Determination of Preliminary Remediation Goals at an Industrial FUSRAP Site - 9164

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ABSTRACT

This paper summarizes the methodologies used to develop site-specific preliminary remediation goals for radionuclides of potential concern (ROPCs) present at the DuPont Chambers Works FUSRAP Site in Deepwater, New Jersey. DuPont Chambers Works processed uranium oxides and uranium scrap to produce uranium tetrafluoride, uranium hexafluoride and a small quantity of uranium metal under contract with the Manhattan Engineer District and the Atomic Energy Commission from 1942 to 1947. These activities resulted in radiological contamination at the site. The residual contamination at the site is currently being addressed under the Formerly Utilized Sites Remedial Action Program managed by the Philadelphia District of the U.S. Army Corps of Engineers. Uranium-234 (U-234), uranium-235 (U-235), uranium-238 (U-238), radium-226 (Ra-226) and thorium-230 (Th-230) were identified as the ROPCs for the site.

INTRODUCTION

The United States Army Corps of Engineers (USACE) – Philadelphia District (CENAP) is currently addressing the cleanup of radiologically contaminated areas at three operable units (OUs) within DuPont Chambers Works facility (referred to as the "Site") under Formerly Utilized Sites Remedial Action Program (FUSRAP). To facilitate further investigations and develop cleanup alternatives, the USACE grouped six potentially impacted areas, referred to as areas of concern (AOCs) into the three OUs. OU 1 consists of Former Building 845 (AOC 1) and F Corral (AOC 2), OU 2 consists of Central Drainage Ditch (CDD) (AOC 3) and Building J-26 Area (AOC 5), and OU 3 consists of Historical Lagoon A (AOC 4) and East Area/East Burial Area (AOC 6).

A number of uranium refinement processes, performed at the Site under contract with the Manhattan Engineer District (MED) and the Atomic Energy Commission (AEC) resulted in radiological contamination at the Site. Both the U.S. Department of Energy (DOE) and the USACE conducted numerous sitewide remedial investigations to determine the nature and the extent of both radiological and chemical contamination present at the Site. The results of those investigations confirmed and identified the presence of radiological contamination at the site [1]. In addition, the USACE conducted a baseline risk assessment to evaluate potential risks to both potential human and ecological receptors present at the Site. The result of the assessments determined an unacceptable level of dose and risk to potential human receptors [2]. Therefore, potential cleanup actions will be considered in a Feasibility Study. As a part of this consideration, the USACE determined the preliminary remediation goal for radiological contaminants. The following sections of the paper summarize the processes for determining the preliminary remediation goals for the radiological contaminants present at the Site.

SITE DESCRIPTION AND HISTORY

DuPont Chambers Works Site is a 700-acre active chemical plant located in Salem County, Pennsville and Carneys Point Townships, on the southeastern shore of the Delaware River, north of the Interstate-295 Delaware Memorial Bridge. The plant is adjacent to the community of Deepwater, New Jersey. Figure 1 shows the location of Chambers Works within the floodplain of the Delaware River, between Helms Cove to the north and the Salem Canal to the south.

The Chambers Works Complex is located in a moderately populated area consisting of light to heavy industry, recreational areas, community service areas, and residential neighborhoods. Situated south of the Chambers Works Complex is the Atlantic Electric Power Plant. East of the Chambers Works Complex are light industrial, residential, and recreational areas. North of the complex are community service and residential areas of Carneys Point Township. Currently, the site is zoned as industrial. The land is assumed to be zoned as industrial for the future.

