

Application of portable X-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites

Introduction

In South Korea, about 936 abandoned metal mines are creating hazards such as soil contamination, acid mine drainage, tailing discharge, ground subsidence, and others (deforestation, abandoned facilities, waste rocks, noise and dust, etc.). Among these hazards, the contamination of farmland soils has mostly occurred because of several factors, such as tailing discharge, overflow of heavy metal-contaminated sludges, usage of contaminated ground and surface water, etc. Tailings have also occasionally been discharged from defective dams into crop fields by severe weather events (mostly typhoons). Heavy metal contamination of paddy or upland fields has the characteristic problem of involving widely spread out properties, resulting in the need to survey large areas. Accordingly, it is expensive to survey a wide range of farmland areas prior to remedial soil processes. In addition, crop contamination occurring by the transfer of contaminants from soils has risen as a social problem.

The Korean Standard Test (KST) for soils is currently applied to investigate soil contamination and regulate the maximum concentration levels of heavy metals in soil (MOE 2002). However, this method is an off-site analysis and has many steps, including the extraction procedure with a strong acid solution. It is also quite complex and expensive, and takes a long time. Accordingly, since a rapid and appropriate analysis of the contaminated area is critical for successfully conducting the remedial operations within a constructed time schedule, it is necessary to have an alternative advanced method to overcome these shortcomings of the KST for soils. The EPA method 6200 using a portable X-ray fluorescence (pXRF) device was incorporated into the SW846 under the Resource Conservation and Recovery Act (RCRA) and is available for field analysis of soils and sediments (EPA 2007). Portable XRF is a non-destructive analytical technique, allowing both qualitative and quantitative analysis of metal species in soils. The mechanism of pXRF analysis can be briefly explained as follows:

(1) an incident X-ray photon produced from a radioisotope source excitation device of the pXRF creates an inner shell vacancy in which an electron leaves the inner shell; (2) when the atom relaxes to the ground state, an outer shell electron falls to make up for the inner shell vacancy; (3) then photons are given off with an energy in the X-ray region of the electromagnetic spectrum that is equivalent to the energy difference between the two shells; (4) the energy level and intensity of these emitted X-rays identify the elements and their concentrations, respectively (Kalnicky and Singhvi 2001; Stallard et al. 1995). More detailed description of the mechanism of metal analysis by pXRF is provided elsewhere (VanCott et al. 1999; Hettipathirana 2004). The heavy metal analysis using a pXRF saves time, and large numbers of heavy metals can be simultaneously detected with high sensitivities. There are two methodologies in the EPA method 6200 using pXRF: field screening (in situ testing) and precise measurements (ex situ testing). Field screening by use of a pXRF could be conducted with in situ or bagged sample testing by measuring many soil samples within a short time, while precise analysis for prepared soil samples takes longer for preparing samples, for example, because of the drying and sieving process. In terms of accuracy, the in situ testing can result in a high range of errors in metal measurement, whereas highly accurate results can be obtained by the precise analysis of pXRF by preparing a homogeneous size distribution of soil grains, as well as deleting the water content of soils. For field screening like in situ testing, a pXRF could also be used in actual crop fields. However, since the measurement of in situ tests could not be as precise as ex situ testing with prepared samples due to the water content and heterogeneous soil size distribution (Kalnicky and Singhvi 2001), we need to develop a proper method to obtain representative concentrations of metal species for crop fields. The in situ pXRF measurement for contaminated soils can be effectively applied to achieve an economical survey by determining hot spots or non-contaminated areas before the refined investigation. For the precise analysis using a pXRF, samples should be

dried and sieved to have a homogeneous fraction ($\leq 125 \mu\text{m}$). However, prior to in situ or ex situ pXRF application for an actual survey of soil contamination, it is necessary to determine the correlation with results of KST for soils that is actually applied to regulate soil quality. In this study, a pXRF was used to measure concentrations of As, Cd, Cu, Pb, and Zn in soils via in situ and ex situ applications, and then the results were compared with data obtained by the KST extraction method for soils to determine linear regression correlations between two different tests. Eventually, applicability with pXRF was assessed for in situ and ex situ testings.

Materials and methods

Soil sampling and pXRF analysis

Following the Soil Environmental Conservation Law, which was established by the Korea Ministry of the Environment in 1995, a zigzag method (Fig. 1) was applied to have a composite sample from paddy or upland fields in an abandoned mine area (MOE 2002). For this method, five to ten soil samples were collected at different locations with 5–10-m intervals and then mixed well to have a soil sample for each field. From this sample, water and other matter such as gravel, leaves, or twigs were removed to get a final composite sample that could be representative for heavy metal concentrations of each field. The collected soil samples were transported to a soil laboratory, spread out with homogeneous thickness on the PE vat, and air-dried for 10 days. After drying, soils were sieved with a 10-mesh sieve ($\leq 2 \text{ mm}$) to obtain soil samples for As, Cu, Pb, and Cd extraction tests, following the KST for soils. According to the KST for soils, soils were sieved with a 100-mesh sieve ($\leq 125 \mu\text{m}$) to conduct total Zn concentration and ex situ pXRF analysis (EPA 6200 method). For ex situ and in situ application, a portable XRF (Innov-X system, alpha-4000 series) equipped with an X-ray tube as an irradiation source and calibrated with the Compton normalization method was used to conduct the analysis of metal species in this study.

Full text is available at :

<http://www.ncbi.nlm.nih.gov/pubmed/19768558>

<http://link.springer.com/article/10.1007/s10653-009-9276-z>