



Proximal sensing provides clean, fast, and accurate quality control of organic and mineral fertilizers

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ABSTRACT

Farms use large quantities of fertilizers from many sources, making quality control a challenging task, as the traditional wet-chemistry analyses are expensive, time consuming and not environmentally-friendly. As an alternative, this work proposes the use of portable X-ray fluorescence (pXRF) spectrometry and machine learning algorithms for rapid and low-cost estimation of macro and micronutrient contents in mineral and organic fertilizers. Four machine learning algorithms were tested. Whole (i.e., as delivered by the manufacturer) (CP) and ground (AQ) samples (429 in total) were analyzed to test the effect of fertilizer granulometry in prediction performance. Model validation indicated highly accurate predictions of macro (N: $R^2 = 0.92$; P: 0.97; K: 0.99; Ca: 0.94, Mg: 0.98; S: 0.96) and micronutrients (B: 0.99; Cu: 0.99; Fe: 0.98; Mn: 0.91; Zn: 0.94) for both organic and mineral fertilizers. RPD values ranged from 2.31 to 9.23 for AQ samples, and Random Forest and Cubist Regression were the algorithms with the best performances. Even samples analyzed as they were received from the manufacturer (i.e., no grinding) provided accurate predictions, which accelerate the confirmation of nutrient contents contained in fertilizers. Results demonstrated the potential of pXRF data coupled with machine learning algorithms to assess nutrient composition in both mineral and organic fertilizers with high accuracy, allowing for clean, fast and accurate quality control. Sensor-driven quality assessment of fertilizers improves soil and plant health, crop management efficiency and food security with a reduced environmental footprint.

1. Introduction

Fertilizers are mineral or organic inputs applied to soil or plant tissues to provide one or more nutrients for improvement of plant growth. Worldwide, fertilizers are highly demanded products used in large quantities to increase and/or maintain agricultural productivity (Majeed, 2018). For instance, the total agricultural use of inorganic fertilizers surpassed 200 million tons in 2020 (FAO, 2022). The poor physical quality of fertilizers is easy to identify by traits such as caking,

discoloration, presence of foreign material, powdered granules, and others. Conversely, chemical quality cannot be visually assessed, creating an opportunity for fraudsters to sell counterfeit, adulterated or expired fertilizers. The use of low quality fertilizers is a grave issue that can lead to poor plant germination, nutrient-weak soils, reduced crop yields, soil and water pollution, and serious problems for human and environmental health (Elahi et al., 2019; Teye et al., 2022).

Organic and mineral fertilizers have heterogeneous chemical composition and different particle sizes and densities, which makes it difficult to standardize. To guarantee consistency, more frequent quality

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Abbreviations

| | |
|-----|-------------------------------|
| CP | whole samples |
| AQ | ground samples |
| PPR | projection pursuit regression |
| RF | random forest |
| XGB | extreme gradient boosting |
| CR | cubist regression |
| RI | relative error increase |

assessment is needed. However, laboratory analyses are costly, requiring highly equipped laboratories, chemical reagents, trained personnel, and careful disposal of the resulting chemical waste (MAPA, 2017; McGrath and Cunliffe, 1985). It is therefore difficult to frequently and accurately verify fertilizer grade (i.e., its guaranteed content of nutrients), especially when used in large quantities. For reference, Brazilian farmers apply around 165 kg of fertilizer per hectare (FAO, 2022), making it impossible to sample each batch of fertilizer and submit it to formal chemical analyses. Long turnaround time of traditional laboratory analysis further increases the problem (analysis usually takes 1–2 weeks after the sample is received by the laboratory) (Vuuren and Groenewald, 2013). Therefore, a rapid and reliable detection technique to assist regulators and consumers to ensure fertilizers quality is necessary.

In the last decades, proximal sensors have been successful in assessing chemical attributes in many scientific fields, such as food science (Herreros-Chavez et al., 2019), water resources (Yarborough et al., 2019), archaeology (Kim et al., 2023), concrete science (Chinchón-Payá et al., 2021), soil health (Liu et al., 2020), etc. Among proximal sensors, portable X-ray fluorescence (pXRF) spectrometer has gained popularity within the soil science research community (Andrade et al., 2022; Mancini et al., 2022; Teixeira et al., 2022). Based on the fluorescence technique, pXRF allows for quantitative measurement of various chemical elements (from Mg to U) in a quickly (60 s) and environmentally friendly way (Silva et al., 2021; Weindorf and Chakraborty, 2018), without destroying the samples. This modern greentech promotes a non-destructive, fast and clean analysis method that could be well suited for quality control of fertilizers, which demand constant and accurate chemical content assessment of a large number of samples. If pXRF data could be modeled to accurately estimate the chemical composition of fertilizers, costly wet-chemistry analyses may be replaced by fast sensor-driven assessment.

Very few studies have reported the use of proximal sensors to assess fertilizer adulteration and nutrient content (Acquah et al., 2022; Han et al., 2009; Teye et al., 2022; Vuuren and Groenewald, 2013). Yet, most of them used near-infrared (NIR) spectroscopy, which is a more expensive tool than pXRF and that generates a large dataset requiring greater computational resources and time for data processing (Andrade et al., 2022). Acquah et al. (2022) used pXRF to determine nutrients and trace elements in fertilizers samples from Kenya and United Kingdom. However, the authors modeled fertilizer types separately and did not account for different particle sizes, as all their samples were ground. If possible, modeling all fertilizers together would make analyses more practical, and investigating the effect of sample grinding is needed, as performed in our study.

Recent research has shown that pXRF can be used for rapid and accurate assessment of Ca and Mg in lime (Benedet et al., 2023), but research reporting pXRF use for inferring organic and mineral fertilizer quality/composition is still rare in the literature. Moreover, the investigation of the effects of particle sizes of fertilizers in predictions of nutrient contents is a novel approach, which may drastically reduce the time needed for chemical evaluation of fertilizers, as they could be analyzed without grinding the samples, i.e., as they are received from the manufacturer. Hence, this work aimed to: i) develop prediction

models through machine learning algorithms [projection pursuit regression (PPR), random forest (RF), extreme gradient boosting (XGB), and cubist regression (CR)] to estimate macro and micronutrient contents in mineral and organic fertilizers using data obtained from pXRF; and ii) test the effect of sample granulometry (i.e., ground samples vs. samples granulometry as delivered by the manufacturer) in prediction accuracy. We hypothesize that pXRF in tandem with machine learning algorithms will constitute a suitable method for clean, fast, and accurate quality control for organic and mineral fertilizers.

2. Material and methods

2.1. Fertilizer samples and acid digestion

A total of 429 organic and mineral fertilizer samples were used in this study, including sulphates, phosphates, nitrates, animal manure, and others (Tables 1 and 2), from several sources and manufacturers. All samples were prepared in two ways: a) as they are delivered by the manufacturer (no preparation), and b) ground and sieved (0.3 mm mesh) (Fig. 1). Hereinafter, grind samples are referred to as AQ, and whole samples that were not ground as CP. These different sample preparation was performed to assess the influence of such procedure on pXRF results (further details on section 2.2).

All the samples were digested in graduated Pyres tubes (150 × 20 mm) with 5 ml of high purity Aqua Regia acid mixture (McGrath and Cunliffe, 1985). Total concentrations of macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) in digested solutions were then determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Analytical Instruments Inc., Kleve, Germany). Further information about the determination of macro and micronutrients in fertilizers can be found in the Brazilian manual of standard methods for fertilizer and amendment analysis (MAPA - Ministério da Agricultura and Pecuária e Abastecimento, 2017).

