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Development and application of an advantageous analytical field methodology.

Mobile Soils Lab: On-site Radiological Analysis Supporting Remedial Activities

Randy Whicker, Michelle Whicker, Janet Johnson, and Bob Meyer*

Abstract: *A mobile, on-site laboratory was used to estimate soil radionuclide concentrations in support of cleanup activities at a former uranium mill site. Respective instrumentation and analytical techniques demonstrated a successful balance between system cost, accuracy, versatility, throughput capacity, and practical simplicity. The methodology involved NaI scintillation gamma spectroscopy measurements calibrated against high-purity germanium analyses by a commercial lab. Statistical comparisons indicated levels of accuracy and precision attained by the on-site lab were similar to that of the commercial lab. Health Phys. 91(Supplement 1):S24–S31; 2006*

Key words: *operational topic; soil; contamination; radionuclide*

INTRODUCTION

Regulatory criteria for remediation at radiologically contaminated sites typically require analysis of radionuclide concentrations in soil. Primary examples include the decommissioning of nuclear power plant facilities or mining/milling sites where naturally occurring radioactive materials (NORM) were produced in support of nuclear power or weapons programs. Other industries that tend

* MFG Incorporated, 3801 Automation Way, Fort Collins, CO 80525.

Randy Whicker has a M.S. degree in environmental health physics and 10 years of radiological assessment experience including a combination of applied research and environmental consulting projects. His work has ranged from assessments of environmental radionuclide contamination and transport pathways, to bioassays of potentially exposed individuals. Currently, Randy is a staff scientist with MFG Incorporated's Radiological Health Group, providing expertise in project planning, experimental design, field sampling, laboratory techniques, radiological measurements, and applied statistical analysis. His efforts have supported entities both public and private in areas of academic research, environmental remediation, and litigation cases. Randy's email is randy.whicker@mfgenv.com.

to concentrate NORM or other radioactive byproducts due to industrial processes are becoming increasingly regulated with respect to radiological issues by State or Federal agencies (e.g., oil production, coal-fired power generation, metals mining, etc.).

Determination of radionuclide concentrations in soil at such sites is normally accomplished through sampling and subsequent analysis at a commercial laboratory. This can be expensive, particularly in cases where a large number of samples may be needed to achieve adequate spatial sampling coverage under guidelines such as those found in MARSSIM, the Multi-Agency Radiation Survey and Site Investigation Manual (U.S. NRC 2000). In addition, obtaining analytical results from a commercial lab can involve considerable delay (weeks or more), which can negatively impact the effectiveness and efficiency of remedial activities.

This paper describes the development of a mobile, on-site soil analysis laboratory and analytical techniques for rapid and accurate

quantification of gamma-emitting radionuclides in soil samples. The system was developed in support of the cleanup of a former uranium mill site but could be applied in other situations provided the radionuclides of interest (or short-lived progeny) have favorable gamma emission characteristics. In this case, the system was successfully used to generate accurate, almost real-time estimates of ^{226}Ra and other radionuclide concentrations in soil samples.

BACKGROUND

The Dawn Mining Company (DMC) processed ore at a uranium mill near Ford, Washington, from the late 1950's to 1982. After that, the mill was intermittently used to recover uranium from water treatment sludges generated at the nearby Midnite Uranium Mine. Following permanent closure in 2001, the planning and implementation process began for mill site reclamation, decommissioning, and termination of DMC's radioactive materials license with the Washington Department of Health (WDOH).

In the summer of 2004, MFG Inc. performed a comprehensive radiological survey of the site in order to characterize the extent of residual (above background) levels of uranium decay products (MFG 2004). From a regulatory standpoint, ^{226}Ra concentration

in soil was a primary criterion for WDOH license termination and, as such, was a primary focus of characterization and cleanup planning efforts. The characterization survey consisted of three elements: (1) A GPS-based gamma scanning/mapping system developed by MFG; (2) soil sampling and radiological analysis by a commercial laboratory; and (3) statistical correlations between gamma measurements and corresponding ^{226}Ra activity concentrations in soil. The correlations, along with gamma survey maps, were used to identify and delineate areas likely to require cleanup (areas likely to exceed the applicable soil ^{226}Ra concentration cleanup criterion of 6 pCi g^{-1}).

