

**Geochemical Evaluation of Uranium Fate and Transport  
Guterl Specialty Steel Site, New York - 12077**

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**ABSTRACT**

Between 1948 and 1952, up to 15,875 metric tons (35 million pounds) of natural uranium metal (U) were processed at the former Guterl Specialty Steel Corporation site in Lockport, New York. The resulting dust, thermal scale, mill shavings and associated land disposal contaminated both the facility and on-site soils. Uranium subsequently impacted groundwater and a fully developed plume exists below the site.

Site soils are composed of anthropogenic fill and re-worked, glacially-derived native soil. This overburden is underlain by the weathered and fractured Lockport Dolostone bedrock. Shallow groundwater levels fluctuate seasonally and allow groundwater to contact U contaminated soil, which promotes transport. This condition is exemplified through coincident increases in specific conductivity and groundwater levels, which flush soluble constituents in the fill/soil to groundwater during recharge events.

In addition, water-level fluctuations affect reduction-oxidation (redox) conditions at the site. The U in soils is subject to wetting and drying cycles that promote oxidation more than stable redox conditions (e.g., dry soil or fully saturated conditions). This oxidizing mechanism increases uranium solubility and mobility. Site groundwater also receives uranium via leaching from near-surface contaminated fill. The strong correlation between nitrate and uranium in groundwater indicates that uranium is mobile where oxidizing conditions occur.

Analytical models of contaminant leaching determined that multiple pathways and transport mechanisms govern site risk. Uranium transport to groundwater involves three mechanisms: 1) direct contact of contaminated soil with groundwater, 2) the oxidation-state or chemical valence of uranium, and 3) the leaching of near-surface contamination to groundwater. These mechanisms require an integrated remedial solution that is sustainable and cost effective.

**INTRODUCTION**

From 1948 to 1956, the former Guterl Specialty Steel Corporation processed up to 15,875 metric tons (35 million pounds) of U ingots in Lockport, NY, which is located approximately 40 kilometers (25 miles) northeast of Buffalo, NY. The on-site land disposal of metallic dust and shavings derived from billet heating and milling has produced contaminated soil conditions throughout the site. Electric furnaces that were used to heat uranium ingots also produced oxide coatings that reportedly resulted in a 0.5 percent loss of oxidized metal to interior dirt floors (potentially 80 metric tons or 175,000 pounds). This interior and exterior soil contamination has led to contaminated groundwater derived from uranium leaching and transport in a carbonate bedrock aquifer below the site. Groundwater investigations associated with a Remedial Investigation (RI) and Feasibility Study (FS) were designed to identify the mechanisms and pathways of uranium transport in groundwater, which are integral to remedial design evaluations and a remedy selection.

## METHOD

### Site hydrogeology

The site is underlain by anthropogenic fill, re-worked glacially-derived native soil, and clayey silt to silty native soil that together overlie the Lockport Dolostone. The fill material and native soil is prevalent throughout the operational areas of the site and ranges from 0.06 to 2.8 meters (m) (0.2 to 9.25 feet [ft]) in thickness. Hydraulic conductivity values common for this silty material normally vary around  $1 \times 10^{-5}$  centimeters per second (cm/s); no site-specific data are available for this overburden layer due to its thinness and previously documented poor yields (New York State Department of Environmental Conservation [NYSDEC], 2000b).

The upper 3 to 4.5 m (10 to 15 ft) of bedrock is a highly weathered and fractured preferential flow zone exhibiting a mean horizontal hydraulic conductivity of  $1.1 \times 10^{-2}$  cm/s (within range of  $7.1 \times 10^{-5}$  to  $8.9 \times 10^{-2}$  cm/s and a geometric mean of  $4.9 \times 10^{-3}$  cm/s) and an effective porosity of 0.09. The rock-core samples from this zone resemble very coarse gravel due to very low rock quality designations (RQD). Literature sources indicate the water-bearing unit at the Guterl

Site normally contains numerous horizontal and vertical weathered fractures, vugs and other solution features (NYSDEC, 2000b). The permeability of this upper flow zone will lessen with depth, as the RQD commonly increases with depth (usually >80% by 6 m or 20 ft).

A deeper groundwater bearing zone exists approximately 9.1 to 12 m (30 to 40 ft) below grade and varies between  $3.0 \times 10^{-7}$  and  $1.0 \times 10^{-2}$  cm/s in hydraulic conductivity. The wide range in hydraulic conductivity reflects the variability of the fractured rock formation; highly productive wells have screens that intersect one or more water producing fractures, whereas poorly producing wells intersect less dense fracture zones or fractures of small aperture. A wide variation in water production was observed in the monitoring wells installed in the deeper water bearing zone during well development activities; a similar variation was observed in the responses to slug tests between individual deep monitoring wells.