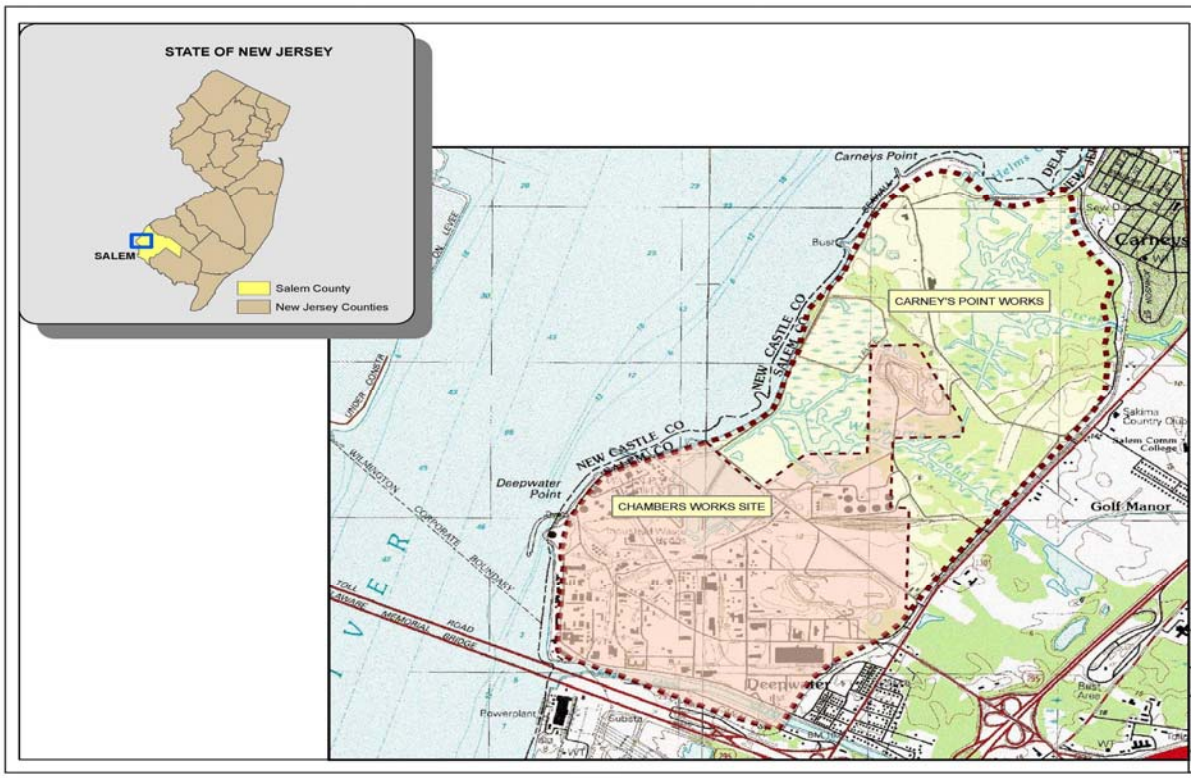

Figure 1: Location of DuPont Chambers Works FUSRAP Site

In 1942, MED contracted with DuPont to perform the following uranium refining processes - brown oxide process, recovery process, green salt process, and metal process. Those processes were performed in an area known as the "Blue Products Area" located in OU 1. In 1946, all MED activities were transferred to the AEC, and DuPont continued its research until late 1947. Chambers Works also converted quantities of green salt (uranium tetrafluoride) to uranium hexafluoride. This process, known as the hexafluoride process, was performed at the former Building J-16 (OU 2). Pilot-scale work on the brown oxide (uranium dioxide), green salt, and recovery processes also took place in the former Building J-16 (currently Building J-26 Area).

The ore concentrate refining process was not conducted at Chambers Works. DOE has estimated that more than half of the MED-related material produced at Chambers Works came from uranium peroxide which was obtained by processing uranium-bearing scrap [3]. Figure 2 is an aerial view of the Chambers Works FUSRAP Site outlining the OUs and the six corresponding AOCs.

