MERCURY AND GAMMA SPECTRA MEASUREMENTS IN FEDERAL SUPERFUND STOCKPILE SOILS

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Abstract

As of October 2001, approximately 7,000 yd^3 of stockpiled soil remained at Brookhaven National Laboratory (BNL) from the 1997 excavation and remedial activities of the BNL Chemical/Animal Pits and Glass Holes disposal area. Characterization identified the soils as non-hazardous low-level radioactive waste, however the confidence in the waste classification was uncertain due to mercury findings exceeding hazardous criteria at the disposal facility. Preliminary characterization was dependent upon what materials had been interred in the original pits, and how the pits were excavated (Bowerman and others, 2003). Beginning in May 2002, BNL initiated an extensive sorting, segregation, and characterization project to ensure debris removal, characterization of the large quantity of heterogeneous soil, and eventual disposal. The focus was to remove "non-conforming" items (vials, needles, glass debris, etc. that did not meet the disposal facility's Waste Acceptance Criteria), and to assure that mercury and radioactive contaminant levels were within acceptable limits for disposal as non-hazardous, low-level radioactive waste.

Sorting and segregation were conducted simultaneously. Large stockpiles (ranging from 150 to 1,200 yd^3) were subdivided into manageable 20 yd^3 units after powered vibratory screening to remove non-conforming items. Soil that passed through the screen was also visually inspected before being moved to a 20yd^3 sub-pile. Eight samples from each sub-pile were collected for analysis. After analyses were completed and the data reviewed, the stockpiles were reconstructed for later disposal (Bowerman and others, 2003).

To provide near real-time data, as well increased confidence levels in soil classification, a field laboratory, equipped with instrumentation to test for total mercury, RCRA metals, gamma spectroscopy, and a tumbler for performing a modified Toxicity Characteristic Leaching Procedure (TCLP) protocol, was set up in a trailer close to the stockpile site. Laboratory instrumentation was used for screening total mercury levels above 260 ppm and for TCLP mercury at levels above 200 μg/L. Radiological instrumentation was used to identify soil contaminants that were above BNL background levels.

The field laboratory completed more than 2,500 analyses of total Hg (XRF) and TCLP/DMA analyses over an 18-week period. For most sub-piles, TCLP tumbling and analyses were completed within two days. One of the most significant aspects of the project success was schedule acceleration. The original schedule projected activities extending from early April until September 30.

Stockpile sorting, analysis, and reconstruction were completed before the end of August (Bowerman and others, 2003). Duplicates of five percent of the samples collected were sent to an off-site laboratory for quality assurance. Both the field laboratory and off-site laboratory results for mercury showed that all of the stockpiled soils were below EPA action levels for hazardous mercury. All stockpiled soils were classified as non-hazardous, low-level radioactive material and are awaiting disposal at Envirocare of Utah.

The field laboratory was instrumental in providing extensive characterization, near real-time data, increased

confidence in soil classification, as well as assisting in project schedule acceleration.

Introduction

Between the years of 1960 and 1976, BNL excavated 55 pits for the disposal of laboratory chemicals, animal carcasses, and spent laboratory metal and glassware. During the pits operational use, the material disposed of in the pits (i.e. laboratory chemicals, animal carcasses, spent laboratory glass and metals) was supposed to be segregated. Historical photographs revealed that
segregation was not always practiced. Because there was poor documentation of disposal practices and disposed material inventories, the presence of chemically hazardous, radioactive, and mixed radioactive materials was considered likely. Pits were covered over with dirt or sandy mixtures when they became full (PWGC, 1997). In 1989, BNL was put on the U.S. Environmental Protection Agency (EPA) National Priorities List (NPL). One of the subsequent remedial activities was a removal action involving the excavation, characterization, and cleanup of the "Animal / Chemical Pits and Glass Holes", which began in 1997 (PWGC, July 2001).

During the 1997
removal action, the 55 pits were fully excavated. Items excavated from the Animal / Chemical Pits and Glass Holes were characterized and segregated into separate soil and debris piles. Large items were removed by with front-end loaders, while a 2-inch vibratory screen was employed to segregate smaller debris items from the soil. The largest waste stream was the excavated soil, which was separated into 18 stockpiles. Stockpile separation depended on field measurements and, ultimately on results from samples sent to off-site analytical laboratories. During the 1997 removal action, 5 out of 18 stockpiles were characterized as non-hazardous, non-radioactive material and were disposed of at a Subtitle D facility. The remaining stockpiles were identified as non-hazardous with residual low-level radioactivity, except for Stockpile 12, which was classified as mixed waste because mercury was observed visually during segregation (PWGC, 1997).

