### Uranium Fate and Transport Modeling, Guterl Specialty Steel Site, New York - 13545

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### ABSTRACT

The Former Guterl Specialty Steel Corporation Site (Guterl Site) is located 32 kilometers (20 miles) northeast of Buffalo, New York, in Lockport, Niagara County, New York. 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. Uranium transport from the site involves legacy on-site pickling fluid handling, the leaching of uranium from soil to groundwater, and the groundwater transport of dissolved uranium to the Erie Canal.

Groundwater fate and transport modeling was performed to assess the transfer of dissolved uranium from the contaminated soils and buildings to groundwater and subsequently to the nearby Erie Canal. The modeling provides a tool to determine if the uranium contamination could potentially affect human receptors in the vicinity of the site. Groundwater underlying the site and in the surrounding area generally flows southeasterly towards the Erie Canal; locally, groundwater is not used as a drinking water resource. The risk to human health was evaluated outside the Guterl Site boundary from the possibility of impacted groundwater discharging to and mixing with the Erie Canal waters. This condition was evaluated because canal water is infrequently used as an emergency water supply for the City of Lockport via an intake located approximately 122 meters (m) (400 feet [ft]) southeast of the Guterl Site. Modeling was performed to assess whether mixing of groundwater with surface water in the Erie Canal could result in levels of uranium exceeding the U.S. Environmental Protection Agency (USEPA) established drinking water standard for total uranium; the Maximum Concentration Limit (MCL).

Geotechnical test data indicate that the major portion of uranium in the soil will adsorb or remain bound to soil, yet leaching to groundwater appears as an on-site source. Soil leaching was modeled using low adsorption factors to replicate worst-case conditions where the uranium leaches to the groundwater. Results indicate that even after several decades, which is the period of time since uranium was processed at the Guterl Site, leaching from soil does not fully account for the currently observed levels of groundwater contamination. Modeling results suggest that there were historic releases of uranium from processing operations directly to the shallow fractured rock and possibly other geochemical conditions that have produced the current groundwater contamination. Groundwater data collected at the site between 1997 and 2011 do not indicate an increasing level of uranium in the main plume, thus the uranium adsorbed to the soil is in equilibrium with the groundwater geochemistry and transport conditions. Consequently, increases in the overall plume concentration or size are not expected.

Groundwater flowing through fractures under the Guterl Site transports dissolved uranium from the site to the Erie Canal, where the groundwater has been observed to seep from the northern canal wall at some locations. The seeps discharge uranium at concentrations near or below the MCL to the Erie Canal. Conservative mixing calculations were performed using two worst-case assumptions: 1) the seeps were calculated as contiguous discharges from the Erie Canal wall and 2) the uranium concentration of the seepage is 274 micrograms per liter ( $\mu$ g/L) of uranium, which is the highest on-site uranium concentration in groundwater and nearly ten-fold the actual seep concentrations. The results indicate that uranium concentrations in the seep water would have to be more than 200 times greater than the highest observed on-site groundwater concentrations (or nearly 55,000  $\mu$ g/L) to potentially exceed the drinking water standard (the MCL) for total uranium in the Erie Canal.

### **INTRODUCTION**

From 1948 to 1956, the former Guterl Specialty Steel Corporation processed up to 15,875 metric tons (35 million pounds) of Uranium ingots in Lockport, NY, which is located approximately 40 kilometers (25 miles) northeast of Buffalo, NY. Soil contamination from on-site land disposal of metallic dust, shavings, and oxide scale derived from billet heating and milling partially led to contaminated groundwater conditions in the underlying carbonate bedrock aquifer. Alleged operational disposal of uranium impacted quenching and pickling fluids in the soil disposal areas evidently enhanced groundwater contamination. Other operational sources for contamination appear evident in historical aerial photographs of the site. All these factors are integral to remedial design evaluations and a remedy selection.

