (II), dissolved oxygen, pH, and oxygen reduction potential (ORP). Analytes for the five-year sampling round include the annual parameters plus methane, sulfate, nitrate, manganese, and carbon dioxide, which provide additional information on the redox state in the monitoring wells.

Data for the JGWMP wells, as provided in the reports mentioned above, show that arsenic concentrations in groundwater for most of the wells have either a declining or stable trend. (See Appendix 1 for a complete set of graphs showing arsenic concentrations in PAC Source Area-related wells as measured during the JGWMP.) As a demonstration that the plume is not expanding, the arsenic concentration in the well at the downgradient edge of the PAC Source Area (see Figure 1), shows a generally declining trend in arsenic concentrations over time.

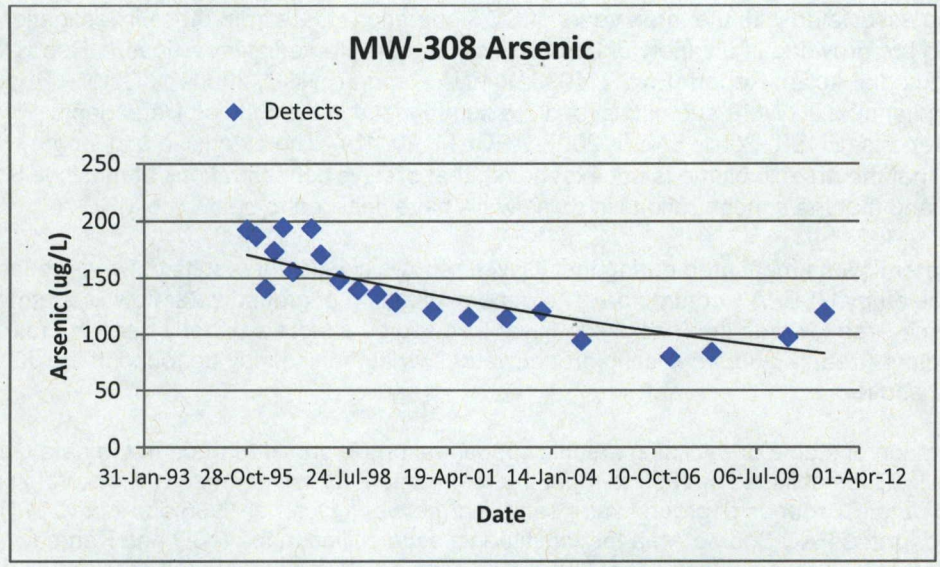

Figure 1: Trend in Arsenic Concentration at MW-308

For several of the JGWMP wells shown in Appendix 1, there is no clear trend or a slightly increasing trend in arsenic concentrations; in each of these wells, methanogenic conditions exist (methane levels over 1,000 ug/l), including the fact that iron hydroxides that control arsenic solubility have yet to re-form (as discussed under Tier II). Such behavior is consistent with the conceptual model of arsenic behavior at the site: the arsenic concentration is expected to be relatively stable until the aquifer becomes more oxidized (and the mass of reduced materials are exhausted) and the iron and manganese hydroxides reform, co-precipitating arsenic. Thus, the concentration of arsenic is expected to behave in a "binary" fashion: it will persist until the controlling solids reform, and then it should decline rapidly.

As discussed below, such behavior has been observed at the site, and the lower concentration of arsenic has been maintained (see the discussion of the Tier III line of evidence). This anticipated behavior is consistent with the literature and with USEPA's review of arsenic at the PAC Source Area. As stated in USEPA Second Five Year Review (USEPA, 2007c) with regard to PAC Source Area arsenic concentrations:

> "*The apparent stable concentration of arsenic…is consistent with results from column studies on arsenic transport reported (Stollenwerk and Colman 2004), where numerous pore volume flushes with oxygenated water were required to reduce arsenic concentrations to 10 µg/L. Furthermore, a nearly stable plume configuration is predictable on the basis of transport models for phosphorous, which has similar transport properties to arsenic (Colman, 2004; John Colman, U.S. Geological Survey, verbal communication, July 2007).*"

In summary, the stable or decreasing trends in arsenic concentrations and groundwater flow data support a static to shrinking area affected by arsenic, satisfying the requirements of Tier I. Based on the results of the site characterization data demonstrating that the arsenic concentrations are generally stable to declining (contaminant removal from groundwater), the PAC Source Area is appropriate for evaluation under Tier II for arsenic attenuation.

Tier II

Under Tier II of the MNA Guidance for inorganics, the mechanism(s) and apparent rate of attenuation should be determined (USEPA, 2007a). The objective under Tier II is "*to eliminate sites where further analysis shows that attenuation rates are insufficient for attaining cleanup objectives estimated for the site within a timeframe that is reasonable compared to other remedial alternatives*" (USEPA, 2007a).

In the following discussion, the geochemical mechanism of arsenic liberation and MNA is defined based on the literature. Site-specific characterization of the redox status of each monitoring well is then considered as it relates to the potential mobility of arsenic in the context of the geochemical mechanisms. This data evaluation provides evidence that the mechanisms are understood and provides a basis for estimating the overall rate of MNA for arsenic across the PAC Source Area. This section also provides a summary of the estimated rate of MNA for arsenic including estimation of "half-lives" for arsenic concentration. The rates presented here were originally presented in the March 27, 2011 Assessment of Arsenic and Total Organic Carbon (TOC) "Decay" in the PAC Source Area at the Peterson/Puritan Superfund Site in Cumberland, RI (AECOM, 2011) and have been updated with the 2011 data.

The mechanism for attenuation is based on the conceptual site model developed for the site. As presented in the Second USEPA Five-Year Review (USEPA, 2007c),

> "*The conceptual model that has been presented for arsenic in groundwater involves local geochemical processes that cause reducing conditions. The reducing conditions, in turn, dissolve arsenic that is present naturally in the rock and sediments. Although analyses for arsenic in overburden soils have not been performed recently at the PAC Source Area, analytical results for soils and bedrock at the LukOil gas station indicate that arsenic is present in both media. Elevated arsenic concentrations in water from wells near operable unit 2 (J.M. Mills landfill) (ARCADIS, 2007) further supports the concept of a natural source for arsenic in valley-fill sediments. Other Site features that could cause the mobilization of arsenic might include release of BTEX chemicals and alteration of ground-water recharge patterns such as by construction of impermeable surfaces.*"

This process of reductive dissolution of arsenic is described in the MNA guidance for arsenic (USEPA, 2007b), where "*Houndslow (1980) and Kinniburge (2002) provide an assessment of geochemical triggers that may lead to arsenic mobilization in subsurface systems.*" These include the trigger occurring in the PAC Source Area: "*desorption/dissolution due to a change to a reducing chemical environment*" (USEPA, 2007b).

As discussed in the ODS Report (ENSR, 2000b), the addition of biodegradable carbon to the aquifer starts the process leading to the release of arsenic through reductive dissolution. The activity of microorganisms in aquifers is usually limited by a lack of carbon. Addition of biodegradable carbon stimulates microbial growth and utilization of oxygen. When oxygen is depleted, microorganisms utilize alternative electron acceptors such as iron and manganese in order to continue degrading available carbon (Table 1). As iron oxides dissolve upon reduction, adsorbed and co-precipitated arsenate is released into solution (Smith, 1998; Massacheleyn, 1991). In addition, the arsenic itself is reduced from arsenic (As)(V) to As(III), which has a lower tendency to bind with mineral surfaces than does As(V).

MICROBIAL ELECTRON ACCEPTORS			
Electron Acceptor	**Oxidized Species (oxidation state)**	**Reduced Species (oxidation state)**	**Water Quality Indicator**
oxygen	O_2 (0)	H_2O (-2)	Dissolved oxygen (DO) present
nitrogen	NO_3^- (+5)	NO_2^- (+3)	low nitrate ([a])
manganese	Mn^{+4} (+4)	Mn^{+2} (+2)	high soluble manganese (Mn)
iron	Fe^{+3} (+3)	Fe^{+2} (+2)	high soluble Fe
sulfur	SO_4^{2-} (+6)	H_2S (-2)	low sulfate, high sulfide([b])
carbon	CO_2 (+4)	CH_4 (-4)	high methane

(a) Subsequent reactions may convert nitrite to nitrogen gas or other reduced nitrogen species.
(b) Sulfide may form insoluble precipitates with iron and arsenic lowering aqueous sulfide concentrations.

More Reducing ↓

Table 1: Indicators of Groundwater Redox Status (ENSR, 2000a)

At the PAC Source Area, at least three septic systems, various sumps and dry wells, underground disposal of boiler blowdown discharge, and the accidental release of isopropanol to the subsurface all added biodegradable carbon to the aquifer; these releases initiated the series of bio-geochemical processes leading to arsenic concentrations in groundwater above the MCL (ENSR, 1995; ENSR, 1996; Bates, 1996, ENSR, 1998b). In addition, there is evidence of other releases of organic substances to the subsurface surrounding the PAC Property (ENSR, 2000a), including the LukOil gasoline spill east (upgradient) of the Peterson/Puritan site in the 1990s, effects of which were seen in PAC Source Area wells (peaks in benzene and arsenic concentrations in between 2001 and 2003) (ENSR, 2007; USEPA, 2007c).

These primary sources of reducing agents led to production of other reducing agents (e.g., reduced iron, sulfide) which must be oxidized before the iron and manganese hydroxides can re-form and reduce arsenic concentrations. As described above, under the conceptual site model of arsenic mobilization in the subsurface, organic carbon present in soils and groundwater results in the depletion of oxygen and the subsequent geochemical reduction of the aquifer. Under reducing conditions, iron and manganese oxides are reduced and dissolved to liberate co-precipitated arsenic. To reverse these conditions, organic carbon must be exhausted, followed by the reintroduction of oxygen, the reformation of iron and manganese hydroxides and the co-precipitation of arsenic.

The literature on similar settings (e.g., Delemos et al., 2006; Welch et al., 2000; Kelly et al., 2005; Smedley and Kinniburgh, 2002) and site-specific data are consistent in showing that arsenic is present at elevated concentrations in groundwater only when manganese and iron are reduced (i.e., iron and manganese hydroxides become unstable, leading to soluble manganese and iron in groundwater). This conceptual model has been used to construct a strategy for characterizing groundwater quality relative to its oxidation-reduction status as well as likely presence of arsenic at elevated concentrations (ENSR, 2000a). To determine the redox state of the aquifer at individual wells, the concentrations of relevant geochemical parameters were compared with their concentrations at wells which did not appear to be affected by groundwater contaminants; these wells are referred to as "unimpacted wells."

Table 2 provides a summary of the evaluation of groundwater quality used to define the redox status of each well and assess the potential for the elevation of arsenic concentration. Based on this evaluation, wells were categorized as shown in Table 3 for data collected up to 1999 (ENSR, 2000a). In some cases, the historical trends in a parameter's concentration is indicated by an arrow indicating an increasing or decreasing trend based on the Mann-Kendall test. The arsenic concentration observed in the various on-site wells correlated well with the presence of reducing conditions (i.e., manganese reducing or more reduced) and is shown in Figure 2.

Well Type - Estimated Redox State	MNA Rating Criteria							
	ORP depressed (likely ORP)	DO (meter) depressed (fraction < 1 mg/L)[a]	Nitrate depressed	Mn elevated (magnitude of conc.)	Fe(II) elevated	Sulfate depressed (value)	Methane (conc. ug/L)	Arsenic elevated
aerobic	no (>350)	no	no	no	no	no, 30	ns	no
aerobic, oxygen low compared to background	no (>350)	yes, 0/4	no	yes, ug/L	no	no, 30	0.4	no
nitrate-reducing	no (>200)	yes, 2/4	yes	yes, ug/L	no	no, 30	30	no
Mn-reducing	no (>200)	yes, 4/4	yes	yes, mg/L	no	no, 30	30	1/4
iron-reducing	yes (<300)	yes, 4/4	yes	yes, mg/L	yes	no, 30	30	yes
sulfate-reducing	yes (<300)	yes, 4/4	yes	yes, mg/L	yes	yes, 5U	30	yes
methanogenic	yes (<150)	yes, 4/4	yes	yes, mg/L	yes	yes, 7	700	yes
iron or sulfate-reducing[c]	no (320)	yes, 4/4	yes	ns	ns	yes, 11	ns	yes
≥ Mn-reducing[b]	no (290)	yes, 4/4	ns	ns	no	no, 30	ns	1/4
≤ sulfate-reducing[b]	yes (<300)	yes, 4/4	yes	yes, mg/L	yes	yes, 5U	ns	yes
≤ iron-reducing[b]	yes (180)	yes, 4/4	yes	yes, mg/L	yes	ns	ns	yes

ns: parameter not measured or data rejected during validation
(a) Fraction of results less than 1 mg/L DO (meter).
(b) Redox state uncertain due to few results &/or because results unavailable for all geochemical parameters.
(c) Redox state uncertain because geochemical parameters are not consistent with a particular redox state. (In this example ORP is high for sulfate-reducing conditions and sulfate concentration is not as depressed as in other wells. Since arsenic is elevated and nitrate depressed, probably at least iron-reducing and may be sulfate-reducing. High ORP reading could be an error.)

