MANAGEMENT OF POTENTIALLY CONTAMINATED WASTEWATER AND IMPLEMENTATION OF AN ALTERNATIVE COMPLIANCE METHODOLOGY FOR GROSS ALPHA AND GROSS BETA AT THE FUSRAP MAYWOOD SUPERFUND SITE

M. S. Winters FUSRAP Maywood Team - Shaw Environmental, Inc. 100 West Hunter Avenue, Maywood, NJ, 07607

D. C. Hays Jr. FUSRAP Maywood Team - United States Army Corp of Engineers 700 Federal Building, 12th St., Kansas City, MO 64106

Dr. B. J. Tucker FUSRAP Maywood Team - Shaw Environmental, Inc. 3 Riverside Drive Andover, MA 0181

ABSTRACT

The management of wastewater that accumulates in radiologically contaminated excavations can be a difficult challenge for teams involved in environmental cleanups. Organizations performing environmental cleanups must consider how best to manage and dispose of potentially contaminated excavation water.

This paper initially identifies the primary sources of potentially contaminated wastewater generated at the FUSRAP Maywood Superfund Site (FMSS) and summarizes the current methods, by which the Maywood Team manages wastewater removal, transport, treatment, and discharge to the local publicly-owned treatment works (POTW), under stringent radionuclide compliance parameters. The focus will then shift to a discussion of the challenges facing the Maywood Team when analyzing treated wastewater for radionuclide parameters. The presentation closes with a specific discussion of the "Alternative Compliance Methodology" established by the Maywood Team, and applied under certain conditions, to overcome adverse radiochemical analysis conditions.

INTRODUCTION

Shaw Environmental and the United States Army Corps of Engineers (USACE) have teamed together to safely and effectively remediate the FMSS. The FMSS waste stream consists primarily of soils contaminated with Thorium-232 and associated daughter progeny. In addition to Thorium-232 (Th-232), lesser concentrations of other naturally occurring radionuclides (i.e., Radium-226 [Ra-226], Uranium-238 [U-238], and their associated daughter progeny) are present in the waste stream. The current effort includes the remediation of the FMSS, which includes the

4.7 hectare Maywood Interim Storage Site (MISS) and 26 vicinity properties located in a densely populated and commercially active area of Bergen County, New Jersey.

Projects involved in outdoor remediation usually must give consideration to the potential for accumulation of potentially contaminated wastewater in excavations and the manner by which it is eventually discharged from site. Typically, the sources of potentially contaminated wastewater, encountered in remedial excavations, are groundwater permeation and/or weather related precipitation. Prior to discharge from the FMSS, potentially contaminated wastewater is routed through a pretreatment process and/or tested for compliance with established release limits.

WASTEWATER MANAGEMENT

Removal

Wastewater management [1] covers impacted water collected during construction activities, generated onsite from decontamination procedures, generated from storm water events, and generated from operation and maintenance of the pretreatment system. Impacted water is classified as any water (i.e., precipitation, groundwater, or decontamination wash water) that contacts contaminated soil or contaminated equipment at the FMSS and is presumed contaminated.

The volume of impacted water to be managed depends on a combination of factors:

- Depth of excavation relevant to groundwater;
- Sequencing of excavation and restoration schedules;
- Weather conditions;
- Decontamination activities; and
- Control of surface water run-off

Transport

Wastewater is typically pumped from remedial excavations directly into fractionation storage tanks (or "frac tanks") located nearby where preliminary settling of solids occurs. Wastewater is then pumped directly into vacuum tanker trucks for transport back to the MISS. The water is placed in frac tanks at the MISS, which not only store the water, but allow for additional settling of solids. Current influent storage capacity on the MISS is approximately 560 cubic meters.

Pretreatment

Potentially contaminated wastewater is pumped from frac tanks to a multi-staged treatment system. Process water passes through several treatment steps, including primary settling, coagulation and clarification, filtration (Stage I), ion exchange (Stage II), and if necessary, purification (Stage III) using granular activated carbon (GAC). To date, the Stage III pretreatment has not been required for FMSS wastewaters.

Discharge

Treated wastewater is transferred directly from the treatment process train to staging frac tanks. Each filled staging tank constitutes a "batch" and is sampled for compliance with POTW discharge permit parameters. Samples are typically collected from treated batches after Stage II to determine if further pretreatment is required. Turn-around of sample results is typically five to seven days.

