A CASE STUDY OF URANIUM MOBILITY IN GROUNDWATER AT THE DUPONT CHAMBERS WORKS SITE

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ABSTRACT

To determine whether uranium mobility via groundwater is a concern at a Manhattan Engineering District (MED) project uranium-processing site, a three step investigative approach was utilized. First, existing data and data sources were analyzed. Second, the site was screened using a Geoprobe® to locate potential problem areas. Finally, a focused investigation is underway using monitoring wells located in suspect areas. This study charts the investigative approach taken to determine if MED-related contamination is present at the DuPont Chambers Works Site in Deepwater, New Jersey. Specific tasks of the investigation will focus on the nature and extent of the contaminants in soil and groundwater and the potential for mobility from site soils to groundwater. The rationale and methodologies for the investigation of soil and groundwater are presented in the following sections of this paper.

In the course of these investigations, soil mineralogies were identified using X-ray diffraction (XRD) analysis. Bulk soil chemistry was determined using Scanning Electron Microscopy (SEM). To determine how strongly other potentially mobile uranium phases are bound to site soils, sequential extraction desorption experiments were performed on soil samples from areas with elevated levels of soil uranium concentrations. Each sample was subjected to progressively stronger extractants designed to dissolve particular chemical phases, and the resultant liquids were analyzed for uranium. This test was a good proxy for field conditions at the Chambers Works site due to the presence of various chemical plumes and a wide range of groundwater Eh and pH. XRD analysis of two samples showed the presence of low solubility/mobility uranium oxides including pitchblend and uraninite. However, in addition to immobile phases, six of the seven samples analyzed by sequential extraction showed that thirty to seventy-five percent of the uranium bearing phases present may be mobilized under dilute to weakly acidic groundwater

conditions. One sample showed forty percent of uranium present may be mobilized by rainwater. These findings suggest that uranium mineralogy at the site does not exclude the presence of uranium plumes, although only localized plumes have been found.

INTRODUCTION

The United States Army Corps of Engineers (USACE) has begun a preliminary Phase I Remedial Investigation (RI) at the DuPont Chambers Works Site under the Formerly Utilized Sites Remedial Action Program (FUSRAP) in Deepwater, New Jersey. The goal of the RI is to determine the nature and extent of the Manhattan Engineer District (MED)-related radiological contamination at the DuPont Chambers Works Site. This goal requires investigation of both soil and groundwater. Although groundwater has not traditionally been investigated at FUSRAP sites, regulators and the public have expressed concerns over groundwater-related ecological and health risks. In addition, DuPont is concerned that their groundwater treatment system may be capturing MED-related radiological contaminants. There are four groundwater related questions to be answered in the RI study:

- Are radiological contaminants at the site mobile in groundwater?
- If so, how far could they travel?
- Which direction(s) could they have gone?
- What is a meaningful uranium distribution coefficient (Kd) for risk assessment models?

SITE BACKGROUND

The DuPont Chambers Works Site, a 700-acre chemical plant active since 1892, contracted with MED to perform several uranium processing activities. These included production of uranium compounds including oxides, metal, peroxides and salts. Enriched compounds were not produced.

Under the FUSRAP program established by the Department of Energy (DOE), six individual areas of concern (AOCs) were defined and some preliminary investigative tasks were performed at the DuPont Chambers Works Site. In October 1997, responsibility for the administration and execution of FUSRAP was transferred to USACE. The AOCs established by DOE were combined for this investigative effort into three separate Operable Units (OU-1, 2, and 3, shown on Figure 1). Two AOCs can be found within each of the three OUs. The Building 845 area and the F Corral AOCs are located within OU-1. The Central Drainage Ditch and Building J-26 area AOCs are found within OU-2, and the historical lagoon and east burial area AOCs are found within OU-3.

SITE PHYSICAL CHARACTERISTICS

The DuPont Chambers Works site is located in Deepwater, NJ in the floodplain of the Delaware River. The shallow soils are of alluvial origin but have been substantially modified by landfilling and construction activities. Shoreline sediments are likely accreted point bar deposits as well as over-bank deposits from periodic flooding of the Delaware River. Tidal marsh deposits consisting of silty clays lie inland of the shore deposits. The Chambers Works site was