In the summer of 2005, soil cleanup operations began. Radiological aspects of the cleanup Work Plan (MFG 2005) called for continued use of the scanning/mapping system to guide excavation operations, as well as the development of an on-site laboratory and analytical technique for rapid estimation of ^{226}Ra activity concentrations in soil. The motivation for development of the on-site soils lab was that gamma scan results and correlations with ^{226}Ra concentrations alone were not considered definitive evidence of compliance with the cleanup criterion. Sending soil samples to a commercial lab for definitive verification during the cleanup would have required lead times that were impractical for assessing the adequacy of the cleanup on a daily basis. A rapid and accurate way to screen soil samples for compliance was needed to minimize the need for re-deployment of work crews and equipment to areas thought to be adequately cleaned up based on gamma scans, but which weeks later could be found to have soil concentrations still exceeding the cleanup criterion.

METHODS

Instrumentation

The first practical consideration in developing the on-site soils lab was to choose appropriate gamma spectroscopy instrumentation in terms of accuracy, speed, and cost. High-purity germanium (HPGe) detection systems have the highest spectral resolution, but also have lower counting efficiency, are very expensive, and generally require a supply of liquid nitrogen (Knoll 2000). Although NaI scintillation systems have lower resolution, they also have higher counting efficiency, lower cost, are generally simpler to maintain, and have better mobility.

The instrumentation chosen for the DMC mill site cleanup was a 3 × 3-inch Ludlum Model 44-20 NaI detector (Ludlum Measurements, Inc., P.O. Box 810, Sweetwater, TX 79556) coupled to a PC-based URSA-II (Radiation Safety Associates, Inc., PO Box 107, Hebron, CT 06248) multi-channel analyzer (MCA) system (Fig. 1). The MCA unit is small and portable and can be run from an equally portable laptop computer. Cost of the MCA and software was about $4,000. The final component of the counting system involved lead rings and plates, arranged such that both sample and detector were shielded from background radiation during counting.

Sampling and sample preparation

Soil samples were collected in the field in a manner consistent
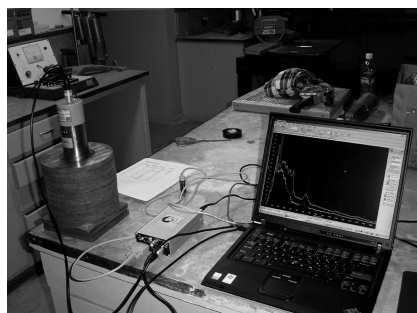

Figure 1. Photo of the NaI-based counting system.

with the cleanup criterion (in this case, composite sampling within a 100 m^2 grid over a depth of 15 cm to represent average corresponding concentrations). Universal Transverse Mercator (UTM) coordinates were taken at the center of each grid with a Garmin Legend GPS instrument (Garmin International Inc. 1200 East 151st Street, Olathe, KS 66062-3426), and recorded for mapping purposes. Samples were dried in ovens at about 100°C then sieved to separate any rock fraction greater than 1 cm diameter. The large rock fraction was reduced by crushing and returned to the sample for homogenization. Aliquots of homogenized samples were weighed, canned in counting tins, and sealed with electrical tape. At each stage of sample collection and processing, equipment was thoroughly cleaned to prevent cross-contamination.

Sample counting and spectral analysis

Determination of optimal sample count times was based on balancing the number of samples that could be analyzed per day against the need to achieve sufficient accuracy (i.e., optimization of spectral resolution, counting statistics, and system detection limits relative to the cleanup criterion). Minimum detectable concentration (MDC) limits were calculated as described in Principles of Radiological Health and Safety (Martin and Lee 2003) and were based on measurements of National Institute of Standards and Technology (NIST)-certified ^{226}Ra soil reference material standards and a background soil sample. With a calculated MDC of 0.75 pCi g^{-1} (well under the cleanup criterion) and the potential to analyze more than 20 samples per day, a 20-min count time was selected as best suited to the project.

Estimation of ^{226}Ra activity concentrations involved analysis

of the number of counts within three energy regions of interest (ROIs) in soil sample gamma emission spectra. These ROIs encompassed energy peaks for short-lived ^{226}Ra decay chain progeny including ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV). Because ^{222}Rn, a noble gas with a half life of 3.8 d, is an intermediate isotope between ^{226}Ra and these decay chain progeny, counts were taken before significant ^{222}Rn ingrowth in sealed samples could occur (0-d counts), as well as after approximate secular equilibrium between ^{222}Rn and ^{226}Ra was achieved (21-d counts). Statistical analysis of the relationship between 0-day and 21-day results allowed ^{226}Ra estimates to be made without any ^{222}Rn ingrowth waiting period.