The Lockport Dolostone is bounded vertically by the Rochester Shale, which acts as a lower aquitard to the dolostone. The logs from two deep core borings indicate that in the up gradient (northern)

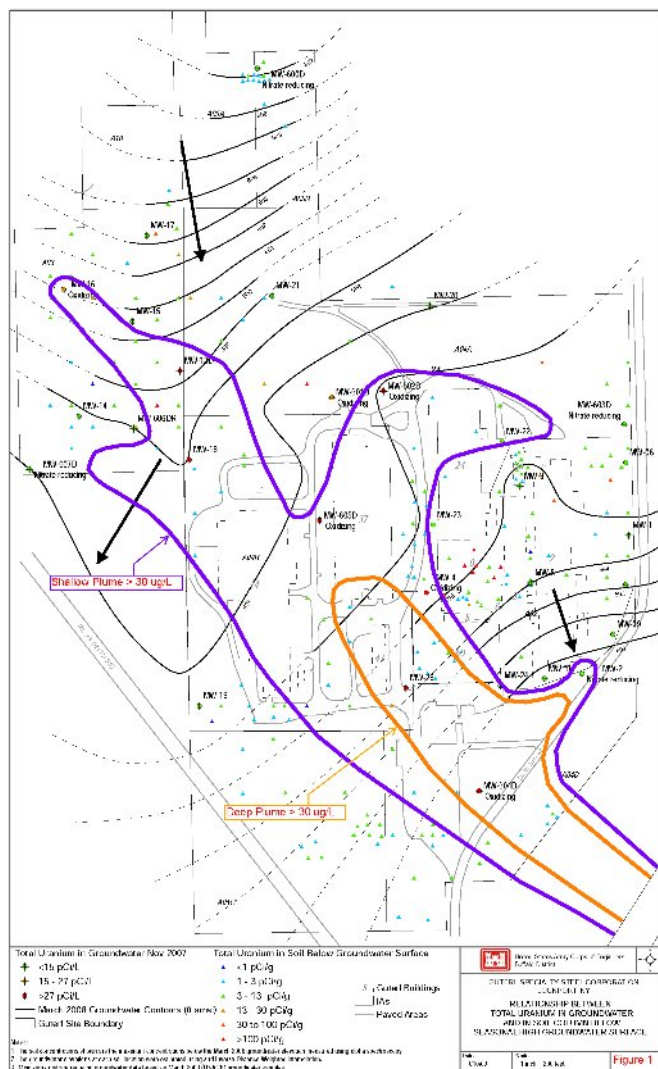


Figure 1. Soil and Groundwater Impacts

part of the site, the bottom of Lockport dolostone is approximately 20.4 m (67 ft) below ground surface, followed by at least 6.1 m (20 ft) of shaley or argillaceous dolostone transitioning to Rochester shale. In the down gradient (southern) part of the site towards the Erie Canal, the bottom of Lockport dolostone is approximately 13.7 m (45 ft) below ground surface, followed by at least 9.1 m (30 ft) of shaley/argillaceous dolostone transitioning to Rochester shale. Observations of this transitional facies (e.g., RQD and bedding) do not indicate significant water bearing zones. Groundwater levels in the shallow bedrock are within 0.6 to 2.4 m (2 to 8 ft) of grade at the site and fluctuate up to 1.2 m (4 ft) seasonally, which can result in groundwater contacting the uranium impacted soils and fill, as illustrated in Figure 1.

Groundwater levels in the deep bedrock are within 0.9 to 10.7 m (3 to 35 ft) of grade, indicating a more variable flow field. Both bedrock zones flow predominantly southeasterly across the site toward the Erie Barge Canal located southeast of the site; a westerly flow region also exists due to pumping stresses from a bedrock quarry to the west. The prevalence of groundwater in the upper zone but divergent water levels (to dry wells) in the lower zone indicates that vertical barriers interrupt the bedrock flow at certain locations, which creates significant vertical gradients in some areas. Contaminant distributions also indicate that the upper and lower zones are not completely vertically integrated since uranium distributions in the upper zone are normally greater than those in the lower zone. Generally, the lower zone is not impacted with U until nearer the Erie Canal (Figure 1).

### **Site contamination**

Increases in specific conductivity commonly occur with groundwater level increases, which indicate groundwater contacts soluble constituents in soil that are then leached into groundwater in conjunction with the normal downward leaching of constituents to groundwater.

Water-level fluctuations also appear to induce changes in redox conditions. Uranium in soil that experiences wetting and drying cycles is more likely to oxidize than if redox conditions are stable. Under oxidizing conditions, uranium mobility can increase, thus increasing the leachability from the contaminated vadose zone.

Groundwater at the Guterl Steel Site also is impacted by volatile organic compounds (VOCs) or chlorinated solvents and related degradation compounds, including trichloroethene (TCE), cis-1,2-dichloroethene (DCE), vinyl chloride, 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCA). Sampling data indicate that chlorinated VOC concentrations are below NYSDEC criteria in and around the landfill, but reveal elevated VOCs in many wells in the Excised Area. Chlorinated compound concentrations are generally highest in the wells installed along the western side of the Excised Area. TCE and 1,1,1-TCA may be considered the parent or source chemical products, while the other chlorinated compounds likely reflect post-release biodegradation (Dong et al., 2006). Many reported concentrations exceed groundwater criteria of 5 micrograms per liter ( $\mu\text{g/L}$ ) for TCE, 1,1,1-TCA, 1,2-DCE, 1,1-DCA; and 2  $\mu\text{g/L}$  for vinyl chloride in the Excised Area.

