

**X-RAY FLUORESCENCE APPLIED TO
TOTAL URANIUM SOIL CHARACTERIZATION
AT THE FUSRAP RATTLESNAKE CREEK SITE**

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ABSTRACT

The U.S. Army Corps of Engineers (USACE) is conducting a cleanup of Rattlesnake Creek, a radiologically contaminated property under the Formerly Utilized Sites Remedial Action Program (FUSRAP). Rattlesnake Creek is located adjacent to the Ashland 2 site in Tonawanda, New York. USACE is using guidance provided in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) to establish that sites satisfy site-specific cleanup requirements and the U.S. Environmental Protection Agency's (EPA) Triad approach to streamline data collection and address decision-making uncertainty at Rattlesnake Creek. The USACE developed site-specific derived concentration guideline level (DCGL) requirements consistent with the cleanup criteria as defined in the Record of Decision. DCGLs for Rattlesnake Creek were developed for radium-226, thorium-230, and uranium-238, which were the principal radionuclides of concern. An analysis of the data from the Rattlesnake Creek area indicates that thorium-230 is the primary remediation driver. The cleanup and closeout process is complicated because a significant portion of the contamination is buried beneath more recent clean sediments, making gamma walkover surveys ineffective. At Rattlesnake Creek, it is not possible to directly detect and quantify thorium-230 at the DCGL levels with in-field instrumentation. The alternative approach was to find a surrogate for thorium-230 that could be addressed using real-time techniques. The selected surrogate was total uranium. While the levels of uranium are not sufficiently high to be quickly and reliably detectable by in-field gamma sensing techniques, they are at levels that can be detected and quantified by x-ray fluorescence (XRF). More than 350 Geoprobe cores were collected within the creek and more than 2,000 XRF analyses were performed at 15-cm individual intervals. The XRF total uranium results displayed a good agreement with uranium concentrations determined by alpha spectroscopy. In those areas of the creek where total uranium was co-located with thorium-230, the XRF analysis provided a cost-effective means of identifying the contaminated soil. The end result of the characterization work was the identification of areas requiring excavation. The excavation footprints were primarily derived from the spatially dense XRF results.

INTRODUCTION

There is often uncertainty associated with decisions regarding remedial action and remedial design at hazardous waste sites. Confidently answering what seems to be straight-forward

questions (e.g., are contaminants of concern present at levels that pose risk concerns? what is the spatial extent of contamination?) becomes difficult when the supporting environmental data sets are sparse. Historically, managing the inherent uncertainties of hazardous waste site remediation has focused on keeping laboratory analytical errors to a minimum [1]. It has been established, however, that in many cases it is the heterogeneity of contaminated media at a site coupled with limited sampling that contributes the bulk of uncertainty when making decisions [2].

Sampling uncertainty is primarily managed by increasing sampling density. Constrained budgets coupled with traditional off-site laboratory analyses that can be very expensive (hundreds to thousands of dollars per sample) make it difficult to achieve desired sampling densities at a reasonable programmatic cost. Traditional laboratory analyses have the added limitation of extended sample result turn-around times, meaning that results are often not available until field crews have been demobilized and making it difficult to resolve “surprises” (e.g., contamination discovered in unexpected locations) when they arise.

New paradigms such as EPA’s Triad have been proposed for addressing characterization and remediation uncertainty through the use of systematic planning, dynamic work strategies, and real-time measurement systems [3]. Real-time here simply refers to the availability of measurement or analytical results in a time frame that allows field work to be modified or adapted to observed conditions. This in turn enables dynamic work strategies, i.e., strategies that promote field work efficiency by guiding work progress on the basis of real-time results. The implementation of these types of strategies at any particular site hinges on the availability of suitable “real-time” measurement systems for the contaminant(s) of concern or a suitable surrogate.

The Rattlesnake Creek (RSC) site provides an example of the use of x-ray fluorescence (XRF) to support real-time decision-making in the field, illustrating both the advantages of real-time measurement systems and their limitations when the targeted analyte is a surrogate for the primary remediation driver.