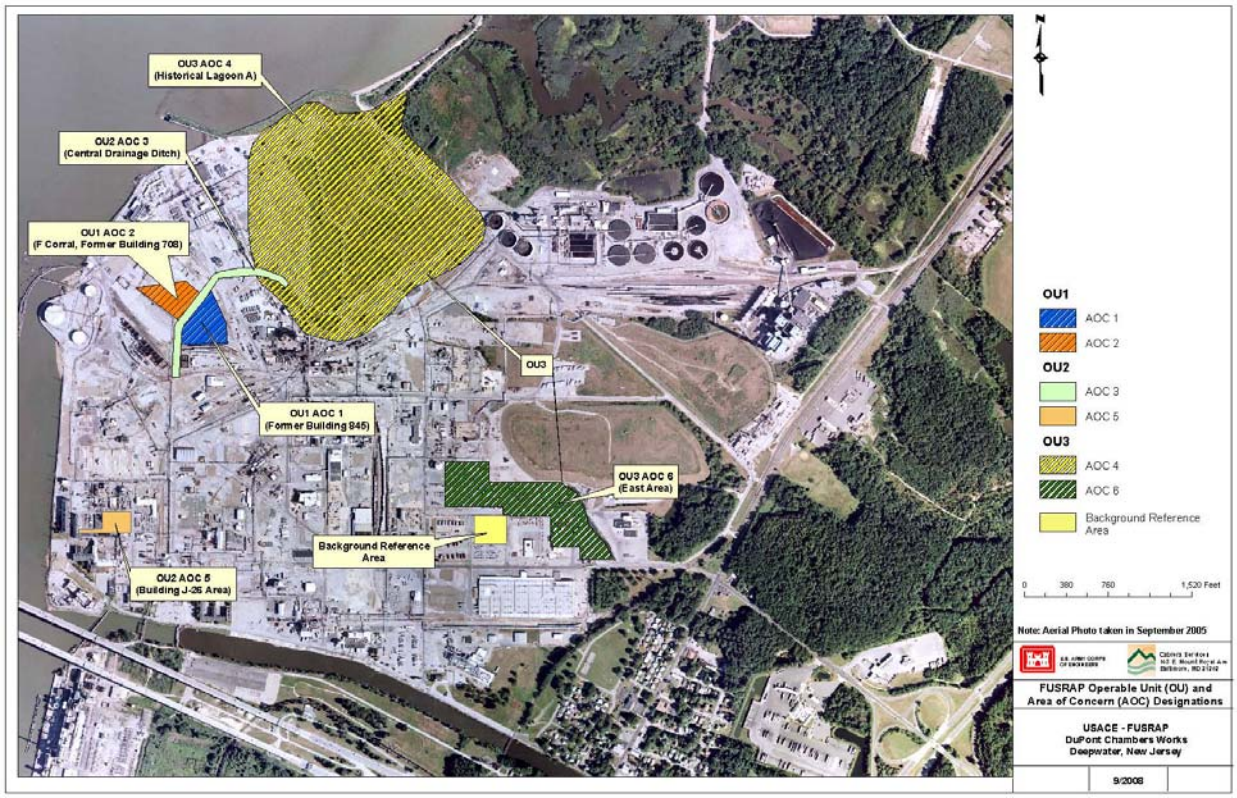

Figure 2: Designation of FUSRAP OUs AND AOCs

IDENTIFICATION OF RADIONUCLIDES OF POTENTIAL CONCERN (ROPC)

The USACE is mandated to investigate and cleanup certain eligible contaminants under FUSRAP. These eligible contaminants are defined as:

- Radioactive contamination resulting from activities performed for the MED or AEC;
- Other radioactive contamination or hazardous substances that are mixed or commingled with MED or early AEC radioactive contamination;
- At federally-owned FUSRAP sites, all radioactive contamination and hazardous substances are within the scope of the FUSRAP response action; and
- Other substances where specifically directed by Congress [4].

The USACE initiated an internal working group for the purpose of evaluating the MED processes used at Chambers Works Site in order to identify FUSRAP eligible contaminants. The group reviewed historical site records, specific compounds and feedstock materials used at Chambers Works, and general industry references describing similar processes at other facilities.

