Automated Groundwater Monitoring of Uranium at the Hanford Site, Washington - 13116

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ABSTRACT

An automated groundwater monitoring system for the detection of uranyl ion in groundwater was deployed at the 300 Area Industrial Complex, Hanford Site, Washington. The research was conducted to determine if at-site, automated monitoring of contaminant movement in the subsurface is a viable alternative to the baseline manual sampling and analytical laboratory assay methods currently employed. The monitoring system used Arsenazo III, a colorimetric chelating compound, for the detection of the uranyl ion. The analytical system had a limit of quantification of approximately 10 parts per billion (ppb, µg/L). The EPA's drinking water maximum contaminant level (MCL) is 30 ppb [1]. In addition to the uranyl ion assay, the system was capable of acquiring temperature, conductivity, and river level data. The system was fully automated and could be operated remotely. The system was capable of collecting water samples from four sampling sources, quantifying the uranyl ion, and periodically performing a calibration of the analytical cell. The system communications were accomplished by way of cellular data link with the information transmitted through the internet.

Four water sample sources were selected for the investigation: one location provided samples of Columbia River water, and the remaining three sources provided groundwater from aquifer sampling tubes positioned in a vertical array at the Columbia River shoreline. The typical sampling schedule was to sample the four locations twice per day with one calibration check per day.

This paper outlines the instrumentation employed, the operation of the instrumentation, and analytical results for a period of time between July and August, 2012. The presentation includes the uranyl ion concentration and conductivity results from the automated sampling/analysis system, along with a comparison between the automated monitor's analytical performance and an independent laboratory analysis.

Benefits of using the automated system as an alternative to traditional sample collection and analysis includes the following:

- Field observations that provide more characterization information than is possible using traditional monitoring methods.
- Potentially significant reductions in labor and analytical costs if traditional methods are complemented by automated systems.
- The reduced cost of acquiring samples will allow for more frequent collection of samples that may be automatically introduced into real-time graphical flux programs allowing site

managers to observe the changes in contaminant concentrations during remediation projects and across discrete river stage events.

INTRODUCTION

Uranium is a significant contaminant of concern at U.S. DOE sites as well as uranium mining and tailings locations. Uranium is present in several groundwater plumes at the Hanford Site, Washington [2]. **Figure 1** shows one of these plumes, located in the 300 Area industrial complex, which lies along the banks of the Columbia River [2]. The fate and transport of uranium through the aquifer are important parameters to characterize for developing long-term corrective actions. Present baseline monitoring methods include manual in-field collection of groundwater samples followed by submittal of the collected samples to a commercial or government operated analytical laboratory for analysis. The turnaround time for analytical results can be several weeks to months. The significant cost of the baseline monitoring method typically limits the sampling frequency to a semi-annual or quarterly basis at the Hanford Site. To adequately characterize the full range of seasonal variability in the dynamic hydrologic environment near the Columbia River requires more frequent sampling events to be performed. Because future remedial action decisions at Hanford will likely include a component of groundwater monitoring, developing methods to efficiently obtain appropriate field data in a cost effective manner is paramount.

Figure 2 shows a chart of the Columbia River water elevations at the 100-H Area of the Hanford Site between 1/1/2012 and 10/31/2012. The river stage is shown to fluctuate through a range of almost 6 meters in elevation during the year. Additionally, there exists a series of dams on the Columbia River located upstream of the Hanford Site. Releases from the hydroelectric dam immediately upstream, Priest Rapids Dam, are responsible for daily, weekly, seasonal, and multiyear cycles in river state within the Hanford Reach of the Columbia. These seasonal and daily fluctuations have a dramatic impact on the contaminant distribution of groundwater discharging into the Columbia River. A hexavalent chromium monitoring system deployed along the Columbia River at the Hanford Site indicated that the hexavalent chromium concentration could vary in a single shallow well from <10 ppb to over 200 ppb over the course of one day [3]. Similar fluctuations in uranium concentrations occur farther downstream at the 300 Area, where the field test of an automated system was undertaken. **Figure 2** shows a boxed region that correlates with the active study period described herein. This region is expanded in **Figure 3** (right axis).

There is an identified need for a field-deployable automated analytical system capable of monitoring the flux of uranium and other radionuclides in groundwater plumes, and long-term monitoring of the effectiveness of corrective actions. The conceptual model for the uranium plume in groundwater beneath the 300 Area reveals a very complex and dynamic plume, thus requiring extra care in developing a strategy for characterizing the plume's behavior currently and in the future. A full description of the physical and hydrologic setting for the plume, and a characterization of the plume's behavior, is presented in a recent remedial investigation report for the 300 Area [4].

