



**JERNIMO JUVÊNIO CHIVALE**

**ASSESSING AND MAPPING THE ELEMENTAL  
COMPOSITION OF COFFEE LEAVES AND FRUITS USING  
PORTABLE X-RAY FLUORESCENCE SPECTROMETRY**

**LAVRAS - MG  
2024**

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SPECTROMETRY**

Master dissertation presented at Federal University of Lavras as part of the requirements of the Graduate Program, in Soils Department, area of concentration Environmental Resource and Land Use, to obtain Master Degree in Soil Science.

Prof. Dr Bruno Teixeira Ribeiro

Advisor

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**JERNIMO JUVÊNIO CHIVALE**

**AVALIAÇÃO E MAPEAMENTO DA COMPOSIÇÃO ELEMENTAR DE  
FOLHAS E FRUTOS DE CAFÉ UTILIZANDO ESPECTROMETRIA DE  
FLUORESCÊNCIA DE RAIOS-X PORTÁTIL**

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## Resumo

A análise foliar é fundamental para monitorar o estado nutricional das plantas, garantindo alta produtividade e qualidade. Tradicionalmente, essa análise é realizada por métodos de digestão úmida, que são demorados e exigem grandes quantidades de reagentes químicos. A espectrometria de fluorescência de raios X portátil (pXRF) tem mostrado alto desempenho na avaliação de materiais terrestres variados e apresenta potencial para caracterizar folhas e frutos de plantas. Este estudo parte da hipótese de que as medições de pXRF em folhas de café frescas e intactas podem contribuir para a avaliação do estado nutricional das plantas em comparação com métodos laboratoriais convencionais. E o objetivo do experimento foi verificar a sensibilidade do pXRF no monitoramento nutricional de plantas de café. O experimento foi conduzido em uma área de 67 hectares de café no distrito de Macaia, em Bom-Sucesso, Minas Gerais (MG), onde 35 pontos georreferenciados foram estabelecidos aleatoriamente. Em cada ponto, oito folhas diagnósticas foram coletadas e analisadas diretamente na superfície adaxial com um modelo pXRF Bruker S1 Titan operando no modo Geoexploration (tempo de 90 segundos). Após as análises in situ com pXRF, as amostras de cada ponto foram secas em estufa a 60 °C, moídas e reanalisadas por: i) pXRF Bruker S1 Titan no modo Geoexploration (90 segundos); ii) pXRF Bruker Tracer 5g com calibração para materiais vegetais; iii) ICP-OES após digestão ácida. Adicionalmente, frutos verdes e maduros dos mesmos pontos foram coletados, secos, moídos e analisados via pXRF Bruker S1 Titan e ICP-OES após digestão ácida. Os resultados mostraram que as medições de pXRF em amostras secas e moídas, utilizando os modelos Titan e Tracer, foram muito semelhantes ao método ICP-OES. Para K, Mg e S, as análises in situ com pXRF foram comparáveis aos demais métodos, embora as concentrações de P e Ca in situ tenham sido subestimadas. Nos micronutrientes, todos os métodos foram comparáveis, exceto para Zinco (Zn). O sensor pXRF foi capaz de diferenciar os frutos verdes dos maduros na análise de componentes principais (PCA) e apresentou forte correlação entre folhas e frutos verdes. Semelhanças foram observadas entre pXRF e ICP-OES em mapas de distribuição espacial da composição elementar.

**Palavras-chave:** Folhas de café. Sensor proximal. Agricultura inteligente.

## Abstract

Foliar analysis is essential for monitoring the nutritional status of plants, ensuring high productivity and quality. Traditionally, this analysis is performed using wet digestion methods, which are time-consuming and require large amounts of chemical reagents. Portable X-ray fluorescence spectrometry (pXRF) has shown high performance in assessing various earth materials and holds the potential for characterizing plant leaves and fruits. This study hypothesizes that pXRF measurements on fresh and intact coffee leaves can contribute to assessing the nutritional status of plants compared to conventional laboratory methods. This experiment aimed to verify the sensitivity of pXRF in monitoring the nutritional status of coffee plants. The experiment was conducted in a 67-hectare coffee area in the Macaia district of Bom-Sucesso, Minas Gerais, where 35 georeferenced points were randomly established. At each point, eight diagnostic leaves were collected and directly analyzed on the adaxial surface using a pXRF Bruker S1 Titan model operating in Geoexploration mode (dwell time of 90 seconds). After in situ pXRF measurements, samples from each point were oven-dried at 60 °C, ground, and re-analyzed using: i) pXRF Bruker S1 Titan in Geoexploration mode (90 seconds); ii) pXRF Bruker Tracer 5g calibrated for plant materials; iii) ICP-OES after acid digestion. Additionally, green and mature fruits from the same points were collected, oven-dried, ground, and analyzed via pXRF Bruker S1 Titan and ICP-OES after acid digestion. Results showed that pXRF measurements on oven-dried and ground samples using the Titan and Tracer models were similar to the ICP-OES method. For K, Mg, and S, in situ, pXRF measurements were comparable to other methods, although P and Ca concentrations in situ were underestimated. All methods were comparable for micronutrients except for Zinc (Zn). The pXRF sensor could differentiate green and mature fruits in principal component analyze (PCA) and showed a strong correlation between leaves and green fruits. Similarities were observed between pXRF and ICP-OES in spatial distribution maps of elemental composition.

