

Cholla Power Plant, Joseph City, Arizona, Voluntary Remediation Program #090050-00

Monitored Natural Attenuation Work Plan

December 2020

Arizona Public Service

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1. Introduction

The Arizona Public Service (APS) Cholla Power Plant (the Site) consists of four coal-fired generators and is located in Joseph City, Arizona, 300 feet north of the railroad tracks that run along the banks of the Little Colorado River. Figure 1-1 is a Site location map, and Figure 1-2 shows groundwater monitoring well locations. Volatile organic compounds (VOCs), including chlorinated VOCs, were identified in the groundwater beneath the Site during previous investigations while assessing contamination resulting from a diesel fuel release, as discussed in Section 1.1.

The purpose of this report is to summarize the evaluation of physical and analytical information at the Site and to present a work plan to implement a monitored natural attenuation (MNA) remedy for VOCs in Site groundwater. APS is conducting activities related to VOCs in Site groundwater under the Arizona Department of Environmental Quality's Voluntary Remediation Program (VRP); the Site has been assigned a VRP site code of 090050-03.

1.1 Summary of Previous Investigations

APS has conducted investigations related to underground storage tank (UST) and petroleum releases and has performed ongoing groundwater monitoring at the Site since the early 1990s, including the following:

- Harding Lawson Associates conducted investigations of a UST release in the early 1990s and installed wells UST-1 through UST-5 (HLA 1995).
- APS conducted investigations in May 1998 and October 2002 to evaluate the extent and magnitude of soil contamination associated with a diesel fuel release from an abandoned, buried pipeline located between Generator Units 2 and 3. In 2005, two monitoring wells, DR-1 and DR-2, were installed to assess potential groundwater contamination associated with the diesel fuel release. (Mogollon 2005).
- Two additional monitoring wells (VRP-1 and VRP-2) were installed in 2007 to assess the extent and degree of VOC contamination in groundwater in the vicinity of well DR-2 (Mogollon 2008).
- A HydroPunch investigation was conducted during November 2011 to assist in delineating the horizontal extent of groundwater contamination and to attempt to identify the source area (Mogollon 2012).
- Three groundwater monitoring wells (VRP-3, VRP-4, and VRP-5) were installed in November 2012 to further assess the extent of groundwater contamination in the vicinity of well DR-2 (Mogollon 2013).
- Five shallow groundwater monitoring wells (VRP-7 through VRP-11) and one deep groundwater monitoring well (VRP-12) were installed in 2016 to further characterize the lateral and vertical extent of trichloroethene (TCE)-impacted groundwater (CH2M 2017). Aquifer tests were performed to evaluate the hydraulic conductivity of the alluvial aquifer.
- Deep groundwater monitoring well VRP-13 was installed in 2017 to evaluate VOC impacts downgradient of well VRP-3 in the deeper zone of the aquifer (CH2M 2018).
- Groundwater monitoring wells CH-MW-1 and CH-MW-2 were installed in 2017 to evaluate potential subsurface impacts of leakage from transformers (ARCADIS 2018a) and shunt reactors (ARCADIS 2018b).
- Intermediate zone groundwater monitoring wells VRP-14 and VRP-15 were installed in 2019 to evaluate VOC concentrations between depths of 40 and 90 feet below ground surface (bgs) (CH2M 2019).

Groundwater monitoring wells at the Site were sampled on a varying schedule after installation. Wells VRP-1, VRP-2, VRP-3, VRP-4, VRP-5, and DR-2 had one or more groundwater samples with a TCE concentration exceeding the Arizona Water Quality Standard (AWQS) of 5 micrograms per liter (µg/L). The maximum TCE concentration reported in groundwater was 140 μg/L in well VRP-3, measured in

June 2013. Groundwater samples collected from VRP-4 have exceeded the tetrachloroethene (PCE) AWQS of 5 µg/L.

Based on these results, the TCE-impacted groundwater appears to extend from well VRP-4 more than 500 feet west to well VRP-3. TCE-impacted groundwater does not appear to extend more than 1,000 feet from well VRP-3, based on HydroPunch sampling results, and does not appear to extend beyond the Site boundaries based on groundwater monitoring data.

1.2 Site Geology and Hydrogeology

The Site geology, hydrogeology, and hydrology were obtained from reports of previous investigations at the Site.

