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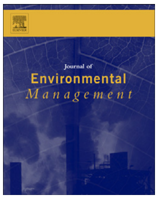

Research article

Elemental assessment of vegetation via portable X-ray fluorescence (PXRF) spectrometry

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ABSTRACT

Elemental concentrations in vegetation are of critical importance, whether establishing plant essential element concentrations (toxicity vs. deficiency) or investigating deleterious elements (e.g., heavy metals) differentially extracted from the soil by plants. Traditionally, elemental analysis of vegetation has been facilitated by acid digestion followed by quantification via inductively coupled plasma (ICP) or atomic absorption (AA) spectroscopy. Previous studies have utilized portable X-ray fluorescence (PXRF) spectroscopy to quantify elements in soils, but few have evaluated the vegetation. In this study, a PXRF spectrometer was employed to scan 228 organic material samples (thatch, deciduous leaves, grasses, tree bark, and herbaceous plants) from smelter-impacted areas of Romania, as well as National Institute of Standards and Technology (NIST) certified reference materials, to demonstrate the application of PXRF for elemental determination in vegetation. Samples were scanned in three conditions: as received from the field (moist), oven dry (70 °C), and dried and powdered to pass a 2 mm sieve. Performance metrics of PXRF models relative to ICP atomic emission spectroscopy were developed to asses optimal scanning conditions. Thatch and bark samples showed the highest mean PXRF and ICP concentrations (e.g., Zn, Pb, Cd, Fe), with the exceptions of K and Cl. Validation statistics indicate that the stable validation predictive capacity of PXRF increased in the following order: oven dry intact < field moist < oven dried and powdered. Even under field moist conditions, PXRF could reasonably be used for the determination of Zn (coefficient of determination, R^2_{val} 0.86; residual prediction deviation, RPD 2.72) and Cu (R^2_{val} 0.77; RPD 2.12), while dried and powdered samples allowed for stable validation prediction of Pb (R^2_{val} 0.90; RPD 3.29), Fe (R^2_{val} 0.80; RPD 2.29), Cd (R^2_{val} 0.75; RPD 2.07) and Cu (R^2_{val} 0.98; RPD of 8.53). Summarily, PXRF was shown to be a useful approach for quickly assessing the elemental concentration in vegetation. Future PXRF/vegetation research should explore additional elements and investigate its usefulness in evaluating phytoremediation effectiveness.

1. Introduction

Soils impacted by metal pollution are common worldwide, often occurring in areas of industrial processing (e.g., petrochemical refining, mining, smelting). Industrial metal pollution can stem from an acute source such as a spill, or via long term accumulation by eolian deposition of dusts (Wuana and Okieimen, 2011). Alternately, metals can also occur naturally in soils as a result of parent material weathering (Micó et al., 2006) or irrigation with metal-laden groundwater or surface waters (Roberts et al., 2007); in fact, some metals are also plant essential elements (e.g., Cu, Mg, Zn, etc.). In the soil, such metals pose limited risks to humans, mostly through dermal exposure and direct contact. However, unique plant species are known to differentially accumulate different metals, via absorption of metal-laden water, whereby the metals accumulate in plant organs (e.g., roots, stems, leaves, fruits, seeds).

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For example, *Alyssum* spp., *Brassica pekinensis, Noccaea (Thlaspi) caerulescens, Arabidopsis halerii, Sedum alfredii,* and *Pteris* spp. have been linked to Ni, Pb, Zn, Cd, and As uptake, respectively (Courbot et al., 2007; Lochlainn et al., 2011; Craciun et al., 2012; Hanikenne et al., 2008; Halimaa et al., 2014; Li et al., 2003; Srivastava et al., 2006; Xiong, 1997; Zhang et al., 2011). Finally, concerns exist over the presence of pesticides, pollutants, and other chemicals in vegetal materials (Zeng et al., 2013, 2016; Schafer and Kegley, 2002; Khan et al., 2008).

While plant uptake of metals can be of concern if the plants are used as food for human consumption (Millis et al., 2004; Podar et al., 2004; Podar and Ramsey, 2005), certain plant species can also be used as an effective phytoremediation option for metal-laden soils (Brooks et al., 1998; Pollard et al., 2014). Furthermore, a metal hyperaccumulator plant species can be utilized for the purpose of phytomining; where a crop is grown to extract metal from the soil to be harvested and processed for metal recovery (Ali et al., 2013; Barceló and Poschenrieder, 2003; Brooks et al., 1998). Ali et al. (2013) note that the quantity of metal recovered by vegetal hyperaccumulators can vary from a few hundred to several thousand mg kg^{-1}; the best choices for active phytomining are plants featuring a rapid growth rate, aboveground biomass production, highly branched root system to exploit the maximum amount of contaminated soil, ability to translocate metals from roots to shoots, and easy cultivation/harvest.

For decades, the analytical standard for elemental analysis of plant materials has been atomic absorption spectrophotometry (AAS) (Hanlon, 1998) or inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Isaac and Johnson, 1998). In such methods, vegetal samples are subjected to acid digestion while heating, placing all elements into an acidic solution which can then be aspirated across a torch for elemental quantification. While accurate, this approach is time consuming and requires extensive laboratory equipment and consumables. Laboratory-based X-ray fluorescence has also been successfully used to quantify elements in plant material (Watson, 1998), though some limitations such as its inability to detect light elements (e.g., N, B) were noted. By contrast, portable X-ray fluorescence (PXRF) spectrometry is a proximal sensor system which has been shown to provide multi-elemental quantification in soils (Weindorf et al., 2014), water (Pearson et al., 2017), and several other matrices. The key advantages of PXRF relative to traditional laboratory based approaches are that it is fast (60–90 s), requires no consumables, and is field portable.