The redox conditions of groundwater are also affected by the presence of the VOCs and as a consequence affect the mobility of uranium in groundwater. Therefore, the fate and transport analysis of the total uranium factored in the co-mingling of the VOC and the uranium plumes. The presence of high VOC concentrations and the movement of the VOC plume through the groundwater, under natural gradients or potential gradients forced by a groundwater extraction remedy, can alter the groundwater redox conditions and thus uranium mobility (Mullen, 2007).

So the presence of the VOC plume affects the modeling of remedial alternatives performed during the FS.

### Uranium geochemistry

Uranium oxide is typically present as uranium dioxide (UO<sub>2</sub>) or triuranium octoxide (U<sub>3</sub>O<sub>8</sub>) in soils; UO<sub>2</sub> slowly converts to U<sub>3</sub>O<sub>8</sub> at ambient air temperatures (Argonne National Laboratory [ANL], undated). Uranium in UO<sub>2</sub> is present in the reduced, tetravalent (U<sup>4+</sup>) form, which has exceedingly low solubility in water (approximately 1 x 10<sup>-26</sup> µg/L at pH 7 [Mullen, 2007]). Uranium in the U<sub>3</sub>O<sub>8</sub> state is present as both U<sup>4+</sup> and oxidized U<sup>6+</sup> valence states; stochastically as (2U<sup>6+</sup>)U<sup>4+</sup>O<sub>8</sub>. U<sub>3</sub>O<sub>8</sub> also is known for low solubility in water, yet can vary with redox-sensitive species (e.g., iron and manganese), pH, and the presence calcium, carbonates, humic substances. Aqueous chemistry variations can increase the U<sup>6+</sup> solubility more readily than U<sup>4+</sup> and produce U concentrations that exceed the groundwater screening level of 30 µg/L. Carbonate ions, in particular, form complexes with uranium and increase its solubility and mobility (Zachara et al., 2007). Since the Lockport Dolostone is a CaMgCO<sub>3</sub> based Silurian bedrock, oxidized uranium will speciate into mobile uranyl-carbonate in the aquifer.

The metallic U source in site soil is assumed to be predominantly in the U<sup>4+</sup> valence state and thus solubility limiting; under reducing conditions U<sup>4+</sup> tends to precipitate. Under oxidizing conditions, U<sup>6+</sup> mobility depends on the pH and other constituents present in groundwater. Table I provides selected parameter concentrations measured in Guterl Site groundwater samples. For wells in the upper part of the table, substantial differences between total and dissolved iron concentrations and detected nitrate indicate conditions are oxidizing. These conditions, along with the presence of bicarbonate alkalinity, are favorable for uranium to be dissolved in groundwater. Where nitrate exceeds 0.5 milligrams per liter (mg/L), uranium exceeds the groundwater screening level.

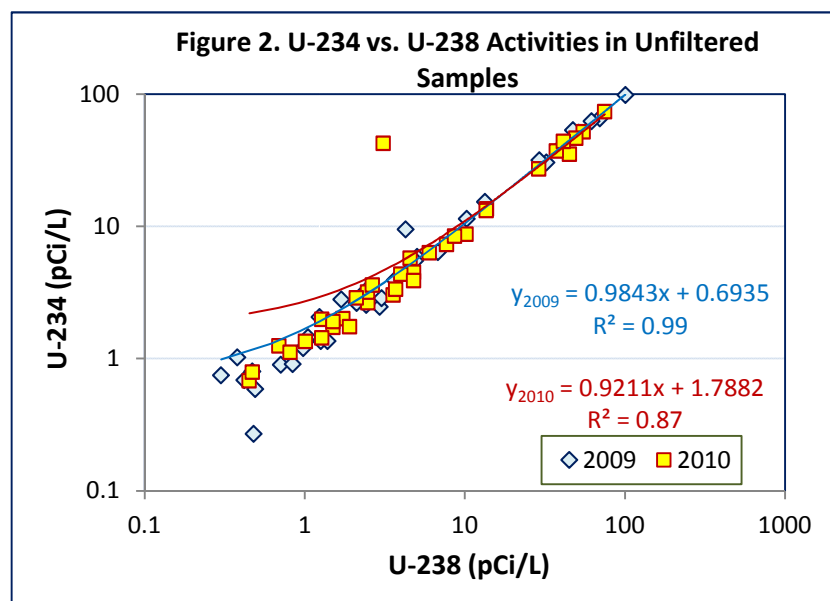
TABLE I. Selected Groundwater Parameters from the Guterl Site.

