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# Application of field-portable-XRF for the determination of trace elements in deciduous leaves from a mine-impacted region

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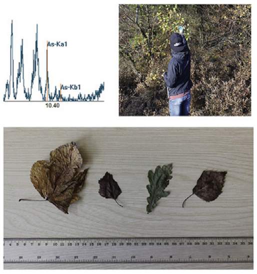
## HIGHLIGHTS

- Field-portable-XRF has been trialled for determining trace elements in intact deciduous leaves.
- In a low density mode detection limits for fresh and dried leaves were generally $<100\ \mu g\ g^{-1}$.
- As and Zn were most commonly detected in leaves from mine-impacted sites.
- Concentrations agreed well with those derived independently from acid digestion-ICP.
- The approach has potential for on-site biomonitoring of deciduous leaves.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Deciduous leaves ($n = 87$) from beech (*Fagus sylvatica*), birch (*Betula* spp.) and oak (*Quercus* spp.) trees have been collected from three metal mine-impacted sites in southwest England and tested for concentrations of trace elements (As, Cu, Pb and Zn) using a field-portable-x-ray fluorescence (FP-XRF) spectrometer configured in a low density mode and housed in a stand. When intact leaves were analysed directly, mean detection limits ranged from about 10 (As) to $70\ \mu g\ g^{-1}$ (Cu) on a fresh weight basis; after freeze-drying, respective limits increased to about 20 and $120\ \mu g\ g^{-1}$ on a dry weight basis. Within these constraints, As and Zn were detected in samples from all genera, with concentration differences between fresh and dry states attributed to the mass of water present and its propensity to attenuate x-rays. A comparison with As and Zn concentrations in local soils and determined by XRF in a higher density mode revealed different accumulation and exclusion characteristics among the three genera of tree. In contrast, and despite soil concentrations that were similar to those of Zn, Cu was detected in only two dried leaves and Pb evaded detection throughout. Pooled results from the study showed good agreement with independent results derived from ICP following acid digestion, with a slope defining the overall relationship that was close to unit value. Accordingly, the XRF approach is able to provide a rapid assessment of the levels of certain trace elements in leaves from contaminated sites, with the configuration deployed on site having potential to deliver immediate results.

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## 1. Introduction

Although mosses and epiphytic lichens have gained widespread use in biomonitoring of airborne trace element pollution, their absence in some urban and industrialised areas has resulted in the study of higher plants (Bargagli et al., 2003; Aničić et al., 2011; Serbula et al., 2014). Many tree species are tolerant of high environmental concentrations of trace elements and leaves are often the main sink for pollutants (Bargagli, 1998). Thus, as well as providing a means of increasing the trace element content of top soils through leaf deposition-decomposition and increasing trace element exposure to consuming organisms, leaves act as potential indicators of both contaminated soil, through uptake via the root system, and polluted air, through wet and dry deposition (Franiel and Babczyńska, 2011; Dimitrijević et al., 2016; Pająk et al., 2017).

At sites impacted by contemporary or historical metalliferous mining, and where the presence of elevated environmental concentrations of many trace elements is a concern, deciduous and evergreen tree leaves have been commonly employed as indictors of soil contamination (Unterbrunner et al., 2007; Dmuchowski et al., 2014; Nirola et al., 2015; Stefanowicz et al., 2016). Here, capture and uptake of a trace element is from a large soil volume, with the concentration in the leaves reflecting availability in the soil rather than total soil concentration. Strictly, and to act as a true bioindicator, uptake through the roots should be relatively constant over a wide gradient of trace element concentrations in the soil such that there should be a linear relationship between concentrations in the leaves and in the soil (Baker et al., 2000; Kabata-Pendias and Pendias, 2001). However, some trees may act as excluders for certain elements by inhibiting their uptake into roots, even at high external concentrations in the soil, while others may act as hyper-accumulators which are able to tolerate high concentrations in their leaves, even at low external concentrations (Madejón et al., 2004; Schmidt et al., 2016); the latter are, therefore, particularly attractive as phytoremediators of highly contaminated soils (Antosiewicz et al., 2008; Dimitrijević et al., 2016).