2.2. pXRF scanning

Analyses were performed in all CP and AQ samples using a Bruker pXRF spectrometer (Analytical Instrumentation, Billerica, MA, USA), model Tracer 5 g, containing a Rh X-ray tube with 50 keV and 100 μ A. The analyses were done in triplicates in "Soil" mode for 60 s each using the inbuilt Geochem software, as described by Weindorf and Chakraborty (2018). The pXRF spectrometer detected the concentration of twenty-six elements in the studied fertilizers: Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn, and Zr.

To guarantee the quality of the data generated using the pXRF spectrometer, pXRF manufacturer's standard soil check sample (CS-M2) and a sample certified by the National Institute of Standards and Technology (NIST) SRM 695 fertilizer check sample had their contents measured using pXRF. Results from these certified check samples obtained by pXRF were compared with the certified values and the recovery values obtained per element were calculated (recovery value = elemental content obtained using pXRF/certified elemental content). The elements obtained using the pXRF analyses and their recovery values (CS-M2/SRM 695) were: Al (–/–), As (0.99/–), Ba (0.95/–), Ca (0.98/0.58), Cd (–/–), Cr (–/–), Cu (0.93/–), Fe (0.95/0.66), Hg (–/–), K (0.98/0.70), Mg (–/–), Mn (0.96/0.71), Ni (–/–), P (1.18/–), Pb (0.98/–), Rb (–/–), S (–/–), Sb (–/–), Se (–/–), Si (–/–), Sn (–/–), Sr (1.00/–), Ti (–/–), V (–/–), Zn (0.84/0.60), and Zr (–/–). Dashes (–) indicate that either the element has no certified content in the reference material, or it was not detected using the pXRF spectrometer.

2.3. Data analysis and modeling

Prior to the development of prediction models of nutrients contained in fertilizers based on pXRF data, an exploratory analysis was performed

Table 1
Number of samples for each macro and micronutrient per fertilizer nature.

| Fertilizer | N | P | K | Ca | Mg | S | B | Cu | Fe | Mn | Zn |
|------------|-----|-----|-----|-----|----|----|----|----|----|----|----|
| Mineral | 93 | 81 | 52 | 88 | 25 | 63 | 49 | 24 | 6 | 11 | 26 |
| Organic | 82 | 77 | 78 | 30 | 29 | 33 | 29 | 29 | 29 | 29 | 29 |
| Total | 175 | 158 | 130 | 118 | 54 | 96 | 78 | 53 | 35 | 40 | 55 |

Table 2
Types of fertilizers analyzed through pXRF to build machine learning prediction models.

| Type of fertilizer | Number of samples | Type of fertilizer | Number of samples |
|-----------------------|-------------------|----------------------------------|-------------------|
| Boron | 3 | NK + sulfur + micronutrients | 45 |
| Castor bean residuum | 3 | NP | 12 |
| Cattle manure compost | 21 | NPK | 51 |
| Charcoal | 3 | NPK + micronutrients | 30 |
| Coffee residuum | 3 | NPK + sulfur + micronutrients | 27 |
| Compost | 33 | Organomineral | 6 |
| K + micronutrients | 36 | Poultry litter | 39 |
| KCl | 12 | Rice residuum | 3 |
| Manure | 15 | Sewage sludge | 3 |
| MAP | 15 | Single superphosphate | 33 |
| Micronutrients | 6 | Slow-release nitrogen N, S and K | 3 |
| Nitrate | 15 | Urea | 6 |
| NK | 3 | Wood residuum | 3 |

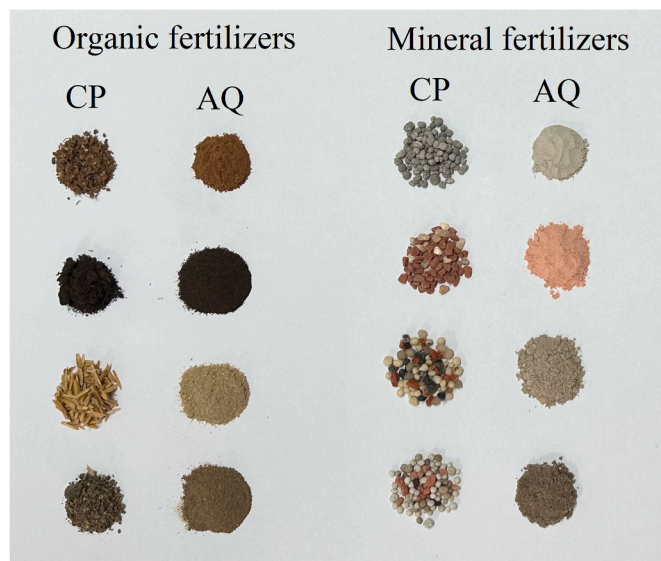


Fig. 1. Examples of the studied organic and mineral fertilizers demonstrating the different granulometry of the samples as they were received from the manufacturer (CP) and after being ground (AQ).

in order to remove outliers and better characterize the dataset. Principal component analysis (PCA) was used to search for trends in data from pXRF analysis of CP and AQ samples. PCA is commonly used to visualize multidimensional data and observe segregation in large datasets (Andrade et al., 2020, 2023). As PCA did not segregate organic from mineral fertilizers through pXRF results, data from both types of fertilizers were modeled together.

Afterwards, the entire dataset was randomly separated into modeling and validation sub-datasets, consisting of 70% and 30%, respectively. Both modeling and validation sub-datasets had samples of organic and

chemical fertilizers. PXRF detected twenty-six elements (variables); however, only the optimal explanatory variables selected through recursive feature elimination were used to build the prediction models. The “boruta” package (Kursa and Rudnicki, 2010) was used to perform feature selection for each nutrient. The method performs a top-down search for relevant features and ranks their importance. Thus, the pXRF variables were classified as Confirmed (important feature), Tentative (the feature does not impact model’s accuracy) or Rejected (not important feature). The Rejected variables were not used in the prediction models. The pXRF variables selected for the prediction of each nutrient can be seen in Fig. 7. The same set of explanatory variables was used for CP and AQ samples aiming to assess granulometry influence on pXRF results and, hence, accuracy delivered by the prediction models per nutrient. Variables’ importance was calculated for the best models for each predicted nutrient using the ‘caret’ package.

The prediction models were created using four different machine learning algorithms: projection pursuit regression (PPR), random forest (RF), extreme gradient boosting (XGB), and cubist regression (CR) using K-fold cross-validation ($K = 10$). All the models were built in R software (version 4.2.1) (R Development Core Team, 2022) using the “caret” package (Kuhn, 2008). Then, external validation was conducted (see section 2.4). These algorithms coupled with pXRF data have been successful for the development of prediction models for varying attributes of different materials, such as lime (Benedet et al., 2023), soils (Silva et al., 2021; Mancini et al., 2022), leaves (McGladdery et al., 2018; Andrade et al., 2023), rocks (Steiner et al., 2017), and other materials (Herreros-Chavez et al., 2019; Kim et al., 2023), but they have not been applied to fertilizers yet. Machine learning algorithms were used herein since they are more powerful for the identification of relationships among data than conventional analysis (Tang and Li, 2023).