Although the MCA manufacturer claims the provided software allows radionuclide quantification based on energy calibrations and counting efficiencies for certified standards, it was not possible to verify the algorithms used for respective calculations and we were unable to obtain satisfactory results using that approach. Instead, actual soil samples from the site were used to calibrate our NaI count data against HPGe gamma spectroscopy results from an accredited commercial lab (Energy Laboratories Inc.). About 10% of soil samples collected during the 2005 cleanup were also analyzed by Energy Laboratories Inc. (ELI). In effect, soil samples from the site that were analyzed by ELI were used as secondary standards for direct cross-calibration of measurement systems. An advantage to this approach is that both the higher counting efficiency of the NaI system and the greater resolution of the HPGe system are statistically reflected in the results.

The cross-calibration of measurement systems involved fitting curves to known ^{226}Ra activity data (HPGe results) and corresponding ROI count data (NaI results). Due to an apparent non-linearity for these data in the low activity range (below about 8 pCi g^{-1}), fitted power functions were used for the cross-calibration (Fig. 2A). For higher activity ranges, fitted linear regression functions were used (Fig. 2B). Respective curve equations for each ROI were used to predict ^{226}Ra concentrations in unknown soil samples. Resulting concentration estimates for each ROI were averaged to take advantage of all relevant count data, help limit the influence of any potential spectral interferences, and provide the best possible overall estimates. Because additional samples were periodically analyzed both by the on-site soils lab and ELI throughout the 2005 cleanup, calibration curves were periodically updated to include these additional data. The accuracy of NaI estimates was continually assessed against new batches of results from ELI, both before and after calibration curve updates.

Quality assurance/quality control

Because NaI-based radionuclide quantification by MFG's on-site soil lab was based on statistical relationships with corresponding HPGe measurements performed by ELI, quality assurance was partially related to ELI's accreditation and QC protocols. ELI is certified by the EPA as well as by seven different States. The laboratory follows a strict chain of custody protocols, uses NIST-certified standards for instrument calibrations, and performs measurements on EPA or other certified reference material standards with each set of client samples to provide information on measurement accuracy. ELI also performs duplicate analyses on 10% of all client samples to provide information on measurement variability. MFG observed details of these QC protocols during a visit to ELI's Casper, Wyoming, facility prior to initiation of the work described here.

A NIST-certified ^{137}Cs source was used to calibrate the NaI counting system at the beginning of each day and to monitor the system for spectral drift every 1–2

(A) $y = 4E-12x^{4.01}$, $R^2 = 0.76$
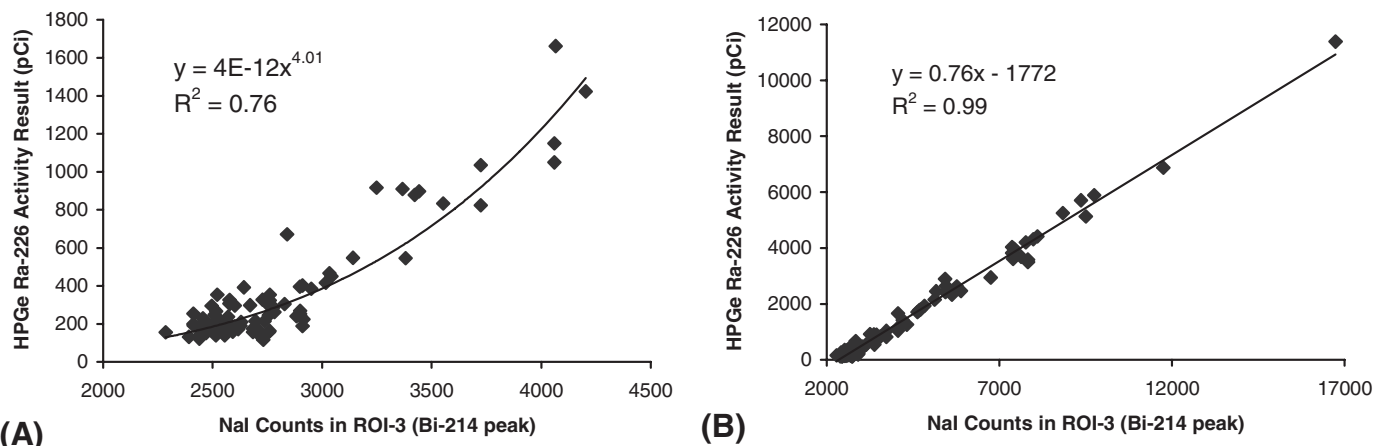
(B) $y = 0.76x - 1772$, $R^2 = 0.99$

Figure 2. Example fitted cross-calibration curve functions for low activity ranges (A) and high activity ranges (B) in secondary reference material standard samples.

h. MCA fine-gain settings were adjusted as needed. Daily system QC checks were also performed at the beginning of each day. This involved taking measurements on secondary "background" (1.2 pCi g^{-1} ^{226}Ra) and "source" (21.1 pCi g^{-1} ^{226}Ra) soil reference material standards and recording the number of counts within the ^{214}Bi energy peak ROI on system control charts. Results falling within ±3 standard deviations from the mean of 20 respective initial control chart measurements indicated that the counting system was working properly. Finally, duplicate measurements were performed by the MFG on-site soils lab for about 3% of samples, while about 1% of samples were split for dual analyses by MFG and/or ELI to assess sample aliquot variability and the effectiveness of sample homogenization.