Well	Dissolved Oxygen mg/L	Nitrate as N mg/L	Total Uranium ug/L	Total Iron ug/L	Dissolved Iron ug/L	Sulfate mg/L	ORP mV	Alkalinity, Total mg/L
MW-605D	0.21	1.4	<b>191.73</b>	25.9 J	<15.4	92	87	350
MW-604D	1.07	1.0	<b>74.07</b>	<15.4	<15.4	59	174	250
MW-602D	5.37	0.62	<b>116.82</b>	29.5 J	<15.4	40	149	250
MW-4	0.42	0.55	<b>47.59</b>	<15.4	44.2 J	56	77	210
MW-16	0.00	0.24	19.19	1990	53.4 J	82	135	400
MW-601D	0.25	0.2	19.42	<15.4	<15.4	150	-201	300
<b>Nitrate Reducing</b>								
MW-2	0.00	<0.1	19.44	119 J	98.4 J	94	-42	290
MW-600D	0.28	<0.1	9.88	457	51.4 J	180	64	520
MW-603 D	0.34	<0.1	2.56	1140	557	77	7	270
MW-607D	0.31	<0.1	0.09	1950	207	110	-94	710
MW-08	0.00	<0.1	0.07	393	390	180	-24	370

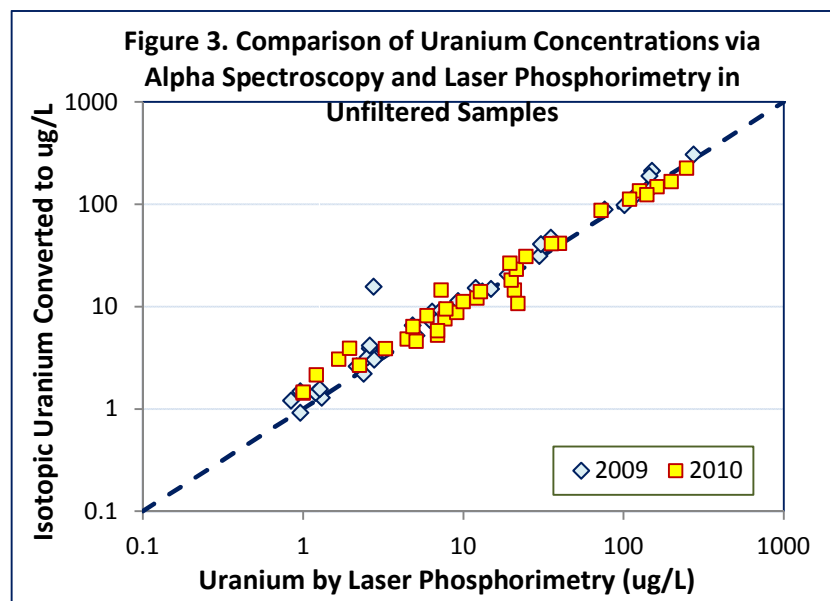
Notes: “J” indicates an estimated concentration; “<” indicates the concentration was not detected. **Bold** values exceed the uranium groundwater screening level.

Where nitrate reducing conditions exist (nitrate not detected and greater soluble iron is seen), uranium concentrations are below the screening level. Uranium reduction from  $U^{6+}$  to  $U^{4+}$  occurs after nitrate reduction; thus uranium as  $U^{6+}$  would be expected only in wells with detected nitrate. In Guterl Site groundwater, there is a strong correlation between nitrate and uranium, indicating that uranium is mobile where oxidizing conditions occur.

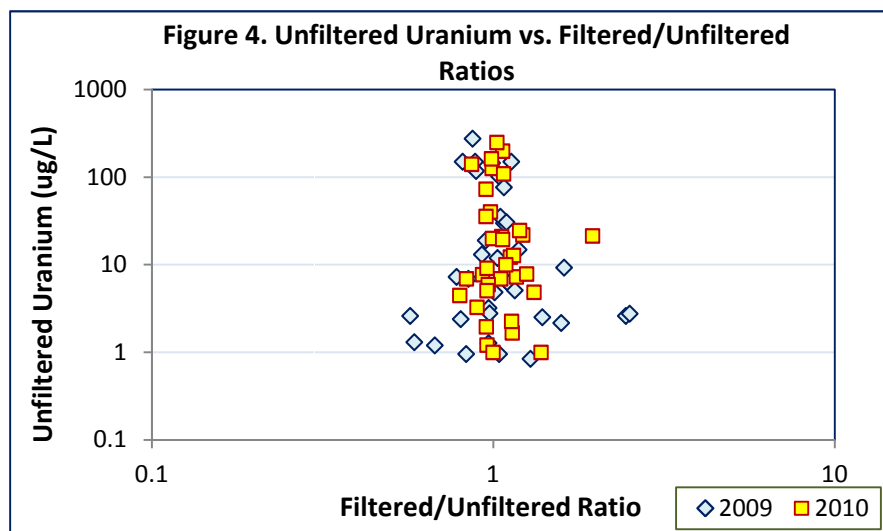
Groundwater sampling conducted in 2009 and 2010 produced results consistent with previous RI sampling, which indicated that only natural uranium ratios are prevalent on site. Figure 2 shows the correlations between the alpha spectroscopy results for U-234 versus U-238 in picoCuries per liter (pCi/L). Samples from both events show strong correlations ( $R^2 > 0.86$ ) between the two isotopes (with the exception of one outlier) and the two trends are coincident. The slopes of the linear regressions of the two data sets, which represent the average U-234/U-238 ratios, are close to 1.0 which is a fingerprint for natural uranium, especially at higher values.