Table 2: Groundwater Quality Ranking Criteria (ENSR, 2000a)

Well	ORP depressed	DO(meter) depressed (fraction < 1 mg/L)[a]	Nitrate depressed	Mn elevated (magnitude of conc.)	Fe(II) elevated	Sulfate depressed (value)	Methane (conc. ug/L)	Arsenic elevated	Estimated Redox State
AD-1	yes ↑	yes, 14/15 ↑	yes	ns	20/23	no	ns	21/22	iron-reducing
AD-2	yes ↓	yes, 6/8	yes	ns	yes ↓	yes, 5U	ns	yes	≤ sulfate-reducing[b]
AW-2	no	yes, 1/3	ns	yes, mg/L	no	ns	ns	2/8 ↓	≥ Mn-reducing[b]
AW-3	yes	yes, 7/8	yes	yes, mg//L	yes ↓	yes, 5.7	ns	yes	≤ sulfate-reducing[b]
DW-1	yes	yes, 3/3	no	yes, ug/L	yes	no	ns	yes	iron-reducing
DW-2	yes	yes, 3/3	yes	yes, mg/L	yes ↓	yes, 10.7	ns	yes	≤ sulfate-reducing[b]
DW-3	yes	yes, 2/3	yes	yes, mg/L	yes ↓	yes, 16.6	ns	1/5	iron-reducing
MW-101C	ns	ns	ns	yes, ug/L	no	ns	ns	4/5	≥ Mn-reducing[b]
MW-302A	7/8	yes, 6/7	yes	yes, mg/L	yes	yes, 5U	ns	yes ↑	≤ sulfate-reducing[b]
MW-302B	yes ↑	yes, 7/7	yes	yes, mg/L	yes	yes, 5U	ns	yes	≤ sulfate-reducing[b]
MW-303	yes ↑	yes, 6/8	yes	yes, mg/L	yes	yes, 5U	ns	yes	≤ sulfate-reducing[b]
MW-304	7/8	yes, 6/8 ↓	no	yes, mg/L	11/12	yes, 5.5	ns	yes ↓	iron or sulfate-reducing[b]
MW-307	No	yes, 1/5	ns	yes, ug/L	no	ns	ns	no	aerobic, oxygen low compared to background[b]
MW-308	Yes	yes, 8/9	yes	yes, mg/L	yes	yes, 10U	ns	yes ↓	≤ sulfate-reducing[b]
MW-401	no	yes, 0/2	ns	yes, ug/L	no	ns	ns	1/4	≥ nitrate-reducing[b]
MW-407	no	no	ns	yes, mg/L	no	ns	ns	no	aerobic

ns: parameter not measured or data rejected during validation
Trends identified in the JGWMP Report for ORP, DO (meter), Fe(II) are indicated by ↑ and ↓ arrows.
(a) Fraction of results less than 1 mg/L DO (meter).
(b) Redox state uncertain due to few results &/or because results unavailable for all geochemical parameters.

Table 3: Estimated Aquifer Redox State 1999 (ENSR, 2000a)

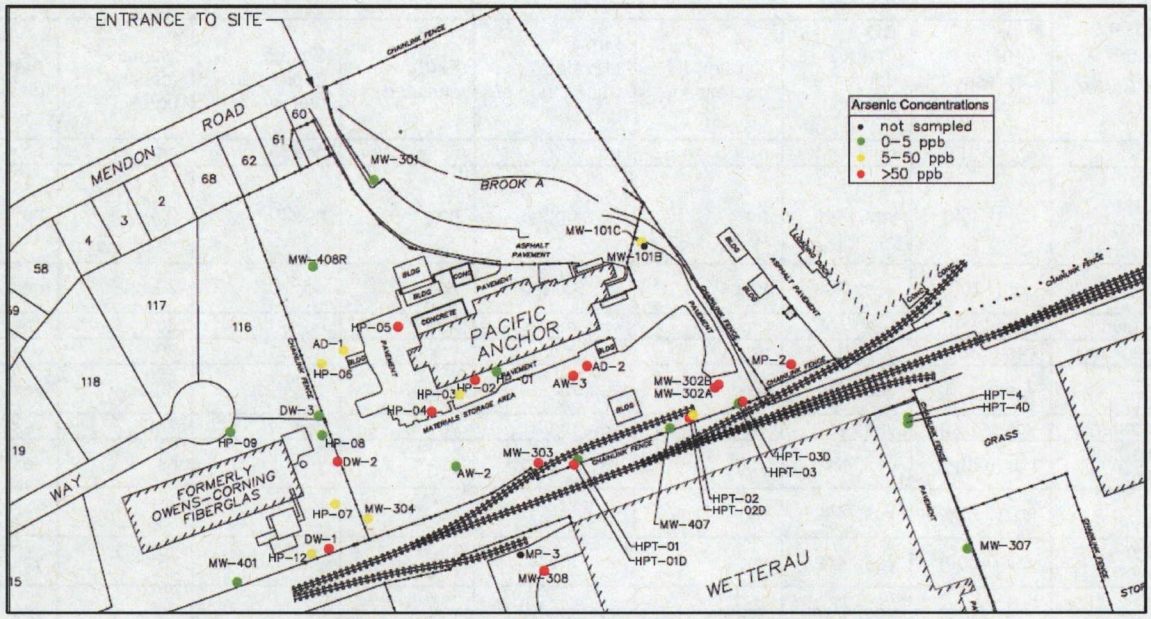

Figure 2: Arsenic Concentrations 1999

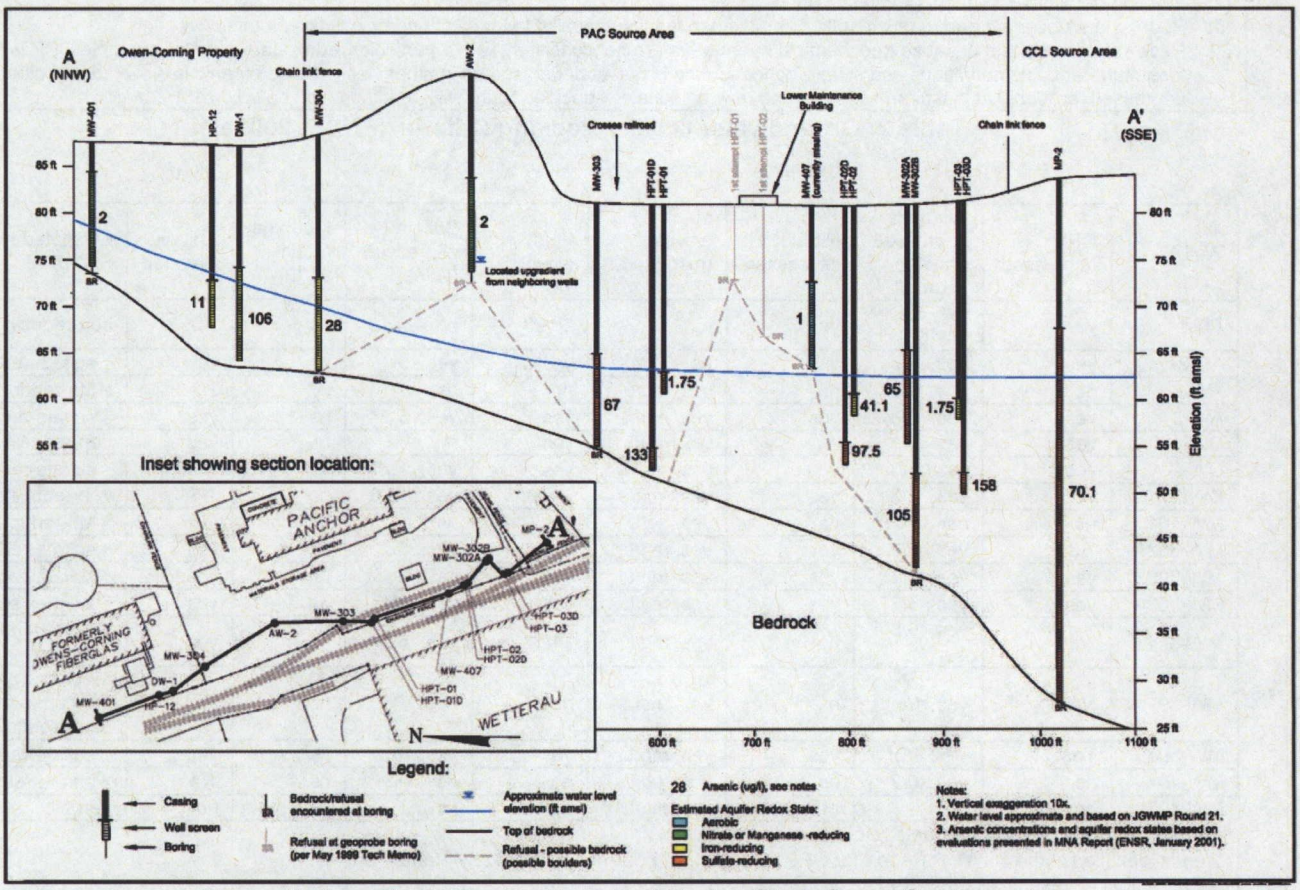

Figure 3: Arsenic Concentrations and Redox State Cross Section

Figure 3 presents the geochemical and arsenic data (ENSR, 2000a) as a cross-section constructed near the lower edge of the PAC Source Area. In this figure, the groundwater redox state and arsenic

concentration are both included as labels on the wells' screened intervals. Generally, elevated arsenic concentrations are associated with iron- and sulfate-reducing conditions[1].

Using the ENSR (2000a) assessment methods, wells were re-evaluated for their redox state based on data collected in 2008. See Table 4 and Figure 4.

Well	ORP depressed (<250)	DO(meter) depressed (<6.2)	Nitrate depressed (<6.2)	Mn elevated	Fe(II) elevated (>2.5)	Sulfate depressed (<27 (<11))	Methane (conc. ug/L)	Arsenic elevated (>4)	2008 Estimated Redox State
AD-1	80.4	1.32	2.2	NA	0	31	not analyzed	2.13	nitrate-reducing
AD-2	NA	NA	0.22 J	NA	5	5	5140	178	methanogenic
AW-1RR	-103.3	0.23	R	NA	15	22	Ns	43.4	iron-reducing
DW-1	-38.1	1.18	0.97	NA	7.5	31	44.7	87.5	iron-reducing
DW-2	-74.4	-0.08	0.1 U	NA	20	26	183	201	methanogenic
DW-3	58.5	0.37	0.32	NA	1	27	10.4	1.67	nitrate-reducing
MP-2	-136.3	0.09	0.1 U	NA	45	1.5	218	65.4	methanogenic
MW-302A	-63.3	0.16	0.1 UJ	NA	NR	1 U	627	66.5	methanogenic
MW-302B	-91.4	0.05	0.1 UJ	NA	25	1 U	542	55.6	methanogenic
MW-304	136.9	6.02	1.4	NA	0	23	NA	2.78	≥ nitrate-reducing
MW-307	147.4	0.22	1.2	NA	0	9.9	55.4	0.5 U	≥nitrate-reducing
MW-308	-69.4	0.15	0.1 U	NA	15	17	1010	85.1	methanogenic
MW-401	123.3	5.65	2.1	NA	0	21	0.3 U	2.84	≥ nitrate-reducing

Table 4: Estimated Aquifer Redox State 2008

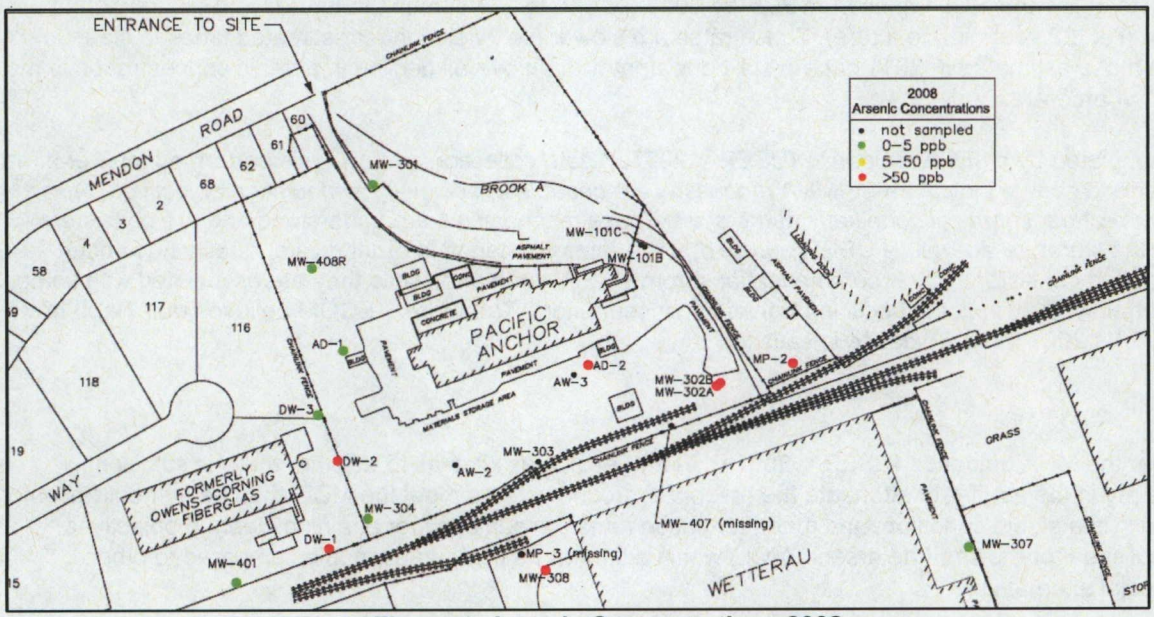

Figure 4: Arsenic Concentrations 2008

Comparisons between 1999 (Figure 3) and 2008 (Figure 4) show that the redox state in several wells has become less reduced (e.g., AD-1, MW-304) and, as a result, arsenic concentrations have decreased.

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[1] Note that methane concentration data were not collected during this period. Several of the wells indicated as sulfate reducing in this assessment were subsequently found to exhibit methanogenic conditions.

