



Systematic review and meta-analysis

Estimating plant-available nutrients with XRF sensors: Towards a versatile analysis tool for soil condition assessment

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ABSTRACT

The timely diagnosis of plant-available soil nutrient contents is crucial in enhancing agricultural intensification and bridging yield gaps. There is a global demand for a practical and easy-to-use analytical tool capable of predicting the nutrient status of agricultural soils to make the soil chemical diagnosis faster, cheaper, and environmentally friendly. A growing body of research has highlighted the potential of energy dispersive X-ray fluorescence (XRF) sensors for monitoring the condition of agricultural soils. This study critically reviews current knowledge on the feasibility of using XRF sensors and suggests ways forward to predict plant-available soil nutrients. The review finds that some challenges need to be addressed, including: (i) mitigating the matrix effect in XRF spectral libraries and (ii) calibrating models that can capture the local context of the ratio between total and available nutrient content (T/A ratio). This study further discusses knowledge gaps related to the above-mentioned challenges and proposes the following future research areas: (i) understanding the impact of soil management on the temporal stability of T/A ratio and XRF model performance; (ii) assessing advanced predictive modelling strategies to address the challenges related to XRF spectral libraries, i.e., to deal with matrix effect and local context of the relationship between total and available content of nutrients, and (iii) evaluating data acquisition and modelling strategies that optimize the *in situ* application of portable XRF. Understanding these points is critical to advancing the technological maturity of predicting available nutrients *in situ* to fulfil plant nutrient requirements along with its development. Finally, portable, easy-to-use analytical tools are key to enhancing soil health/condition monitoring and proposing best management practices in agricultural areas worldwide, particularly in regions with limited infrastructure of soil laboratories. Soil monitoring is critical to preserve, sustain and recover soil condition/health, one of the main manageable drivers of soil and food security.

1. Introduction

Ensuring soil health and security is paramount for maintaining soil functions and providing related ecosystem services, including addressing the challenges posed by climate change (Evangelista et al., 2023). Maximizing soil carbon sequestration by optimizing its management must be rapidly scaled up worldwide (Lal, 2004). Agricultural soils from tropical regions, e.g., Sub-Saharan Africa, Brazil, SE Asia, and NW-China, have great potential for carbon storage (Bossio et al., 2020;

Padarian et al., 2022); since these areas have considerable yield gaps and a long history of organic carbon losses (Amelung et al., 2020). In these countries, closing yield gaps through intensifying agriculture in degraded crop and pasture lands — instead of expanding it to carbon-rich lands and forests — is being prioritized in their climate-change agendas (Amelung et al., 2020; Marin et al., 2022; Suh et al., 2020).

The yield gap in tropical areas is attributed to climate constraints and soil and crop management (Sentelhas et al., 2015). The main issue related to soil management is the inherent low chemical fertility and

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high acidity levels due to the highly weathered characteristics of soil in tropical regions (Fageria and Nascente, 2014). Optimizing soil fertility management is critical to intensifying agriculture in these areas (Oliveira et al., 2023; Suh et al., 2020), and for that, it is fundamental to monitor the status of key soil fertility attributes (McBratney et al., 2014). Paradoxically, regions with poor soil fertility often are the ones where farmers have the most limited access to soil testing infrastructure and assistance for formulating fertilization programs (Dimkpa et al., 2017; Van Rooyen et al., 2021). Laboratory soil testing is traditionally carried out using wet-chemistry procedures (i.e., extractions using resin or weak acids followed by elemental determination), which are the most accurate means for determining plant-available (av-) nutrients. Conversely, these analyses could be faster (i.e., taking a few days to provide the results and reports), use reagents, and require execution in a controlled environment because they involve potentially toxic products. In addition, crop fields are often located hundreds or even thousands of kilometres from the nearest laboratory, increasing the cost and time required to obtain the nutrient status of samples from the field (Dimkpa et al., 2017).

To facilitate soil monitoring, several initiatives are being conducted worldwide to develop mobile laboratories by using proximal soil sensing (PSS) technologies (Viscarra Rossel et al., 2010), e.g., AgroMobile in Brazil (Instituto BioSistêmico®, Brazil), SoilCares Mobile soil testing laboratory in Kenya (van Erp et al., 2014), and soil-testing mobile van in Nepal (Pandey et al., 2018), amongst others (see Dimkpa et al., 2017). PSS technologies capable of assessing soil fertility would benefit not only the scenario described above, but also support the automation and regular soil monitoring in digital agriculture (Molin and Tavares, 2019; Nawar et al., 2017). However, reliable technology for predicting available nutrients in agricultural soils remains a significant challenge within soil science and plant nutrition.

This paper reviews the advances and perspectives of using energy dispersive X-ray fluorescence spectroscopy (XRF) for soil nutrient quantification across the main agricultural regions around the world. This paper first outlines the advantages and limitations of instantaneous nutrient monitoring using XRF over other sensing techniques and then presents a systematic review to summarize state-of-the-art achievements in the scientific literature that assessed nutrient prediction via XRF. The review also points out the knowledge gaps for the use of XRF in soil nutrient diagnosis and the challenges to establishing effective X-ray fluorescence spectral libraries, which are to: (1) mitigate the physical and chemical matrix effects that affect the relationship between X-ray fluorescence signals (i.e., counts of photons per unit of time) and the total content of soil elements; and (2) develop agronomic models capable of transforming XRF data into available nutrient contents to plants. The first challenge is related to the physical fundamentals of this technique, while the second is an agronomic challenge associated with the development of pedotransfer functions (Minasny and Hartemink, 2011). It is important to consider that the abovementioned points are challenges related to the XRF technique, i.e., once they have been overcome, nutrient prediction can be carried out with portable or benchtop XRF equipment. Finally, some considerations for *in situ* application of portable XRF equipment are outlined.

2. Towards an easy-to-use and versatile analysis tool for monitoring soil nutrients

2.1. Benefits of instantaneous nutrient monitoring

Sensors based on dry chemistry allow precise analysis with reduced sample preparation and without needing reagents (Gredilla et al., 2016), making its analytical procedures compatible with instantaneous and easy-to-use data acquisition (Gatuszka et al., 2015), encouraging research that seeks to transform sensor output into agronomic information (e.g., soil nutrient levels). Accurate nutrient analyses via sensors would make it possible to “bring the lab to the field” and eliminate the

logistical challenge of transporting samples to commercial laboratories (Molin and Tavares, 2019; Pandey et al., 2018). Scenarios for instant analysis of agricultural soils using sensors are illustrated in Fig. 1.

The availability of portable and user-friendly tools for soil analysis would empower agronomists to conduct instant diagnosis assessments, enabling them to identify critical nutrient levels and optimize fertilizer recommendations. In addition to reducing costs associated with sample transportation and using wet chemistry reagents, these tools would enable extension officers or consultants to better address the economic and social aspects specific to each landowner’s unique situation (Van Rooyen et al., 2021).

Developing and testing a proximal-sensing method for soil analysis is a topical subject for soil scientists. Although this research area has significantly advanced in the last decade, showing many successful applications of sensors for predicting various attributes, such as texture, and organic carbon, among others (Demattè et al., 2019; Ng et al., 2022a; Paiva et al., 2022), the prediction of available soil nutrients remains as a critical challenge (McBride, 2022).

2.2. Monitoring soil nutrients: a new horizon with XRF sensors

Some sensing techniques have been evaluated for diagnosing soil nutrient status, such as diffuse reflectance spectroscopy (DRS) in the near- and mid-infrared range, electrochemical sensors, and, more recently, the elemental analysis techniques energy dispersive X-ray fluorescence spectroscopy (also known as ED-XRF) and laser-induced breakdown spectroscopy (LIBS). All these techniques have advantages and drawbacks for assessing soil available nutrients; however, recent research with ED-XRF (referred to in this paper as XRF) has obtained reliable results and brings a promising perspective (Nawar et al., 2019; Silva et al., 2021; Tavares et al., 2021).

Diffuse reflectance spectroscopy using visible (vis; 400–700 nm), near-infrared (NIR; 700–2500 nm), and mid-infrared (MIR; 2500–25000 nm) ranges do not present absorption features directly related to soil nutrients (Stenberg et al., 2010). Nevertheless, satisfactory predictions for available nutrients could be obtained with these techniques in some circumstances, such as local models (Mouazen and Kuang, 2016) or advanced modelling strategies (Ng et al., 2022a). However, accurate predictions are uncommon since satisfactory models depend on the covariation of nutrients with spectrally active attributes (Kuang et al., 2012). This is a major limitation of the nutrient predictive models via DRS. More complete discussion about the main advancements and limitations of DRS techniques can be found in the recent papers from McBride (2022) and Viscarra Rossel et al. (2022).

Electrochemical sensors, such as ion-selective electrodes (ISE) and the ion-sensitive field-effect transistor (ISFET), can measure the content of specific ions (e.g., H^+ , K^+ , and NO_3^-) and therefore; allow direct predictions of available nutrients (Viscarra Rossel et al., 2011). However, their limitations are related to the reduced lifetime (e.g., 2–9 months) and the influence of soil texture on their results (Archbold et al., 2023). In addition, this technique requires extra sample preparation, e.g., extractions using deionized water or an extractant and an agitator (Sinfield et al., 2010).