1.2.1 Geology

The following description is summarized from the *Arizona Public Service Cholla Power Plant Point of Compliance Evaluation* (POC Evaluation) (Montgomery 2011). The geology of the Site consists of floodplain alluvium overlying bedrock. The POC Evaluation describes the Holocene-age alluvium as *"heterogeneous, comprised chiefly of interbedded sand, silt and clay layers; some gravel beds have also been reported along the Little Colorado River."* All of the monitoring wells associated with the UST, diesel release, and VOC-impacted groundwater at the Site are screened in this alluvial unit. Groundwater in this unit is not used to a significant extent for water supplies but is important for riparian habitat. The thickness of the alluvium in the area of the VOC plume is not known, but based on thickness contours presented in the POC Evaluation, could be in excess of 150 feet.

Bedrock at the Site consists of the following units in descending order: Moenkopi Formation, Coconino Sandstone, Schnebly Hill Formation, and Supai Formation. The Moenkopi Formation is divided into three members: Holbrook, Moqui, and Wupatki. The Moqui member is the thickest of the three at about 250 to 300 feet thick and consists primarily of mudstone. The Moqui member acts as a confining bed, hydraulically separating the shallower alluvial unit and the deeper Coconino Sandstone.

The Coconino Sandstone is the principal water-bearing unit for this region. It consists of fine-grained, cross-bedded, eolian sandstone and is about 400 feet thick in the vicinity of the Site. The permeability varies greatly and depends on the degree of fracturing and cementation.

The Schnebly Hill Formation is about 300 to 350 feet thick and consists primarily of very fine-grained sandstone, with a permeability between 10 and 28 percent of that calculated for the Coconino Sandstone. The Supai Formation is about 600 feet thick and consists of halite and anhydrite.

1.2.2 Hydrogeology

Groundwater in the alluvial unit is present in the vicinity of the Site at a depth of approximately 40 feet bgs. The groundwater elevation in this unit decreased about 4 feet between 2006 and 2014 and increased about 3 feet between 2014 and 2020. The upper 35 to 40 feet of the alluvial unit consists of predominantly clayey sediments, below which fine sand extends to at least 120 feet bgs (CH2M 2017). Groundwater flow is generally westerly, with a very flat gradient of approximately 0.0009 (Jacobs 2020).

The Wupatki member of the Moenkopi Formation, located beneath the confining Moqui member and the underlying Coconino Sandstone, are saturated in the vicinity of the Site. Groundwater in these units generally flows to the northwest. Groundwater in the Coconino Sandstone occurs under confined conditions beneath the Site (Montgomery 2011).

2. Natural Attenuation Evaluation

Natural attenuation includes a variety of physical, chemical, or biological processes that act to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water (EPA 1998). The primary biological attenuation mechanism for chlorinated solvents is reductive dechlorination, which degrades contaminants such as TCE by sequentially removing chlorine atoms. Reductive dechlorination typically requires anaerobic aquifer conditions and often results in changes in groundwater chemistry. These changes can be measured by analysis of groundwater samples for parameters such as iron, manganese, sulfate, nitrate, and others.

Cometabolism (a biological process), abiotic transformation on reactive minerals (a chemical process), and the physical processes of dispersion, dilution, and sorption also can act to reduce VOC concentrations in groundwater.

Multiple lines of evidence were evaluated to assess the potential for natural attenuation of VOCs (primarily TCE) in groundwater. Data collected during field investigation and groundwater monitoring activities indicate that natural attenuation is occurring at the Site due to both biological and abiotic mechanisms. Key lines of evidence supporting this evaluation include the following:

- Field measurements of dissolved oxygen (DO) and oxidation-reduction potential (ORP) collected during well development indicate that anaerobic conditions exist in Site groundwater, which would be expected to facilitate reductive dechlorination of TCE and PCE.
- Groundwater monitoring data from October 2014 indicated that the highest concentrations of dissolved iron, dissolved manganese, and sulfate in samples collected from onsite wells (that is, not including well CR-1, which is located near the Little Colorado River) were found in the sample collected from downgradient well VRP-1. This suggests that these compounds may be generated during natural attenuation of the VOCs present in groundwater (CH2M 2015).
- The presence of cis-1,2-dichloroethene (DCE) indicates that reductive dechlorination is occurring in Site groundwater.
- The magnetic susceptibility analyses indicated that reactive minerals, such as magnetite, are present in the aquifer. The estimated half-life of TCE due to abiotic degradation ranges from 0.28 to 17 years.

The following sections describe evaluations of these lines of evidence.