### METHOD

#### Site hydrogeology

The site is underlain by a sandy silt to clayey silt 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 are prevalent throughout the operational areas of the site and ranges from 0.06 to 2.8 meters (m) (0.2 to 9.25 ft) in thickness. Hydraulic conductivity (K) values common for this silty material vary around 1 x  $10^{-5}$  centimeters per second (cm/s); no site-specific data are available for this overburden layer due to its thinness and previously documented poor yields [1].

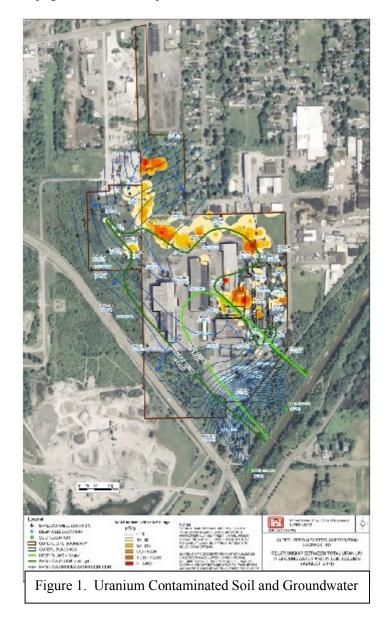
The upper 3 m to 4.5 m (10 ft to 15 ft) of the Lockport Dolostone is a highly weathered and fractured preferential flow zone exhibiting a mean horizontal K of  $1.1 \times 10^{-2}$  cm/s; the K data vary between 7.1 x  $10^{-5}$  cm/s and to  $8.9 \times 10^{-2}$  cm/s and exhibit a geometric mean of  $4.9 \times 10^{-3}$  cm/s. This zone has an estimated effective porosity of 0.09 [2]. Literature sources indicate the water-bearing unit at the Guterl Site normally contains numerous horizontal and vertical weathered fractures, vugs and other solution widened features [1]. Groundwater levels in the shallow bedrock are within 0.6 m to 2.4 m (2 ft to 8 ft) of grade 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 in this zone flows mainly southeasterly under a 0.0602 m/m (ft/ft) gradient.

A deeper groundwater bearing zone occurs from 9.1 m to 12 m (30 ft to 40 ft) below grade and exhibits a K range from  $3.0 \times 10^{-7}$  cm/s to  $1.0 \times 10^{-2}$  cm/s. 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. Groundwater levels in the deep bedrock are within 0.9 m to 10.7 m (3 ft to 35 ft) of grade, indicating a more variable flow field. Flow in this zone is southeasterly (toward the Erie Canal) under a 0.0891 m/m (ft/ft) gradient [3].

The Lockport Dolostone is bounded vertically by the Rochester Shale, which acts as a lower aquitard. On-site boring logs show the Lockport extends approximately 13.7 m (45 ft) to 20.4 m (67 ft) below ground surface, where it transitions into a 6.1-m (20-ft) to 9.1-m (30-ft) thick argillaceous dolostone that conformably overlies the Rochester Shale. Observations of this transitional facies (e.g., rock quality designation [RQD] and bedding) do not indicate significant water bearing zones.

Groundwater in both zones flows 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 the bedrock quarry to the west. Groundwater in the upper zone can be coincident with or greatly higher than the lower

zone, indicating that vertical barriers interrupt the bedrock flow at certain locations. Contaminant distributions also indicate that the upper and lower zones are not vertically integrated since uranium distributions in the upper zone are up to three-times greater than the lower zone. Generally, the lower zone is not impacted with U until nearer the Erie Canal. Figure 1 shows the shallow and deep groundwater uranium plumes exceeding the MCL of 30  $\mu$ g/L superimposed on the shallow groundwater potentiometric surface map, groundwater flow paths, and soil sources of uranium.



### Site contamination

Uranium contamination at the site 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 [4]. 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  $10^{-26} \mu g/L$  at pH 7) [5]. 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 of calcium, carbonates, and 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 [6]. Since the Lockport Dolostone is a CaMgCO<sub>3</sub> based Silurian bedrock, oxidized uranium will speciate into mobile uranyl-carbonate in the aquifer [2]. The on-site pH ranges from 6.6 to11.1 and reduction-oxidation (redox) conditions vary from -285 millivolts (mV) to 192 mV, which is a range that can lessen uranium mobility. However, the presence of high sulfate in the bedrock groundwater mitigates the lower redox conditions and thus hexavalent uranium transport still is promoted in the aquifer.

