Research Paper

Validation of handheld X-ray fluorescence for in situ measurement of mercury in soils

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ABSTRACT

Handheld X-ray fluorescence (XRF) devices hold promise for quick field screening of contaminated sites, but so far, these devices have not been successfully used for mercury screening because of poor sensitivity and questionable accuracy. This paper describes a site-specific calibration method and demonstrates the successful field use of XRF for measuring mercury in the soils of contaminated sites. The method achieved a detection limit of 7.4 mg/kg Hg with a 60-s analysis time. This improves upon earlier attempts and is sufficient for detecting mercury at generic risk assessment soil screening levels (23 mg/kg Hg). The study also demonstrated levels of accuracy and precision for the method that rivaled traditional laboratory methods. In a split-sample comparison with laboratory Method 7471A, field XRF results agreed with an R^2 of 0.93 and a median coefficient of variation of 15%. Precision estimates from duplicate and triplicate samples were not statistically different between the two methods and were constrained by sample heterogeneity and not method capabilities. This study demonstrates that handheld XRF can be successfully used at contaminated sites to achieve high quality Hg results that are accurate, precise, and at a level of sensitivity that is commensurate with generic risk assessment screening levels.

1. Introduction

The principles and use of X-ray fluorescence spectroscopy (XRF) for elemental analysis have been well-established for many years [1–3]. While XRF analysis began as a laboratory-based analytical method, field portable or handheld XRF instruments have been developed over the past several decades [4] and continue to improve in technology and the quality of measurement results [5,6]. Initial uses of handheld XRF devices were primarily for positive material identification of metal alloys and for identification of lead-based paint [4,7]. Use in these areas is still widespread, but handheld XRF use has expanded to numerous other applications including: screening of toxic elements in foods [8] and personal care products [9], identification of trace metals in waste electrical equipment [10], screening of mining ores [11], characterization of agricultural soils [12], analysis of power plant bottom ash [13], identification of treated lumber [14], analysis of geologic samples [15], analysis of dust and air samples [16], extensive use as a forensic tool in art and archeology [17], use as a sourcing tool for geological artifacts [18], and widespread use in the screening and analysis of soils and sediment at contaminated sites [5,19–25].

Handheld XRF devices offer significant advantages for use in the environmental characterization of contaminated sites. These instruments provide broad element selectivity, so sites can be quickly screened for nearly any element in the periodic table [8]. The instruments are relatively rugged and portable to remote or physically challenging sites. There is no (or very little) sample preparation required, which speeds analysis and may provide more environmentally relevant results than laboratory methods that require significant sample processing [12]. Certainly, the greatest advantage of handheld XRF devices is that these field instruments can provide immediate results to support real-time

remediation decisions [20]. Field instruments can greatly reduce the overall cost and investigation time by quickly locating hotspots, developing more targeted sampling strategies, and efficiently delineating contaminated areas in the field [25]. Reducing the turnaround time of sample reporting and decision-making can greatly impact the overall pace of remediation at contaminated sites, which is important considering that over 1300 sites are currently on the Superfund National Priority List and an additional 3779 Resource Conservation and Recovery Act (RCRA) corrective action sites are targeted for cleanup by 2020.

The primary disadvantage of handheld XRF use at contaminated sites is that these instruments typically do not achieve the accuracy, precision, and level of detection obtained with laboratory-based methods [6]. These performance characteristics, however, differ according to the target element and the instrument. Some researchers have reported very good performance of XRF devices for certain metals and major compositional elements [26]. Parsons et al. demonstrated acceptable levels of detection, accuracy, and precision for As measured in soils by XRF [19]. Higueras et al. reported excellent performance for As, Cd, Cu, Pb, and Zn in soils [27]. Radu and Diamond reported good agreement between XRF and atomic absorption spectrometry for As, Cu, Pb, and Zn [24]; while DiScenza et al. found good agreement for Pb but not for As [28]. Based on comparisons with National Institute of Standards and Technology (NIST) standards and ICP analysis, Weindorf et al. concluded that XRF can be used to accurately identify most heavy metals in soils [12]. While this conclusion was true for As, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Ti, and Zn; results were not accurate for Cd, Co, and Hg. Similarly, Vanhoof et al. demonstrated good accuracy and level of detection for Pb and Zn, but failed to achieve sufficient levels of detection for Cd, Cr, Ni, and Hg to properly evaluate accuracy in field samples [25].