Rattlesnake Creek

The U.S. Army Corps of Engineers (USACE) is conducting cleanup of RSC, a radiologically contaminated property, under the Formerly Utilized Sites Remedial Action Program (FUSRAP). RSC is an intermittent stream in Tonawanda, New York, and is adjacent to the Ashland 2 FUSRAP site. RSC’s watershed includes the Seaway, Ashland 1, and Ashland 2 sites, all of which contained soils affected by radionuclide contamination. Contamination found within the creek bed and low-lying floodplain originated from ore residuals placed on the Seaway and Ashland properties. Radionuclide-contaminated material migrated via erosional processes into RSC, which is the drainage feature for the area. Limited sampling conducted in the late 1990s identified contamination in creek sediments at levels that were of potential human health concern. Figure 1 is an aerial photograph of RSC, and the area of concern associated with its floodplain. The area of concern was approximately 10 acres in size.

The USACE developed site-specific derived concentration guideline level (DCGL) requirements consistent with the cleanup criteria as defined in the *Record of Decision (ROD) for the Ashland 1*

(Including Seaway Area D) and Ashland 2 Sites [4]. DCGLs for Rattlesnake Creek were developed for the following three principal radionuclides of concern: radium-226 (Ra-226), thorium-230 (Th-230), and uranium-238 (U-238) [5].

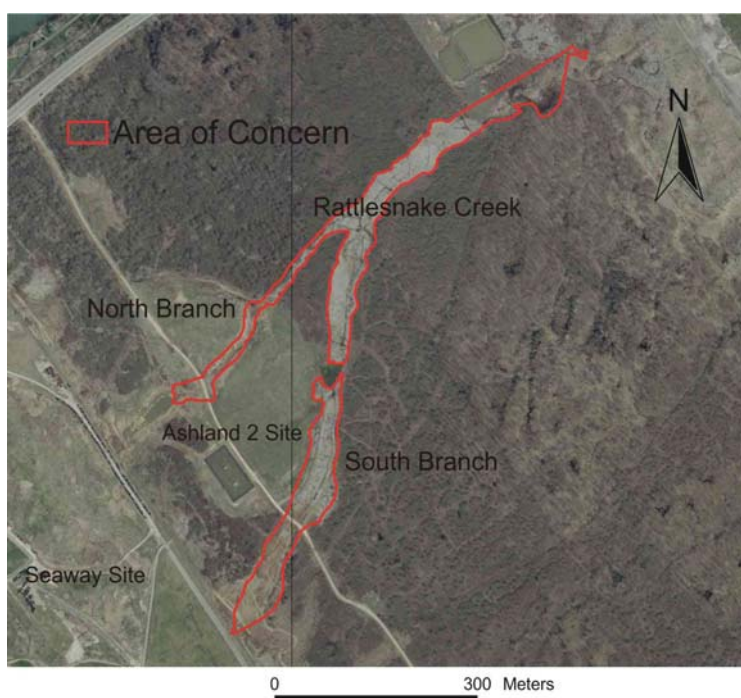


Fig. 1. Rattlesnake Creek

An analysis of the data from the RSC area indicated that Th-230 was the primary remediation driver. The cleanup and close out process was complicated because a significant portion of the contamination was buried beneath more recent, clean sediments, making gamma walkover surveys ineffective in those areas. In addition, the presence of standing water and/or saturated soil conditions made segments of the creek inaccessible for gamma walkover surveys.

The historical sampling at RSC was too limited to either determine the extent of contamination or to confidently “close” those portions of the creek believed not to be contaminated. For most of the creek bed the limited amount of data prevented USACE from developing volume estimates of contaminated soil as part of the remedial design. A data collection effort was planned to serve two primary purposes: (1) to better define the extent of soil contamination and (2) to provide sufficient data to “close” portions of the creek where no contamination was encountered above cleanup requirements.

The primary analytical method for determining Th-230 activity concentrations is alpha spectroscopy. Alpha spectroscopy is expensive (several hundred dollars per analysis) and usually associated with relatively long turn-around times (usually 21 days). The cleanup requirements for RSC required evaluating 100-m² areas for the presence of Th-230 contamination from the surface to a depth of 1 m. Designing a data collection program solely on alpha spectroscopy analyses of soil samples would have been both very costly and rigid. The field work (i.e., collection of the soil samples) would have been complete before results of the

laboratory analyses became available. The challenge was to find a real-time measurement option for RSC that would control the analytical costs and introduce flexibility in the overall characterization and closure strategy.