2.1 Reducing Conditions in Site Groundwater

The DO and ORP of groundwater were measured during development of several monitoring wells in 2016 and 2017 (CH2M 2017, 2018). Table 2-1 summarizes the measurements. The final DO measurements made at the end of well development ranged from 1.00 milligrams per liter (mg/L) in well VRP-8 to 3.81 mg/L in well VRP-13, and the final ORP measurements ranged from -98.5 millivolts (mV) in well VRP-11 to -3.4 mV in well VRP-12. These measurements indicate that anaerobic conditions that can facilitate reductive dechlorination exist in Site groundwater.

	. .			
Well	Date	Time	DO (mg/L)	ORP (mV)
VRP-7	8/25/2016	15:20	2.52	-74.2
VRP-8	8/27/2016	12:10	1.00	-53.2
VRP-9	8/27/2016	16:00	1.84	-85.4
VRP-11	8/24/2016	11:15	1.14	-98.5
VRP-12	8/23/2016	14:35	3.09	-3.4
VRP-13	11/6/2017	11:25	3.81	-70.2

Table 2-1. Dissolved Oxygen and Oxidation Reduction Potential in Groundwater

2.2 Attenuation Parameters

Several groundwater samples collected in August 2014 were analyzed for natural attenuation parameters including dissolved iron and manganese, nitrate and nitrite, methane, sulfate, and total organic carbon. Table 2-2 summarizes the laboratory analytical results from these samples. The following points summarize the interpretation of these data:

- Concentrations of iron are generally greater than 1 mg/L, indicating that the reductive pathway is possible.
- Concentrations of nitrate and sulfate are low enough not to compete with the reductive pathway.
- Concentrations of iron and manganese are generally highest in wells located within the VOC plume, indicating that they may act as electron acceptors during the reductive dechlorination pathway.
- Methane concentrations were above 0.5 µg/L in wells VRP-5 and VRP-3, suggesting anoxic conditions favorable to reductive dechlorination in these wells.
- Well CR-1 appears to have a different geochemistry than other wells at the Site. Concentrations of iron, sulfate, and total organic carbon are much lower in this well compared to other Site wells.

These parameters support the reductive dechlorination pathway in Site groundwater.

Table 2-2. 2014 Groundwater Geochemistry

Notes:

Wells are listed in approximate order from upgradient to downgradient.

Ethane and ethene were not detected in any of the samples

a Assumes iron is present as iron(II)

Meets screening criteria (EPA 1998)

2.3 Presence of Daughter Products in Groundwater

The presence of daughter products can be used to show that parent compounds, such as TCE, are degrading through natural processes. In particular, the presence of cis-1,2-DCE and vinyl chloride provide evidence of reductive dechlorination.

Table 2-3 summarizes the concentrations of PCE, TCE, various forms of DCE, and vinyl chloride measured in samples collected during the fall 2020 sampling event. Table 2-3 also calculates the ratio of cis-1,2-DCE to total DCE, the concentrations of organic chlorine and ethene, the molar ratio of chlorine to ethene, and the fraction of chlorine atoms removed from TCE. Although PCE concentrations are included in the table, they are not used in the daughter product ratio because TCE is assumed to be the primary

compound released to the environment. The analysis likely underestimates the percentage of chlorine removed because vinyl chloride was not detected in any of the samples and groundwater samples were not analyzed for ethene. The absence of vinyl chloride in groundwater containing parent products is not uncommon and may be due to rapid aerobic degradation of vinyl chloride to ethene and ethane or mineralization to carbon dioxide, water, and chloride. Omitting concentrations of these degraded compounds from the analysis likely underestimates the amount of degradation.

The ratio of cis-1,2-DCE to total DCE ranged from 94 percent to 100 percent. Ratios above 80 percent indicate that the DCE likely was generated through reductive dechlorination (EPA 1998). The DCE ratios for some wells could not be calculated because cis-1,2-DCE was not detected in the samples from those wells.