From September 1999 through January 2000, Stockpile 10 and most of 13 were loaded into 29 railcars for transport to Envirocare in Utah for low-level radioactive waste (LLW) disposal. During routine sampling (every 10th railcar), Envirocare identified levels of mercury above 0.2 mg/L in TCLP leachate. Mercury above this level means that the soil was a mixed (radioactive and chemically hazardous) waste, and required treatment prior to disposal. This incident increased BNL's disposal costs by approximately $450,000. Following this incident, and to assure that the rest of Stockpile 13 was characterized properly, 380 cubic yards were screened by hand raking prior to loading and subsequent disposal. Hand raking was successful at segregating residual non-conforming items, but proved to be labor intensive, slow, and costly. After the secondary segregation, the remainder of Stockpile 13 was disposed of at Envirocare without incident (Bowerman and others, 2003).

During 2001, additional sampling was carried out on the remaining stockpiles, and a ½ inch vibratory power-screen was
tested on Stockpile 6B. The power-screen was tested to accelerate the removal of non-conforming items at a low cost. Samples were collected according to the August 2000 BNL guidance document, *Bulk Waste Characterization for Offsite Disposal Sampling Guidance*, which had been created in response to the Stockpile 10 and 13 disposal incidents. The guidance document recommends use of a "Toolbox," a copyrighted interactive spreadsheet in which data are statistically evaluated. Evaluation results indicate whether additional samples are required to achieve assurance that the average value for a quantity of materials is within a 95% confidence interval. For the 2001 campaign, an initial 10 random samples were collected, as required by the "Toolbox". Additional results from the 1997 characterization and sampling campaign were also used for statistical analysis. The "Toolbox" calculates the standard deviation between each sample result per stockpile. If standard deviations between samples are low, then the "Toolbox" reduces the number of additional samples needed for characterization. The number of samples called

for by the “Toolbox” continues to decrease as the standard deviation decreases, but never reaches zero. A low number of additional samples (recommended by the “Toolbox” indicates that the stockpile is characterized and overall homogeneous. In July 2001, after a successful demonstration of the power-screen and the “Toolbox,” Stockpile 6B was shipped for disposal without incident.

After the 2001 sampling campaign, seven of
the 10 remaining stockpiles were re-classified as low-level radioactive waste. Stockpiles 3, 6R and 7 were characterized as hazardous with residual radioactivity. Stockpile 12’s classification was maintained as mixed waste, due to the observation of liquid mercury during the 1997 removal action (Bowerman and others, 2003). Table 1 lists the original and changed classifications for the stockpiles.

Table 1

Stockpile Classification Summary

Stockpile No.	Estimated Volume (Yd^3)	1997 Classification	2001 Classification*
3	150	Hazardous (Dioxin), Residual Radioactivity	Hazardous (Dioxin), Residual Radioactivity
4	450	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity
6A	900	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity
6C	320	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity
6R	1200	Non-Hazardous, Residual Radioactivity	Hazardous, Residual Radioactivity
7	270	Non-Hazardous, Residual Radioactivity	Hazardous, Residual Radioactivity
8	700	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity
11	1800	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity
12	700	Non-Hazardous, Residual Radioactivity (contains visible mercury)	Non-Hazardous, Residual Radioactivity (contains visible mercury)
15	300	Non-Hazardous, Residual Radioactivity	Non-Hazardous, Residual Radioactivity

* Classification based on Stockpile Characterization – 2001 performed in accordance with Waste Management Department's Bulk Waste Determination Guidance Document, 2000.

To prevent further incidents during subsequent disposal activities and to increase confidence in these stockpile

classifications, BNL extended sorting and segregation to all the stockpiles in 2002,
and increased the number of samples per stockpile. A ½ inch vibratory power-screen was used again to segregate non-conforming items, and a field laboratory was established near the stockpiles for cost effective, near-real time characterization. Samples taken from the stockpiles were delivered daily to the field laboratory for rapid (one-day turn-around time) analyses for total mercury, TCLP mercury, and gamma-emitting radionuclides. The BNL Environmental Restoration program and the Department of Energy (DOE) Office of Science and Technology, Accelerated Site Technology Deployment (ASTD) program, co-funded these activities (Bowerman and others, 2003).

2002 Stockpile Sorting and Sampling Procedures

A ½ inch vibratory powerscreen was employed to separate non-conforming items (generally intact, closed vials containing powders, liquids, or mercury) from the ten remaining stockpiled soils. After the soils were screened, they were collected into 20 yd^3 sub-piles on 3-millimeter polyethylene sheets by a front-end loader. Segregation rates were projected to be 100 yd^3 per day, or approximately 5 sub-piles created per day, based on 2001 power-screen experience with Stockpile 6B. Field laboratory throughput was designed for 60 samples per day, corresponding to a sampling frequency of three per 5 yd^3
(Bowerman and others, 2003).