Real-Time Measurement Strategies for RSC

At RSC, it is not possible to directly detect and quantify Th-230 with in-field instrumentation at the DCGL levels. The alternative was to find a surrogate for Th-230 that could be detected in the field using real-time techniques. Two possible options were Ra-226 and uranium. Historical information indicated that Ra-226 and uranium were both commingled with Th-230, albeit at low levels. Historical characterization activities at RSC had attempted to use Ra-226 as a Th-230 surrogate with very little success. Therefore, total uranium was selected as the surrogate for additional characterization and closure activities.

While the uranium concentrations at RSC were not sufficiently high to be quickly and reliably detectable by in-field gamma detectors, they were at concentrations that could be detected and quantified by XRF. XRF per-analysis costs are significantly less than the cost of alpha spectroscopy or gamma spectroscopy. XRF can be field deployed, with measurement times on the order of a few minutes per sample. Although some sample preparation (e.g., sample drying, homogenization, etc.) is advisable to improve analytical quality, XRF sample preparation does not include an extraction step, a requirement for alpha spectroscopy. Unfortunately, thorium is not directly quantifiable by XRF at the levels that would have been required for DCGL evaluation.

XRF has made steady gains in regulatory acceptance for heavy metal characterization, as evidenced by its inclusion in EPA SW-846 as Method 6200 [6]. EPA's Method 6200 reports excellent performance for some metals (e.g., arsenic, copper, lead, and zinc) as compared to confirmatory laboratory analyses, and it is widely used to characterize heavy metals (particularly lead) in environmental media. Method 6200 lists 26 analytes that it identifies as amenable to analysis by XRF. Although uranium is not among these, XRF has been used with success at the U.S. Department of Energy (DOE) Ashtabula site both as a laboratory-based and field-deployed system to estimate total uranium concentrations in soils. When controlling for sample homogenization affects, the Ashtabula site reported a correlation coefficient of 0.96 for XRF results as compared to gamma spectroscopy. Detection limits were estimated to be in the range of 10 to 40 parts per million (ppm) total uranium.

XRF measures the total elemental mass of the target analyte present in a sample. Uranium is the target analyte at RSC. For XRF to successfully characterize soils and sediments at RSC, a reliable relationship was required between total uranium, which the XRF would measure, and Th-230 activity concentrations, the remedial action driver. Existing historical data sets included gamma spectroscopy results for U-238, and alpha spectroscopy results for both U-238 and Th-230. It was assumed that the uranium isotopes in soils and sediments at RSC were present in their natural abundances, so the total uranium mass concentration was inferred based on either gamma or alpha spectroscopy results for U-238. A review of historical sample results suggested a relationship between the presence of uranium contamination and the presence of Th-230 contamination in RSC soils and sediments. Specifically, the historical data indicated that 80% of

samples with total uranium concentrations greater than 300 ppm also had Th-230 above DCGL requirements; 83% of all samples with Th-230 DCGL exceedances also had uranium greater than 90 ppm.

The analysis of historical results suggested two important investigation levels that could be applied to XRF total uranium analyses at RSC. XRF results less than 90 ppm for total uranium meant that Th-230 contamination was unlikely. XRF results greater than 300 ppm for total uranium meant that Th-230 contamination was likely present. XRF results between 90 and 300 ppm were inconclusive regarding the presence of Th-230 above DCGL requirements. The historical data analysis had its limitations. Primary among these was the fact that the analysis was based on a relatively small number of sample results that were not evenly distributed across the area of concern. There were also questions about the potential performance of the XRF for the site-specific soils present at RSC, and the relatively low total uranium detection levels that would be required. For these reasons, a methods applicability study was performed using existing archived historical samples for the site. As part of the applicability study, 20 archived samples were analyzed with an XRF unit using protocols similar to those expected for later work. The 20 samples were selected to span a range of total uranium values of interest, from 30 to 238 ppm. The purposes of the applicability study were to better define expected detection limits for the instrument, to establish the XRF's ability to provide reliable total uranium concentration estimates, to identify any potential implementation issues that might either complicate the deployment of the XRF or affect XRF data quality, and to verify the relationship observed between uranium and Th-230 in the historical gamma and alpha spectroscopy results.

The results of the applicability study are presented in more detail later. The general conclusions were that: (1) detection limits were well below 90 ppm total uranium with a 120-second measurement; (2) the XRF did provide reliable total uranium concentration estimates for uranium values above its detection limits; and (3) the relationship between uranium and Th-230 observed in historical results was also found in the archived samples by using XRF to determine total uranium concentrations.