Several wells also became more reduced (e.g., MW-302A, MW-302B, AD-2, and MP-2); however, this is attributed to the addition of organic carbon to the subsurface (LukOil gasoline spill upgradient of the site) impacting those wells (AECOM, 2011a).

Based on the conceptual site model, as we evaluate temporal trends in order to estimate a rate of attenuation of arsenic, we expect that declines in arsenic should lag the decline in TOC concentration and the change in aquifer redox status. Therefore, the concentration of arsenic may be relatively stable in concentration until the necessary geochemical changes have occurred. AECOM notes that this sequence of necessary conditions, as well as the spatial/temporal geochemical variability in the aquifer (i.e., both soil and groundwater) and the difficulty in predicting the rates of several critical processes (e.g., rate of oxygen recharge), make prediction of future trends in arsenic concentration uncertain (ENSR, 2000a; ENSR, 2000b).

The variations in arsenic and TOC are readily apparent in the data, and the uncertainty is manifested in the variability in the projected times to reach the MCL for arsenic. Having said that, the trend at most wells indicates a decline in the concentration of arsenic. This has been acknowledged by USEPA's expert in arsenic dynamics, Dr. Robert Ford, who suggested during a technical call on October 8, 2010 that using trend analysis such as the one described in this assessment may be helpful to support an application for MNA.

In order to evaluate temporal trends, the March 2011 assessment of arsenic and TOC "decay" was updated to include the April 2011 groundwater monitoring data. For the assessment, up to 22 separate results were evaluated at 15 groundwater monitoring wells. The updated assessment is provided in Appendix 2. For each well, the predicted year of decline below the MCL depends upon the rate constant itself (which is the same for all wells), the amount by which the concentration used as a starting point exceeds the MCL, and the year of the latest observation. As shown in Appendix 2, the predicted year of decline below the MCL varies from 2027 to 2041 (i.e., 15 to 29 years in the future) with an average of 2034 (i.e., 22 years in the future). These rates are slower (i.e., yield longer estimated times to cleanup) than those estimated in 2011 but are still consistent with an overall decline in arsenic concentration in the PAC Source Area.

As stipulated by USEPA Guidance (USEPA, 2007b), data collection and analysis performed for Tier II (as described above) indicate that "*MNA processes are capable of achieving remediation objectives, based on current geochemical conditions at the site.*" These mechanisms are understood and are consistent with the literature as well as USEPA (2007b). The rates of change in groundwater quality have been estimated consistent with recommendations from USEPA staff and, while they are associated with some uncertainty, they indicate declining trends in concentration. Therefore, AECOM believes that Tier II of USEPA's 2007 MNA Guidance is satisfied.

Tier III

Under the MNA guidance (USEPA, 2007a), Tier III evaluates sites as to whether there is sufficient capacity in the aquifer to attenuate the arsenic in groundwater to meet the MCL, that the immobilization of arsenic is a stable condition, and that attenuation rates are sufficient for attaining cleanup objectives established for the site (the arsenic MCL) within a timeframe that is reasonable compared to other remedial alternatives.

The data collected in and around the PAC Source Area indicate that PAC Source Area conditions are consistent with meeting the Tier III criteria. The reducing conditions seen in parts of the PAC Source Area are primarily the result of anthropogenic carbon sources that changed the natural geochemistry of the groundwater and enabled the dissolution of the native arsenic. AECOM believes that the presence of arsenic-containing iron and manganese hydroxides in the subsurface prior to the release of anthropogenic carbon strongly suggests that such solids were present in a stable form under "natural" conditions. It is reasonable to infer that once the introduced organic compounds are exhausted and the aquifer redox status returns to oxidized, the arsenic-containing solids will be stable. This is illustrated in

upgradient wells (e.g., MW-301 and MW-401) which show oxidized conditions and low levels of arsenic. This effect was also seen at wells in the southwest corner of the PAC Source Area, where the influx of carbon from LukOil caused temporary increases in arsenic concentrations and then a subsequent decline.

The lowering of the arsenic levels in the groundwater in the PAC Source Area is occurring and will continue to occur as the process of reductive dissolution is reversed and the aquifer returns to its natural state where the arsenic will be resorbed by iron and manganese hydroxide minerals. As biodegradable carbon levels drop, microbial activity will decrease (the natural influx of oxygen from the atmosphere and from upgradient groundwater will be greater than the reduction of oxygen by biodegradation). As the aquifer's redox state rises, iron and manganese oxidize and form solid hydroxides. Arsenic is expected to be scavenged from the groundwater through co-precipitation with and adsorption onto the newly formed iron and manganese minerals (Oscarson, 1980; Fuller, 1993). Soluble iron and manganese are present in the wells containing arsenic, suggesting that these elements will not be limiting to the formation of iron and manganese hydroxides. In the absence of a new source of reducing agents (e.g., another hydrocarbon release), the reformed iron and manganese hydroxides should be stable.

There are two examples of the stable reversal of redox conditions and decline in arsenic concentrations within and near the PAC Source Area. First, in three wells in the PAC Source Area located near a former leachfield, arsenic concentrations have decreased substantially since the removal of that leachfield and have maintained low to nondetect concentrations since the decrease. These reversals include changes in arsenic concentrations from 600 ug/L in 1987 to not detected beginning in 1996 (in AW-2) (Figure 5); from 550 ug/L in 1992 to below the MCL of 10 ug/L beginning in 2008 (in MW-304) (Figure 6), and from 35.1 ug/l in 2003 to below the MCL beginning in 2007 and not detected in 2011 (in AD-1) (Figure 7). These changes have been preceded by the expected changes in redox conditions and have been maintained in a stable fashion since they occurred. AECOM believes that these three wells represent a good, site-specific model for how future arsenic concentrations are likely to evolve under the MNA remedy.

Note that the behavior of the arsenic concentration prior to the decline associated with redox change is characteristic of that observed in wells exhibiting elevated arsenic and low redox: there is typically substantial variation in arsenic concentration with the mean concentration well above the MCL. As seen in the discussion of the Tier II criterion, this variation contributes to the uncertainty in estimating the time to clean up.

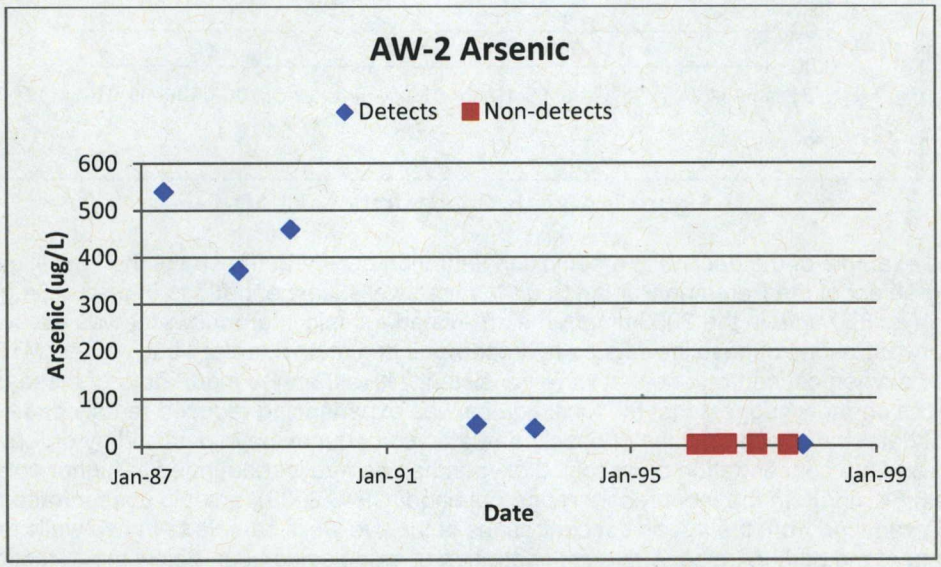

Figure 5: Arsenic Concentrations at AW-2.

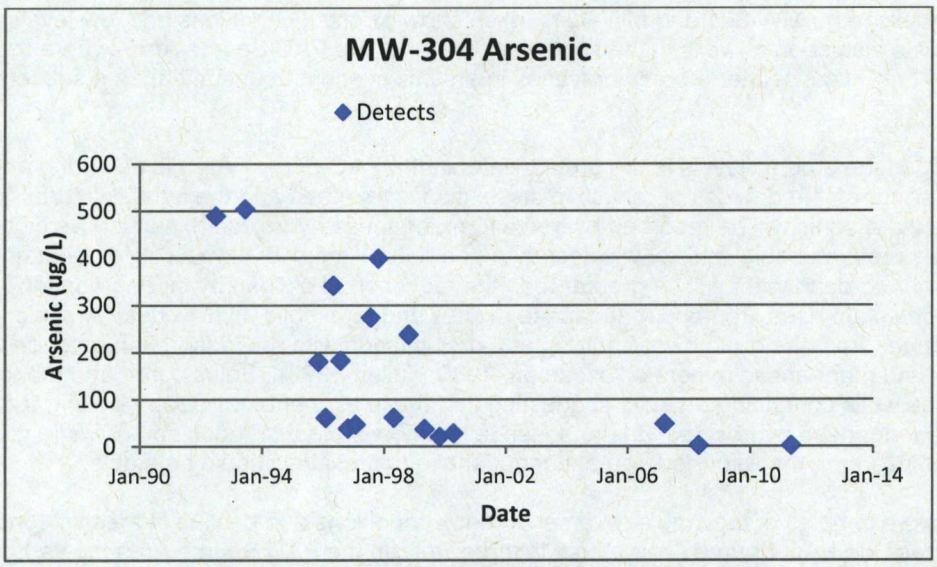

Figure 6: Arsenic Concentrations at MW-304.

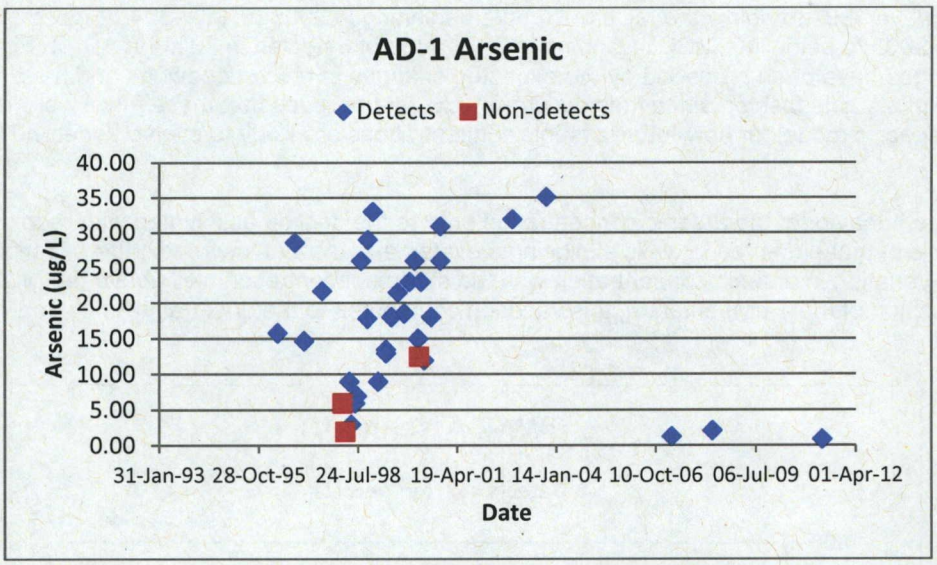

Figure 7: Arsenic Concentrations at AD-1.

The second example of the decline in arsenic concentration occurs at the site of the LukOil gasoline spill, in wells upgradient of the Peterson/Puritan Site. In these wells, concentrations of arsenic in groundwater were as high as 850 ug/L in the 2003 timeframe. Elevated arsenic in groundwater was associated with elevated concentrations of gasoline-related hydrocarbons and methyl tertiary-butyl ether (MTBE) as well as dissolved oxygen concentrations that were consistently less than 1.0 mg/l. Both of these circumstances strongly suggest that the local aquifer was experiencing reduced redox conditions. In more recent data, the concentrations of gasoline-related compounds have declined by orders of magnitude, and the concentration of dissolved oxygen has generally rebounded to higher concentrations (as high as 8.84 mg/l). In the most recent report obtained (CEA, 2009), arsenic concentrations had been substantially reduced from their peak concentrations in the five wells sampled. In two wells located downgradient of the point of release, the concentration of arsenic has been below the detection limit[2] for

[2] Detection limits were either 5 ug/l or 10 ug/l.

eight of the last nine sampling rounds and five of the last seven sampling rounds, respectively. Again, the observed behavior at these wells suggests that declines in arsenic concentration, once they occur, will be stable.

Both of these examples show the capacity of the aquifer to attenuate the arsenic in groundwater to meet the MCL and, that once attenuated, the immobilization of arsenic generally appears to be a stable condition. This behavior is consistent with the site-specific conceptual site model as well as the literature on reductive dissolution as a source of arsenic in the subsurface (USEPA, 2007b).

As discussed in the evaluation of the Tier II criterion, the estimated attenuation rates for arsenic result in predicted times to meet the MCL that are reasonable and consistent based on previous estimates. The reasonableness of these timeframe is substantially bolstered by the finding that, with the institutional controls in place and groundwater not being a drinking water source, arsenic in groundwater does not currently pose a threat to human health or the environment and is not likely to pose such a threat in the future.

Based upon the PAC Source Area meeting the criteria in Tier III, development of a performance monitoring plan for the PAC Source Area under Tier IV is appropriate.