Both XRF and LIBS techniques have spectra related to the total content of the chemical elements present in the soil (e.g., Fe, Ca, K, P, Si, Al, among others). Regarding their usage feasibility, XRF has a greater versatility over LIBS since it allows for analyzing loose soil samples (e.g., grain size ≤ 2 mm), while LIBS require soil to be compressed in pellets to ensure analytical replicability (Jantzi et al., 2016). Preparing pellets is time-consuming and laborious as it requires fine grinding (e.g., using cryogenic or ball grinding) followed by pressing of the milled materials. Sandy soils still require the addition of a binding agent (e.g. microcrystalline cellulose powder) to aggregate the particles during the pressing step (see Tavares et al., 2019). These procedures make LIBS unfeasible for *in situ* analysis and limit its use in mobile laboratories. In contrast, analyses using XRF do not require these preparatory

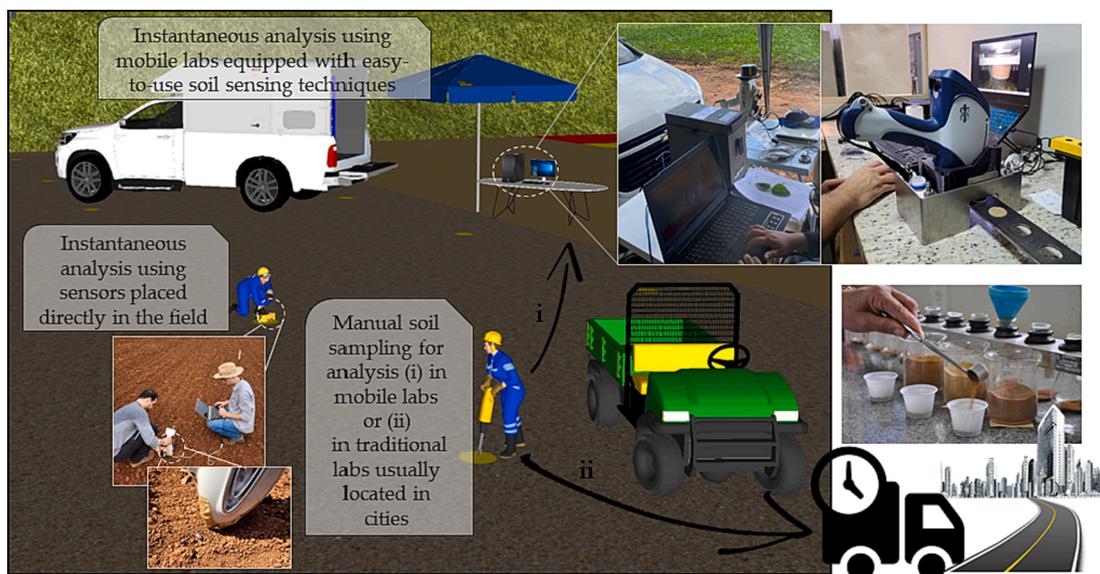


Fig. 1. A conceptual framework for instantaneous soil analysis using smart soil sensors compared to traditional soil analysis carried out in commercial laboratories.

procedures (Tavares et al., 2019), making it more versatile and attractive for developing easy-to-use approaches for instant analysis. The versatility of XRF technology combined with the availability and good

performance of portable XRF sensors (Bueno Guerra et al., 2014; Rouillon and Taylor, 2016) makes this equipment promising for the development of PSS applications to monitor soil fertility (Rouillon and

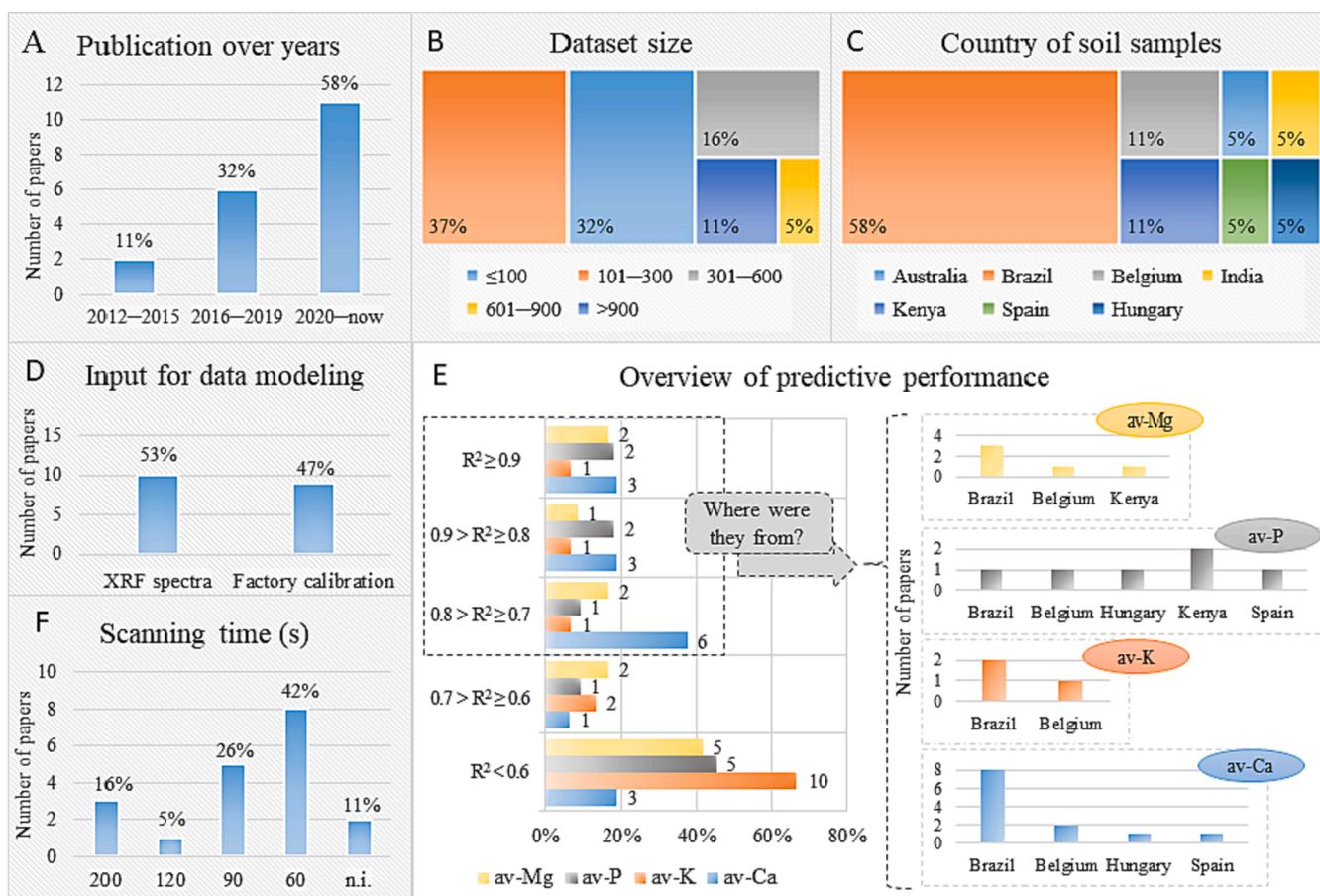


Fig. 2. Overview of publications that used XRF sensors for the prediction of available (av-) nutrients (av-Mg, av-P, av-K, and av-Ca), showing (A) the number the publications over years counting from the first publication in 2012; (B) the size of soil sample bank used; (C) the country from which the soil samples were obtained; (D) the data used as input for model calibration; and (F) the scanning time used for data acquisition. It was also shown (E) an overview of the predictive performance obtained from the publications, detailing the country of the studies that reported good performance ($R^2 \geq 0.7$); details regarding the range of nutrient variation reported by these publications are shown in Fig. 3.

Taylor, 2016; Weindorf et al., 2014a).

2.3. XRF for nutrient analysis: advances, challenges, and perspectives

A systematic review on studies that assessed soil available nutrients prediction using XRF was conducted considering peer-reviewed original articles that were accessed via Web of Science, Scopus, and Science Direct employing the terms “XRF” OR “pXRF” OR “X-ray fluorescence” OR “ED-XRF” AND “soil fertility” OR “soil nutrient” OR “soil available nutrient”, which were searched in the title, abstract, and keywords. Articles from the same research group that utilized the same dataset but have already been published were excluded from the review. The final database, comprising 19 publications, is shown in Table S1 (Supplementary Material).

The summary of the number of publications over years, size of soil dataset, country of soil samples, type of data used as input for model calibration, XRF scanning time for data acquisition, as well as the overall predictive performance achieved was shown in Fig. 2. The review revealed that the first paper to suggest XRF as a tool for analyzing available nutrients in agricultural soils was published by Kaniu et al. (2012) in the early 2010s. Subsequently, there has been a notable increase in the number of papers focusing on this application (Fig. 2A), with a significant spike observed in 2020. In fact, 58% of the papers published in this field were from that particular year.

In general, extraction of av-Ca and av-Mg was predominantly performed via 1 M potassium chloride (KCl), while extractions with Mehlich-1, Mehlich-3, ion exchange resin, and ammonium lactate extract were also used in some studies (Table S1). For the determination of av-K and av-P, the predominant method was Mehlich-1, with some papers using Mehlich-3, ion exchange resin, and ammonium lactate extract (Table S1).

An overview of the performance obtained (Fig. 2E) shows satisfactory predictions ($R^2 \geq 0.7$) of av-Ca in 75% of the papers (12 out of 16); for av-K, 20% of the papers (3 out of 15); while for av-P, 45% of the

papers (5 out of 11); and for av-Mg, 42% of the papers (5 out of 12). For all tested nutrients, most of these satisfactory performances were obtained in studies conducted in Brazil and Kenya, i.e., tropical climate regions (Fig. 2E). However, satisfactory performances are also observed in some investigations conducted in temperate regions, such as Belgium (Javadi and Mouazen, 2021), Hungary (Vona et al., 2022), and Spain (Kandpal et al., 2022). Although better performance was expected in databases with a wider range of nutrient contents, this was not confirmed in the papers gathered in the present bibliometric review (Fig. 3).