**Keywords:** Coffee leaves. Proximal sensor. Smart agriculture.

## **Impactos sociais, tecnológicos, econômicos e culturais**

A aplicação da espectrometria de fluorescência de raios-X portátil (pXRF) no setor agrícola tem causado significativos impactos sociais, tecnológicos e econômicos. O presente estudo teve como objetivo avaliar a eficácia do pXRF para monitorar em tempo real os níveis nutricionais de folhas e frutos em plantações de café, realizado na fazenda Morro Grande, localizada em Macaia, Bom-Sucesso, Minas Gerais, em colaboração com a UFLA. No aspecto social, o pXRF possibilitou um monitoramento rápido e acessível do cultivo de café, melhorando as decisões dos produtores e fortalecendo as práticas de agricultura de precisão. Ao analisar os macronutrientes (P, K, Ca, Mg e S) e micronutrientes (Fe, Mn, Cu e Zn), os dados obtidos mostraram-se semelhantes aos do método convencional ICP-OES, com exceção de P, Ca e Zn, que apresentaram resultados subestimados. Essa tecnologia contribuiu para a sustentabilidade, promovendo um uso mais racional de fertilizantes e minimizando os impactos ambientais, resultando em benefícios para as comunidades rurais. Do ponto de vista tecnológico, o pXRF representou um progresso significativo ao possibilitar análises *in situ* e em tempo real, diminuindo a necessidade de laboratórios e produtos químicos. Essa inovação está em sintonia com os objetivos da ONU (redução da fome e a luta contra as mudanças climáticas), visando um aumento sustentável da produtividade agrícola. Sob a perspectiva econômica, o pXRF demonstrou a capacidade de diminuir custos operacionais, reduzindo a demanda por insumos e otimizando a utilização dos recursos. Um monitoramento nutricional eficiente contribui para uma produção agrícola mais lucrativa e de alta qualidade, fortalecendo a competitividade e a autossuficiência de pequenos e médios agricultores. Desta maneira, o pXRF se estabelece como uma ferramenta-chave para uma agricultura contemporânea e sustentável

## **Social, technological, economic and cultural impacts**

The use of portable X-ray fluorescence spectrometry (pXRF) in agriculture has generated significant impacts on social, technological, and economic levels. This study aimed to assess the sensitivity of pXRF in real-time nutritional monitoring of leaves and fruits in coffee plantations, conducted at Morro Grande farm in Macaia, Bom-Sucesso, Minas Gerais, in partnership with UFLA. Socially, pXRF facilitated rapid and accessible monitoring of coffee crops, enhancing farmers' decision-making and strengthening precision agriculture practices. In analyzing macronutrients (P, K, Ca, Mg, and S) and micronutrients (Fe, Mn, Cu, and Zn), the results were similar to the conventional ICP-OES method, except for P, Ca, and Zn, which were underestimated. This technology promoted sustainability by enabling the rational use of fertilizers and reducing environmental impacts, benefiting rural communities. On the technological front, pXRF represented an advancement by allowing *in situ* and real-time analyze, reducing dependency on laboratories and chemical products, and aligning with UN goals (hunger reduction and climate change mitigation) to sustainably increase agricultural productivity. Economically, pXRF demonstrated potential for lowering operational costs, minimizing the need for inputs, and optimizing resource use. Effective nutritional monitoring supports a more profitable and high-quality agricultural production, promoting the competitiveness and self-sufficiency of small and medium-sized farmers. Thus, pXRF is establishing itself as a strategic tool for modern, sustainable agriculture.

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## LIST OF ABBREVIATIONS

**In situ pXRF Titan:** pXRF Titan on Fresh and intact leaves analyzes

**Ex situ pXRF Titan:** pXRF Titan on oven-dried leaves analyzes

**Ex situ pXRF Titan:** pXRF Tracer on oven-dried leaves analyzes

**Gdry Titan:** pXRF Titan on oven-dried green fruits analyzes

**Gconventional:** conventional acid digestion analyses on oven-dried green fruits

**Mdry Tracer:** pXRF tracer on oven-dried mature fruits analyzes

**Mconventional:** conventional acid digestion analyses on oven-dried mature fruits

**PCA:** Principal components analyze

**GLS:** Generalized linear square

**OM:** Organic Matter

**SB:** Sum of bases

**V %:** Bases saturation

**CEC<sup>1</sup>:** Effective cation exchange capacity

**CEC<sup>2</sup>:** Potential cation exchange capacity

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## 1.0 Introduction

Worldwide information on coffee plant nutrition is essential in agriculture. Brazil is widely known for its high coffee crop productivity, good soil management, and use of input fertilizers to supply plants with nutrients (Borges *et al.*, 2023). Coffee (Arabica and canephora/Robusta) is a significant contributor to the Brazilian economy, both domestically and internationally (Figueiredo *et al.*, 2022; Bunn *et al.*, 2014; Borges *et al.*, 2020; Winter *et al.*, 2020). For optimal growth and high productivity, coffee plants require well-managed, well-drained soil rich in nutrients and organic matter. Well-nourished coffee plants are more resilient to pests, diseases, and adverse environmental conditions (e.g., soil water scarcity) (Borges *et al.*, 2020; Alves *et al.*, 2022; Borges *et al.*, 2023).

However, to monitor the nutritional of this crop traditional or conventional methods of analyzes are commonly used but are time-consuming, requiring numerous samples, using chemical reagents, and necessitating sample pre-treatment (Swetha *et al.*, 2022). In addition to traditional methods, complementary sensor technologies such as portable X-ray fluorescence (pXRF) offer accurate analyzes that can improve and enhance the mapping of the chemical elemental composition in coffee crops. Conventionally, many analyzes are conducted using the *ex situ* pXRF method, which involves drying, grinding, and placing samples in containers before analyze. Yet, foliar *in situ* pXRF analyzes are a solution to enhance this approach and accelerate the optimization of the coffee crop's nutritional management.

This technique allows for high-yield analyze on a large scale in a short time, facilitating quick decision-making (Cubero *et al.*, 2020; Pallottino *et al.*, 2019; Kopačková, 2019; Barbedo *et al.*, 2019). Furthermore, pXRF sensor analytical method is rapid, can be used in the field, and provides reliable, accurate elemental composition data for different earth materials (Ribeiro *et al.*, 2021; Acosta *et al.*, 2023; Swetha *et al.*, 2022).