Tier IV

Tier IV requires the design of a performance monitoring plan. "*The objective under Tier IV analysis to develop a monitoring program to assess long-term performance of the MNA remedy and identify alternative remedies that could be implemented for situations where changes in site conditions could lead to remedy failure*" (USEPA, 2007a).

There is currently, and has been for 17 years, an ongoing monitoring program in place in the PAC Source Area, the JGWMP, which will serve as a performance monitoring program and which is expected to continue to support monitoring the effectiveness of the remedy. Consistent with USEPA guidance, this monitoring program contains locations that provide adequate aerial and vertical coverage to verify that arsenic concentrations in the PAC Source Area are stable or decreasing and provide the ability to monitor groundwater chemistry where the arsenic attenuation is occurring to show that MNA processes are continuing (USEPA, 2007b).

As part of this monitoring program, and as specified in the MNA guidance (USEPA, 2007a), a subset of wells that represent the site's heterogeneity is selected for annual sampling and a more comprehensive set of wells is sampled every five years. Groundwater flow as measured during previous JGWMP rounds, and particle tracking examples using the 2008 USEPA groundwater flow model for the site, indicate that the existing sampling locations are appropriate for the monitoring of arsenic mobilized as a result of activities at the PAC Source Area (AECOM, 2009).

Monitoring parameters for the annual round include: TOC, arsenic, Fe(II), dissolved oxygen, pH, and ORP. Monitoring parameters for the five-year sampling round include the annual parameters plus methane, sulfate, nitrate, manganese, and carbon dioxide. These parameters serve to assess attenuation efficiency and the attenuation mechanism (USEPA, 2007a). As part of the monitoring, groundwater levels across the site are measured to demonstrate consistency in groundwater flow behavior (USEPA, 2007b).

According to USEPA guidance, the performance monitoring program must include conditions that might trigger a re-evaluation of the adequacy of the monitoring program (USEPA, 2007a). For the PAC Source Area, these conditions include sustained upward trends in arsenic and TOC concentrations in groundwater.

Conclusion

Implementation of MNA in the PAC Source Area is an appropriate remedy as demonstrated within the four-tiered framework (USEPA, 2007a and 2007b) as follows:

- The PAC Source Area has been fully characterized, and it has been demonstrated that arsenic concentrations are generally stable or decreasing (Tier I);
- The apparent rate and mechanism of attenuation has been demonstrated (Tier II);
- The capacity of aquifer to continue and sustain attention has been shown (Tier III); and
- A monitoring plan, along with triggers for reevaluation, has been developed (Tier IV).

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Appendix 1 Arsenic Graphs

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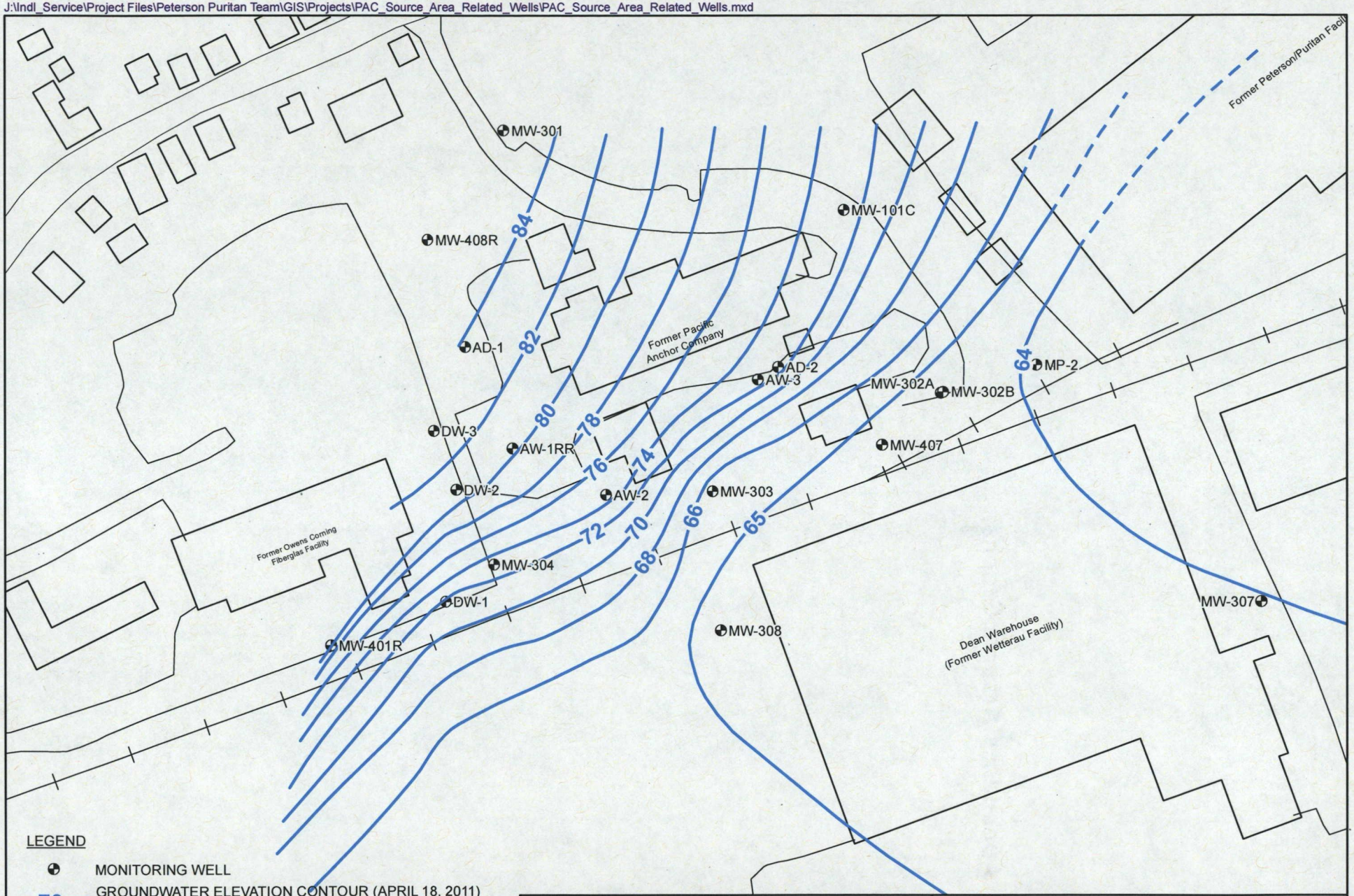


LEGEND

MONITORING WELL

—70— GROUNDWATER ELEVATION CONTOUR (APRIL 18, 2011) (DASHED WHERE INFERRED)

AECOM

N E S W

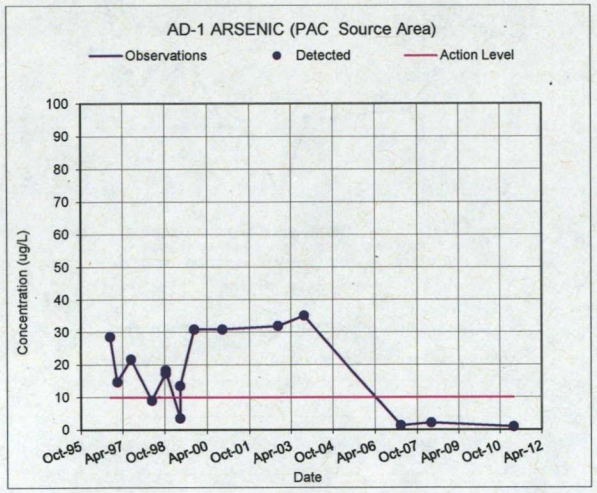
0 80 160 Feet

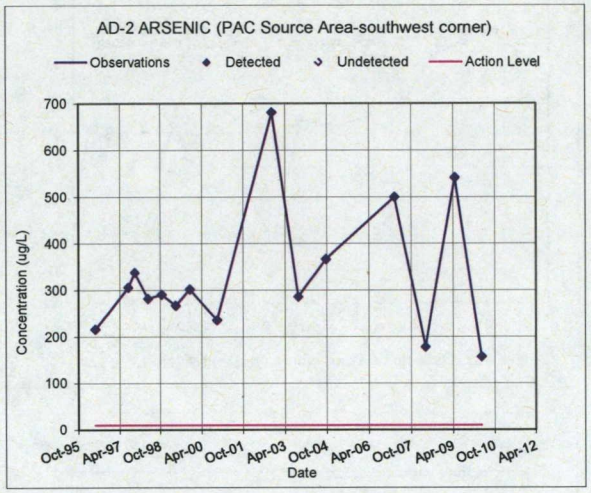
PETERSON/PURITAN SUPERFUND SITE
OPERABLE UNIT 1
CUMBERLAND, RHODE ISLAND
60197448.4

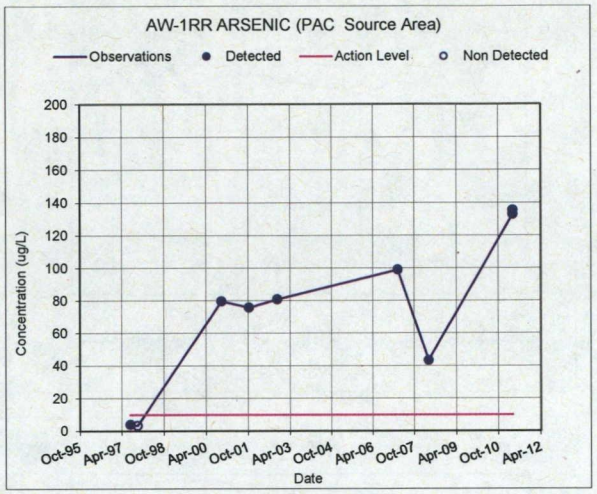
PAC SOURCE AREA - RELATED WELLS

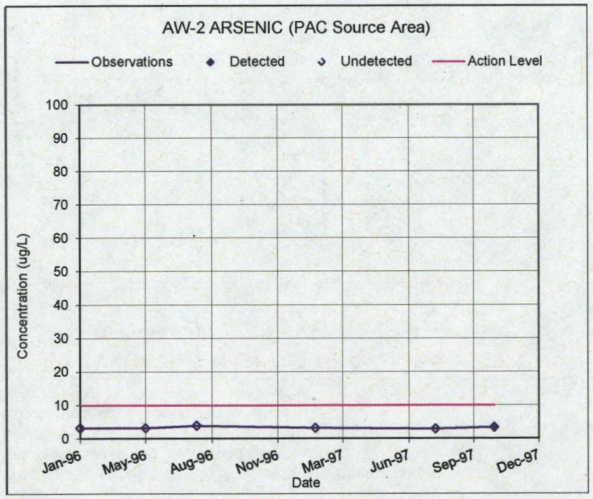
DATE: 04/24/12 | DRWN: J.E.B. | FIGURE 1

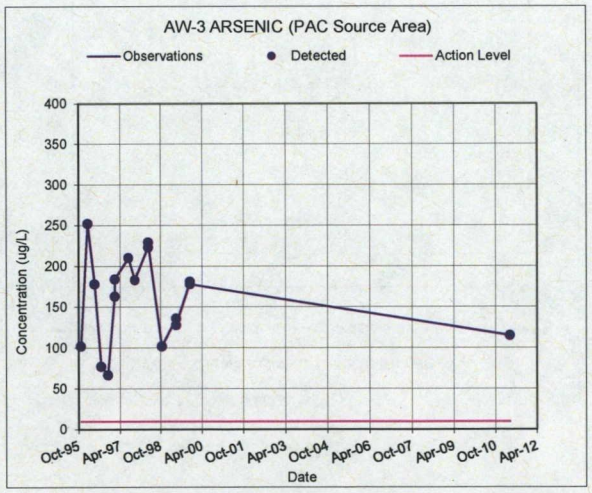
Appendix 1
PAC Source Area-Related Wells Arsenic Concentrations
Peterson/Puritan, Inc. Superfund Site
Operable Unit 1
Cumberland and Lincoln, Rhode Island

