High-resolution Groundwater Investigation at a FUSRAP Site with an Aging Water-supply Infrastructure: Former Harshaw Chemical Company, Ohio - 16146

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ABSTRACT

The Former Harshaw Chemical Company (HCC) Site is located in Cleveland, Ohio, approximately 5 kilometers (km) (3 miles) south of downtown Cleveland, in an industrialized area adjacent to the Cuyahoga River and Big Creek. Developed site parcels include former production areas with legacy buildings, former production area foundations, parking areas associated with previously demolished buildings, and re-developed privately-owned commercial properties.

The HCC Site was initially developed 1905 and commercially manufactured chemical solvents, metal salts, fluorides, hydrofluoric acids, and other chemical products. HCC began production activities for the Manhattan Engineer District (MED) in late 1942 in support of the United States' early atomic weapons program. The primary process conducted by the HCC consisted of the refining of uranium oxide to produce several uranium-bearing materials, including uranium hexafluoride (UF6), uranium tetrafluoride (UF4), and uranium tetrachloride (UCl4). The HCC also conducted numerous chemical and radiological research and production activities for the MED and later for the Atomic Energy Commission (AEC). Groundwater and soil contamination resulting from these activities is characterized in the site Remedial Investigation Report (USACE 2009) and primarily found near the G-1 process building.

A Feasibility Study (USACE 2012) evaluated soil remediation alternatives and their potential impacts to future groundwater conditions. Since there is no groundwater pathway in the assumed industrial future land use, groundwater evaluations are intended to demonstrate that further degradation of groundwater will not occur after potential soil remediation. Total uranium is the primary MED-based groundwater contaminant and was numerically simulated using a site-specific groundwater flow and transport model. Remedial results are judged in terms of no significant impact, significant positive impact (i.e., significantly decreased extent of contamination), or significant negative impact (i.e., significantly increased extent of contamination).

A complicating factor in the groundwater simulation and decision-making process for this site is the existence of municipal water-line leakage on and around the site. This aging infrastructure, in conjunction with the generations of modifications, promoted leakage and fresh-water contact with contaminated soils. To optimize the groundwater conceptual site model for numerical model updates, a high-density groundwater well network was installed in conjunction with the demolition of the G-1 building. The results of the detailed groundwater investigation, coincident soil sampling, utility-line termination, municipal water-line repairs, water-level collection, and uranium sampling indicates the groundwater is re-equilibrating and will lead to optimal decisions and site remediation.

INTRODUCTION

The Former Harshaw Chemical Company (HCC) Site is located in an industrialized area adjacent to the Cuyahoga River and Big Creek approximately 5 km (3 miles) south of downtown Cleveland, Ohio, USA. Developed site parcels include former production areas with legacy buildings, former production area foundations, parking areas associated with previously demolished buildings, and re-developed privately-owned commercial properties (Figure 1) [1].

Figure 1. HCC Site Components

The HCC Site was industrialized initially in 1905 and used to manufacture chemical solvents, metal salts, fluorides, hydrofluoric acids, and other chemical products. HCC expanded production in late 1942 to support the United States' early atomic weapons program under the Manhattan Engineer District (MED). The HCC refined uranium oxide to produce several uranium-bearing materials, including uranium hexafluoride (UF6), uranium tetrafluoride (UF4), and uranium tetrachloride (UCl4). The HCC also conducted numerous chemical and radiological research and production activities for the MED and subsequently the Atomic Energy Commission (AEC).

Groundwater and soil contamination resulting from these activities is characterized in the site Remedial Investigation Report (USACE 2009) and primarily found near the G-1 process building (USACE 2012) (Figure 2) [1, 2]. Geochemical indicators (pH and specific conductance) implied that leakage from the municipal water-supply infrastructure to the north was flowing along legacy site utilities and producing a hydraulic mound under and near the G-1 complex, which influenced the transport of uranium at the site (see notation on Figure 1). These water-supply lines are dual 61-centimeter (24-inch) 1100 kiloPascal (160 PSI) pipes and an associated 20-centimeter [8-inch] fire line. Subsequent investigations [3], in concert with water-line termination and repairs by municipal stakeholders, indicate a new baseline is emerging for subsequent geochemical rebound analysis that may influence remedial design components.

