PORTLAND HARBOR RI/FS

# ROUND 3A
# UPSTREAM & DOWNSTREAM SEDIMENT DATA REPORT
# ADDENDUM 1: RADIOISOTOPE CORES

## APPENDIX A
## DATA VALIDATION REPORT

DRAFT

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Table A-1. $^{7}$Be Samples Qualified for Holding Time Exceedances

# LIST OF ACRONYMS

| | |
|---|---|
| $^{7}$Be | beryllium-7 |
| $^{137}$Cs | cesium-137 |
| dpm | disintegrations per minute |
| EDD | electronic data deliverable |
| EPA | U.S. Environmental Protection Agency |
| keV | kiloelectronvolts |
| LWG | Lower Willamette Group |
| MARLAP | Multi-Agency Radiological Laboratory Analytical Protocols |
| NRC | U.S. Nuclear Regulatory Commission |
| $^{210}$Pb | lead-210 |
| $^{209}$Po | polonium-209 |
| QA | quality assurance |
| QC | quality control |
| QAPP | quality assurance project plan |
| $^{226}$Ra | radium-226 |
| RI/FS | remedial investigation and feasibility study |
| RPD | relative percent difference |
| SRM | standard reference material |
| TAMU-G | Texas A&M University, Galveston |

# 1.0 DATA EVALUATION PROCESS

The radioisotope data were validated in accordance with guidance specified by the United States Nuclear Regulatory Commission's (NRC's) Regulatory Guide 4.15 – Quality Assurance for Radiological Monitoring Programs (NRC 2006), by the Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP; EPA et al. 2004), and by the U.S. Environmental Protection Agency's (EPA's) *Guidance on Environmental Data Verification and Validation* (EPA 2002). Results for quality control (QC) samples were evaluated against applicable control limits in general accordance with the EPA data validation guidelines and the QC requirements included in the referenced methods.

All electronic data deliverable files (EDD) were verified by comparing all of the field sample results and QC sample results to the hardcopy data package. One-hundred percent of the data received a full (Level IV) validation, which included evaluation of:

- Sample chain-of-custody
- Analytical holding times
- Instrument performance
- Blank contamination
- Precision (replicate analyses)
- Accuracy (compound recovery)
- Detection limits
- Package completeness.

The following laboratory deliverables were reviewed during the full data validation:

- The case narrative discussing analytical problems (if any) and procedures
- Chain-of-custody documentation and laboratory sample receipt logs
- Instrument standard reference material results for beryllium-7 ($^{7}$Be), radium-226 ($^{226}$Ra), and cesium-137 ($^{137}$Cs) analyses, and internal standard results for $^{210}$Pb analysis
- Instrument background and blank results
- Results for laboratory replicates
- Radioisotope results for the sediment samples
- Verification of intermediate transcriptions and reported concentrations for the field and QC samples

- Review of instrument data to verify radioisotope results.

# 2.0 DATA QUALITY EVALUATION

A total of 111 samples (35 samples from core RC01, 38 samples from core RC02, and 38 samples from core RC483) were analyzed for $^{7}$Be, $^{226}$Ra, $^{137}$Cs, and $^{210}$Pb radioisotope analyses at Texas A&M University at Galveston's (TAMU-G) Laboratory for Oceanographic and Environmental Research. These samples were collected as part of the Portland Harbor remedial investigation/feasibility study (RI/FS) Round 3A upstream and downstream sediment investigation for the Lower Willamette Group (LWG).

## 2.1 CHAIN-OF-CUSTODY AND SAMPLE HOLDING TIMES

Chain-of-custody was maintained for all samples analyzed. The methods for analysis do not contain guidance on sample holding times for radioisotope analyses due to the relatively long half-lives of radioisotopes. However, for isotopes with relatively short half-lives, a general guideline of twice the half-life of the isotope was used. For this set of samples, $^{7}$Be has the shortest half-life (53 days) of all the isotopes measured. Given the above guideline a holding time of 106 days was considered acceptable for $^{7}$Be samples. All samples were analyzed for $^{7}$Be within 106 days, except for the samples listed in Table 2-1. These results were assigned a "*J*" qualifier and are considered usable as estimates. These results may be biased low.

MARLAP does provide guidance on sample storage conditions for sediment samples, suggesting that they be kept on ice or refrigerated. All samples from this project were stored on ice while in the field and were transferred to refrigerators once they arrived at TAMU-G.