2.4. Evaluating model performance

The accuracy of the predicted macro and micronutrient contents by the different machine learning algorithms (PPR, RF, XGB, and CR) was assessed by comparing predicted versus observed values through the coefficient of determination (R^2), root mean square error (RMSE) (Eq. (1)), and residual prediction deviation (RPD) (Eq. (2)). Their equations are given as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - m_i)^2} \quad (1)$$

$$RPD = SD/RMSE \quad (2)$$

where, n : number of observations, y_i : estimated value by the model, m_i : measured value by the chemical analysis, SD : standard deviation of the observed values. RPD has been characterized into three classes: $RPD > 2$, prediction models delivering accurate results, $1.4 \leq RPD \leq 2$, prediction models providing moderately accurate results, and $RPD < 1.4$, prediction models being non-reliable (Chang et al., 2001). The models with greater R^2 and lower RMSE were considered optimal for predicting laboratory analysis.

2.5. Relative error increase

The percentage of RMSE increase (Eq. (3)) was calculated to compare how the different machine learning algorithms performed. This index

was calculated by using the lowest RMSE value achieved by the most accurate model as a reference to assess the Relative Increase (RI) of RMSE. That is, the RMSE of the most accurate model was compared to the RMSE values from the other models to evaluate differences in prediction accuracy among models (Eq. (3)). As the calculations were made for models trained with CP and AQ samples, the influence of fertilizer granulometry on the accuracy of the algorithms was also evaluated. The RI equation follows:

$$RI = \frac{RMSE_{compared} - RMSE_{most\ accurate}}{RMSE_{most\ accurate}} * 100 \quad (3)$$

where $RMSE_{most\ accurate}$ is the lower RMSE value achieved by a specific algorithm, and $RMSE_{compared}$ is the RMSE values from the other algorithms.

3. Results

3.1. Chemical characterization of organic and mineral fertilizers through pXRF

The summary statistics of macro and micronutrients contents in organic and mineral fertilizers determined via wet-chemistry analysis is shown in Table 3. The results showed great variability in the contents of both macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) (CV% > 70). The variability reported here is similar to that reported by Acquah et al. (2022). This high data variability can help create robust models applicable to a broad variety of fertilizers, since the samples represent a wide range of fertilizer types. The PCA of nutrient contents showed no patterns that distinguished organic and mineral fertilizers (Fig. 2).

3.2. Accuracy of macro and micronutrients predictions

The prediction performance of macro and micronutrients in mineral and organic fertilizers calculated from the external validation (samples not used for calibrating the models) is shown in Table 4. All prediction models achieved $R^2 > 0.80$. Sample granulometry influenced the accuracy of predictions. For N, P, K, S, B, Cu, and Mn, the RMSE values were lower when training models with AQ samples, resulting in highly accurate predictions (N: $R^2 = 0.92$ and RPD = 3.45; P: 0.97 and 5.37; K: 0.99 and 9.23; S: 0.96 and 4.89; B: 0.99 and 7.29; Cu: 0.99 and 6.90; Mn: 0.91 and 2.86) (Table 4, Fig. 3).

Similarly, models trained with CP samples were also accurate (N: $R^2 = 0.91$ and RPD = 3.08; P: 0.91 and 3.29; K: 0.97 and 5.59; S: 0.88 and 2.90; B: 0.91 and 2.68; Cu: 0.86 and 1.98; Mn: 0.85 and 1.63), although comparatively less accurate than AQ models. Thus, both types of sample preparation (with and without gridding) are suitable for accurate macro and micronutrient predictions using pXRF data. In most cases, models

Table 3

Descriptive statistics of macro and micronutrients for organic and mineral fertilizers determined via wet-chemistry analysis.

| Element (%) | n | Min | Max | Mean | SD | CV% |
|-------------|-----|------|-------|-------|-------|-------|
| N | 175 | 0.01 | 46.25 | 9.88 | 10.29 | 104.2 |
| P | 158 | 0.00 | 23.83 | 6.43 | 5.72 | 89.0 |
| K | 130 | 0.00 | 44.49 | 12.79 | 14.83 | 115.9 |
| Ca | 118 | 0.00 | 44.70 | 13.38 | 9.53 | 71.3 |
| Mg | 54 | 0.00 | 7.07 | 1.91 | 2.29 | 119.7 |
| S | 96 | 0.00 | 16.68 | 4.88 | 5.15 | 105.4 |
| B | 78 | 0.00 | 2.17 | 0.46 | 0.74 | 111.4 |
| Cu | 53 | 0.00 | 0.71 | 0.18 | 0.22 | 123.5 |
| Fe | 35 | 0.00 | 6.78 | 1.99 | 2.38 | 119.9 |
| Mn | 40 | 0.00 | 0.55 | 0.14 | 0.13 | 93.5 |
| Zn | 55 | 0.00 | 0.75 | 0.22 | 0.24 | 108.0 |

n: number of samples, Min: minimum, Max: maximum, SD: standard deviation, CV: coefficient of variation.

trained with AQ samples were slightly more accurate. The exceptions were Ca ($R^2 = 0.94$ and RPD = 4.03), Mg (0.98 and 7.01), Fe (0.98 and 7.19), and Zn (0.94 and 4.00), for which the best results were delivered by models trained with CP samples (Table 4). It is important to mention that even nutrients not detected by pXRF (N and B) could be accurately predicted based on the other elements detected by pXRF in such N- or B-containing samples.

Results obtained herein were as good as those reported by Acquah et al. (2022), and for some elements predictions were even more accurate. Acquah et al. (2022) used pXRF to predict macro and micronutrients in fertilizer samples segregated by fertilizer type (e.g., sulphates, phosphates, nitrates, etc). The authors could accurately predict Mg, P, S, K, Ca, Zn, and Mn contents ($R^2 > 0.97$); however, low accuracy was obtained for Fe ($R^2 = 0.55$) and Cu ($R^2 = 0.10$). Acquah et al. (2022) did not analyze N and B contents in fertilizer samples. Similarly, Benedet et al. (2023) used pXRF to predict Ca and Mg contents in lime samples and obtained accurate results ($R^2 > 0.68$). Further extending these other studies, our results emphasize that pXRF can be used to estimate the content of several elements in a wide variety of geochemical and organic products used in agriculture.

The Relative Increase (RI%) of RMSE was overall higher for PPR and XGB models (Fig. 4), i.e., PPR and XGB had the poorest performances (Fig. 5). CR and RF performed better than the other algorithms (Fig. 5). The highest RI values for XGB were observed for P, Mg, S and B. PPR models presented relatively poor performance when estimating N, K, Ca, Fe and Mn. In most cases where high RI was observed, models trained with AQ samples presented comparatively higher error. Exceptions were PPR models trained to estimate K, Ca, Fe and Zn, and XGB models when estimating Mg; all of which had higher error increase when trained with CP samples. CR and RF consistently presented lower RI, except for Mn predictions, for which CR models presented high RI (Fig. 4).

3.3. Influence of fertilizer granulometry on pXRF scanning

The elemental composition detected by pXRF varied with sample granulometry. Differences were observed especially for the elements Cu, K, Mg, Mn, P, S, Sr, and Zn (Fig. 6). In AQ samples, comparatively lower contents were detected by pXRF for Cu, Mn, Sr, and Zn than that obtained in CP samples. In CP samples, lower contents were detected for K, P and S than in AQ samples. Although the total observed content varied depending on the granulometry of the samples (Fig. 6), prediction results indicated that data acquired from both AQ and CP samples can be used to build accurate prediction models (Table 4, Fig. 3).