The most prevalent oxidation state of uranium in oxic groundwater systems is U(VI); it exists as the uranyl ion (UO_2^{+2}). The uranyl ion can be found in combination with nitrate, carbonate and phosphate ions. The carbonate and phosphate complexes have relatively high stabilities [5]. The presence of anions determines the uranyl ion mobility and, therefore, its flux through the aquifer. At the Hanford Site 300 Area, U(VI) is predominantly present as mobile anionic carbonate complexes, which include $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ [6].
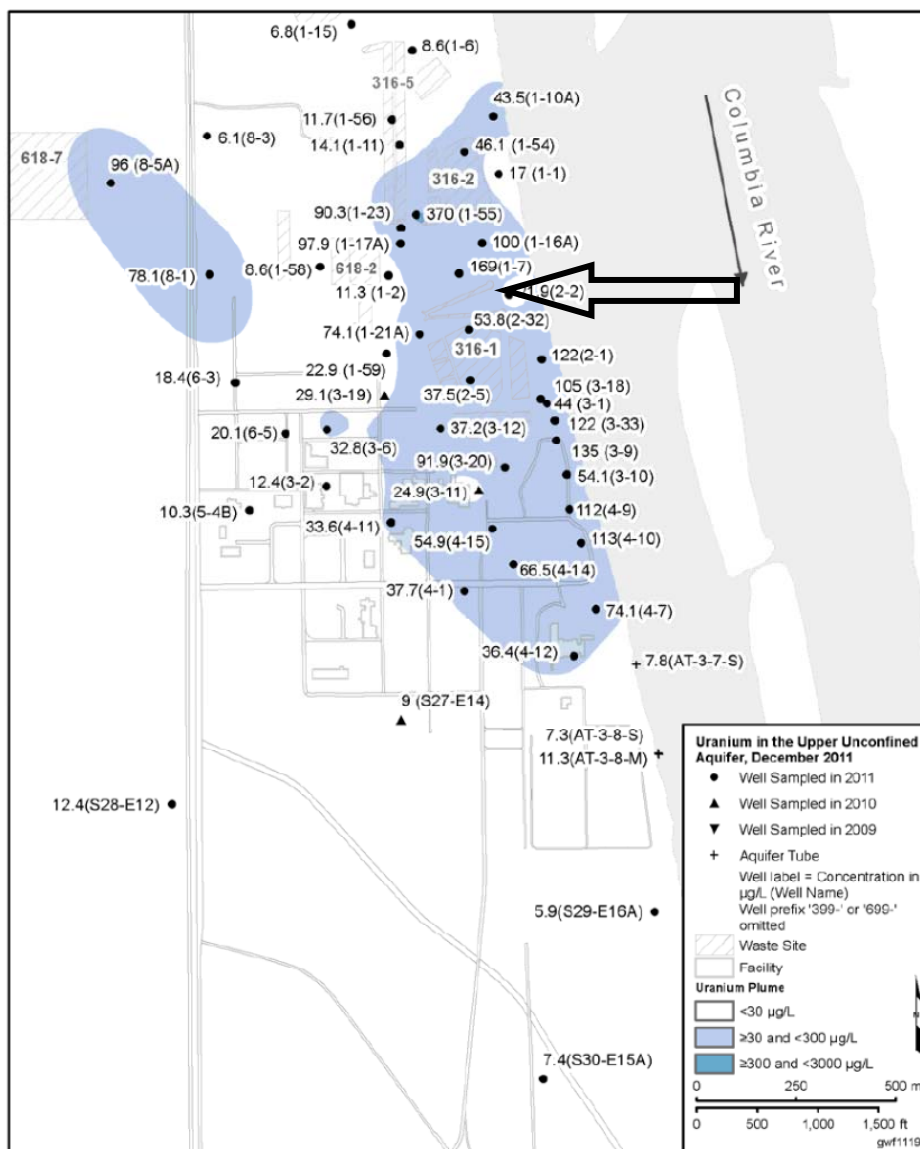

Figure 1. Location of U plume at the 300 Area industrial complex, Hanford Site, Washington. Image taken from the *Hanford Site Groundwater Monitoring for 2011* for 2011, Figure 2.7-7B. Approximate location of Burge Monitor and aquifer tubes is indicated by the arrow.

Contaminant flux, which represents the concentration times the seepage velocity at a given location, is a metric that yields powerful insight for understanding contaminant transport, considering remediation design strategies, and for developing long-term monitoring approaches

[7, 8]. When an initial flux distribution survey is conducted, remedial action optimization can be driven by reducing risk through hydraulic containment, or targeted removal of highly contaminated zones. When coupled to a flux distribution survey, follow-on monitoring activities, designed to automatically document flux reduction and changes in contaminant mass over time, can decrease the time period required for site closure, significantly reducing future costs to the federal government.

A uranyl ion detection system was designed as a "plug and play" component of a "universal" sensor platform developed by Burge Environmental, Inc. This system has been successfully used for the field deployment of trichloroethene (TCE) and hexavalent chromium detection systems [3, 9, 10]. Additionally, two radionuclide (^{90}Sr and ^{99}Tc) detection systems were designed, fabricated, and tested for measuring the radionuclides in groundwater at the Hanford Site [11, 12]. The ^{90}Sr monitor was deployed near the Columbia River bank in the 100-N Area, while the ^{99}Tc system was deployed as a prototype process monitoring system within a pump and treat plant in the 200-ZP-1 Operable Unit at Hanford. The actual radiochemical sensor modules within these deployed monitoring systems were designed and engineered as a collaboration between Burge Environmental and the Pacific Northwest National Laboratory (PNNL) [13, 14]. PNNL originally developed the preconcentrating mini-column sensor for measurement of β-emitting radionuclides in groundwater [15].
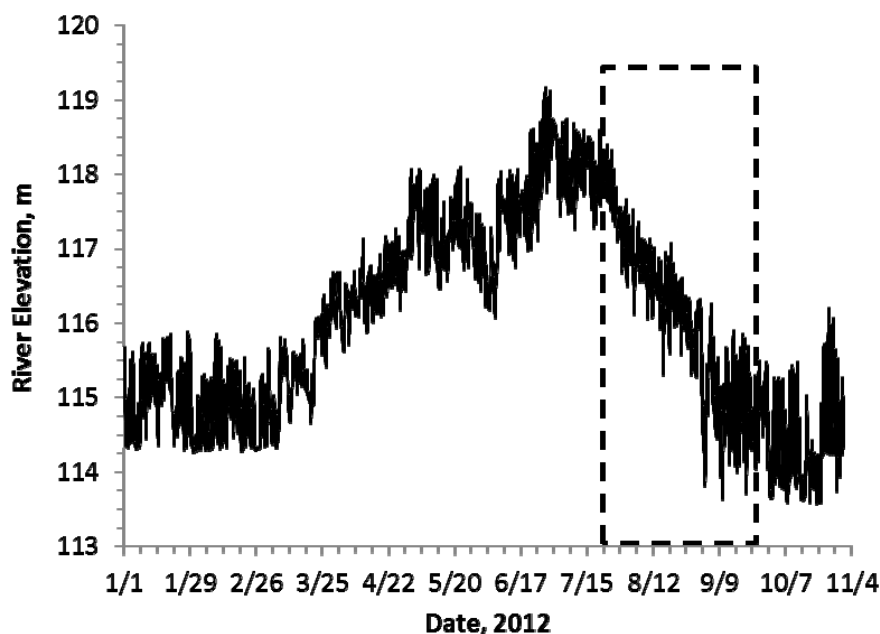