A wide variation in the range of nutrient contents is observed among the different papers (Table S1). Although this is influenced by local soil-forming processes, it was found that, in general, temperate soils had higher ranges of av-Ca and av-K contents than tropical soils, while av-Mg and av-P contents do not show clear behaviour relative to locality. More specifically, for av-Ca, the range varied between 1000–65,000 mg kg⁻¹ in Spain and Belgium and between 0–40,000 mg kg⁻¹ in Hungary (Table S1). While in Brazil and India, av-Ca contents ranged between 20–7398 mg kg⁻¹. Plant-available contents of K ranged from 0 to 1367 mg kg⁻¹ in temperate soils (e.g., Australia, Hungary, Belgium, and Spain), and from 0 to 901 mg kg⁻¹ in studies conducted in Brazil and India (Table S1). In turn, plant-available contents of P ranged around 0–2262 mg kg⁻¹ and 0.8–125 mg kg⁻¹ in different Brazilian fields, between 0–2262 mg kg⁻¹ in Belgium and Spain, and 8–43 mg kg⁻¹ in Kenya. For av-Mg, the largest ranges were from ±20 to >3000 mg kg⁻¹, reported for Indian, Australian, and Brazilian soils. While smaller ranges (e.g., from ±50 to <500 mg kg⁻¹) were observed in both Brazilian and Belgian soils.

It is worth mentioning that a large number of papers (9 out of 19, or 47%) used the total content result obtained via factory calibration (instead of the raw spectrum) as input for modelling (Fig. 2D). These pre-developed measurement packages (e.g., Soil Mode, Innov-X Systems, Inc., MA, USA) have specific routines for spectra acquisition and processing. Therefore, they do not allow adaptation of optimal

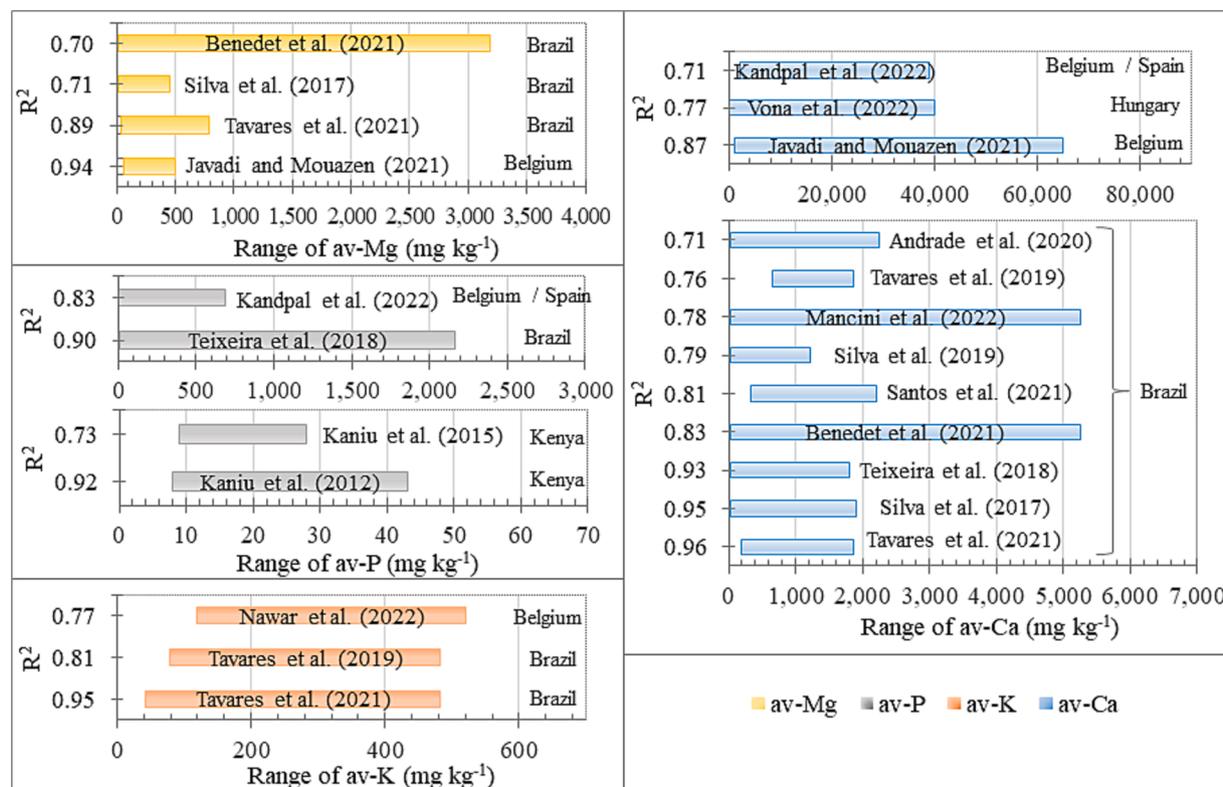


Fig. 3. Range of nutrient variation as a function of the coefficient of determination reported by studies that obtained R^2 greater than 0.7.

instrumental conditions, such as X-ray tube configurations, which will be necessary for applications related to the instantaneous prediction of soil nutrients. In addition, all studies used scanning times greater than 60 s, which is a time-consuming analysis within the context of proximal soil sensing. A recent study has indicated that excellent predictions of av-Ca and av-K can be achieved with scanning times shorter than 10 s (e.g., 7, 4, and 2 s) (Tavares et al., 2023). The possibility of this drastic reduction in analysis time should encourage research addressing *in situ* applications. The advances, challenges, and perspectives of the studies gathered were discussed in the following section.

2.3.1. Challenge 1: Dealing with physical and chemical matrix effects in spectral libraries

To ensure accurate prediction of nutrient contents in soil samples from various agricultural fields, calibration of XRF models should rely on robust spectral libraries (Shepherd and Walsh, 2002). These databases should contain a sufficiently large number of samples that represent the diversity of soils to be analyzed (Guerrero et al., 2016). Gathering X-ray fluorescence spectra from these soils will encompass a diverse matrix effect. This effect refers to the influence of physical (e.g., variations in density and particle size) and chemical properties (i.e., variations in the contents of Si, Al, K, Ca, Fe, Ti, Zr, among others) of the samples on the sensor's output. In the scenario where the soil matrix is uniform, the relationship between the concentration of an analyte and the resulting spectra would be straightforward and linear. However, various soil matrices exhibit absorptions or enhancements of specific energies (USEPA, 2007). In other words, the matrix effect influences the relationship between an analyte's concentration and fluorescence emission's intensity.

The matrix effect can be mitigated. Most of the research that evaluated XRF to predict available nutrients used factory calibrations (e.g., Soil Mode, Innov-X Systems, Inc., MA, USA). These pre-programmed packages have routines for spectra acquisition and processing and provide the total contents of the elements present in the samples (Andrade et al., 2020; de Lima et al., 2019; O'Rourke et al., 2016; Silva et al., 2018). However, these algorithms lack transparency and do not provide information about the soils used for the calibration. Thus, open-source and collaborative X-ray fluorescence spectral libraries and models are preferred.

A common practical mistake is constructing calibration curves using soils with lower average atomic numbers, such as those abundant in Al and Si. Subsequently, these curves were erroneously applied to estimate element concentrations in soils containing greater levels of heavier elements like Fe, Mn, and Ti. Hence, calibration must be performed with soil samples whose chemical composition is similar to those that will be analysed.

A more comprehensive exploration of the matrix effect in XRF data is provided in the reviews by Rousseau (2006) and Bowers (2019), which offer insights into various correction strategies. These strategies include spectral preprocessing techniques such as Compton normalization, as demonstrated by Yilmaz and Boydaş (2018), as well as the utilization of correction factors, as proposed by Markowicz (2008). Additionally, as discussed Aidene et al. (2021), multivariate modeling strategies can also be employed to address the matrix effect.

In a recent investigation conducted on tropical soils, Tavares et al. (2020b) examined the impact of the matrix effect on av-Ca and av-K prediction. The study highlighted the effectiveness of employing a combination of Compton normalization and multivariate models. Modelling using XRF spectra after Compton normalization also yielded more accurate results for predicting key fertility attributes in temperate soils (Javadi et al., 2021). These studies indicate the importance of the Compton $K\alpha$ peak (i.e., which has energy around 19 keV in Rh tubes), which should be incorporated in the spectra and their analysis (Tavares et al., 2020a). It is worth mentioning that the Compton and Thomson scattering region, as well as the background of the XRF spectra, is influenced by the anode of the X-ray tube used, e.g. while an XRF spectra

obtained with a Rh X-ray tube will show Compton and Thomson scattering of the Rh- $K\alpha$ peak around 18–21 keV, a spectra obtained with an Au tube will show Compton and Thomson scattering of the Au- $L\alpha$ peak around 7–10 keV.

While the studies mentioned above demonstrated the effectiveness of matrix-effect mitigation, most of their datasets were limited to no more than 267 samples. Therefore, to determine the feasibility of mitigating this effect for a range of soils, evaluating these strategies using more extensive databases that exhibit more complex levels of the matrix effect is crucial. In databases containing diverse soil types, it may be worthwhile to consider modelling strategies that aim to “localize” samples with similar spectral characteristics. Approaches such as memory-based learning (MBL) methods (Ramirez-Lopez et al., 2013), localized PLSR (Ng et al., 2022b), and transfer learning (Padarian et al., 2019) could be effective and should be considered for future research.

Variations in particle size, organic matter (OM) content, and moisture content also lead to absorption or enhancement effects on fluorescence emission, thus causing matrix effects. Finer particle sizes of soil samples can exhibit higher elemental concentrations than unground or coarser samples. This effect is particularly noticeable for elements with small atomic numbers, such as K, Ca, V, and Cr (Laiho and Peramaki, 2005). In laboratory analyses, the effect of grain size and moisture is minimized by standardizing the sample preparation with drying and sieving (e.g., < 2 mm). Furthermore, as demonstrated by Tavares et al. (2019), this simple preparation can be as effective as soil pelletizing — a preparation that aims to reduce physical matrix effects and homogenize the sample — for nutrient prediction. This standard preparation of drying and sieving the samples was applied in all papers evaluated in this review (Table A1). Sample sieving may be feasible in a mobile laboratory setting, particularly when working with relatively dry soils. However, drying and sieving may not be practical for *in situ* analyses. Therefore, future research should assess the trade-off between nutrient prediction accuracy and the elimination of sample preparation.