RESULTS AND DISCUSSION

MFG on-site laboratory estimates of ^{226}Ra concentrations in soil samples collected during the DMC mill site cleanup proved more accurate than originally anticipated. Samples measured both by MFG and ELI (after full ^{222}Rn ingrowth) had a mean NaI:HPGe ^{226}Ra result ratio of 1.02 ± 0.29, indicating that NaI-based estimates had no significant tendency to over-predict or under-predict HPGe results. Regression statistics between MFG's NaI-based estimates and ELI's corresponding HPGe-based estimates (Fig. 3A) demonstrated a nearly perfect linear relationship. The spread of data about the regression line showed relatively small average residuals, resulting in a 95% prediction band width of about ±3 pCi g^{-1} on either side of the regression (Fig. 3B). This indicates that a given measurement result from ELI using HPGe gamma spectroscopy has a 95% probability of falling within ±3 pCi g^{-1} of a corresponding NaI-based estimate generated by MFG's on-site soils lab.

For high concentrations, the ±3 pCi g^{-1} prediction band width can imply a high level of relative accuracy (e.g., within ±5% at 60 pCi g^{-1}), but for low concentrations it can imply a high relative potential for error (e.g., within ±50% at 6 pCi g^{-1}). As demonstrated in Fig. 3B, however, most ELI measurements were significantly closer to MFG estimates than ±3 pCi g^{-1}, even in the lowest concentration range. The respective spread of data indicates an 80% probability that an ELI result will fall within ±2 pCi g^{-1} of an MFG NaI-based estimate. Deviations between ELI's duplicate analysis QC measurements averaged 0.6 ± 0.8 pCi g^{-1}, and with some individual deviations at or near ±2 pCi g^{-1}, the 95% prediction band width for the NaI system does not appear far beyond the range of measurement variability for the HPGe system. ELI's reported range of acceptable accuracy for HPGe QC measurements on certified soil reference material standards is ±30% (e.g., within ±2.1 pCi g^{-1} for a 7 pCi g^{-1} reference standard). These results and observations suggest that by calibrating our NaI-based measurements against ELI results, the general level of accuracy and precision attained by MFG's on-site soils lab is similar to that demonstrated by the HPGe system used by ELI.

With all analytical techniques, it is normal for measurement variability or estimation error to have greater relative impact in the lowest range of values. For
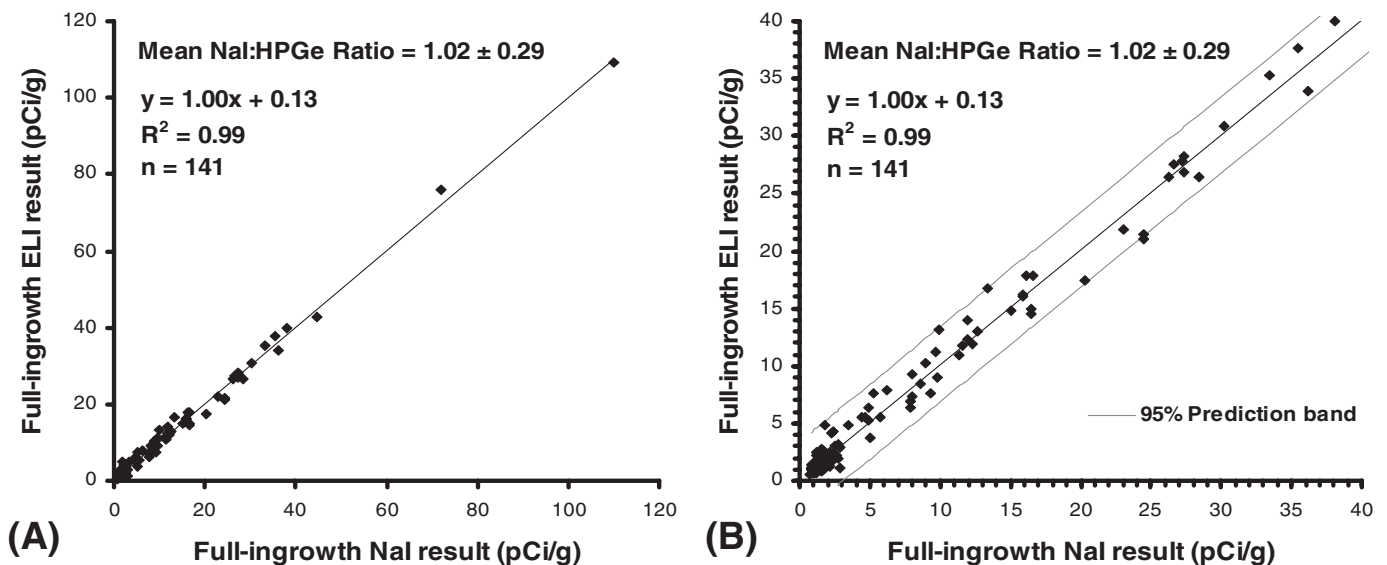