Figure 2. Columbia River water elevations taken at the 100-H Area (upstream of the 300 Area) between 1/1/12 and 10/31/12. Boxed region indicates time of uranyl ion monitoring evaluation period.
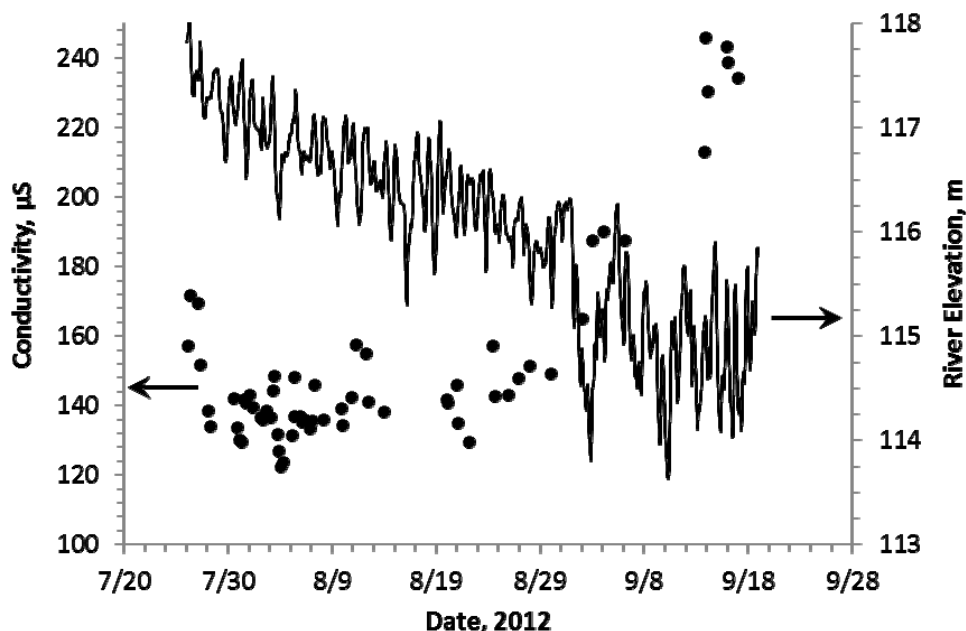
Figure 3. (Right axis) Columbia River water elevations between 7/26/12 and 9/18/12. Water levels measured at the 100 H Area of the Hanford Site, approximately 40 km upstream. (Left axis) Burge groundwater monitoring system measured conductivity values during the same interval (aquifer tube C6342).

The most commonly used analytical methods to determine dissolved uranium in environmental waters includes ICP-optical emission spectrometry (ICP-OES), ICP-mass spectrometry (ICP-MS), radiochemical methods (liquid scintillation, alpha spectroscopy, etc.), and kinetic phosphorescence analysis (KPA). In general, these instruments are not suitable as the basis of detection for field-deployable, long-term monitoring instrumentation due to their expense, power requirements, and complexity.

The analytical methodology selected for use in the uranyl monitoring system was a colorimetric method. The colorimetric reagent selected was Arsenazo III, which is capable of efficiently and selectively chelating with the uranyl ion under acidified (~pH 2) conditions [16]. Additionally, the monitoring system was designed to operate conductivity, temperature and water level probes.

An overview of the scope of work prior to the field deployment included:

- Selection of the most sensitive and robust colorimetric reagent
- Determine instrumental parameters necessary for obtaining a limit of quantification (LOQ) at or below the 30 ppb drinking water limit (DWL)
- Attain a precision of $\pm$ 15 % RSD using actual ground-water samples