The technique is environmentally friendly as it does not involve chemical reagents, preventing pollution. Soil science has embraced using pXRF sensors to optimize soil fertility and plant nutritional management (Acosta *et al.*, 2023; Ribeiro *et al.*, 2021). Can determine plants' critical, optimal, abundant nutrient and toxicity levels (Sousa *et al.*, 2018).

The pXRF sensor analyzes present an excellent alternative for the chemical characterization of plant materials, such as coffee leaves and fruits allowing the real-time monitoring of coffee's nutritional status and facilitating the mapping of elemental composition within the growth area.

This work aims to: i) Apply pXRF sensors on in situ and ex situ to analyze coffee leaves and fruits; ii) Compare the pXRF sensors results with conventional ICP-OES analyzes of plant materials (leaves and fruits) for macro- (P, K, Ca, Mg, and S) and micronutrients (Fe, Mn, Cu, and Zn); iii) Model the variable data obtained via conventional methods and pXRF sensors using generalized linear square (GLS) model; iv) Spatialize the elemental composition maps to illustrate the nutritional status distribution of coffee leaves using a spline interpolator in ArcMap 10.8 software.

## 2.0 Bibliography Review

### 2.1 Conventional Analyses

According to Hong *et al.* (2020), conventional wet digestion-based methods for soil characterization exhibit significant limitations, particularly in their capacity to deliver rapid soil information or generate laboratory spectral data. According to Swetha *et al.* (2022), these methods are inherently time-consuming, costly, and labor-intensive, primarily due to the extensive sample preparation required. Despite their widespread use, they fail to provide the efficiency needed for high-throughput soil analyzes, which is increasingly demanded in research and agricultural applications (M. *et al.*, 2018).

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) represents a more advanced analytical approach that has been widely adopted (Douvris *et al.*, 2023), for the simultaneous determination of multiple essential macro and micronutrients, including P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn (Moragano *et al.*, 1999; Karasakal, 2020). ICP-OES offers high sensitivity and precision, making it suitable for assessing the elemental composition of various materials (AMORIM *et al.*, 2024). However, the technique is not without drawbacks. The use of chemical reagents in wet digestion before ICP-OES analyzes poses environmental hazards, as these chemicals contribute to pollution and may present disposal challenges (Lee *et al.*, 2022). Additionally, the need for careful calibration and the potential for matrix effects are further considerations that complicate its use.

Despite these concerns, wet chemistry digestion methods remain indispensable for assessing plant nutritional status and soil fertility attributes (Pereira *et al.*, 2024). These methods allow for the extraction and quantification of elemental composition in soil and plant tissues (Tarantino, *et al.*, 2016), providing critical data for understanding nutrient dynamics and informing fertilization practices (Antonangelo *et al.*, 2021). Studies such as those by Vaccaro *et al.* (2004) and Galeriani *et al.* (2020) have highlighted the importance of these techniques in agricultural research and soil science, where precise nutrient analyze is essential for optimizing crop yields and maintaining soil health.

The ongoing reliance on wet digestion methods underscores the need for continued research into more efficient, less hazardous alternatives that can meet the demands of modern soil analyzes without compromising environmental integrity. Emerging technologies, such as

portable X-ray fluorescence (pXRF) and near-infrared spectroscopy (NIRS), are being explored as potential solutions that could complement or replace traditional methods, offering faster, non-destructive analyzes with minimal sample preparation.

### **2.2.0 Potable X-ray Fluorescence Spectrometry (pXRF)**

X-rays, discovered by German physicist Wilhelm K. Rontgen (1845–1923), have been used for commercial elemental analyzes since 1950 (Shackley, 2011). The applicability of XRF spectroscopy is widespread in geochemistry, material science, and archaeology. The method is based on the interaction of X-ray radiation with atoms, with typical analyzes times between 30 and 90 seconds (Panchuk *et al.*, 2018; Tavares *et al.*, 2023). The spectrometer has a detection range from 100% down parts per million (ppm-mg Kg<sup>-1</sup>) and, in some cases, parts per billion (ppb-ug Kg<sup>-1</sup>) levels (An *et al.*, 2021). XRF's main advantage is its ability to detect elemental composition directly, even at concentrations slightly below environmental limits, providing feasible and effective results (An *et al.*, 2021; Qingya *et al.*, 2022). The method simultaneously quantifies numerous elements in a short time, is non-destructive, and does not require complex sample preparation.

The pXRF spectrometer is widely employed in soil science and recognized as the official method (USEPA 6200) for soil and leaf nutrient concentration analyze. Factors influencing equipment analyzes (e.g., water content, operational conditions, thickness, and light elements) have been well-researched and clarified (Ribeiro *et al.*, 2021; Costa *et al.*, 2023).

The pXRF sensor offers a sophisticated solution that is fast, precise and does not require sample preparation. It presents numerous benefits compared to conventional methods, such as speed, portability, a wide dynamic range for elemental quantification, and the ability to perform analyzes on-site (Weindorf *et al.*, 2013; Weindorf *et al.*, 2014).

When the atoms within the material structures are exposed to high-energy X-rays, electrons are displaced from their orbits. As these electrons return to their initial orbits, they release energy in the form of characteristic fluorescence for each element. Consequently, the elements in the materials under analyze can be identified (Weindorf *et al.*, 2014). The use of pXRF sensors enables the analyze of the total concentration of certain elements in soil and food samples, including Mg, Fe, Al, Si, Ca, K, and U (Frydrych & Jurowski, 2023; Tavares *et al.*,

2023). Additionally, these sensors can be used to indirectly evaluate other soil characteristics like pH, cation exchange capacity (CEC), and texture (Tavares *et al.*, 2023). However, these technologies still face challenges in terms of accuracy and the ability to measure a wide range of elements, particularly at low concentrations.