Figure 3. (A) Relationship between ELI's HPGe-based ^{226}Ra results and MFG's NaI-based ^{226}Ra results for fully equilibrated samples; (B) a 95% prediction band for the same graph, zoomed in at the low range of values to better illustrate the spread of the data about the regression line.
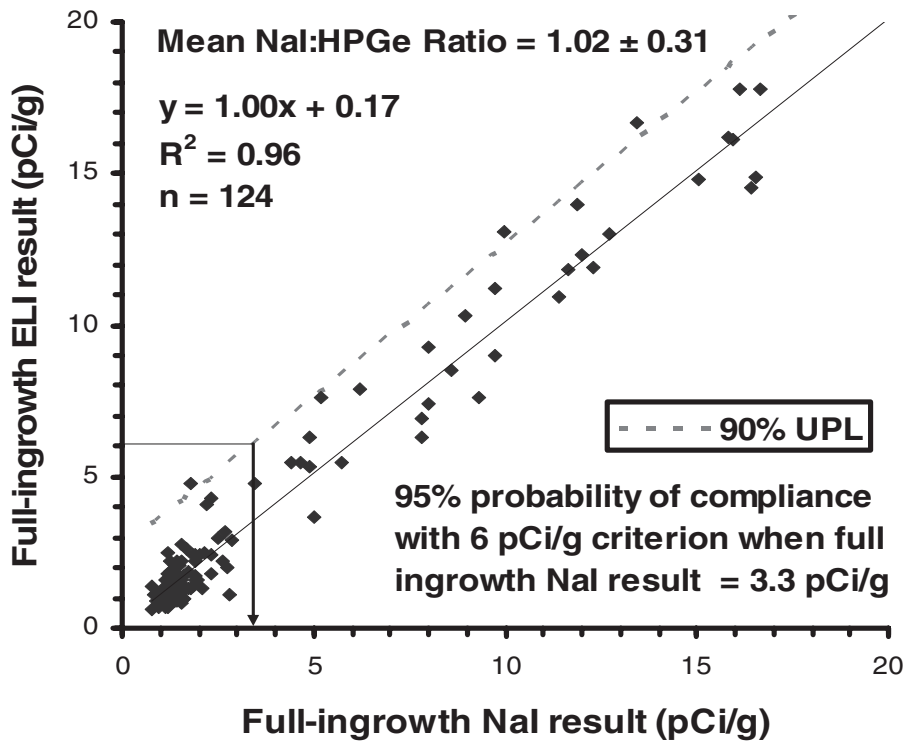
Figure 4. Development of cut-off value for [226]Ra estimates based on full [222]Rn ingrowth measurements.

Along with the estimation accuracy demonstrated for fully [222]Rn-equilibrated samples and the ability to support high-density sampling, immediate estimates of full-ingrowth [226]Ra concentrations generated the same day samples were processed and sealed (0-d estimates) were an important feature of the on-site soils lab. These estimates were used throughout the project to assess the adequacy of the cleanup on a daily basis. The relationship between full-ingrowth HPGe results and "day zero" NaI measurements is shown in Fig. 5A. This regression equation was used to convert day zero NaI measurements into full-ingrowth [226]Ra concentration estimates. A comparison of HPGe results and these 0-d estimates is shown in Fig. 5B. Although the linear relationship was still very strong, 0-d estimates had somewhat less agreement with HPGe results compared to NaI estimates generated from full-ingrowth measurements (see Fig. 3A for comparison).