INSTRUMENTATION

The uranyl monitoring system was capable of collecting and analyzing samples, and cleaning the system between each analysis (**Figure 4**). Additionally, the uranyl monitoring system performed periodic (usually daily) calibrations of the uranyl detection system using a uranyl ion standard. A photograph of the detection system illustrates the primary components of the monitoring system, including the sampling components (peristaltic pump and valves), the uranyl sensing system (sample mixing chamber, analytical cell, and colorimetric solution and delivery valves), the calibration system (standard bottle and delivery valves) and the auxiliary sensors (conductivity cell and water level sensors) (**Figure 5**, left). The entire system was mounted in a trailer located adjacent to the Columbia River at the 300 Area of the Hanford Site (**Figure 5**, right). The interior of the trailer was temperature controlled by the monitoring system via an electric heater.
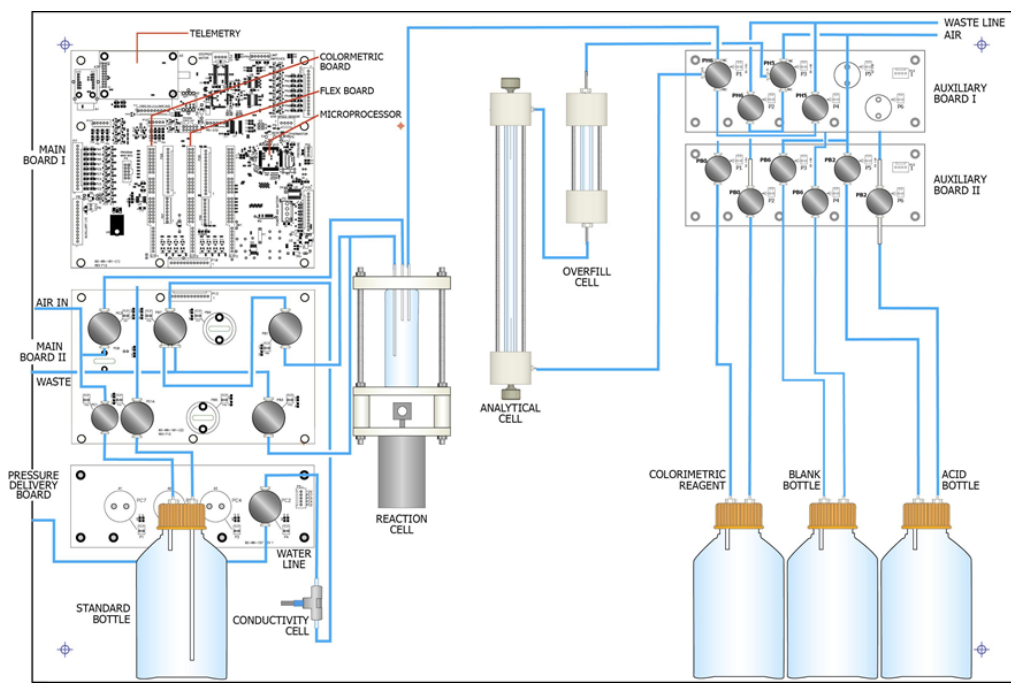

Figure 4. Uranyl monitoring system schematic.

Sampling: The system was capable of collecting water samples from four locations using a single peristaltic pump and four selection valves. The sampling system collected groundwater samples from three aquifer sampling tubes buried at increasing depths below the riverbed along the Columbia River. A fourth tube was anchored to the top of the river bed that supplied Columbia River water (**Table 1**). The aquifer tubes were 1/4" fluorocarbon tubes. The water samples were collected an on-board peristaltic pump and passed through a 0.45 μm cartridge filter. The filtered samples were directed to a flow-through conductivity cell. The water was passed through the conductivity cell until the conductivity readings of the sensor stabilized (+3 μS for 30 seconds). This was to ensure that the water sample was representative of the groundwater being sampled, and not stagnant water within the sampling lines. The sample water was then introduced into a volume-metered sample chamber where the sample was reacted with a metered volume of the colorimetric reagent solution. A magnetic stir bar within the sample chamber was activated via a small electric motor residing immediately below the chamber. After the sampling

event was complete, a vent valve was activated and the water in the sampling lines was gravity drained back into the formation.
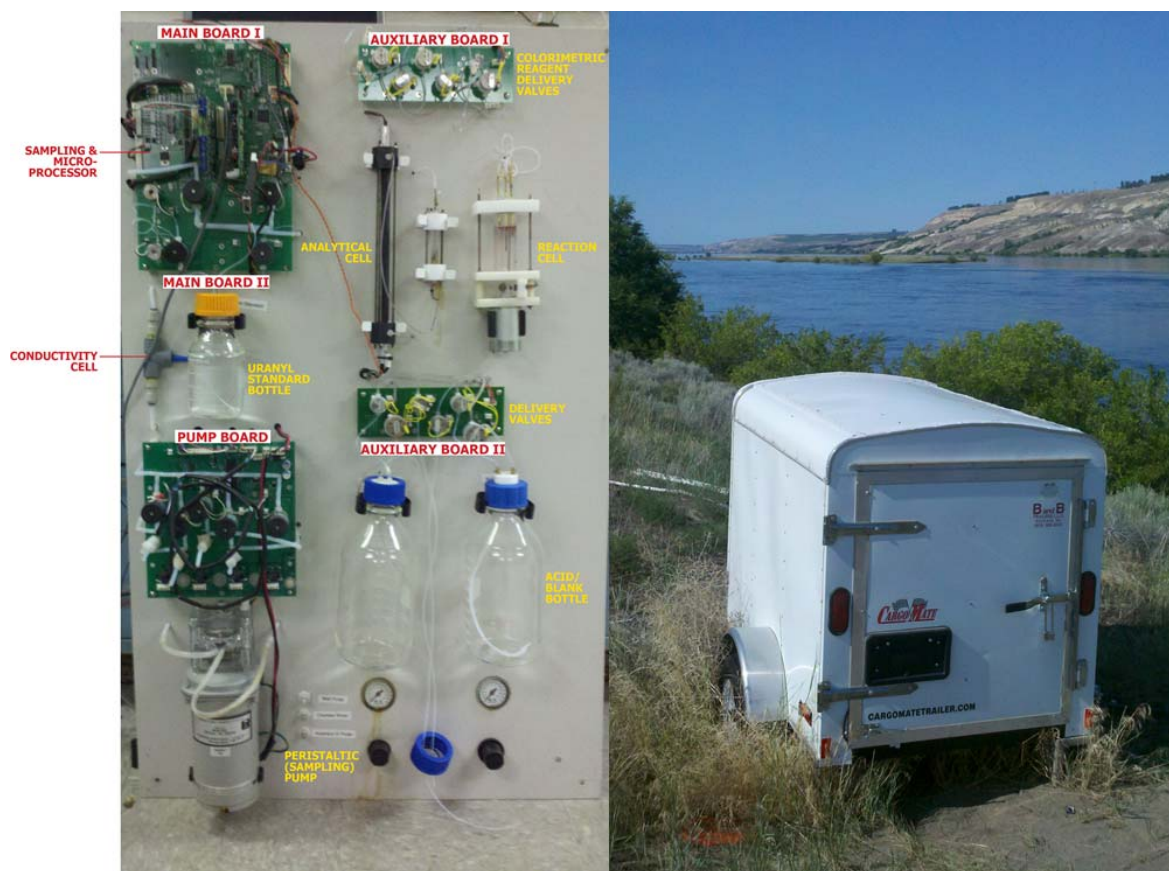