According to Jang (2009), and Antonangelo *et al.* (2021) foliar diagnosis for evaluating plant nutritional status is crucial, and pXRF is continually useful in actual crop fields. The matrix condition of the coffee plant, the targeted element, and the energy of the incident X-rays imply that even qualitative analyze of intact plant leaves can be useful for in-field exploration (Ribeiro *et al.*, 2021).

### **2.3 Digital Mapping of Coffee Elemental Composition and Nutritional Status**

Based on the nutritional leaf composition of coffee, it's possible to diagnose the plant's status and calculate the fertilizer requirements necessary to optimize management and enhance productivity (Silva *et al.*, 2020). However, plants exhibiting high nutrient imbalances negatively impact agronomic indices, which can result in reduced economic returns (Martins *et al.*, 2019). To achieve high yields and maintain economic efficiency, it's crucial to monitor coffee plant nutrition closely, manage soil inputs and fertilizers thoughtfully, and utilize comprehensive elemental composition mapping. These practices can help farmers standardize their budgets and improve overall crop performance.

Over time, yield estimates are continuously refined based on the annual harvest of coffee grains (Zanela *et al.*, 2024). Beyond traditional methods, advanced technologies such as remote and proximal sensors, as well as digital platforms, are increasingly employed (Martins *et al.*, 2023) to provide real-time nutritional information and streamline field management (Silva *et al.*, 2011). The agronomic system has integrated agricultural production knowledge, thereby enhancing the applicability of software, autonomous robots, satellites, aerial vehicles, and machinery supported by Big Data analytics in agriculture (Basso *et al.*, 2019). That involves precision and digital agricultural smart techniques (Kolling and Rapim, 2021).

The integration of the Internet of Things (IoT) further enhances precision and enables intelligent agricultural practices. By leveraging real-time data on the nutritional status of coffee

plants, farmers can make informed, flexible decisions to address field conditions proactively, optimizing both yield and economic outcomes.

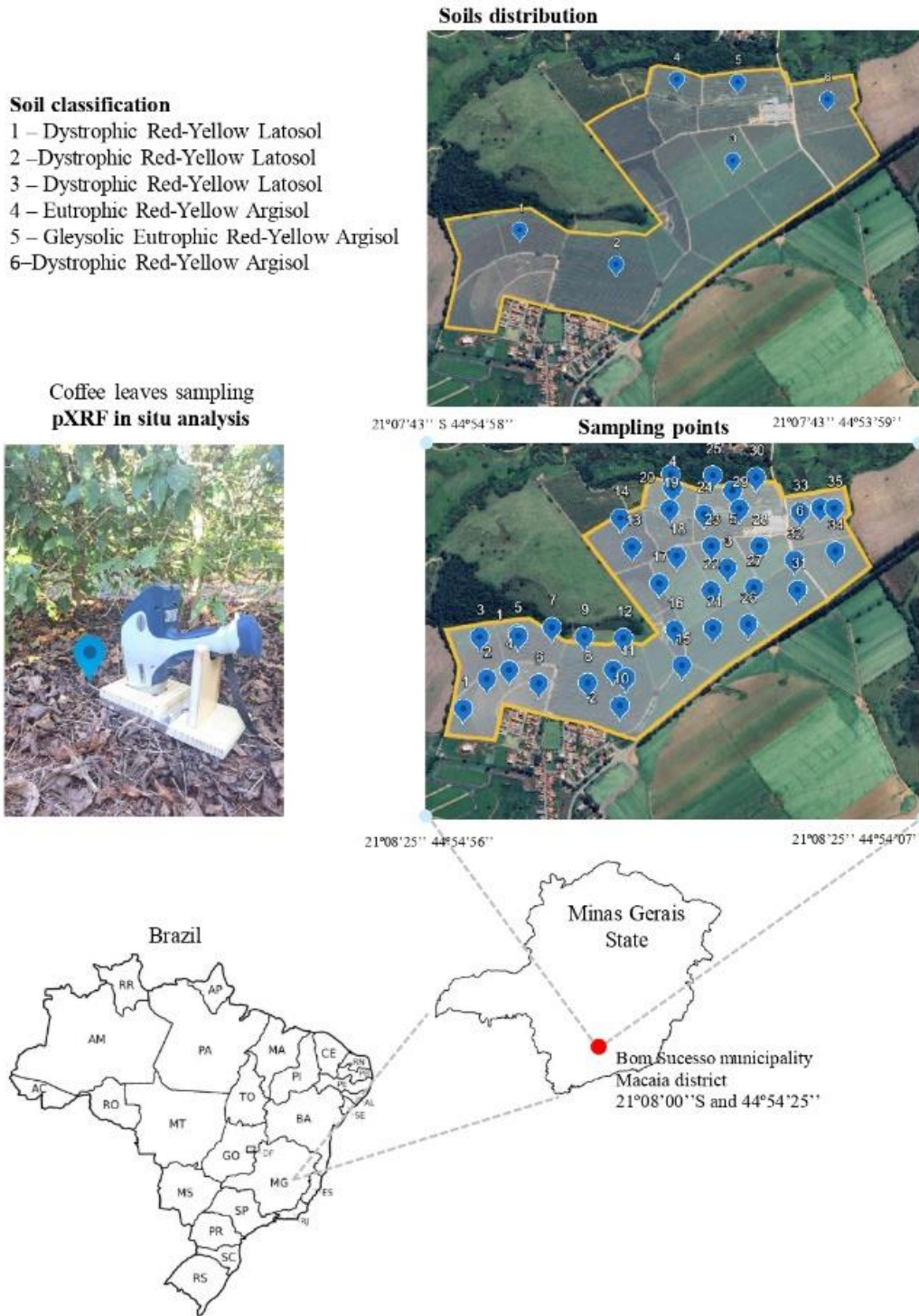
### 3.0 Material and Methods

#### 3.1 Description of the Studied Area

A coffee farm located in Bom Sucesso (Macaia District), Minas Gerais state, was selected (Fig. 1). The experimental area (67 ha), is geographically located at 21°08'19.92''S and 44°54'30.19''W, in an altitude of 826 meters above the sea level. The Atlantic Forest biome predominantly characterizes the region, (IBGE, 2015) with features of alluvial Dystrophic soils along the river margin, Cambisols, and Red Argisols at higher elevations within the forest (Carvalho et al., 1995; Rodrigues *et al.*, 2003).