The fraction of chlorine removed from TCE were calculated by first converting the concentrations of TCE and its degradation products from micrograms per liter to moles per liter of chlorine and moles per liter of chloroethene. For TCE, there are 3 moles of chlorine for each mole of chloroethene (three chlorine atoms per molecule); for cis-1,2-DCE, trans-1,2-DCE, and 1,1-DCE, there are 2 moles of chlorine for each mole of chloroethene (two chlorine atoms per molecule); and for vinyl chloride there is 1 mole of chlorine per mole of chloroethene (one chlorine atom per molecule). The overall ratio for each well is the total moles of chlorine divided by the total moles of ethene based on concentrations of TCE and each of its degradation products. The percentage of chlorine removed is 1 minus the overall ratio divided by the ratio for pure TCE (which is 3), and that difference multiplied by 100:

$$
\% \text{ Chlorine Remove } d = \left(1 - \left[\frac{Cl_{TCE} + Cl_{cDCE} + Cl_{tDCE} + Cl_{1,1DCE} + Cl_{VC}}{ETH_{TCE} + ETH + ETH_{1,1DCE} + ETH_{VC}} \right] \right) \times 100
$$

Where:

CI_{TCE} is the total moles of chlorine in TCE in the sample.

Cl_{cDCE} is the total moles of chlorine in cis-1,2-DCE in the sample.

CltDCE is the total moles of chlorine in trans-1,2-DCE in the sample.

ClVC is the total moles of chlorine in vinyl chloride in the sample.

 ETH_{TCE} is the total moles of ethene in TCE in the sample.

ETHcDCE is the total moles of ethene in cis-1,2-DCE in the sample.

ETH_{tDCE} is the total moles of ethene in trans-1,2-DCE in the sample.

ETHVC is the total moles of ethene in vinyl chloride in the sample.

Table 2-3 summarizes the molar ratio calculations. The percentages of chlorine atoms removed from TCE ranged from 0 to 24 percent, and the average chlorine removal was 9 percent. These calculations suggest that reductive dechlorination is occurring in Site groundwater.

Table 2-3. Daughter Product Evaluation

Notes:

Nondetected results were replaced with a concentration of 0 µg/L for calculation purposes

PCE concentrations are not used in the calculations since it is rarely detected and TCE is assumed to be the primary released compound

Analytical results reported above the reporting limit are in **bold.**

Bold text indicates compound was detected.

Bold underlined text indicates the concentration exceeds the AWQS.

 $J =$ estimated value

"<" denotes that the compound was not detected; the value given is the reporting limit

bmp = below measuring point

ID = identification number

 $mol/L = mole(s)$ per liter

PDB = passive diffusion bag

2.4 Abiotic Attenuation

Magnetite, the most abundant mineral in natural sediments that exhibits magnetic behavior (Microbial Insights 2015), has been shown to degrade a variety of chlorinated alkenes including TCE (EPA 2009). In contrast to anaerobic biodegradation, abiotic degradation by magnetite does not go through a sequential reductive dechlorination (for example, TCE to cis-1,2-DCE to vinyl chloride) so the effects of this mechanism cannot be evaluated using the daughter product ratio method. This process has been shown to be adequate to support MNA as a remedy or part of a remedy at a site (Wiedemeier et al. 2017).

Magnetic susceptibility is a measure of the amount of magnetite present in the aquifer sediment. The results of the magnetic susceptibility analysis can be used to estimate the range of first-order decay rate for TCE and other VOCs through an empirical relationship (Lebron et al. 2015). Two soil samples collected when drilling wells VRP-7 and VRP-11 were analyzed for magnetic susceptibility, and the values were 5.79E-07 cubic meters per kilogram (m^3/kg) and 3.25E-07 m^3/kg (CH2M 2017). This indicates that the reactive mineral magnetite is present in the aquifer (EPA 2009) and likely facilitates abiotic degradation of VOCs at the Site. These measurements equate to a first-order decay rate constant of approximately 0.04 to 2.5 per year (Lebron et al. 2015). The decay constant is converted to a half-life using the following equation:

$$
t_{1/2} = \frac{\ln(2)}{\lambda_{\rm t}}
$$

Where:

t1/2 is the half-life.

λ*^t* is the first order decay rate constant.

The half-life is the time required for the concentration to reduce to half of its original value. Based on the range of the estimated decay rate constant, this equation yields a half-life ranging from 0.28 to 17 years.

2.5 Trend Evaluation and Regression Analysis

Jacobs Engineering Group Inc. (Jacobs) evaluated TCE concentration trends for selected wells using the Mann-Kendall trend analysis and calculated point attenuation rates using a regression analysis. This section summarizes the results of those evaluation focusing on wells that currently or historically contained TCE at concentrations exceeding its AWQS. These wells include DR-2 and VRP-1 through VRP-5.