Uncertainty in environmental characterization is often a trade-off involving the number of samples and sampling methods, field screening analysis methods, and certified analytical laboratory methods (Crumbling, D.M. et al, 2001). While precision in analytical methods has been steadily increasing with improved technology, accuracy in characterization is much more dependent on how well the sample reflects the actual condition of the waste. Uncertainty in the data therefore is closely tied to the extent of sampling. In many environmental remediation characterization efforts, sampling uncertainty offsets analytical laboratory reliability. Explicitly: “If representativeness cannot be established, the quality of the chemical analysis is irrelevant.” Data quality in support of remediation decisions can be improved considerably with increased sampling and field screening methods to supplement certified laboratory results (Bowerman and others, 2003).
Sub-pile sample locations were located at top, center, and bottom quadrants (north, south, east, west). After the completion of the first stockpile, Stockpile 8, center quadrants were dropped,
because the rate of sorting and sample production was far more than the field laboratory capacity of 60 samples per day. Five percent of the samples were collected in triplicate as quality assurance samples; one was sent off-site to a state-certified laboratory, and one was used in the field laboratory as a blind field duplicate (Bowerman and others, 2003).

Field crew sorting operations and sample production
were much greater than anticipated. Sub-pile creation rates exceeded the estimated 100 yd^3 per day; on their most productive days, the field crew sorted approximately 200 yd^3 per day, therefore boosting sample collection per day from the estimated 60 to approximately 100 plus. Stockpile reconstruction was projected to be completed by the end of September 2002, but was completed in the third week of August 2002 (Bowerman and others, 2003).

Field Laboratory Equipment and Methods

The field laboratory and its equipment were located in a stationary trailer, approximately ¼ mile west of the stockpiles. Because most of the soils had residual radioactive contamination, appropriate controls and staff training

were required for opening and handling samples. The major objective of the 2002 project was analysis for total mercury and TCLP mercury, as shown in the process flow diagram (Figure 1.) This paper focuses further on Stockpile 12, which had reportedly visible mercury mixed in with the soil, after a brief description of the experimental methods.