The POTW discharge permit limitations for radionuclide parameters [2] are established in coordination with the New Jersey Department of Environmental Protection and are similar to the stringent "National Primary Drinking Water Regulations" [3] established for community water systems. The POTW radionuclide discharge criteria for the FMSS are presented in Table I:

 Table I. POTW Radionuclide Discharge Parameters for the FMSS [2, 3]

Radionuclide Parameter	Maximum Contaminant	Method Detection
	Level (MCL)	Level (MDL)
Gross Alpha	15 pCi/l	3 pCi/l
(excluding uranium & radon)		
Gross Beta	50 pCi/l	4 pCi/l
(excluding natural potassium-40)		
Combined Ra-226 + Ra-228	5 pCi/l	1 pCi/l each
Uranium	30 µg/l	$1 \ \mu g/l^a$ or 0.5 pCi/l ^b

^a mass analysis

^b alpha spectrometry

If the concentrations/activities and the analysis MDLs are <u>within</u> the not-to-exceed permit values, the "batch" may be discharged to the POTW via the sanitary sewer system.

COMPLIANCE CHALLENGES

Impact of Increased Solids Content to Analysis Data Quality

Obtaining radioanalytical sample results, within the required analysis MDLs for gross alpha (GA) and gross beta (GB), can be highly challenging when dissolved and suspended solids are present in treated wastewater. Solids in wastewater interfere with GA and GB detection due to the absorption of radioactive particle emissions. By nature of the seasonal manifestation of increased solids content, it is postulated that the primary source of the solids build-up in FMSS wastewater is the use of de-icing "salts" on road surfaces around the site and surrounding community. Wastewater samples to be analyzed for GA and GB are evaporated, leaving a solid residue that is deposited on a planchet. As the mass of the evaporated sample increases, the associated radioactive particle absorption increases, resulting in reduced instrument sensitivity. This reduction in sensitivity results in an increase in the instrument Minimum Detectable Activity (MDA), synonymous for this discussion with the term "MDL". Radioanalytical labs typically develop absorption curves, based on a range of evaporated sample masses, to correct

for solids interference. Unfortunately, there is an upper limit to the evaporated mass allowed on a sample planchet. A mass limit of five milligrams per square centimeter is established for GA/GB analysis. Limiting the amount of solids from sample evaporation reduces the overall volume of water that may be evaporated for sample analysis. Since sample volume is inversely proportional to MDA, reducing the sample volume increases the MDA. To some degree, smaller sample volumes can be partially offset by increased instrument counting periods. However, there is a point of diminishing returns and a practical limit to how long a single sample can be counted in a production laboratory.

Proposed Solution

As discussed previously, the presence of <u>non</u>-radioactive solids in processed wastewater has resulted in problems with meeting required detection limits established in the POTW discharge permit. Considering the turn-around time for repeat sampling evolutions, the potential need to retreat a processed batch purely to resolve a data quality issue, and the costs to the Project associated with delaying batch discharge, the need to consider compliance alternatives was identified. To that end, the following permit compliance process modification was developed by the Maywood Team and subsequently proposed to, and accepted by, the NJDEP and the POTW Authority:

- If the GA or GB analysis result is <u>less than or equal to</u> the permit discharge limit, and the analysis MDA <u>does not exceed</u> the permit MDL, the batch would be released. This constitutes the standard compliance methodology.
- If the GA or GB analysis result is <u>less than or equal to</u> the permit discharge limit, <u>but</u> the analysis MDA <u>exceeds</u> the permit MDL, the Project would utilize the "Alternative Compliance Methodology (ACM)" described in the next section.
- If either of the GA or GB analysis results are <u>greater</u> than the permit discharge limit, the batch will <u>not</u> be released without additional treatment and/or sampling.

It is important to note that compliance with the other radionuclide and chemistry parameters specified in the POTW discharge permit, remains a consistent requirement, regardless of the manner by which GA and GB data is evaluated.

ALTERNATIVE COMPLIANCE METHODOLY (ACM)

In the case of the second bullet presented in the "Proposed Solution" above, the Project proposed to derive GA/GB concentrations, when necessary, from elemental and/or isotopic analysis of naturally occurring radioactive materials known to be present, either in Maywood wastes, or in the natural environment.