Elemental uranium concentrations were also analyzed via laser phosphorimetry (LP) using Method ASTM D 5174 in the 2009 and 2010 samples. These LP results allow an independent comparison of uranium concentrations by two different methods in each sample. Figure 3 shows the uranium concentrations in each of the unfiltered samples as determined via LP (x axis) versus activities determined by alpha spectroscopy converted to mass concentration units ( $\mu\text{g/L}$ ) and summed (y axis). The dashed line on the figure is the trend expected for perfect agreement ( $x=y$ ) between the two methods. The majority of the points fall close to the dashed line, and the median alpha spectroscopy/LP ratio for the 71 samples is 1.16. The closeness and symmetry of the points about the dashed line indicates general agreement and lack of bias in either method for most of the samples.



The ratios of uranium concentrations (LP method) in filtered versus unfiltered sample splits in the 2009 and 2010 samples is shown as a function of the unfiltered concentrations in Figure 4.

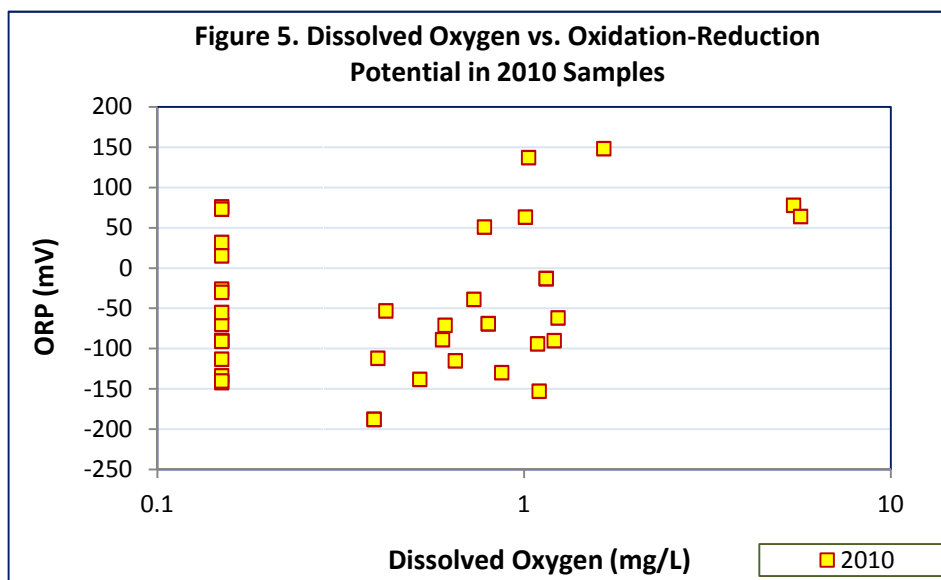


Samples with uranium present in a mostly dissolved state should have ratios close to 1.0, and samples with uranium present as suspended particulates should have ratios below 1.0.

Greater scatter in the filtered/unfiltered ratios is observed at lower concentrations where the uncertainties in concentrations increase. However, the majority of

the samples line up as a vertical trend over a ratio of 1.0, indicating that the uranium detected in the samples is not removable by filtration, and is therefore mostly present in a dissolved state.

The mobility of uranium in groundwater is most sensitive to pH, redox conditions, and the concentrations of carbonate, which is a strong complexing agent for the  $U^{6+}$  form of uranium. Of these parameters, redox is the most important because the solubility of  $U^{6+}$  is about six orders of magnitude higher than the solubility of  $U^{4+}$ , so an understanding of small-scale redox conditions along potential groundwater flow paths is important. Estimation of the redox conditions at samples locations are commonly based on dissolved oxygen (DO) and oxygen reduction potential (ORP) measurements performed in the field, which are subject to interferences from contamination of reducing samples with atmospheric oxygen. This can be seen in Figure 5, which shows the correlation between the DO versus ORP field measurements



in the 2010 samples. Reported DO values of zero are assigned a value of 0.15 mg/L and form the vertical stack of points on the left side of the figure. The lack of strong agreement between the two parameters indicates that one or both have high uncertainties. In addition, optical DO probe are used in the field instead of the standard electro-chemical DO probes.

The newer optical probe design yields more accurate results. Continued annual collection of these data and enhanced (quarterly) sampling is being performed.



