



Heavy metal availability assessment using portable X-ray fluorescence and single extraction procedures on former vineyard polluted soils

Elena Peralta^a, Gustavo Pérez^a, Gerardo Ojeda^{b,c}, Josep Maria Alcañiz^{b,d}, Manuel Valiente^a, Montserrat López-Mesas^a, María-Jesús Sánchez-Martín^{a,*}

^a GTS Research Group, Department of Chemistry, Faculty of Science, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola del Vallès, Spain

^b CREA, E08193 Bellaterra, Cerdanyola del Vallès, Spain

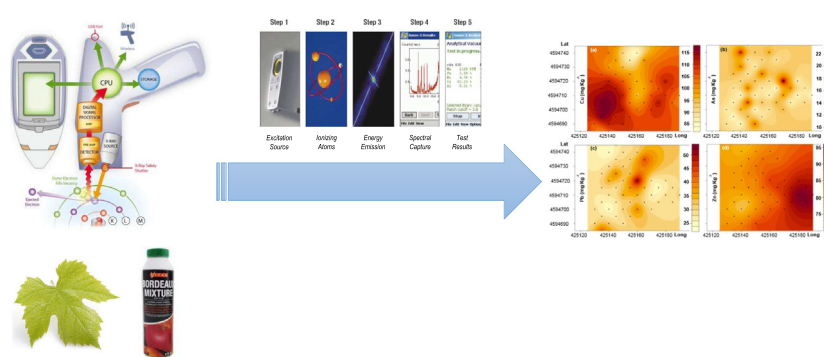
^c Escuela de Ciencias Agrícolas, Pecuarias y de Medio Ambiente ECAPMA, Universidad Nacional Abierta y a Distancia, Cl. 17 sur # 33-24, Bogotá, DC, Colombia

^d Departament Biologia Animal, Biologia Vegetal i Ecologia, Universitat Autònoma de Barcelona, E08193 Bellaterra, Cerdanyola del Vallès, Spain

HIGHLIGHTS

- *In situ* total soil heavy metals assessment by portable X-ray fluorescence.
- FP-XRF combined with leaching test for fast risk assessment of metals' soil pollution.
- Mapping and monitoring of polluted areas in a fast and cheap way.
- Copper concentration found on soil was above the regional governmental limits.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 December 2019

Received in revised form 10 April 2020

Accepted 10 April 2020

Available online 12 April 2020

Editor: D. Barcelo

Keywords:

X-ray fluorescence

FP-XRF

Soil pollution

Metal bioavailability

Heavy metals maps

ABSTRACT

The periodic application of copper-based fungicides (Bordeaux mixture) to vineyards of the Mediterranean region has generated an important pollution source that in some cases requires a quick intervention due to the high bioavailable copper content measured. Despite some vineyards were abandoned 40 years ago, noticeable amounts of Cu and other man-related metals are still nowadays detected in soils. In the present work, the development of a mobility test for the available heavy metal (Cu, Pb, Zn and As) content in soil has been performed using portable X-ray fluorescence (FP-XRF) combined with single leaching test, and was applied to a calcareous soil of a former vineyard area in Catalonia (NE Spain). The combined methodology has provided useful information for fast and detailed risk assessment, in terms of mobility and bioavailability of metals. The anthropogenic contribution was evaluated by means of the Concentration Enrichment Ratios (CER) in soil. The results reflect a clear anthropogenic contribution for Cu, a partial anthropogenic contribution for Pb proceeding from an external pollution source, and a non-significant external contribution for As and Zn. The topsoil concentration ranges for Cu (70–128 mg kg⁻¹) were found to be above the background level and several samples above the regional governmental limits (Generic Reference Levels or GRL values) for soil ecosystem protection and for human health (90 mg kg⁻¹). The present study reveals that the use of FP-XRF equipment constitute a highly valid option for quick decision making during the field location, characterization and quantitative elemental analysis of soil samples for screening of potential pollutants such as heavy metals.

© 2020 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: mariajesus.sanchez@uab.cat (M.-J. Sánchez-Martín).

1. Introduction

In the Mediterranean region, vineyards are one of the most erosion-prone crops (Salomé et al., 2016) that need a use of agrochemicals. The most used pesticides in this crop are those to prevent and treat fungal diseases, like downy mildew. For this purpose, the Bordeaux mixture, a copper-based fungicide, has been routinely used in Europe since the end of the 19th century, and is one of few treatments permitted in ecological agriculture (Kelly and Bateman, 2010). This mixture comprise $\text{Ca}(\text{OH})_2$ and CuSO_4 and other less soluble compounds, such as Cu_2O , $\text{Cu}(\text{OH})_2$ and $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (Chaignon et al., 2003; Pietrzak and McPhail, 2004) being an important source of Cu contamination. As a result of its long-term use in the Mediterranean region, Cu concentrations above the background level have been mapped in traditional vineyard areas (Ballabio et al., 2018). Moreover, the Bordeaux mixture contains other metals that should be also monitored (Mirlean et al., 2007); including arsenic, lead, zinc and nickel, all of which can be harmful to human health if certain thresholds are exceeded (Rocha et al., 2015). Among them, As is a widely occurring environmental contaminant with inorganic-As recognized as a class-one carcinogen (National Research Council (U.S.). Board on Environmental Studies and Toxicology, 2007). But As in the soil also comes from parent material and other anthropogenic sources such as the use of animal manures or irrigation with As-contaminated groundwater (Meharg and Zhao, 2012). Arsenic contamination in soil may cause phytotoxicity and yield losses (Panaullah et al., 2009).

Once marginal agricultural areas have been abandoned due to social and economic change, the continuous use of agrochemicals containing pollutants has resulted in contaminated soils (Arias-Estévez et al., 2008; Komárek et al., 2010; Silva et al., 2019). In a long-term, persistent pollutants as heavy metals, such as copper, arsenic, lead and cadmium (Yang et al., 2018) are cases of major concern, requiring, in some cases, risk assessment (Fernández-Calviño et al., 2008). Therefore, analytical tools for a fast diagnosis of soil pollution by heavy metals and other trace elements could be useful.

To determine low concentrations of these metals in minerals, spectrometric methods are mainly used. These methods include electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) (Bobrowski et al., 2015). However, several decades ago laboratory based X-ray fluorescence (XRF) spectrometry has been applied to analyse major and minor elements in fields such as geochemistry, forensic science and archaeology (Langford, 2005; Shackley, 2011). XRF has several advantages when compared to other multi-elemental techniques such as ICP-MS like the limited preparation required for solid samples, non-destructive analysis, increased total speed and throughput, the decreased production of hazardous waste and the low start-up and running costs (Parsons et al., 2013). Field portable X-ray fluorescence (FP-XRF) retains these advantages while additionally provides data on-site and hence reducing costs associated with sample transport and storage. Rapid *in situ* analysis also facilitates elemental mapping at the field scale in order to target areas of interest for further laboratory based analysis. Since the last decade, the application of FP-XRF for metals contamination assessment has become a reliable solution for *in-situ* soil analysis (Brent et al., 2017; Gutiérrez-Ginés et al., 2013; Melquiades and Appoloni, 2004; Potts et al., 2005; Shand and Wendler, 2014; Weindorf et al., 2013; Weindorf et al., 2012). The application of such technique allows to quickly assess metals contamination at a definitive or screening level (Kilbride et al., 2006), as well as contamination patterns. This fact let to perform a high volume of field tests, minimizing off-site analytical costs and without destroying the samples that can be later used for further tests. Other advantages involve faster turn-around of results, first-hand information on pollutants spatial distribution and on heterogeneity degree in undisturbed sites (Harper et al., 2006; Mitchell et al., 2012). However, it is important to take into account some limitation of the FP-

XRF technique, for example: the heterogeneity of the sample may affect the results, the detection limits require careful considerations and it is more reliable/sensible to some metals than others (Lemiere and Lemière, 2018). Therefore, appropriate sample treatment and quality control procedures must be put in place to reduce as much as possible such limitations.