enlarged during its history by filling in these localized marsh areas. Generally, the soils at the site that exist at or below sea level elevations are naturally occurring marsh deposits, while sediments occurring above sea level are fill materials.
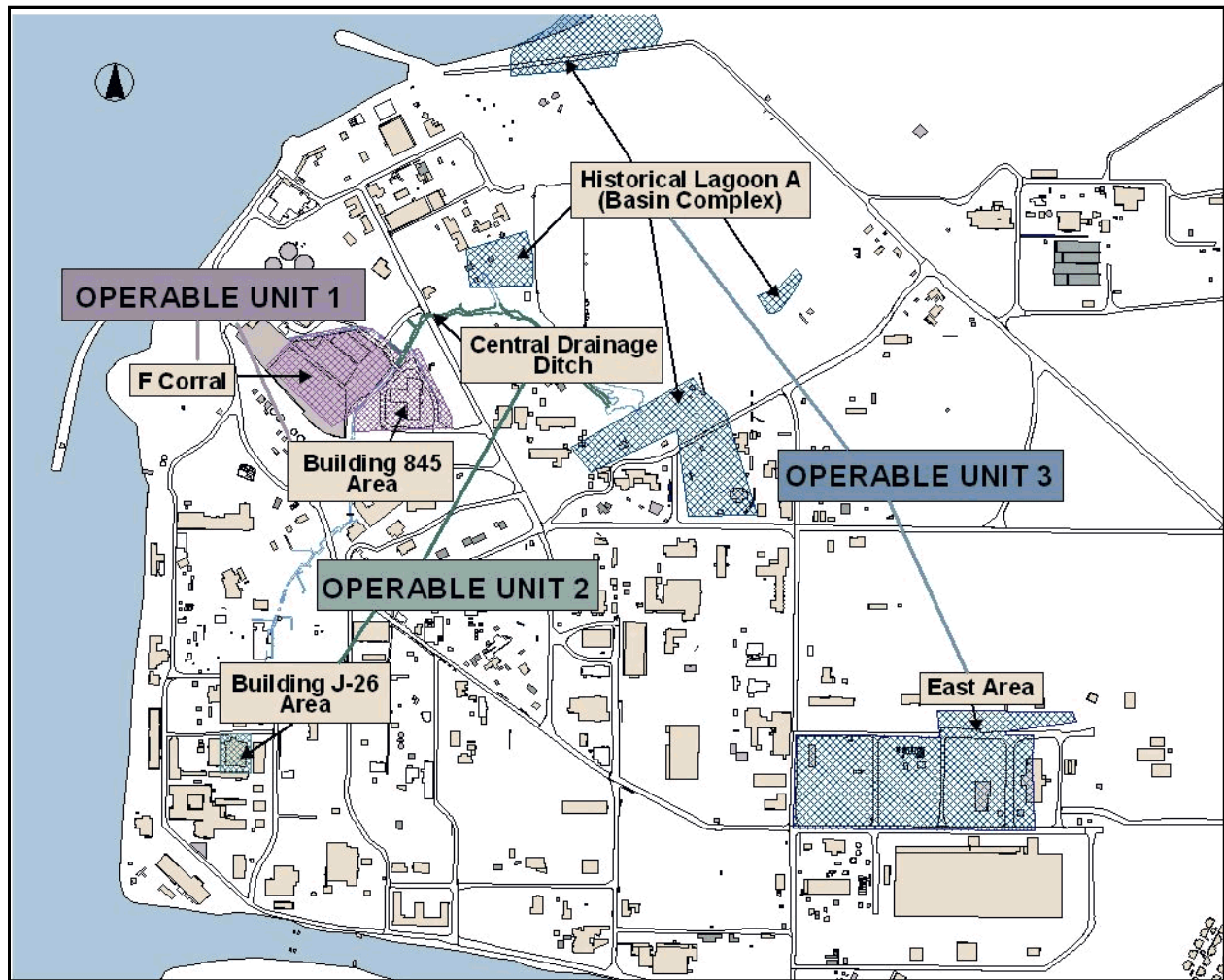

Fig. 1. Chambers Works Areas of Concern.

The hydrostratigraphic units encountered beneath the site consist of sedimentary deposits that have been divided into five major sequences [1]. The first major sequence consists of the A and B aquifers separated by the AB aquitard and underlain by the BC aquitard. This sequence represents the vertical extent of MED-related contaminants presented in this RI. The A aquifer consists primarily of fill material of Holocene age, composed of silty sands, rubble and debris, and ranges in thickness at the site from 0-17 ft. The AB aquitard consists of Holocene age naturally deposited organic silt, clay and peat and ranges in thickness from 0-12 ft. The AB aquitard is discontinuous and either thins or is eroded in various places and represents a leaky aquitard. The B aquifer consists of Holocene age sands and is interpreted to be Delaware River Alluvium. The B-aquifer ranges in thickness from 1-30 ft. across the site.

DISCUSSION OF FACTORS INFLUENCING URANIUM MOBILITY

Uranium Geochemistry
Uranium is one of the more geochemically complex chemicals in the water and soil environment. It can form a mobile ion or an immobile mineral depending on several key variables [2, 3]. The redox state of the water is one of the most important variables because most of the immobile mineral phases form when uranium is in reducing conditions. There is no specific threshold oxidation reduction potential for uranium mobility, because mobility is also influenced by other key factors: pH, aqueous complex formation, and sorption (see definition below) to various mineral surfaces. Uranium is amphoteric, meaning that it can mobilize at either high or low pH. Again, the specific value depends on additional factors such as redox and complexes. Among the most important uranium complexes leading to mobilization are the carbonate species (bicarbonate (HCO_3^-), carbonate ($CO_3^=$)) [4]. Uranium can also complex with phosphate and hydroxyl (OH^-) ions (and several other anions). Carbonate is one of the more common anions that can form strong aqueous complexes with uranium (especially. at pH greater than 6.5). Surprisingly, there were no carbonate data available for the site before this study. Although specific values cannot be given for mobile ranges, with the dependency on multiple factors, some general trends are observed. Immobile uranium minerals tend to form when dissolved oxygen is less than 1 milligram per liter (mg/L) and further soil investigative techniques (i.e. XRD and SEM) are warranted under these conditions. The circumneutral pH (6 to 8) is more likely to mobilize uranium. Significant carbonate concentrations can form complexes with sorbed uranium and remobilize it; however, uranium occurring in mineral form is much more difficult to remobilize.