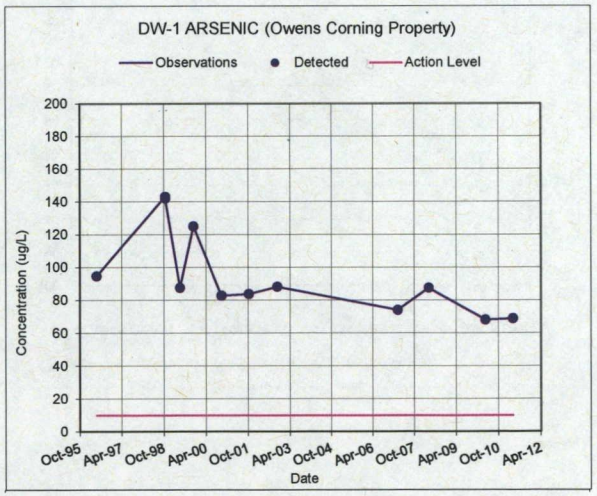












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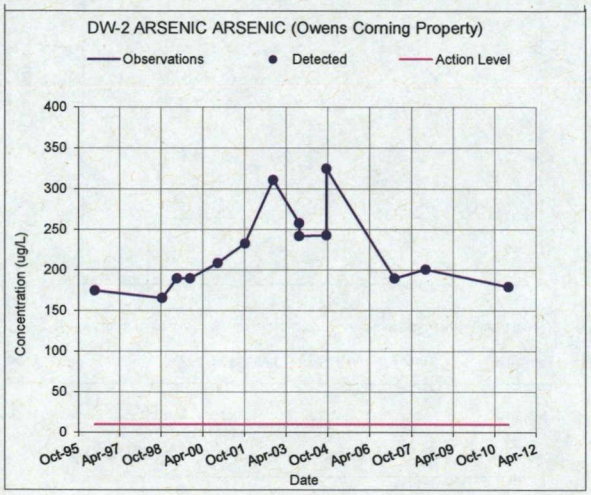
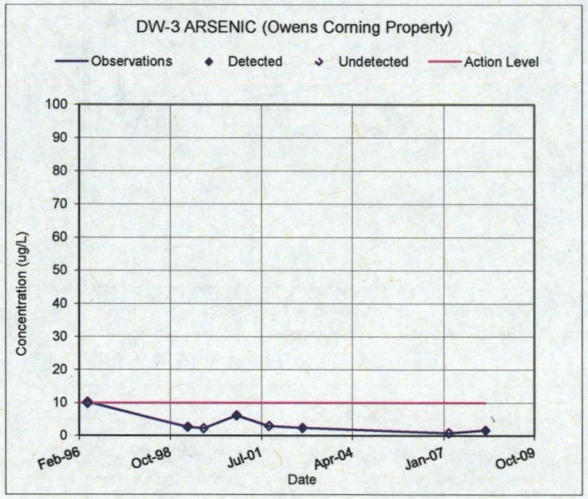
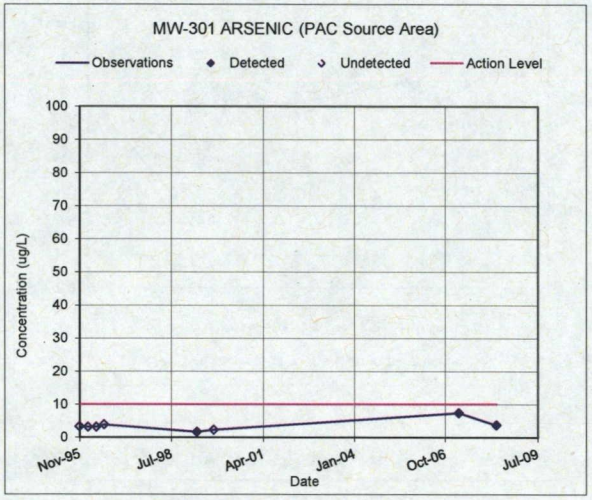
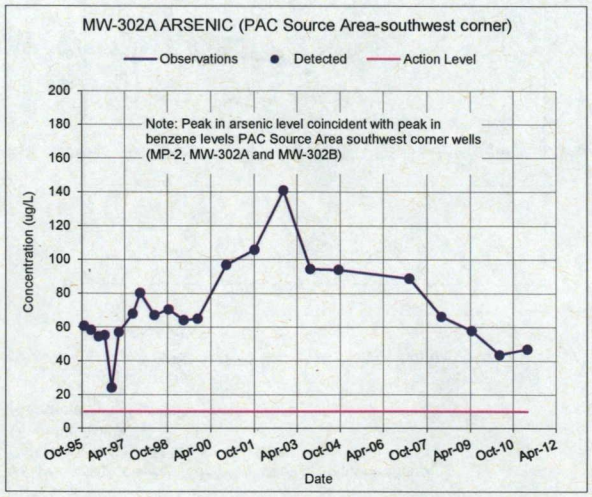
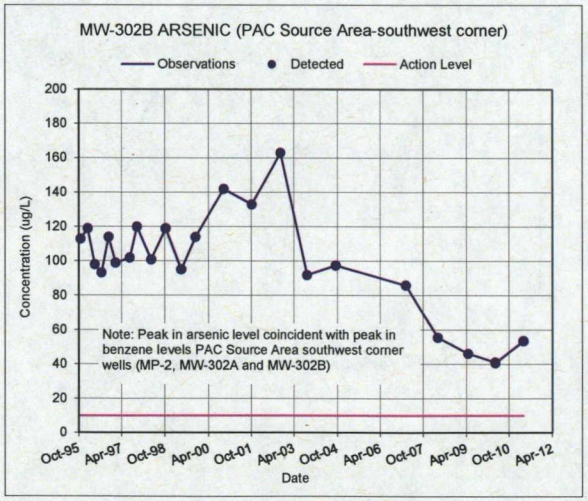
Cumberland and Lincoln, Rhode Island

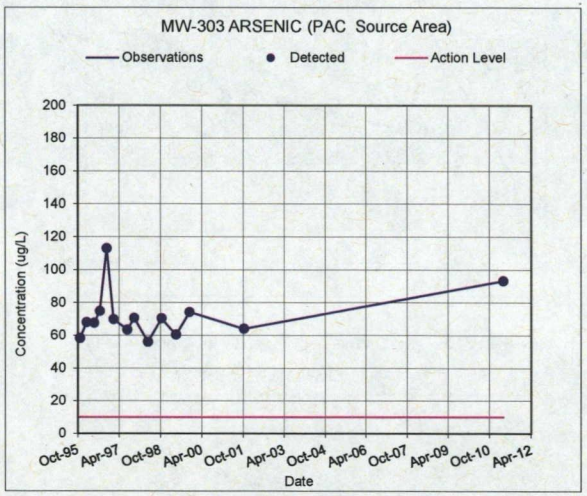












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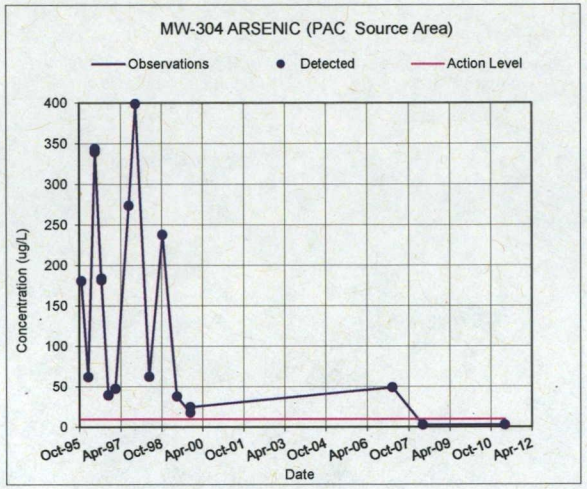
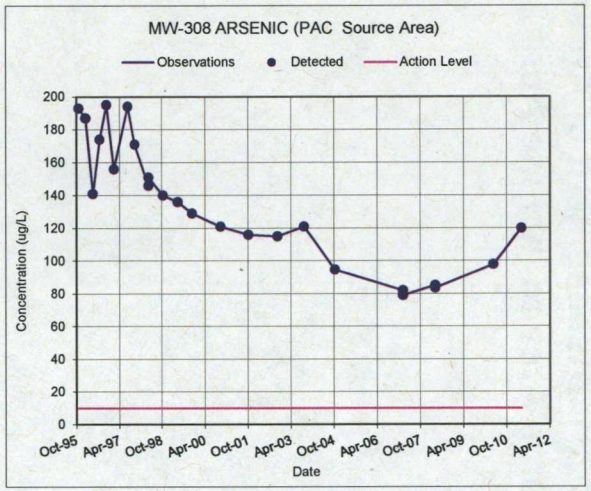
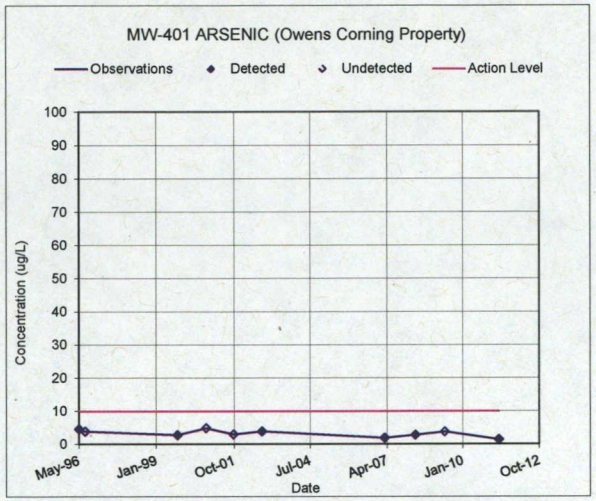
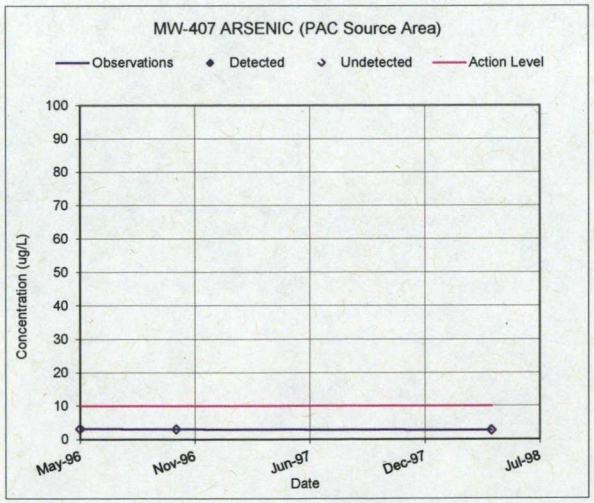
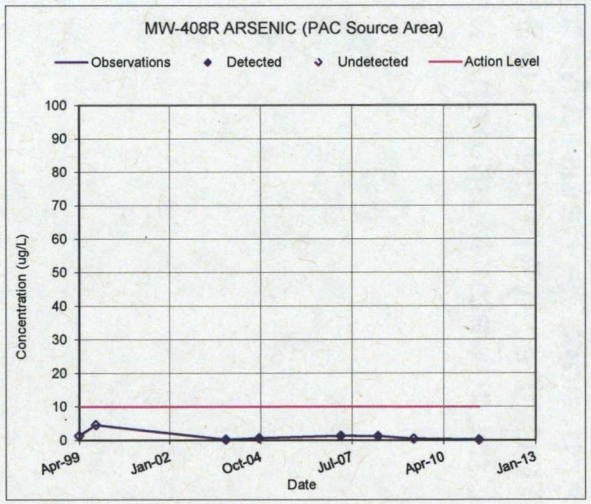
Peterson/Puritan, Inc. Superfund Site
Operable Unit 1
Cumberland and Lincoln, Rhode Island

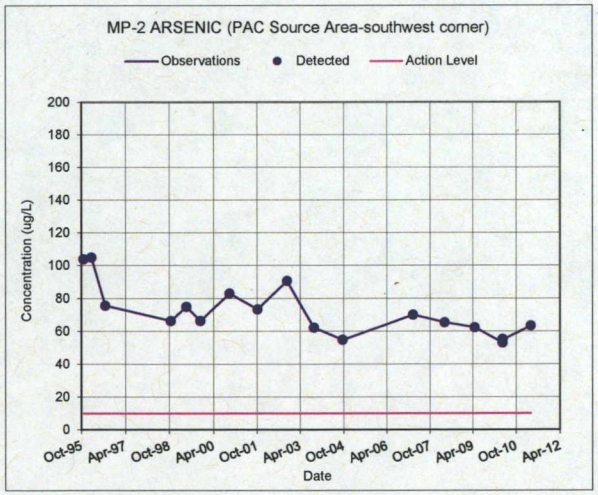












Appendix 2 – Revised March 2011 Assessment of Arsenic and TOC "Decay" in the PAC Source Area to include April 2011 Groundwater Monitoring Data

The following assessment updates the March 29, 2011 evaluation of arsenic and TOC "decay" in the PAC Source Area at the Peterson/Puritan Superfund Site in Cumberland, RI.

In order to evaluate temporal trends, up to 22 separate results were evaluated at each of 15 groundwater monitoring wells. Samples were collected as early as October 1995 and as late as April 2011. It is important to note that the frequency of data collection effort has not been uniform in time and that at some locations (e.g., MW-303) data were not collected during a period of ten years or more. The methods used to collect and analyze groundwater samples have been consistent for all of the data employed in this assessment. In addition, data pre-dating the Joint Ground Water Monitoring Program, when arsenic concentrations were significantly higher at many locations, were not used. At each location, time series (i.e., arsenic and TOC concentration vs. time) plots were created and the resulting data fit to a first order decay[3] equation (i.e., $C_t = C_o e^{-kt}$). For each location, the decay coefficient (k – units of yr^{-1}) and the correlation coefficient (r^2) were calculated. Generally, the entire data series was used in the analysis. However, where the impacts of other sources of TOC (e.g., LukOil) were apparent as later peaks in concentration (e.g., at MW-302A and MW-302B), the time series were truncated to start with the later peak and evaluate the trend after that peak.

A relatively favorable fit to the data for arsenic is presented as Figure 1. The results for all 15 wells are presented in Table 1.

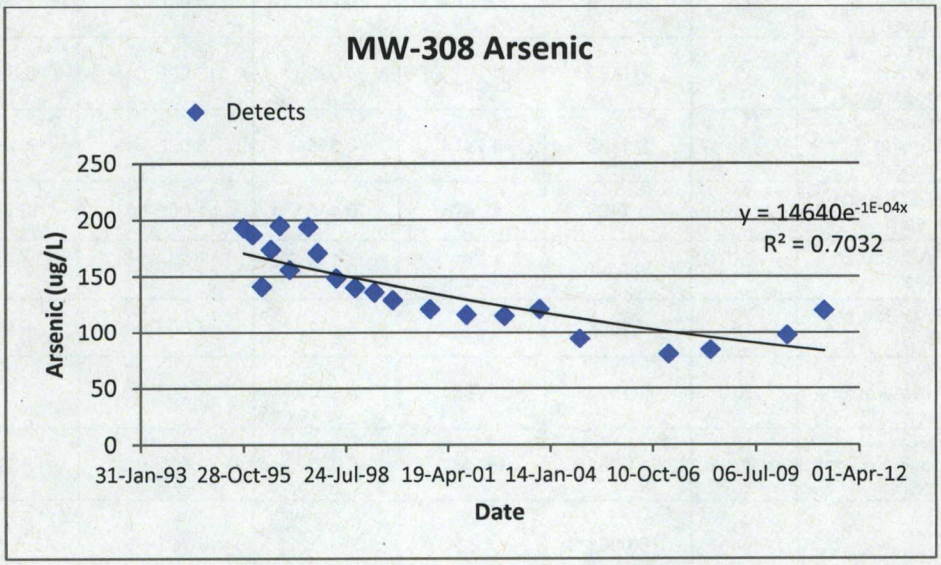


Figure 1: Trends in Arsenic Concentration at MW-308. Note that k is calculated by Excel on a daily basis on this figures but has been converted to an annual basis in Table 1.