The assessment of the impact of trace elements in soils and sediments, is based not only in the total metal content, but also in its mobility and bioavailability, due to the biogeochemical and ecotoxicological significance of a given element. These metal characteristics are determined by its specific binding form and coupled reactivity rather than by its total concentration (Batley, 1989). One of the most successful attempts to consider labile fractions and pollutants partition, among the different phases present in soils, has been provided by sequential extraction schemes (SEs) (Bacon and Davidson, 2008). Simultaneously, single non-selective extractions methods that target groups of labile or mobile phases have also gained interest. Such an approach can provide a useful assessment for screening purposes to identify trace metal pollution (Pérez et al., 2008), without the inconvenience of SEs procedures and with some advantages mainly related to their cost efficiency, usability and a reduction on bias induced by reduced sequential translation and accumulation of procedural errors.

In this paper, the results of field and laboratory studies on heavy metals availability assessment using portable X-ray fluorescence and single extraction procedures on former vineyard polluted soil are presented. The principal aim of the present study focuses on a quick assessment of metals pollution, specifically Cu, Pb, Zn and As, considering their spatial distribution as well as their availability. Such assessment has been possible by the combination of FP-XRF equipment and single leaching tests. FP-XRF analysis performed before and after a simple extraction procedure has allowed the development of a mobility test for the available heavy metal content in the soil.

2. Materials and methods

2.1. Site and soil characteristics

An abandoned vineyard area of 3000 m² in Catalonia (NE Spain) was subjected to detailed study. The area is located in the experimental fields of the Universitat Autònoma de Barcelona (Cerdanyola del Vallès, Barcelona), at geographical coordinates 41.5004 N and 2.10331E. Currently this area is devoted to experimental crops for research purposes but in the time of sampling the area was let fallow.

The soil has an Ap-Bwk-Ck profile and can be classified as Typic Calcixercept according to Soil Taxonomy System (Soil Survey Staff, 1999). Only topsoil was subjected to study. It has a clay loam texture, an alkaline pH, high carbonate content, and low organic carbon content and cation exchange capacity.

2.2. Field sampling

A total of 48 soil samples were collected, following a 5 × 5 m UTM grid (Fig. 1). At each point, a core of 10 cm diameter was obtained by using a sampling ring of 2 cm depth, after removing organic debris if present. This sample is representative of topsoil (Ap horizon) as it is mixed every year by tilling at a depth of 20–30 cm. About 0.3 kg of surface soil sample was collected, mixed thoroughly, and stored in a sealed and coded plastic bag in order to transfer them to the laboratory to determine soil parameters and perform single leaching tests. Additionally, 3 background samples were collected in the same area at 60 and 80 cm depth using an Edelman auger to calculate Concentration Enrichment Ratios (CERs) values following the same procedure. The soil blank samples are of the same lithology and soil type, taken very close to the experimental area, at a depth that correspond to the base of Bwk horizon, at enough depth to prevent suspected pollution influences.

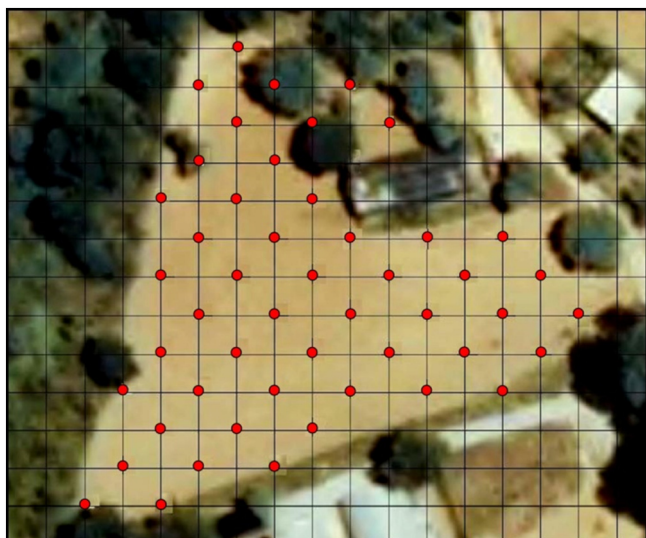


Fig. 1. Sampling grid map of the studied area showing soil sampling points (5 × 5 m UTM grid).

To analyse the moisture effect, the metal concentration was measured in the original samples and after a preliminary step involving a drying process using an air forced oven at 105 °C for 24 h or until constant weight (dried samples). Conversely, for the particle size study, samples were air-dried (30 °C) for 48 h, disaggregated and sieved through a 2 mm stainless steel sieve in order to remove coarse particles and then oven dried. For total elemental analysis, subsamples were ground and sieved below 100 µm as required.

2.3. Mobility tests

The soil contained in each sample cup used for the FP-XRF analysis was treated with HCl 0.5 mol l⁻¹ with a soil to HCl ratio of 1:20 and shaking at 30 rpm for 1 h. The choice of this methodology was based on its effectiveness, efficiency in terms of resource consumption and reduction of experimental time (Pérez et al., 2008). After the leaching test, the suspension was centrifuged at 3000g for 10 min with a model C-5 centrifuge (Pacisa, Barcelona, Spain). The suspension was filtered by means of 0.22 µm filter and the resulting extracts from the filtering process were stored in polypropylene bottles at 4 °C prior to analysis with Thermo Elemental ICP-OES (model Intrepid II XLS, Franklyn, MA, USA), measuring correction standards periodically to correct for any drift or any external influences interfering the sensitivity of the instrument. As methodological blank samples, silicon dioxide matrix at concentrations above the established lower limit of detection was employed. These samples were used to monitor for cross-contamination and laboratory-induced contaminants or interferences, as well as to determine LOD and LOQs, following EPA Method 6200 US EPA, E.P.A., 2007. Standard soil certified reference material (CRM), NIST2710, was also analyzed to validate the extraction procedure.

The remaining soil residue was washed twice with MilliQ water and recovered by filtration. After a drying period in an oven at 105 °C, until constant weight, the soil residue was reintroduced in the sample cup. In order to establish the new methodology, FP-XRF measurements were performed at the laboratory facility before and after the acidic extraction. In the last case, the value obtained by FP-XRF was mathematically corrected for dissolved mass weight loss. The observed differences between both measurements, initial and final, using FP-XRF were employed to estimate and correlate the *in-situ* mobility measurements with those provided by the single leaching test.

