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Rapid assessment of smelter/mining soil contamination via portable X-ray fluorescence spectrometry and indicator kriging

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ABSTRACT

Industrial pollution is a worldwide problem, especially near mining/smelter sites where toxic metals tend to accumulate in soils, sediments, and water. These elements pose a risk both for humans and other organisms' health. In Eastern Europe, assessment of toxic elements such as Pb, Cu, Zn, and others remain challenging because traditional methods are costly and time consuming due to sample collection, chemical digestion, and quantification in laboratories. To reduce these limitations, new assessment methods are needed for deployment in impacted areas. The study conducted herein is the first of its kind to combine portable X-ray fluorescence (PXRF) spectrometry with non-parametric indicator kriging for rapid soil pollution hotspot mapping in Eastern Europe. PXRF was used to assess As, Cu, Cr, Mn, Pb, Zn, and V at 131 georeferenced points (121 impacted; 10 control) in and around the city of Baia Mare, Romania. For spatial variability analysis, ordinary kriging interpolation was used to predict elemental levels in unsampled locations. Pb exceeded the action limit in 91.09% of the area, followed by As (81.20%), Cu (41.52%), Zn (26.69%), and Cr (5.58%). Indicator kriging was then used to estimate the probabilities of data exceeding certain threshold levels. As a result, the pollution hotspots were quickly identified. The highest estimated probabilities of surpassing the Romanian action limits were found around the smelting plant and dispersal stack. Results indicated a likelihood of exceeding action limits of 75% for Cu and between 50 and 75% for Zn. A major portion of the study area showed high probabilities for As and Pb surpassing the Romanian action limits by 75%. Summarily, the PXRF/indicator kriging approach proved effective at rapidly assessing the potential of metal-laden soils to exceed government mandated limits. Using this approach, other cities impacted by similar operations can quickly and cost effectively map areas of concern.

1. Introduction

Toxic metals are pervasive throughout the environment and pose serious threats to both human health and ecological sustainability. The sources of toxic metals in soils are numerous, some naturally occurring from geologic deposits. However more commonly, toxic metals accumulate in soils due to anthropogenic impacts via metallurgy, industrial pollution, petrochemical refining, fertilizer application, and irrigation practices with metal laden waste. The term "heavy metals" is often used to describe such elements based upon their density, though no consensus exists on the exact definition of which elements meet such criteria. As such, we will refer to such elements as "toxic metals" herein, the most commonly cited of which are As, Cd, Hg, and Pb (As is considered a metalloid); the toxicity of which is related to their relative concentrations within the soil. However, exposure to high levels of the aforementioned elements and even other more benign elements such as Zn, Cu, and Ni can also cause health problems.

Many studies have been conducted worldwide focusing on the anthropogenic causations of toxic metal pollution in soils (Kabata-Pendias, 2011; Wuana and Okieimen, 2011). For example, Sallaku et al. (2009) found that smelting plants around Elbasani, Albania produced high levels of soil contamination up to 20 km away from the production facilities through fine particle and gas emissions. Moreover, industrial pollution by toxic metals from rapid industrialization in China has been shown to denude soil quality (Hu et al., 2013). Disposal of some 270 billion pounds of petrochemical refining waste into containment

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pools and waste sites has increased toxic metal deposition on site when compared to that of various reference sites (Schroder et al., 2000). Furthermore, commercial fertilizers, especially those that use phosphate rock as a source of P, have also been shown to contain toxic metals which can be detrimental to soils and the food chain (Mortvedt, 1996). The application of sewer sludge and associated byproducts is of great concern as toxic metals often persist and contaminate the soil (Lake et al., 1984). Plants taking up nutrients via soil solution also absorb toxic metals, thus introducing them into the food chain (Hooda et al., 1997). Surface waters and irrigation practices with metal laden waste can also contribute to high toxic metal levels in soils (Khan et al., 2008). For example, Nazif et al. (2006) reported that contaminated manure and pesticides containing toxic metals associated with industrial wastewater migrated into soils of Pakistan.

Though there are many sources of anthropogenic toxic metals in the soils of Eastern Europe, smelting activities have been a major contributor to toxic metal accumulation in soils of Romania in particular. For example, Krüger and Carius (2001) identified 14 villages and small cities in rural Romania with substantive environmental pollution to include: Copşa Mică, Baia Mare, Zlatna, Ploieşti-Brazi, Oneşti, Bacău, Suceava, Piteşti, Târgu Mureş, Turnu Măgurele, Tulcea, Işalniţa, Braşov, and Govora. While the problem of toxic metals is generally known and accepted in the villages, limited information exists as to the spatial extent of the pollution, effectiveness of remediation or isolation efforts, and the impacts that the toxic metals are having on the health of the local populations. Furthermore, spatial variability assessment is constrained by the time and cost associated with traditional laboratory analysis. To date, only a few studies have used portable X-ray fluorescence (PXRF) spectrometry for soil analysis in Romania. Several methods have established the technique for scientific study whereby a handheld spectrometer featuring low power X-rays is used to scan soil samples in-situ and provide total concentration for multiple elements simultaneously (US-EPA, 2007; Weindorf and Chakraborty, 2016; Soil Survey Staff, 2014). Ene et al. (2011) used a handheld Thermo Scientific XLTj-700 series NITON energy dispersive PXRF to evaluate soils of Galati, Romania in a zone of iron and steel production. All samples featured elevated levels of Ni, Cr, and As relative to local background levels, while some other samples exceeded Romanian alert levels for Hg, Cd, and Se. Ulmanu et al. (2011) used an Oxford Instruments X-MET 3000 TX analyzer to evaluate soils collected from an old metallurgical industrial area of Bucharest, Romania. Comparing PXRF results to those obtained by laboratory analysis (AAS), they concluded that the best correlations were obtained for Pb and Mn. Furthermore, they found that disparity between PXRF and laboratory results was larger at low elemental concentrations. Paulette et al. (2015) and Weindorf et al. (2013) used a Delta Premium DP-6000 PXRF to evaluated anthropogenically impacted soils in Copşa Mică and Zlatna, Romania, respectively. These two studies have served as comparative precursors to the present study, demonstrating the environmental assessment power of combining PXRF with spatial interpolation for rapid delineation of impacted areas. In a pilot study by Weindorf et al. (2015) near the Baia Mare Cuprom smelter, both Cu and Pb were noted to be > 30 times the action limit established by Romanian guidelines. A few other studies in Romania (e.g., Huzum et al., 2012) have utilized laboratory based XRF instruments such as the PANalytical Epsilon 5.