Moreover, differences in the detection of total contents due to the granulometry of samples led algorithms to rank the importance of the explanatory variables (pXRF variables) differently (Fig. 7). Moreover, as expected, the algorithms defined different explanatory variables according to each nutrient predicted. Interestingly, not always the nutrient predicted had the content of that same element delivered by pXRF as the most important variable for the model to predict its content. For instance, while the prediction of P using CP samples had P detected by pXRF as the most important variable for the model (as expected), for Cu prediction, Ca delivered by pXRF was chosen by the model as the most important variable.

4. Discussion

4.1. Potential of pXRF to assess macro and micronutrients in fertilizers

Despite granulometry, density, bulk density, particle shape, surface characteristics, flow characteristics, friability, and state of agglomeration of the samples of mineral and organic fertilizers used herein, models trained with pXRF data could accurately predict macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) in both organic and mineral fertilizers (Table 4, Fig. 3), even with pXRF not detecting B and N (the best R^2 values were 0.99 and 0.92, respectively). Benedet et al.

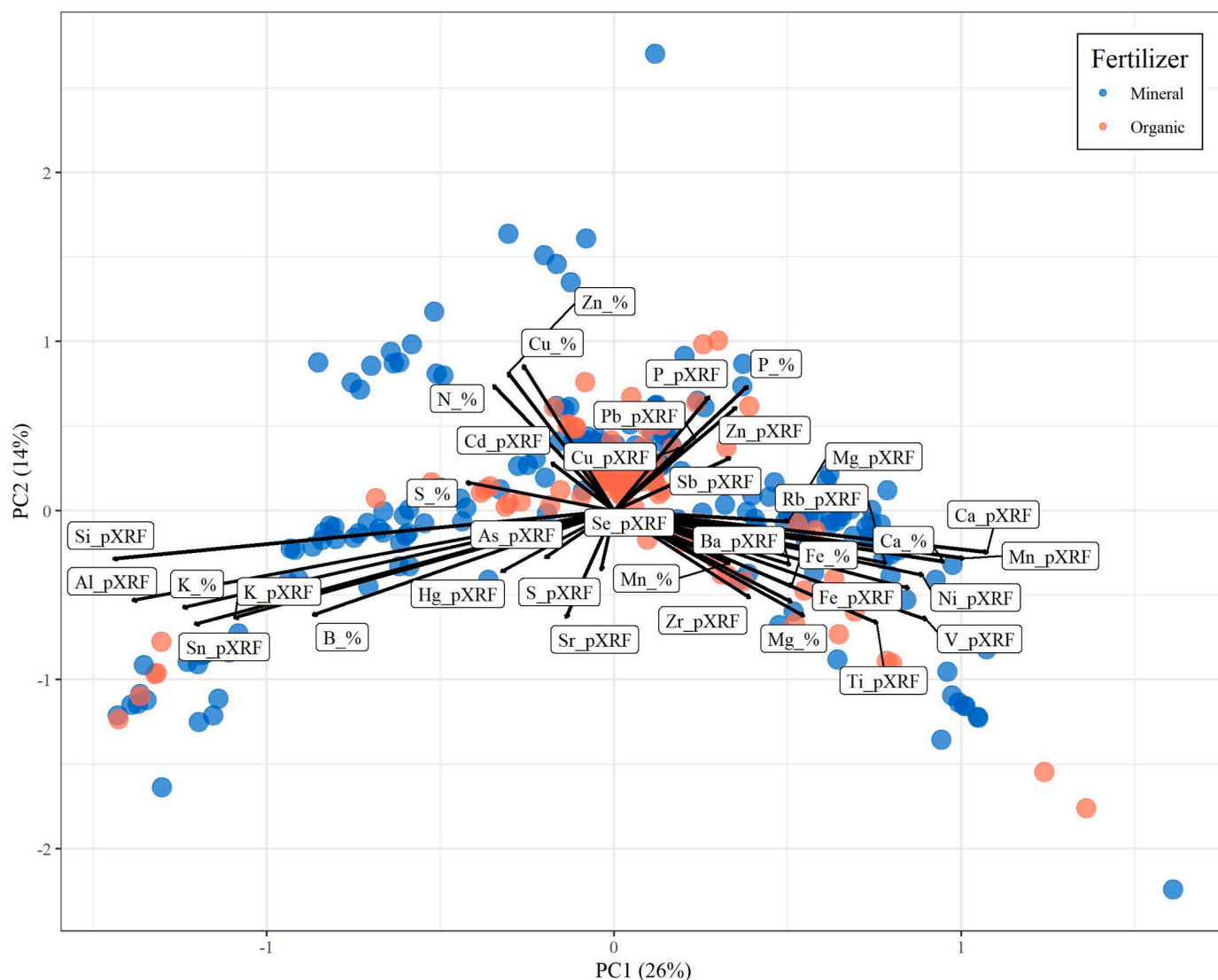


Fig. 2. Principal component analysis (PCA) of portable X-ray fluorescence (pXRF) spectrometer data and macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) for samples of organic and mineral fertilizers.

(2023) used pXRF data to assess lime quality regarding the contents of Ca and Mg and also concluded that samples without grinding delivered suitable results. The literature reports studies that used a proxy analysis to predict other fertilizer properties (Halder et al., 2017; Vuuren and Groenewald, 2013), but very rare studies conducted so far used pXRF for the assessment of nutrient contents in fertilizers (Acquah et al., 2022), as the current approach. For instance, Vuuren and Groenewald (2013) used near-infrared spectroscopy (NIRS) as a quality control indicator for bulk blended inorganic fertilizers. Teye et al. (2022) used portable NIRS and multivariate data analysis to discriminate and quantify adulteration in fertilizer samples. The authors successfully used support vector machine (SVM) and RF for the identification of unexpired and expired fertilizers, and different types of partial least squares regression to quantify the levels (10–50%) of adulteration. However, in addition to needing pre-treatment of NIRS spectra (the authors used first derivative), NIRS generates larger datasets (wavelength range of 740–1070 nm), which require longer time and higher computation power (Andrade et al., 2022) compared to pXRF-derived data (Mancini et al., 2022).

Besides, Acquah et al. (2022) used a pXRF to assess the certification and homogeneity of standard reference materials for fertilizers. Mackey et al. (2007) used XRF to measure the K-L_{2,3} characteristic X-ray lines of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Ti, V, and Zn and the

L₂-M₄ line of Pb to develop a fertilizer reference material, namely NIST SRM 695. In their study, results obtained by XRF for Mo and Co showed much less variation than ICP-OES and instrumental neutron-activation analysis (INAA), respectively; those observed variations were attributed to measurement reproducibility rather than material heterogeneity.

In addition to overcoming some challenges regarding the fertilizer material, this green technology presents many advantages: no highly specialized personnel or sample preparation are required, the probe is easy to operate, and the scanning results are instantly available. Besides, as a handheld device, it can be taken to the field for *in situ* scanning. Calibration, preparation and especially proper maintenance are essential to guarantee continued reliable results; lack of sensitivity for minor concentrations below the limit of detection (LOD) and intricacy in data treatment are some challenges of this approach, although the combination of machine learning algorithms with pXRF data surpassed them.