In addition to aqueous complexes, the mobility of uranium depends on soil characteristics. In other words, certain soils and sediments can form a chemical bond with uranium (referred to as sorption), removing it from solution. Among the likely sorption sites for uranium are iron oxides, clays, and organic matter [5, 6]. Both the types of sorption sites and their surface area are factors in the degree of sorption. Furthermore, sorption sites compete with aqueous complexes to bind uranium [7]. Because of the multiple factors influencing sorption, a lumping term is often used to describe the distribution of uranium between the solution and the solid phases. This distribution factor is known as the K_d. It has the advantage of describing multiple factors, but the disadvantage of not being able to adequately predict site-specific behavior when any of these factors varies. It is important therefore to examine the factors individually to improve predictions [8].

The soil chemistry and groundwater chemistry need to be examined together. Uranium sorbed to soil may be desorbed by changes in local groundwater chemistry. When an "aggressive" groundwater comes into contact with sediment that contains sorbed uranium, desorption may occur. This is a particular concern at a contaminated site where the chemistry of the water is not constant (and predictable), but instead contains contaminant plumes with varying pH, redox, and complexing agents. Thus, as shown in Figure 2, the form of uranium in soil is important for predicting whether it can be mobilized. The pie diagrams show forms of uranium based on sequential leaching by progressively more aggressive solutions ranging from de-ionized water to aqua regia. The soil sample 3-SS-28-R has mostly insoluble forms of uranium and groundwater passing through will not dissolve uranium, while the Elevator Shaft sample has soluble,

exchangeable, and carbonate forms of uranium. Aggressive groundwater can dissolve uranium and lead to high concentration in solution.
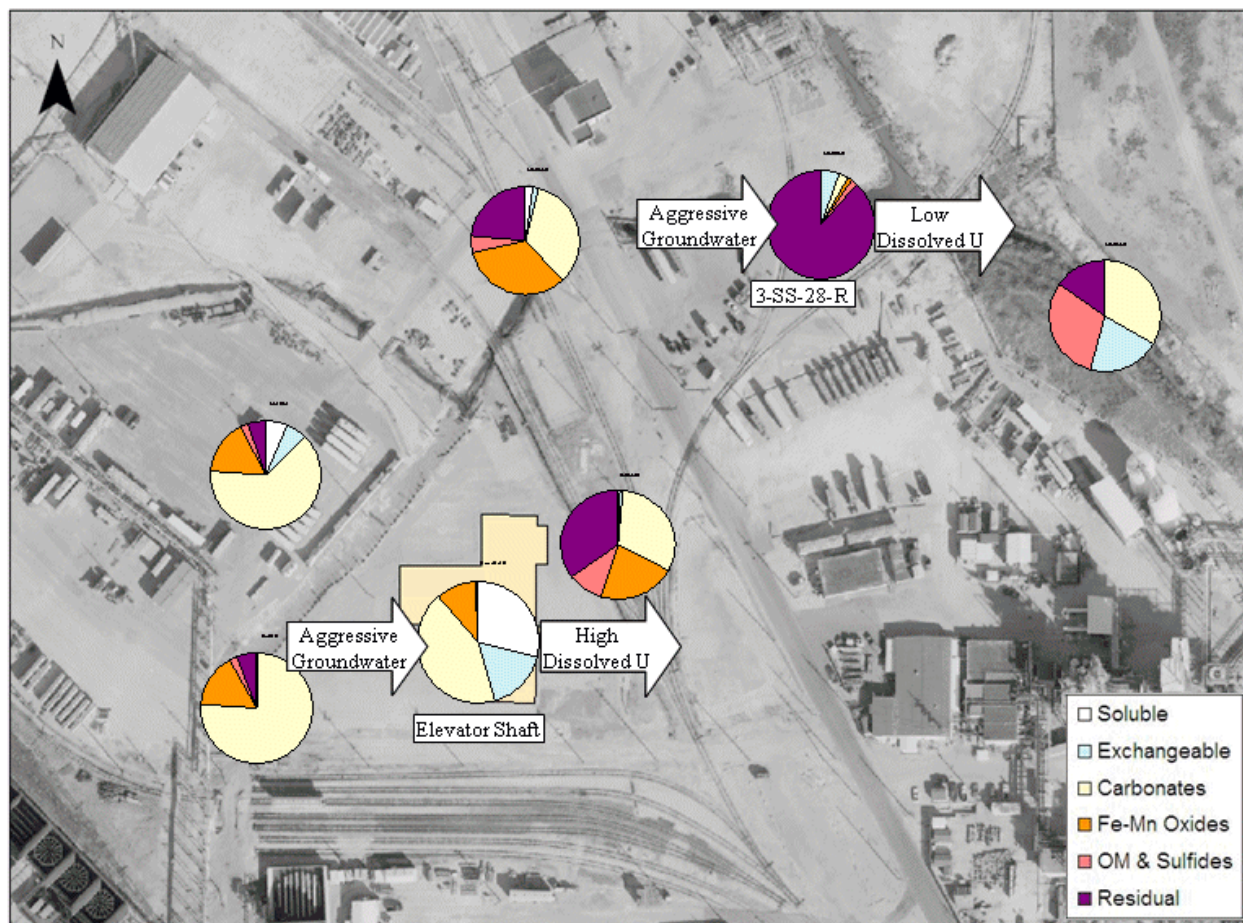

Fig. 2. OU-1 Sequential Extraction Results.