Prolonged exposure to metals such as Cu, Pb, Ni, V, and Zn can cause deleterious health effects in humans, many with both acute and chronic effects (Singh et al., 2011). Lead is one of the most pervasive toxic metals found in urban soils. The literature contains numerous examples of Pb accumulation in urban settings as well as peri-urban landscapes impacted by industrial activity (Clark and Knudsen, 2014; Laidlaw and Filippelli, 2008). Even in 2015, the city of Flint, Michigan in the United States endured a public health crisis related to Pb entering the public drinking water supply. Given the serious, long lasting health implications of metal exposure, governments worldwide have established health limits for maximum allowable concentrations of metals in soils. The Romanian Ministry of the Forest, Waters, and Environment (1997) established government mandated alert and action limits for soil elemental concentrations [see Supplementary material (SM), Table SM-1). The former is the value at which increased scrutiny should be applied to soils indicating that concentrations are likely above geochemical background levels while the latter should trigger action in the form of isolation or remediation to protect human health. Less sensitive land use includes all existing commercial and industrial uses, and land surfaces provided for such use in the future. Sensitive land is best conceived of as land supporting agronomic production, gardens, pastures, or wilderness. Background (normal) soil values for Romania as well as topsoil median values for Europe and worldwide are given in Table SM-1 (Salminen et al., 2005; Bowen, 1979; Romanian Ministry of the Forest, Waters, and Environment, 1997). It is important to note that total elemental content in soils may or may not coincide with its environmental availability/mobility. However, as the former is used in establishing government mandated limits, it will be the focus of this study.

Given the widespread, well documented problems of toxic metal contamination in the soils of Baia Mare, Romania (Weindorf et al., 2015) the application PXRF spectrometry coupled with geographic information system spatial interpolation to rapidly acquire and model toxic metals data in surface soils seems timely. As the third of a three part investigation (Weindorf et al., 2013; Paulette et al., 2015), this study aims to establish a novel approach of combining PXRF results and non-parametric indicator kriging (IK) for rapid soil pollution hotspot mapping. Recently, Chakraborty et al. (2017) established the potential of another proximal sensing approach called diffuse reflectance spectroscopy combined with indicator kriging for rapid identification of soil As pollution hotspots. Since the combination of PXRF and IK has not been tested for soil contamination assessment yet, this study aims to validate the viability of this approach for widespread application in areas of Eastern Europe where use of the PXRF is not yet well understood (especially by field-level scientists) nor widely deployed. Specifically, the objectives of this study were to: 1) evaluate the utility of PXRF for qualitatively separating contaminated soils from uncontaminated soils, 2) identify soil heavy metal pollution hotspot areas by combining PXRF results and IK interpolation, and 3) compare elemental abundances of the Baia Mare industrial site with similar impacted sites in Romania. We hypothesize that the combination of PXRF and IK interpolation will be highly effective at identifying of soil pollution hotspots, more quickly and inexpensively than traditional laboratory approaches.

2. Materials and methods

2.1. General occurrence and features

Baia Mare is a small city located in Maramureș County, northern Romania, in the Baia Mare Depression (228 m altitude) (Fig. 1). It is positioned near the middle of the Săsar River at the foot of the Gutâi Mountains. The depression is surrounded by a 50 km long mountain chain: Văratec - Gutai - Oaş, formed during the Neogene, the result of intense volcanic activity. Igneous rocks of these mountain massifs contain metallic ores of lead, zinc, copper, gold, and silver, some of which occur in the free state. In the southeast and southwest extents of the depression, sedimentary rocks, clay, marls, and alluvial deposits (gravel, coarse grained sand) are common (Damian et al., 2008).

Climate of the area is Mediterranean-like, with mild winters (average temperature − 2.4 °C in January) and long summers (19.9 °C average temperature in June), due to the Carpathian Mountains shielding against colder weather from the northeast. Precipitation is generally constant throughout the year, averaging 976 mm. Winds are minimal, with no outstanding features. Air masses tend to immobilize in the depression offering long periods of calm conditions across the city, a circumstance that has negatively impacted pollution in the city