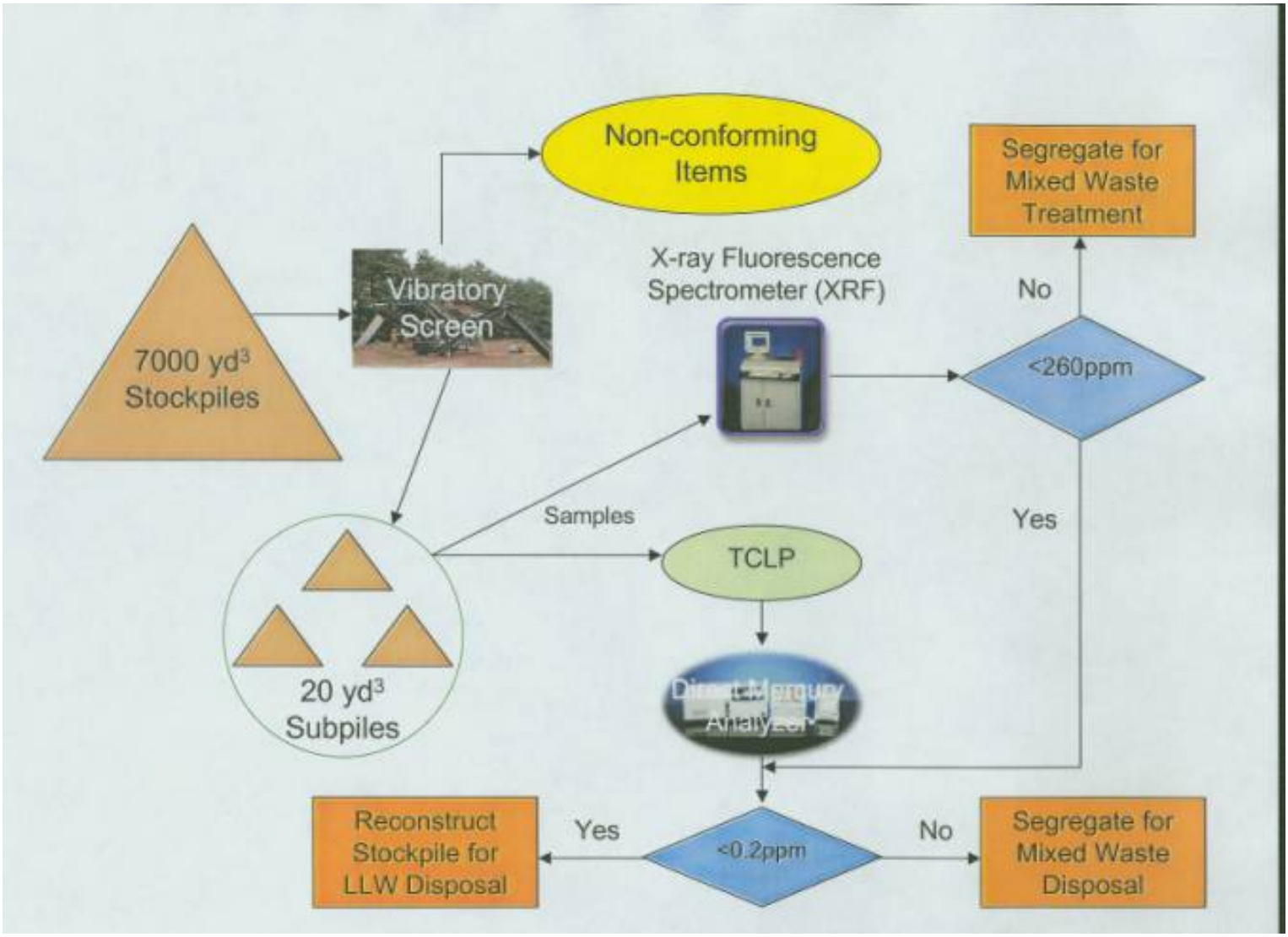

Figure 1. Sorting and analysis flow diagram for Field Laboratory

X-ray Fluorescence (XRF)

The X-ray Fluorescence system was used to analyze for total mercury in the stockpiles. XRF is a mature technology, capable of elemental detection of heavier elements (atomic weight greater that sodium) in solids and liquids, both qualitatively and quantitatively. The detection limit is typically in the range of low parts per million (ppm) for most metals and was reported at 1.5 ppm for mercury at maximum count time per sample. The XRF system (Jordan Valley, model EX-6600A) allows for rapid detection of lower concentrations, because it has a high intensity x-ray source. Other advantages of XRF are that it can quantify broad concentration ranges (ppm levels up to 100%), it is non-destructive to the sample, does not create any secondary waste, requires minimal sample preparation, and total analysis time is often less than 30 minutes per sample (G. Walsh, 2002).

Approximately 10 grams of each sample was sieved to less than 2 millimeters and loaded into a disposable polyethylene cup with a 0.5 mm Mylar bottom liner. Soil was then compressed using a press equipped with a torque wrench for uniform and reproducible packing of the soil in the cup. The Jordan Valley system has a 10-position

automatic sample changer. Eight to nine sub-pile samples were tested in each batch, along with a soil standard spiked with a known quantity of mercury for quality assurance. In order to analyze 60 samples per day, count time was 3 minutes per sample, which resulted in a lower detection limit of 50.5 mg/kg mercury (Bowerman and others, 2003).

Modified Toxicity Characteristic Leaching Procedure (TCLP)

The modified Toxicity Characteristic Leaching Procedure (TCLP) used was essentially a $1/10^{th}$ scale version of the test recommended by the U.S. Environmental Protection Agency (EPA). The scaled version limited the amount of secondary wastes produced and maximized tumbler capacity and sample throughput. Extraction fluid #1, with a pH of 4.94, was used for all tests, as determined by the related EPA procedure (Bowerman and others, 2003). The tumbler held a total of sixty 250 mL polyethylene bottles. After tumbling, a small amount of the sample liquid was filtered (0.7 •), and then tested using the Direct Mercury Analyzer (DMA).

Direct Mercury Analyzer (DMA)

The Milestone DMA-80 measures low concentrations of mercury in environmental samples, in accordance with EPA Method 7473, "Mercury In Solids And Solutions By Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry". Its reproducibility, low detection limits, rapid throughput, and the fact that it does not generate any secondary waste, makes it ideally suited for environmental applications (Bowerman and others, 2003).

The method involves placing a weighed sample in a small "boat" for drying and thermal treatment in a stream of heated oxygen gas. The gas stream is passed through a gold that captures all mercury in by amalgamation with the gold. The gold amalgam is subsequently heated and mercury vapor detected with an atomic absorption spectrophotometer tuned to the absorption wavelength for mercury, 254 nanometers. The Milestone DMA absolute detection limit is 0.11 nanograms mercury. For the listed maximum 0.5-gram sample size, the theoretical detection limit is 0.00022 ppm (0.22 ppb) (Bowerman and others, 2003). The DMA sample changer holds 40 boats. Generally, 32 TCLP samples could be analyzed during one DMA batch run, and the 8 remaining boats were quality assurance tests - either empty boats (blanks) or National Institute of Standards and Technology Certified Reference Materials.