Figure 2. Soil and Groundwater Impacts

METHOD

Site hydrogeology

The hydrogeologic zones of interest at the HCC site include the overburden units and, to a lesser extent, the underlying weathered shale bedrock [1]. The overburden zone nearest the G-1 complex consists of two surficial coarse-grained fill layers, an underlying finer-grained layer of native sediments (or a native-fill soil mix), and a basal zone of variably coarse-grained shaly gravel and/or alluvium that blankets bedrock. The surficial fill produces a perched groundwater zone that varies up to seven feet in thickness under and around G-1, but is not contiguous across the site (i.e., the layer pinched out to 46 centimeters (cm) (18 inches) in test pits to the north). The underlying clayey layer varies up to 2.5 meters (m) (8 feet [ft]) in thickness and

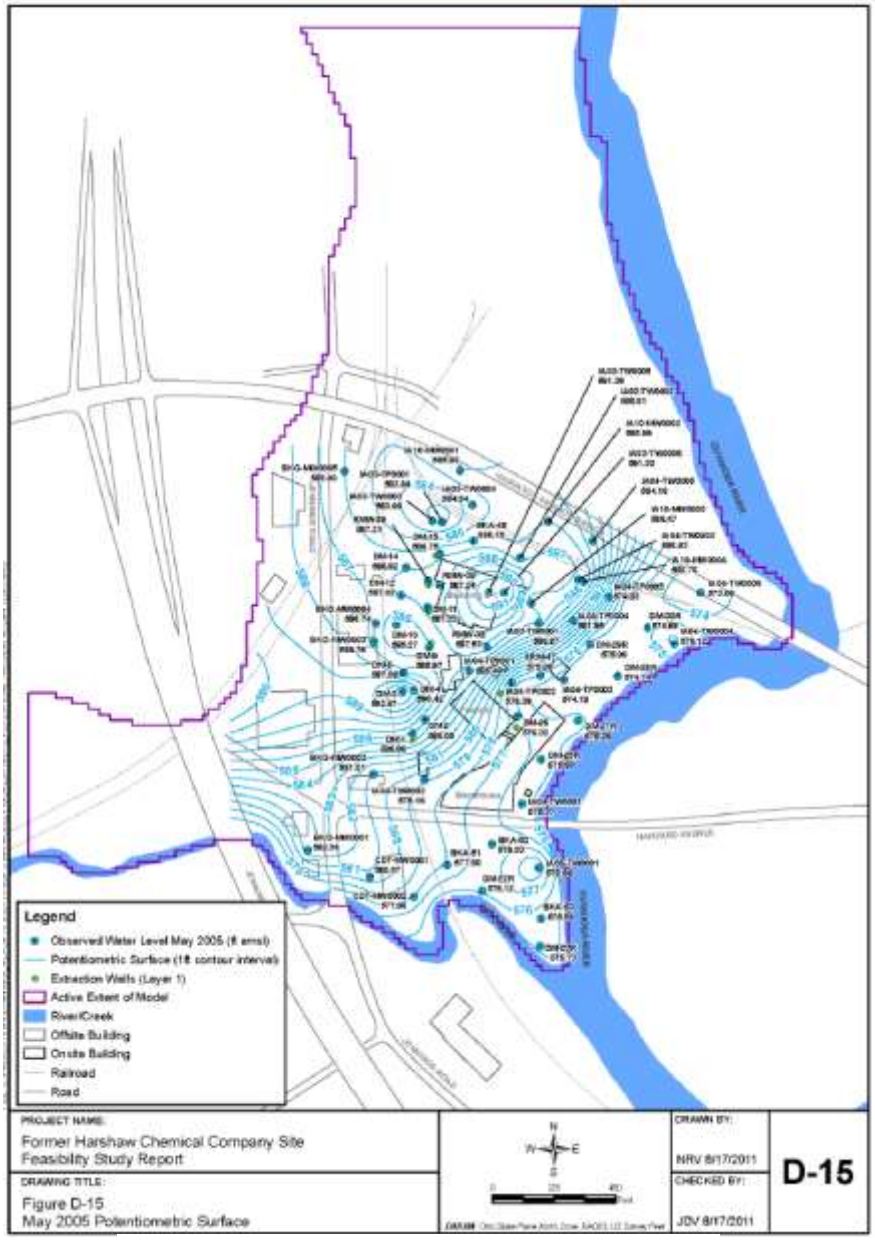

Figure 3. May 2005 Groundwater Levels

separates the perched zone from the underlying groundwater zone above bedrock. This fine-grained layer is thin to absent under and immediately near the G-1/G-2 footprint due to building foundation construction and utility trenching. Consequently, the subsurface conditions near G-1 (less distinct layering), in concert with water-main leakage evidently following legacy water lines, produced a groundwater mound under the G-1 area (Figure 3), which then dissipated in both the perched and deeper groundwater zones (Figure 4).