2.4. FP-XRF measurements

The total heavy metals content in soil samples (Cu, Pb, Zn and As) was analyzed by FP-XRF using an Alpha 6500 (Innov-X Systems, Woburn, Massachusetts, USA). This equipment consists in a tube-type energy dispersive instrument with a tungsten cathode and a silver anode that can generate X-rays in the energy range 10 to 40 keV and electric current range 10–50 µA. The instrument has a 1.4 cm diameter circular probe window (1.54 cm² area). The instrument employs a Si-PIN diode detector with an energy resolution of 230 eV at the full-width at half-maximum intensity (FWHM) of the manganese (Mn) K X-ray line. The improved energy resolution of the detector allows for efficient use of a Fundamental Parameters (FP)-based method to calculate elemental concentrations. FP is a mathematical treatment of chemical matrix effects used in conjunction with pure element or known standard element responses to develop an iterative algorithm for analysis of a specific sample type (e.g., soil, oil, thin film, paint). The FP method, chosen from a menu of the application, does not require calibration. Applications for soils, Pb-in-paint (K- and L-lines), and thin films are provided with the instrument.

Measurements using FP-XRF were performed at different stages of the study, *in situ* (in the field), after drying (in order to evaluate the moisture), after grinding and sieving (to evaluate particle size effect) and after mobility test.

Measures performed in the field were done by shooting directly on the sampling spot. When measuring at the laboratory facility, ten milliliter high density polyethylene sample cups (Chemplex, FL, USA) were filled with 8 g of soil samples. Sample cups were sealed using pre-cut Mylar® circles film and placed in the testing stand of the benchtop docking station. The instrument was set for 120 s analyzing time for each sample in standard operation mode, using the soil programme in the sequential mode and the LEAP (Light Element Analysis Program) module, for the measurement of heavy metals and light elements (below Al). LEAP works by changing the X-ray tube beam conditions to settings which are optimized for the detection of elements lighter than iron. This time-period is considered the best trade-off between accuracy and speed of analysis. Quality assurance of FP-XRF measurements was performed following QC procedures indicated by EPA Method 6200QC which include, energy calibration check (Alloy 316), instrument and method blank, calibration verification check and precision sample and confirmatory sample every 10 samples. The FP-XRF limit of detection (LoD) and limit of quantification (LoQ) for the different metals were calculated from the measurement of a soil matrix blank at the start and end of analysis, and after approximately every ten samples (for a minimum of eight measurements per set of sample).

LoD and LoQ were defined as three and ten times, respectively, the calculated standard deviation value of the mean for each target element. Ideally, the sample should have a target analyte concentration near the site action level. NIST 2710 standard reference samples were employed as calibration verification checks, providing results within specified tolerances (Mackey, 2010).

2.5. Pollution degree assessment

The natural concentration of heavy metals in the soil (background concentration) differs significantly from one place to another, so the value of the Generic Reference Level (GRL) for heavy metals is conditioned by the geochemical composition. Following Spanish regulations, these GRL levels correspond to the concentration of a polluting substance in the soil that does not carry a risk higher than the maximum acceptable for human health or ecosystems, according to Spanish and Catalan laws and based on Commission Regulation EC 1488/94 (Real Decreto 9/2005, 2005). The General Reference Levels (GRL) 186 for both human health and ecosystems on agricultural soils specified by

Catalonia Governmental Regulation of the study metals are: Cu (90 mg kg^{-1}), Pb (60 mg kg^{-1}), Zn (170 mg kg^{-1}) and As (30 mg kg^{-1}).

Complementary reliable information can be obtained by considering the variation of metals concentration within the different geological substrates or soil horizons. In this sense, an evaluation by concentration enrichment ratios (CERs) using both, total and available concentrations of the pollutants, led to better establish anthropogenic contribution to the site contamination (Sutherland and Tolosa, 2000). CERs are calculated by Eq. (1).

$$CER_n = \frac{\left[\frac{C_n \text{ sample}}{C_c \text{ sample}} \right]}{\left[\frac{C_n \text{ Background}}{C_c \text{ Background}} \right]} \quad (1)$$

Considering the concentration of a given element, C_n , in both target and background sample, normalized with respect to the concentration of a lithogenic conservative element such as Al, Fe, Ti or Zr expressed as C_c (Horowitz et al., 1988; Trefry et al., 1985; Vega et al., 2009; White and Tittlebaum, 1985). The selected lithogenic element must be characterized by an accurate and precise determination, by a reduced anthropogenic contribution compared with its natural occurrence and by its resistance to the weathering processes. Fe was chosen as conservative element representing ambient or natural elemental levels (background), once confirmed its accurate and precise determination and a constant concentration along all the strata of the collected soil samples.

An accepted classification allows differentiating samples by the anthropogenic contribution: minimal or no anthropogenic enhancement when $CER < 2$, moderate for $2 < CER < 5$, significant when $5 < CER < 20$, very strong for $20 < CER < 40$ and extreme when $CER > 40$ (Sutherland and Tolosa, 2000).

2.6. Statistical analysis

Significant differences of soil metal concentrations between wet and dry soil samples and between sieved and grinded soil samples were estimated by *t*-test using Microsoft Excel 2016 software (Microsoft Corporation, Redmon, Washington). Simple linear regressions were developed by *lm* function and Graphics package of R software from Vienna (Austria) (R

Core Team, 2013), in order to establish the influence of soil moisture and physical protection of metals by soil aggregation on the measurement of soil metals.

A geostatistical analysis of metal distribution was developed by GeoR - a package for geostatistical analysis by R software (R Core Team, 2013). A sample grid between latitude (4,594,690, 4,594,740) vs longitude (425,120, 425,180) UTM coordinates was selected to analyse the spatial distribution of soil metals. The R-package Variog computing an omnidirectional semi-variogram (exponential model) between sampling distances and As, Cu, Pb and Zn values (mg kg^{-1}), which was used to develop a spatial interpolation by kriging. The R-package Contour was used to obtain maps of soil metal distribution from the data analysis made by kriging.

For the CER values, Kruskal-Wallis procedure was used to determine significant differences among the metals. Kruskal-Wallis test was performed using Infostat© software (Di Rienzo et al., 2018).

3. Results and discussion

3.1. Soil moisture and particle size effects

3.1.1. Moisture effect

The intensity of characteristic X-rays of analytes decreases as water content of the sample increases, owing to the stronger X-ray absorption by water than by air in fractures and pores of samples. It is also known that the concentration result of a given element is lower than expected due to the sample dilution effect produced by the humidity content and decreases as the moisture increases (Shefsky, 1997). In order to know the effect of the moisture in the present analysis, the metal concentration was measured before (original field moisture content) and after a drying process at 105°C (dried samples). The LoD obtained for each metal was: $13.6 \pm 0.2 \text{ mg kg}^{-1}$ for As, $37.9 \pm 0.7 \text{ mg kg}^{-1}$ for Cu, $12.2 \pm 0.4 \text{ mg kg}^{-1}$ for Pb and $14.8 \pm 0.5 \text{ mg kg}^{-1}$ for Zn.

As it is shown in Fig. 2 Zn, Cu and Pb concentrations for most of the 48 samples, were found to be higher when samples were dried. Arsenic data do not show the previous trend and no differences are observed (it must be considered that As values were very close or below the LoD) (Table 1).