According to the Köppen climate classification, the region experiences a Cwb mesothermic climate marked by mild summers and generally temperate conditions. Additionally, two distinct seasons are characterized by wet and rainy summers with a cold dry winter (IBGE, 2015). The average annual precipitation is 1776 mm, primarily occurring between October and March, with a mean annual temperature of 19°C (Guimarães *et al.*, 2019).

The predominant lithology region includes gneiss and kaolinite minerals in Argisols, and Cambisols overlying mica-schist, itabirite, and quartzite. Additionally, oxides, meta-limestone, gabbro, and serpentinite are found in Latosols (Araujo *et al.*, 2014).



**Figure 1:** Location of the collection samples, 6 random geo-referenced points for soil collect and 35 for coffee vegetable materials in growth coffee area in Macaia Bom-Sucesso MG.

### 3.2 Sampling Scheme and Procedures

Thirty-five (35) points were randomly established in the studied area (Fig. 1). At each point, eight (8) diagnostic coffee leaves from the third or fourth (3/4) pair and 300g of green fruits from the productivity branches at the beginning of April. At the end of April 2024, an additional 300g of mature fruits were collected from the same points. Also, at each point soil samples from 0-20 cm and 20-40 cm layers were collected. Additionally, based on the relief of the studied area, six points were established for soil classification. The soil samples were collected from 0 to 20 cm up to 100 cm along the soil profile. For points 5 and 6 added 100 to 120 cm layer was also sampled. Soil sampling was performed under the coffee canopy using a stainless-steel hand auger (Malavolta *et al.*, 1997). The soil was classified per the Brazilian System of Soil Classification (Embrapa, 2018).

A total of 137 samples were collected:

- 76.5% for coffee leaves and fruits;
- 23.5% for soil.

### 3.3 Foliar in situ Analyze

After collection, the leaves were cleaned using wet wipes. Each intact and fresh leaf collected at each point was analyzed using pXRF Bruker S1 Titan model (Geoexploration mode and dwell time of 90 s) in the field. After pXRF measurements, the eight (8) coffee leaves from each point were packed into paper bags constituting composite samples. These samples were oven-dried (60° C) and ground for further analyze (pXRF and conventional method).

### 3.4 Foliar and Fruits ex situ Analyzes

The oven-dried leaves (ex-situ pXRF Titan), green (Gwet Titan), and mature fruits (Mdry Titan) were analyzed using the Geo-exploration mode of pXRF S1 Titan 800 with a 90-second dwell time. These analyzes were performed after checking samples using certified reference materials CS-M2 (National Institute of Standards) and NIST 2710a from Bruker. Additionally, the pXRF-Tracer 5g plantF1 mode (ex-situ pXRF Tracer) standardized only for plant analyzes was used to oven-dried leaves with a 60-second dwell time method.

### 3.5 Conventional (ICP-OES) Analyzes of Dried Plant Materials

After being ground, the samples were subjected to conventional assessment using a wet digestion method in nitro-perchloric acid (Miller, 1998; Malavolta *et al.*, 1997). For this, 0.5g sub-samples were transferred to 50 mL digestion glass tubes and treated with 6 mL of an acid solution (HNO<sub>3</sub>, 2:1 v/v). The samples were then digested using a heating block digestion system (Borges *et al.*, 2021; Recena, 2018). After digestion, the samples were cooled to 22-24°C room temperature (Borges *et al.*, 2020; Costa *et al.*, 2023) and transferred to 50 mL volumetric flasks. The macronutrient (P, K, Ca, Mg, and S) and micronutrients (Fe, Cu, Mn, and Zn) concentrations of plant materials (leaves, green and mature fruits) were determined by ICP-OES Ciro Vision (Spectro Analytical Instruments Inc., Kleve, Alemanha).

### 3.6 Soil Sample Preparation

The soil samples were air-dried, ground, and sieved through a 2 mm sieve. A subsample was taken for the conventional laboratory method: soil texture and fertility properties.

### 3.7 Conventional Soil Assessment

Soil analyzes were conducted using conventional methods. The pH was measured in a 1:2.5 (v/v) soil-to-water ratio. Exchangeable cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup>) were extracted using 1 mol/L<sup>-1</sup> KCl. The soil-to-extracting ratio was 1:10 (v/v), and the soil suspensions were placed in 250-mL Erlenmeyer flasks, vibrated for 20 minutes, and then left to equilibrate for 16 hours. Al<sup>3+</sup> was determined by titration with 0.025 mol/L<sup>-1</sup> NaOH (Wright & Stuczynski, 1996), and available K<sup>+</sup>, P, Fe, Mn, Cu, and Zn were extracted using the Mehlich-1 solution. The concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Fe, Mn, Zn, and Cu were quantified via ICP-OES (Toppel *et al.*, 2018). Phosphorus (P), and Sulphur (S) were determined via the same equipment, with S being extracted by Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The effective cation exchange capacity (CEC<sup>1</sup>) was determined by the sum of exchangeable cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Al<sup>3+</sup>), and the potential cation exchange capacity (CEC<sup>2</sup>) by the sum of Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and (H<sup>+</sup> + Al<sup>3+</sup>). Soil organic matter (SOM), clay, silt, and total sand were determined using a calibrated Vis-NIR infra-red spectrometry (Santana *et al.*, 2019), customized for this purpose, titled SpecSolo-Scan® (SpecSolo, 2018) from the IBRA (Brazilian Institute of Agronomic Analyze).