Jacobs evaluated TCE concentration trends using the Mann-Kendall analysis in 10 groundwater monitoring wells where TCE is routinely detected (Jacobs 2020). Among the three wells that contained TCE at concentrations exceeding its AWQS of 5 µg/L in September 2020, the analysis identified a decreasing trend for well VRP-2, a stable trend for well VRP-3, and no trend for well VRP-4. None of the wells containing TCE at concentrations exceeding its AWQS exhibited an increasing concentration trend. Among wells that did not contain TCE at concentrations exceeding its AWQS in September 2020, the analysis identified a decreasing concentration trend for wells DR-2 and VRP-1 and no trend for well VRP-5.

Jacobs calculated point attenuation rates for TCE using the methods described in the U.S. Environmental Protection Agency (EPA) guidance document, *An Approach for Evaluating the Progress of Natural Attenuation in Groundwater* (EPA 2011). Appendix A contains the regression spreadsheets, and Table 2-4 summarizes the calculated rate constants.

The rate constants were converted to half-life values using the formula in Section 2.4 (half-lives could not be calculated for wells VRP-4 and VRP-5 because their attenuation rates were negative, indicating a slight increasing concentration trend). The half-life values for wells DR-2, VRP-1, and VRP-2, which ranged from 11 to 13 years, were similar to the average of those obtained from the magnetic susceptibility analysis. The half-life for well VRP-3 was 144 years, which is consistent with the stable trend identified for this well from the Mann-Kendall analysis.

These analyses indicated stable or decreasing TCE concentration trends in four of the six wells that currently or historically contained TCE at concentrations exceeding its AWQS. Wells VRP-4 and VRP-5 showed no trend from the Mann-Kendall analysis and a slight increasing trend from the regression analysis. This is likely due to a short-term increasing trend in TCE concentrations observed in these wells between roughly October 2017 and February 2020.

2.6 Prevention of Offsite Volatile Organic Compound Migration

The attenuation rate can be compared to the estimated velocity of TCE in groundwater to assess whether natural attenuation could prevent migration of TCE at concentrations exceeding the AWQS beyond the Site boundary. Using Site hydraulic conductivity, hydraulic gradient, and porosity data, it is possible to estimate the average linear groundwater velocity for the Site using the following equation:

$$
v = k \frac{dh/dl}{n}
$$

Where:

 $v =$ groundwater velocity

 $k = h$ ydraulic conductivity

dh/dl = horizontal hydraulic gradient

 $n =$ porosity

Inserting the hydraulic conductivity of 130 feet per day, the hydraulic gradient of 0.0009 feet per foot, and the porosity ranging from 0.26 to 0.30 into this equation yields an estimated average linear groundwater velocity between 142 and 164 feet per year. This does not take into account sorption of TCE to organic material or degradation of TCE through microbial or abiotic pathways, both of which would result in a longer time required to reach the Site boundary. Using an approximate distance of 1,800 feet between well VRP-3 and the Site boundary, and an average groundwater velocity of 153 feet per year, it would take about 12 years for VOCs to migrate offsite.

However, such migration has not been observed. The TCE concentration in well VRP-3 was 51 µg/L when the well was installed in 2012. Given that TCE was detected at a concentration that exceeded its AWQS in well DR-2 when that well was installed in 2005, TCE likely has been present at well VRP-3

since at least this time. Assuming a groundwater velocity of 153 feet per year and a starting date of 2005, TCE at well VRP-3 should have been observed in wells CH-MW-2 or VRP-9 by 2013. TCE was detected once in well CH-MW-2 at a concentration of 0.51 µg/L in February 2020 and has never been detected in samples from well VRP-9 (these wells were installed in 2017 and 2016, respectively). This suggests that either the groundwater velocity is slower than estimated from site parameters or attenuation is occurring rapidly.

The concentration of TCE in well VRP-3 (100 µg/L in September 2020) would have to be reduced by half just over four times to reach a concentration below the AWQS. For this to occur within 12 years, the halflife would need to be less than 3 years, which is shorter than the half-lives estimated using the regression analysis, but is within the range of half-lives obtained from the magnetic susceptibility analyses. Other attenuation mechanisms, including reductive dechlorination, dilution, and dispersion, would act to reduce the half-life.

2.7 Summary

Multiple lines of evidence indicate that natural attenuation is occurring in Site groundwater. Primary mechanisms likely include reductive dechlorination and abiotic transformation on reactive minerals in addition to physical mechanisms such as dilution, dispersion, and sorption. Abiotic degradation alone may reduce the TCE concentrations in groundwater sufficiently to prevent offsite migration of TCE exceeding the AWQS. Other attenuation mechanisms are expected to further reduce TCE concentrations in groundwater.