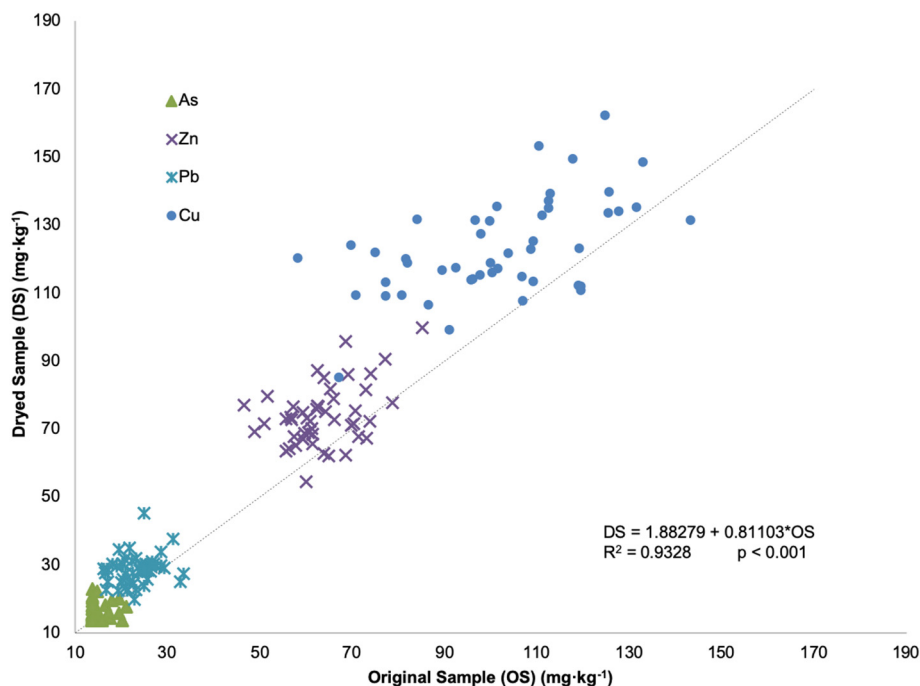


Fig. 2. Concentration of the different metals measured by FP-XRF in original (field moisture) and dried samples. Linear correlation by *lm* function and Graphics package of R software.

Table 1

Average concentration and standard deviation, of the different metals in original (field moisture) and dried soil samples ($n = 48$). *t*-Test for paired samples ($p < .05$) results.

	Concentration (mg kg ⁻¹)		t-test ($p < .05$)	
	Original samples	Dried samples	Value p	Significant(S)/not significant (NS)
Cu	102 ± 19	123 ± 14	7 · 10 ⁻¹²	S
Pb	23 ± 4	28 ± 4	2 · 10 ⁻⁸	S
Zn	63 ± 8	74 ± 9	2 · 10 ⁻¹⁰	S
As	14 ± 2	15 ± 2	2 · 10 ⁻²	S

The average values and standard deviations for each metal are shown in Table 1, where it is observed that the differences between original and dried samples are significant for all the analyzed metals. Thus, the moisture content of the collected samples (range between 9 and 18%) affect significantly the results of the present analysis. Previous work suggests that soil moisture does not have a significant impact on the accuracy of FP-XRF analysis until a threshold value of 20% moisture content is reached and that errors resulting from soil moisture below this threshold are minor (Kalnicky et al., 1992). This 20% threshold has been approved and reproduced in many official protocols since its original publication (Sackett and Bedford, 1998), but other works suggest that the values measured for the soil dried for 24 h at 60 °C show that moisture influence in the concentration values may reach 20%, which cannot be neglected if measurements with some accuracy are aimed (Bastos et al., 2012). In the present study, soil moisture resulted in a decrease in recorded concentration of up to 18.2% (for Pb with an average

of 14% of humidity) compared to the same dry sample (Table 1). These results are in agreement with the bibliography that indicate that previous studies have severely underestimated the importance of soil moisture (Parsons et al., 2013).

3.1.2. Particle size effect

When grinding the soil samples below 100 µm, significant differences in the concentrations for Cu, Pb and Zn are observed (Table 2), showing an effect of the particle size on the XRF response. Zn concentration of grinded samples presents a generalized increment compared to the respective <2 mm sieved ones (Fig. 3) suggesting an exposition by grinding of metal located inside the particles. For Cu, all the samples show a higher value when sieved than grinded, what can be explained owing to Cu is mainly adsorbed in the surface of soil particles or aggregates, due to its anthropogenic procedence. On the other hand, Zn and Pb are mainly distributed in the inner part of the soil particles, determining its lithogenic origin. For As no differences are observed, probably because the values are very close to the LoD.

The effect of particle size is an important factor when considering data quality during XRF analysis. There are two main reasons for this, the first is due to sample heterogeneity, the second to surface effects. As the FP-XRF analysis window is relatively small (approximately 2 cm²) it is important that the average composition of the sample is well represented within this area. A well homogenized sample with small particle size better represents average sample composition within this small visible area, but dilute the metal sorbed to surfaces of particles.

3.2. Heavy metals content and pollution degree assessment

Total copper concentration in soil samples ranged between 70 and 128 mg kg⁻¹, similar amounts to those observed at Piemonte and Tuscany in other vineyard soils (Brun et al., 1998). These values are higher than the mean of vineyards in European countries (49.3 mg kg⁻¹) reported by Ballabio et al. (2018) in a wider Cu survey that includes other crops and land uses. Other studies have shown greater concentrations of total copper: between 96 and 583 mg kg⁻¹ (Fernández-Calviño et al., 2008), 157–434 mg kg⁻¹ (Fernández-Calviño et al., 2008) or above 140 mg kg⁻¹ (Nogueirol et al., 2010) due to different climate conditions, ageing of the vineyard area, decades of fungicides application

Table 2

Average concentration and standard deviation of the different metals in sieved and grinded soil samples ($n = 48$). *t*-test for paired samples ($p < .05$) results.

	Concentration (mg kg ⁻¹)		t-Test ($p < .05$)	
	Sieved samples	Grinded samples	Value p	Significant (S)/not significant (NS)
Cu	118 ± 15	105 ± 12	2 · 10 ⁻⁹	S
Pb	28 ± 4	31 ± 9	4 · 10 ⁻²	S
Zn	74 ± 8	85 ± 9	2 · 10 ⁻¹²	S
As	16 ± 2	16 ± 4	0.2	NS

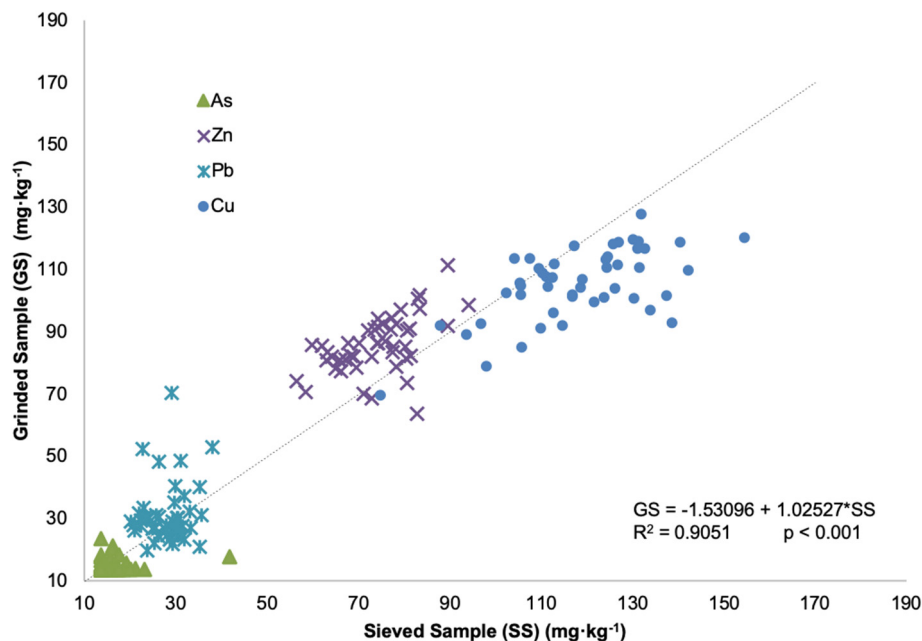


Fig. 3. Concentration of the different metals measured by FP-XRF in sieved and grinded samples. Linear correlation by lm function and Graphics package of R software.