Ninety-five percent probability cut-off values for 0-d estimates, used to "release" areas from further need for excavation on a daily basis, periodically changed throughout the project as more data became available with which to refine and strengthen predictive statistical relationships. The final 0-d estimate cut-off for all available data at the end of the project was 2.0 pCi g^{-1} (Fig. 6). This cut-off value, like the 3.3 pCi g^{-1} cut-off value for full-ingrowth NaI estimates, was subject to potential U-nat interference limitations. An analysis of how increasing U-nat concentrations might influence [226]Ra cut-off values due to spectral interferences is shown in Table 1. When samples with estimated U-nat concentrations above 100 pCi g^{-1} were excluded from the analysis, data scatter was slightly reduced, 90% upper prediction limits decreased accordingly, and
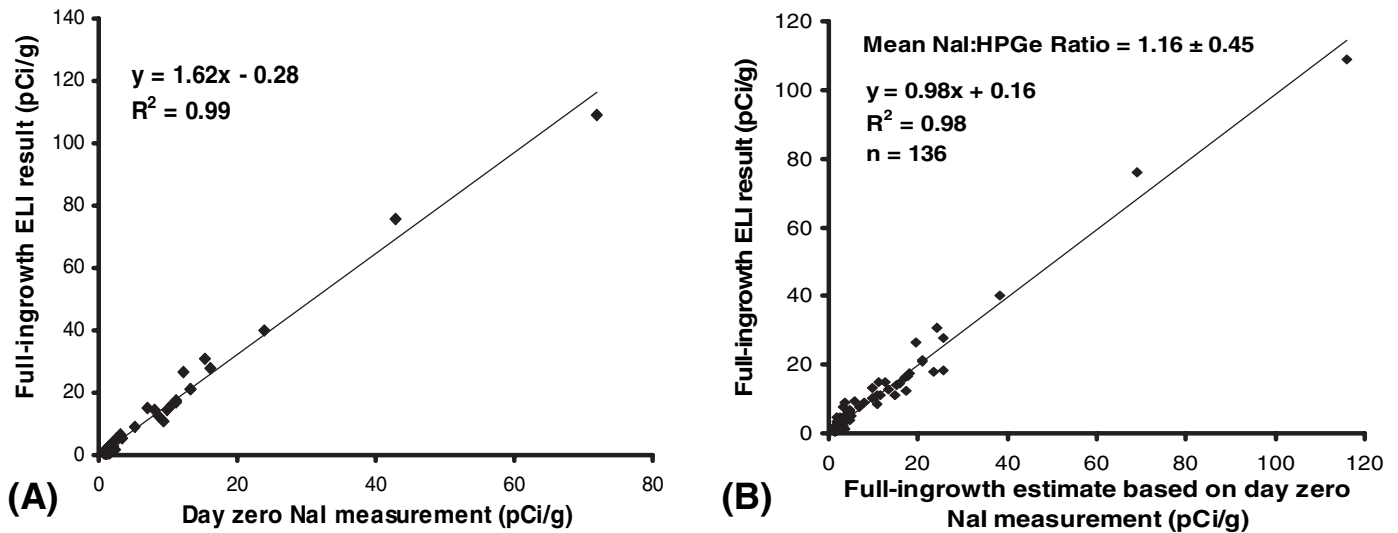
samples with low activity, it also becomes more difficult to distinguish analyte signal from background "noise" such as Compton scatter. In a regulatory application like the DMC mill site cleanup, these issues are relatively easy to deal with using statistically based cut-off values, provided the regulatory "criterion" is sufficiently large relative to system detection limits.

Fig. 4 again shows corresponding full-ingrowth [226]Ra estimates from ELI and MFG's on-site soils lab, but here the data are limited to values less than 20 pCi g^{-1} in order to specifically model the relationship near the 6 pCi g^{-1} cleanup criterion. The 90% upper prediction limit (UPL) shown in Fig. 4 indicates a 95% probability of compliance with the cleanup criterion for a full-ingrowth NaI-based estimate of 3.3 pCi g^{-1}. This represents a cut-off value that can provide statistically defensible evidence of compliance to regulators and the public, particularly where high density sam-

pling and on-site analysis were conducted, but only a fraction of respective samples were analyzed by a commercial lab.

A limitation of this or any NaI-based cut-off value used to assess regulatory compliance at the DMC mill site is that the presence of high levels of natural uranium (e.g., in former ore stockpile areas) can affect and sometimes invalidate NaI-based [226]Ra estimates. There were several instances where NaI estimates showed very poor agreement with HPGe results, yet in each case high levels of natural uranium (U-nat) were present. Large [230]Th and [235]U peaks associated with high U-nat concentrations appeared to inflate counts in [226]Ra progeny ROIs. However, these same peaks enabled clear identification and reasonably accurate quantification of U-nat concentrations. As a result, it was fairly simple to identify samples that required HPGe analysis for accurate quantification of [226]Ra concentrations.