Figure 5. Uranyl monitoring system image (left) and location along Columbia River at the Hanford Site 300 Area (right).

Analysis: After the colorimetric reaction was completed in the sample chamber, the reacted sample (or standard) was transferred into the analytical cell where the colorimetric analysis was performed. The design of the analytical cell included a light source emitting within the Arsenazo III / uranyl ion complex's maximum absorbance region (red LED, 660 nm) on one end and a detector (photocell) on the opposite end. The path length of the analytical cell was ~25 cm, with a 0.55 cm inner diameter.

Cleaning and Waste Handling: The monitoring system drained and then rinsed the sample chamber and analytical cell with a dilute acid solution. The cleaning system segregated the different waste streams based on whether the waste streams contained Arsenazo III and/or uranyl standard solutions. Arsenazo III and uranyl-bearing solutions were passed through cation exchange and activated charcoal columns placed in tandem to remove uranyl ion and Arsenazo III, respectively. Finally, the solutions were passed through a one gallon glass reservoir containing marble chips in order to neutralize the acid in the water.

Calibration: Calibration of the analytical cell was performed by the following method. First, filtered river water was metered into the sampling chamber, mixed with Arsenazo III / acid, and

delivered to the analytical cell in order to obtain the reference light intensity (I_o) level from the red LED through the blank solution. The cell was purged and cleaned. Next, the sampling chamber received the filtered river water again, along with a metered volume of uranium standard, and the Arsenazo III / acid solution. Solution was mixed. This created a uranium standard of known concentration, which was subsequently delivered to the analytical cell for determination of light intensity (*I*) of the uranyl ion-bearing solution. The final uranyl ion standard concentration was set to 150 µg/L (ppb), which was expected to be approximately double that of the highest uranium concentration within the contamination plume. The Beer-Lambert Law was used to ascertain absorbance (*A*) of the uranyl standard, and the ratio of *A* to the known uranyl ion concentration of the spike, *c* (in µg/mL), provided the calibration parameter, or measurement efficiency (*Em*), which is in units $(\mu g/mL)^{-1}$ as per the equation below:

$$Em = A \cdot c^{-1} = -\log_{10}\left(\frac{I}{I_0}\right) \cdot c^{-1}$$

The flow-through conductivity sensor (Cole-Parmer), with resistance temperature detector (RTD), was calibrated using two calibration standards at 100 and 1000 µS. The standardized KOH solutions were manually injected through the calibration sensor using a 20 mL syringe, and sensor signal was recorded within the Burge software, where it was converted to conductivity values (in µS). Calibration was periodically checked via the delivery of 150, 250, and 500 µS standardized groundwater solutions through the sensor. The conductivity sensor maintained its calibration through the entire duration of the study.

Communication: The system has the capability of communicating with a user by radio telemetry or cellular data link. This enables a remote user to control the unit, monitor the unit's operation in real time, and download data from the monitoring system. Data downloaded using the cellular data link may be loaded directly onto the web. This capability allows the data to be directly interfaced with groundwater contaminant distribution and mass flux visualization programs. Therefore, the final analytical results of the monitoring system can be translated into intuitive graphics to support remedial actions and site management decisions.

RESULTS AND DISCUSSION

The Arsenazo III colorimetric analytical approach was evaluated and optimized at PNNL. Optimization included the determination of optimal Arsenazo III concentration and acidification level in representative groundwater samples. The resulting targeted sample concentration was ~5 µg/mL Arsenazo III and ~0.02 M HCl. The field deployable uranyl monitoring system prototype was designed and engineered at Burge Environmental, Inc., and was later tested in the PNNL laboratory to ensure the system met the criteria of linearity, accuracy, and precision. The limit of quantification was determined to be ~10 ppb. The system was deployed at the 300 Area industrial complex (**Figure 1**, arrow) and was housed inside a small trailer near the river bank (**Figure 5**, right). The system was operated and tested from July to September, 2012.

The monitoring system was programmed to collect samples from three aquifer tubes and the Columbia River (**Table 1**). The river water was sampled to represent essentially uranium-free water (i.e., water that contained uranium at concentrations below the limit of detection for the automated system).