and mineral composition. The narrowest range is for arsenic with values from 10 to 24 mg kg⁻¹, levels that are quite similar to the observed in the background samples (14 mg kg⁻¹), revealing its lithogenic source rather than its origin from a continuous Bordeaux application or from other agrochemicals. In the case of zinc, a wider concentration range was observed 64–111 mg·kg⁻¹, higher than the background level (70 mg kg⁻¹) for the 96% of the analyzed samples. However, the obtained amounts are lower than those observed in other bibliographic vineyard soils studies with zinc affection (Mirlean et al., 2007). Lead presents a higher range concentration (20–70 mg kg⁻¹) over the background levels (19 mg kg⁻¹) and also higher than the amounts found in other studies (Mirlean et al., 2007).

The representation of the heavy metals total concentration when applying FP-XRF to the milled 48 soil samples (particle size below 100 µm) is given in Fig. 4. It can be observed that copper is generally above the GRL values, showing risk of soil be contaminated, and therefore a detailed evaluation of the risk should be performed. Meanwhile, As and Zn in all the studied samples and Pb in all except one, indicated that monitoring or deeper studies are not necessary because the concentration of these metals is below the GRL levels.

In order to properly estimate the pollution degree as well as the anthropogenic contribution, CER values were determined considering factors such as geochemical variability. The representation of CER values for each metal, given in Fig. 5, clearly outlines the anthropogenic character of copper, which present half of the population data with CER values between 2 and 5, showing a moderate anthropogenic contribution, and the remaining 50%, between 5 and 8 showing a significant anthropogenic contribution.

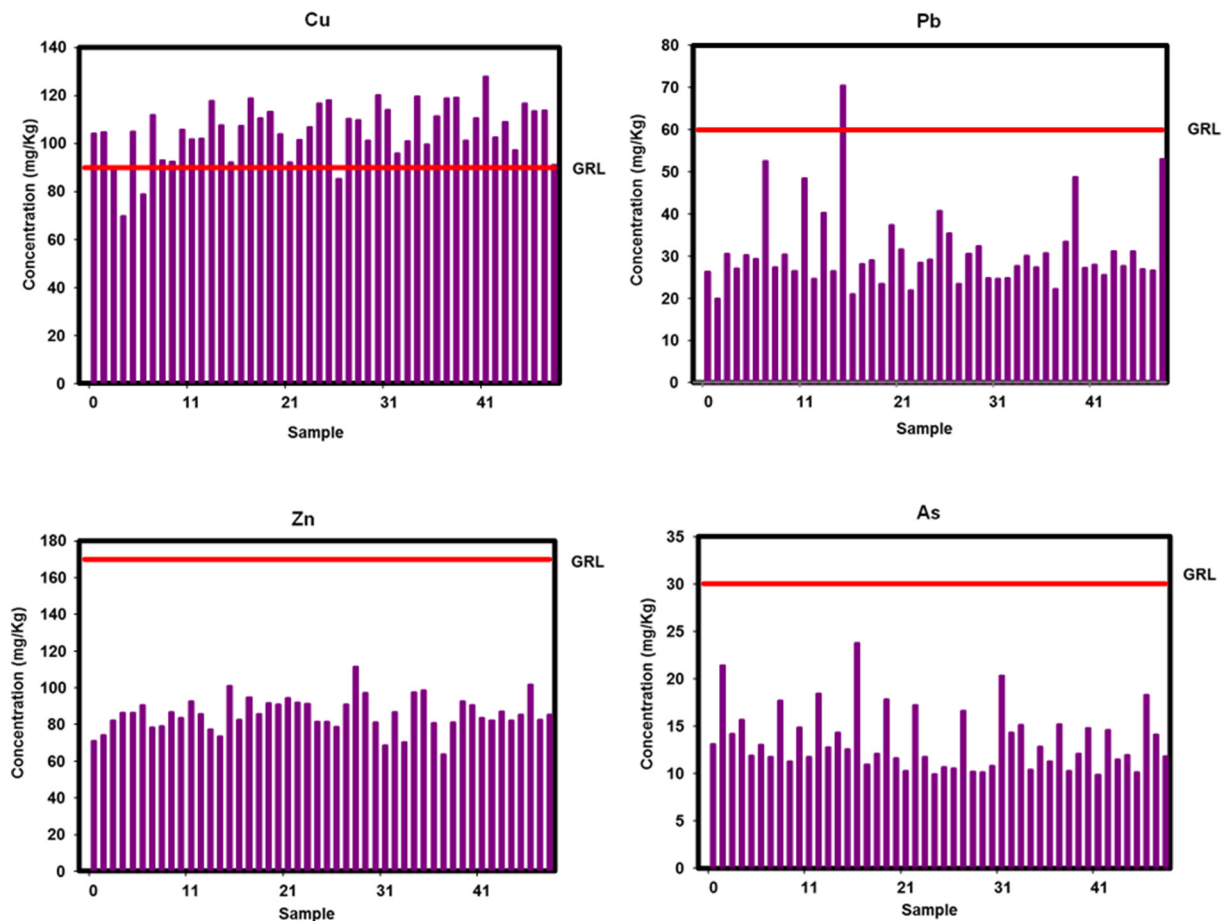


Fig. 4. Concentration values for Cu, Pb, Zn and As in all soil samples. Red line shows the values for GRL for these metals and protection to the human health and ecosystems applicable to Catalonia.

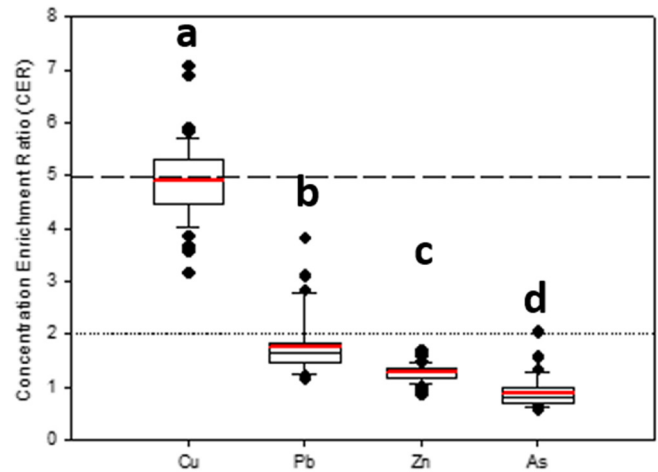


Fig. 5. Representation of CER values for the 48 soil samples for Cu, Pb, Zn and As. Dotted line represents minimal anthropogenic contribution; dash line represents moderate anthropogenic contribution. Means with a common letter are not significantly different ($p > .05$).