## 2.2 INSTRUMENT PERFORMANCE

Instrument performance was assessed by evaluating the balance calibration certificate for the balance used for determining sample mass, standard reference material results for the detectors measuring radioactive decay emissions, and through the evaluation of detector background levels.

The analytical balance used for determining sample mass is calibrated yearly. The calibration certificate indicated that the balance was within the manufacturer's specifications.

A total of 12 detectors were used: two for the measurement of alpha particle emissions ($^{210}$Pb at 46.5 kiloelectronvolts [keV]) and 10 for the measurement of gamma particle emissions ($^{7}$Be, $^{137}$Cs, and $^{226}$Ra; 352-662 keV). The $^{210}$Pb method specifies the addition of an internal standard (polonium-209 [$^{209}$Po]) of known

activity to correct for any loss of chemical yield and instrument efficiency during analysis. The internal standard was added to every sample analyzed. Each sample result was then corrected for any inherent bias based on the amount of standard added to the sample and the instrument response.

Standard reference materials (SRMs) for $^{137}$Cs and $^{226}$Ra were analyzed to evaluate the performance of the gamma detectors used to measure $^{7}$Be, $^{137}$Cs, and $^{226}$Ra radioactive decay emissions. The response efficiencies of the SRMs were compared between two different standards (SRM 4350B and SRM 4357) for $^{137}$Cs and $^{226}$Ra that were analyzed for each detector. The relative percent differences (RPDs) for $^{137}$Cs were 4.1 and 5.3 for detectors 01 and 02, respectively. The RPDs for $^{226}$Ra were 9.1 and 19 for detectors 01 and 02, respectively. In addition, the percent recovery (%R) of the standard was evaluated for each detector with $^{137}$Cs %R of 104 and 105 for detectors 01 and 02, respectively; and $^{226}$Ra %R of 91 and 121 for detectors 01 and 02, respectively. These were within the control limits established by the agency that issued the standard, except for $^{226}$Ra which exceeded the upper control limit of 118 %R for detector 02.

For both alpha and gamma emission measurements, background levels were measured for all detectors prior to running the sediment samples. Background corrections were not necessary, because they were either not detected or were negligible compared to the sample counts (sample counts were greater than 10 times the background counts).

## 2.3 METHOD BLANK ANALYSES

Method blanks were evaluated to assess instrument performance and analytical procedures and their possible impact on the sample results. To assess the impact of blank readings on the reported sample results, an action level of 5 times (5x) the decay emission value calculated for each blank was used.

Decay emission values were calculated for every blank analyzed and varied between 0.000 and 0.103 disintegrations per minute (dpm). Calculated decay emission values for all samples were greater than 5x 0.103 dpm, thus indicating no bias in the sample results due to instrument performance or analytical procedures.

## 2.4 ACCURACY

Accuracy of the gamma radioisotope data was determined by evaluating the SRM results. The control limits for the SRMs were established by the issuing agency. All SRM results were within the control limits specified for the standards, except for $^{226}$Ra which exceeded the upper control limit of 118 %R for detector 02 by 3%.

As mentioned previously, the $^{210}$Pb method specifies the addition of an internal standard ($^{209}$Po) of known activity to correct for any loss of chemical yield and instrument efficiency during analysis. The internal standard was added to every sample analyzed. Each sample result was then corrected for any inherent bias based on the amount of standard added to the sample and the instrument response.

## 2.5 PRECISION

Precision was assessed by evaluating laboratory sample replicate results for $^{210}$Pb. Laboratory sample replicates were not prepared for $^{7}$Be, $^{137}$Cs, and $^{226}$Ra. However, a subset of the samples were prepared, epoxied for 2 weeks time, and measured for the purpose of improving the $^{226}$Ra results. Sealing the samples inhibits the loss of radon-222, which is the daughter product of $^{226}$Ra. $^{7}$Be and $^{137}$Cs are not as volatile as $^{226}$Ra, thus sealing would not improve the results of these isotopes and one would not expect a significant difference in decay emissions between the sealed and non-sealed samples. Thus, the epoxied results for the non-volatile radioisotopes, $^{7}$Be and $^{137}$Cs, were evaluated to determine the measurement precision for those radioisotopes. Precision could not be assessed directly for $^{226}$Ra. All $^{226}$Ra results were qualified "*J*" and are considered usable as estimates.