Subsequent data collection programs for RSC were designed around the assumption that the XRF would provide relatively inexpensive and rapid results on the contamination status of individual sampling locations from the surface down to a depth of 1 meter (m). The overall strategy was to collect one GeoProbe core per 100-m² area, down to a depth of 1 m, with core locations based on a triangular grid superimposed over the area of concern. Each 15 centimeter (cm) interval from each core was dried to a moisture content of less than 20% (consistent with SW846 Method 6200 [6]), homogenized, and then sub-sampled and analyzed via XRF in a mobile laboratory on site using 120 second measurement times. If any interval yielded an XRF total uranium result greater than 300 ppm, that location was identified for excavation. If all intervals were less than 90 ppm, confirmatory surface and subsurface samples were collected and analyzed using alpha spectroscopy analysis, with the expectation that the results would confirm that the location met cleanup requirements. If there was an interval with total uranium between 90 and 300 ppm (but none above 300 ppm), a sample from the interval with the highest XRF result was analyzed to determine if excavation was required.

XRF RESULTS

The data collection work was implemented in the spring of 2004. More than 350 GeoProbe cores were collected within the creek and more than 2,000 XRF analyses were performed on 15-cm individual intervals. Figure 2 shows the XRF system in use at the mobile laboratory. Sample preparation included heat-lamp open-air drying of samples, homogenization using a blender, and then sub-sampling into XRF measurement cups. Samples selected for alpha spectroscopy analysis were packaged, shipped, and prepared at a commercial laboratory using steps that included homogenization, sub-sampling, and extraction steps. It is important to note that both alpha spectroscopy and XRF analyze a relatively small sub-sample of the original sample mass. For both analyses, heterogeneity of uranium contamination within samples becomes an important source of analytical error.

The XRF was used to screen 15-cm intervals for the likely presence of contaminants of concern above DCGL levels. Off-site analysis of soil samples involved both alpha and gamma spectroscopy at a combined analytical cost of \$260 per sample. The XRF per sample costs were on the order of \$80 per sample. Use of the XRF reduced the number of soil intervals requiring off-site alpha and gamma spectroscopy analysis.



Fig. 2. XRF unit

XRF Analytical Quality

The applicability study data yielded a Pearson correlation coefficient of 0.93, indicating a high degree of linear correlation between the XRF total uranium concentrations and the total uranium concentrations inferred from alpha spectroscopy U-238 results for the 20 samples analyzed. A linear regression, using XRF results to predict alpha spectroscopy results, yielded a slope of 1.07, a y-intercept of 14 ppm, and an adjusted R^2 of 0.86. The adjusted R^2 is a measure of the goodness

of fit for a regression line. An adjusted R^2 equal to one occurs when all data points fall on a straight line. The characterization work produced 230 samples that were analyzed by both alpha spectroscopy and XRF and that yielded detectable concentrations of total uranium. The XRF total uranium concentrations for these samples ranged from 16 ppm (the lower limit of uranium detectability for most samples) to 308 ppm. The Pearson correlation coefficient for these data was 0.86. A linear regression, using XRF results to predict alpha spectroscopy results, yielded a slope of 1.02, a y-intercept of -3 ppm, and an adjusted R^2 of 0.74.

An interesting side note on analytical data quality and “definitive” methods is that 10 of the 20 historical samples used in the applicability study had both alpha and gamma spectroscopy results for U-238. Both alpha and gamma spectroscopy are commonly accepted “definitive” methods for U-238 sample analysis. The Pearson correlation coefficient for the gamma and alpha spectroscopy results for these 10 samples was only 0.66, significantly lower than the 0.93 observed between XRF and alpha spectroscopy results. Poor correlation coefficients are typically blamed on poor analytical quality associated with “field” analytical techniques, but in fact they also reflect analytical variability inherent in traditional analyses.