Previous historical investigations at the Site indicated that MED-related radiological contamination is limited to natural uranium (U_{nat}) isotopes (i.e., Uranium-234 (U-234), uranium-235 (U-235), and uranium-238 (U-238)) and their short-lived decay progeny. Refined natural uranium, the primary site contaminant, is in a state of secular equilibrium with its short-lived decay progeny, which consist of daughter radionuclides with half-lives short enough to allow them to decay at the same rate at which they are produced. Based on the assumption that the original uranium refinement processes were performed approximately 60 years ago, the following short-lived uranium decay progeny may be present:

- Short-lived decay progeny of U-238 expected to be present are Thorium-234 (Th-234) (24-day half-life), and Protactinium -234m (Pa-234m) (1.17-minute half-life).
- Short-lived decay progeny of U-235 expected to be present is Th-231 (25-hour half-life).
- U-234 has no short-lived decay progeny expected to be present.

Therefore, all three uranium isotopes were selected initially as the radionuclides of potential concern (ROPCs) for the site. However, long-lived thorium isotopes (specifically Th-230) are ROPC at other FUSRAP sites where uranium ore or where ore concentrates were used as feedstock. The black oxide (triuranium octaoxide) feedstock was used at the site; and therefore thorium-230 was identified as a possible contaminant in the feedstock and added to the ROPC list for the Site by the working group.

Radium-226 was also added as an ROPC as it is a daughter product in the decay chain of U-238 and is present in unrefined uranium ore. Ra-226 has been identified as a co-contaminant of uranium at other FUSRAP sites, and is also a potential contaminant in black oxide feedstock. Ra-226 appears to be a contaminant primarily where ore beneficiation has occurred (i.e., where ores or ore concentrates were initially processed) and may be present in MED wastes.

The working group performed an additional data evaluation by comparing maximum site sampling results of Ra-226 and Th-230 with respect to the potential in-growth concentration of those radionuclides from their parent products, U-234 and U-238. The data evaluation discovered that the relative concentrations of Ra-226 and Th-230 found in AOC 2 samples exceeded what would be expected from uranium-series progeny decay alone. For example, if the uranium feedstock (in the form of sodium uranate) received at the Site was ‘pure’ refined uranium, it would be expected that all nonuranium progeny would have been stripped away, leaving only the U-238 (~99.3 % abundance) and U-235 (~0.7% abundance).

Table I shows the results of theoretical in-growth for ‘pure’ refined uranium after a 65-year decay period [5]. This example mimics what would be expected in Site samples collected during the RI if theoretical in-growth was the only source of Th-230 and Ra-226.

Table I. Decay Series Activities and In-growth of Pure Refined Uranium (U-234 and U-238)[a] after 65 years

Nuclide	Half-Life	Activity (Bq)	Activity (µCi)	In-growth (%)
U-238	4.50E+09 yr	1.24E+04	3.34E-01	---
Th-234	24 d	1.24E+04	3.34E-01	100%
Pa-234m	1.2 min	1.24E+04	3.34E-01	100%
U-234	2.40E+05 yr	1.24E+04	3.34E-01	100%
Th-230	**7.70E+04 yr**	**7.23E+00**	**1.95E-04**	**0.0585%**
Ra-226	**1.60E+03 yr**	**1.01E-01**	**2.72E-06**	**0.0008%**
Rn-222	3.80E+00 d	1.01E-01	2.72E-06	0.0008%
Po-218	3.10E+00 min	1.01E-01	2.72E-06	0.0008%
Pb-214	2.70E+01 min	1.01E-01	2.72E-06	0.0008%
Bi-214	2.00E+01 min	1.01E-01	2.72E-06	0.0008%
Po-214	1.60E-04 sec	1.01E-01	2.72E-06	0.0008%
Pb-210	2.20E+01 yr	4.40E-02	1.19E-06	0.0004%
Bi-210	5.00E+00 d	4.39E-02	1.19E-06	0.0004%
Po-210	1.40E+02 d	4.30E-02	1.16E-06	0.0003%

[a] Initial Activity (t=0) for U-234 and U-238 = 1.24E+04 Bq = 3.34E-01 µCi

Table I shows that the in-growth of the decay series progeny below U-234 is quite marginal given only 65 years (relative to the 4.4 billion year half-life of series parent U-238). The theoretical abundance of Th-230 in the decay chain would be 0.0585% while the abundance of Ra-226 only reaches 0.0008%. This is due to the relationship of the half-lives of the intermediate daughter U-234 (2.4E+05 yrs) versus the next daughter in the series Th-230 (7.7E+04 yrs). The relatively small difference in their half-lives stunts the in-growth of the remainder of the series over the short time period being investigated (65 yrs).