Routine groundwater sampling conducted since 2009 produced results consistent with previous RI sampling, which shows natural isotopic signatures in a mostly dissolved state. The uranium concentrations in most wells show steady-state conditions; only two wells show upward trends.

### **Groundwater exposure**

Site groundwater is not used as a drinking water or industrial source, yet other exposure pathways exist and long-term uncertainties of site use over this potable water supply raises concerns due to the large-scale, above-MCL ( $30 \mu g/L$ ) conditions under the site (Figure 1). The Erie Canal is 91 m (300 ft) southeast of the site and excavated into bedrock along the reach adjacent to the site. The potential influx of contaminated site groundwater to the canal is a concern because the emergency drinking water intake for the City of Lockport is located across the canal from the Guterl site [8].

The Niagara County Health Department noted that the intakes were used seven (7) times from 1990 to 1997 [8]. Since this emergency water intake may act as a potential exposure pathway for the residents served by the City of Lockport water district, the groundwater seepage downgradient of the site and canal water were sampled for uranium multiple times since 2007. The results showed groundwater seepage varies from  $3.5 \mu g/L$  to  $44.9 \mu g/L$  and averages  $17.4 \mu g/L$ , whereas canal water averages  $0.5 \mu g/L$ , or background concentrations. Figure 2 shows the monitoring results used to assess the uranium flux from the site to the Erie Canal and ensure the protection of the emergency drinking water source.

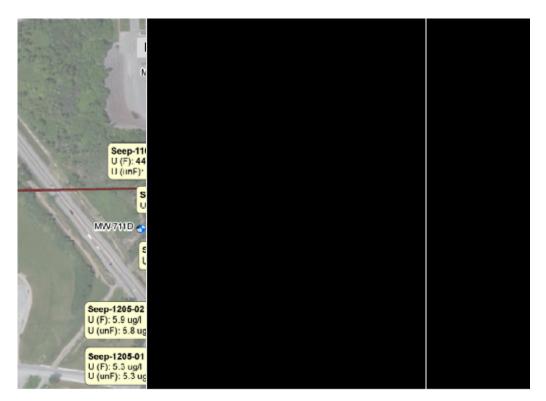


Figure 2. Groundwater Seep Sampling

### RESULTS

### Groundwater flux to the Erie Canal

The Erie Canal proximal to the site flows from west to east and fluctuates by several feet due to the seasonal control of the navigable water level. From November 20 through April 20, the canal near the site is dewatered to less than 0.6 m (2 ft) of standing water and no measurable flow occurs along the emergency water intake. From April 20 through November 20, the Erie Canal becomes navigable by raising the water levels to 3.7 m (12 ft) deep, which is approximately 2.4 m to 6.4 m (8 ft to 21 ft) lower than the shallow bedrock groundwater elevations along the southeastern Guterl Steel Site boundary. Therefore, a locally steep gradient in the contaminated shallow bedrock zone forces groundwater to discharge to the Erie Canal at rates derived from normal groundwater fluctuations. During normal operation periods, the average surface-water flow rate in the canal is 61 cm/s (2 ft per second, ft/s) due to upstream and downstream locking of shipping and boating traffic [2].

The hydrogeologic conceptualization of the flow system shown on Figure 3 provides a basis to estimate the risk of exposure from the ingestion of uranium released from the Guterl Steel Site. Mixing calculations used site uranium concentrations in groundwater and Erie Canal flow parameters to determine if site groundwater would elevate the uranium concentrations in the Erie Canal to or above 30  $\mu$ g/L.