The analytical quality of the XRF results was monitored in a variety of ways, including the use of prepared standards, analysis of blanks, analysis of duplicates, and repeated measurement of selected samples. Analysis of prepared standards containing known concentrations allows monitoring of the system calibration over time. Blanks guarantee that laboratory contamination and/or some forms of calibration problems are not an issue. Repeated measurements are important because they provide estimates of measurement precision. Through the course of the field work, 13 samples from 13 different locations were subjected to multiple measurements. In each case, the selected sample (represented by its sub-sample) was analyzed 10 times, using 120 seconds for each measurement. The average uranium concentration for these 13 samples ranged from 40 to 270 ppm. The standard deviation ranged from 3.7 to 9.0 ppm, with standard deviations in general increasing with increasing average concentrations, as one would expect. The average uranium concentration over these 13 samples was 110 ppm, while the average standard deviation was 5.9 ppm. This suggests a relative standard deviation (RSD) of less than 6%. SW-846 Method 6200 defines an acceptable RSD as less than 20%.

The applicability study results and the experience gained during the characterization work suggest that the XRF's analytical performance in reliably quantifying total uranium was acceptable.

Relative Sources of Uranium Variability

The 13 sample locations with intervals analyzed multiple times by XRF for total uranium allow an evaluation of the relative sources of the variability observed in XRF total uranium results for RSC. These 13 core locations were scattered across the site and represented 75 individual 15-cm core intervals. As mentioned earlier, one sample from each core had its sub-sample analyzed multiple times to address analytical precision. The average standard deviation observed among these replicate measurements was approximately 6 ppm. The overall standard deviation observed across all 75 samples from the 13 cores was 44 ppm. This 44-ppm standard deviation encompasses the effects of natural spatial variability, variability introduced by sample handling

and preparation and analytical imprecision. Applying an analysis of variance to these data indicates that analytical imprecision accounts for only 2% of the overall variability observed in sample results. This is basically insignificant from a decision-making perspective when those decisions involve drawing conclusions about the contamination status of specific areas of the RSC site.

Uranium as a Predictor of Th-230 Concerns

While XRF proved to be an excellent real-time method for reliably and quickly quantifying total uranium concentrations down to relatively low levels, its effectiveness as a predictor of Th-230 concerns for the site was not as consistent as anticipated. Figure 3 shows the footprint of uranium contamination throughout the RSC area of concern based on XRF results.

The original conceptual site model of contamination at RSC assumed that all contamination present shared a common source and so would share common characteristics. As alpha spectroscopy results began returning from off-site laboratory analysis, however, it became clear that the situation at RSC was not that simple. In particular, contamination characteristics in the south branch of the creek were significantly different than those encountered in the north branch. In the case of the south branch, contamination was encountered at depth and total uranium was almost always present at activity concentrations greater than Th-230 for samples that showed indications of contamination. In contrast, contamination in the north branch was almost exclusively surficial and displayed very little evidence of impacts from uranium contamination, despite the presence of Th-230 elevated above cleanup guidelines. Contamination characteristics from the confluence of the two branches downstream reflected the commingling of contamination characteristic of the north and south branches.