Fortunately there are more reliable methods of estimating groundwater redox conditions based upon selected elemental ratios and the ratios of redox-sensitive element concentrations in filtered versus unfiltered sample splits. These methods are based on comparisons of unfiltered iron versus aluminum correlations, iron filtered/unfiltered ratios, and manganese filtered/unfiltered ratios, were used at the Guterl Steel Site to assess the redox conditions in the groundwater.

### Groundwater exposure

Site groundwater is not used as a drinking water or industrial source, yet other exposure pathways exist. Groundwater seepage into the Erie Canal was observed at two locations in August 2011, as shown on Figure 6. The seep elevations (174.26 m 173.56 m or 571.72 ft and 570.72 ft) are in the range of groundwater elevations measured at the deeper downgradient wells MW-708 DD, MW-709 DD, MW-710DD, MW-711 DD, and MW-712 DD (172.53 m to 179.66 m or 566.15 to 589.45 ft) and may represent a fraction of the site groundwater that discharges to the Canal, either via natural seepage flow paths or as groundwater flowing to the Canal via preferential flow paths created by subsurface utilities. A subsequent seep sampling event occurred in November 2011 after the canal was drained for winterization; the August and November sampling results indicate the uranium plume has advanced to this flow boundary.

Figure 6  
Locations of Seeps on August 8, 2011



Notes:

1. Seep 01 is downgradient of site and downstream from the pipeline crossing. This was the only seep between the pipeline crossing shown above and the downstream Stevens Street bridge.
2. Seep02 is located between the Lockport Bypass and the pipeline crossing. It may not reflect site groundwater and was collected for comparison to the Seep 01 analytical results.

This is a concern because the emergency drinking water intake for the City of Lockport is located across the canal from the seepage areas. Canal water sampled during the RI did not show elevated U near these locations, yet will continue to be a monitored media.

### Modeling assessment

Uranium leaching through the vadose zone was evaluated analytically during the RI and will be numerically modeled during the FS (see Table II) to determine if remedial goals for soil are protective of groundwater (i.e., ensure residual uranium concentrations in soil will not cause groundwater to exceed 30 µg/L at the point of compliance). The modeling assessment was extended to include a no-action or baseline flow and transport model that will serve as a tool to evaluate the effects of potential remedial alternatives. The original models were designed using RI data, whereas additional groundwater data being acquired throughout 2011 will enhance the site baseline condition for the FS. Consequently, the FS modeling will be more sophisticated and better predict impacts from potential alternatives such as pump and treat, slurry walls, and permeable reactive barriers. The total simulation time for each of the FS alternatives is 1,000 years, sufficient to allow assessment of the groundwater exposure pathway(s).

TABLE II. Models Used to Evaluate Leaching of Uranium to Groundwater.

Model	Application
SESOIL	Vadose zone transport (RI and FS)
AT123D	Saturated zone transport (RI)
MINEQL+	Uranium solubility – input for SESOIL (RI and FS)
RESRAD	Estimate risk and dose from radioactivity; infiltration necessary to match observed time of occurrence of uranium in groundwater (RI)
HELP	Generate recharge estimates for calibrating SESOIL (RI)
SEVIEW	Combines SESOIL and AT123D and simplifies input (RI)
MODFLOW	3-dimensional saturated zone flow (FS)
MT3D	3-dimensional saturated zone transport (FS)

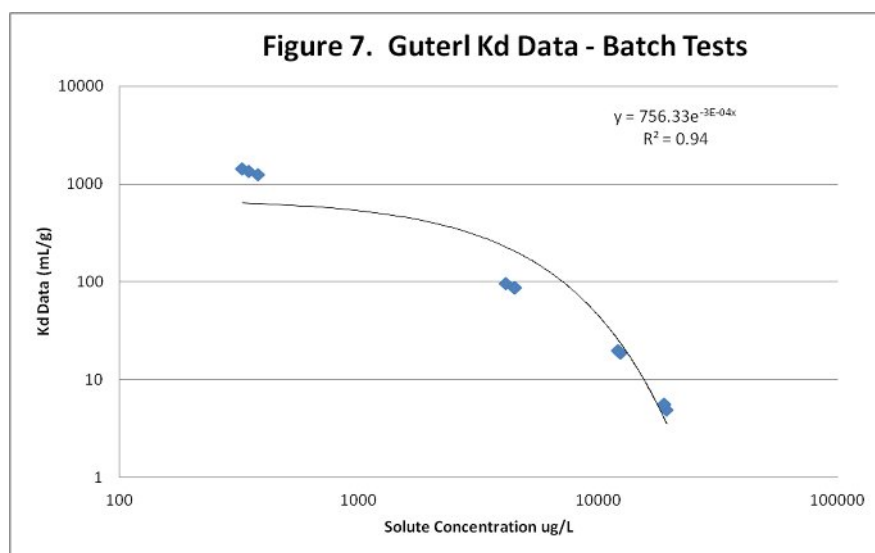
A generalized multi-dimensional soil model was developed to conservatively reflect the entire Guterl Site. The contaminated soil area was defined as 67,000 square meters (16.6 acres) and the vadose zone soil was divided into an upper one-meter thick contaminated zone (considered fill) that overlies a 0.3-meter thick uncontaminated zone (considered native silty soil) derived from on-site borings. Input parameters for soil properties were derived directly or indirectly from Guterl Site data and SESOIL guidance (Bonazountas, M., and J. Wagner. 1981, 1984). During the performance of the FS and post RI data gap investigation, the SESOIL simulations were modified to incorporate the variability in the soil uranium concentrations across the site. Since the half-lives for uranium are long, only advection, dispersion, and adsorption were modeled for metallic uranium (i.e., first-order decay was ignored).