With different possible sources of trace elements (from the atmosphere and soil) and potentially confounding issues of hyper-accumulation and exclusion, the analysis of a large number of leaf samples is often required at contaminated sites, with repeat visits sometimes necessary. Conventional analysis of leaves involves digestion of the matrix in concentrated mineral acid followed by trace element determination by, for example, inductively coupled plasma spectrometry or atomic absorption spectrometry, but this approach can be time- and resource-consuming and may generate large quantities of hazardous waste. As an alternative, plant material may be determined non-destructively by x-ray fluorescence (XRF) spectrometry. Here, samples are typically dried, milled and packed before being excited by an x-ray beam, with the expulsion of inner electrons of an atom accompanied by electrons cascading from higher orbitals and the emission of characteristic fluorescent x-rays (Sacristán et al., 2016; Towett et al., 2016).

In order to further minimise sample preparation, it may be assumed that the plant matrix has similar characteristics to thin plastic films in terms of the absorption, scattering and fluorescence of x-rays, and analyse material intact (i.e. without milling or packing) using an XRF algorithm that is calibrated for low density matter. This approach was recently tested and validated both in the laboratory and in the field on coastal and marine macroalgae (Bull et al., 2017; Turner et al., 2017) and is trialled in the present study on deciduous leaves. Specifically, the current investigation focuses on the trace metalloid, As, and the trace metals Cu, Pb and Zn, in both common leaves and in soils (with the latter employing more established XRF protocols) at three sites impacted by historical, non-ferrous mine waste. Although tests were performed solely in the laboratory, the potential for applying the approach in the field is also addressed.

## 2. Materials and methods

### 2.1. Sampling

Sampling of leaves and soils was undertaken at three sites impacted by historical (19th century), non-ferrous metal mining activities in west Devon, south west England. The geology of the region is dominated by fine-grained sedimentary sequences and chert with outcrops of granite and slates, and soils are mainly brown earths that are well-drained but subject to slight seasonal waterlogging (Rawlins et al., 2003). The region is sparsely populated, with occasional small settlements and farms, and current land use is dominated by agriculture and managed woodland. The first site (S1) was on Dartmoor National Park in the vicinity of a series of relatively small, disused copper mines (digital coordinates: 50.5130, −4.1116; 85 m asl). The second and third sites were within the UNESCO district of the Tamar Valley at locations influenced by more extensive mining and processing facilities for both copper and arsenic; specifically, S2 was adjacent to an old but functional adit (50.5361, −4.2081; 50 m asl) and S3 was along the northern edge of a large spoil tip (50.5385, −4.2214; 78 m asl).

Each site was visited during mid-autumn (early November) in 2016, following a period of dry weather and as deciduous foliage was being shed. A total of 87 leaves were collected by hand and using plastic tweezers from trees that were common to all sites and that usually occurred in clusters but were occasionally solitary: namely, beech (*Fagus sylvatica*), birch (*Betula* spp., including *B. pendula*) and oak (*Quercus* spp.). Specifically, three leaves were taken from lateral branches at a height of about 2 m from between one and five trees of each genus (depending on their abundance and accessibility) and stored in individual zip-lock specimen bags in a dark polyethylene box. Soil samples, of about 300 g and to depths of around 10 cm, were collected from under the canopies of three trees from each location using a plastic trowel and were stored likewise.

### 2.2. Leaf sample processing and XRF analysis

On return to the laboratory, leaf surfaces were wiped gently with three-ply blue roll to remove any visibly adherent material and weighed on a five-figure Sartorius balance. Fresh samples were then analysed for a suite of elements, of which As, Cu, Pb and Zn as important contaminants of non-ferrous mining are the focus of the present study, by energy dispersive, field-portable (FP-)XRF using a battery-powered Niton XRF analyser (model XL3t 950 He GOLDD+) which was configured, nose-upwards, in a bench-top accessory stand and activated remotely by a laptop connected via USB. In order to minimise any artefacts arising from variations in geometry or thickness, an area of the upper blade midway between the midrib and margin, and free from any sign of infection, was selected for analysis. This area was measured for thickness using Allendale digital callipers before being positioned directly above the XRF detection window, a process aided by imagery from an integrated CCD camera and, where necessary, polyethylene blocks outside of the x-ray beam acting as weights. Once the shield of the stand was closed, measurements, with appropriate thickness correction and in a low-density plastics mode, were undertaken for equal counting periods in a main energy range (50 kV/40 μA) and low energy range (20 kV/100 μA). Counting was trialled up to ten minutes but a total period of 120 s was selected as a suitable timescale that appeared to provide sufficiently low counting errors yet maximise the number of elements detected. Spectra arising from both energy ranges were