Considering the other metals, Pb present a 90% of CER values below 2, as well for the 100% of the Zn and As data, indicating a minimum or no anthropogenic contribution for these three cases. In the case of Cu, the great dispersion of CER values suggests a partial contribution of an external pollution source in some samples. Kruskal Wallis test showed significant differences between the different studied metals ($p > .05$).

3.3. Assessment of metal availability: comparison between both mobility tests

In order to compare the performance of the developed methodology against the single extraction mobility test, a linear regression model was employed. RSD, r^2 and inferential statistics allow to set a data quality level (definitive, quantitative and qualitative screening) to each relationship depending on set criteria given by United States Environmental Protection Agency in 1998 (Billets, 2006).

A clear correlation between the data of *in situ* mobility and laboratory mobility tests, can only be depicted from the Cu data $r^2 = 0.9925$. Additionally, a reduced RSD value, the slope and intercept values ($y = 1.703x + 4.220$), indicate that Cu data can be classified within the definitive quality level. The obtained result indicates that the combined method of simple extraction and analysis by FP-XRF is feasible to assess the mobility and availability of this element *in situ*. Conversely, data dispersion is observed for Zn, Pb and As, with r^2 values below 0.70, indicating a qualitative screening level. The arsenic poor linearity is explained due to its concentration at or below the detection limit of the equipment, thus the related inaccuracy. Additionally, the main lithogenic source of Zn, Pb and As, sample concentrations similar to the background, and their reduced mobility are the responsible for a poor correlation for those elements.

3.4. Heavy metals spatial distribution

Elemental spatial distribution maps, three-dimensional images and interpretive hazard maps of pollutants, or even more anthropogenic contribution of each element in the studied area, can be obtained when combining FP-XRF measurements for both total and mobile pollutants content with geographical information given by GPS equipment (Darko et al., 2017).

The obtained results are illustrated in Fig. 6. The copper distribution map of grinded samples shows the greatest pollution points and suggests the anthropogenic contribution. Through the studied area, a tendency of cluster distribution of copper is observed, probably due to a non-homogeneous and repetitive application of the Bordeaux mixture. Thereby, a zone at the southwest corner of the vineyard area, illustrate the greatest observed concentrations, owing to the proximity of a former tank employed for manufacture and distribution of the fungicide. As and Pb present the same spatial distribution pattern with homogeneous concentrations along the area, similar to those of background samples. But Zn present a completely different distribution, being the east area the most polluted due to the corrosion of a greenhouse structure (buildings visible at the image) and the runoff flux due to terrain slope.

4. Conclusions

By developing a new methodology to monitor polluted soils, a persistent Cu pollution derived from a recurrent application of Bordeaux mixture to the former vineyard area has been determined. The characterization of Cu pollution degree by means of GRL and determination of CER values has let to ascertain the main anthropogenic contribution to the identified Cu content. The total copper concentration in the analyzed soil samples is consistent with results reported by other authors when studying vineyards soils. For other metals, different distribution trends have been observed in relation to their lithogenic or anthropogenic contribution.

The present study reveals that the use of FP-XRF equipment constitute a highly valid option for quick decision making during the characterization and quantitative elemental analysis of soil samples for screening of potential pollutants such as heavy metals. Further, the present methodology can be used for quick metal availability tests, by the use of a combination of FP-XRF measurements and single leaching

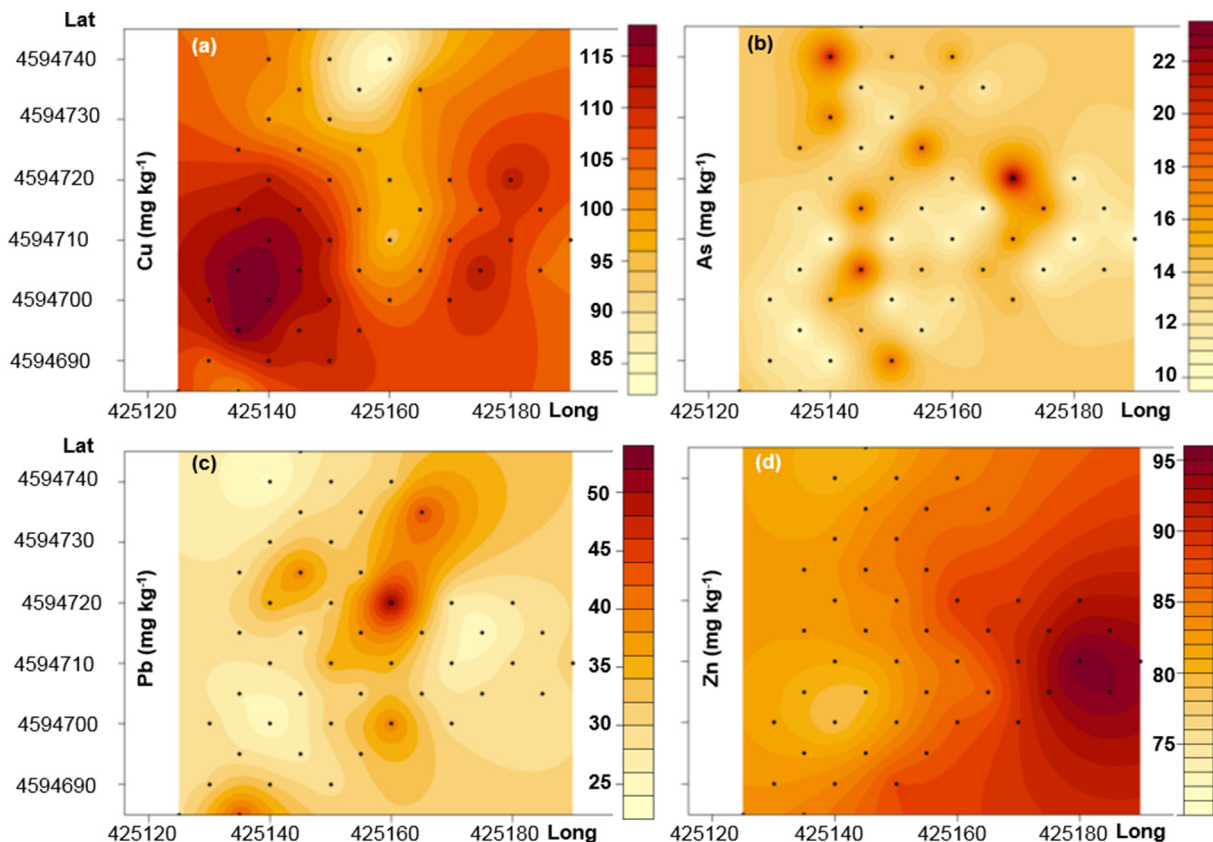


Fig. 6. Metals concentration (mg kg^{-1}) distribution maps within the studied area.

test employing HCl, giving reliable and useful information *in situ* regarding the real hazard of heavy metals in soils, since the *in situ* measurement of the leaching process using FP-XRF, agrees with the ICP-OES determination of the corresponding HCl leachates. Additionally, the methodology allows the identification and monitorization of polluted areas in a fast and inexpensive way, being directly applied to the studied area. Both, soil moisture content and particle size effects, affect significantly the FP-XRF measurements of target elements. The effect of soil moisture has been underestimated in previous works, so it must be corrected to have good estimates of the total concentration of metals. The way to eliminate these effects of humidity would be to carry out a drying procedure of the sample *in situ*. Therefore, the described methodology can be used for risk assessment of agricultural soils regarding the presence of heavy metals as pollutants.

