

June 20, 2013

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Florida Department of Environmental Protection  
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Re: Review of Applications and Guidance on the Measurement of Arsenic in Soil Using XRF

Dear Ms. Mora-Applegate:

Recently there has been interest in an expanded role for the use of field-portable x-ray fluorescence (XRF) instruments to assess site soil contamination. XRF offers potential advantages over conventional fixed-based laboratory analyses in terms of cost and speed with which soil concentration data can be obtained. However, field portable XRF devices are currently considered to provide primarily screening level data, to be used in conjunction with confirmatory analysis by other U.S.EPA-approved methods. The ability of XRF-generated data alone to support decision-making at sites (e.g., whether or not remediation in specific areas is required), is dependent on the precision of the individual instrument and its ability to identify the specific analyte of concern and to determine the true concentration of the analyte in the specific matrix. To facilitate Department review of any proposed expanded use of XRF beyond field screening, we have summarized existing guidance and relevant peer-reviewed literature with particular attention to methods for assessing the quality of data from XRF. We have included information specific to arsenic, as the use of XRF for assessment of arsenic soil contamination has been recently proposed.

#### **General Recommendations on the Use of XRF**

The portable XRF can be used in the field to assess metals in soil using three different procedures: 1) *in-situ* soil testing - the XRF measures the metal concentrations in soil directly by placing the instrument on the surface of the ground, without any sample processing, 2) bagged soil testing - the soil sample is placed in a thin plastic bag, the XRF is used to measure the metal concentrations through the bag and 3) prepared soil - the soil samples are dried (if necessary), sieved and homogenized prior to analysis by XRF. The prepared soil is considered the most accurate method, while the *in-situ* and bagged soil sample testing are considered field-screening methods (Innov-X Systems 2003; Olympus/Innov-X Systems 2010).

EPA Reference Method 6200 (U.S. EPA 2007) provides guidance on the use of XRF for measuring metals in soil and sediment. It indicates that XRF is intended as a screening method, recommending confirmatory analysis by a total-digestion EPA analytical protocol. However, if comparisons with laboratory-based measurements indicate that XRF meets definitive data quality objectives, it could potentially be used to make a decision based upon an action level with respect to site remediation.

### **Criteria Used to Evaluate XRF Field Performance**

The applicability of field XRF technologies to measure trace elements in the soil have been previously evaluated by the U.S. EPA under the Superfund Innovative Technology Evaluation (SITE) Program (U.S. EPA 1998; U.S. EPA 2006). However, individual instrument performance is dependent on the analyte being measured as well as the physical and chemical properties of the matrix of concern, and therefore XRF performance should be characterized for the analyte of interest, under field-specific conditions.

Evaluation criteria used by the U.S. EPA to assess instrument performance based on method detection limit (MDL), accuracy and precision are summarized below.

#### ***Method Detection Limit***

The usefulness of XRF for site characterization depends in part on the limits of detection for elements of interest. MDL of the instrument is dependent on a number of factors, including the sample matrix, the analyte being measured, inter-elemental interferences, and measuring time. The detection limits reported for each instrument by the manufacturer, are based on a clean spiked SiO<sub>2</sub> matrix, with a 1-2 min measuring time, in the absence of interfering elements (Olympus LOD brochure; U.S. EPA 2007). These detection limits will not necessarily apply to field samples due to potential matrix interferences. EPA Method 6200 indicates that limits of detection for a given instrument should to be established in the matrix of interest based upon spike recoveries. Alternatively, certified reference material from the appropriate matrix can be used.

#### ***Accuracy of the instrument***

To evaluate the accuracy of the instrument, data obtained using XRF is compared with paired laboratory data obtained using EPA-approved analytical methods. The accuracy of the instrument is assessed based on the absolute value of the relative percent difference (RPD), and correlation plots between the XRF and laboratory data.

As an example, the U.S. EPA evaluated the accuracy of XRF measurements for several elements in soil (U.S. EPA, 1998). The RPD between the reference laboratory results and the paired XRF value was calculated for 70 samples, using the following equation:

$$RPD = \frac{(M_R - M_D)}{\text{Average}(M_R - M_D)}$$

$M_R$  = mean reference laboratory measurement  
 $M_D$  = mean XRF instrument measurement

The median and absolute RPD values were used to classify the data quality in the following categories:

*Excellent*- Median RPD 0%-10%  
*Good*- Median RPD 10-25%  
*Fair*- Median RPD 25-50%  
*Poor*- Median RPD above 50%

To assess the effects of analyte concentrations on the accuracy of the instruments the data were grouped based on concentration ranges (ie. low, medium and high). Comparability of the XRF data with the laboratory results was also analyzed using linear correlation plots. The linear regression calculation and correlation coefficient ( $r^2$ ) were used to assess general bias of the instrument.

### ***Instrument Precision***

The precision of the XRF instrument was evaluated for the target analytes by calculating the relative standard deviation (RSD) for replicate samples, using the equation below:

$$RSD = \left| \frac{SD}{\bar{C}} \right| * 100$$

RSD = Relative standard deviation

SD = Standard deviation

$\bar{C}$  = Mean concentration

In the U.S. EPA's evaluation of XRF instruments (U.S. EPA 1998), the precision of the XRF technology for each analyte was classified based on the median RSD from high to low, using the following criteria:

*High*- Median RSD: 0%-5%  
*Moderate*- Median RSD 5%-10%  
*Low*- Median RSD- 10%-20%  
*Very Low*- Median RSD above 20%

U.S. EPA Method 6200 also has precision criteria. In order for XRF data to be considered adequately precise, the RSD should be no greater than 20%, with the exception of chromium (which should be no greater than 30%).