4.2. The effect of granulometry of fertilizers sample

An important objective of our study was to verify if ground samples (AQ) would deliver more faithful data through pXRF scanning and more accurate models compared with no grinding samples (CP) (i.e., as they

Table 4

Root mean square error (RMSE), coefficient of determination (R^2) and residual prediction deviation (RPD) of the prediction of macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) contents in whole (CP) and ground (AQ) fertilizers through portable X-ray fluorescence (pXRF) spectrometer using four machine learning algorithms: PPR = projection pursuit regression; RF = random forest; XGB = extreme gradient boosting; CR = cubist regression.

| Algorithm | Granulometry | RMSE | R^2 | RPD | RMSE | R^2 | RPD | RMSE | R^2 | RPD |
|-----------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | N | | | P | | | K | | |
| PPR | CP | 4.26 | 0.80 | 2.18 | 2.63 | 0.81 | 2.30 | 5.07 | 0.89 | 2.98 |
| RF | CP | 3.01 | 0.91 | 3.08 | 2.37 | 0.87 | 2.55 | 3.41 | 0.95 | 4.44 |
| XGB | CP | 3.37 | 0.87 | 2.75 | 2.65 | 0.82 | 2.28 | 3.90 | 0.93 | 3.89 |
| CR | CP | 3.49 | 0.86 | 2.66 | 1.84 | 0.91 | 3.29 | 2.71 | 0.97 | 5.59 |
| PPR | AQ | 7.12 | 0.60 | 1.30 | 1.78 | 0.91 | 3.41 | 2.37 | 0.98 | 6.40 |
| RF | AQ | 3.36 | 0.87 | 2.76 | 1.78 | 0.92 | 3.39 | 1.64 | 0.99 | 9.23 |
| XGB | AQ | 2.87 | 0.91 | 3.23 | 2.49 | 0.84 | 2.42 | 2.74 | 0.97 | 5.52 |
| CR | AQ | 2.69 | 0.92 | 3.45 | 1.13 | 0.97 | 5.37 | 2.09 | 0.98 | 7.23 |
| | | Ca | | | Mg | | | S | | |
| PPR | CP | 6.86 | 0.72 | 1.51 | 0.53 | 0.97 | 4.56 | 2.47 | 0.78 | 2.12 |
| RF | CP | 4.28 | 0.89 | 2.42 | 0.35 | 0.98 | 7.01 | 2.14 | 0.84 | 2.44 |
| XGB | CP | 2.85 | 0.94 | 3.64 | 0.97 | 0.91 | 2.49 | 2.15 | 0.83 | 2.43 |
| CR | CP | 2.57 | 0.94 | 4.03 | 0.58 | 0.97 | 4.15 | 1.80 | 0.88 | 2.90 |
| PPR | AQ | 4.23 | 0.85 | 2.44 | 1.21 | 0.82 | 2.01 | 1.08 | 0.96 | 4.84 |
| RF | AQ | 4.80 | 0.83 | 2.16 | 0.65 | 0.94 | 3.71 | 1.75 | 0.89 | 2.98 |
| XGB | AQ | 3.93 | 0.88 | 2.64 | 0.88 | 0.94 | 2.74 | 3.13 | 0.66 | 1.67 |
| CR | AQ | 2.58 | 0.94 | 4.01 | 0.57 | 0.96 | 4.28 | 1.07 | 0.96 | 4.89 |
| | | B | | | Cu | | | Fe | | |
| PPR | CP | 0.35 | 0.82 | 2.30 | 0.22 | 0.44 | 1.07 | 1.52 | 0.58 | 1.57 |
| RF | CP | 0.32 | 0.91 | 2.53 | 0.12 | 0.86 | 1.98 | 0.44 | 0.99 | 5.41 |
| XGB | CP | 0.52 | 0.80 | 1.53 | 0.21 | 0.13 | 1.11 | 0.33 | 0.99 | 7.17 |
| CR | CP | 0.30 | 0.91 | 2.68 | 0.16 | 0.51 | 1.42 | 0.33 | 0.98 | 7.19 |
| PPR | AQ | 0.11 | 0.99 | 7.29 | 0.17 | 0.49 | 1.38 | 1.03 | 0.91 | 2.33 |
| RF | AQ | 0.15 | 0.99 | 5.29 | 0.03 | 0.99 | 6.90 | 0.44 | 0.97 | 5.38 |
| XGB | AQ | 0.34 | 0.94 | 2.35 | 0.22 | 0.00 | 1.04 | 0.42 | 0.98 | 5.63 |
| CR | AQ | 0.13 | 0.99 | 6.35 | 0.05 | 0.95 | 4.50 | 0.51 | 0.97 | 4.67 |
| | | Mn | | | Zn | | | | | |
| PPR | CP | 0.14 | 0.08 | 0.65 | 0.25 | 0.37 | 1.00 | | | |
| RF | CP | 0.06 | 0.85 | 1.63 | 0.09 | 0.88 | 2.64 | | | |
| XGB | CP | 0.10 | 0.00 | 0.96 | 0.11 | 0.88 | 2.18 | | | |
| CR | CP | 0.11 | 0.61 | 0.82 | 0.06 | 0.94 | 4.00 | | | |
| PPR | AQ | 0.17 | 0.06 | 0.55 | 0.12 | 0.84 | 2.02 | | | |
| RF | AQ | 0.03 | 0.91 | 2.86 | 0.11 | 0.80 | 2.31 | | | |
| XGB | AQ | 0.09 | 0.00 | 0.99 | 0.17 | 0.90 | 1.49 | | | |
| CR | AQ | 0.17 | 0.05 | 0.56 | 0.11 | 0.80 | 2.31 | | | |

Optimal validation values obtained for each parameter are given in bold.

are delivered by the manufacturer), as fertilizers are not always a homogeneous material, such as granular fertilizers (lower homogeneity) vs. powder fertilizer (greater homogeneity). The literature has reported that the particle size affects the homogeneity of the generated data, with standard deviation values increasing as particle size increases (Touzé et al., 2022). Fertilizers are challenging matrices for pXRF scanning. Not only some fertilizers have a cover (wrap) for slow release, which may have interfered on total elements scanning on whole samples (CP), but also the different material density may have affected the depth of penetration for emitted X-rays returning from the samples.

Results showed that this quick and clean approach can enable fertilizer quality control even without sample grinding. This can aid manufacturers to ensure that high quality mineral and/or organic fertilizer is supplied, even in the field (analyzing samples as they are delivered to the consumer). This method can be applied worldwide by enabling area-specific modeling for fertilizer formulas commonly found in a particular area. Furthermore, it could also be used by the final consumer, for example a farmer, who could make sure that the purchased product is not substandard.

4.3. Green analysis in organic and mineral fertilizers: future perspectives

Worldwide, the concern with fertilizer quality control has been present, such as in China (Han et al., 2009), Tanzania (Michelson et al., 2021), USA (Mukome et al., 2013), Ghana (Teye et al., 2022), Canada (Verenitch and Mazumder, 2012), etc. Generally, fertilizer missing nutrients can result from either manufacturing impurities or adulteration by wholesalers or agro-dealers (Michelson et al., 2021; Sanabria et al.,

2013).

Michelson et al. (2021) reported that beliefs about adulteration push down farmer willingness-to-pay for fertilizer, with farmers willing to pay more if the fertilizer's quality is verified. Besides, these authors also found some evidence of misperceived quality. Many fertilizers present an undesirable appearance, and farmers appear to rely on these observable attributes to incorrectly infer nutrient contents. Therefore, the method proposed here can play an important role in solving those issues since macro and micronutrient contents in fertilizers can be rapidly and accurately assessed through machine learning models trained with pXRF data.