Increases in OM content could lead to matrix effects as they alter soil physical properties (e.g., density reduction) and decrease the sample's average atomic number (Morona et al., 2017). Higher OM concentrations would lead to an increase in the spectra scattering region and attenuation of the fluorescence emission lines (Ravansari and Lemke, 2018). The matrix effect of OM was evaluated by Costa et al. (2019) and Rosin et al. (2022). Both studies suggest that spectral interference is only noticeable when the soil OM content exceeds 5%, which is usually considered a high value in agricultural soils, particularly in tropical regions. Nevertheless, further investigations are still needed for organic-rich soils, and a possible alternative for these cases is to combine XRF and vis-NIR spectra, given the close relationship between vis-NIR data with organic components. In this regard, a recent patent by Weindorf and Chakraborty (2017) combined vis-NIR and XRF sensors with remote sensing data to analyse some soil attributes.

To date, no studies have been carried out on *in situ* prediction of soil fertility attributes using portable XRF equipment. When collecting fluorescence data directly in the field, it is important to consider the variations in moisture and the irregularities in soil surface and aggregates. Water in soil enhances the absorption of X-rays, reducing the intensity of the X-ray signal (Weindorf et al., 2014b). However, it is possible to correct the soil moisture effect. For example, theoretically, the reduction in X-ray intensity is proportional to the increase in water content of the sample (Ge et al., 2005). However, Stockmann et al. (2016) showed that the response of intensity decreases with moisture content is inconsistent across all soil types; thus, a universal correction factor for soil moisture cannot be derived. Another potential approach is to employ spectra pretreatment techniques and advanced modelling methods, similar to those used in removing external effects in DRS techniques, as discussed by Mouazen et al. (2020) and Nawar et al. (2020). These techniques should be investigated further, especially in soil samples exceeding 20 % gravimetric moisture content or when the target element has fluorescence emission lower than 5 KeV (Ravansari

et al., 2020). In addition, the combination of vis-NIR data, which is sensitive to soil moisture variation, may also be an alternative to mitigate the effect of moisture on XRF data and is worthy of further study. Progress in these areas may drive the development of portable equipment specifically designed for soil data collection directly in the field, similar to the CheMin prototype used in the Mars Science Laboratory mission (Sarrazin et al., 2005).

2.3.2. Challenge 2: Algorithms for predicting available nutrients

Determining available nutrients involves measuring the amount of plant-accessible elements in soils. This is achieved through partial extractions utilising specific extractants, such as Mehlich 1, Mehlich 2, resin, and other methods. These extractants simulate plants' uptake (ion absorption) behaviour, allowing for an estimation of nutrient availability in the soil solution (Barber, 1995). The ratio between the total and plant-available contents (T/A ratio) of a given nutrient can vary depending on soil mineralogy characteristics (e.g., minerals present in the parental material that are nutrient sources), soil weathering level, as well as on the soil fertility management (e.g., fertilizer and lime application) (Barber, 1995; Marschner and Rengel, 2023). Considering that X-ray fluorescence spectra are intrinsically related to the total content of elements present in the soil, the second challenge for predicting nutrients via XRF is developing agronomic algorithms that consider the local context of the T/A ratio. Local and regional spectral libraries will certainly have different levels of T/A ratio complexity. Although local models are anticipated to have lower complexity, it is important to acknowledge that they can still be impacted by variations in soil management practices. These changes in soil management can potentially influence the temporal stability of the local XRF performance. Therefore, it is crucial to consider the dynamic nature of soil management factors when evaluating and utilizing local models for XRF analysis.

2.3.2.1. Inferences in tropical and temperate soils. Studies using XRF to predict plant-available nutrients on tropical soils attribute the successful predictions to the highly weathered nature of these soils compared to those in temperate regions (Hartemink, 2002). The prevalence of Fe and Al oxides and kaolinite in tropical soils, which lack plant nutrients such as Ca, K, and Mg in their structure, means that soil management becomes the primary driver of the T/A ratio (de Lima et al., 2019). Conversely, this behaviour is not observed for phosphorus (P), which exhibits complex chemistry in tropical soils. P strongly binds with oxides in the clay fractions, leading to the variable T/A ratio affected by clay type and content. The review by Silva et al. (2021) discussed key differences between tropical and temperate regions regarding the potential use of XRF.

On the other hand, soils in temperate regions typically have greater mineralogical complexity due to their lower degree of weathering compared to tropical soils (Hartemink, 2002). This characteristic results in a greater range of nutrient variation in studies carried out in countries such as Belgium (e.g., Javadi and Mouazen, 2021; Nawar et al., 2022), Hungary (e.g., Vona et al., 2022), and Spain (e.g., Kandpal et al., 2022), particularly for av-Ca and av-K (Table S1), as discussed in Section 2.1. Thus, a greater complexity of the T/A ratio is also expected, which might reflect in a lower predictive performance for spectral libraries of temperate soils compared to those of tropical soils. For example, estimating the plant-available contents of Ca and K can be challenging in cases where the soil contains minerals rich in these elements, such as muscovite, mica, or calcite. Nevertheless, studies on temperate soils also report the successful prediction of plant-available nutrients, such as Kandpal et al. (2022) and Vona et al. (2022) for av-Ca ($R^2 \geq 0.71$), Nawar et al., (2022) for av-K ($R^2 = 0.77$), Kandpal et al. (2022) and Vona et al. (2022) for av-P ($R^2 = 0.83$), and Javadi and Mouazen (2021) for av-Mg ($R^2 = 0.94$). More research should be conducted to understand the factors behind the success and failure of each studied case. Mineralogical analysis can be key in this process, even for tropical areas.

Mineralogical identification using, e.g., vis-NIR, MIR, or XRD spectra can serve as an option to identify soil samples that are suitable or unsuitable for the analysis of available nutrient contents through XRF. In addition, as pointed out for the challenge 1 (Section 2.3.1), advanced models that localize similar samples [e.g., Ng et al. (2022b) and Padarian et al. (2019)] may be an alternative to deal with the local context of the T/A ratio in X-ray fluorescence spectral libraries and should be further investigated.

2.3.2.2. Possible effects of soil management on T/A ratio. While satisfactory nutrient predictions in tropical soils are linked to the strong connection between the T/A ratio and soil management practices rather than soil processes (de Lima et al., 2019; Tavares et al., 2020a), it is important to note that management practices implemented in subsequent years can potentially modify the T/A ratio. These changes in management practices, such as fertilisation, liming or application of other amendments, can influence nutrient availability and alter the relationship between total nutrient content and available nutrient content in the soil (Riebe et al., 2019). The effect of soil management on the temporal stability of XRF model performance to predict plant-available nutrients has not yet been addressed in the literature.

Future studies need to understand how much agricultural soil management influences the model performance over time. For example, the effects of an increase in OM over time (fundamental to the increase of soil C stocks) should also be evaluated in local models, since it promotes changes in soil chemical (i.e., an increase of light elements, such as C, H, and O) and physical composition (e.g., reduction of bulk density); consequently, altering matrix effects in the spectra.

Another important management that should reflect on XRF models is the application of fertilizers and amendments (e.g., rock powder or lime application). These interventions can alter some nutrients' T/A ratio, consequently reducing the performance of previously calibrated models. Understanding these aspects is fundamental to adapting and developing methods to mitigate performance loss or suggest the need to continuously update the prediction models, e.g., updating the calibration database enriched with new samples, e.g., Guerrero et al. (2014).

2.3.2.3. A case study in Brazilian tropical soils. Fig. 4, as presented by Tavares et al. (2022), provides compelling evidence that supports the theoretical aspects related to the potential for nutrient prediction using XRF in tropical soils, which have been discussed previously in Sections 2.3.1 and 2.3.2. The figure shows the T/A ratios obtained from two distinct agricultural areas in Brazil (Fig. 4C). These areas are geographically distant from each other (Fig. 4A), representing both tropical (Field 2 with Aw climate) and subtropical (Field 1 with Cfa climate) regions. Both fields have simple mineralogy (Fig. 4B), typical of tropical areas (i.e., Fe and Al oxides and kaolinite), but differ in elemental composition. In both areas, the T/A ratio has a linear response and shows low values of Ca (ranging between 1.0 and 1.3 in Field 1 and between 1.2 and 2.0 in Field 2), K (ranging between 1.3 and 3.5 in Field 1 and between 1.2 and 3.4 in Field 2), and Mg (ranging between 1.4 and 5.6 in Field 1 and between 1.2 and 3.0 in Field 2). Using an XRF sensor to determine the contents of plant-available nutrients, this dataset achieved excellent predictions ($R^2 \geq 0.89$; shown in Table S1) for all of these nutrients (Tavares et al., 2021). The successful prediction of av-Ca and av-K is due to the linear relationship between total and plant-available contents observed in both fields. These successful predictions are an example of an agronomic model that dealt with the matrix effect and captured the relationships between XRF data and plant-available nutrients. Although Mg showed a linear T/A ratio in both areas, its prediction was only possible due to its correlation with Ca ($r = 0.93$), since the XRF data did not have the Mg emission line.