### 3.8 Statistical Analyzes

The plant materials data from the conventional ICP-OES and pXRF sensor were subjected to descriptive statistical analyze. The following parameters were calculated to identify significant variability between the methods: minimum, mean, maximum, coefficient of variation (CV %), and standard deviation (s.d). Concentrations measured by pXRF sensor and conventional ICP-OES were reported in  $\text{g}\cdot\text{kg}^{-1}$  for macronutrients and  $\text{mg}\cdot\text{kg}^{-1}$  for micronutrients and all analyzes were performed using R software version 4.5.1 (2024.04.1).

### 3.9 Data Modelling

The generalized least squares (GLS) model in the “nmls” version 3.1-164 package (Pinheiro *et al.*, 2022) was selected as the best fit for modelling data, effectively minimizing variance heterogeneity compared to a linear model (LM) as determined by an ANOVA test. The model efficiency was based on a lower Akaike Information Criterion (AIC) value and high log-likelihood (logLik). Residuals from the model were extracted and plotted on a Q-Q plot with a QQ line to assess normality and heteroscedasticity. Logarithmic (log) transformations were performed on conventional and pXRF sensor data, and the Dunnett test was used for multiple comparisons between the conventional ICP-OES method (as the control) and the pXRF sensor results on the observation variables. This was followed by extracting emmeans (estimated marginal means) from the statistical models using the “emmeans” version 1.10.1 (Lenth, 2021) package. The `geom_errorbar` function from the `ggplot2` package (Wickham, 2016) was used to plot bar graphs with the least significance levels at  $p\text{-value} < 0.05$ .

#### 3.1.0 Principal Components Analyzes (PCA) and Correlations

To evaluate the sensitivity of the pXRF equipment for measuring concentrations in plant materials relative to the conventional ICP-OES method, and to determine the correlation between these methods, correlation plots and PCA were performed using the standard scale function in R (R Core Team, 2024). The PCA was conducted via the “Mass” package, version 7.3-60.01 (Ripley *et al.*, 2024), and visualized using “ggplot2” (Wickham, 2016).

### 3.1.1 Mapping the Elemental Composition

The data values obtained from conventional ICP-OES, in situ pXRF Titan, ex situ pXRF Tracer coffee leaves, and conventional ICP-OES Soil attribute analyzes were processed using the geoprocessing software ArcMap 10.8. The Spline interpolator was employed to determine the spatial distribution maps, which, according to Matos (2008), consist of a set of polynomials that fit a surface to known point values using polynomial expressions. Thus, based on the maximum and minimum values found in each analyze, it was possible to input them into the tool and establish a distribution model across the environment. Root means square error (RMSE) was used to predict and compare the performance of in situ pXRF Titan and ex situ pXRF Tracer methods across conventional ICP-OES analyzes of the spatial distribution variable maps.

$$\text{RMSE} = \frac{\sqrt{\sum_{i=1}^n (y_i - \hat{y})^2}}{n} \text{ where: } y_i \text{-Observed values of conventional analyzes; } \hat{y} \text{ -}$$

pXRF predicted values; and n – number of observations.

## 4.0 Results and Discussion

### General Description of the Studied Area

The samples were collected from an area characterized by varying relief, including flatlands, and undulating terrain. The predominant soil types in this area were identified as Dystrophic Red-Yellow Latosol on points 1, 2, and 3 with low base saturations ( $V < 50\%$ ) in most of the first 100 cm of the B horizon (including BA). Eutrophic Red-Yellow Argisol and Gleysolic Eutrophic Red-Yellow Argisol on points 4 and 5 respectively, with base saturations ( $V \geq 50\%$ ) in most of the first 100 cm of the B horizon (including BA). Point 6 is Dystrophic Red-Yellow Argisol on point 6 with low base saturations ( $V < 50\%$ ) in most of the first 100 cm of the B horizon (including BA), (Embrapa, 2018). Other soil attributes are summarized in Table 1

**Table 1:** Soil attributes organic matter (OM), effective cation exchange capacity (CEC<sup>1</sup>), potential cation exchange capacity (CEC<sup>2</sup>), sum of bases (SB), bases saturation (V %), and Munsell color charts

Soil depths	Points	Relief Classification	OM g/kg	Clay g/kg	PH (H <sub>2</sub> O)	CEC <sup>2</sup> cmolc/kg	CEC <sup>1</sup> cmolc/kg	SB cmolc/kg	V %	Munsell Color Charts
0-20 cm			19	398	4.8	109.1	37.1	27.1	25	5/6 (2.5YR)
20-40 cm			14	410	4.6	85.5	18.5	10.5	12	5/4 (2.5YR)
40-60 cm	1	Soft wavy	13	458	4.6	71.9	16.9	8.9	13	5/8 (2.5YR)
60-80 cm			15	429	4.5	54.6	14.6	6.6	12	5/8 (2.5YR)
80-100 cm			9	412	4.3	45.4	10.4	4.4	10	4/8 (2.5YR)
0-20 cm			17	477	4.4	72.7	18.7	10.7	15	3/3 (2.5YR)
20-40 cm			22	373	4.5	73.7	16.7	12.7	17	3/4 (2.5YR)
40-60 cm	2	Soft wavy	16	390	4.4	69.7	13.7	9.7	14	4/4 (2.5YR)