The relative percent difference (RPD) was calculated for each replicate sample reported above the method reporting limit. All replicate results detected at less than 2 times the reporting limit were within ±2 times the reporting limit value. All replicate results detected above 2 times the reporting limit were within 30 RPD, with the exception of the last sample analyzed on detectors 10 and 12 for $^{210}$Pb with 34 RPD and 38 RPD, respectively. No data were qualified because the exceedances were not large and the results from the $^{210}$Pb replicates analyzed two days prior were well within 30 RPD (ranging from 2.1 to 19 RPD).

## 2.6 METHOD DETECTION LIMITS AND METHOD REPORTING LIMITS

Project specific target detection limits were not established for radioisotope analyses. The method reporting limits were estimated by the laboratory for each sample and each radioisotope. The method reporting limit ranges (in parentheses) for each radioisotope are as follows: $^{7}$Be (1.1 to 5.4 dpm per gram [dpm/g]), $^{137}$Cs (0.1 to 0.2 dpm/g), $^{226}$Ra (0.2 to 0.4 dpm/g), and $^{210}$Pb (0.1 to 2.2 dpm/g).

## 2.7 FIELD QUALITY CONTROL SAMPLES

No field quality control samples were submitted for radioisotope analysis.

## 2.8 COMPLETENESS OF DATA SET

Completeness is calculated by comparing the total number of acceptable data (non-rejected data) to the total number of data points generated. Completeness for the Round 3A radioisotope data is 100%, which exceeds the QAPP completeness objective of 95%.

# 3.0 QA ASSESSMENT SUMMARY

Data qualification was necessary based on holding time exceedances for several samples analyzed for $^{7}$Be, and for all $^{226}$Ra samples based on the lack of replicate analyses to measure analytical precision. All radioisotope data are considered acceptable as qualified, and are fully usable for all data uses summarized in the Round 3A FSP for Upstream & Downstream Sediment Sampling (Integral 2006).

# 4.0 REFERENCES

EPA. 2002. Guidance on Environmental Data Verification and Validation. EPA AQ/G-8. U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC.

EPA, DOD, DOE, FDA, DHS, NRC, FDA, USGS, and NIST. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual Volume II. EPA 402-B-04-001B. NTIS PB2004-105421. U.S. Environmental Protection Agency, U.S. Department of Defense, U.S. Department of Energy, U.S. Department of Homeland Security, U.S. Nuclear Regulatory Commission, U.S. Food and Drug Administration, U.S. Geological Survey, and National Institute of Standards and Technology, Washington, DC.

Integral. 2006. Portland Harbor RI/FS Preliminary Upstream & Downstream Sediment Data Evaluation and Round 3A Field Sampling Plan for Upstream & Downstream Sediment Sampling. IC06-0019. Prepared for the Lower Willamette Group, Portland, OR. Integral Consulting Inc., Mercer Island, WA.

NRC. 2006. U.S. Nuclear Regulatory Commission Regulatory Guide 4.15 – Quality Assurance for Radiological Monitoring Programs (Inception through Normal Operations to License Termination) Effluent Streams and the Environment. U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research, Washington, DC.

Table A-1. $^{7}$Be Samples Qualified for Holding Time Exceedances

| **Sample ID** | **Holding Time Exceeded by:** | **Sample ID** | **Holding Time Exceeded by:** |
|---|---|---|---|
| LW3-RC02-069 | 17 days | LW3-RC483-013 | 4 days |
| LW3-RC02-073 | 6 days | LW3-RC483-017 | 5 days |
| LW3-RC02-077 | 10 days | LW3-RC483-021 | 6 days |
| LW3-RC02-105 | 11 days | LW3-RC483-069 | 8 days |
| LW3-RC02-109 | 13 days | LW3-RC483-073 | 9 days |
| LW3-RC02-113 | 7 days | LW3-RC483-077 | 12 days |
| LW3-RC02-129 | 8 days | LW3-RC483-105 | 14 days |
| LW3-RC02-133 | 14 days | LW3-RC483-109 | 15 days |
| LW3-RC02-137 | 15 days | LW3-RC483-113 | 16 days |
| | | LW3-RC483-129 | 17 days |
| | | LW3-RC483-133 | 1 day |
| | | LW3-RC483-137 | 2 days |