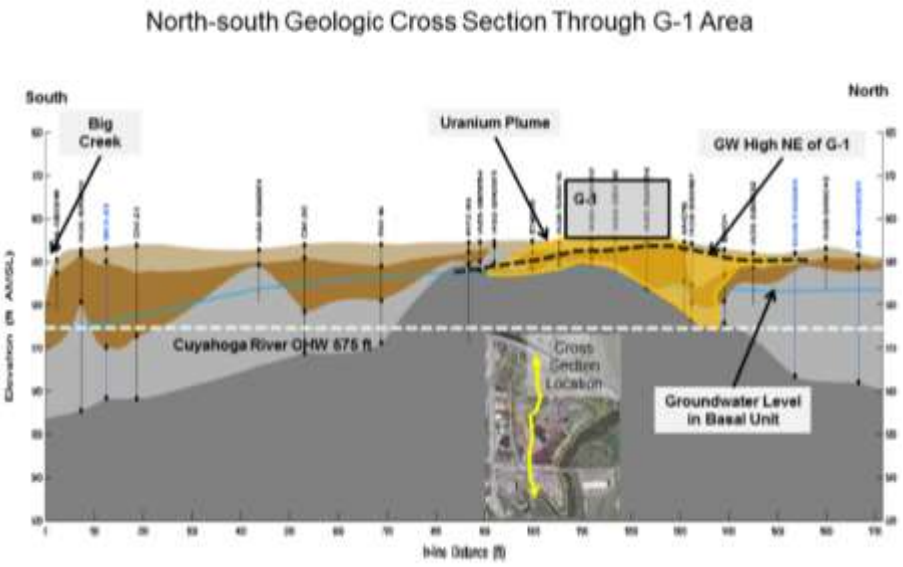

Figure 4. Conceptual Hydrogeologic Model

Groundwater-level trends generally indicate the water main repair to the north of the site, coupled with site water-line reconfiguration and termination at Harvard Avenue, are reflected in the declining groundwater elevations near G-1.

Potentiometric surface maps used as the baseline in the RI and FS decision making and modeling were derived from a near-average hydraulic condition (May 2005) that is depicted in Figure 3 [1, 2]. A potentiometric map reflecting current conditions (October 2015) is seen in Figure 5 and includes data from 18 new wells and 13 new piezometers (Figure 6). The new groundwater elevations are generally lower than previous datasets and thus indicates the site baseline is changing to reflect the absence of water-line leakage (i.e., the historic groundwater mound is dissipating).

A numerical groundwater flow and contaminant-transport model constructed for the RI and FS coalesced the overburden units into one single model layer that dominantly reflected the coarse-grained flow zone above bedrock (i.e., the perched zone was not represented in the model) [1, 2]. The weathered bedrock (Cuyahoga Shale) is represented as a second low-permeability layer in the model. The near-average groundwater elevations from May 2005 (Figure 3) were used as calibration targets since they reflect an overall higher (more conservative) horizontal hydraulic gradient from the Building G 1 area to the Cuyahoga River. To simulate current conditions, 2016 water levels (Figure 5) were input to the numerical model as calibration targets. Additionally, the numerical model was updated to reflect the new conceptual site model, where water-line leakage is terminated, the recharge distribution omits an artificial high-input zone (0.5 gallons per minute), and a new uranium distribution is predicted for decision-making purposes. These impacts are discussed below and in the results section.

Figure 5. 2016 Groundwater Elevations

Site contamination

The historical G-1 area operations produced subsurface soil impacts (Figure 2) that became partially saturated under G-1 due to the groundwater mound (Figure 5). Uranium dissolved in groundwater and eventually infiltrated storm-sewers that discharged to the Cuyahoga River. The uranium plume also dispersed westward towards an eight-well nickel recovery system designed to prevent nickel-impacted groundwater from infiltrating the sanitary sewers. Figure 2 also presents the interpreted total-uranium plume used in the RI and FS, whereas the reconfigured plume and soil extents using the 2014-2015 monitoring well and test-pit data show some shrinkage in the west but slight expansion in the north and east.