Global events, like the Covid-19 pandemic and the war in Ukraine, can disrupt exports, pushing fertilizer prices further up and reducing its availability in the global market (FAO, 2022). Thus, advances in research and development of technologies that can contribute to reduce costs throughout the fertilizer production chain are very helpful. The novel approach addressed in this paper has strong economic implications, since it can provide reliable information about the quality of traded fertilizer without increasing the production costs.

Besides economics, the use of pXRF-driven models to control fertilizer quality also has remarkable environmental implications. By promoting a cleaner industrial process (without chemical waste generation), this approach prevents soil, water and plant pollution, and helps mitigate resources depletion (due to non-consumption of reagents) both further upstream in the supply chain (for manufacturer standards) and also for the end users (e.g., farmers).

As a promising technique for fertilizer quality control, further research about this novel approach is encouraged. Questions about the

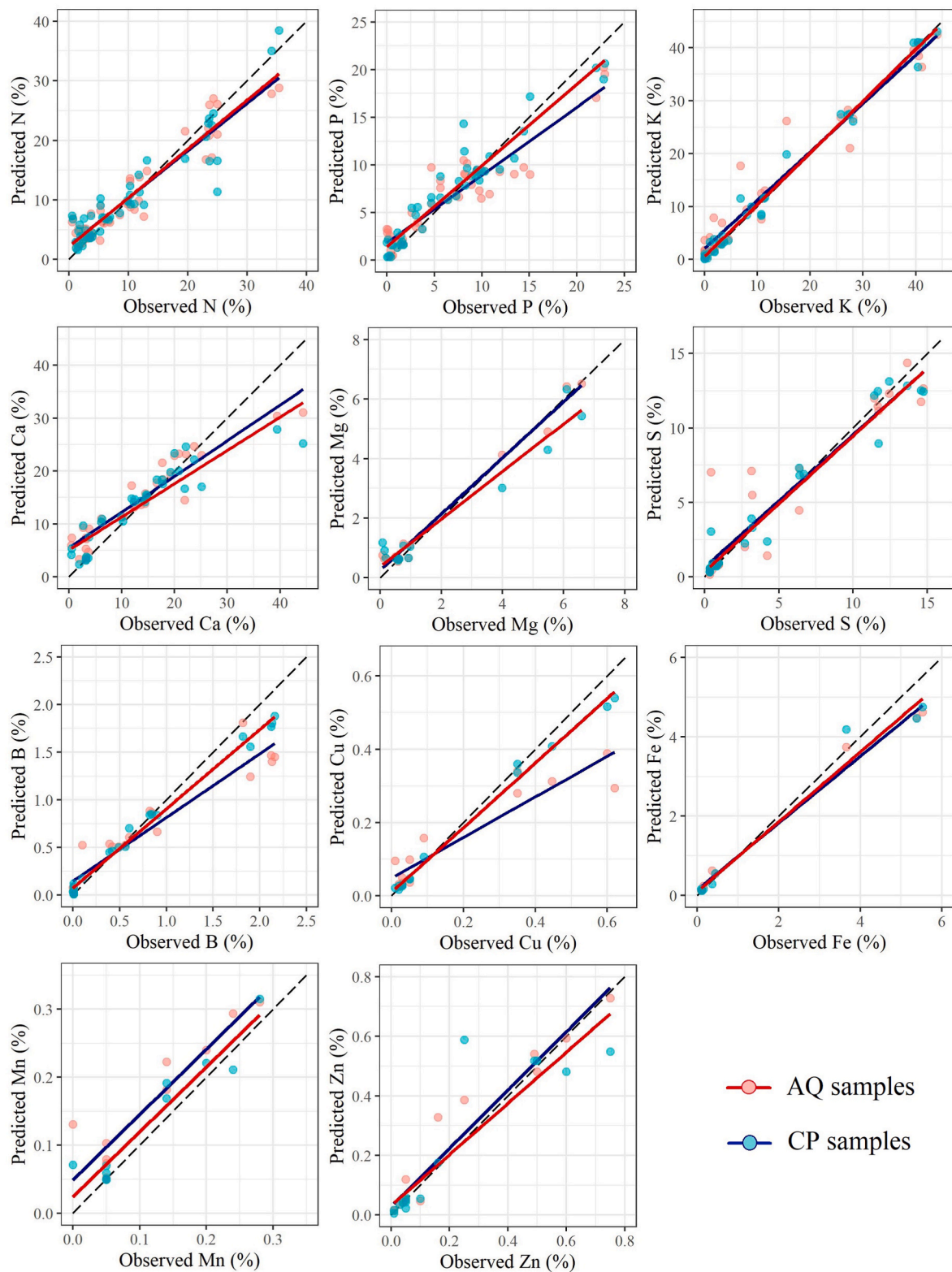


Fig. 3. Observed versus predicted scatter plots for the best prediction models for macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) of whole (CP – no grinding) and ground (AQ) samples of mineral and organic fertilizers based on portable X-ray fluorescence (pXRF) spectrometry data and four machine learning algorithms.

use of other proximal sensors (including sensor fusion), modeling methodologies (since the chosen algorithm interferes in prediction models accuracy), and the effect of moisture in predictions still require further investigation, especially for the development of a certified

methodology by the competent authorities.

Furthermore, pXRF allows for the detection of non-nutritive elements (potentially toxic) in fertilizers (Acquah et al., 2022). In Brazil, there are established maximum limits of toxic heavy metals allowed in