Table 1. Selected aquifer tubes in the 300 Area, Hanford Site Washington

Water Source	Depth, meters	Geologic Unit [2]	Within Contamination Plume?
River	---	---	---
C6341	3.8	Hanford Gravels	Yes
C6342	5.4	Hanford Gravels	Yes
C6343	6.2	Ringold Formation, Unit E	No

The system was primarily operated in the late evening and early morning, as it was easier to maintain a constant temperature within the trailer. The colorimetric analysis is temperature dependent. The red LED used for the source of the colorimetric detection system is sensitive to temperature variation. A 2-3° C variation in the operating temperature of the LED would result in a 5 to 8% variation in the measured uranyl concentrations. The daily ambient temperature variation during the operational period ranged from 38° C during the day to below 15° C in the evenings. The interior of the trailer was typically 6° C warmer than the outside temperature during sunlight hours. Although the interior of the trailer was air conditioned, the initial temperature control of this system was not sufficient to reduce the temperature variation to acceptable levels for performing colorimetric analyses. A temperature control system was implemented that allowed the uranyl monitoring system to use a temperature sensor embedded near the source LED to control a small heater in the trailer. This system was capable of regulating the temperature of the LED to within 1° C of a selected temperature (26-28° C) from approximately 11 PM to 7 AM during the testing period. The system was not operated during the daylight hours when temperatures in the interior of the trailer rose above this temperature threshold. It should be noted that during much of this period of time, the water levels in the Columbia River were low (**Figure 2**) and the highest uranyl concentrations were expected to be present in the groundwater.

The design and operation of the monitoring system included a calibration module that was capable of the preparation and analysis of a blank and spiked blank. The uranyl standard used in this investigation was a uranyl nitrate solution that was diluted by the calibration system with the blank water to a final concentration of 150 ppb. The analysis of the blank and spiked blank resulted in the calculation of a calibration factor (*Em*) that was used to quantify the uranyl concentrations in the samples collected from the aquifer tube. The system could be programmed to prepare and determine a new *Em* on a daily or less frequent basis. The calibration factors established during the investigation period are illustrated in **Figure 6**. The *Em* values averaged 1.33 ± 0.082 (µg/mL)$^{-1}$ (1σ, n = 29).
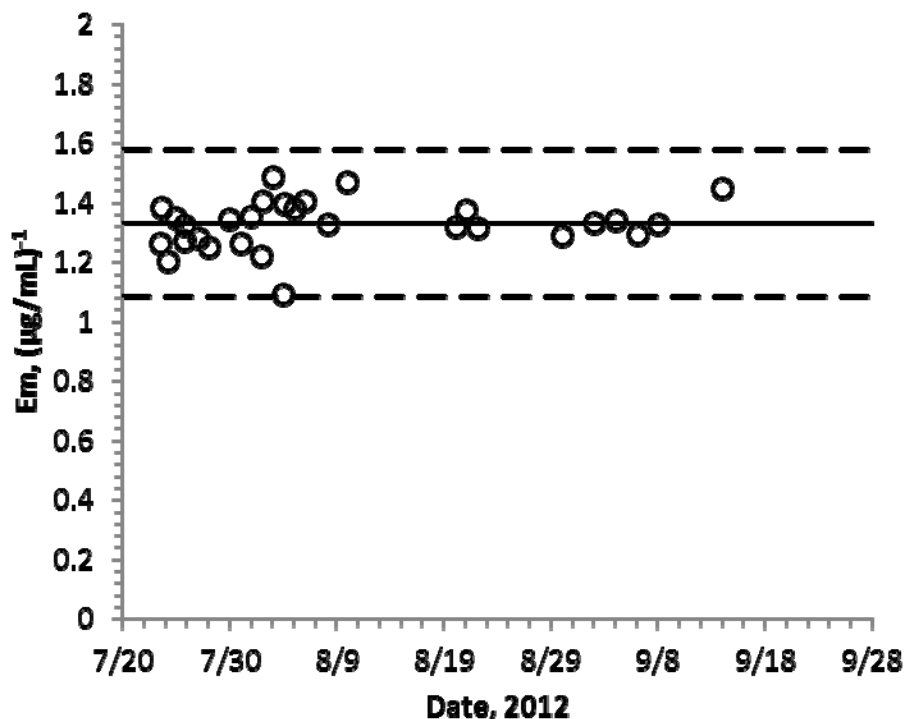
Figure 6. Calibration factor (*Em*) for the uranyl monitoring system between July and September, 2012. Average *Em* ± 3 standard deviations are shown.

The testing procedure included periodic collection of water samples for laboratory analysis of uranium by Kinetic Phosphorescence Analysis (KPA), along with water conductivity. A comparison of the analytical results of the monitoring system and the laboratory analysis for samples from aquifer tube C6342 is illustrated in **Table 2**.

Table 2. Comparison of analytical data between Burge uranium monitor and PNNL laboratory assay for aquifer tube C6342.