Historical laboratory analytical data demonstrate that TCE has not been detected in downgradient wells VRP-8, VRP-9, VRP-14, CH-MW-2, or CR-1 at concentrations exceeding its AWQS of 5 µg/L. These data confirm that the combination of low groundwater velocity and attenuation of TCE in groundwater have been effective at preventing migration of TCE offsite at concentrations that exceed the AWQS.

3. Proposed Remedy

The proposed remedy for the site is MNA. This section escribes the monitoring plan, metrics for the remedy, and contingency actions related to the metrics.

3.1 Groundwater Monitoring Plan

The proposed monitoring plan consists of continuing to sample Site groundwater semiannually for VOC analysis and adding analysis of natural attenuation parameters in selected wells. The depth to groundwater will be measured semiannually in wells UST-2, DR-2, M-62A, VRP-1 through VRP-5, and VRP-7 through VRP-15 . Samples will be collected semiannually from these wells using PDB samplers and will be analyzed for VOCs using EPA Method 8260B.

Wells UST-2, DR-2, VRP-3, VRP-4, VRP-9 and CH-MW-2 will be sampled annually using the low-flow purge method and will be analyzed for MNA parameters. These wells were selected to provide two upgradient monitoring locations, two in-plume locations, and two downgradient locations to compare geochemical parameters along the axis of the plume. MNA parameters and typical analytical methods include the following:

- DO and ORP (field measurements)
- Dissolved iron and manganese (EPA Method 6010B)
- Sulfate, nitrate, nitrite, and chloride (EPA Method 300.0)
- Sulfide (SM4500S2-D)
- Total organic carbon and total dissolved carbon (EPA Method 9060A)
- Alkalinity (SM2320B)
- Methane, ethane, ethene, and carbon dioxide (RSK-175)

Parameters may be removed from this list if results indicate they do not support the MNA evaluation.

Sampling will be conducted in accordance with procedures described in Appendix B, and data validation and management will be conducted in accordance with the *Arizona Public Service Quality Assurance Project Plan* (Jacobs 2019).

3.2 Metrics

The proposed metrics for the remedy are based on demonstrating the stability or reduction of the TCE plume in groundwater and the lack of offsite migration. The proposed metrics are as follows:

- A decreasing or stable trend in the TCE concentration at well VRP-3
- No offsite migration predicted, based on the estimated groundwater flow velocity, TCE attenuation rates, and TCE concentrations and trends in downgradient wells, particularly VRP-9 and CH-MW-2

3.3 Contingency Triggers and Actions

Contingency actions may be triggered based on periodic evaluations of the metrics. The proposed contingency triggers and actions are as follows:

- If the TCE concentration at well VRP-3 shows an increasing trend above historical concentrations, additional source area investigations will be evaluated. Access to potential source areas may be insufficient to conduct a thorough source area investigation.
- If the TCE concentrations in a perimeter well such as VRP-9 or CH-MW-2 show an increasing trend and offsite migration of the TCE was predicted, the sampling frequency in the affected well(s) will be increased to quarterly, and the addition of additional downgradient wells will be considered.

3.4 Schedule

Groundwater monitoring events are currently scheduled for February and August of each year. MNA parameters will be collected once per year during the February event. Results will be reported within 60 days of receipt of validated laboratory data. Each report will include a summary of the field activities, tabulated groundwater elevations and laboratory results, and maps showing groundwater elevation contours and selected VOC concentrations. The second semiannual report will also include historical groundwater elevation and VOC data, an update of the Mann-Kendall trend analysis, daughter product ratio evaluation, groundwater elevation and TCE concentration hydrographs, and an evaluation of Site metrics.