60-80 cm			12	462	4.7	51.8	10.8	8.8	17	4/6 (2.5YR)
80-100 cm			8	440	4.6	40.2	6.2	5.2	13	4/6 (2.5YR)
0-20 cm			19	400	4.1	117.6	14.6	3.6	3	3/2 (2.5YR)
20-40 cm			15	560	4.05	94.7	19.7	5.7	6	3/2 (2.5YR)
40-60 cm	3	Flat	14	373	4.1	120.8	16.8	3.8	3	3/4 (2.5YR)
60-80 cm			14	439	4	107.5	13.5	3.5	3	3/4 (2.5YR)
80-100 cm			9	397	4	99.8	13.8	3.8	4	4/6 (2.5YR)
0-20 cm			31	212	6.4	121.7	97.75	97.7	80	2.5/1 (2.5YR)
20-40 cm			10	212	5.3	74.5	50.55	50.5	68	5/3 (2.5YR)
40-60 cm	4	Wavy	8	284	5.3	50.5	25.5	24.5	49	5/8 (5YR)
60-80 cm			6	200	5	39.9	18.9	17.9	45	6/8 (5YR)
80-100 cm			5	235	5.2	40.7	21.75	21.7	53	5/8 (2.5YR)
0-20 cm			25	119	6.3	150.2	135.25	135.2	90	2.5/1 (2.5YR)
20-40 cm			14	145	6.3	94.2	79.25	79.2	84	4/4 (5YR)
40-60 cm	5	Wavy	9	186	6.1	54	38.05	38	70	6/8 (5YR)
60-80 cm			5	94	5.9	53.6	34.6	32.6	61	7/8 (5YR)
80-100 cm			1	162	5	37.1	23.1	18.1	49	8/4 (5YR)
100-120 cm			1	250	5.9	49.5	29.5	25.5	52	5/8 (2.5YR)
0-20 cm			17	353	6.1	97.4	77.45	77.4	79	3/2 (5YR)
20-40 cm			12	284	6.1	49.1	31.15	31.1	63	5/8 (2.5YR)
40-60 cm	6	Wavy	7	304	6	29.5	12.55	12.5	43	4/6 (2.5YR)
60-80 cm			5	454	6	30.5	13.55	13.5	44	4/6 (2.5YR)
80-100 cm			3	247	5.2	28.6	11.65	11.6	41	5/8 (2.5YR)
100-120 cm			3	82	5.4	33.6	15.6	7.6	23	5/8 (2.5YR)

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#### 4.1.0 Descriptive Statistical Results of Plant Materials

After obtaining results from conventional ICP-OES and pXRF sensor methods, descriptive statistical analyzes were applied to coffee leaves and fruits (Tables 2 and 3). The descriptive statistical analyzes obtained via the pXRF sensor for macronutrients and micronutrients (Table 2), on in situ pXRF Titan and ex situ pXRF Tracer methods showed significant variability for P, Mg and Ca. For Mn was high in both ex situ Titan and Tracer. The elements K, S, Fe, Cu, and Zn showed inconsistent variability across all pXRF methods compared to the conventional ICP-OES method.

Additionally, a log transformation was applied for Ca, however, Fe and Zn did not satisfy the statistical premises models. The variable discrepancy values observed probably influenced the variance heterogeneity in these elements. In oven-dried green and mature fruits (Table 3), the macronutrient (P, K, Ca, Mg, and S) and micronutrient (Mn, Cu, and Zn) concentrations expressed significance models providing acceptable premises. Except Ca which has a limit of detection. The GLS modelling, provided robust results for the majority of macronutrient and micronutrient concentrations in both leaves and fruits, demonstrating statistical validity (Costa *et al.*, 2023).

**Table 1:** Descriptive statistics of the elemental composition obtained via the conventional method (Conventional ICP-OES) on oven-dried leaves and portable X-ray fluorescence spectrometry (pXRF) on intact and fresh leaves (in situ pXRF Titan), oven-dried leaves (ex situ pXRF Titan and ex situ pXRF Tracer)

Parameter	P (g/kg <sup>-1</sup> )	K (g/kg <sup>-1</sup> )	Ca (g/kg <sup>-1</sup> )	Mg (g/kg <sup>-1</sup> )	S (g/kg <sup>-1</sup> )	Fe (mg/kg <sup>-1</sup> )	Mn (mg/kg <sup>-1</sup> )	Cu (mg/kg <sup>-1</sup> )	Zn (mg/kg <sup>-1</sup> )
<b>Conventional ICP-OES</b>									
Min.	1	15.3	6.5	1.68	0.17	50	15	10	9.5
Max.	1.5	28	18	4.5	1.98	155	125	23.5	39.5
Mean	1.2	21.3	9.84	2.74	0.72	74.86	67	15.5	18.35
s.d.	0.1	3.09	1.92	0.5	0.39	24.48	18.6	2.99	7.03
cv(%)	11	14.5	19.5	18.1	51.8	32.7	27.7	19.3	38.3
<b>In situ Titan</b>									
Min.	0.2	14.4	0	8.87	0.86	489.5	101	14.4	7.75
Max.	0.8	27.3	6.65	12.0	1.87	1261	196	19	10
Mean	0.4	19.9	2.53	10.2	1.31	1012	133	16	8.72
s.d.	0.11	2.42	2.11	0.69	0.22	168.8	20.65	1.22	0.55
cv(%)	29	12.2	83.1	6.73	16.9	16.65	15.5	7.67	6.34
<b>Ex situ pXRF Titan</b>									
Min.	0.83	16.34	8.27	2.42	1.53	<LOD	36	7	14
Max.	1.54	26.38	15.77	4.55	2.27	<LOD	138	21	14
Mean	0.97	21.97	11.54	3.63	1.73	<LOD	66.26	13.37	14
s.d.	0.08	2.04	1.78	0.56	0.16	<LOD	21.85	3.16	0
cv(%)	8.7	9.3	15.5	15.5	8.84	<LOD	32.9	23.6	0
<b>Ex situ pXRF Tracer</b>									
Min.	0.9	13.9	7.11	0	1.52	74	40	8	7
Max.	1.3	22.9	13.6	4.29	2.25	186	152	19	12
Mean	1.0	18.6	9.74	1.36	1.78	94.4	7906	14.6	9.49
s.d.	0.1	1.83	1.53	1.48	0.18	20.51	24.3	2.49	1.22
cv(%)	10	9.87	15.7	108.7	10.13	21.73	30.71	17.04	12.88