An understanding of the background water chemistry and the forms in which the uranium occurs is needed to predict where the uranium is now and whether it might become mobile in the future. Each of these mobility factors has been examined in this study and will be discussed below.

APPROACH TO CHARACTERIZING URANIUM CONTAMINATION AT THE SITE

The primary objective of the RI is to define the nature and extent of MED-related radiological contamination in OUs-1, 2, and 3 (the OU-3 RI has not been completed as of the writing of this paper).

Existing monitoring wells are not located in MED areas. To determine if and where to place new monitoring wells, a three-step approach was used to investigate the nature and extent of contaminants in each of the AOCs. **Step I** involved evaluation of existing site information. **Step II** investigations involved screening tasks for site characterization, including soil and water analysis to define the existence and extent of the contamination. **Step III** involved more focused investigative tasks to determine contaminant mobility, direction, and extent. Some geochemical

investigations of soil and groundwater for Step III began during Step II, essentially piggy-backing on the sample collection for site characterization. Samples were also collected from existing monitoring wells not located in the OUs. Step III also included installation of monitoring wells in the OUs as warranted by findings in Steps I and II. The detailed tasks and the results of these investigative steps are discussed below.

Step I Evaluation of Existing Site Information
A historical record review, a gamma walkover survey and a geophysical survey to help identify underground utilities and soil heterogeneity were conducted. Part of the historical record review included locating areas of radiological contamination identified by walkover surveys and soil analyses conducted by Oak Ridge National Laboratory (ORNL) in 1977 and Bechtel National, Inc. (BNI) in 1983. These investigations lead to the definition of the AOCs previously described.

Step II Soil Screening Investigation Tasks

Step I results were used to create a sampling grid that included both biased and unbiased sample locations. Site sampling patterns were developed according to the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM). Additional sampling locations were added to re-test locations from previous studies were uranium was found and are considered "biased" sample locations. These locations needed to be free of concrete, underground utilities and debris in order to facilitate the use of Geoprobe® direct push sampling of soil and groundwater.

The OU-1 field effort was conducted in 2002. The OU-1 remedial investigation included Building 845 and F-Corral AOCs, which formerly housed scrap uranium processing and by-product recovery operations, and production of brown oxides, green salts and uranium metal.

Twenty-four grid and 12 biased locations were sampled at the Building 845 Area and 37 grid and six biased locations were sampled at the F parking Corral. Seventy-nine surface and 230 subsurface soil samples were collected during the OU-1 field effort.

The OU-2 sampling effort was completed in 2003. At OU-2 (AOCs-3 and 5), sampling patterns were developed along the drainage features that comprised the Central Drainage Ditch and drains in the area of Building J-26. These areas were chosen for investigation because they may have received uranium processing wastes and were potential uranium transport pathways.

At AOC-3, the sample locations were placed 75 feet apart while at AOC-5 the spacing was approximately 50 feet apart. Twenty-seven borings were completed in AOC-3, from which 164 soil samples were collected. At AOC-5, 11 soil borings were advanced from which 64 soil samples were collected. Borings were advanced to a planned depth of 10 feet below ground surface (bgs).

The soil samples from both the OU-1 and OU-2 investigations were screened in an on-site gamma spectroscopy lab. The on-site results were used to select soil samples of varying soil textures and uranium concentrations for off-site analysis.

Step II Groundwater Screening Tasks

Groundwater samples were collected from Geoprobe boreholes at the former Building 845 Area and F Corral, as well as at AOC-3 and AOC-5. The sampling strategy was to check for potential MED-related radionuclide contamination of groundwater. Step II began with the direct push sampling of soils at the gridded and biased sampling locations. Next, a temporary piezometer was inserted into the open borehole and a groundwater sample was extracted using low flow sampling techniques. Groundwater samples were collected from approximately 50 percent of the Geoprobe® sampling locations. Uranium isotopic concentrations in groundwater were determined using alpha spectroscopy. Gross alpha, gross beta, and radium isotopic concentrations were also determined.

Samples taken from open holes during Step II Geoprobe® direct push sampling were considered screening samples and were more prone to contain colloidal and solid phases than samples collected from a permanently-constructed monitoring well that includes a well screen and sand filter pack. Analytical results for samples taken from open boreholes may be biased high for metals even utilizing low flow sampling procedures. Therefore, a filtered and an unfiltered sample were collected at each sampling location. More weight was given to the filtered samples during screening for dissolved uranium.

Step III Specialized Soil Analyses

The following supplementary soils analyses were developed to obtain information on potential mobility of uranium. This task goes beyond looking at where the uranium is located and addresses the question of why it is there and whether it will remain in place. To do so, we have examined the form of uranium in the soil by the following methods:

1. Sequential extraction uses progressively more aggressive solutions to dissolve uranium in a soil sample. Some forms of uranium are more mobile than others under different chemical conditions and the forms can be distinguished by this technique.
2. XRD identifies the mineralogy of the soil contaminated with uranium. If uranium is present as a mineral (rather than as a sorbed phase) it can also be identified by XRD.
3. SEM/EDS (Scanning Electron Microscopy / Energy Dispersive Spectroscopy) provides microscopic evidence for forms of uranium that might not be identified by XRD. Specifically, if uranium is sorbed onto amorphous phases, it cannot be identified by XRD but can be identified by SEM/EDS. High iron content in association with uranium would be evidence for sorption.
4. TOC and CEC are soil analyses for Total Organic Carbon and for Cation Exchange Capacity, respectively. These analyses can be performed on contaminated or uncontaminated soil samples to provide background characteristics of soil. High values increase the potential for the soil to immobilize uranium if present..
5. K_d is the distribution coefficient, or the ratio of the amount of contaminant sorbed to the amount in solution, used to calculate a retardation factor. This is more specific and more time consuming than the TOC and CEC measurements because it identifies how uranium attaches to the soil under different geochemical conditions and uranium concentrations.