A few studies have previously established the applicability of PXRF to vegetation. McLaren et al. (2011) used a Bruker Tracer III-V PXRF (equipped with He purge and Si-Pin detector) to evaluate elemental concentrations in cotton, corn, and wheat. They found significant linear relationships between PXRF and acid digest datasets for Ca, Co, Cr, Fe, K, Mn, Ni, P, S, Si, and Zn, concluding that PXRF "provides an efficient alternative to traditional plant digestion." Paltridge et al. (2012a) used laboratory based energy dispersive XRF to determine Fe and Zn in rice and pearl millet grain. They found strong R^2 values (0.79–0.98) between XRF and ICP methods, concluding that XRF is a convenient and economical approach for elemental determination. Similarly, Paltridge et al. (2012b) found strong correlations between the two methodologies for Zn, Fe, and Se in wheat. Moreover, Sacristán et al. (2016) successfully used PXRF to predict Cu in lettuce (*Lactuca sativa* L.). Finally, Towett et al. (2015) reported reliable measurement of S, K, and Ca on dry vegetal powders via PXRF without the use of vacuum, though they concede that lower detection limits may be compromised.

In Romania, extensive metals pollution has been documented in soils; the result of mining and smelting operations in numerous communities (Krüger and Carius, 2001). Previous studies have applied PXRF to examine the spatial variability of metal pollution in soils (Weindorf et al., 2013; Paulette et al., 2015; Chakraborty et al., 2017a), but fewer studies have evaluated the vegetation supported therein and none have applied PXRF for such evaluation. Importantly, areas in the immediate vicinity of the smelters are used today for active agricultural production, causing concerns over potential metal contamination of harvested crops. Such contamination could occur as soil attached to the outer epidermis of root (e.g., carrots, *Daucus carota*) or underground stems (e.g., potatoes, *Solanum tuberosum*), as dust deposited on the leaves of leafy vegetables (e.g., lettuce, *Lactuca sativa*; spinach, *Spinacia oleracea*; cabbage, *Brassica oleracea*), or accumulated in the shoots by transporters for plant nutrient analogs (Krupa et al., 2002) (e.g., Pb^{2+} substituting for Zn^{2+}; Cd^{2+} entering Ca^{2+} transporters).

While previous studies established the potential for PXRF analysis of vegetal materials, they stopped short of evaluating a broad range of organic matrices, variation in elemental concentration caused by vegetal condition (e.g., field moist intact, oven dry intact, oven dry powdered), or considering its use for quantification of toxic metals contained therein. As PXRF quickly gains in popularity, consideration of its broader use on organic matrices seems timely. Thus, the objective of this study was to statistically evaluate the relationships between ICP- and PXRF-determined elemental data under different scanning conditions (moisture, homogenization) to establish the validity of PXRF for direct elemental analysis of vegetal matrices. We hypothesize that PXRF will provide qualitative estimations of elemental concentrations for field moist samples, and more definitive (quantitative) elemental determinations for samples which have been dried and/or homogenized.

2. Materials and methods

2.1. General occurrence and features

Fieldwork for this study was conducted in two locations, Zlatna and Copşa Mică, Romania (Fig. 1). Both cities, located in central part of the country, are known as polluted areas due to industrial mining, ore processing, and smelting operations.

2.2. Zlatna, Romania

Zlatna processed non-ferrous ores between 1747 and 2002. The main industrial unit in Zlatna was represented by Ampelum S.A. producing H_2SO_4, Cu, $FeSO_4$, and $MgSO_4$. Mining and processing activities generated silica dust, gases (e.g., SO_2, CO_2, CO, and various N oxides), and metals released as powders and aerosols (especially Pb). Zlatna is situated in Alba County in the Zlatna-Ighiu depressional corridor of the Ampoi River Valley, a narrow valley with an east-west orientation (Popa, 2005), where the low wind (0.06 m s^{-1}) creates frequent periods (approx. half year) of atmospheric calm allowing metal deposition throughout the valley. The climate is generally wet and cool, with average annual temperature and precipitation between 6 and 8 °C and 800–1000 mm, respectively (Roşu, 1973). The main vegetation is forest, consisting largely of beech (*Fagus sylvatica*) and sessile oak (*Quercus petrea*). Per the *Romanian System of Soil Taxonomy*, Florea and Munteanu (2012) [US Taxonomic equivalent given per Soil Survey Staff, 2014] characterize 63% of soils in the area as Luvisols [Hapludalfs] (mostly on hills) and 27% as Cambisols [Inceptisols] (mostly Dystricambosols [Dystrudepts] developed on acid rocks and Eutricambosols [Eutrudepts] developed on carbonatic diluvium). On steep slopes, Regosols and Lithosols [Udorthents] comprise ~2.5% while floodplain Alluviosols [Udifluvents] cover ~7.5% of the area (Paulette