Depending on the derived value needed (i.e., GA or GB), the following analyses are required to implement the ACM:

- Isotopic thorium by separation chemistry and alpha spectrometry (Th-232, Th-230, and Th-228);
- Ra-226 by separation chemistry and gross alpha counting (i.e., total alpha-emitting radium) or by alpha spectrometry (Ra-226 only);

- U-238 by separation chemistry and alpha spectrometry or, by kinetic phosphorescence analysis (KPA), an elemental uranium measuring technique requiring additional calculation to quantify the U-238 concentration.
- Ra-228 via radium separation chemistry and gross beta counting

The following assumptions/conditions apply to the ACM:

- As a conservative measure, equilibrium conditions are assumed to exist, in the Thorium and Uranium Decay Series, between measured parent and associated daughter progeny. For example, bismuth-212 (Bi-212) is assumed to be in equilibrium with the measured parent nuclide Th-228.
- Daughter progeny of the Actinide Decay Series (U-235) are disregarded due to their very limited contribution to the overall GA/GB under natural uranium conditions.
- Due to their limited abundances (i.e., branching ratios less than five percent) [4], astatine-218 (At-218), thallium-206 (Tl-206), Tl-210, and the isomeric transitional phase of Protactinium-234 (Pa-234 IT) are excluded from this evaluation.
- The alpha emission from Pb-210 is excluded from the evaluation due to an alpha decay rate of approximately 0.000002 percent [4].
- Consistent with BCUA Permit criteria and the National Primary Drinking Water Regulations, GA concentrations exclude alpha emissions from the decay of any isotope of uranium or radon.
- It is acknowledged that there is a documented non-equilibrium condition between U-238 and U-234 in groundwater. However, considering the minimal impact of variability in this application, the concentration U-234 and U-238 may be assumed to be equivalent. Therefore, as accepted by the POTW and NJDEP, the specific activity of U-238 is 0.3365 pCi/µg of elemental uranium.
- Treated wastewater contains only those radionuclides present in the natural environment and Maywood waste stream (i.e., thorium and uranium decay series isotopes).
- All analyses are performed in a NJDEP approved radiochemistry laboratory using industry recognized methods.

From the analytical methods and assumptions noted previously, the ACM can be implemented to establish derived values for the following parameters:

- GA Concentration
- GA MDA
- GB Concentration
- GB MDA

Determination of the ACM-GA Concentration and MDA

Table II presents the relevant alpha emitting isotopes, of the uranium and thorium decay series, that provide the basis for calculating the ACM-GA concentration and associated MDA:

Table II. Gross Alpha by Isotopic Reference

Alpha	Lab Reported Analyte for Equilibrium	Effective Alpha Decay Rate
Emitter	Assumption	(%) [4]
Th-232	Th-232	100
Th-228	Th-228	100
Ra-224	Th-228	100
Po-216	Th-228	100
Bi-212	Th-228	35
Po-212	Th-228	65
Th-230	Th-230	100
Ra-226	Ra-226	100
Po-218	Ra-226	100
Po-214	Ra-226	100
Po-210	Ra-226	100

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Considering Table II above and the assumptions made in previous sections, Equation 1 presents the method for calculating the ACM-GA concentration:

ACM-GA Concentration =
$$A_{Th-232} + (4*A_{Th-228}) + A_{Th-230} + (4*A_{Ra-226})$$
 (Eq. 1)

Equation Notes:

- "A" represents the measured activity of the specified isotope.
- Th-228 activity is multiplied by four, instead of five, because Bi-212 decays by alpha emission approximately 35 percent of the time and beta decays 65% of the time. Bi-212 decays to the alpha emitter Po-212 approximately 65 percent of the time, and to the beta emitter, Tl-208, 35 percent of the time. Combined, Bi-212 and Po-212 effectively yields one total alpha particle emission, for each decay of Th-228.

The ACM-GA MDA value is calculated as an analyte data quality verification step and is derived from the sum of the reported MDA values for each analyte used to determine the ACM-GA concentration (i.e., Th-232, Th-230, Th-228, and Ra-226).

