Editorial

Development and Application of X-rays in Metal Analysis of Soil and Plants

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Metals in soil and plants may have divalent roles as essential macro- and micronutrients or dangerous pollutants, depending on their nature and concentration. Assessment of the concentration of such metal elements is considered an important analytical determination in evaluating soil fertility and pollution, as well as plant nutritional status, to define correct fertilization strategies or remediation actions. In addition, the content of metal nutrients and potentially toxic elements (PTEs) influences the quality and safety of vegetal products.

Metal analysis is also important in the study of soil–plant interactions. An understanding of the processes underlying the exchange of metal elements between soil and plants can shed light on plant nutrition mechanisms and the strategies used by plants to acquire mineral nutrients. This is important not only under normal physiological conditions, but also in the case of biotic (e.g., pathogen attacks) and abiotic (e.g., draught, nutrient deficiency, temperature changes, salinity) stresses. The study of the plant–soil system can also facilitate the identification of possible strategies to biofortify the edible parts of plants and to avoid the uptake of PTEs, which can affect the health of consumers. At the same time, metal analysis is important for the study of soil characteristics and environmental issues related to PTE contamination, mobility, bioavailability and speciation. In recent decades, we have observed fast progress in soil–plant system research, and new research challenges have been accompanied by the rapid development of new techniques, methods and data analysis strategies. Among the available techniques, X-ray spectroscopies have been demonstrated to be powerful tools for the study of metals and metalloids in the soil–plant system, for both agricultural and environmental applications [1]. According to the interaction of X-rays with matter, different physical phenomena can be exploited for analytical purposes, each of them providing different information about the studied sample [1].

Among these techniques, X-ray fluorescence spectroscopy (XRF) is used for the elemental characterization of samples. Unlike other atomic spectroscopies such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS), XRF has the advantage of enabling direct analysis of the sample without the need for matrix dissolution (via acid or alkaline digestion). This reduces the risks of sample modification, contamination and loss of information (e.g., oxidation state, speciation). Moreover, XRF analyses are faster and cheaper, with much lower consumption and disposal of chemicals, and therefore, a lower environmental impact.

Two types of XRF spectroscopy are available, depending on the way in which the fluorescent signal is detected: wavelength-dispersive XRF (WD-XRF), where the emerging fluorescence beam is recorded depending on its wavelength (separated by a diffracting

crystal), and energy-dispersive XRF (ED-XRF), where the fluorescence signal is detected depending on its energy. Compared to WD-XRF, ED-XRF has the advantage of simultaneously collecting and recording all the fluorescence signals coming from the excited sample, allowing fast elemental analysis. In the last decade, the continuous development of silicon drift detectors (SDDs) and Peltier cooling systems has resulted in ever-increasing analytical performance and instrumental miniaturization, also leading to the development of portable XRF spectrometers (pXRF). Usually, in XRF, the detectors are placed at 90° from the incident beam, which commonly strikes the sample at an angle of 30–45°. However, the incident beam can be tilted at different angles, obtaining so-called grazing incidence X-ray fluorescence spectroscopy (GI-XRF), which can be used for layer analysis. By moving the incident beam to an angle below the critical angle, the incident beam can be totally reflected. This phenomenon is employed in so-called total-reflection X-ray fluorescence spectroscopy (TXRF). It allows the quantification of trace elements at the ppb level and is therefore widely used for the analysis of plants and soils.

XRF can also be used to study the element distribution in a sample, and for this purpose, a scanner is used to move the sample along two orthogonal axes or to perform the analysis while the sample is rotating. The first strategy is used in micro- (μXRF) or macro-XRF (MA-XRF) to obtain 2D elemental maps, while the second strategy is employed in XRF tomography to study the 3D distribution of the elements.

X-rays can be used also to perform speciation of the metal, and in this case, X-ray absorption spectroscopy (XAS) is used.

While there are several commercially available instruments for XRF that can be used for laboratory analyses, synchrotron radiation is usually required for XAS.