[3] Decay is used in a generic manner to capture declines in aqueous concentration. Declines in arsenic concentration in water are not due to destruction but are associated with sorption to solids and to groundwater transport.

Well ID	Location	Times sampled (1995 to 2011)	Arsenic Decay Constant (per year)	Arsenic Half Life (years)	Arsenic r^2	Total Organic Carbon Decay Constant (per day)	Total Organic Carbon Half Life (years)	Total Organic Carbon r^2
AD-2	PAC Source Area	19	0.1095	6.3301	0.2350	3.00E-04	6.3301	0.7138
MP-2	CCL Near Source Area	21	0.0292	23.7379	0.2827	-3.00E-04	-	0.4927
MW-302A	PAC Source Area	22	0.1095	6.3301	0.9102	-9.00E-05	-	0.7938
MW-302B	PAC Source Area	22	0.1460	4.7476	0.8330	-7.00E-05	-	0.0894
AD-1	PAC Source Area	17	0.2190	3.1651	0.5997	2.00E-04	9.4952	0.5862
AW-1RR	PAC Source Area	12	0.0365	18.9903	0.0120	6.00E-04	3.1651	0.8353
AW-3	PAC Source Area	13	0.0146	47.4758	0.0242	4.00E-04	4.7476	0.7369
DW-1	Owens Corning Property	12	0.0329	21.1004	0.4876	5.00E-05	37.9807	0.0805
DW-2	Owens Corning Property	13	-0.0073	Not declining	0.0220	3.00E-04	6.3301	0.6370
DW-3	Owens Corning Property	9	0.1460	4.7476	0.6554	6.00E-04	3.1651	0.6514
MW-101C	PAC Source Area	6	0.1460	4.7476	0.4954	1.00E-04	18.9903	0.0928
MW-303	PAC Source Area	14	-0.0146	Not declining	0.1084	4.00E-04	4.7476	0.7075
MW-304	PAC Source Area	15	0.2555	2.7129	0.6123	4.00E-04	4.7476	0.5134
MW-307	PAC Downgradient Area	20	0.1825	3.7981	0.7117	-7.00E-05	-	0.1333
MW-308	PAC Downgradient Area	21	0.0365	18.9903	0.7032	3.00E-04	6.3301	0.3608
		Mean	0.0961	12.8		3.76E-05	9.6	

Table 1: Summary of Estimated Trends in Arsenic and TOC

Inspection of Table 1 shows that the first-order decay fit shown in Figure 1 for MW-308 is stronger than those evident at most other wells. In fact, despite the general decline in arsenic concentration across the PAC Source Area, in some wells, the trend in arsenic concentration is weakly positive. This behavior is consistent with the conceptual site model (i.e., organic carbon decline precedes arsenic decline). An example that illustrates the site conceptual model is presented in Figure 4. In this figure, the earlier decline in TOC is demonstrated for MW-304 followed by a decline in arsenic that lags by three years or more.

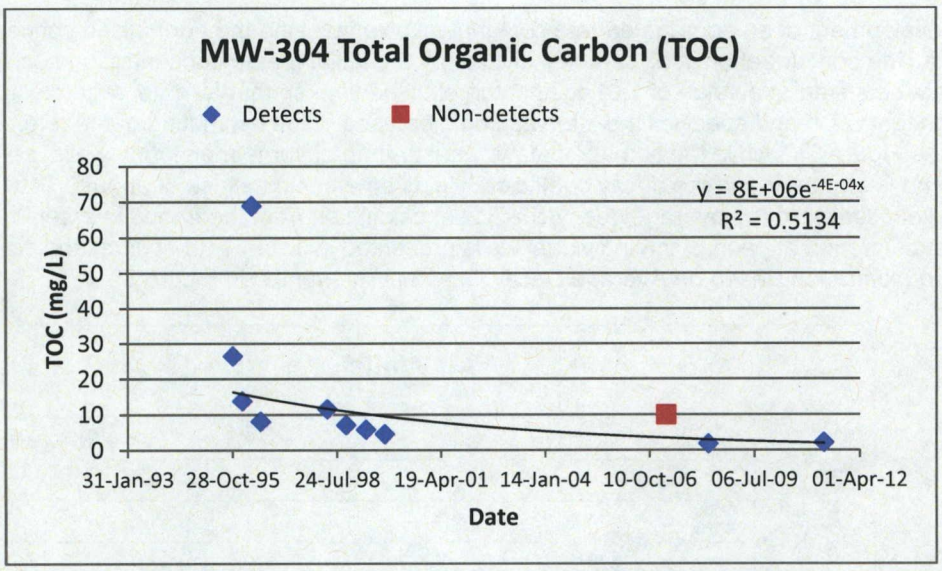


Figure 2a: Trends in TOC Concentration at MW-304.

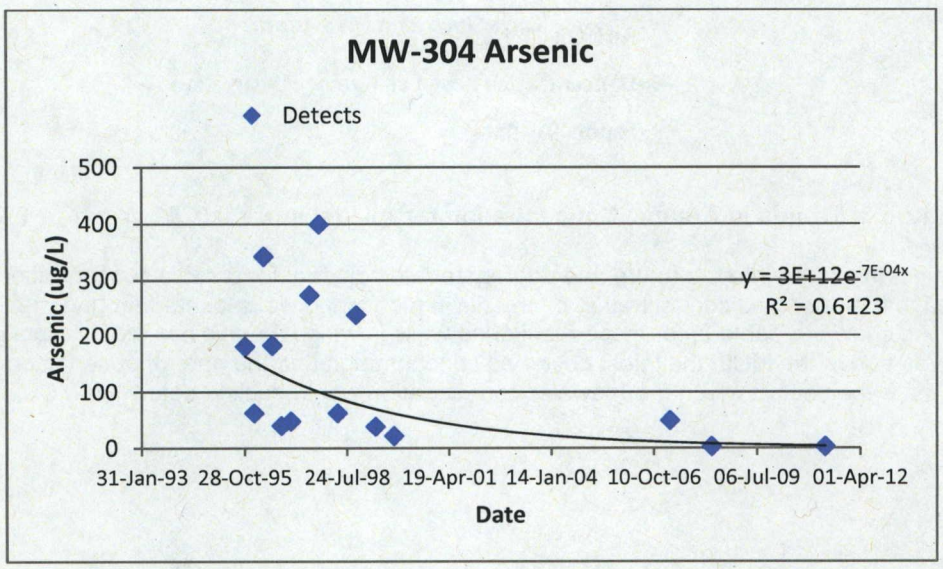


Figure 2b: Trends in Arsenic Concentration at MW-304.

While the temporal trends in arsenic concentration are relatively strong at some wells, the site conceptual model indicates that arsenic will remain elevated over the volume of the aquifer affected by elevated organic carbon until the oxidizing conditions are re-established. This suggests that the soundest approach to estimating a decay constant for the decline in arsenic concentration is to aggregate the data on arsenic trends with time across the relevant wells in order to estimate an aggregate rate constant. This approach accounts for the rates of decline of wells including those that are already below the MCL and those that have a slightly positive trend in arsenic concentration.

Development of an aggregated rate constant involved plotting the normalized concentration (i.e., the concentration in all samples divided by the initial (peak) concentration such that all data sets start at a value of 1.0) against the elapsed time so that all data, regardless of the concentration and specific time interval, could be used in the estimating of the rate constant (see Figure 3). While the fit to the data is weaker than at some monitoring wells, an overall trend is apparent and the decay coefficient yields an arsenic half-life of about 9.21 years. This is very similar to the average decay coefficient calculated from the trends in arsenic concentration at each of the individual wells presented in Table 1 (the curve labeled "Concentration Based on Average Decay Constant" presented in Figure 3).

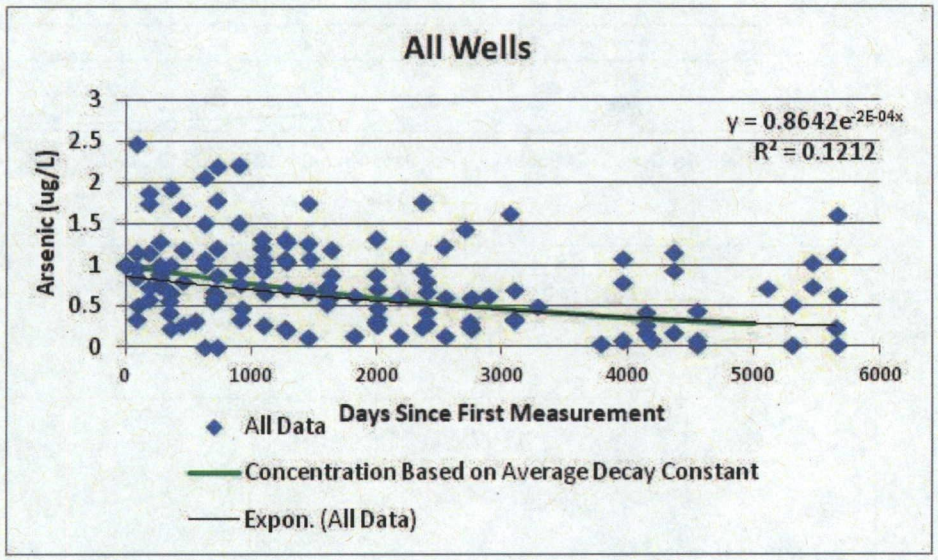


Figure 3: Trends in Arsenic Concentration for All Wells ($k = 0.0752\ yr^{-1}$, $t_{1/2} = 9.21$ years)

To project this trend into the future, the aggregate rate constant for arsenic concentration was then applied to the observed concentration of arsenic in monitoring wells located around the PAC Source Area. As shown in Table 2, for those monitoring wells in which arsenic has most recently been observed above the MCL, the latest observed concentration and the date of observation were used to estimate the year at which groundwater concentration would decline below the MCL.

Well ID	Location	Value on Trend (date)	Value on Trend (concentration ug/L)	Estimated Year when Arsenic Concentration = 10 ug/L
AD-2	PAC Source Area	5/5/2010	156.7	2038
MP-2	CCL Near Source Area[3]	4/25/2011	63.4	2030
MW-302A	PAC Source Area	4/26/2011	47.2	2027
MW-302B	PAC Source Area	4/26/2011	53.65	2028
AD-1	PAC Source Area	-	-	Already Below 10 ug/L
AW-1RR	PAC Source Area	4/27/2011	134.05	2038
AW-3	PAC Source Area	4/27/2011	115	2036
DW-1	Owens Corning Property	4/28/2011	68.8	2031
DW-2	Owens Corning Property	4/28/2011	179.8	2041
DW-3	Owens Corning Property	-	-	Already Below 10 ug/L
MW-101C	PAC Source Area	-	-	Already Below 10 ug/L
MW-303	PAC Source Area	4/28/2011	93.2	2034
MW-304	PAC Source Area	-	-	Already Below 10 ug/L
MW-307	PAC Downgradient Area[3]	-	-	Already Below 10 ug/L
MW-308	PAC Downgradient Area	4/26/2011	120	2037
		Mean	92.125	2034

Table 2: Estimated MNA Timeframe Using Aggregate Arsenic Rate Constant (k = 0.0752 yr^{-1}, $t_{1/2}$ = 9.21 years)

For each well, the predicted year of decline below the MCL depends upon the rate constant itself (which is the same for all wells), the amount by which the concentration used as a starting point exceeds the MCL, and the year of the latest observation. As shown in Table 2, the predicted year of decline below the MCL varies from 2027 to 2041 (i.e., 15 to 29 years in the future) with an average of 2034 (i.e., 22 years in the future).

The general behavior of the TOC and arsenic data, including their variability, are consistent with the site conceptual model articulated for the site over the last nearly 20 years. As demonstrated previously, the concentrations of organic carbon and arsenic are generally declining within the PAC Source Area and in the downgradient monitoring wells. While the approach used to estimate the time frames is reasonable and their range is generally consistent with the estimate from 2001 (i.e.,

10 to 30 years), uncertainty remains. In particular, co-precipitation of arsenic from groundwater is a complex, multi-step process, the rate of which is difficult to predict and likely to vary in space.

AECOM

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March 29, 2011

Mr. Larry Brill
Branch Chief, OSRR Branch I
United States Environmental Protection Agency – Region I
5 Post Office Square - Suite 100
Boston, MA 02109-3912

Subject: Prediction of MNA Effectiveness at the PAC Source Area of the Peterson-Puritan Superfund Site to Support Potential Remedy of Monitored Natural Attenuation Peterson/Puritan, Inc. Superfund Site, OU1 Cumberland and Lincoln, Rhode Island

Dear Mr. Brill,

USEPA has requested that Lonza evaluate the feasibility and utility of updating its previous estimate of the time frame for Monitored Natural Attenuation (MNA) for arsenic. This previous estimate was presented as an appendix to a document prepared to support the First Five Year Review in 2001. We understand that that USEPA is considering whether MNA may be an appropriate alternative remedy for arsenic in groundwater in the PAC Source Area.