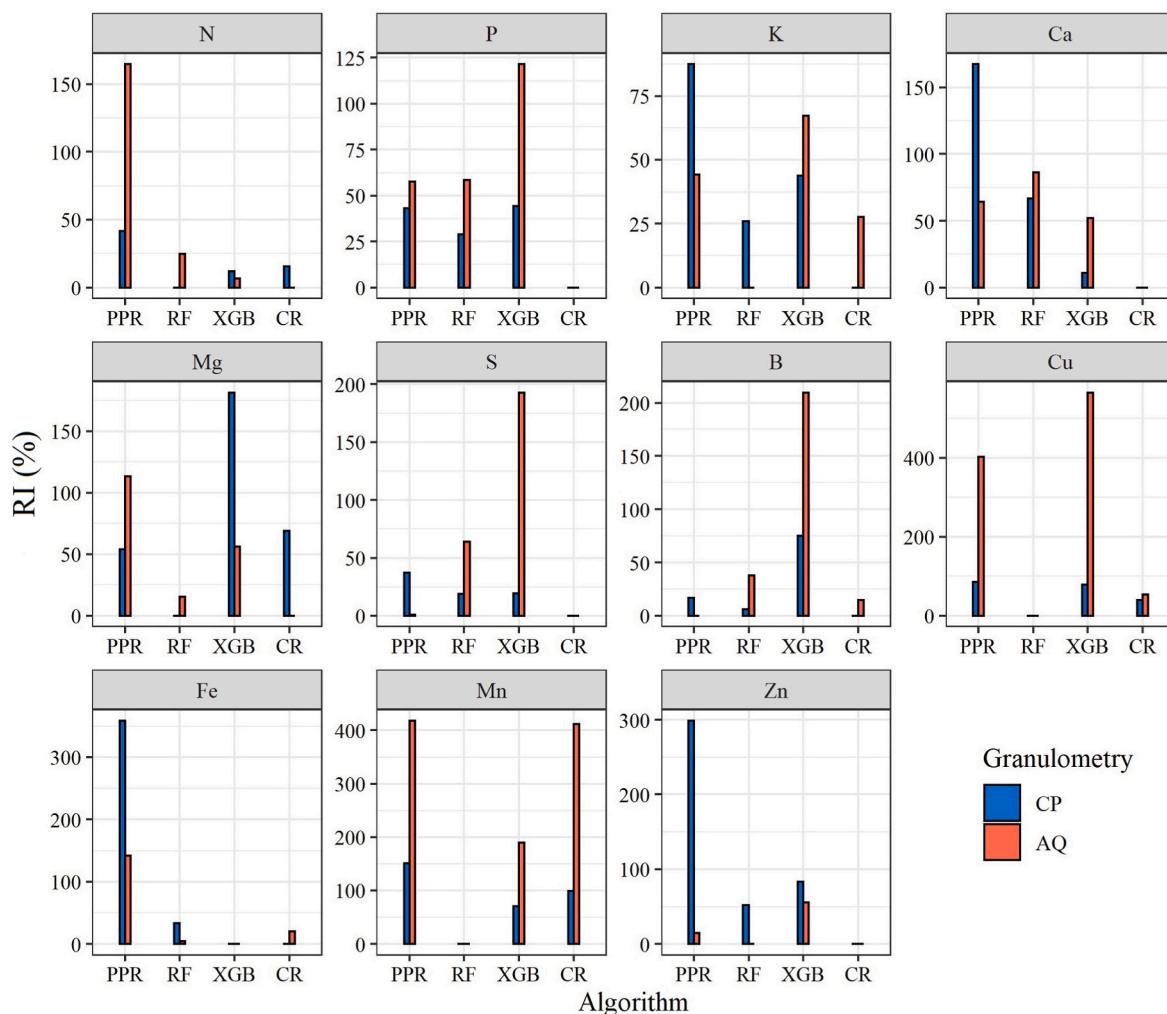


Fig. 4. Relative Increase (RI) of root mean square error (RMSE) showing the increase of RMSE in all models compared to the best performing model for that nutrient. Models were trained using whole (CP) and ground (AQ) samples of mineral and organic fertilizers based on portable X-ray fluorescence (pXRF) spectrometry data. PPR = projection pursuit regression; RF = random forest; XGB = extreme gradient boosting; CR = cubist regression.

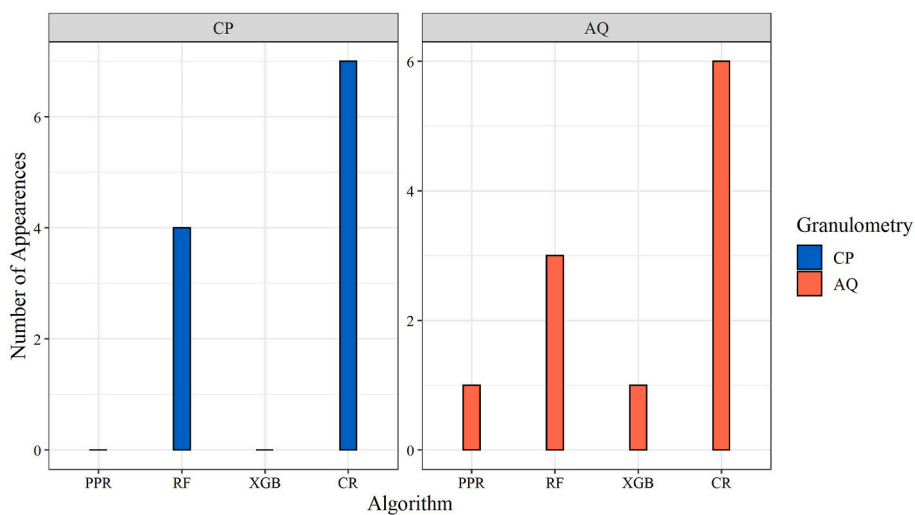


Fig. 5. Number of times each machine learning algorithm delivered the most accurate prediction model for whole (CP) and ground (AQ) samples of mineral and organic fertilizers based on portable X-ray fluorescence (pXRF) spectrometry data. PPR = projection pursuit regression; RF = random forest; XGB = extreme gradient boosting; CR = cubist regression.

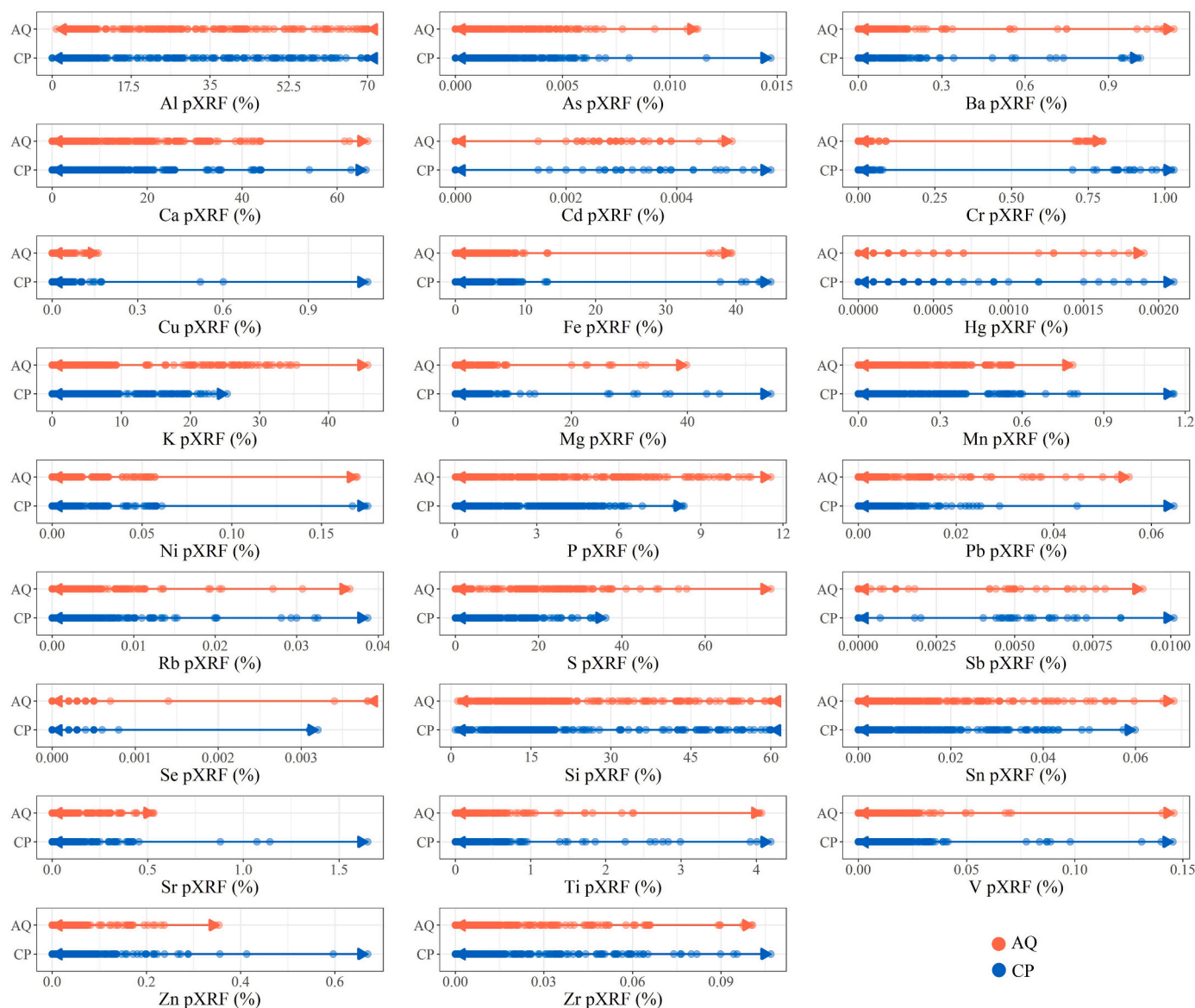


Fig. 6. Differences of chemical elemental characterization of whole (CP – no grinding) and ground (AQ) samples of mineral and organic fertilizer by portable X-ray fluorescence (pXRF) spectrometry.

mineral fertilizers containing phosphorus and micronutrients. Internationally, USA, Japan, China, Australia and the European Union have also enacted regulations that limit the amounts of non-nutritive elements in fertilizers, such as of As, Cd, Co, Cr, Hg, Mo, Ni, Pb, and Se. Future studies are encouraged to use this green analysis method to assess non-nutritive elements in mineral and organic fertilizers, since it could help fertilizer manufacturers and state regulatory authorities to rapidly verify these limits, after proper calibration with the traditional analytical methods.