In summary, each of these techniques detects a different form of uranium that may be present. K_d, sequential extraction, TOC, and CEC are quantitative, but because they measure different types of sorption, analytical results may not be numerically similar. Due to soil heterogeneity, multiple analyses are needed to identity variability between sampling locations in addition to overall characteristics for the soil.

Step III Focused Groundwater Investigation Tasks
Groundwater samples were collected from existing monitoring wells not located in the OUs and from Step II sampling locations. In addition to the sample collected for radionuclide screening, basic water chemistry analysis was included to better understand the geochemical factors controlling uranium chemistry. Groundwater samples submitted for Target Analyte List (TAL) metals were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and for anions using ion chromatography or titration (for alkalinity). Parameters measured in the field included pH, conductivity, temperature, oxidation reduction potential (ORP), turbidity and dissolved oxygen.

Step III Monitoring Well Installation and Sampling
Monitoring well locations were chosen based on results from the Geoprobe® investigation, to locate wells in areas where uranium was detected in groundwater. The monitoring wells also allowed for measurement of water levels to determine the direction of groundwater flow. Sixteen two-inch PVC monitoring wells were installed as part of a field effort undertaken during the summer and fall of 2004. Six locations had well pairs nested the A and the B aquifer units. Of the 16 monitoring wells installed in OU-1, seven were screened within the A aquifer and nine were screened within the B aquifer. The wells were installed using hollow stem auger and split spoon techniques. The monitoring wells were surveyed and sampled in late fall of 2004. The results of the groundwater sampling event were pending as of this report.

Once the monitoring wells were installed and completed, they were developed until the resultant water measured less than 10 nephelometric turbidity units (NTU). This was done to "set" the filter pack and ready the well for sample collection. Samples were collected using low flow sampling techniques; one set was unfiltered and another set of samples was passed through a 0.45 micron (µm) in-line filter. Although not required by the New Jersey Department of Environmental Protection (NJDEP) regulations, filtered groundwater samples were collected in order to distinguish "colloidal" and "suspended particulate" from "dissolved" phase uranium. Filtered contaminant data are necessary to begin to deduce how uranium moves under a given set of site conditions using geochemical speciation codes. It should be noted that 0.45 µm is an environmental industry standard of "practicality" and represents an artificial separation of colloidal and particulate phases from dissolved phases. Various definitions exist as to the size of suspended and colloidal particles. However, it is generally accepted that some colloidal particles will pass through a 0.45 µm filter [9] and that certain metals (e.g. iron and aluminum) will have results that are biased high and may effect charge balance calculations and subsequent geochemical modeling results.

Two monitoring wells were installed within OU-2. They were screened within the B aquifer along the Central Drainage Ditch. The purpose of well installation in this area was to determine if the Central Drainage Ditch represented a potential pathway for contaminants to migrate to the B aquifer.

RESULTS

Step I   Evaluation of Existing Site Information

Previous investigations at Building J-26 and F-Corral performed by ORNL and BNI. for DOE indicated that MED-related contamination is limited to natural uranium isotopes (i.e. U-234, U-235 and U-238) and their short-lived progeny. These investigations identified potentially elevated uranium concentrations in surface and subsurface soils, concrete slab foundations, and shallow groundwater. ORNL conducted a radiation survey of the Chambers Works Site in 1977 and found gamma radiation exposure rates to be consistent with background levels. Part of the survey included the area around Building J-26 (OU-2). In 1983, BNI performed a radiation survey of the Chambers Works Site and found near-surface gamma radiation to be less than twice background. Soils were not sampled and analyzed from the Building J-26 area during the two investigations. Both studies also included soil sampling and analyses in the F-Corral and Building 845 areas (OU-1) and the Central Drainage Ditch (OU-2). Soil analytical results for Uranium from samples taken in the F-Corral ranged from not detectable to 6.8 picocuries per gram (pCi/g) during the ORNL study and 0.9 to 105 pCi/g during the BNI study. Soil analytical results for uranium from samples taken in the Building 845 Area ranged from non-detectable to 6,920 pCi/g during the ORNL study and from 1 to 8,057 pCi/g during the BNI study. Soil and sediment analytical results for Uranium from samples taken in the Central Drainage Ditch ranged from non-detectable to 12,600 pCi/g during the ORNL study and 1 to 1.9 pCi/g during the BNI study.

Step II Soil and Groundwater Screening results at OU-1

A complete summary of all results from the soil screening analyses associated with the DuPont Chambers Works RI is not warranted for the limited scope of this paper; and only the results of uranium analyses will be presented in the following sections. Only where necessary (i.e., discussion of uranium mobility below) will other analytical data be presented.