Lonza's updated analysis to estimate of the time frame for MNA for arsenic is included as an attachment to this letter. Please note that the original 2001 analysis focused on a specific groundwater quality parameter, Chemical Oxygen Demand, which is no longer collected as part of the Joint Groundwater Monitoring Program. We have performed a similar analysis, attached, which focuses on a similar parameter, Total Organic Carbon, as well as arsenic itself.

The results of the updated analysis are consistent with the site conceptual model of arsenic liberation in the sub-surface and the estimated timeframes, while variable, are generally consistent with the 2001 estimate. For this reason, they are reasonable estimates of the time frame over which MNA will be an effective remedy at the PAC Source Area.

We look forward to discussing this analysis and working with USEPA to implement an MNA remedy for the PAC Source Area. Please call us if you have any questions or comments on the attached document.

Yours sincerely,

Carolyn K. Scott

Mark Gerath
Technical Director

Carolyn K. Scott
Program Manager

cc: Mike Jasinski, USEPA
David Newton, USEPA
Ruthann Sherman, USEPA
John Hultgren, USEPA
David Freeman, Paul, Hastings, Janofsky & Walker

Paul Sieracki, Lonza Inc.
Elizabeth Perry, AECOM
Doug Bright, AECOM
Project File

Evaluation of Arsenic and TOC "Decay" in the PAC Source Area

Summary

In order to evaluate the potential for natural processes to affect Monitored Natural Attenuation (MNA) of arsenic concentrations elevated above the Maximum Contaminant Level (MCL) in groundwater in the PAC Source Area, temporal trends in organic carbon and arsenic have been evaluated in data collected over 15 years in several monitoring wells. Concentrations of organic carbon and arsenic are both generally declining, consistent with the site conceptual model of arsenic mobility. The average rate of decline (as expressed as a "decay" coefficient) was applied to the most recent groundwater data collected at each of several wells to predict future arsenic concentrations. The year at which groundwater at the well would reach the MCL (10 µg/l for arsenic) was predicted. For the average well, the predicted date to reach the MCL is 2026 (15 years in the future). The predicted date for the various wells ranges from 2019 to 2036. These predictions are generally consistent with an estimate made earlier as part of the 2001 Five Year Review.

Evaluation

USEPA has expressed an interest in updating a relatively simple analysis of temporal trends in groundwater quality that was performed in 2001[1]. That analysis evaluated apparent temporal trends in chemical oxygen demand (COD) and used the observed trends to estimate a time at which the concentration of COD could be expected to fall below the estimated background concentration (a value estimated at 9 mg/l). This analysis was predicated on the site conceptual model that at elevated COD concentration, arsenic concentration would also remain elevated. Using temporal trends in COD and the assumption that arsenic would remain elevated until COD returned to background, the 2001 analysis concluded that between 10 and 30 years would be necessary for natural processes to be effective at reducing elevated arsenic concentrations (i.e., an MNA remedy). The following discussion presents AECOM's use of the more current groundwater quality data to develop a similar analysis and prediction of MNA time frames.

With the approval of USEPA, COD has not been analyzed for several years in groundwater samples from the PAC Remediation Area. For that reason, this current analysis focuses on arsenic itself as well as total organic carbon (TOC). It is important to recall that under the conceptual site model of arsenic mobilization in the subsurface, organic carbon present in soils and groundwater results in the depletion of oxygen and the subsequent geochemical reduction of the aquifer. Under reducing conditions, iron and manganese oxides are reduced and dissolved to liberate co-precipitated arsenic. To reverse these conditions, organic carbon must be exhausted, followed by the reintroduction of oxygen, the reformation of iron and manganese oxides and the co-precipitation of arsenic. Therefore, as we evaluate temporal trends in arsenic and TOC, we expect that declines in arsenic should lag those in TOC and that arsenic may be relatively stable in concentration until TOC has declined to low concentrations.

AECOM has noted on several occasions that this sequence of necessary conditions, as well as the spatial/temporal geochemical variability in the aquifer (i.e., both soil and groundwater) and the difficulty in predicting the rates of several critical processes (e.g., rate of oxygen recharge), make prediction of future trends in arsenic concentration uncertain. The variations in arsenic and TOC are readily apparent in the data, and the uncertainty is manifested in the variability in the projected times to reach the MCL for arsenic. Having said that, the trend at most wells (as previously defined using a non-parametric statistical analysis) indicates a decline in the concentration of arsenic. This

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[1] ENSR, 2001. Monitored Natural Attenuation Report. Five Year Review Evaluation October 1995 to October 1999. Peterson/Puritan Superfund Site. Cumberland, RI. First Operable Unit. PAC Remediation Area. Appendix F: Estimation of Remediation Timeframes for Natural Attenuation.

has been acknowledged by USEPA's expert in arsenic dynamics, Dr. Robert Ford, who has suggested that using trend analysis such as the one below may be helpful to support an application for MNA.

In order to evaluate temporal trends, up to 21 separate results were evaluated at 15 groundwater monitoring wells. Samples were collected as early as October 1995 and as late as May 2010. It is important to note that the data collection effort has not been uniform in time and that at some locations (e.g., MW-303) data have not been collected for ten years or more. In addition, data pre-dating the Joint Ground Water Monitoring Program, when arsenic concentrations were significantly higher at many locations, were not used. At each location, time series (i.e., arsenic and TOC concentration vs. time) plots were created and the resulting data fit to a first order decay[2] equation (i.e., $C_t = C_o e^{-kt}$). For each location, the decay coefficient (k – units of yr^{-1}) and the correlation coefficient (r^2) were calculated. Generally, the entire data series was used in the analysis. However, where the impacts of other sources of TOC (e.g., LukOil) were apparent as later peaks in concentration (e.g., MW-302A and MW-302B), the time series were truncated to start with the later peak.

A relatively favorable fit to the data for arsenic is presented as Figure 1. The results for all 15 wells are presented in Table 1.

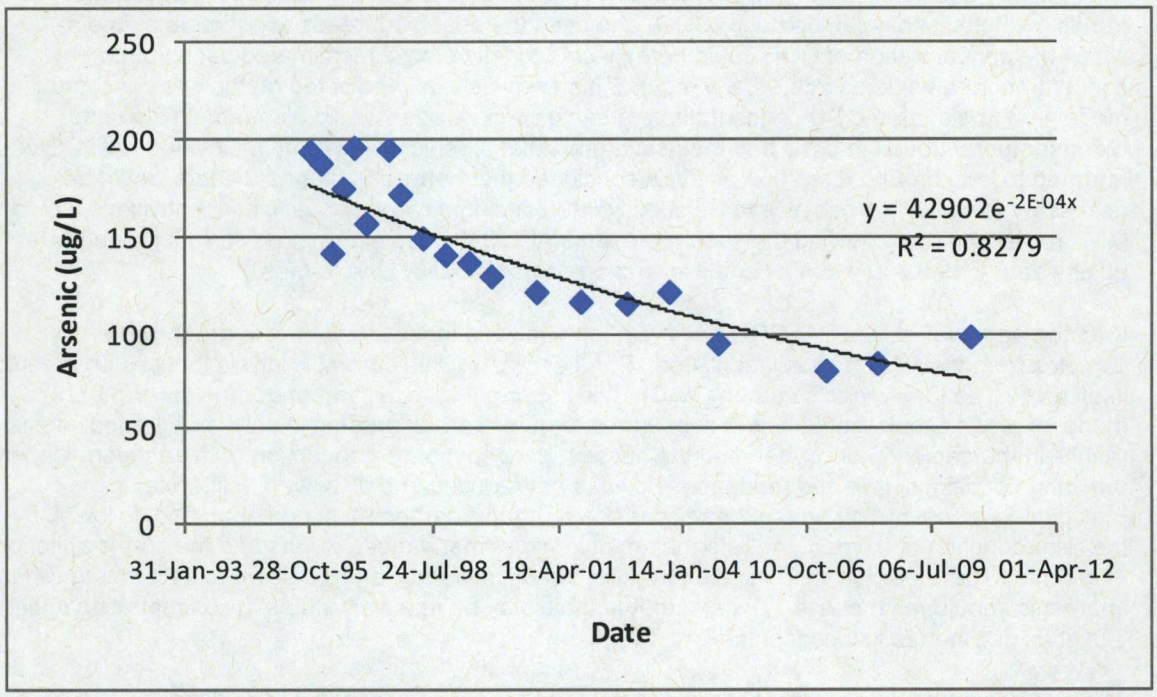

Figure 1: Trends in Arsenic Concentration at MW-308. Note that k is calculated by Excel on a daily basis on this figures but has been converted to an annual basis in Table 1.

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[2] Decay is used in a generic manner to capture declines in aqueous concentration. Declines in arsenic concentration in water are not due to destruction but are associated with sorption to solids and to groundwater transport.

Well ID	Location	Times sampled (1995 to 2010)	Arsenic Decay Constant (per year)	Arsenic Half Life (years)	Arsenic r2	Total Organic Carbon Decay Constant (per year)	Total Organic Carbon Half Life (years)	Total Organic Carbon r2
AD-2	PAC Source Area	19	0.1095	6.3301	0.2350	0.1095	6.3301	0.7558
MP-2	CCL Near Source Area[3]	20	0.0365	18.9903	0.3530	-0.1825	-	0.7269
MW-302A	PAC Source Area	21	0.1095	6.3301	0.8906	-0.0365	-	0.7325
MW-302B	PAC Source Area	21	0.1460	4.7476	0.8941	-0.0365	-	0.1689
AD-1	PAC Source Area	16	0.1825	3.7981	0.4151	0.1095	6.3301	0.6441
AW-1RR	PAC Source Area	11	0.0730	9.4952	0.0395	0.2555	2.7129	0.8550
AW-3	PAC Source Area	12	-0.0183	Not declining	0.0026	0.3650	1.8990	0.8458
DW-1	Ow ens Corning Property	11	0.0329	21.1004	0.4058	0.0110	63.3011	0.0228
DW-2	Ow ens Corning Property	12	-0.0219	Not declining	0.1536	0.1460	4.7476	0.7049
DW-3	Ow ens Corning Property	9	0.1460	4.7476	0.6554	0.2190	3.1651	0.6514
MW-101C	PAC Source Area	5	0.2920	2.3738	0.5078	-0.0110	-	0.0014
MW-303	PAC Source Area	13	0.0183	37.9807	0.0309	0.2555	2.7129	0.6952
MW-304	PAC Source Area	14	0.2190	3.1651	0.4457	0.1460	4.7476	0.4009
MW-307	PAC Dow ngradient	20	0.1825	3.7981	0.7117	-0.0256	-	0.1333
MW-308	PAC Dow ngradient	20	0.0730	9.4952	0.8279	0.1095	6.3301	0.3069
		Mean	0.1054	10.2		0.0956	10.2	

Table 1: Summary of Estimated Trends in Arsenic and TOC

Inspection of Table 1 shows that the first-order decay fit (shown in Figure 1) is stronger than those evident at most other wells. In fact, despite the general decline in arsenic concentration across the study area, in some wells, the trend in arsenic concentration is weakly positive. This behavior is consistent with the conceptual site model (i.e., organic carbon decline precedes arsenic decline). An example that illustrates the site conceptual model is presented in Figure 2. In this figure, the earlier and steeper decline in TOC is demonstrated for MW-303, a well with a relatively low rate of decline for arsenic concentration.

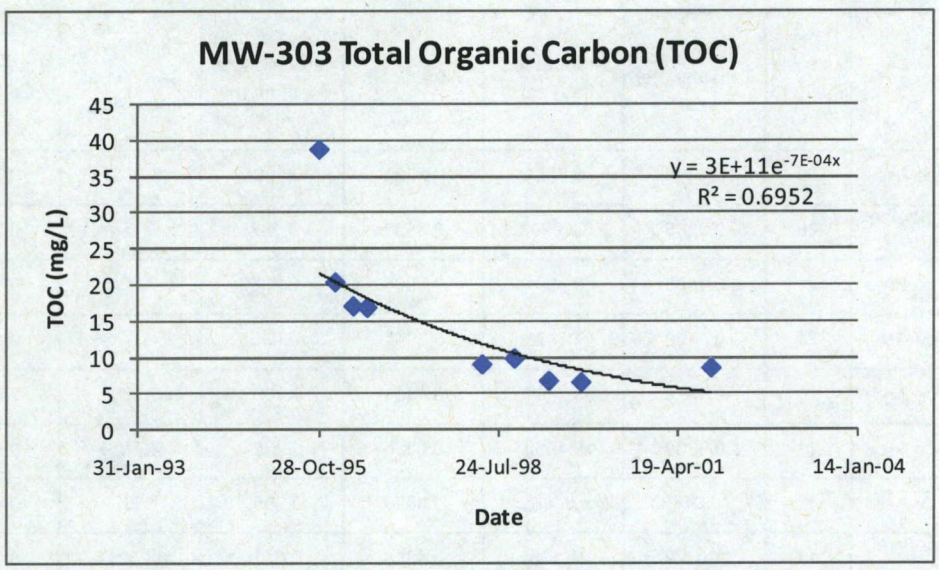


Figure 2a: Trends in TOC Concentration at MW-303.