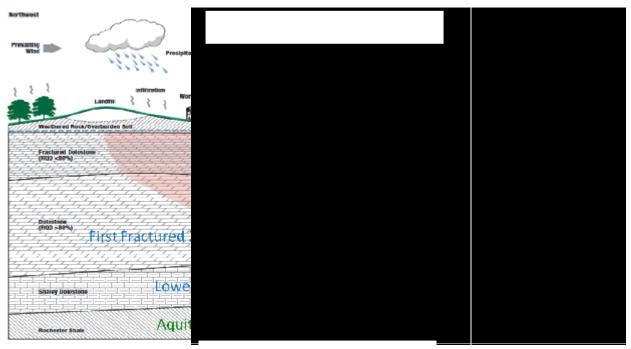


Figure 3. Conceptual Flow Model

The transport of uranium contaminated groundwater from the site to the Erie Canal occurs in the upper weathered zone and deeper fracture flow zone. Groundwater velocities through a fractured network can be high since the fractures usually occupy only a very small fraction of the bedrock groundwater system (i.e. low porosity). So, even when groundwater velocities through individual fractures may be high, the average volumetric flow rates through the groundwater in a fractured system can be low. The upper weathered zone is analogous to a very coarse grained medium and the deeper zone a discrete fractured system promoted by bedding planes and facies changes.

Groundwater seepage into the Erie Canal has been observed at discrete locations since September 2011; these seeps vary in volumetric discharge and are limited to two to eight distinct locations. This seepage mixes with a much larger volume of water in the Erie Canal and is diluted. The mixing calculations assumed the seeps discharge to the canal along the entire width of the uranium plume delineated above 30 ug/L (Figure 1).

The average groundwater discharge rate from the shallow site groundwater to the Erie Canal was calculated using Darcy's Law.

= — = — [Equation 1]

where:

is the average groundwater discharge rate [L3/T] *K* is the hydraulic conductivity [L/T] *i* is the hydraulic gradient [L/L] *A* is the cross-sectional area through which groundwater flows [L2] *w* is the width of the groundwater discharge zone [L] *b* is the depth of the discharge zone [L]  $n_e$  is effective porosity of shallow bedrock [dimensionless]

The following inputs were used:

K = 3.0 m/day (10 ft/day), geometric mean of the shallow bedrock slug tests i = 0.0602 m/m, measured from wells MW-604D and MW-712D toward the Erie Canal w = 229 m (750 ft), measured as the width of the uranium plume above 30 µg/L b = 5.6 m (18.5 ft), estimated as the entire vertical extent between the average seep elevation (174.1 m, 571.2 ft) and the Erie Canal bottom elevation (168.5 m, 552.7 ft)  $n_e = 0.09$ , estimated for fractured shallow bedrock with RQD<80%

The average groundwater flow rate ( ) was calculated to be 2,628 m<sup>3</sup>/day (92,808 ft<sup>3</sup>/day) or 0.03 m<sup>3</sup>/second (1.07 cubic ft per second [cfs]). This is a conservatively high estimate for the plume discharge area, as seeps are discrete flows from the full rock face, as measured from the top of the observed seeps to the Erie Canal bottom.

### Erie Canal discharge and dilution factor

The volumetric flow rate in the Erie Canal was estimated as follows.

=

[Equation 2]

where:

is the Erie Canal discharge rate [L3/T] *W* is the width of Erie Canal [L] *D* is the height of water column in the Erie Canal [L] *V* is the velocity of water in the Erie Canal [L/T]

The following inputs were used:

W = 28.7 m (94 ft), width of the Erie Canal upstream of Lock 34/35, New York State Canal Corporation communication to USACE, dated April 6, 2012 D = 3.7 m (12 ft), height of water in the Erie Canal upstream of Lock 34/35, New York State Canal Corporation communication to USACE dated April 6, 2012 V = 0.61 m/second (2 ft/sec), (USACE, 2010)

The Erie Canal flow, , was calculated to be  $63.9 \text{ m}^3$ /second (2,256 cfs).