Figure 6. Monitoring Well and Well Point Array

The current uranium plume is derived using the maximum of the unfiltered total uranium results in groundwater and test-pit water (Figure 7), which is acceptable since filtered and unfiltered groundwater results for uranium are generally similar, as exemplified by an average filtered to unfiltered ratio of 0.96. The contamination in the perched zone is dispersed farther north due to preferential pathways in the near-surface fill, which was seen varying from clean sand to granular ash to clayey soils. The basal groundwater zone exhibits a more constrained plume, indicating the transport from the G-1 area, even under a mounded condition, is inhibited by the local hydrostratigraphy and geochemistry.

RESULTS

New conceptual groundwater model

The removal of the G-1 structure was followed by a detailed groundwater investigation and sampling regimen. The origin of the groundwater mounding is not overly definitive, yet the investigative activities included the hydraulic isolation of site utilities and separate repair of the water main north of the site. Only a new 2-inch water line serves the nickel treatment facility.

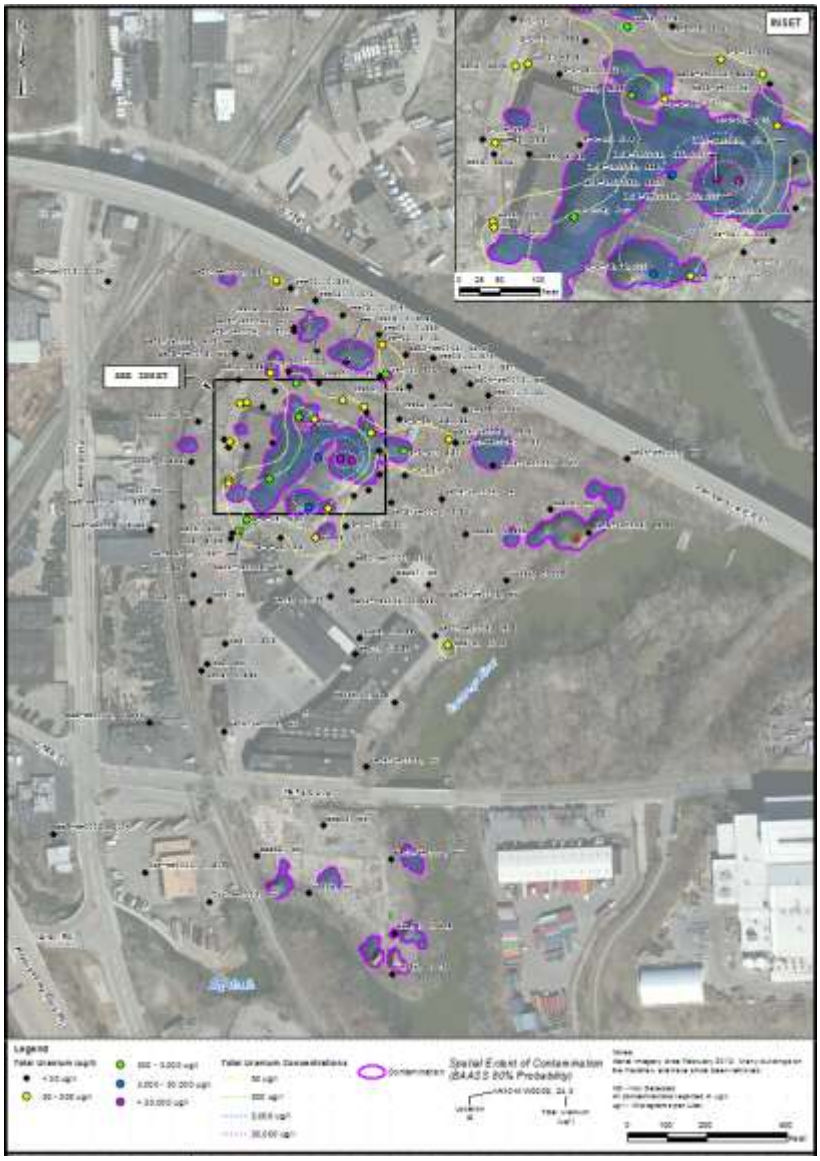

Figure 7. Site Soil and Groundwater Contamination

The combined activities, executed separately by the City of Cleveland and USACE, reduced the variables that were promoting the transport of uranium at the site. In addition, the site owner (BASF, Inc.) removed a series of storm-water sewers throughout the site, specifically the system that discharged to the Cuyahoga River (i.e., USACE sampling location IA09-SW0008 or BASF Outfall 007) (Figure 8).