Results for uranium in soil from OU-1 are presented on Figure 3. An investigative screening value (ISV) of 14 pCi/g was established. In AOC-1, the ISV was exceeded at 15 of 36 borehole locations and in 17 soil samples. Of the 17 samples exceeding the ISV, 15 were surface samples and two were subsurface samples. Total uranium analytical results varied from non-detectable to 99,000 pCi/g. In AOC-2 (F Parking Corral) the ISV was exceeded in 9 of 43 borehole locations and in a total of 21 soil samples. Of the 21 samples exceeding the ISV, nine were surface samples and 12 were subsurface samples. Total uranium analytical results varied from non-detectable to 16,600 pCi/g.

The results for filtered groundwater samples in Building 845 area indicated no exceedances of USEPA for uranium (30 micrograms per liter (µg/L) or 20.3 pCi/L). The results from unfiltered groundwater samples at the Building 845 area indicated higher concentrations. Unfiltered uranium concentrations ranged from non-detectable to 46.3 pCi/L. The results for filtered

(dissolved) groundwater samples in the F Parking Corral Area indicated three exceedances of USEPA MCLs as shown on Figure 4. Again, the results for unfiltered groundwater analyses were consistently higher: total uranium ranged from 0.78 to 2,390 pCi/L.

Step II Soil and Groundwater Screening Results at OU-2

At AOC-3, 11 of the 164 samples or 7 percent of the samples, exceeded the ISV. Sediment sample 3-SB-04 had the highest activity (98 pCi/g) and was collected from the bottom of a wooden trough. Exceedances of the ISV ranged from 14.7 to 98 pCi/g. All boreholes were completed to 10 feet bgs in AOC-3. Most samples that exceed the ISV were shallow
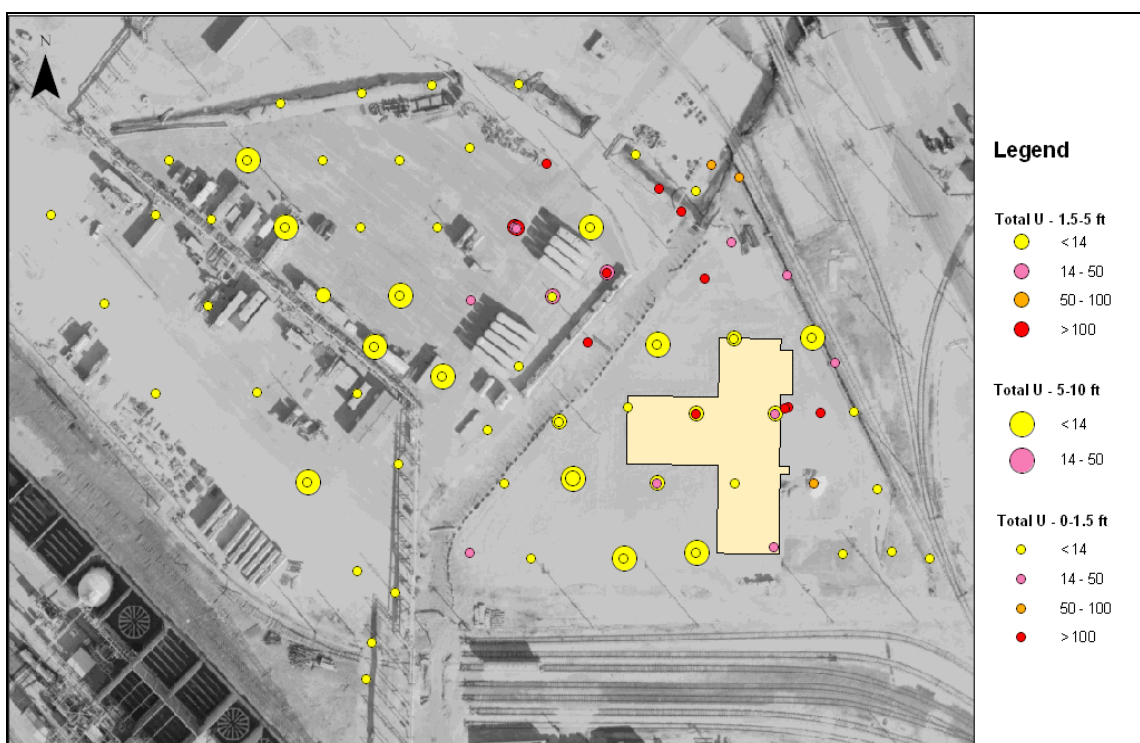

Fig. 3. Total Uranium in Soils (pCi/g).

samples collected from between 0 and four ft bgs. Three samples that exceeded the ISV were found between four and eight ft bgs. No soil samples collected and submitted for analysis in AOC-5 exceeded the ISV.

Groundwater analytical results for OU-2 showed that the maximum uranium concentration in filtered groundwater samples was 7 pCi/L (at 3-SB-14). Two unfiltered samples from AOC-3 had total uranium concentrations greater than 20 pCi/L. None of the unfiltered groundwater samples at AOC-5 had uranium concentrations greater than 2 pCi/L. One unfiltered sample had a uranium concentration greater than 20 pCi/L.

Fig. 4. Total Uranium in Groundwater Samples (Filtered) (pCi/L).