In contrast to the behaviour observed for Ca, K, and Mg, the T/A ratio for P (Fig. 4C) is high and non-linear for both studied fields (ranging from 16.0 to 72.4 for Field 1 and from 3.8 to 30.4 for Field 2). As a result,

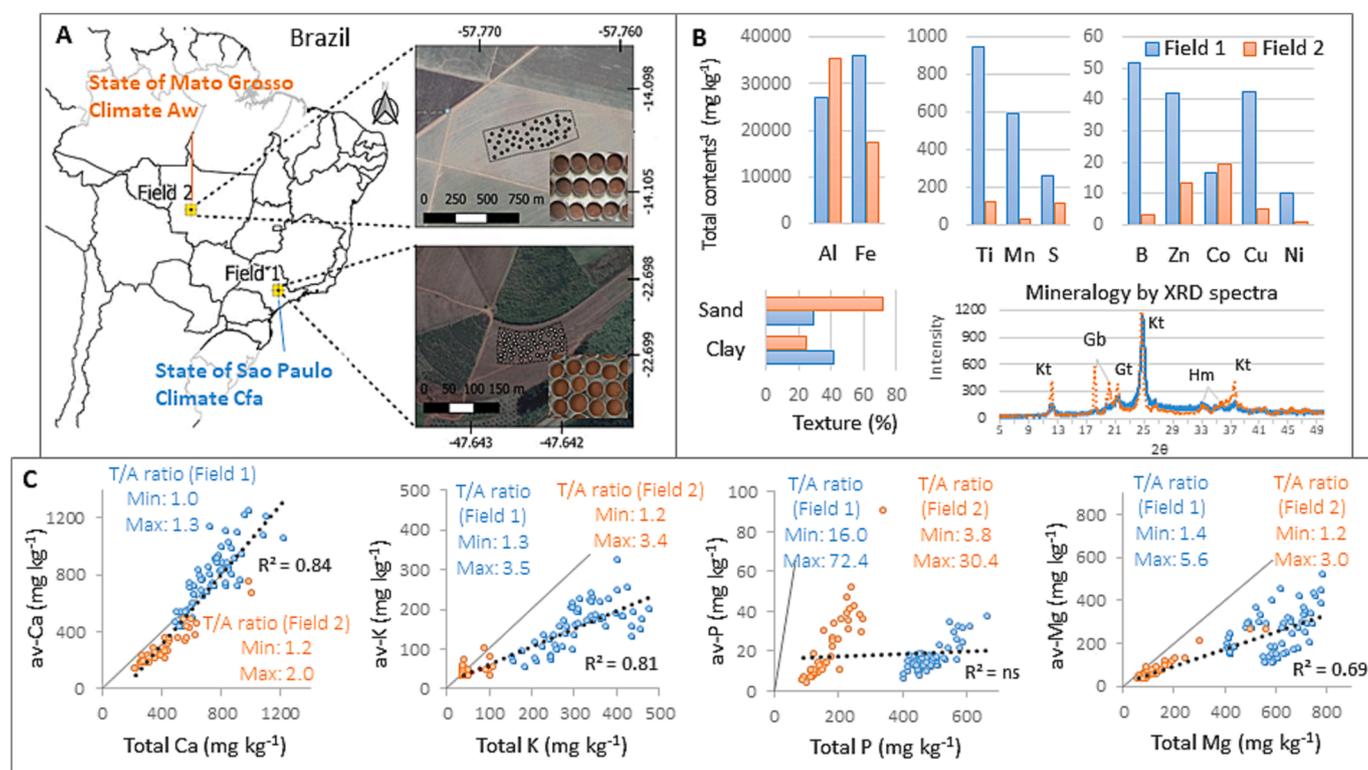


Fig. 4. Overview of results published by Tavares et al. (2022) showing the ratio between total and available (av-) content (T/A ratio) obtained from two agricultural areas in Brazil (C), which are geographically distant (A), with mineralogy predominantly composed of hematite (Hm), gibbsite (Gb), goethite (Gt), and kaolinite (Kt) (B), but differ in elemental composition (B). The acronyms of the climate indications followed Köppen's classification.

poor prediction ($R^2 = 0.01$; shown in Table S1) was obtained for this nutrient with the XRF sensor (Tavares et al., 2021). In contrast to av-Mg, av-P did not show a correlation with other elements, and the XRF sensor did not detect because it was below the limit of detection. The effectiveness of av-P prediction using LIBS sensors is demonstrated in the

study by Tavares et al. (2022), where satisfactory results with an R^2 value of 0.72 were obtained for the same dataset. Unlike XRF, LIBS exhibited well-defined P emission lines, enabling more precise measurements. Although the total and plant-available P in both areas did not show a linear relationship, local calibration is achievable. In this

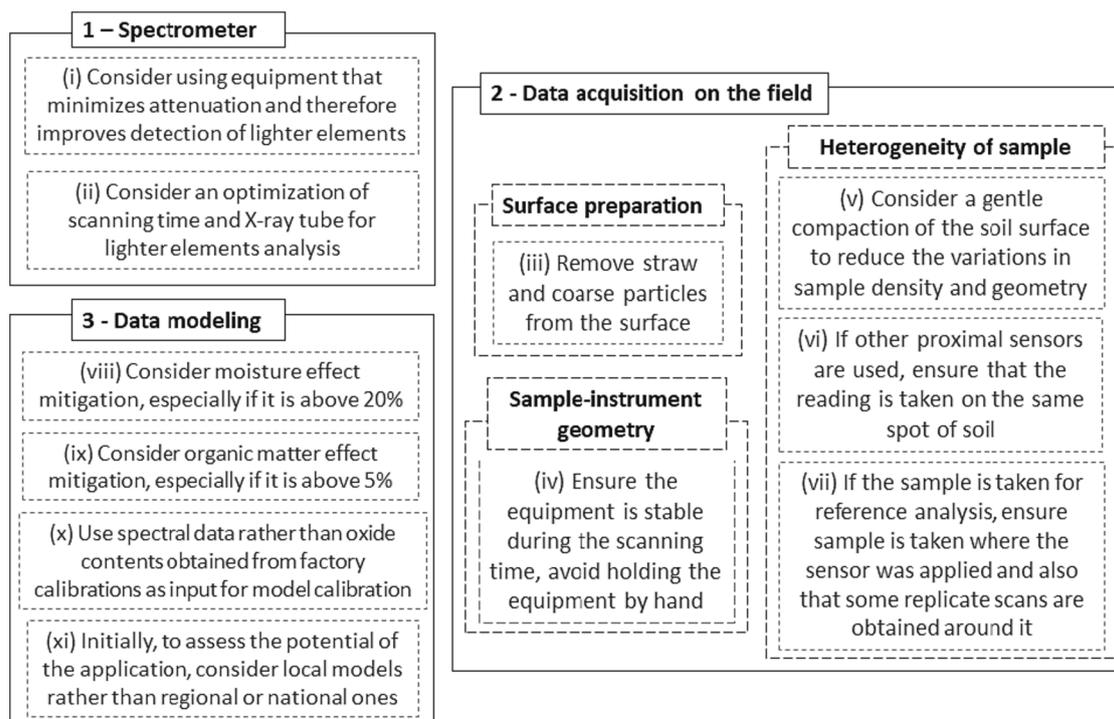


Fig. 5. Flowchart of key considerations to improve the quality of *in situ* data collection and modelling for predicting soil nutrients using portable XRF sensors.

context, advancements in X-ray tube and detector technology, such as performing analysis under vacuum condition (Gozetto et al., 2023), which help reduce the limit of detection for P, are possibilities for enabling accurate av-P prediction using XRF.

2.4. *In situ* XRF measurements for soil nutrients prediction: some considerations for future research

Results from *in situ* measurements often require more meticulous attention to ensure their quality compared to those obtained through laboratory measurements (Potts and Sargent, 2022). Predictive performance may be lower for *in situ* applications compared to laboratory studies. This is because oscillations in factors that alter the fluorescence emission intensity of a given analyte, e.g., moisture content, sample heterogeneity, sample-instrument geometry, among others, are more likely to occur during in-field scans. This is particularly important for the prediction of plant-available nutrients as their predictive models often use lighter elements (e.g., Si, Al, Ca, K, and Ti) as the most important variables (Andrade et al., 2020; de Lima et al., 2019; Tavares et al., 2020a), which are particularly more influenced by external effects due to their lower energies of fluorescence emission (i.e., below 5 KeV) (Ravansari et al., 2020).

Fig. 5 lists the key aspects that researchers might wish to consider to reduce sources of variability in *in situ* measurements using portable XRF equipment. The points raised are related to three groups: (1) hardware design and instrumental optimisations of the **spectrometer**; (2) procedures to be performed during the **data acquisition on the field**; and (3) **data modelling** for nutrient prediction. Regarding the spectrometer, it should have facilities that minimise attenuation of the fluorescence emission caused by the atmosphere and by the equipment's internal windows, e.g., using a vacuum chamber, and a thin graphene foil as a detector window (Adams et al., 2020). In addition, conducting tests to optimize the X-ray tube voltage and current and the detector dwell time may promote increases in the signal-to-noise ratio of lighter elements (Tavares et al., 2023, 2020a).

Regarding *in situ* data acquisition, it is necessary to (i) prepare the soil surface by removing straw and possible coarse particles, (ii) ensure that the sensor is physically stable during its scanning to avoid oscillations in the sample-instrument geometry, and (iii) use strategies that consider the heterogeneities of physical structure and grain size distribution, e.g., lightly compacting and smoothing the soil surface to be analyzed. In addition, to account for micro-scale heterogeneities that may lead to readings with nugget effects, analysis can be performed using replicates a few centimetres apart (Ravansari et al., 2020).

Regarding data modelling, one should consider techniques to mitigate the effects of moisture and organic matter contents (especially where variation in these elements exceeds the critical limits discussed in Section 2.3.1). Hence, using spectral data instead of oxide contents obtained from factory calibration is essential to dealing with these external effects on the spectra. Furthermore, it is recommended to use local models rather than regional or national ones, at least in the first instance that the potential of *in situ* measurements needs to be assessed. Lastly, it is worth noting that the points mentioned here aim to provide guidance for future studies which should focus on evaluating the potential of portable XRF sensors for predicting soil fertility attributes in the field and refining best practice protocols for this specific application.