### **Data quality requirements**

The 1998 U.S. EPA Technology Verification Report for field XRF analyzers categorized the data based on one of the following three data quality levels: 1) definitive, 2) quantitative screening and 3) qualitative screening (U.S. EPA 1998).

Definitive level data is considered analyte-specific, and has a high degree of quantitative accuracy. Quantitative screening data provide analyte-specific identification; however the concentration quantification is not precise. The Quality Assurance/Quality Control Guidance for Removal Activities (U.S. EPA 1990) recommends that a minimum of 10% of the screening level data samples be verified using an EPA-approved method with QA/QC criteria associated with definitive data. Qualitative screening level data provide information regarding the presence or absence of contaminants. They do not, however, provide accurate concentration estimates. The statistical requirements for each of these data quality levels are summarized in the table below.

**Table1. Quality criteria used by the U.S. EPA to validate field XRF data based on confirmatory laboratory values.**

<b>Data Quality Level</b>	<b>Statistical requirements</b>
Definitive Level	$r^2 = 0.85$ to 1.0. Relative standard deviation (RSD) less than or equal to 10%. Inferential statistics indicate that the two sets of data are statistically similar.
Quantitative Screening Level	$r^2 = 0.70$ to 1.0. Relative standard deviation (RSD) < 20%. Inferential statistics indicate that the two sets of data are statistically different.
Qualitative Screening Level	$r^2 > 0.70$ . Relative standard deviation (RSD) > 20%. The data should have less than 10% false negative rate.

From U.S. EPA 1998

### **Application of field- portable XRF technology to evaluate arsenic in soil**

Portable XRF technology has been shown to be a promising method that can be used in the field to measure soil levels of arsenic (U.S. EPA 1990; U.S. EPA 1998; U.S. EPA 2004), even at trace concentrations (low ppm) (Parsons et al. 2012). The commercially available Delta Handheld XRF Analyzers report the limits of detection (LODs) for arsenic ranging between 1 and 4 ppm in a bulk SiO<sub>2</sub> matrix free of any interfering elements (Olympus 2013). The LOD for arsenic reported for the 2003 Delta XRF model is 9 ppm. The correlation between soil arsenic concentration measured using Delta XRF analyzer and laboratory results has a calculated  $r^2$  value of 0.99 according to the manufacturer. However, the LODs and accuracy of the XRF devices for the analysis of arsenic in the field can be affected by different factors. Consequently, instrument performance should be evaluated on a site-specific basis.

A recent study by Parsons et al. (2012) evaluated the effects of instrument parameters, sample preparation techniques and matrix characteristics on the level of detection and the data quality for measuring trace levels of arsenic in a floodplain soil. The method for arsenic characterization *in situ*, where the soil was homogenized, sieved (<2 mm) and compacted in the field reported an estimated

MDL of 6.8 ppm with 14.4% RSD precision. Comparison between the paired field and laboratory data resulted in an  $r^2$  of 0.93. Improvements in the MDL, precision and  $r^2$  were observed with increased soil preparation steps, such as drying and homogenization and grinding the samples.

The lowest MDL for arsenic reported in this study was 5.8 ppm, with an  $r^2 = 0.96$  when XRF results from extensively prepared samples were compared with measurements using ICP-MS. The soil preparation method with the lowest MDL involved homogenization, sieving (<2 mm), lyophilization, grinding to >63  $\mu\text{m}$ , compaction, and measuring the arsenic concentrations using XRF sample cups. The study concluded that careful sample preparation and instrument calibration based on site-specific standards can improve the limits of detection for arsenic, accuracy and precision.

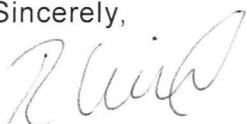
### **Lead interferences with arsenic measurements**

The presence of lead in the soil interferes with arsenic measurements by overlapping the arsenic  $K\alpha$  spectral peak (U.S. EPA 2007; Olympus 2010). However, the instrument's software is designed to correct for the lead interference, and it may only be of concern when the arsenic concentrations measured are low, or if the lead to arsenic ratio is above 10. The presence of lead in soil is reported by the manufacturer to result in higher detection levels for arsenic, and decrease the precision of the instrument.

In summary, XRF instrument performance can vary depending upon the instrument, analyte, and site-specific conditions. The performance of the instrument on a site-specific basis, along with the data quality objectives for the site, determine the limits on the use of XRF data (i.e., screening versus definitive). The U.S. EPA provides guidance for determining XRF instrument accuracy, precision, and MDL, as well as data quality requirements for its intended uses.

We hope that this background information is helpful to the Department when considering proposals for expanded use of XRF, in particular for generating definitive data. Please let us know if you have any questions.

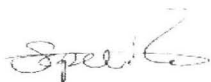
Sincerely,



Roxana E. Weil, Ph.D.



Leah D. Stuchal, Ph.D.



Stephen M. Roberts, Ph.D.

## References

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