ASTD Laboratory Results

Soil sorting activities produced 283 sub-piles, which were then re-assembled into 10 new stockpiles, corresponding to the original 10 (Bowerman and others, 2003). For the purpose of this paper, the discussion of results will be limited to TCLP mercury and total mercury results for Stockpile 12. The field laboratory analyzed two hundred and sixty samples from Stockpile 12 and the off-site laboratory analyzed twelve samples from Stockpile 12.

Total Mercury and TCLP Mercury Results

Figure 2 depicts average TCLP mercury results for the 31 sub-piles created from Stockpile12. The highest single-sample value for Stockpile 12 was 613 µg/L, found in sub-pile 17. Sub-pile 17 had the highest sub-pile average result at 145 µg/L. Only four sub-piles of the 31 from Stockpile 12 had TCLP mercury averages greater than 100µg/L. Average results for every Stockpile 12 sub-pile was below EPA mercury action levels of 200 µg/L.

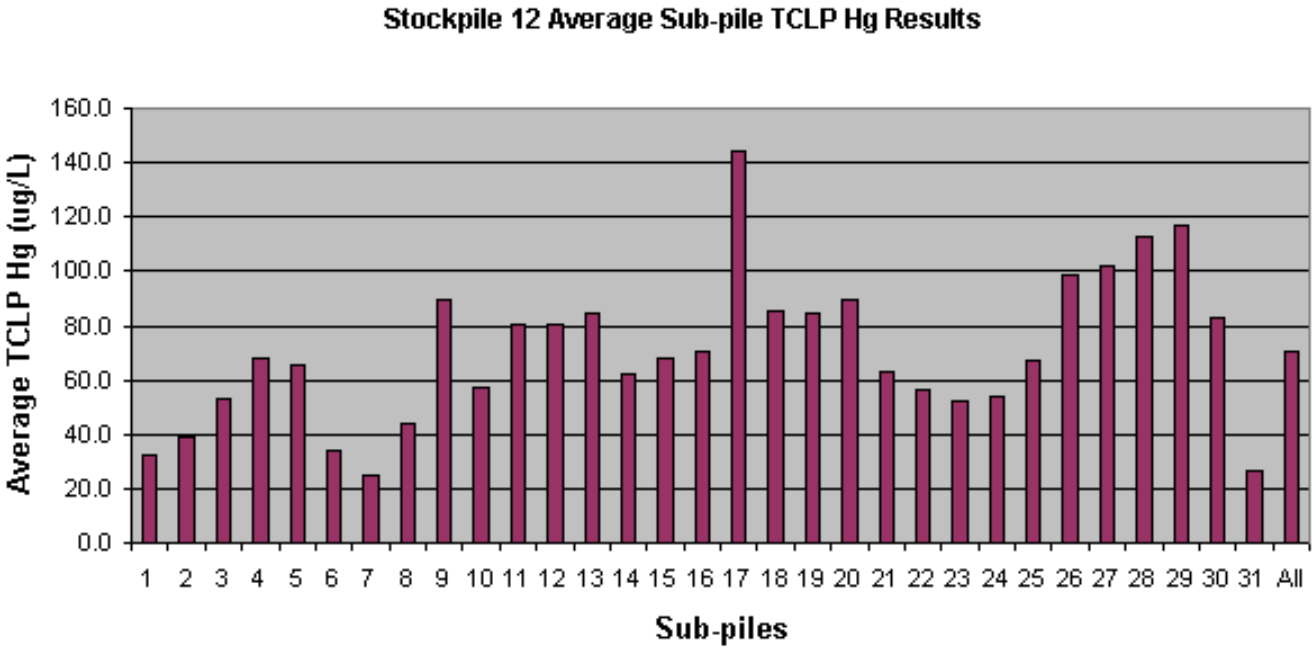

Figure 2.

Average TCLP Mercury Results for Stockpile 12 sub-piles.