Uranium adsorption (distribution) coefficients ( $K_d$ ) were estimated using two rounds of laboratory tests of site soil. The first test employed a twenty-four hour batch test method using uranium spiked groundwater of differing concentrations (380 µg/L to 25,665 µg/L) shaken with site soils having a narrow range of uranium concentrations (RI activity). Those tests produced the following results:



- Native uncontaminated soil  $K_d$ : 1247 and 1452 milliliters per gram (mL/g), with a three point average of 1356 mL/g
- Contaminated soil/fill  $K_d$ : 5 to 97 mL/g, with a nine point average 39 mL/g.
- Lockport Dolostone (gravel-sized grains)  $K_d$ : 0.22 mL/g.

The lower  $K_d$  values for fill, with respect to the native soils, are caused by a slightly larger grain size distribution for the fill and higher concentrations of the solute exposed to the fill. The  $K_d$  values showed an exponential decline using higher solute concentrations due filled adsorption capacity, whereas the native soil exposed to lower solute concentrations produced higher  $K_d$  values due to continued availability of exchange sites throughout the test. Figure 7 exemplifies this non-linear  $K_d$  condition derived from the batch tests. This condition is important when evaluating the potential for leaching from high U-concentration soils, where interstitial pore-water concentrations would be high and leaching rates that may advance faster than ambient soil data would predict.



The second set of uranium  $K_d$  tests collected for FS activities used undisturbed contaminated soil samples obtained during well installations. These soils were exposed to simulated precipitation in the form of synthetic rain water, as used in the Synthetic Precipitation Leach Procedure (EPA Method 1312), via column testing to define actual leaching concentrations from on-site soils. These eight samples were tested

in triplicate and produced the following soil  $K_d$  values that will be used in the FS leaching models:

- $K_d$ : 1,052 to 95,667 mL/g, with an average of 17,699 mL/g.

These newer and higher  $K_d$  values will be used preferentially in the FS modeling efforts for remedial alternative analyses because the procedure replicates the leaching of uranium by the infiltrating rainwater through the process of desorption.

Uranium solubility was evaluated in the RI using MINEQL+ (Schecher and McAvoy, 2003), which conservatively assumed that the uranium source was fully oxidized ( $U^{6+}$ ); the actual oxidation state of uranium in site soil was not determined due to resource constraints. Modeling results indicated that elevated uranium concentrations are associated with oxidizing conditions and elevated anion concentrations. Similar groundwater conditions are seen at wells MW-602D and MW-605D (Table I); well-specific model results calculated a maximum solubility of about 150 milligrams per liter (mg/L) for uranium.

A RESRAD dose model (ANL,2001) was compiled for the RI to estimated the peak dose to residents and construction workers resulting from groundwater exposure. RESRAD was

calibrated to produce the current groundwater concentrations that were developed over the 58 years since FUSRAP related operations. The RI fate and transport models listed in Table II were aligned using the select parameters derived by the RESRAD calibration. The HELP model (Schroeder et al., 1994a, 1994b) estimated groundwater recharge that was then used as a calibration target in the SESOIL vadose zone leaching model.

In SESOIL and RESRAD, the fill and native soil layers were treated as “vertical percolation layers.” SESOIL was calibrated to an average groundwater recharge of 0.37 meter per year (m/yr) (14.5 inches per year), which was close to the recharge rate of 0.39 m/yr determined by RESRAD. The SESOIL calibration employed a hydraulic conductivity of  $5.5 \times 10^{-5}$  cm/s, a soil disconnectedness index of 10, an effective porosity of 0.20, and soil moisture of 15%. These input generally reflected the characteristics of the contaminated fill. To produce sufficient transport of uranium to groundwater within the 58-year timeframe, a  $K_d$  of 25 mL/g for both contaminated and uncontaminated vadose zone soils was applied to the SESOIL modeling, which is lower than tested values.

The vadose zone flux estimated by SESOIL was then input to a simplified AT123D model (Yeh, 1981); this flux was applied to the top of the water table directly below the modeled uranium source in soil. The AT123D model assumed the upper 3 to 4.6 m (10 to 15 ft) of the Lockport Dolostone was a highly weathered and fractured porous media equivalent, as defined by RQD data. Since the groundwater concentrations are only modeled directly below the source area and not downgradient, this assumption was considered to be acceptable.