5. Conclusions

Fast and accurate ($R^2 > 0.92$) estimation of macro and micronutrient contents in a wide variety of mineral and organic fertilizers was achieved using pXRF without producing chemical waste. Grinding fertilizer samples was not required to obtain accurate predictions. The proposed method can reduce time, cost and the environmental footprint of the quality control of fertilizers.

Results demonstrated the remarkable potential of models trained with pXRF data in predicting macro (N: $R^2 = 0.92$; P: 0.97; K: 0.99; Ca:

0.94; Mg: 0.98; S: 0.96) and micronutrients (B: 0.99; Cu: 0.99; Fe: 0.98; Mn: 0.91; Zn: 0.94) in both organic and mineral fertilizers. Although for N, P, K, S, B, Cu and Mn the best prediction models were achieved for ground samples (AQ), the results for the samples without prior preparation (CP – as they are received by the consumer) were also consistent and accurate.

Machine learning models (mainly cubist regression and random forest) trained with pXRF data provided accurate estimations of the chemical composition of fertilizers. We have shown that this green technology is a promising alternative to traditional wet chemistry, facilitating large-scale quality control of both organic and mineral fertilizers. Reliable and visionary fertilizer quality control based on proximal sensors data can ensure the adoption of certified fertilizers, which can raise regional agricultural productivity and improve household and national food security.

Credit author statement

The corresponding author declares the following contributions from the authors: Renata Andrade: Writing – Original draft, Investigation,

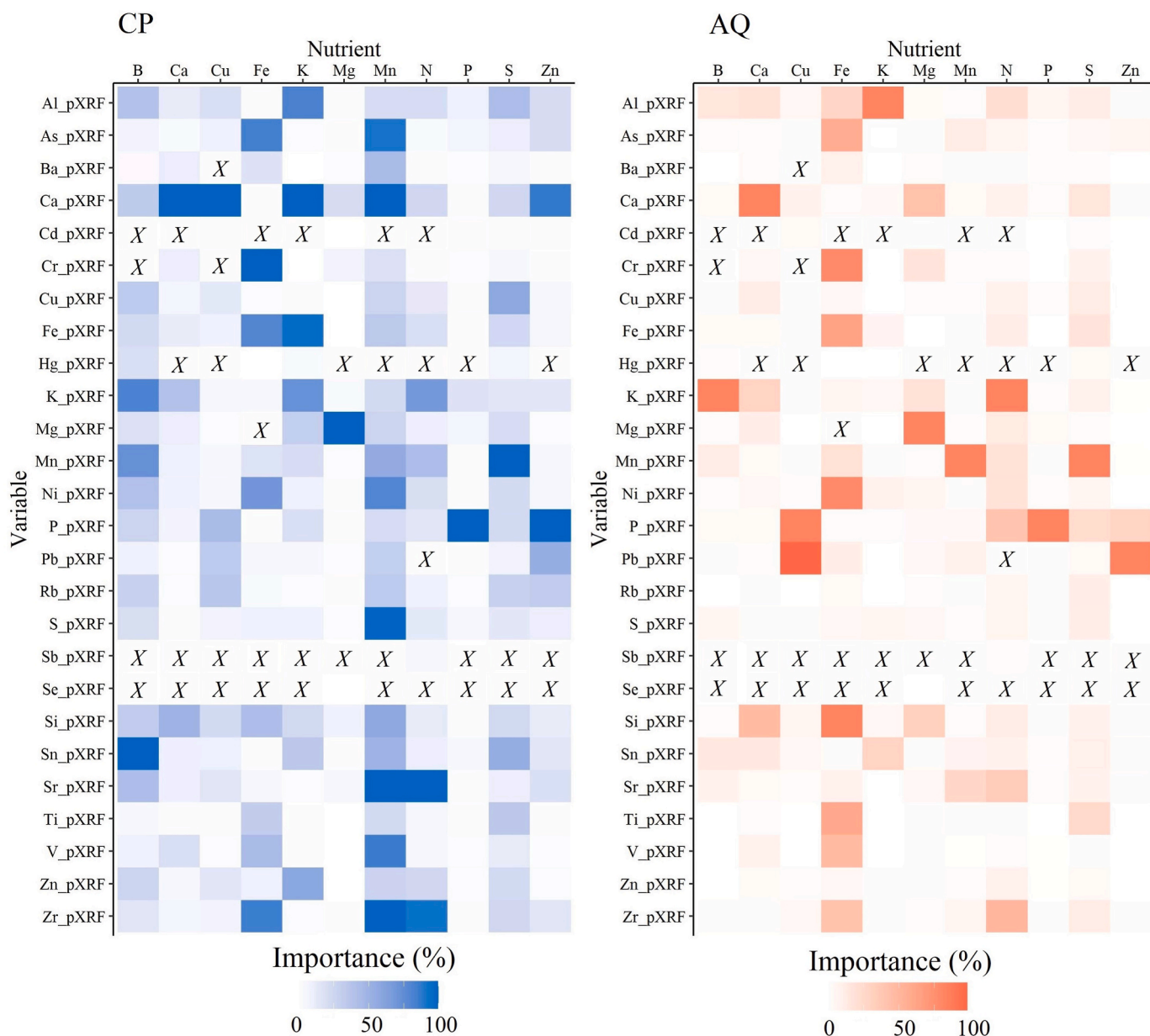


Fig. 7. Explanatory variables (portable X-ray fluorescence (pXRF) spectrometry results) and their respective importance for the best macro (N, P, K, Ca, Mg, and S) and micronutrients (B, Cu, Fe, Mn, and Zn) prediction of whole (CP) and ground (AQ) samples of mineral and organic fertilizers based on pXRF data. X means that the variable was not used for the prediction model for that nutrient.

Visualization, Software. Sérgio Henrique Godinho Silva: Conceptualization, Writing – review and editing, Methodology, Supervision. Lucas Benedet: Conceptualization, Investigation, Resources. Marcelo Mancini: Writing – review and editing. Geraldo Jânio Lima: Data curation and Formal analysis. Kauan Nascimento: Data curation and Formal analysis. Francisco Hécio Canuto Amaral: Data curation and Formal analysis. Douglas Ramos Guelfi Silva: Writing – review and editing. Marta Vasconcelos Ottoni: Writing – review and editing, Resources. Marco Aurélio Carbone Carneiro: Project administration, Supervision, Resources. Nilton Curi: Conceptualization, Writing – review and editing, Project administration, Supervision.

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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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