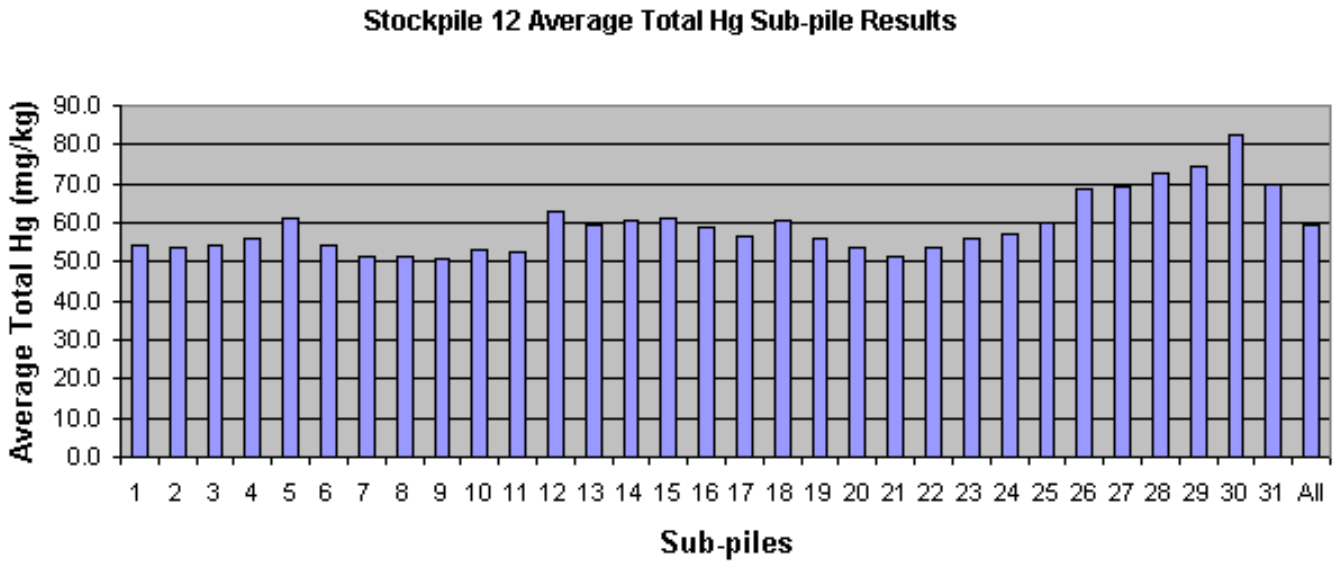

Figure3.

Average Total Mercury Results for Stockpile 12 sub-piles.

Average total mercury results for
the 31 sub-piles created from Stockpile 12 are shown in Figure 3. The highest total mercury result was 129 mg/kg or ppm in a single sample from sub-pile 30 of Stockpile 12. The highest average total mercury result was also found in sub-pile 30 of Stockpile 12 at 83 mg/kg or ppm. All results for Stockpile 12 sub-piles were below EPA mercury action limits of 260 mg/kg.

Comparison of Field Laboratory Data with Offsite Laboratory Data

The BNL EM Directorate Quality Assurance Plan generally requires that one field duplicate sample be sent to a contract lab for every 20 samples, or five percent. For this project, a duplicate for analysis in the field laboratory,

and a duplicate for independent off-site total mercury and TCLP mercury analyses were collected every 20 samples (Bowerman and others, 2003).

There are several approaches for inter-laboratory data comparisons. For the purposes of this discussion, the approach used involves comparisons of Stockpile 12 averages obtained from the two data sets, to see if similar characteristics apply (i.e. do the data sets agree that the soils are not hazardous) (Bowerman and others, 2003). Data comparisons for Stockpile 12 TCLP mercury are listed in Figure 4. Data comparisons for Stockpile 12 total mercury are listed in Figure 5.

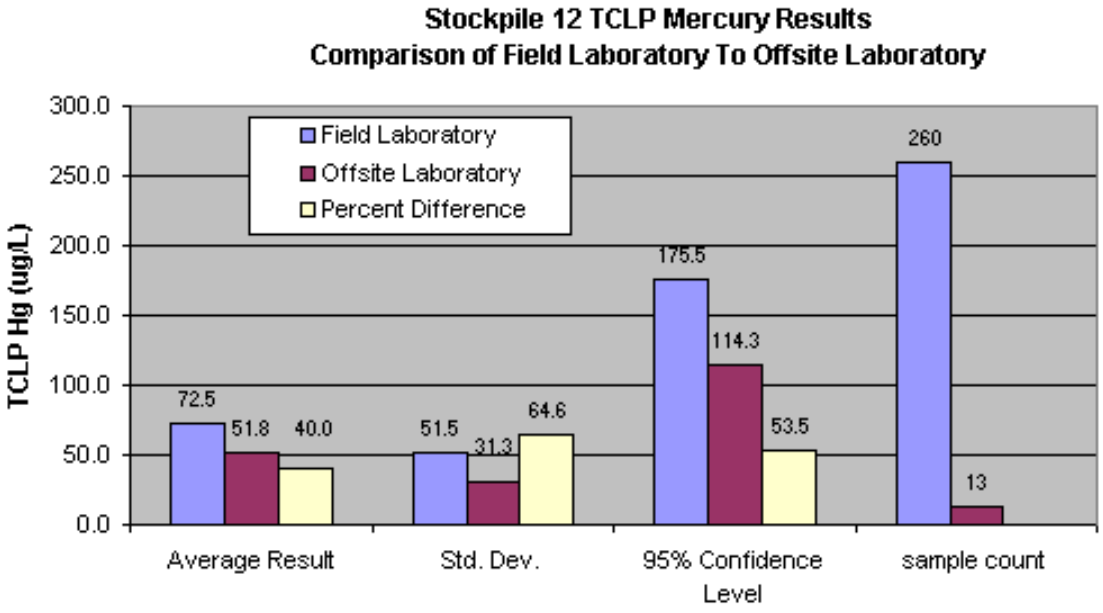

Figure 4. Field Laboratory and Offsite Laboratory TCLP Mercury Results – Stockpile 12.