Figure 5. (A) Relationship between ELI's HPGe ^{226}Ra analysis results for fully equilibrated samples and corresponding NaI measurements performed the same day samples were sealed (day zero measurements); (B) relationship between full-ingrowth HPGe results and estimated full-ingrowth ^{226}Ra concentrations based on day zero NaI measurements (0-d estimates).

cut-off values slightly increased. This finding is important because cleanup standards also state a secondary criterion of 100 pCi g^{-1} for U-nat. It is thus reasonable to consider estimates for both analytes and only apply the higher ^{226}Ra cut-off values since any areas with U-nat concentrations exceeding 100 pCi g^{-1} will require cleanup anyway.

The final element of the on-site soils lab in terms of practical application involved mapping the soil concentration estimates. MFG Gamma Viewer 2.77, a software program developed for mapping gamma scan data, also allows soil sampling locations and respective concentration data to be mapped immediately in the field and updated daily as needed.

Color-coded maps with soil concentration estimates superimposed on gamma scan results were an important assessment and cross-verification tool, supporting continual development of strategies to maximize the efficiency and effectiveness of the cleanup. Fig. 7A shows a Gamma Viewer map of gamma exposure rate status at the mill site prior to the 2005 cleanup and Fig. 7B shows both gamma status and ^{226}Ra soil concentration data at the end of 2005 cleanup efforts.
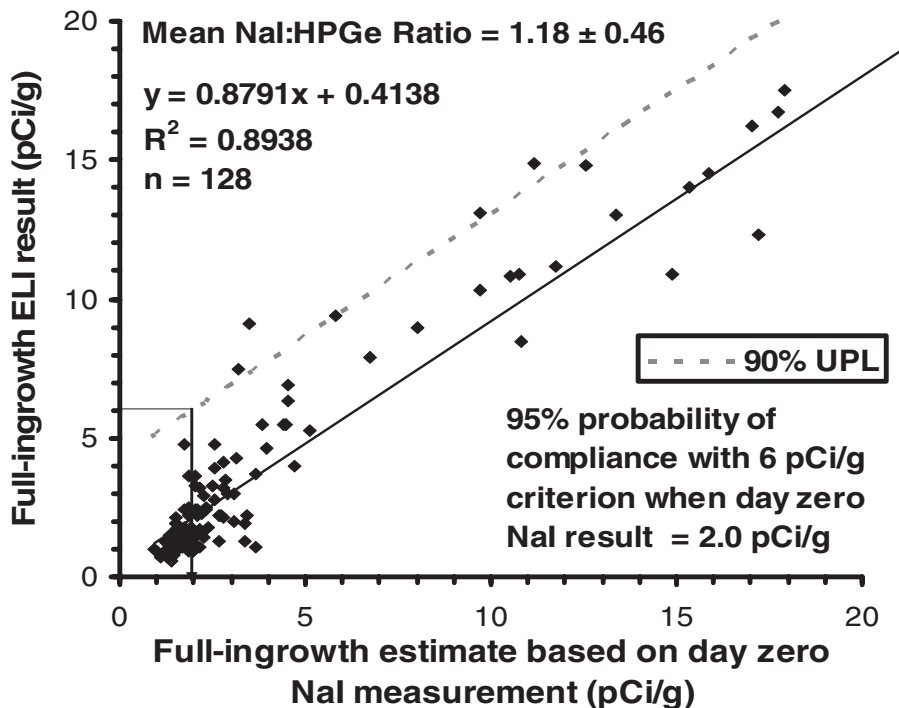
CONCLUSION

A mobile, on-site soil analysis laboratory based on gamma spectroscopy with a NaI scintillation

Figure 6. Development of a cut-off value for estimated full-ingrowth ^{226}Ra concentration based on day zero measurements (0-d estimates) for all data.

Table 1. Ninety-five percent probability ^{226}Ra cut-off values calculated for all data and for subsets of data with various (higher) levels of estimated natural uranium concentration excluded.

	^{226}Ra cut-off values (pCi/g)	
	Full-ingrowth cut-off	0-day estimate cut-off
All data	3.3	2.0
Data <300 pCi/g U-nat	3.3	2.0
Data <200 pCi/g U-nat	3.3	2.0
Data <100 pCi/g U-nat	3.4	2.6