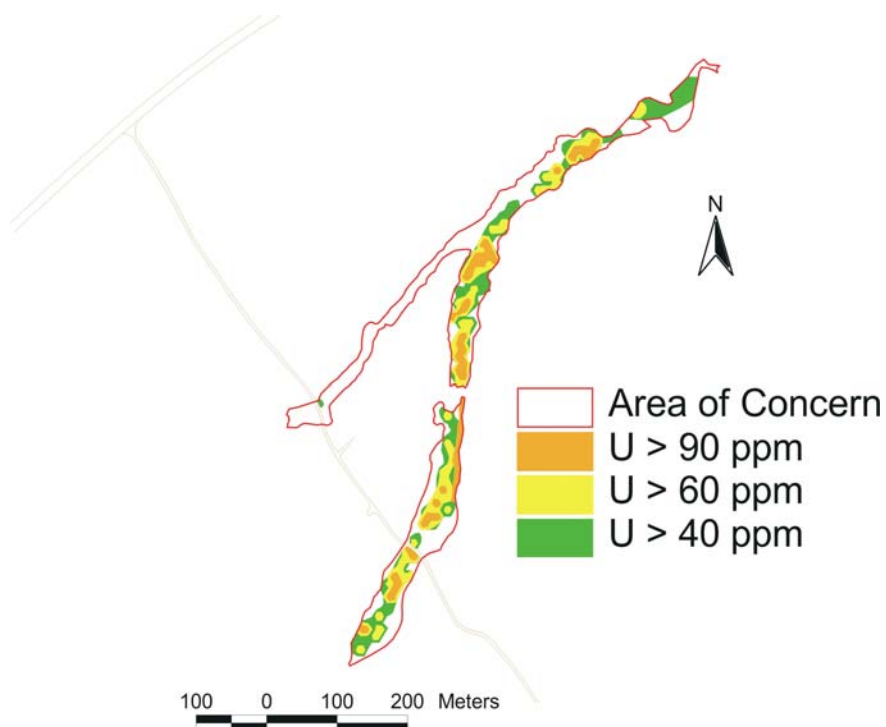


Fig. 3. Total uranium footprint

As a result, the XRF was deemed ineffective for identifying Th-230 contamination that posed health concerns in the north branch because of the relative absence of uranium. In the south branch the XRF clearly identified the impacted soil/sediment footprint both laterally and vertically. However, even in this case it became apparent that investigation levels derived from the limited historical data sets were not performing as expected. In a retrospective review of surface samples from the south branch (these for the most part had both XRF and alpha spectroscopy results), the lower investigation level needed to be dropped to 40 ppm total uranium in order to capture the preponderance of Th-230 contamination. Because of the time lag associated with the return of alpha spectroscopy results, this modified investigation level was not applied to the actual data collection but was applied to the interpretation of XRF results once data collection was complete.

The availability of real-time XRF results allowed field crews to address unexpected situations as they arose during characterization activities. These included several borings in the south branch where contamination appeared to extend deeper than the expected 1 m. These cases were flagged by the XRF analyses and the locations revisited and re-cored to ensure the extent of contamination for those locations was vertically bounded. In another instance, suspicious soil mounds were observed along the banks of the south branch. XRF analysis of soil samples from those mounds identified contamination, suggesting that the mounds were spoilage piles from previous creek trenching work. Finally, the XRF not only quantified uranium but also several other heavy metals, including lead and cadmium, that were found to be present at levels that potentially would pose RCRA disposal concerns. The XRF data supported the selection of waste profile samples for toxicity characteristics leaching procedure (TCLP) analysis.

CONCLUSIONS

The availability of real-time measurement and analytical methods provides the potential opportunity for reducing analytical costs and improving decision-making as part of hazardous waste site characterization and remediation activities. The RSC site experience underscores how well these types of techniques can perform from an analytical quality perspective, but also highlights the types of problems one can encounter when attempting to use real-time methods to guide decision-making. In the case of RSC, the use of an on-site XRF system provided excellent, cost-effective analytical performance for quantifying the presence of total uranium. Observed precision and accuracy for the XRF was equivalent to that observed in off-site laboratory analytical results. Total uranium detection limits were well below the requirements for RSC, and in general were below uranium cleanup standards that are typically encountered at contaminated sites. The XRF accomplished this at significantly reduced per-sample analytical costs and quickly enough so that the results were available while field work was underway.

The use of uranium as a surrogate, for the primary RSC remediation driver, Th-230, was not as successful as expected. Differences in contaminant ratios for different stream branches made the XRF ineffectual for identifying Th-230 contamination in the north branch. The XRF investigation levels initially derived from limited historical data sets proved incorrect for the bulk of the creek, and required adjustment as additional off-site analytical data became available. Despite these shortcomings, however, the XRF still provided essential information regarding contaminant footprints in the south branch of the stream (particularly the vertical extent of contamination) and assisted in identifying and responding to several different unexpected situations encountered while field work was underway.

REFERENCES

1. Crumbling, D.M., 2001/2002 “In Search of Representativeness: Evolving the Environmental Data Quality Model,” *Quality Assurance*, 9:179-190.
2. Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, T.A. Ranney, and P.W. Schumacher, 1996, *Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at Explosives-Contaminated Sites*, Special Report 96-15, USACE Cold Regions Research & Engineering Laboratory, September.
3. Crumbling, D.M., C. Groenjes, B. Lesnik, K. Lynch, J. Shockley, J. Van Ee, R. Howe, L. Keith, and J. McKenna, 2001, “Managing Uncertainty in Environmental Decisions,” *Environmental Science and Technology*, October.
4. USACE, 1998, *Record of Decision for the Ashland 1 (including Seaway Area D) and Ashland 2 Sites*, Tonawanda, New York, April.
5. USACE, 2004, *Rattlesnake Creek Final Status Survey Plan*, Tonawanda, New York, February.
6. U.S. Environmental Protection Agency, 1998, *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*, Method 6200, Revision 0.