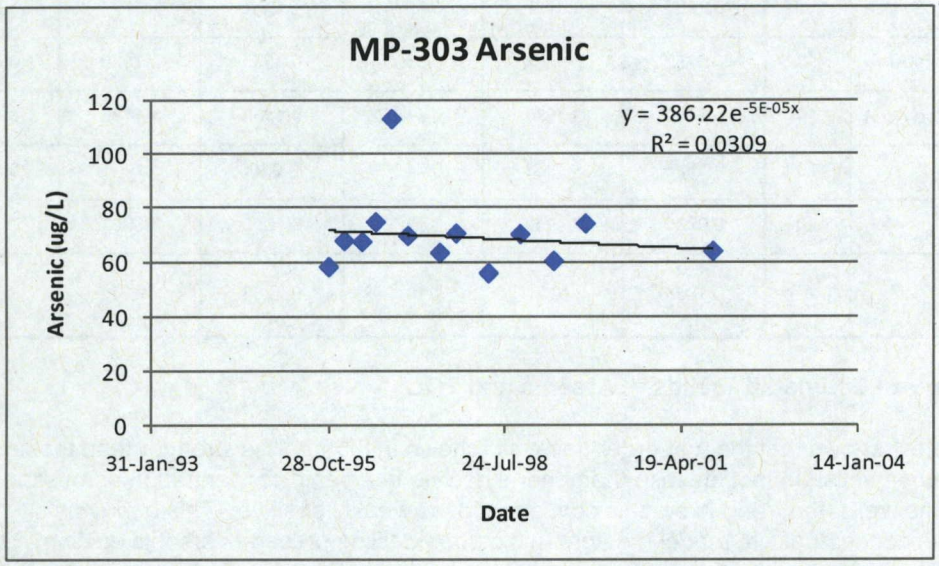


Figure 2b: Trends in Arsenic Concentration at MW-303.

While the temporal trends in arsenic concentration are relatively strong at some wells, the site conceptual model indicates that arsenic will remain elevated over the volume of the aquifer affected by elevated organic carbon until the oxidizing conditions are re-established. This suggests that the soundest approach to estimating a decay constant for the decline in arsenic concentration is to aggregate the data on arsenic trends with time across the relevant wells in order to estimate an aggregate rate constant. This approach accounts for the rates of decline of wells including those that are already below the MCL and those that have a slightly positive trend in arsenic concentration.

Development of an aggregated rate constant involved plotting the normalized concentration (i.e., the concentration in all samples divided by the initial concentration such that all data sets start at a value of 1.0) against the elapsed time so that all data, regardless of the concentration and specific time interval, could be used in the estimating of the rate constant (see Figure 3). While the fit to the data is weaker than at some monitoring wells, an overall trend is apparent and the decay coefficient yields an arsenic half-life of about 10.2 years. This is very similar to the average decay coefficient calculated from the trends in arsenic concentration at each of the individual wells presented in Table 1 (the curve labeled "Concentration Based on Average Decay Constant" presented in Figure 3).

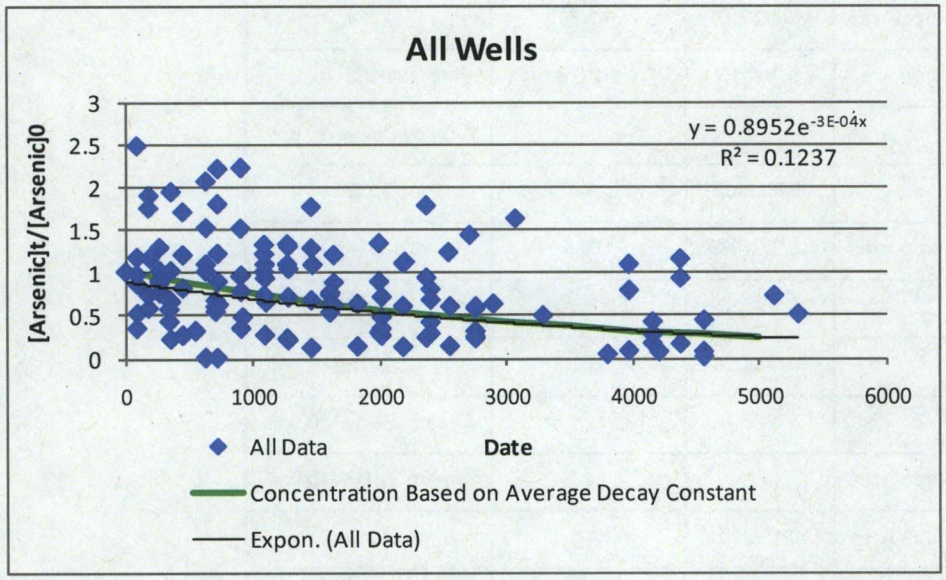


Figure 3: Trends in Arsenic Concentration for All Wells ($k = 0.1054\ yr^{-1}$, $t_{1/2} = 10.2$ years)

To project this trend into the future, the aggregate rate constant for arsenic concentration was then applied to the observed concentration of arsenic in monitoring wells located around the PAC Source Area. As shown in Table 2, for those monitoring wells in which arsenic has most recently been observed above the MCL, the latest observed concentration and the date of observation were used to estimate the year at which groundwater concentration would decline below the MCL. For example, at MW-303, the last available measurement was 64.1 µg/l observed in October 2001. Using that concentration as an initial one and applying the aggregate rate constant yields approximately 18 years as the time necessary to reach the MCL at that location. Therefore, as shown in Table 2, the estimated year to reach the MCL at MW-303 is 2019 (i.e., 18 years from 2001).

Well ID	Location	Value on Trend (date)	Value on Trend (concentration ug/L)	Estimated Year when Arsenic Concentration = 10ug/L
AD-2	PAC Source Area	5/5/2010	156.7	2036
MP-2	CCL Near Source Area[3]	5/5/2010	55	2026
MW-302A	PAC Source Area	5/4/2010	43.8	2024
MW-302B	PAC Source Area	5/4/2010	41.05	2023
AD-1	PAC Source Area	-	-	Already Below 10 ug/L
AW-1RR	PAC Source Area	4/23/2008	43.4	2022
AW-3	PAC Source Area	10/27/1999	179.5	2027
DW-1	Owens Corning Property	5/4/2010	68.1	2028
DW-2	Owens Corning Property	4/24/2008	201	2036
DW-3	Owens Corning Property	-	-	Already Below 10 ug/L
MW-101C	PAC Source Area	-	-	Already Below 10 ug/L
MW-303	PAC Source Area	10/19/2001	64.1	2019
MW-304	PAC Source Area	-	-	Already Below 10 ug/L
MW-307	PAC Downgradient	-	-	Already Below 10 ug/L
MW-308	PAC Downgradient	5/5/2010	97.9	2031
		Mean	71.25625	2026

Table 2: Estimated MNA Timeframe Using Aggregate Arsenic Rate Constant ($k = 0.1054\ yr^{-1}$, $t_{1/2} = 10.2$ years)

For each well, the predicted year of decline below the MCL depends upon the rate constant itself (which is the same for all wells), the amount by which the concentration used as a starting point exceeds the MCL, and the year of the latest observation. As shown in Table 2, the predicted year of decline below the MCL varies from 2019 to 2036 (i.e., 8 to 25 years in the future) with an average of 2026 (i.e., 15 years in the future).

The general behavior of the TOC and arsenic data, including their variability, are consistent with the site conceptual model articulated for the site over the last nearly 20 years. As demonstrated previously, the concentrations of organic carbon and arsenic are generally declining within the PAC Source Area and in the downgradient monitoring wells. While the approach used to estimate the time frames is reasonable and their range is consistent with the estimate from 2001 (i.e., 10 to 30 years), uncertainty remains. In particular, co-precipitation of arsenic from groundwater is a complex, multi-step process, the rate of which is difficult to predict and likely to vary in space.

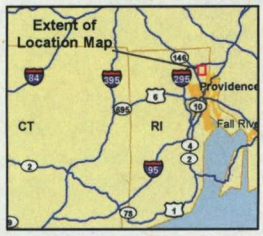
Conclusion

Subject to the above-stated caveats, we believe that 10 to 30 years is a reasonable estimate of the time frame over which MNA will be an effective remedy at the PAC Source Area of OU 1 at the Peterson/Puritan Superfund Site.

ATTACHMENT 3

SITE FIGURES

Flow
Ashton Dam
Town of Cumberland
Ashton Mill
Boundary of Potential OU 3
Mackland Farm/ Kelly House Property
116
Blackstone River
Pacific Anchor Chemical Facility (PAC)
(Former) Peterson/Puritan Facility (CCL)
Dean Wharehouse
Boundary of OU 1
Town of Lincoln
Okonite
Boundary of OU 2
(Former) Martin St Municipal Wellfield
Hope Global
Blackstone River
Blackstone Canal
Lenox St. Well
Quinnville Municipal Wellfield
J.M. Mills Landfill
Pratt Dam



Notes:
1. Boundaries depicted are estimated and are for general descriptive purposes only.
2. OU1 includes the Quinnville wellfield as a receptor of OU1 groundwater contaminants.
3. For OU-1, this map depicts an estimated site boundary configuration indicating extent of future Institutional Controls (deed restrictions) to be implemented.

Aerial Photo Date 4/14/03 from RIGIS

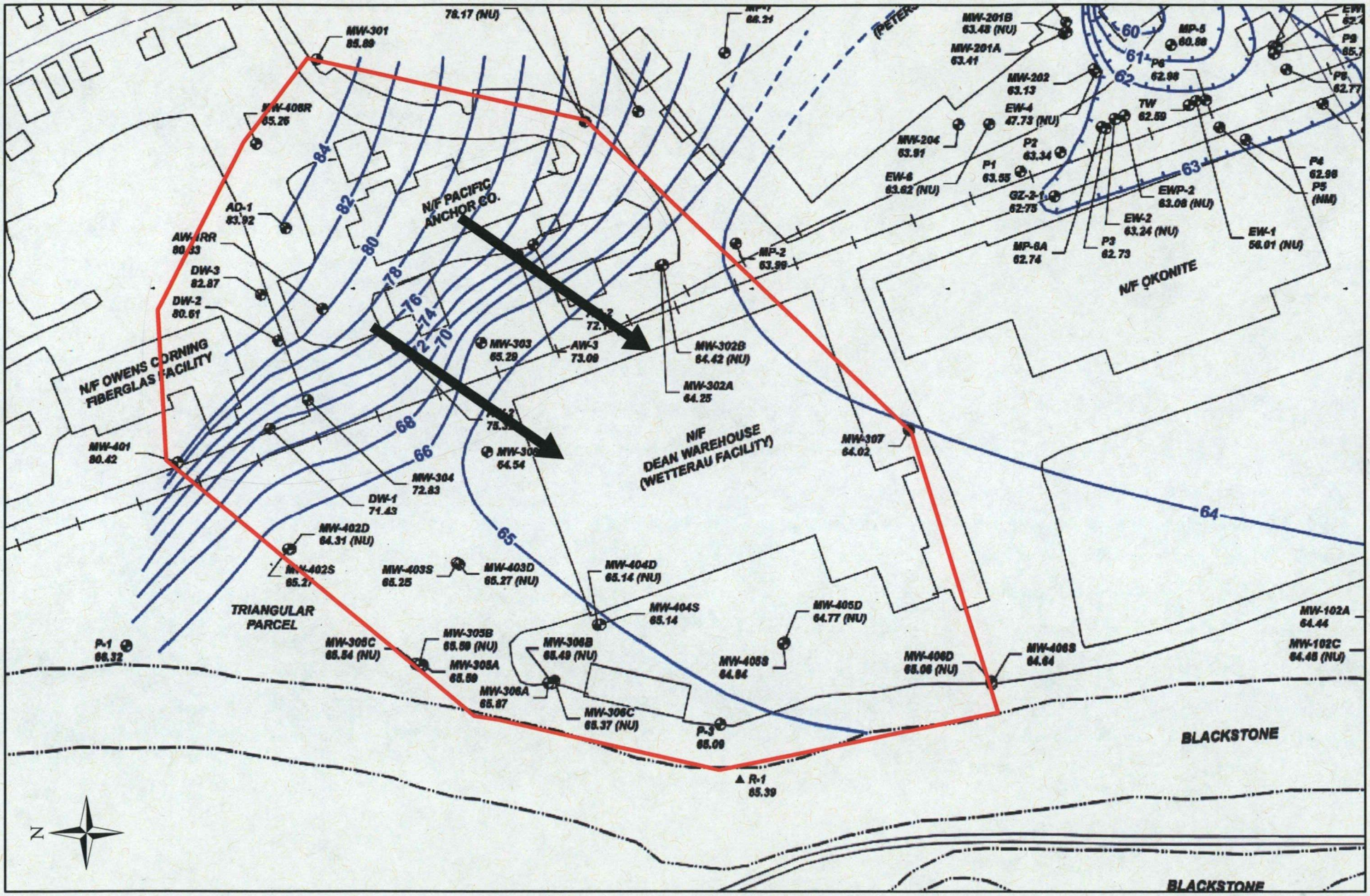
N

0 1,000 Feet

US Army Corps of Engineers
New England District

M:\Projects\Superfund\PetersonPuritan\Figures\PetersonPuritanLocationMapAerial091912.pdf
M:\Projects\Superfund\PetersonPuritan\MXDs\PetersonPuritanLocationMapAerial062112.mxd
September 19, 2012 DWN: MTW CHKD: KJH

Figure 1
Location Map with Aerial Photo
Peterson/Puritan Superfund Site
Cumberland, RI



0 100 200 400 600 800 Feet

Groundwater Flow Direction

MNA Compliance Zone

Round 22 Groundwater Contours (feet)

Figure 2:
Proposed MNA Compliance Zone
PAC Remediation Area
Peterson Puritan Superfund Site
Cumberland, Rhode Island