The field laboratory average TCLP mercury data is more conservative than the off-site average TCLP mercury data by 40 percent. This comparison is supported by a similar difference in comparison of the field and off-site 95 percent upper confidence level for TCLP mercury. The standard deviation of average TCLP mercury was higher for the field laboratory than the standard deviation of average TCLP mercury for the off-site laboratory.

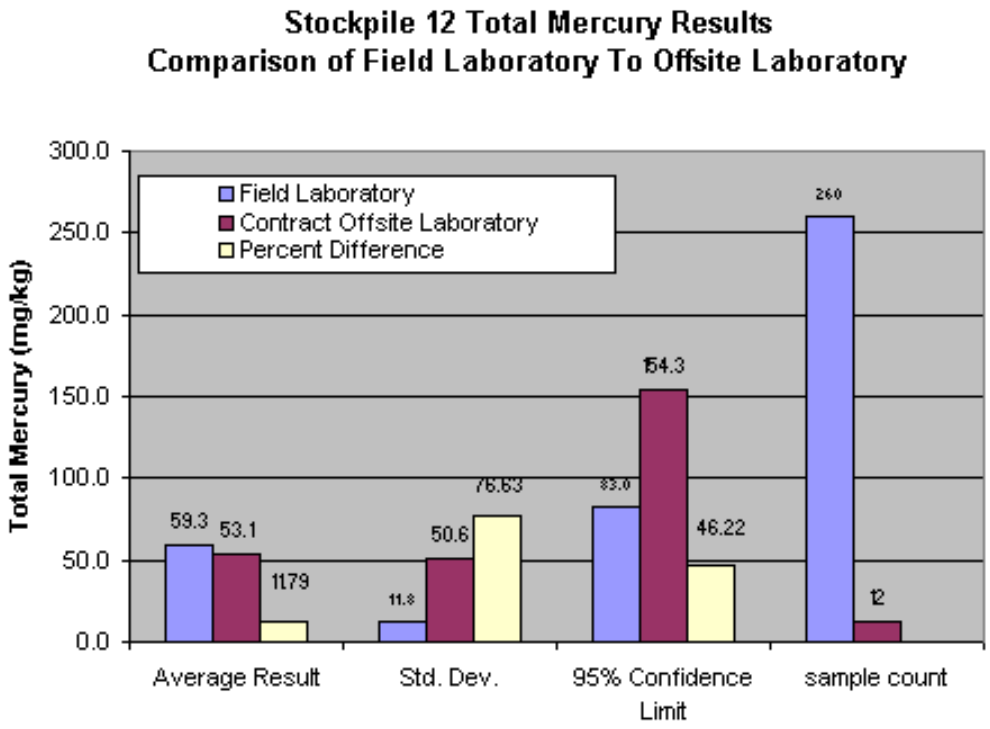

Figure 5. Field Laboratory and Offsite Laboratory Total Mercury Results – Stockpile 12.

A twelve percent difference is noted between the average total mercury data for the field and off-site laboratories. The standard deviation of the field laboratory is much smaller than that of the off-site laboratory due to the high detection limit (50.5 ppm) imposed by the field laboratory to improve sample throughput. Because of the higher standard deviation in the off-site lab, the calculated 95% confidence level value (average value plus twice the standard deviation) is correspondingly higher.

Waste Characterization

Both field laboratory and off-site laboratory mercury results showed that Stockpile 12 average mercury results were below EPA action levels of 200 µg/L for TCLP mercury and 260 mg/kg or ppm for total mercury, therefore the Stockpile 12 soils on average are classified as non-hazardous. However, waste disposal facilities require that a certified laboratory must provide characterization data for waste disposal purposes. Thus, the Quality Assurance program for the field laboratory included sending samples to a certified off-site laboratory for analysis. In this way, the field laboratory data serves as broad statistical support for higher confidence levels in limited sampling and analysis at an off-site laboratory (Bowerman and others, 2003).