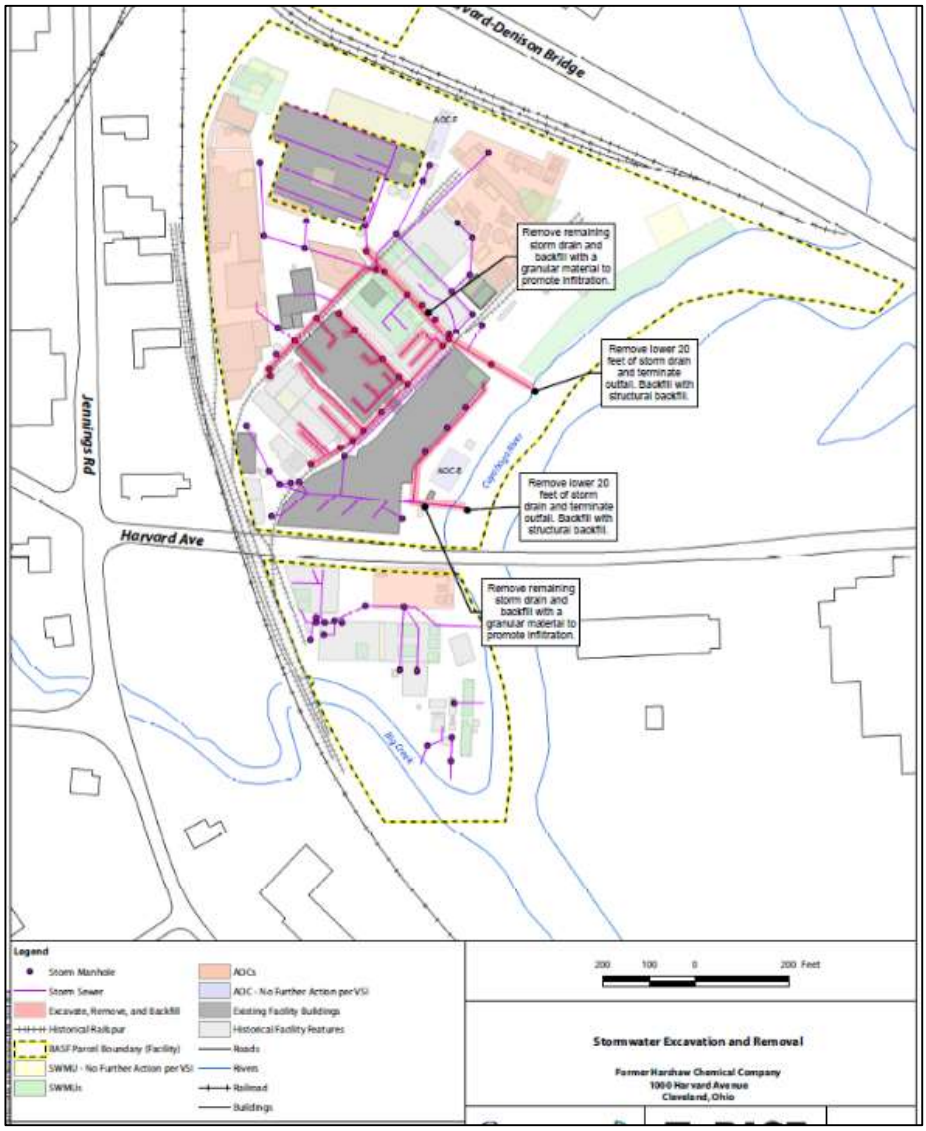

Figure 8. BASF Storm Sewer Removal

The utility trenches varied from 3 m to 4.3 m (10 to 14 ft) deep and were backfilled to grade with angular coarse gravel to cobble-sized quarried limestone. This configuration provides preferential recharge zones and groundwater flow pathways during the seasonally high groundwater periods (e.g., late-fall rains to spring melt-off). However, groundwater levels near G-1 are now declining, so the trenches may not promote plume expansion, but rather dispersion (dilution) due to higher recharge along the trenches. Current groundwater sampling and water-level data do not show perceptible influences from flow or transport in this utility-trench network (i.e., no groundwater depressions or plume lengthening).