While XRF performance results for some elements have been promising, specific attempts to use XRF for the analysis of Hg in soils have been particularly disappointing. Kalnicky and Singhvi [20], Stosnach [5], Weindorf et al. [12], Vanhoof et al. [25], and the U.S. Environmental Protection Agency (EPA) [29] all initially failed to achieve Hg detection limits low enough to provide relevant results for contaminated site screening. Even when Hg detection levels were sufficient (20 mg/kg Hg), Miller et al. concluded that the XRF method was unreliable for the analysis of Hg due to poor accuracy and could result in the underestimation of Hg concentrations by more than an order of magnitude [21]. Other authors cited soil moisture as a potential interference with XRF results [20].

In this study, a handheld XRF device was evaluated as a field screening tool for soil Hg as a part of on-going remedial investigations along the South River in Waynesboro, Virginia (USA). To improve the XRF performance over previously published attempts, instrument parameters were optimized for Hg detection, and a site-specific calibration was developed using previously collected samples with known Hg concentrations. XRF performance measures of sensitivity, accuracy, and precision were evaluated across 239 field samples that were split for field and laboratory XRF analysis and confirmation using the laboratory-based cold vapor atomic absorption method (EPA SW-846 Method 7471A) [30].

2. Materials and methods

2.1. Field site

Historical Hg releases from a textile manufacturing facility in Waynesboro, Virginia (USA), have resulted in widespread downstream contamination of a 25-mile stretch of the South River [31]. While the original discharge of mercury to the river ceased more than 60 years ago, elevated mercury concentrations continue to be measured in a number of different biota, including invertebrates [32], amphibians [33], reptiles [34], fish [35], birds [36], and mammals [37]. The Virginia Department of Health posts the entire 25-mile stretch of the South River and an additional 100 miles of the adjoining South Fork Shenandoah River with a fish consumption advisory to protect human health.

Remedial investigations at the site have identified erosion of the contaminated stream banks as the primary source of mercury currently entering the river [38]. Periodic flooding during the mercury release period (1929–1950) stored large amounts of inorganic mercury in floodplain soils and river banks. As these contaminated bank soils erode, inorganic mercury enters the river and is temporarily stored in fine-grained river sediments. During storage, mercury within anoxic sediment deposits is methylated to provide a readily available source of organic mercury for biological uptake and accumulation. Studies have estimated from 97 kg/yr [38] to 188 kg/yr [39] of inorganic mercury loading to the South River from bank erosion. For this reason, interim remediation measures are focused on reducing or eliminating Hg loading to the river through removal and stabilization of Hg-impacted bank soils.

To identify Hg-impacted bank soils and delineate areas for potential remediation, field sampling campaigns have sampled surficial soils at 1-ft to 2-ft intervals along bank transects placed at approximately 100-ft along the first 2-miles of river downstream from the historic discharge. In areas with high Hg concentrations, additional bank transects have been sampled and 1-ft interval vertical bank cores have been taken to better delineated the three-dimensional extent of Hg contamination. In all, more than 2500 bank soil samples have been collected and analyzed for Hg content at fixed laboratories. During two recent investigations, a Bruker Tracer III-SD Handheld XRF Spectrometer was evaluated as a field screening tool for real-time analysis of Hg in soils as a part of on-going remedial investigations.

2.2. Experimental design

The objective of the current study was to develop site-specific Hg calibration data and evaluate the precision and accuracy of the field XRF method compared to conventional laboratory analysis using EPA Method 7471A [30]. In 2015, a site-specific empirical calibration for the XRF was developed using bank soil samples collected from the South River and analyzed for Hg using Method 7471A. In 2016, a field and laboratory validation study of the calibrated XRF method was conducted. For this validation study, a total of 239 bank soil samples were collected from the South River remediation site, analyzed for Hg in the field using the XRF, shipped to a laboratory for confirmatory Hg analysis using EPA Method 7471A, and then shipped to James Madison University for follow-up laboratory testing using the XRF.

2.3. Field sampling

Fifty-one surficial soil and soil core samples were collected in 2015 for preliminary XRF testing. An additional 239 surficial soil and soil core samples were collected in March 2016 as a part of the field and lab validation study. Surficial soils were collected using a stainless steel trowel, while bank cores were collected using a 2-in bucket auger. For surficial samples, 2-ft intervals along the bank face were composited in a stainless steel bowl and homogenized by hand. For bank cores, 1-ft depth intervals were composited on a plastic sheet and homogenized by hand. Homogenized samples were split into two subsamples; one was used on-site for real-time XRF analysis, and the other was placed in 250-ml plastic containers and shipped on ice to Eurofins/Lancaster Laboratories (Lancaster, PA) for total Hg and moisture analysis.