Step III Results of Focused Groundwater Sampling

The uranium concentrations in borehole water are discussed above, but uranium was also measured in existing wells outside of the OUs as part of the stepped investigation. The uranium concentrations in existing wells were all low. The highest concentration (26 pCi/L at I17-M01A) was more than an order of magnitude below the suggested water contamination criteria for FUSRAP sites of 600 pCi/L. Naturally occurring uranium is also present in local aquifers [10]. While this data may suggest the presence of some low-level MED-related uranium, there is no evidence in the external wells to suggest large plumes of uranium moving beyond the OU boundaries. The results of the monitoring well sampling within OU-1 and OU-2 are pending.

The additional focused sampling elucidated groundwater parameters that influence mobility of uranium; these parameters vary across the site (Table I). For the site-wide study, pH varied from six to ten, generally falling in the circumneutral range, which enhances mobility. For OU-1, the pH range was somewhat higher, from four to ten. For OU-2, the range was narrower, with pH values from five to eight, mostly in the mobile region. Alkalinity is primarily a measure of carbonate concentration, one of the dominant uranium complexes. However, at high concentrations other species may contribute to alkalinity. Alkalinity was highly variable, with values from less than 1 milimole per liter (mmol/L) to 24 mmol/L. Only a few samples were above 10 mmol/L and most samples fell in the 2 to 6 mmol/L range. These concentrations are significant for complexing uranium and the higher concentrations would be very important in

remobilizing sorbed uranium. Some of the samples with the highest dissolved uranium also had high alkalinity; however, the uranium concentration is controlled both by source term availability and complexation, so not all samples with high alkalinity will have high uranium concentrations.

Table I. Summary of Geochemical Data by Site

	2000 Plant	2002 OU-1	2003 OU-2
pH	5.7 to 9.9	4.3 to 9.9	4.8 to 7.9
Alkalinity, mmol/L	0.1 to 23	0.04 to 24	1.8 to 8.8
Eh, mV	-160 to 206	-94 to 221	-54 to 434
DO, mg/L	0.2 to 11.3	Probe failure	0.4 to 7.3
Filtered U, pCi/L	0 to 39	0 to 906	0 to 7.4

Redox measurements are difficult to make, so data reliability is questionable. Field instruments have to be carefully calibrated, the water sample must be secluded from the atmosphere before measurement, and the measurement may not reflect an equilibrium value and could be unstable. For example, dissolved oxygen measurements and oxidation reduction potential measurements did not always follow the same trend. With these caveats, only a limited understanding of the redox potential of these waters can be deduced. In OU-1, the waters tended to have low redox potential or be reducing. In OU-2, where the shallow aquifer was sampled near the drainage ditch, the redox potential was more variable from oxidizing to reducing. There was an attempt to measure individual redox couples to better understand redox potentials, but again, the different couples did not follow the same trend so an equilibrium value could not be established. Thus, one of the most important measures of uranium mobility has significant constraints. However, direct measurement of the form of uranium in soil gives an indication of the redox control on mobility. This is discussed further below.

The samples were checked for ion dominance by calculating the percentage of the cations and anions with the highest concentrations (trace concentrations are by definition negligible). The ion dominance indicates geochemical processes controlling the water chemistry and can be used to group samples of similar origin. Most of the samples had Sodium (Na) as the dominant ion with some mixed Na-calcium (Ca). The location of the different water types showed that the shallow A wells are more likely to have Ca as the dominant cation and the B aquifer has Na as the dominant cation. A few samples had a mixture of HCO3 type water or a mixture of chloride (Cl) and HCO3, but Cl was more commonly the dominant anion. The Na-Cl type waters occurred throughout the site; the B Aquifer communicates with the Delaware River, which is brackish at Deepwater. An unusual Iron (Fe) and Na-sulfate(SO4) water occurs in some locations (e.g., the 3-SB-14 area in the B aquifer), which is indicative of some type of chemical processing. These data indicate that plumes moving through the site alter the "typical" groundwater chemistry and need to be considered as an important geochemical variable.

Unfiltered uranium concentrations were nearly always higher than filtered uranium concentrations. In the open bore-hole samples, the unfiltered uranium was often ten times greater, and sometimes one hundred times greater. Preliminary data from the developed piezometers installed in 2004 show a correlation coefficient of 0.995 between filtered and

unfiltered uranium, with unfiltered results being higher. However, the data from open boreholes are scattered, with no correlation between filtered and unfiltered (correlation coefficient is 0.01 when one outlier point is removed). These data show the importance of colloidal transport of uranium. The high (but noisy) filtered concentrations also reflect sampling from open boreholes where the sediment has been disturbed rather than cased boreholes that have been purged. The more consistent trend in the 2004 data points to the need for properly constructed piezometers to better understand the geochemical processes that are important in these soils.

Water chemistry data from samples with ion balances better than 10 percent were entered into the geochemical speciation program PHREEQC to check for mineral equilibria. When a mineral is saturated, it suggests that mineral might control the ion concentrations in solution. The WATEQF database was used because it contains uranium species and minerals. Carbonate minerals (calcite and dolomite) were sometimes supersaturated or close to saturation, suggesting the presence of carbonate cements in the sediments. The uranium mineral saturation was controlled by the measured redox potential value. Schoepite (uranium hydroxide) and rutherfordine (uranium carbonate) were undersaturated. Uraninite was occasionally supersaturated, but a more likely initial precipitate would be the amorphous form, $UO_2(a)$. Only three of the 60 analyses modeled were supersaturated with respect to amorphous uranium oxide.