In the center of the AOC 2 source zone, the maximum concentration of U-238 is 15,000 pCi/g. Therefore, if it is assumed that the presence of Th-230 and Ra-226 were from in-growth alone, the derived concentrations (using the calculated fractions in Table I) would approach 9 pCi/g and 0.12 pCi/g, respectively. However, measured concentrations of Th-230 within AOC 2 range up to 32 pCi/g while Ra-226 concentrations have been found to be present up to approximately 3 pCi/g. Since the actual progeny activities are greater than the calculated values from daughter-in-growth alone, it is assumed that the excess concentrations of Th-230 and Ra-226 are due to the presence of impurities within the sodium uranate feedstock. Therefore, five ROPCs have been identified as eligible contaminants for FUSRAP investigation and cleanup at the DuPont Chambers Works FUSRAP Site: U-234, U-235, U-238, Th-230, and Ra-226.

DEVELOPMENT OF PRELIMINARY REMEDIATION GOALS FOR ROPCs

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the selection of a cleanup action that is protective of human health and the environment and complies with "applicable or relevant and appropriate requirements (ARARs)." The requirements for cleanup actions are provided in 40 Code of Federal Registrar (CFR) 300.430. According to those requirements, the Environmental Protection Agency (EPA) defines the CERCLA acceptable target risk range as 10^{-6} to 10^{-4} for carcinogenic chemicals. However, a potential ARAR was identified which could guide the cleanup for the Site. Based on *Soil Remediation Standards for Radioactive Materials* (N.J.A.C 7:28-12), a dose limit criterion of 15 millirem per year (mrem/yr) was identified as a potential ARAR for the Site [6]. Therefore, this 15 mrem/yr dose criterion was used to derive site-specific preliminary remediation goals for ROPCs present at the Site.

Due to the absence of Ra-226 and Th-230 sampling results for samples analyzed during initial site investigations, USACE performed a surrogate evaluation to develop a preliminary remediation goal for a surrogate ROPC. Under surrogate evaluation, it is possible to measure just one of the contaminants instead of all while demonstrating overall compliance for all other ROPCs present at the Site. The surrogate evaluations were performed in four steps.

- Identification of the surrogate ROPC;
- Establishment of relationships between the surrogate ROPC with respect to the other ROPCs;
- Determination of derived concentration guideline level (DCGL) for all ROPCs; and
- Calculation of an effective site-specific preliminary remediation goal for the surrogate ROPC that accounts for all ROPCs at the Site.

Each step is summarized in the following subsections.

Step 1: Identification of Surrogate ROPC

Uranium-238 has already been used as a surrogate for total uranium at the Site. As Ra-226 and Th-230 are daughter products of U-238, U-238 was once again chosen as the surrogate ROPC for the Site. Continuation of its use is supported by the following:

- It has a higher relative abundance with respect to other isotopes;
- It is the easiest ROPC to detect at the site through both alpha and gamma spectrometry analysis.

Step 2: Establishment of Relationship of Surrogate ROPC with Respect to Other ROPCs

During this step, the relationships between the surrogate ROPC (U-238) and the other four ROPCs were determined. The relationships were summarized in the following.

Relationship among Uranium Isotopes

The relationships between three uranium isotopes were determined by utilizing their radioactive isotopic activity ratios for natural uranium (approximately 2.2 % comes from uranium-235, 48.6 % uranium-238, and 49.2 % uranium-234).