The transient status of the groundwater at the HCC site (i.e., declining mound, gradient changes, less contaminated soil contact, rebounding native geochemistry, and utility pathways) and the impacts on predictive modeling are discussed below.

Groundwater modeling of the new CSM

The groundwater flow and contaminant-transport model used in the FS will be modified to account for the following changes in the conceptual site model:

- An artificially high recharge area under the eastern end of G-1 was previously set at 63.5 cm per year (25 inches per year) to manifest the groundwater mound near G-1; this area was modified to reflect the estimated recharge entering through the G-1 slab in other portions of the model (i.e., 2.54 cm or 1 inch per year).
- The storm-sewer excavations that are backfilled with cobble-sized stone were assigned recharge values previously estimated for degraded concrete, or 30.5 cm (12 inches) per year.
- The October 2015 water-level data were input as the new calibration targets for predictive transport analyses.
- The starting plume in the transport analysis was updated to reflect the higher density sampling data from 2014-2015.
- The hydraulic conductivity of the fill and soils below G-1 was increased to a uniform value of 5.0E-3 centimeter per second (cm/s) (14.1 feet per day [ft/d]), where less than 3 m (10 ft) in thickness, to conservatively reflect the influence of coarse-grained shallow fill versus deeper interlayered (coarse- and fine-grained layers) seen in boring logs and test pits.
- The subsurface bedrock topography will be re-contoured to reflect new boring log data near G-1 and along the northern railroad right-of-way.

During recalibration, the balance of model input was not updated, including residual leachate influxes, surface-water components, and assigned flow boundaries [1, 2].

Modeling results

The updated calibration and subsequent uranium transport prediction was slightly different for the long-term simulation. The uranium plume expanded more easterly towards the Cuyahoga River, but initiated with less overall mass in the plume due to plume re-delineation. This lower mass indicates greater long-term attenuation is possible (i.e., cation competition from high-concentration groundwater saturation is less pronounced than the previous RI and FS models).

In addition, the groundwater sampling data were evaluated to produce geochemical plots that support decision-making at the HCC site (Figure 9). The potential for uranium transport declines with lower nitrate (<1.1 mg/L), dissolved oxygen (< 0.94 mg/L), and oxygen reduction potential (<38 milliVolts and optimally <-5 milliVolts) that reflect reductive conditions, where uranium can complex with sulfides, oxides, and chlorides (and carbonates to a lesser extent). The ORP mapping at the site indicates that reductive conditions dominate the site groundwater in 2015 and should increase in size and strength (further lowering ORP values) to reflect what appears to be a normal background condition for this hydrogeology.