3. Final remarks

- Measuring plant-available soil nutrients is crucial to agricultural intensification, closing yield gaps, and consequently contributing to soil and food security and climate-change mitigation. The development of user-friendly analytical approaches that allow instant diagnosis of nutrient status *in situ* is vital. It also facilitates the adoption of best management practices to enhance soil fertility, soil health, and plant nutrition. Soil chemical monitoring is vital to avoid

degradation (or restore degraded soils) to sustain soil functionality and related ecosystem services. However, predicting available nutrients remains challenging for current proximal soil sensing technologies.

- XRF sensors have emerged as promising tools for predicting nutrient availability in agricultural soils. The sensor is robust, and the measurement time can be as short as a few seconds and still produce reliable performance. However, gaps in knowledge still exist, and it is essential to gather ground truth data to strengthen the application of XRF sensors.
- Some key issues that need attention include: (i) evaluating the temporal stability of local models to account for fertilizer management; (ii) expanding the X-ray fluorescence spectral libraries to include diverse soil samples is also a pressing issue; (iii) testing advanced modeling strategies to address matrix effects and the local context of the ratio between the total and plant-available contents (T/A ratio); (iv) to evaluate the potential fusion with other sensing techniques that can serve as auxiliary data to improve predictive performances and extend the monitored attributes; and (v) to assess the potential of *in situ* applications and approaches to mitigate external effects (e.g., soil moisture and roughness).
- Exploring these themes will enhance the understanding of the factors contributing to successful and unsuccessful predictions, enabling us to identify soil samples suitable for XRF analysis and optimize data acquisition and processing strategies for improved results.

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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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data (Table S1 presents a list of the articles and key information gathered in our bibliometric review.) to this article can be found online at <https://doi.org/10.1016/j.geoderma.2023.116701>.

References

- Adams, C., Brand, C., Dentith, M., Fiorentini, M., Caruso, S., Mehta, M., 2020. The use of pXRF for light element geochemical analysis: a review of hardware design limitations and an empirical investigation of air, vacuum, helium flush and detector window technologies. *Geochem. Explor. Environ. Anal.* 20, 366–380. <https://doi.org/10.1144/geochem2019-076>.
- Aidene, S., Khaydukova, M., Pashkova, G., Chubarov, V., Savinov, S., Semenov, V., Kirsanov, D., Panchuk, V., 2021. Does chemometrics work for matrix effects correction in X-ray fluorescence analysis? *Spectrochim. Acta Part B At. Spectrosc.* 185, 106310 <https://doi.org/10.1016/j.sab.2021.106310>.
- Amelung, W., Bossio, D., de Vries, W., Kögel-Knabner, I., Lehmann, J., Amundson, R., Bol, R., Collins, C., Lal, R., Leifeld, J., Minasny, B., Pan, G., Paustian, K., Rumpel, C., Sanderman, J., van Groenigen, J.W., Mooney, S., van Wesemael, B., Wander, M., Chabbi, A., 2020. Towards a global-scale soil climate mitigation strategy. *Nat. Commun.* 11, 5427. <https://doi.org/10.1038/s41467-020-18887-7>.
- Andrade, R., Faria, W.M., Silva, S.H.G., Chakraborty, S., Weindorf, D.C., Mesquita, L.F., Guilherme, L.R.G., Curi, N., 2020. Prediction of soil fertility via portable X-ray fluorescence (pXRF) spectrometry and soil texture in the Brazilian Coastal Plains. *Geoderma* 357, 113960. <https://doi.org/10.1016/j.geoderma.2019.113960>.
- Archbold, G., Parra, C., Carrillo, H., Mouazen, A.M., 2023. Towards the implementation of ISFET sensors for in-situ and real-time chemical analyses in soils: A practical review. *Comput. Electron. Agric.* 209, 107828 <https://doi.org/10.1016/j.compag.2023.107828>.
- Barber, S.A., 1995. *Soil Nutrient Bioavailability: A Mechanistic Approach*. John Wiley & Sons.
- Bossio, D.A., Cook-Patton, S.C., Ellis, P.W., Fargione, J., Sanderman, J., Smith, P., Wood, S., Zomer, R.J., von Unger, M., Emmer, I.M., Griscom, B.W., 2020. The role of soil carbon in natural climate solutions. *Nat. Sustain.* 3, 391–398. <https://doi.org/10.1038/s41893-020-0491-z>.
- Bowers, C., 2019. Matrix effect corrections in X-ray fluorescence spectrometry. *J. Chem. Educ.* 96, 2597–2599. <https://doi.org/10.1021/acs.jchemed.9b00630>.
- Bueno Guerra, M.B., de Almeida, E., Carvalho, G.G.A., Souza, P.F., Nunes, L.C., Júnior, D. S., Krug, F.J., 2014. Comparison of analytical performance of benchtop and handheld energy dispersive X-ray fluorescence systems for the direct analysis of plant materials. *J. Anal. At. Spectrom.* 29, 1667–1674. <https://doi.org/10.1039/C4JA00083H>.
- Costa, Y.T., Ribeiro, B.T., Curi, N., de Oliveira, G.C., Guilherme, L.R.G., 2019. Organic matter removal on oxide determination in oxisols via portable X-ray fluorescence. *Commun. Soil Sci. Plant Anal.* 50, 673–681. <https://doi.org/10.1080/00103624.2019.1589479>.
- de Lima, T.M., Weindorf, D.C., Curi, N., Guilherme, L.R.G.G., Lana, R.M.Q.Q., Ribeiro, B. T., 2019. Elemental analysis of Cerrado agricultural soils via portable X-ray fluorescence spectrometry: Inferences for soil fertility assessment. *Geoderma* 353, 264–272. <https://doi.org/10.1016/j.geoderma.2019.06.045>.
- Demattê, J.A.M., Dotto, A.C., Paiva, A.F.S., Sato, M. V, Dalmolin, R.S.D., Maria do Socorro, B., da Silva, E.B., Nanni, M.R., ten Caten, A., Noronha, N.C., 2019. The Brazilian Soil Spectral Library (BSSL): A general view, application and challenges. *Geoderma* 354, 113793.
- Dimkpa, C., Bindraban, P., McLean, J.E., Gatere, L., Singh, U., Hellums, D., 2017. *Methods for rapid testing of plant and soil nutrients*. Springer International Publishing, Cham, pp. 1–43. https://doi.org/10.1007/978-3-319-58679-3_1.
- Evangelista, S.J., Field, D.J., McBratney, A.B., Minasny, B., Ng, W., Padarian, J., Román Dobarco, M., Wadoux, A.-M.-J.-C., 2023. A proposal for the assessment of soil security: Soil functions, soil services and threats to soil. *Soil Secur.* 10, 100086 <https://doi.org/10.1016/j.soisec.2023.100086>.
- Fageria, N.K., Nascente, A.S., 2014. Management of soil acidity of South American soils for sustainable crop production. *Adv. Agron.* 128, 221–275. <https://doi.org/10.1016/B978-0-12-802139-2.00006-8>.
- Gatuszka, A., Migaszewski, Z.M., Namięśnik, J., 2015. Moving your laboratories to the field – Advantages and limitations of the use of field portable instruments in environmental sample analysis. *Environ. Res.* 140, 593–603. <https://doi.org/10.1016/j.envres.2015.05.017>.
- Ge, L., Lai, W., Lin, Y., 2005. Influence of and correction for moisture in rocks, soils and sediments on in situ XRF analysis. *X-Ray Spectrom.* 34, 28–34. <https://doi.org/10.1002/xrs.782>.
- Gozetto, J.D., de Almeida, E., Brasil, M.A.S., Virgilio, A., Santos, E., Furlan, G.R., Pereira de Carvalho, H.W., 2023. In-house manufactured benchtop <scp>XRF</scp> spectrometer. *X-Ray Spectrom.* <https://doi.org/10.1002/xrs.3375>.