Comparison with 2001 Sampling and Characterization Campaign Results

A significant point of comparison is the sampling and characterization campaign during 2002 with 2001 sampling results, using the “Toolbox.” The more extensive field laboratory data in general reduced the uncertainty for all total mercury data. The general conclusion from the field laboratory TCLP data was that all Stockpiles were within acceptable levels for classification as non-hazardous (Bowerman and others, 2003). The discrepancy with the “Toolbox” is that it characterizes large volumes of soil based on few samples taken, and assumes homogeneity.

Conclusions

The field laboratory completed more than 2,200 analyses for total mercury (XRF) and more than 2,400 TCLP mercury (DMA) analyses throughout the 2002 effort. For most of the sub-piles TCLP, DMA, and XRF analyses were completed within two days. One of the most significant aspects of the project success was schedule acceleration. The original schedule projected activities extending from early April 2002 until September 30, 2002. Stockpile reconstruction was completed in the third week of August 2002 (Bowerman and others, 2003).

Reliable statistical verification of the original characterization of Stockpile 12 as non-hazardous, low-level radioactive wastes was accomplished. Stockpile 12 was originally characterized as mixed waste, but due to extensive sample analysis, it was later classified as non-hazardous, low level radioactive waste. T
he ASTD field laboratory provided extensive characterization of the stockpiles could not have been completed without the grant provided by the DOE ASTD program. The BNL ER group did not have the baseline funding for extensive characterization of the stockpiles using an off-site laboratory for analyses. The advantages of the ASTD field laboratory included shorter sample turnaround times, a more flexible laboratory schedule that can adapt to changes in the field, purchased equipment and supplies for future use at BNL, and increased waste characterization confidence.

Acknowledgements

The authors would like to thank the U.S. Department of Energy for supporting the work described here (Contract No. DE-AC02-98CH10886).

References

Bowerman, B.S., Adams, J.W., Kalb, P.D., and Lockwood, A.C., “The BNL ASTD Field Lab – Near-Real-time Characterization of BNL Stockpiled Soils to Accelerate Completion of the EM Chemical Holes Project”, Brookhaven National Laboratory, Upton, NY, 2003.

Brookhaven National Laboratory, “Animal/Chemical Pits and Glass Holes Project Stockpile Characterization Summary Report, Final”, March 28, 2002.

Brookhaven National Laboratory, “Chemical Holes Project Waste Management Plan”, July, 2002.

BNL EM Directorate, “Environment, Safety and Health Plan: Glass Holes Stockpiles Inspection, Loading & Disposal,” Brookhaven National Laboratory, September, 2001.

BNL EM Directorate, “Sampling And Analysis Plan For Waste Characterization Of Stockpiled Soil,” Brookhaven National Laboratory, January 2002.

BNL EM Directorate, “Sort, Inspect, Load & Ship Chemical Holes Soil Stockpiles: Technical Work Document,” EM-GH-TP-02-01, Rev. 0, Brookhaven National Laboratory, March 2002.

BNL EM Directorate, “Environment, Safety and Health Plan, ASTD Field Laboratory,” Brookhaven National Laboratory, March 2002.

BNL EM Directorate, “Glass/Chemical/Animal Holes Project ASTD Field Laboratory Technical Work Document,” EMD-GH-TP-02-02, Rev.0, Brookhaven National Laboratory, March 2002.

BNL Waste Management Division, “Bulk Waste Characterization for Offsite Disposal Sampling Guidance,” Brookhaven National Laboratory, August 2000.

Crumbling, D.M., et al “Managing Uncertainty in Environmental Decisions,” Environmental Science and Technology, American Chemical Society, pp. 405-409, October 1, 2001.

P. W. Grosser Consulting Engineer and Hydrogeologist, P.C., “Waste Characterization Report for the Animal/ Chemical Pits and Glass Holes, Draft Final”, April 1999.

P. W. Grosser Consulting Engineer and Hydrogeologist, P.C., “Mercury-Contaminated Soil Evaluation of Treatment Alternatives – Chemical Holes Stockpiles 6B & 12, Draft”, June 1999.

U.S. Environmental Protection Agency, “Toxicity Characteristic Leaching Procedure,” Method 1311, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm

U.S. Environmental Protection Agency, “Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test,” Method 1310A, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm

Walsh, Geanene, and Bowerman, B.S., “Presentation: Mercury Characterization of Stockpile Soils”, The Richard Stockton College of New Jersey, Energy Research Undergraduate Laboratory Fellowship, Brookhaven National Laboratory, Department of Environmental Sciences, 2002.

Walsh, Geanene, “Mercury Characterization of Stockpile Soils”, Richard Stockton College of New Jersey, Energy Research Undergraduate Laboratory Fellowship, Brookhaven National Laboratory, 2002.

W. de Laguna, “Geology of Brookhaven National Laboratory and Vicinity, Suffolk County, New York,” Geological Survey Bulletin 1156-A, U.S. Geological Service (1963).