The 3-dimensional MODFLOW and MT3D models developed for the FS have two major layers based on occurrence of groundwater, the mapped fracture density, and RQD calculations. This hydrostratigraphy corresponds to water bearing units that are monitored by shallow and deep wells. Fractured dolostone showing RQD values <80% are water bearing, whereas dolostone with >80% RQD layers are less productive to “tight.” The model grid is aligned with the local flow field and uranium plume axis that approximately coincides with regional northwest to southeast fracture trends.

The vertical boundaries for the model consist of a precipitation based recharge boundary at the model top and a flux boundary as the bottom of the model. The flux boundary was determined on the basis of water balance evaluation conducted as part of the modeling. A fraction of site groundwater is discharged to the canal as seeps while another component is migrating to deeper rock. The lateral boundaries of the model are a combination of constant head and specified head boundaries based on the physical conditions and flow model calibration.

## RESULTS

Soil concentrations input to SESOIL were adjusted to predict a groundwater concentration equal or close to the screening level of 30  $\mu\text{g/L}$ , which resulted in a soil uranium-238 activity of 0.17 pCi/g (0.5 milligrams per kilogram [mg/kg] elemental uranium). This value would represent an  $\text{U}^{6+}$  state in soil that is actually less than background data. A soil value of 1 pCi/g would result in an elevated uranium activity of 163 pCi/L in bedrock groundwater, which is not realistic (i.e., natural conditions do not produce this concentration).

Since the RI models over-predicted observed conditions by assuming all uranium is mobile  $\text{U}^{6+}$ , future assessments will account for mixed valence conditions and alternative contaminant flux pathways. The ratio of metallic  $\text{U}^{4+}$  to  $\text{U}^{6+}$  in site soil is unknown, yet should lessen with time (source oxidation). The representation of soil with a singular solubility for U will be modified to a

temporally varying uranium solubility, which is logical but includes significant numeric uncertainty. The analyses may require more qualitative analyses if the models cannot effectively simulate this complex transient condition.

The uranium values above the groundwater MCL consistently occur at eight bedrock monitoring wells that generally show oxidizing conditions that promote a  $U^{6+}$  uranyl-carbonate complex. These wells are also downgradient of impacted soils in contact with groundwater on a seasonally fluctuating basis, so continual transport to bedrock by means of infiltration through the vadose zone is enhanced by seasonal flushing of contaminated pore water from the soil. This is especially prevalent where native soils are sparse and contaminated fill with possibly lower  $K_d$  can more readily transport U to groundwater.

The geochemical conditions indicated on Figure 1 may change as groundwater levels fluctuate up to 4 feet at numerous locations. Field measurements of dissolved oxygen and field redox data indicate that increases in water levels were accompanied by changes in groundwater conditions from reducing to oxidizing. These changes likely affect transport of contaminants because wetting and drying soil cycles can cause corrosion of uranium metal due to cycling between oxidizing and reducing conditions. Uranium present as  $U^{4+}$  in soil (dominant in the original metallic source term) may be oxidized to  $U^{6+}$  under such seasonal fluctuations, resulting in more soluble uranium being present and available for transport by groundwater. The mixed oxidation states of the uranium detections in soil create numerical modeling uncertainty because the interim partially oxidized states do not have defined solubility.

## DISCUSSION

The analytic modeling of general site conditions during the RI were calibrated to an average infiltration rate of 0.38 m/yr and indicated that uranium-238 activities less than 1 pCi/g uranium in the upper 1 m of soil would violate the groundwater MCL for total U (30 ug/L) in bedrock groundwater. Since this does not match the observed groundwater condition, the input assumptions were either overly conservative or the main mechanism for uranium transport to groundwater is direct contact between bedrock groundwater and contaminated soil.

The models assumed a fully oxidized (entirely  $U^{6+}$ ) form of uranium, which actually varies throughout the site and soil column in a mixed valence state via  $U_3O_8$  ( $U^{4+}$  and  $U^{6+}$ ) and fully oxidized uranyl-carbonates. Historical land disposal and disturbance practices allows direct contact of contaminated material containing  $U^{4+}$  and  $U^{6+}$  with the dolostone aquifer or with soil that is seasonally in contact with groundwater. Changes in redox conditions appear induced by water level fluctuations, which promote an oxidized U condition in site soil via wetting and drying cycles. Increases in specific conductivity when groundwater levels rise indicate that soluble constituents are being flushed into groundwater.

Consequently, uranium in bedrock groundwater results from two sources: 1) uranium that was oxidized during milling operations and leached to groundwater through soil, and 2) ongoing oxidation of uranium metal in soil, present due to historical disposal and disturbance practices, that is seasonally in contact with groundwater. Both conditions have produced a groundwater plume that flows from soil source areas to a surface-water sink adjacent to the site. The lessons learned from the initial modeling effort will be redressed in an updated analysis that will account for the uniqueness of the multiple source condition and remedial efforts to control the existing uranium plume.

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