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Figures

Figure 1-1**. Site Location Map**

Source: ESRI World Imagery (Clarity)

Figure 1-**2. Well Location Map** APS Cholla Power Plant Joseph City, Arizona

- \bigcirc Shallow Monitoring Well (screened from top of aquifer to 60 feet or less)
- \bigcirc Intermediate Monitoring Well (screened from top of aquifer to 90 feet or less)
- \bullet Deep Monitoring Well (screened interval is below 90 feet and above 120 feet)

Solution Inactive Well

Source: ESRI World Imagery (Clarity)

LEGEND

Appendix A Regression Analysis

DR‐2

VRP‐1

VRP‐2

VRP‐3

Appendix B Groundwater Sampling Procedures

Appendix B. Groundwater Monitoring Program

This appendix describes procedures for collecting groundwater samples as part of the routing groundwater monitoring program for the Arizona Public Service Cholla Power Plant site in Joseph City, Arizona. The monitoring program consists of semiannual groundwater sampling for volatile organic compounds (VOCs) using passive diffusion bags (PDBs) and annual sampling of six wells for monitored natural attenuation (MNA) parameters.

The depth to groundwater will be measured semiannually in wells UST-2, DR-2, M-62A, VRP-1 through VRP-5, and VRP-7 through VRP-15. Samples will be collected from these wells semiannually using PDBs and will be analyzed for VOCs using U.S. Environmental Protection Agency (EPA) Method 8260B.

In addition, wells UST-2, DR-2, VRP-3, VRP-4, VRP-9, and CH-MW-2 will be sampled annually using the lowflow purge method and will be analyzed for MNA parameters. These wells were selected to provide two upgradient monitoring locations, two in-plume locations, and two downgradient locations to compare geochemical parameters along the axis of the plume. MNA parameters and typical analytical methods include the following:

- Dissolved oxygen (DO) and oxidation-reduction potential (ORP) (field measurements)
- Dissolved iron and manganese (EPA Method 6010B)
- Sulfate, nitrate, nitrite, and chloride (EPA Method 300.0)
- Sulfide (SM4500S2-D)
- Total organic carbon and total dissolved carbon (EPA Method 9060A)
- Alkalinity (SM2320B)
- Methane, ethane, ethene, and carbon dioxide (RSK-175)

Table B-1 summarizes the sampling program.

Table B-1. Groundwater Sampling Program Summary

Well	Measuring Point Elevation (feet amsl)	Screened Interval (feet bgs)	Depth of PDB for Semiannual Sampling for VOCs (feet btoc)	Annual Sampling for MNA Parameters
VRP-9	5011.78	20-60	53	Yes
VRP-10	5015.42	20-60	53	No
VRP-11	5019.53	20-60	53	No
VRP-12	5019.62	108-118	113	No.
VRP-13	5013.93 ^a	110-120	115	No.
VRP-14	5014.42 ^a	60-70	65	No.
VRP-15	5018.89a	$71 - 81$	76	No.

Table B-1. Groundwater Sampling Program Summary

a Elevation was adjusted from the North American Vertical Datum of 1988 to match the power plant's internal coordinate system by subtracting 2.28 feet from the survey measurements

amsl = above mean sea level

bgs = below ground surface

 b toc = below top of casing

B.1 Passive Diffusion Bag Samplers

B.1.1 Installation

PDBs should not be installed unless the top of the sampler is at least 1 foot below the water table when the sampler is suspended above the bottom of the well, including any sediment that may have accumulated. The 1-foot thickness of water column above the PDB allows for fluctuations in the water table elevation during the equilibration period. It may be necessary to adjust the depth of the sampler from the values listed in Table B-1 based on the amount of water in the well at the time the PDB is installed. An example field sampling form is included in Appendix C.

The following procedures will be followed to install PDBs:

- 1. Measure the depth to groundwater and total depth of each monitoring well using an electronic water level meter. Record the measurements and ensure that the planned placement depth is completely below the water level.
- 2. Fill the PDB sampler by removing the plug from the sampler, inserting the provided funnel into the sampler, and pouring deionized water into the sampler. The sampler should be filled until water rises and stands at least halfway into the funnel. Remove excess bubbles from the sampler, and then remove the funnel and securely replace the plug.
- 3. Slide the filled PDB sampler into a clean, protective mesh sleeve if it is not already in one.
- 4. Attach a pre-measured harness or polyethylene rope to the well head to secure the PDB sampler during deployment. Next, attach the pre-measured harness and a stainless-steel weight to the PDB sampler. If a pre-measured harness is not used, attach a hangar assembly and/or a measured length of polyethylene rope and a stainless-steel weight to the PDB sampler. To keep the PDB sampler submerged a stainlesssteel weight should be attached to the bottom of the PDB sampler.
- 5. Slowly lower the stainless-steel weight, PDB sampler, and line into the well riser until the line holding the PDB sampler is taut.
- 6. Close the well casing to prevent precipitation from entering the well during the equilibration period. Based on the flat groundwater gradient at the Site, a minimum equilibration time of at least 2 weeks is recommended. PDB samplers may be left in wells for more than 1 year, and for routine groundwater

sampling a new PDB sampler can be installed immediately after the previous sampler is removed from the well for sampling.