Relationship among Ra-226, Th-230 and U-238

The radiological data collected at the Site were evaluated to determine the relationship between measured concentrations of U-238, Ra-226, and Th-230. At first, detected sampling results were used to calculate the ratios of Ra-226/U-238 and Th-230/U-238. The calculated ratios were then fitted against standard normal and standard log-normal distributions to evaluate which distribution would be the best input assumption in the statistical analysis using the Pro-UCL software (version 4.0) [7]. It was determined that the data were best represented by a log-normal distribution. Therefore, lognormal ratios of Ra-226/U-238 and Th-230/U-238 were utilized to establish the relationship between Ra-226 and Th-230 with respect to U-238.

Prior to establishing relationship, Rosner outlier test, available in ProUCL 4.0 was utilized to identify any potential outlier that may be present in the lognormal datasets for both ratios. The results of the Pro-UCL analysis on both ratio distributions determined that no outliers were present, meaning that all calculated ratio values appear to be part of the same log-normal distribution. By comparison, the results of the Rosner test on the individual nuclide distributions (also assumed log-normal) resulted in nine assumed outliers for U-238, 40 for Ra-226 and 21 for Th-230. Thus, the behavior of the ratios allowed all values, without exclusion, to be used in the surrogate calculations.

The mean values of 0.11 and 0.16 for Ra-226/U-238 and Th-230/U-238 ratio distributions, respectively, were chosen for predicting both Ra-226 and Th-230 from measured U-238 values. The mean value was chosen instead of a UCL-95 or other qualified statistical level in order to avoid potential biasing of the derived Ra-226, and Th-230 values. These values, along with the abundance values of uranium isotopes in natural uranium (0.486 U-238, 0.022 U-235, and 0.492 U-234), were used to calculate the relationship, or the activity fraction of each ROPC with respect to U-238.

Step 3: Determination of DCGL for Individual ROPC

Residual Radioactivity (RESRAD) dose modeling code (version 6.3) was utilized for determining site-specific DCGLs for the ROPCs, including refined natural uranium, Ra-226, and Th-230 based on a dose limit criterion of 15 mrem/yr [8]. Since the site is zoned as industrial, an industrial worker scenario, excluding active groundwater usage, was considered the most appropriate dose model for inclusion within the site conceptual model. Site specific characteristics that also support this decision include:

- Current groundwater conditions preclude its active use. The two uppermost aquifers beneath the Site exhibit high dissolved solids as well as high organic and metal contamination due to DuPont operations;
- DuPont and the State of New Jersey designated the aquifers beneath the Site as a Classification Exception Area (CEA) as part of DuPont's groundwater remediation plan (CEA list of DuPont contaminants does not include radionuclides);
- The Site is not within the capture zone of current municipal drinking water well systems; and
- Dissolved MED uranium in Site aquifers has been shown to be immobile, both vertically and horizontally, due to the reactive nature of uranium peroxide, but also due to the reducing conditions encountered in both aquifers. This fact has been clearly established by extensive groundwater sampling in the A and B aquifers.

Under the industrial worker scenario, the worker is modeled as a typical site worker who spends most of the time indoors. The worker may be exposed to the residual radioactive contamination that may be present in surface soil but is not expected to have regular contact with subsurface soil. The industrial worker is at the site for 250 days per year for 25 years [9]. During a typical working day, the worker is assumed to spend 7 hours indoors and 1 hour outdoors and will ingest 50 milligram (mg) of soil [10]. The inhalation rate for the receptor is 20 cubic meter (m^3) per day [9]. Exposure pathways evaluated for the industrial worker scenario include:

- External gamma radiation from radionuclides in the surface soil;
- Incidental ingestion of surface soil; and
- Inhalation of airborne contaminated dust or emissions from surface soil.

Table II presents the results of site-specific individual ROPC DCGL for an industrial worker without groundwater usage.