CRediT authorship contribution statement

Elena Peralta: Methodology, Investigation, Formal analysis, Conceptualization, Writing - original draft. **Gustavo Pérez:** Investigation, Conceptualization, Formal analysis, Writing - review & editing. **Gerardo Ojeda:** Formal analysis, Writing - review & editing. **Josep Maria Alcañiz:** Resources, Writing - review & editing. **Manuel Valiente:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Montserrat López-Mesas:** Formal analysis, Writing - review & editing, Visualization, Project administration, Funding acquisition. **María-Jesús Sánchez-Martín:** Formal analysis, Writing - review & editing, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial support for this study was provided by a project of the Ministry of Science and Innovation, Spain (grant reference: CTM2015-65414-C2-1-R). This research also is associated to the Colombian projects PIE 7 2018_2 and PIE 7 2018_2 (Universidad Nacional Abierta y a Distancia - UNAD).

References

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agric. Ecosyst. Environ.* 123, 247–260. <https://doi.org/10.1016/j.agee.2007.07.011>.

Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? *Analyt.* 133, 25–46. <https://doi.org/10.1039/b711896a>.

Ballabio, C., Panagos, P., Lugato, E., Huang, J.-H., Orgiazzi, A., Jones, A., Fernández-Ugalde, O., Borrelli, P., Montanarella, L., 2018. Copper distribution in European topsoils: an assessment based on LUCAS soil survey. *Sci. Total Environ.* 636, 282–298. <https://doi.org/10.1016/j.scitotenv.2018.04.268>.

Bastos, R.O., Melquades, F.L., Biasi, G.E.V., 2012. Correction for the effect of soil moisture on *in situ* XRF analysis using low-energy background. *X-Ray Spectrom.* 41, 304–307. <https://doi.org/10.1002/xrs.2397>.

Batley, G.E., 1989. *Trace Element Speciation Analytical Methods and Problems*.
 Billets, S., 2006. *Innovative Technology Verification Report Innov-X XT400 Series XRF Analyzer*.

Bobrowski, A., Królicka, A., Maczuga, M., et al., 2015. Anodic stripping voltammetric determination of copper traces in carbonate minerals and fly ash extracts using a screen-printed electrode modified *in situ* with antimony film. *Insights Anal. Electrochem.* 1 (1). <https://doi.org/10.21767/2470-9867.100006>.

Brent, R.N., Wines, H., Luther, J., Irving, N., Collins, J., Drake, B.L., 2017. Validation of hand-held X-ray fluorescence for *in situ* measurement of mercury in soils. *J. Environ. Chem. Eng.* 5, 768–776. <https://doi.org/10.1016/j.jece.2016.12.056>.

Brun, L., Maillet, J., Richarte, J., Herrmann, P., Remy, J., 1998. Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils. *Environ. Pollut.* 102, 151–161. [https://doi.org/10.1016/S0269-7491\(98\)00120-1](https://doi.org/10.1016/S0269-7491(98)00120-1).

Chaignon, V., Sanchez-Neira, I., Herrmann, P., Jaillard, B., Hinsinger, P., 2003. Copper bio-availability and extractability as related to chemical properties of contaminated soils from a vine-growing area. *Environ. Pollut.* 123, 229–238.

Darko, G., Dodd, M., Nkansah, M.A., Aduse-Poku, Y., Ansaah, E., Wemegah, D.D., Borquaye, L.S., 2017. Distribution and ecological risks of toxic metals in the topsoils in the Kumasi metropolis, Ghana. *Cogent Environ. Sci.* 3, 1354965. <https://doi.org/10.1080/23311843.2017.1354965>.

Di Rienzo, J.A., Casanoves, F., Balzarini, M.G., Gonzalez, L., Tablada, M., C., R., 2018. *Infostat - Statistical Software*.

Fernández-Calviño, D., Pateiro-Moure, M., López-Periago, E., Arias-Estévez, M., Nóvoa-Muñoz, J.C., 2008. Copper distribution and acid-base mobilization in vineyard soils and sediments from Galicia (NW Spain). *Eur. J. Soil Sci.* 59, 315–326. <https://doi.org/10.1111/j.1365-2389.2007.01004.x>.

Gutiérrez-Ginés, M.J., Pastor, J., Hernández, A.J., 2013. Assessment of field portable X-ray fluorescence spectrometry for the *in situ* determination of heavy metals in soils and plants. *Environ. Sci. Process. Impacts* 15, 1545–1552. <https://doi.org/10.1039/c3em00078h>.

Harper, M., Pacolay, B., Hintz, P., Andrew, M.E., 2006. A comparison of portable XRF and ICP-OES analysis for lead on air filter samples from a lead ore concentrator mill and a lead-acid battery recycler. *J. Environ. Monit.* 8, 384–392. <https://doi.org/10.1039/b518075a>.

Horowitz, A.J., Elrick, K.A., Callender, E., 1988. The effect of mining on the sediment - trace element geochemistry of cores from the Cheyenne River arm of Lake Oahe, South Dakota, U.S.A. *Chem. Geol.* 67, 17–33. [https://doi.org/10.1016/0009-2541\(88\)90003-4](https://doi.org/10.1016/0009-2541(88)90003-4).

Kalnicky, D.J., Patel, J., Singhvi, R., 1992. Factors affecting comparability of field XRF and laboratory analyses of soil contaminants. *Proceedings of the Forty-First Annual Conference on Applications of X-Ray Analysis* (Colorado Springs, CO, USA).

Kelly, S.D., Bateman, A.S., 2010. Comparison of mineral concentrations in commercially grown organic and conventional crops – tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*). *Food Chem.* 119, 738–745. <https://doi.org/10.1016/j.foodchem.2009.07.022>.

Kilbride, C., Poole, J., Hutchings, T.R., 2006. A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP-OES and *ex situ* field portable X-ray fluorescence analyses. *Environ. Pollut.* 143, 16–23. <https://doi.org/10.1016/j.envpol.2005.11.013>.

Komárek, M., Cadková, E., Chrástný, V., Bordsas, F., Bollinger, J.-C., 2010. Contamination of vineyard soils with fungicides: a review of environmental and toxicological aspects. *Environ. Int.* 36, 138–151. <https://doi.org/10.1016/j.envint.2009.10.005>.

Langford, A., 2005. *Practical Skills in Forensic Science*.

Lemiere, B., Lemiére, B., 2018. A review of pXRF (field portable X-ray fluorescence) applications for applied geochemistry. *Appl. Geochemistry. J. Geochemical Explor.* 10. <https://doi.org/10.1016/j.gexplo.2018.02.006>.

Mackey, E.A., 2010. Certification of Three NIST Renewal Standard Reference Materials for Element Content: SRM 2709a San Joaquin Soil, SRM 2710a Montana Soil I, and SRM 2711a Montana Soil II, NIST Special Publication. U.S. Department of Commerce, National Institute of Standards and Technology.

Meharg, A.A., Zhao, F.-J., 2012. Sources and losses of arsenic to Paddy fields. *Arsenic & Rice*. Springer, Netherlands, Dordrecht, pp. 51–69. https://doi.org/10.1007/978-94-007-2947-6_4.