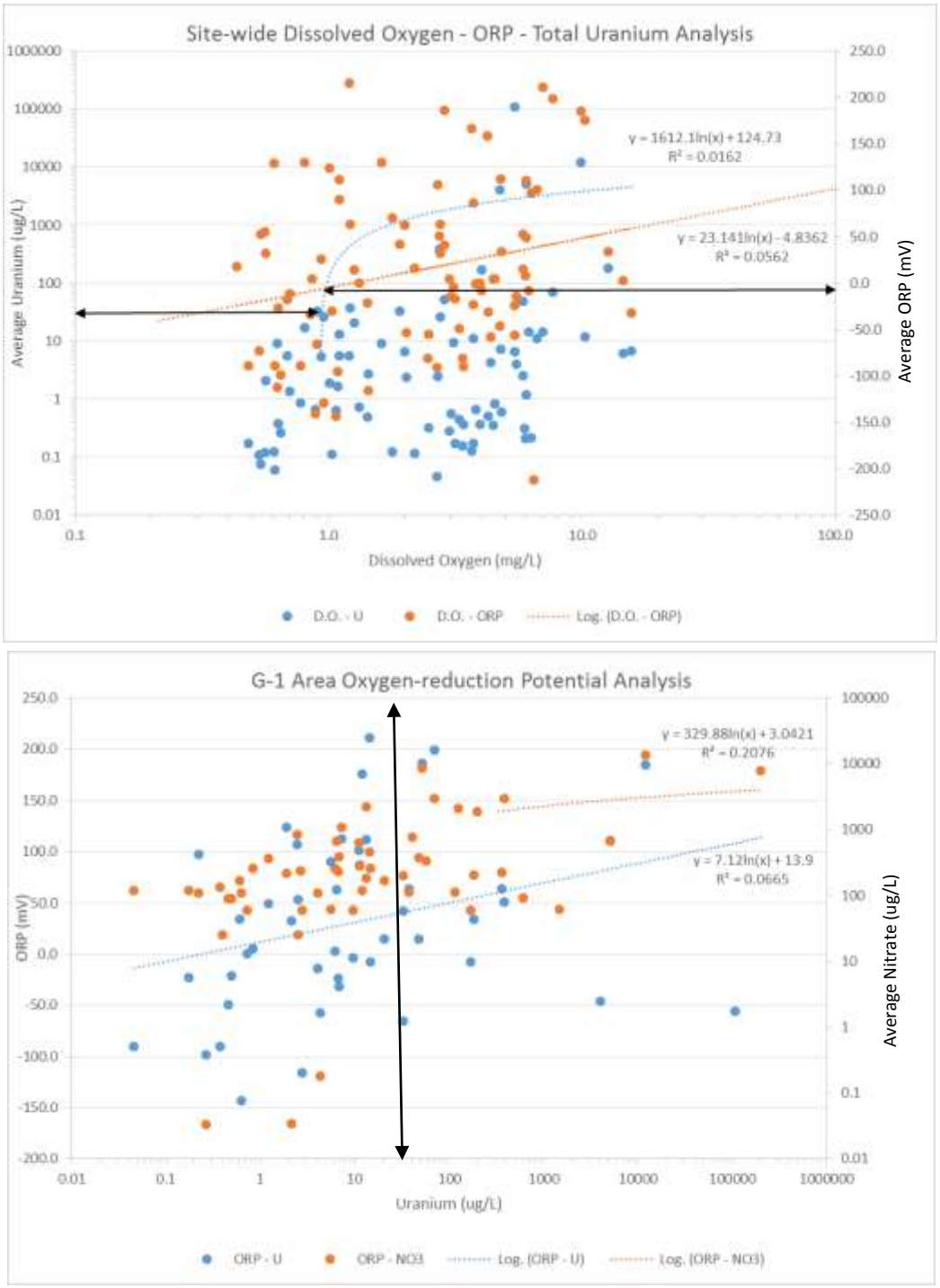

Figure 9. Geochemical Characteristics

CONCLUSION

The groundwater contamination at the HCC site was complicated by anthropogenic influences (water-main leakage), utility-line pathways, the saturation of contaminated soils, and storm-sewer discharges. The lithologic layering near the G-1/G-2 building area constrained the uranium plume and promoted dispersion into the shallow perched zone in the surficial fill and deeper coarse-grained zone that is the dominant transport zone at the site. The termination of water lines on the site, cessation of construction activities, removal of storm sewers, and re-configuration of surface-water features at the site all have affected the groundwater condition by depressing water levels near G-1, which then de-saturated the contaminated soil sources for the G-1 uranium plume.

The re-establishment of reductive geochemistry should progress without the influence of water-line leakage and further suppress uranium transport from below G-1. The current plume should theoretically attenuate as the groundwater mound drains from impacted soils and the uranium mass is re-distributed in the soils below and around G-1.

The groundwater monitoring program in place at HCC will be modified by utilizing unattended water-quality sondes that will routinely record pH, specific conductance, ORP, dissolved oxygen, and water level. ORP will be used as an indicator to predict uranium transport conditions, which will be used to guide modifications in the number of wells and the sampling methods (e.g., passive diffusion bags or other no-purge methods in lieu of low-flow sampling).

The intended outcome is the final dismissal of groundwater as a media of concern through geochemical data and transport modeling results.

REFERENCES

1. USACE 2009. Former Harshaw Chemical Site Remedial Investigation Report, Revision 1. October.
2. USACE 2012. Former Harshaw Chemical Site Feasibility Study Report, Revision 1. September.
3. USACE 2015. Former Harshaw Chemical Site Further Investigation of Site Water Lines and Test Pit #4 Addendum - Building G-1 Deconstruction and Groundwater Investigation. November.