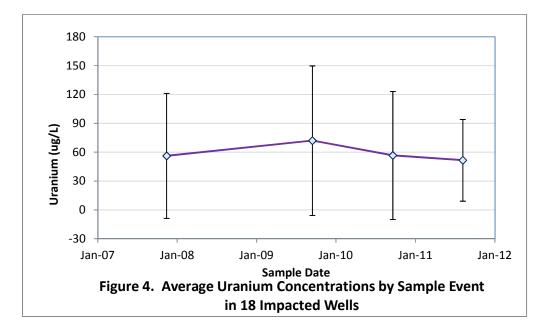
To estimate the dilution of uranium tainted groundwater flux to the Erie Canal, the following dilution ratio was calculated:

Dilution Factor =  $Q_{canal} / Q_{gw}$  [Equation 3] = 63.88 m<sup>3</sup>/second (2,256 cfs) / 0.03 m<sup>3</sup>/second (1.07 cfs) = 2,108\*

\* The original calculations were performed in English units, thus the deviation from metric conversion (and rounding) that would equate to a 2,129 dilution factor.

#### Erie Canal uranium risk

Temporal trends in uranium concentrations at the Guterl Steel Site were evaluated using graphical and statistical methods. Only 3 of the 30 wells showed significant trends: 1) MW-3 is a cross-gradient well with a significant downward trend, 2) MW-603D is cross-gradient well with a significant upward trend, and 3) MW-24 is a down-gradient well with a significant upward trend (e.g., concentrations increased from 5.49 to 35.08  $\mu$ g/L in the four successive samples). The site-wide results indicate that no statistically significant trends in uranium concentrations are detectable at during the four-year monitoring period, with the exception of MW-24. Figure 4 provides an additional perspective, which shows mean uranium concentrations for each of the four sample events calculated from the 18 impacted wells. Error bars are set equal to plus and minus one standard deviation for each sample event. This plume-wide mean perspective shows that 1) the standard deviations in uranium concentrations at each sample event are of the same magnitude as the mean concentrations of the individual means. These results imply that any trend in the plume-wide averages, if present, would not be detectable over the four-year monitoring period.



The highest measured total uranium concentration at the site was measured at 274.24  $\mu$ g/L on February, 2012 in MW-9. Uranium data do not show an increasing trend, so the plume appears in equilibrium with potential site sources (past and present) and thus increases in groundwater concentrations above 274  $\mu$ g/L are not expected. Consequently, 274  $\mu$ g/L was used as the highest groundwater uranium concentration that could migrate toward the Erie Canal and discharge through a seep. Applying a dilution factor of 2,108, this would result in a maximum concentration of 0.13  $\mu$ g/L in the Erie Canal water, which would be indistinguishable from background (0.5  $\mu$ g/L).

To determine the seepage concentration needed to cause the Erie Canal water to exceed the MCL, a reverse loading calculation was performed. The uranium concentration needed to meet the  $30 \mu g/L$  drinking water limit was calculated as follows:

Therefore, as long as groundwater concentrations at the Guterl Steel Site do not exceed 63,000  $\mu$ g/L, the mixing of groundwater seeps with Erie Canal water will not result in an exceedance of the 30  $\mu$ g/L limit in the Erie Canal, and thus put the emergency water intake at risk for use.

### Conclusion

The groundwater contamination at the Guterl site is above the drinking water standard of  $30 \ \mu g/L$  for uranium and discharges to the nearby Erie Canal at concentrations near and above this standard. The emergency drinking water intake for the City of Lockport is across the Erie Canal from these seepage areas and thus generated concern regarding the water quality in the Erie Canal. Groundwater flow and contaminant distribution assessments indicate that the uranium flux from the Guterl site will continue until a contaminated soils remedy is completed and a groundwater remediation strategy is in place. To ensure the risk to receptors is minimal during the interim period, groundwater flux and Erie Canal flow calculations were performed to verify the observed sampling results from Erie Canal water.

The resulting estimates of uranium inflow to the canal during periods when the emergency intake would be operable do not indicate a risk to receptors. The estimate of uranium effects to Erie Canal water is indistinguishable from background conditions, as shown by collocated groundwater seepage and canal water samples. The dilution potential in the canal greatly overcomes the capability of groundwater discharge from the site to pose a risk to receptors.

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