B.1.2 Removal and Sampling

The following procedures will be followed to collect groundwater samples using PDBs:

- 1. Slowly remove the PDB sampler from the well by pulling up the weighted line. Avoid exposing the sampler to heat or agitation.
- 2. Examine the exterior of the sampler for tears in the membrane material. Make a detailed observation in the field notes of any residues or discoloration on the exterior of the sampler. Water from samplers in which the membrane has been damaged cannot be submitted for analysis.
- 3. Remove the sampler from the weighted line.
- 4. To minimize cross contamination, remove any excess liquid from the exterior of the sampler by wiping off the PDB sampler with a paper towel.
- 5. To transfer the water from the sampler to sample containers, insert the sampling straw into the bottom of the sampler. Flow may be controlled by tilting the sampler or straw. Fill and cap each sample container.
- 6. Immediately upon collection, all samples for chemical analysis are to be placed in a closed container on ice unless it is not possible to do so. In these instances, the samples should be placed on ice as soon as practical and during the time between collection and placing the samples on ice, the samples should be kept as cool as possible.
- 7. Any unused water in the PDB sampler should be transferred to a 55-gallon drum or other container and managed with other liquids, such as decontamination fluids. Minimal amounts of unused groundwater (for example, less than the volume of one sample container), or groundwater from wells with no history of impacts above the Arizona Water Quality Standard, may be discharged to the ground surface.
- 8. Dispose of the PDB sampler membrane and gloves properly. Reinstall tether with a new PDB or place in a sealable plastic bag and mark with the well number for storage until the next sampling event.

B.2 Purge and Sample

Groundwater samples will be collected from the monitoring wells UST-2, DR-2, VRP-3, VRP-4, VRP-9, and CH-MW-2 using dedicated or decontaminated submersible pumps. The following procedure will be used:

- 1. Measure the depth to groundwater in the well using an electronic water level meter.
- 2. Lower the pump into the well, placing the pump intake at about the middle of the wetted screen interval. The pump depth may need to be adjusted during the purge to maintain the flow of water if the well goes dry during purging.
- 3. Insert the water quality measurement probes into the flow-through cell and place in a shaded area. The purged groundwater must enter the flow through the cell by the lower port and exit via the upper port.
- 4. Begin purging the well at 0.2 to 0.5 liter per minute. Avoid surging. Purging rates for more transmissive formations could be started at 0.5 to 1 liter per minute.
- 5. Measure the water level, purge rate, and field parameters including pH, temperature, specific conductivity, ORP, and DO frequently (about every 5 minutes). The water level should indicate little drawdown in the well (less than 0.3 foot).
- 6. Water quality parameters are considered stable when consecutive measurements of pH are within 0.1 pH units and measurements of temperature and conductivity are consistent within 10 percent.
- 7. To collect a sample, reduce the flow rate to 100 milliliters per minute or less if possible. Fill sample containers completely, and cap the bottles. For vials, invert and tap to verify that no air bubbles are present. If air bubbles are larger than roughly pea-size, the bottle may be opened once and topped off. If bubbles are still present, discard the bottle and fill a new container.

8. Turn off the pump and record the volume of water purged.

B.3 Decontamination Procedures

Nondedicated or nondisposable field equipment used during sampling will be decontaminated prior to installation, in between wells, and again after the sampling event has been completed to prevent crosscontamination between sampling locations. Decontamination procedures for field personnel are described in the site Health and Safety Plan.

Nondisposable sampling equipment used for groundwater sampling will go through the following decontamination procedure:

- 1. Scrub with Alconox or equivalent laboratory-grade detergent and water.
- 2. Rinse with potable water.
- 3. Rinse with distilled deionized water.
- 4. Air dry on a clean surface or rack if possible.

Appendix C Field Sampling Forms

Passive Diffusion Bag Retrieval Data Sheet Arizona Public Service Cholla Power Plant Event: 2020 Second Semiannual

Notes:

Example Sample IDs

a Measure to the top of the well casing, not the pipe connector, at well M62-A CH-DR-2-1020 Regular sample collected from well DR-2 in October 2020 CH-FD01-102420 Duplicate sample collected on October 24, 2020