In addition to these techniques, the diffraction of X-rays (XRD) is largely used to study crystalline materials such as soil minerals or metal ores. X-rays can also be used for 3D imaging such as in X-ray computed tomography (XCT), with applications ranging from large objects, such as trees, to nanoscale objects [1].

In this Special Issue, different topics related to the soil–plant system are investigated using X-ray-based methods, highlighting the advantages of these techniques.

In the field of plant nutrition, Hernàndez-Pinto at al. [2] studied the process of germination of habanero pepper seeds (*Capsicum chinense*). By means of a laboratory μXRF, they monitored the distribution of macronutrients (Mg, P, K and Ca) and micronutrients (Mn and Fe) in the seed at different levels of fruit maturation, and during the germination process. Moreover, using the fundamental parameter method, they were able to quantify the elements' concentrations in the different anatomical parts of the seed (hypocotyl, cotyledons, hypocotyl–radicle and radicle). The monitoring of the elements' migration during the germination process suggested that the enrichment of the seedling with macro- and micronutrients increased during germination, and that the best conditions were obtained when the seeds were extracted 14 days after fruit harvesting. These findings support the activity of seedling growers and are particularly helpful in choosing the best period for fruit harvesting and, consequently, the extraction of seeds.

Plants can also become a biowaste, but this kind of waste can be often transformed in a new resource. Marijan et al. [3] studied the possibility of extracting valuable cosmetic ingredients from plants in urban parks, which constituted the majority of biowastes in the investigated areas. Raw materials must be characterized prior to processing in order to avoid introducing hazardous elements into the new material. To monitor the presence and the concentration levels of PTE, TXRF was used for the analysis of plants. TXRF was also used to study the presence of elements that are useful for cosmetics, such as Ca, Zn and Sr.

Many studies are being conducted to investigate the soil–plant system. For these kinds of studies, different calibrations and strategies should be applied to ensure reliable quantification of the elements present in two matrixes: soil and plants. This issue was described by Chubarov et al. [4]. In this paper, two methods were used to analyze the elemental concentration in soils and pine needles from an industrial site in Siberia (Russia). The soil and pine needles were analyzed using both WD-XRF and TXRF, each with a

different purpose. For both samples, WD-XRF was employed for the analysis of major elements, while TXRF was used for the determination of minor elements. A series of reference materials were analyzed to test the reliability of the calibrations performed for the two types of matrixes. The obtained data on soil and pine needles were used to determine parameters such as the normalized enrichment factor (EF), which enables identification of the anthropogenic origin of elements such as Cr, Ni, Zn and Pb.

A solution to the problem of performing different calibrations according to the studied matrix was proposed by Antonangelo and Zhang [5]. In fact, in this paper, a single calibration was used to perform elemental analysis of both soils and plants using a portable XRF spectrometer. The spectra were processed using different models such as linear regression, second-degree polynomial regression and power regression; the information obtained on the recovery of the different element concentrations suggests the possibility of applying this calibration strategy to the determination of nutrient elements in both soils and plants.

Finally, using a multi-analytical approach, Pellinen et al. [6] investigated the migration of PTE in soils of the Priolkhonye Region (Lake Baikal, Russia) via the "field–landslide–coast" pathway caused by gravitational processes.

The geochemistry of the site was investigated almost completely using WD-XRF. However, for Cd and Hg, AAS was used instead of WD-XRF since for some elements, XRF is limited in terms of its detection limits and sensitivity.

In conclusion, this Special Issue demonstrates that X-ray-based analytical methods are important tools for scientists in different fields who study soils and plants, and that the versatility and complementarity of these techniques enable important information to be obtained in both agricultural and environmental research. However, as shown in some of the papers presented in this Special Issue, limitations in the detection and quantification of some elements, which are important in understanding nutritional and environmental problems, are still an issue. These constraints should serve as a starting point for the development of new X-ray-based instrumentation and sample preparation strategies; this could broaden the range of applications of X-ray analyses of the soil–plant system, which are also directly applicable in the field.

Conflicts of Interest: The authors declare no conflict of interest.

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