Date / Time	Uranium Concentration, ppb		Conductivity, µS	
	Monitor	**PNNL** [1]	**Monitor**	**PNNL**
7/26/12 1:07	44.6	38.0	158	159
7/27/12 0:00	30.5	37.5	152	151
7/28/12 5:55	32.6	26.5	134	130
7/30/12 1:28	24.0	21.5	NA	128
7/31/12 6:13	25.5	26.7	129	131
8/01/12 7:35	28.8	25.6	140	136

1. Analysis by kinetic phosphorescence analyzer (KPA)

The uranyl ion concentrations measured during the ~53 day testing period for the three aquifer tubes (C6341, C6342 and C6343) with measurable (>10 ppb) uranyl concentrations are illustrated in **Figure 7**. It was observed that C6341 and C6342, which both reside within the Hanford Gravels formation, tracked closely in uranium concentration, while C6343, which resides within the Ringold Formation, exhibited low concentrations of uranium. This is

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consistent with the findings reported in the *Hanford Site Groundwater Monitoring for 2011* report (figure 2.7-11), which provides a vertical cross section of geological units and aquifer tube positions / depths along the 300 Area shoreline [2]. The uranium concentrations in samples from C6341 and C6342 are observed to generally increase toward the end of August and September, which corresponds to lower Columbia River water levels and greater influence of groundwater under the shoreline region (**Figure 3**).
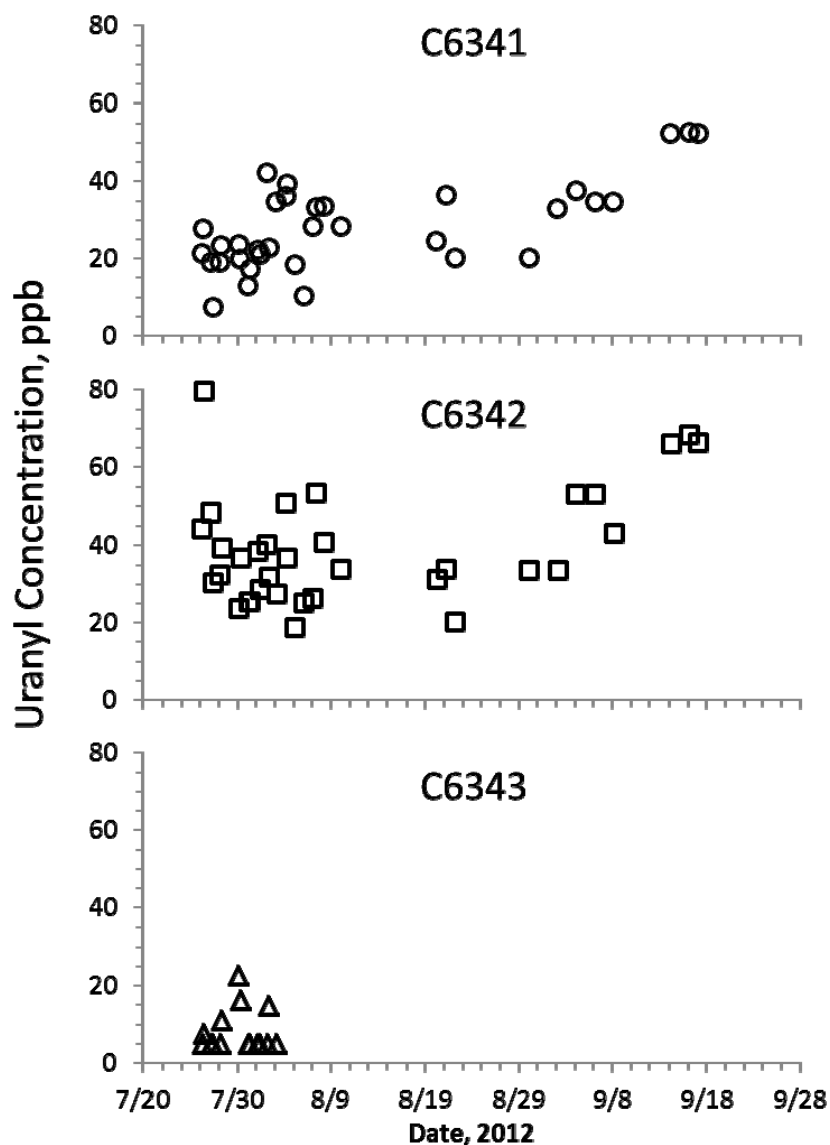
Figure 7. Measured uranyl ion concentration versus time for aquifer tubes C6341, C6342, and C6343 between July and September, 2012.

The conductivity data for the aquifer tube (C6342) is illustrated in **Figure 3**, overlaid with the Columbia River water levels during the same interval. The illustration indicates a strong correlation between aquifer tube conductivity and river stage that is consistent with a hyporheic zone interface: falling river water levels (low conductivity) result in an increase in aquifer tube

water conductivity, as the hydraulic gradient is lowered and results in a greater influx of groundwater (higher conductivity).
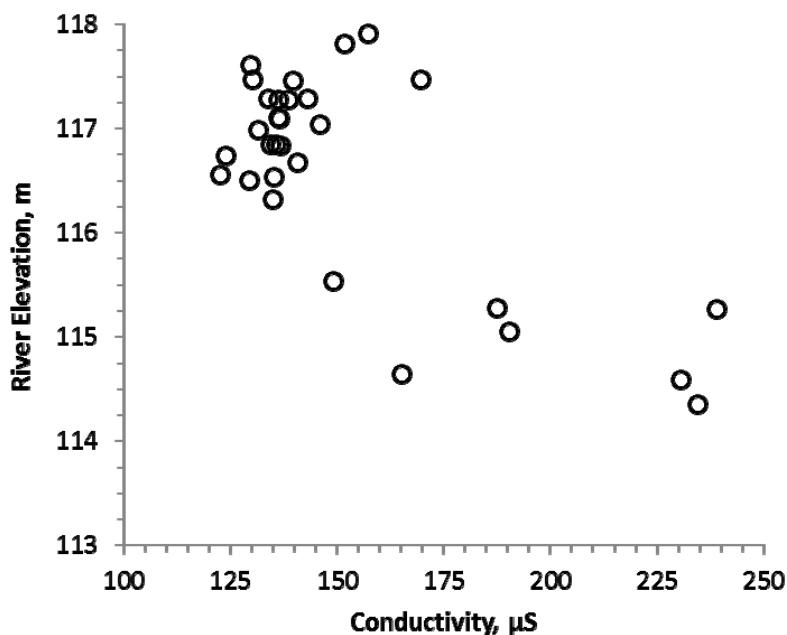