- Gredilla, A., Fdez-Ortiz de Vallejuelo, S., Elejoste, N., de Diego, A., Madariaga, J.M., 2016. Non-destructive Spectroscopy combined with chemometrics as a tool for Green Chemical Analysis of environmental samples: A review. *TRAC Trends Anal. Chem.* 76, 30–39. <https://doi.org/10.1016/j.trac.2015.11.011>.
- Guerrero, C., Stenberg, B., Wetterlind, J., Viscarra Rossel, R.A., Maestre, F.T., Mouazen, A.M., Zornoza, R., Ruiz-Sinoga, J.D., Kuang, B., 2014. Assessment of soil organic carbon at local scale with spiked NIR calibrations: effects of selection and extra-weighting on the spiking subset. *Eur. J. Soil Sci.* 65, 248–263. <https://doi.org/10.1111/ejss.12129>.
- Guerrero, C., Wetterlind, J., Stenberg, B., Mouazen, A.M., Gabarrón-Galeote, M.A., Ruiz-Sinoga, J.D., Zornoza, R., Viscarra Rossel, R.A., 2016. Do we really need large spectral libraries for local scale SOC assessment with NIR spectroscopy? *Soil Tillage Res.* 155, 501–509. <https://doi.org/10.1016/j.still.2015.07.008>.
- Hartemink, A.E., 2002. Soil science in tropical and temperate regions—Some differences and similarities. *Adv. Agron.* 77, 269–292. [https://doi.org/10.1016/S0065-2113\(02\)77016-8](https://doi.org/10.1016/S0065-2113(02)77016-8).
- Jantzi, S.C., Motto-Ros, V., Trichard, F., Markushin, Y., Melikechi, N., De Giacomo, A., 2016. Sample treatment and preparation for laser-induced breakdown spectroscopy. *Spectrochim. Acta Part B At. Spectrosc.* 115, 52–63. <https://doi.org/10.1016/j.sab.2015.11.002>.
- Javadi, S.H., Mouazen, A.M., 2021. Data fusion of XRF and Vis-NIR using outer product analysis, Granger-Ramanathan, and least squares for prediction of key soil attributes. *Remote Sens.* <https://doi.org/10.3390/rs13112023>.
- Javadi, S.H., Munnaf, M.A., Mouazen, A.M., 2021. Fusion of Vis-NIR and XRF spectra for estimation of key soil attributes. *Geoderma* 385, 114851. <https://doi.org/10.1016/j.geoderma.2020.114851>.
- Kandpal, L.M., Munnaf, M.A., Cruz, C., Mouazen, A.M., 2022. Spectra fusion of mid-infrared (MIR) and X-ray fluorescence (XRF) spectroscopy for estimation of selected soil fertility attributes. *Sensors*. <https://doi.org/10.3390/s22093459>.
- Kaniu, M.I., Angeyo, K.H., Mwala, A.K., Mangala, M.J., 2012. Direct rapid analysis of trace bioavailable soil macronutrients by chemometrics-assisted energy dispersive X-ray fluorescence and scattering spectrometry. *Anal. Chim. Acta* 729, 21–25. <https://doi.org/10.1016/j.aca.2012.04.007>.
- Kuang, B., Mahmood, H.S., Quraishi, M.Z., Hoogmoed, W.B., Mouazen, A.M., van Henten, E.J., 2012. Chapter four - Sensing soil properties in the laboratory, in situ, and on-line: A review. In: Sparks, D.L.B.T.-A. in A. (Ed.), *Advances in Agronomy*. Academic Press, pp. 155–223. <https://doi.org/https://doi.org/10.1016/B978-0-12-394275-3.00003-1>.
- Laiho, J.V., Peramaki, P., 2005. Evaluation of portable X-ray fluorescence (PXRF) sample preparation methods. *Spec. Pap. Surv. Finl.* 38, 73.
- Lal, R., 2004. Soil carbon sequestration to mitigate climate change. *Geoderma* 123, 1–22. <https://doi.org/10.1016/j.geoderma.2004.01.032>.
- Marin, F.R., Zanon, A.J., Monzon, J.P., Andrade, J.F., Silva, E.H.F.M., Richter, G.L., Antolin, L.A.S., Ribeiro, B.S.M.R., Ribas, G.G., Battisti, R., Heinemann, A.B., Grassini, P., 2022. Protecting the Amazon forest and reducing global warming via agricultural intensification. *Nat. Sustain.* 5, 1018–1026. <https://doi.org/10.1038/s41893-022-00968-8>.
- Markowicz, A.A., 2008. *Quantification and correction procedures. Portable X-ray Fluoresc. Spectrom. Capab. Situ Anal. R. Soc. Chem. Cambridge* 13–38.
- Marschner, P., Rengel, Z., 2023. Nutrient availability in soils. In: Rengel, Z., Cakmak, I., White, P.J.B.T.-M.M.N. of P. (Fourth E. (Eds.), *Marschner's Mineral Nutrition of Plants*. Elsevier, San Diego, pp. 499–522. <https://doi.org/10.1016/B978-0-12-819773-8.00003-4>.
- McBratney, A., Field, D.J., Koch, A., 2014. The dimensions of soil security. *Geoderma* 213, 203–213. <https://doi.org/10.1016/j.geoderma.2013.08.013>.
- McBride, M.B., 2022. Estimating soil chemical properties by diffuse reflectance spectroscopy: Promise versus reality. *Eur. J. Soil Sci.* 73 <https://doi.org/10.1111/ejss.13192>.
- Minasny, B., Hartemink, A.E., 2011. Predicting soil properties in the tropics. *Earth-Science Rev.* 106, 52–62. <https://doi.org/10.1016/j.earscirev.2011.01.005>.
- Molin, J.P., Tavares, T.R., 2019. Sensor systems for mapping soil fertility attributes: challenges, advances, and perspectives in Brazilian tropical soils. *Eng. Agrícola* 39, 126–147. <https://doi.org/10.1590/1809-4430-eng.agric.v39nep126-147/2019>.
- Morona, F., dos Santos, F.R., Brinatti, A.M., Melquiades, F.L., 2017. Quick analysis of organic matter in soil by energy-dispersive X-ray fluorescence and multivariate analysis. *Appl. Radiat. Isot.* 130, 13–20. <https://doi.org/10.1016/j.apradiso.2017.09.008>.
- Mouazen, A.M., Alexandridis, T., Buddenbaum, H., Cohen, Y., Moshou, D., Mulla, D., Nawar, S., Sudduth, K.A., 2020. Monitoring. In: Castrignano, A., Buttafuoco, G., Khosla, R., Mouazen, Abdul M, Moshou, D., Naud, O.B.T.-A.I. of T. and D.S. for P.S.F. (Eds.), *Agricultural Internet of Things and Decision Support for Precision Smart Farming*. Elsevier, pp. 35–138. <https://doi.org/10.1016/B978-0-12-818373-1.00002-0>.
- Mouazen, A.M., Kuang, B., 2016. On-line visible and near infrared spectroscopy for in-field phosphorus management. *Soil Tillage Res.* 155, 471–477. <https://doi.org/10.1016/j.still.2015.04.003>.
- Nawar, S., Corstanje, R., Halcro, G., Mulla, D., Mouazen, A.M., 2017. Delineation of soil management zones for variable-rate fertilization. *Adv. Agron.* 143, 175–245. <https://doi.org/10.1016/bs.agron.2017.01.003>.
- Nawar, S., Delbecq, N., Declercq, Y., De Smedt, P., Finke, P., Verdoodt, A., Van Meirvenne, M., Mouazen, A.M., 2019. Can spectral analyses improve measurement of key soil fertility parameters with X-ray fluorescence spectrometry? *Geoderma* 350, 29–39. <https://doi.org/10.1016/j.geoderma.2019.05.002>.
- Nawar, S., Abdul Munnaf, M., Mouazen, A.M., 2020. Machine learning based on-line prediction of soil organic carbon after removal of soil moisture effect. *Remote Sens.* 12, 1308. <https://doi.org/10.3390/rs12081308>.
- Nawar, S., Richard, F., Kassim, A.M., Tekin, Y., Mouazen, A.M., 2022. Fusion of Gamma-rays and portable X-ray fluorescence spectral data to measure extractable potassium in soils. *Soil Tillage Res.* 223, 105472 <https://doi.org/10.1016/j.still.2022.105472>.
- Ng, W., Minasny, B., Jeon, S.H., McBratney, A., 2022a. Mid-infrared spectroscopy for accurate measurement of an extensive set of soil properties for assessing soil functions. *Soil Secur.* 6, 100043 <https://doi.org/10.1016/j.soisec.2022.100043>.
- Ng, W., Minasny, B., Jones, E., McBratney, A., 2022b. To spike or to localize? Strategies to improve the prediction of local soil properties using regional spectral library. *Geoderma* 406, 115501. <https://doi.org/10.1016/j.geoderma.2021.115501>.
- O'Rourke, S.M., Stockmann, U., Holden, N.M., McBratney, A.B., Minasny, B., 2016. An assessment of model averaging to improve predictive power of portable vis-NIR and XRF for the determination of agronomic soil properties. *Geoderma* 279, 31–44. <https://doi.org/10.1016/j.geoderma.2016.05.005>.
- Oliveira, D.M. da S., Tavares, R.L.M., Loss, A., Madari, B.E., Cerri, C.E.P., Alves, B.J.R., Pereira, M.G., Cherubin, M.R., 2023. Climate-smart agriculture and soil C