The rest were undersaturated, suggesting that redox is not low enough to precipitate uranium in these samples. Because it is difficult to obtain reliable redox measurements, and there are no data to confirm the field values (e.g., independent measures of redox species), the validity of the uranium mineral equilibria calculations is uncertain. XRD data on mineralogy are discussed below. The modeling also showed that the dominant dissolved complexes in these solutions are $U(OH)_4$ or $U(CO3)_2^{-2}$.

Step III Results of Specialized Soil Analyses
Sorption was not modeled in the work discussed above, but could be added to the model if site-specific sorption characteristics become available. Some of the soil characteristics needed to model sorption are types of binding sites (to select appropriate equilibrium constants) and surface area. Binding sites can be Fe-hydroxides or organic matter. As such, the TOC/CEC of soil samples was measured in OU-1 and OU-2. Available TOC and CEC data suggest low to moderate sites available for sorption. CEC ranges from <5 meq/100 g to 33 meq/100 g. TOC ranged from 600 to 200,000 milligrams per kilogram (mg/kg), but most were less than 25,000 mg/kg. XRD of a limited number of samples was used to confirm uranium mineral assemblages. Two samples with high concentration of uranium in soil from OU-1 had uranium oxides (uraninite, pitchblende, and metastudite) plus a uranium silicate (uranophane). The six samples from OU-2 (Central Drainage Ditch, low uranium in soil) had no detectable uranium mineral phases. X-ray diffraction cannot detect sorbed phases.

As discussed in the methods section, the sequential extraction studies give an indication of the form of uranium in soil and how tightly it is bound to the soil matrix. Soluble and exchangeable uranium are weakly bound and likely to be mobilized by slightly aggressive waters. The carbonate phases are those that can be dissolved in acid solution and the iron and manganese phase are sorbed but could be released under reducing conditions (reductive dissolution of the

oxide phase). The sulfide and organic matter phase requires strong oxidizing conditions to release uranium, and the residual phase is unlikely to be mobilized.

Seven samples have been analyzed to date, and more analyses are planned. The samples come from both OU-1 and OU-2. Based on the operational geochemical definitions from sequential extraction, the four samples from the drainage ditch have less mobile phases of uranium and significant residual uranium. 3SB19 and 3SB10 also have phases that might be dissolved in acid water (carbonate phase). The samples from OU-1 (Figure 2) have more mobile phases of uranium, especially acid soluble (carbonate phase). The elevator shaft has significant potential to be a source of mobile uranium.

Leaching studies to estimate Kd have been conducted on site soils. However, these are not considered a reliable indicator of Kd because they are more aggressive than typical batch Kd experiments and do not account for site-specific groundwater chemistry. Work is underway to obtain site-specific Kd values from each aquifer and from sites with high uranium in soil. These analyses will account for site groundwater conditions, and will consider both sorption and desorption of uranium. Uranium can also sorb to colloids, but unlike soils, colloids will be mobile. This work will be repeated at the sites selected for Step III monitoring well sampling. The analysis is underway and will be reported in future work.

CONCLUSIONS

This study demonstrates the benefits of a stepped approach to investigating a FUSRAP site with uranium contamination. At this site, in addition to soil and building site contamination, there were concerns that uranium might be mobile in the groundwater. In the first step, gamma walkover surveys and soil sampling were conducted to help locate sampling sites for follow on work. Also early in the project, some focused geochemical sampling was conducted using existing wells on the 700-acre site. No large uranium plumes were found outside the contaminated area. The second step consisted of soil and water sampling in boreholes within AOCs. Both a regular grid and biased samples to better delineate contamination were collected in the AOCs. Although the water samples were from undeveloped boreholes open to multiple aquifers, the water quality data provided preliminary information on important geochemical parameters that was not available from previous sampling. The data showed that there was dissolved uranium at some locations and that factors that could mobilize uranium were present. The third step of the project was to use these data to select sites for monitoring wells that can provide better water chemistry data, contaminant information and head and permeability estimates to better determine flow paths. This step would not have been necessary if uranium mobility was not indicated from the previous stages of work.

One of the lessons learned from the stepped approach is that there are limitations to quality of data from open boreholes. For example, the high concentrations of uranium in unfiltered water indicated high turbidity in the borehole and the dissolved uranium concentration could not be associated with a specific contamination zone because mixed layers were sampled. The difficulty in obtaining reliable redox measurement in particular limited geochemical predictions of mobility. Thus, further data were needed from dedicated monitoring wells.

One of the more useful analyses for sorting out mobility questions was the sequential extraction of uranium-contaminated soil, which uses progressively more aggressive waters to dissolve uranium in a soil sample. Seven samples were analyzed by sequential extraction, and the samples vary across the AOCs. This demonstrates the heterogeneous nature of both the site soils and the contaminant form. The four samples from the drainage ditch have less mobile phases of uranium and significant residual uranium. The samples from OU-1 have more mobile phases of uranium, especially acid soluble (carbonate phase). Sequential extraction of uranium from soil near the elevator shaft had a large portion of water-soluble uranium. In contrast to K_d, which evaluates the *potential* of a soil to sorb uranium, the sequential extraction data directly evaluate the uranium that is already sorbed or in mineral form to see if it could be remobilized. Knowing whether the form of uranium in soil is mobile can help in planning future monitoring and remediation efforts.

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