Figure 8. Columbia River elevation vs. conductivity for aquifer tube C6342.
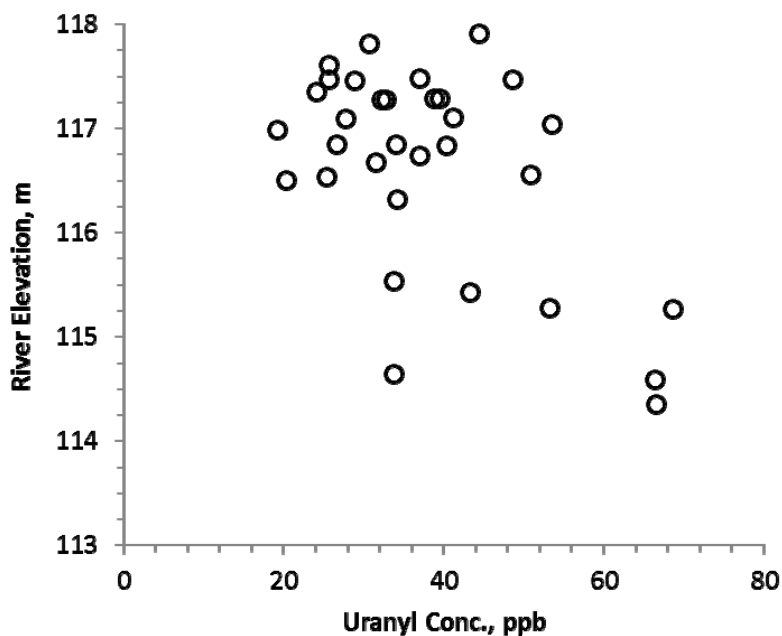

Figure 9. Columbia River elevation vs. uranium concentration for aquifer tube C6342.

Figures 8 and **9** plot river elevation against aquifer tube water conductivity and uranyl concentration, respectively. Each illustrates a negative correlation to river water level, though the uranium correlation is less well defined. A correlation plot of uranyl concentration versus

water conductivity (C6342) is presented in **Figure 10**. A linear regression of the data shows an approximated slope of 0.36 ppb UO_2^{-2} per µS of water conductivity. The correlation of the data appears to be less defined at lower uranyl concentrations. This may be due to analytical error at lower uranyl concentrations, or possibly transport mechanisms of uranyl ion between the water and the aquifer materials.
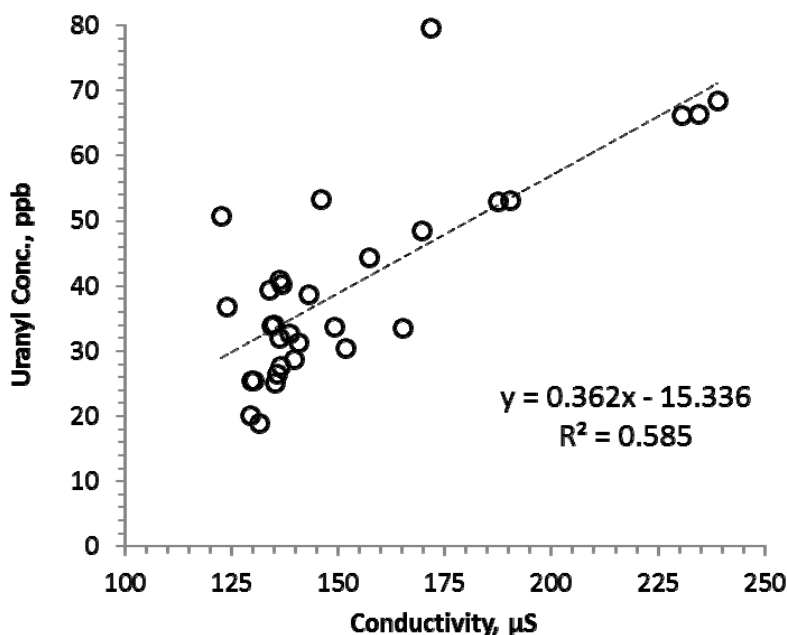

Figure 10. Uranyl concentration vs. conductivity in aquifer tube C6342 between 7/26/12 and 9/18/12.

CONCLUSION

An automated monitoring system was developed for the analysis of the uranyl ion within a shallow contamination plume as it enters the Columbia River at the Hanford Site, Washington. Results of a two-month operational period indicated the system had sufficient sensitivity and precision to determine trends between uranyl ion concentrations versus time, water conductivity, and river stage. The fully-contained on-site groundwater monitoring system was capable of self-calibration routines and unattended groundwater sampling, analysis, waste handling, and data reporting. Such a system represents a novel tool in the advancement of remote monitoring systems for long-term determination of contaminant flux through aquifers and determination of the efficacy of remediation actions.

ACKNOWLEDGEMENTS

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