Melquades, F.L., Apolloni, C.R., 2004. Application of XRF and field portable XRF for environmental analysis. *J. Radioanal. Nucl. Chem.* 262, 533–541. <https://doi.org/10.1023/B:JRNC.0000046792.52385.b2>.

Mirlean, N., Roisenberg, A., Chies, J.O., 2007. Metal contamination of vineyard soils in wet subtropics (southern Brazil). *Environ. Pollut.* 149, 10–17. <https://doi.org/10.1016/j.envpol.2006.12.024>.

Mitchell, D., Grave, P., Maccheroni, M., Gelman, E., 2012. Geochemical characterisation of north Asian glazed stonewares: a comparative analysis of NAA, ICP-OES and non-destructive pXRF. *J. Archaeol. Sci.* 39, 2921–2933. <https://doi.org/10.1016/j.jas.2012.04.044>.

National Research Council (U.S.). Board on Environmental Studies and Toxicology, 2007. *Scientific Review of the Proposed Risk Assessment Bulletin from the Office of Management and Budget*. National Academies Press.

Nogueiro, R.C., Alleoni, L.R.F., Nachtigall, G.R., de Melo, G.W., 2010. Sequential extraction and availability of copper in Cu fungicide-amended vineyard soils from Southern Brazil. *J. Hazard. Mater.* 181, 931–937. <https://doi.org/10.1016/j.jhazmat.2010.05.102>.

Panaullah, G.M., Alam, T., Hossain, M.B., Loeppert, R.H., Lauren, J.G., Meisner, C.A., Ahmed, Z.U., Duxbury, J.M., 2009. Arsenic toxicity to rice (*Oryza sativa* L.) in Bangladesh. *Plant Soil* 317, 31–39. <https://doi.org/10.1007/s11104-008-9786-y>.

Parsons, C., Margui Grabulosa, E., Pili, E., Floor, G.H., Roman-Ross, G., Charlet, L., 2013. Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: considerations for sample preparation and measurement conditions. *J. Hazard. Mater.* 262, 1213–1222. <https://doi.org/10.1016/j.jhazmat.2012.07.001>.

Pérez, G., López-Mesas, M., Valiente, M., 2008. Assessment of heavy metals remobilization by fractionation: comparison of leaching tests applied to roadside sediments. *Environ. Sci. Technol.* 42, 2309–2315.

Pietrzak, U., McPhail, D.C., 2004. Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma* 122, 151–166. <https://doi.org/10.1016/j.geoderma.2004.01.005>.

Potts, P.J., Ellis, A.T., Kregsamer, P., Strelly, C., Vanhoof, C., West, M., Wobrauschek, P., 2005. Atomic spectrometry update. X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* 20, 1124. <https://doi.org/10.1039/b511542f>.

R Core Team, 2013. R: a language and Environment for Statistical Computing [WWW Document]. R Found. Stat. Comput URL <https://www.r-project.org/>, Accessed date: 12 February 2019.

- Real Decreto 9/2005, 2005. . de 14 de enero. por el que se establece la relación de actividades potencialmente contaminantes del suelo y los criterios y estándares para la declaración de suelos contaminados. BOE núm 15. Sección Ip. 1833.
- Rocha, G.H.O., Lini, R.S., Barbosa, F., Batista, B.L., de Oliveira Souza, V.C., Nerilo, S.B., Bando, E., Mossini, S.A.G., Nishiyama, P., 2015. Exposure to heavy metals due to pesticide use by vineyard farmers. *Int. Arch. Occup. Environ. Health* 88, 875–880. <https://doi.org/10.1007/s00420-014-1010-1>.
- Sackett, D., Bedford, M.A., 1998. EPA method 6200 and field portable X-ray fluorescence. A Presentation Developed for the EPA Technology Innovation Office and on-Site Insights Workshops for Innovative Field Characterization Technologies.
- Salomé, C., Coll, P., Lardo, E., Metay, A., Villenave, C., Marsden, C., Blanchart, E., Hinsinger, P., Le Cadre, E., 2016. The soil quality concept as a framework to assess management practices in vulnerable agroecosystems: a case study in Mediterranean vineyards. *Ecol. Indic.* 61, 456–465. <https://doi.org/10.1016/j.ecolind.2015.09.047>.
- Shackley, M.S., 2011. X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology – Bookmetrix Analysis. <https://doi.org/10.1007/978-1-4419-6886-9>.
- Shand, C.A., Wendler, R., 2014. Portable X-ray fluorescence analysis of mineral and organic soils and the influence of organic matter. *J. Geochemical Explor.* 143, 31–42. <https://doi.org/10.1016/j.gexplo.2014.03.005>.
- Shelsky, S., 1997. Comparing field portable X-ray fluorescence (XRF) to laboratory analysis of heavy metals in soil. [WWW Document]. Present. Int. Symp. F. Screen. Methods Hazard. Wastes Toxic Chem URL. <https://clu-in.org/download/char/dataquality/sshelsky02.pdf>, Accessed date: 5 September 2016.
- Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – a hidden reality unfolded. *Sci. Total Environ.* 653, 1532–1545. <https://doi.org/10.1016/j.scitotenv.2018.10.441>.
- Soil Survey Staff, 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. U.S. Department of Agriculture Handbook.
- Sutherland, R., Tolosa, C., 2000. Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu, Hawaii. *Environ. Pollut.* 110, 483–495. [https://doi.org/10.1016/S0269-7491\(99\)00311-5](https://doi.org/10.1016/S0269-7491(99)00311-5).
- Trefry, J.H., Metz, S., Trocine, R.P., Nelsen, T.A., 1985. A decline in lead transport by the Mississippi river. *Science* 230, 439–441. <https://doi.org/10.1126/science.230.4724.439>.
- US EPA, E.P.A., 2007. SW-846 Test Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.
- Vega, F.A., Covelo, E.F., Cerqueira, B., Andrade, M.L., 2009. Enrichment of marsh soils with heavy metals by effect of anthropic pollution. *J. Hazard. Mater.* 170, 1056–1063. <https://doi.org/10.1016/j.jhazmat.2009.05.074>.
- Weindorf, D.C., Zhu, Y., McDaniel, P., Valerio, M., Lynn, L., Michaelson, G., Clark, M., Ping, C.L., 2012. Characterizing soils via portable x-ray fluorescence spectrometer: 2. Spodic and Albic horizons. *Geoderma* 189–190, 268–277. <https://doi.org/10.1016/j.geoderma.2012.06.034>.
- Weindorf, D.C., Paulette, L., Man, T., 2013. *In-situ* assessment of metal contamination via portable X-ray fluorescence spectroscopy: Zlatna, Romania. *Environ. Pollut.* 182, 92–100. <https://doi.org/10.1016/j.envpol.2013.07.008>.
- White, K.D., Tittlebaum, M.E., 1985. Metal distribution and contamination in sediments. *J. Environ. Eng.* 111, 161–175. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1985\)111:2\(161\)](https://doi.org/10.1061/(ASCE)0733-9372(1985)111:2(161)).
- Yang, Q., Li, Z., Lu, X., Duan, Q., Huang, L., Bi, J., 2018. A review of soil heavy metal pollution from industrial and agricultural regions in China: pollution and risk assessment. *Sci. Total Environ.* 642, 690–700. <https://doi.org/10.1016/j.scitotenv.2018.06.068>.