If the calculated ACM-GA concentration and MDA values are <u>within</u> required limits, 15 pCi/l and 3 pCi/l respectively, the batch is considered to be in compliance with the GA discharge parameters. **If** either of the specified limits is <u>exceeded</u>, the batch must be retreated and/or resampled prior to additional discharge evaluation.

Determination of the ACM-GB Concentration and MDA

Table III presents the relevant beta emitting isotopes of the uranium and thorium decay series that provide the basis for calculating the ACM-GB concentration and associated MDA:

Beta	Lab Reported Analyte for Equilibrium	Effective Beta Decay Rate (%)
Emitter	Assumption	[4]
Ra-228	Ra-228	100
Ac-228	Ra-228	100
Pb-212	Th-228	100
Bi-212	Th-228	65
T1-208	Th-228	35
Th-234	U-238	100
Pa-234	U-238	100
Pb-214	Ra-226	100
Bi-214	Ra-226	100
Pb-210	Ra-226	100
Bi-210	Ra-226	100

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The ACM-GB concentration and MDA values are calculated in a reasonably similar manner to the GA methods discussed previously. Considering Table III above and the assumptions made in previous sections, Equation 2 presents the method for calculating the ACM-GB concentration:

ACM-GB Concentration = $(2*A_{Ra-228}) + (2*A_{Th-228}) + (2*A_{U-238}) + (4*A_{Ra-226})$ (Eq. 2)

Equation Notes:

- "A" represents the measured activity of the specified isotope.
- Th-228 activity is multiplied by two, instead of three, because Bi-212 decays by beta emission approximately 65 percent of the time and alpha decays 35 percent of the time. Bi-212 decays to the alpha emitter Po-212 approximately 65 percent of the time, and to the beta emitter, Tl-208, 35 percent of the time. Combined, Bi-212 and Tl-208 effectively yields one total beta particle emission, for each decay of Th-228.
- Within the ACM, there are two accepted methods for quantifying the U-238 concentration. The first method is isotopic analysis which directly measures the concentration of U-238 via alpha spectrometry. The second method, KPA, measures total elemental uranium (U-Mass). If a value for U-Mass by KPA is provided in units of µg/l, multiply the reported value by the specific activity of U-238, 0.3365 pCi/µg, to calculate the U-238 activity in units of pCi/l.

The ACM-GB MDA value is calculated as an analyte data quality verification step and is derived from the sum of the reported MDA values for each analyte used to determine the ACM-GB concentration (i.e., Ra-228, Th-228, U-238 or U-Mass, and Ra-226).

If the calculated ACM-GB concentration and MDA values are <u>within</u> required limits, 50 pCi/l and 4 pCi/l respectively, the batch is considered to be in compliance with the GB discharge parameters.

If either of the specified limits is <u>exceeded</u>, the batch must be retreated and/or re-sampled prior to additional discharge evaluation.

CONCLUSION

The management of potentially contaminated wastewater can be challenging for teams performing outdoor environmental remediation. USACE and Shaw Environmental have established a positive working relationship with regulatory stakeholders and the local discharge authority where all can feel confident that Maywood wastewater is managed in a manner that is protective of the environment and community treatment systems without undue burden to the Project. Institution of an "Alternative Compliance Methodology" to overcome radioanalytical method interferences, maintain operational productivity, and meet compliance limits is an example of this positive working relationship in action. Other projects may benefit from taking a similar approach to compliance testing, in direct coordination with oversight authorities, should similar problems arise.

REFERENCES

- [1] Stone & Webster, Water Management Plan, prepared for the U.S. Army Corps of Engineers, November, 2001.
- [2] Bergen County Utilities Authority Treated Groundwater Discharge Permit for the FUSRAP Maywood Superfund Site; revised by letter dated 11/5/04.
- [3] National Archives and Records Administration, Code of Federal Regulations, Title 40, Protection of the Environment, Part 141, National Primary Drinking Water Regulations, Section 141.26, Monitoring frequency and compliance requirements for radionuclides in community water systems, and Section 141.66, Maximum contaminant levels for radionuclides, July 1, 2004.
- [4] B. SHLEIEN, L.A. SLABACK, B.K. BIRKY, "Handbook of Health Physics and Radiological Health," ISBN 0-683-18334-6, published by Williams & Wilkins (1998).