system can achieve levels of accu-
racy and precision approaching
those of HPGe measurements in a
commercial lab. The analytical
technique of calibrating NaI-based
measurements against HPGe re-
sults is a relatively simple, yet ef-
fective way of achieving this level
of performance. NaI systems are
less expensive, mobile, and are
easy to use and maintain. Advan-
tages of the on-site NaI-based soils
lab include the ability to produce
reliable high-density spatial char-
acterizations of soil concentrations
at relatively low cost, and the abil-
ity to produce accurate, nearly
real-time estimates without any
waiting periods for sample equili-
bration or analytical lead time
from a commercial lab. Some lim-
itations of the NaI-based soils
lab are that radionuclides of
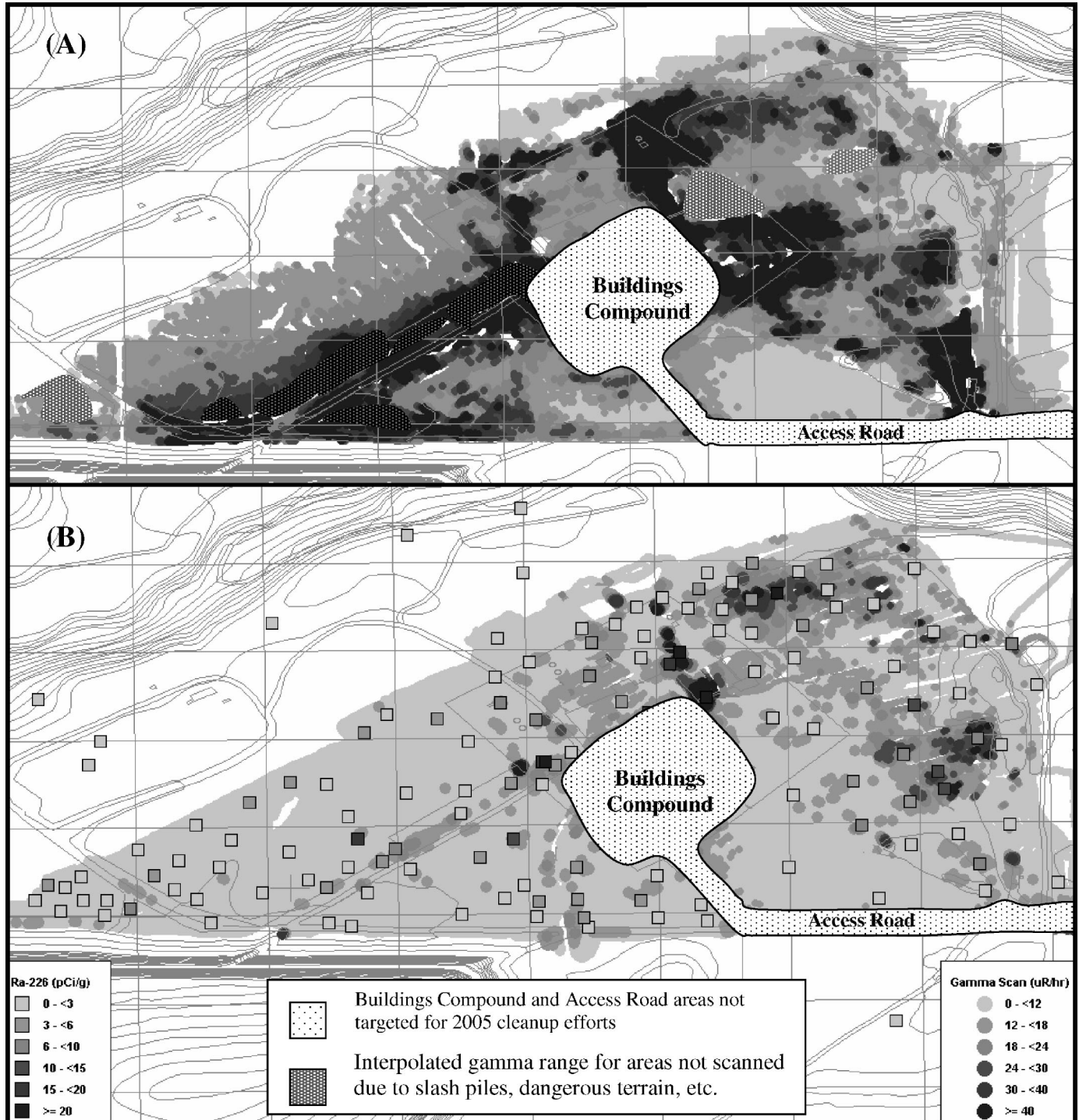interest (or their appropriate

Figure 7. (A) DMC mill site gamma status before the 2005 cleanup commenced (2004 characterization data); (B) gamma + ^{226}Ra status at the end of the 2005 cleanup (4 November 2005).

decay progeny) must have favorable spectral gamma emission characteristics, and estimates can be inaccurate if elements with spectral interferences are present. While potential interferences from other radionuclides can pose analytical problems, they also have the potential to be accurately identified and quantified. This can lead to analytical solutions as well as increased understanding of overall radiological complexities that can be important in terms of regulatory compliance.

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