- sequestration in Brazilian Cerrado: A systematic review. *Rev. Bras. Ciência do Solo* 47. <https://doi.org/10.36783/18069657rbc20220055>.
- Padarian, J., Minasny, B., McBratney, A.B., 2019. Transfer learning to localise a continental soil vis-NIR calibration model. *Geoderma* 340, 279–288. <https://doi.org/10.1016/j.geoderma.2019.01.009>.
- Padarian, J., Stockmann, U., Minasny, B., McBratney, A.B., 2022. Monitoring changes in global soil organic carbon stocks from space. *Remote Sens. Environ.* 281, 113260 <https://doi.org/10.1016/j.rse.2022.113260>.
- Paiva, A.F. da S., Poppiel, R.R., Rosin, N.A., Greschuk, L.T., Rosas, J.T.F., Demattê, J.A. M., 2022. The Brazilian Program of soil analysis via spectroscopy (ProBASE): Combining spectroscopy and wet laboratories to understand new technologies. *Geoderma* 421, 115905. <https://doi.org/10.1016/j.geoderma.2022.115905>.
- Pandey, S., Bhattacharya, N.P., Paudel, P., Pariyar, R., Maskey, K.H., Khadka, J., Thapa, T.B., Rijal, B., Panday, D., 2018. Improving fertilizer recommendations for Nepalese farmers with the help of soil-testing mobile van. *J. Crop Improv.* 32, 19–32. <https://doi.org/10.1080/15427528.2017.1387837>.
- Potts, P.J., Sargent, M., 2022. In situ measurements using hand-held XRF spectrometers: a tutorial review. *J. Anal. At. Spectrom.* 37, 1928–1947. <https://doi.org/10.1039/D2JA000171C>.
- Ramirez-Lopez, L., Behrens, T., Schmidt, K., Stevens, A., Demattê, J.A.M., Scholten, T., 2013. The spectrum-based learner: A new local approach for modeling soil vis-NIR spectra of complex datasets. *Geoderma* 195–196, 268–279. <https://doi.org/10.1016/j.geoderma.2012.12.014>.
- Ravansari, R., Lemke, L.D., 2018. Portable X-ray fluorescence trace metal measurement in organic rich soils: pXRF response as a function of organic matter fraction. *Geoderma* 319, 175–184. <https://doi.org/10.1016/j.geoderma.2018.01.011>.
- Ravansari, R., Wilson, S.C., Tighe, M., 2020. Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. *Environ. Int.* 134, 105250 <https://doi.org/10.1016/j.envint.2019.105250>.
- Riebe, E., Brinkmann, B., Löhmannsröben, G., Riebe, D., Eler, A., Brinkmann, P., Beitz, T., Löhmannsröben, H.G., Gebbers, R., 2019. Comparison of calibration approaches in laser-induced breakdown spectroscopy for proximal soil sensing in precision agriculture. *Sensors* 19, 5244. <https://doi.org/10.3390/s19235244>.
- Rosin, N.A., Demattê, J.A.M., Leite, M.C.A., de Carvalho, H.W.P., Costa, A.C., Greschuk, L.T., Curi, N., Silva, S.H.G., 2022. The fundamental of the effects of water, organic matter, and iron forms on the pXRF information in soil analyses. *CATENA* 210, 105868. <https://doi.org/10.1016/j.catena.2021.105868>.
- Rouillon, M., Taylor, M.P., 2016. Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? *Environ. Pollut.* 214, 255–264. <https://doi.org/10.1016/j.envpol.2016.03.055>.
- Rousseau, R.M., 2006. Corrections for matrix effects in X-ray fluorescence analysis—A tutorial. *Spectrochim. Acta Part B At. Spectrosc.* 61, 759–777. <https://doi.org/10.1016/j.sab.2006.06.014>.
- Sarrazin, P., Blake, D., Feldman, S., Chipera, S., Vaniman, D., Bish, D., 2005. Field deployment of a portable X-ray diffraction/X-ray fluorescence instrument on Mars analog terrain. *Powder Diffr.* 20, 128–133. <https://doi.org/10.1154/1.1913719>.
- Sentelhas, P.C., Batissti, R., Camara, G.M.S., Farias, J.R.B., Hampf, A.C., Nendel, C., 2015. The soybean yield gap in Brazil – magnitude, causes and possible solutions for sustainable production. *J. Agric. Sci.* 153, 1394–1411. <https://doi.org/10.1017/S0021859615000313>.
- Shepherd, K.D., Walsh, M.G., 2002. Development of reflectance spectral libraries for characterization of soil properties. *Soil Sci. Soc. Am. J.* 66, 988–998. <https://doi.org/10.2136/sssaj2002.9880>.
- Silva, S.H.G., Silva, E.A., Poggere, G.C., Guilherme, L.R.G., Curi, N., 2018. Tropical soils characterization at low cost and time using portable X-ray fluorescence spectrometer (pXRF): Effects of different sample preparation methods. *Ciência e Agrotecnol.* 42, 80–92. <https://doi.org/10.1590/1413-70542018421009117>.
- Silva, S.H.G., Ribeiro, B.T., Guerra, M.B.B., de Carvalho, H.W.P., Lopes, G., Carvalho, G. S., Guilherme, L.R.G., Resende, M., Mancini, M., Curi, N., Rafael, R.B.A., Cardelli, V., Cocco, S., Corti, G., Chakraborty, S., Li, B., Weindorf, D.C., 2021. pXRF in tropical soils: Methodology, applications, achievements and challenges. *Adv. Agron.* 167, 1–62. <https://doi.org/10.1016/bs.agron.2020.12.001>.
- Sinfield, J.V., Fagerman, D., Colic, O., 2010. Evaluation of sensing technologies for on-the-go detection of macro-nutrients in cultivated soils. *Comput. Electron. Agric.* 70, 1–18. <https://doi.org/10.1016/j.compag.2009.09.017>.
- Stenberg, B., Viscarra Rossel, R.A., Mouazen, A.M., Wetterlind, J., 2010. Visible and near infrared spectroscopy in soil science. *Adv. Agron.* 107, 163–215. [https://doi.org/10.1016/S0065-2113\(10\)07005-7](https://doi.org/10.1016/S0065-2113(10)07005-7).
- Stockmann, U., Cattle, S.R., Minasny, B., McBratney, A.B., 2016. Utilizing portable X-ray fluorescence spectrometry for in-field investigation of pedogenesis. *CATENA* 139, 220–231. <https://doi.org/10.1016/j.catena.2016.01.007>.
- Suh, S., Johnson, J.A., Tambjerg, L., Sim, S., Broeckx-Smith, S., Reyes, W., Chaplin-Kramer, R., 2020. Closing yield gap is crucial to avoid potential surge in global carbon emissions. *Glob. Environ. Chang.* 63, 102100 <https://doi.org/10.1016/j.gloenvcha.2020.102100>.
- Tavares, T.R., Nunes, L.C., Alves, E.E.N., de Almeida, E., Maldaner, L.F., Krug, F.J., de Carvalho, H.W.P., Molin, J.P., 2019. Simplifying sample preparation for soil fertility analysis by X-ray fluorescence spectrometry. *Sensors* 19, 5066. <https://doi.org/10.3390/s19235066>.
- Tavares, T.R., Molin, J.P., Nunes, L.C., Alves, E.E.N., Melquiades, F.L., de Carvalho, H.W.P., Mouazen, A.M., de Carvalho, H.W.P., Mouazen, A.M., 2020a. Effect of X-ray tube configuration on measurement of key soil fertility attributes with XRF. *Remote Sens.* 12, 963. <https://doi.org/10.3390/rs12060963>.
- Tavares, T.R., Mouazen, A.M., Alves, E.E.N., Dos Santos, F.R., Melquiades, F.L., De Carvalho, H.W.P., Molin, J.P., 2020b. Assessing soil key fertility attributes using a portable X-ray fluorescence: A simple method to overcome matrix effect. *Agronomy* 10. <https://doi.org/10.3390/agronomy10060787>.
- Tavares, T.R., Molin, J.P., Nunes, L.C., Wei, M.C.F., Krug, F.J., de Carvalho, H.W.P., Mouazen, A.M., 2021. Multi-sensor approach for tropical soil fertility analysis: comparison of individual and combined performance of VNIR, XRF, and LIBS spectroscopies. *Agronomy* 11, 1028. <https://doi.org/10.3390/agronomy11061028>.
- Tavares, T.R., Mouazen, A.M., Nunes, L.C., dos Santos, F.R., Melquiades, F.L., da Silva, T. R., Krug, F.J., Molin, J.P., 2022. Laser-Induced Breakdown Spectroscopy (LIBS) for tropical soil fertility analysis. *Soil Tillage Res.* 216, 105250 <https://doi.org/10.1016/j.still.2021.105250>.
- Tavares, T.R., Molin, J.P., Alves, E.E.N., Melquiades, F.L., de Carvalho, H.W.P., Mouazen, A.M., 2023. Towards rapid analysis with XRF sensor for assessing soil fertility attributes: Effects of dwell time reduction. *Soil Tillage Res.* 232, 105768 <https://doi.org/10.1016/j.still.2023.105768>.
- USEPA, 2007. Method 6200: Field portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.
- van Erp, P.J., Terhoeven-Urselmans, T., van der Meer, R., 2014. Soil fertility status and NPK blends at planting for maize growing in the Western Kenyan Counties Uasin Gishu and Busia. *Electron. Int. Fertil. Corresp.* 15–23.
- Van Rooyen, A.F., Bjornlund, H., Pittock, J., 2021. Beyond fertilizer for closing yield gaps in sub-Saharan Africa. *Nat. Food* 2, 756–757. <https://doi.org/10.1038/s43016-021-00386-7>.
- Viscarra Rossel, R.A.A., Adamchuk, V.I.I., Sudduth, K.A.A., McKenzie, N.J.J., Lobsey, C., 2011. Proximal soil sensing: an effective approach for soil measurements in space and time. *Adv. Agron.* 113, 243–291. <https://doi.org/10.1016/B978-0-12-386473-4.00005-1>.
- Viscarra Rossel, R.A., Behrens, T., Ben-Dor, E., Chabrilat, S., Demattê, J.A.M., Ge, Y., Gomez, C., Guerrero, C., Peng, Y., Ramirez-Lopez, L., Shi, Z., Stenberg, B., Webster, R., Winowiecki, L., Shen, Z., 2022. Diffuse reflectance spectroscopy for estimating soil properties: A technology for the 21st century. *Eur. J. Soil Sci.* 73 <https://doi.org/10.1111/ejss.13271>.
- Viscarra Rossel, R., McBratney, A., Minasny, B., 2010. *Proximal Soil Sensing*. Springer Science+ Business Media BV.
- Vona, V., Sarjant, S., Tomczyk, B., Vona, M., Kalocsai, R., Kulmány, I.M., Jakab, G., Ver, A., Milics, G., Centeri, C., 2022. The effect of local samples in the accuracy of mid-infrared (MIR) and X-ray fluorescence (XRF) -based spectral prediction models. *Precis. Agric.* 23, 2027–2039. <https://doi.org/10.1007/s11119-022-09942-y>.
- Weindorf, D.C., Chakraborty, S., 2017. Portable apparatus for soil chemical characterization. *US 2017/0122889 A1*.
- Weindorf, D.C., Bakr, N., Zhu, Y., 2014a. Chapter One - Advances in portable X-ray fluorescence (pXRF) for environmental, pedological, and agronomic applications. *Adv. Agron.* 128, 1–45. <https://doi.org/10.1016/B978-0-12-802139-2.00001-9>.
- Weindorf, D.C., Bakr, N., Zhu, Y., McWhirt, A., Ping, C.L., Michaelson, G., Nelson, C., Shook, K., Nuss, S., 2014b. Influence of ice on soil elemental characterization via portable X-ray fluorescence spectrometry. *Pedosphere* 24, 1–12. [https://doi.org/10.1016/S1002-0160\(13\)60076-4](https://doi.org/10.1016/S1002-0160(13)60076-4).
- Yilmaz, D., Boydağ, E., 2018. The use of scattering peaks for matrix effect correction in WDXRF analysis. *Radiat. Phys. Chem.* 153, 17–20. <https://doi.org/10.1016/j.radphyschem.2018.08.035>.