Table II. DCGLs for Individual ROPC for Industrial Worker Scenario

Radionuclides	Dose per unit concentration		DCGL (Based on 15 mrem/yr)		Site-Specific DCGL (pCi/g)
	T=0 Years	T=1000 Years	T=0 Years	T=1000 Years	
	(mrem/yr)/(pCi/g)		pCi/g		
Ra-226+C[a]	1.15E+00	2.61E-01	1.28E+01	5.75E+01	12.8
Th-230	3.19E-03	2.64E-01	4.70E+03	5.68E+01	56.8

U-234	1.23E-03	9.04E-04	1.22E+04	1.66E+04	12175.3
U-235	7.91E-02	1.01E-02	1.90E+02	1.49E+03	189.5
U-238	1.66E-02	1.95E-03	9.04E+02	7.68E+03	903.6

[a] '+C' means including decay progeny. Ra-226 assumed to be in equilibrium with Pb-210 +C.

Step 4: Calculation of Effective Site-specific Preliminary Remediation Goal

The effective DCGL for the surrogate ROPC was established as site-specific preliminary remediation goals for use as a part of site cleanup process. The effective DCGL for U-238 was calculated by using the following equation [11]:

$$DCGL\,(U-238) = \frac{1}{\left(\frac{f_{Ra-226/U-238}}{DCGL_{Ra-226}} + \frac{f_{Th-230/U-238}}{DCGL_{Th-230}} + \frac{f_{U-234/U-238}}{DCGL_{U-234}} + \frac{f_{U-235/U-238}}{DCGL_{U-235}} + \frac{1}{DCGL_{U-238}} \right)} \qquad \text{(Eq. 1)}$$

where

f = activity fraction of ROPC with respect to U-238

By utilizing the relationship determined in Step 2 and the individual DCGL for each ROPC calculated during Step 3, the effective DCGL for U-238 was determined to be 77 pCi/g. The effective DCGL for U-238 was selected as the site-specific preliminary remediation goal for the Site. Therefore, the site sampling results for U-238 will be compared against the site-specific preliminary remediation goal to demonstrate overall compliance for all ROPCs present at the Site.

CONCLUSION

The USACE is conducting response actions to identify and cleanup or otherwise control residual radioactive material present at the DuPont Chambers Works FUSRAP Site. The site is contaminated with residual radioactivity due to work performed for the MED/AEC. The initial site investigations were primarily focused on refined natural uranium isotopes and their short-lived decay progenies. However, reviews of historical documents and existing documents from similar FUSRAP sites identified Ra-226 and Th-230 as potential contaminants in the black oxide feedstock. USACE working group then performed an additional evaluation by comparing site sampling results with theoretical in-growth concentration of Ra-226 and Th-230 from their parent radionuclide, U-238. The results of the evaluation showed that the relative concentration of Ra-226 and Th-230 at the site exceeded what would be expected only from uranium-progeny decay. As a result, two additional radionuclides (Ra-226 and Th-230) were added as separate ROPCs for the Site. Therefore, the USACE identified five radionuclides - U-234, U-235, U-238, Th-230, and Ra-226 as the ROPCs for the Site.

Due to limited Ra-226 and Th-230 analytical results from initial site investigations, the USACE performed a surrogate evaluation in order to develop an effective site-specific DCGL for all Site ROPCs. As a part of the surrogate evaluation, U-238 was first selected as the surrogate for the other four ROPCs present at the Site. Secondly, relationships were established for the other ROPCs with respect to U-238. During the third step, a RESRAD model was used to derive site-specific DCGLs for the individual ROPCs under an industrial worker scenario. Finally, the relationships for each ROPC with respect to U-238 and individual ROPC DCGL were then utilized to derive an effective DCGL for U-238. The effective DCGL for U-238 will be used as the preliminary remediation goal for the Site during the Feasibility Study evaluations, however, it may be refined if additional data is gathered during remedial

design or other phases of the project. During site cleanup actions the sampling results of U-238 for all soil samples will be compared against the preliminary remediation goal. If the sampling result of U-238 for any sample exceeds the preliminary remediation goal, further cleanup may be appropriate for the Site.

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