Min: Minimum, Max: maximum, S.d, standard deviation, cv(%): coefficient of variance and LOD: limit of detection

For pXRF Titan analyzes on oven-dried green (Gdry) and mature (Mdry) coffee fruits (Table 3), significant variability was observed for Ca and Mn on the Gdry Titan analyzes. P, K, Mg, S, Cu, and Zn exhibited the lowest considerable variability for all pXRF methods. while

Fe was below the limit of detection (<LOD). The leaves and fruits' low variability data can be attributed to balanced coffee plant treatment and effective soil management in the study area (Resende *et al.*, 2016), despite the soil's varying topography, which includes flat areas, and undulating terrain.

**Table 2:** Descriptive statistics of the elemental composition obtained via conventional ICP-OES method on oven-dried green coffee fruits (Gconventional), mature coffee fruits (Mconventional) and pXRF on oven-dried green fruits (Gdry Titan) and mature fruits (Mdry Titan) and mature fruits (Mdry Titan).

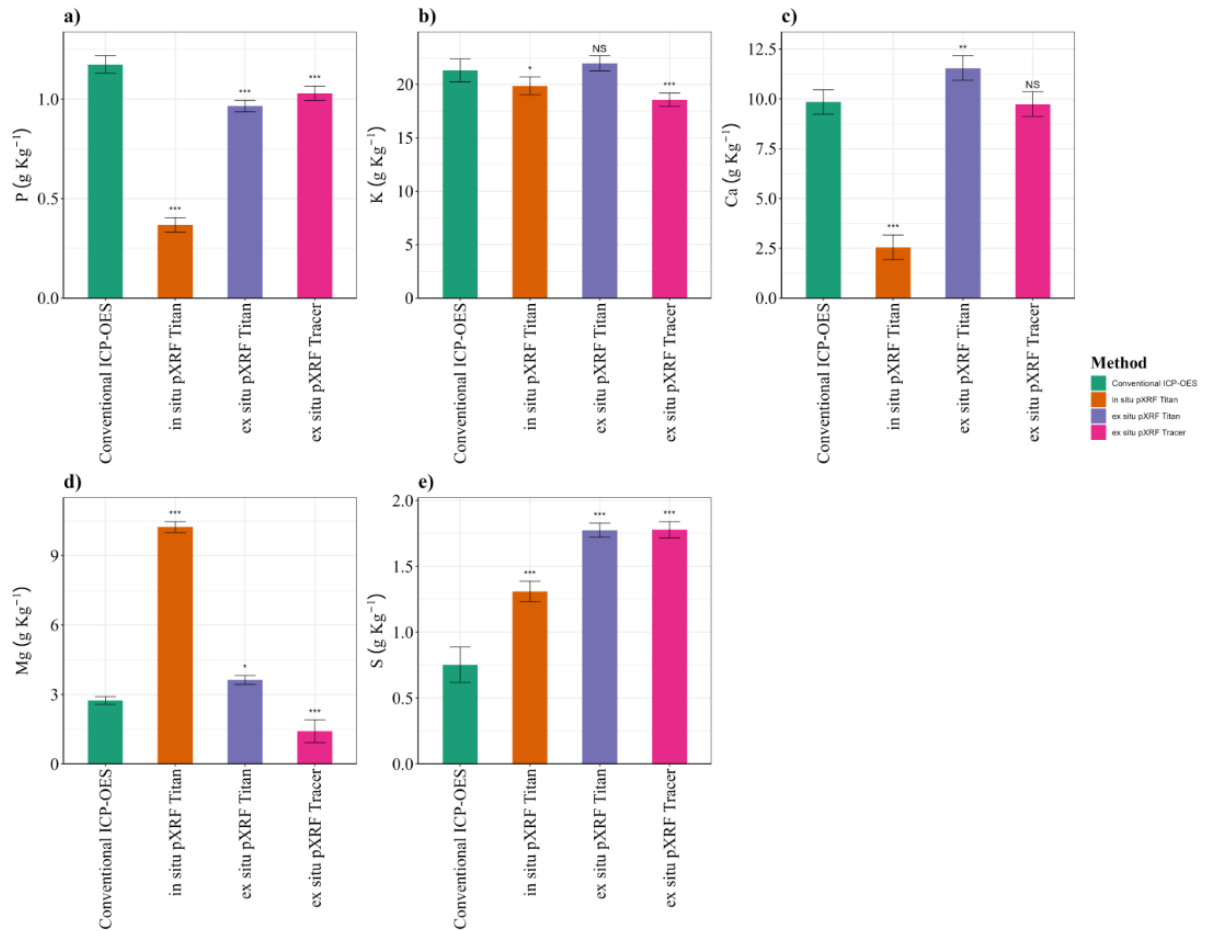
Parameter	P (g/kg-1)	K (g/Kg-1)	Ca (g/Kg-1)	Mg (g/Kg-1)	S (g/Kg-1)	Fe (mg/Kg-1)	Mn (mg/Kg-1)	Cu (mg/Kg-1)	Zn (mg/Kg-1)
<b>Gconventional</b>									
Min.	0.9	17.25	2.25	0.93	0.12	15	10	11.5	10
Max.	1.13	45	4.25	1.63	0.79	45	35	21	23.5
Mean	1.11	25.82	2.99	1.31	0.3	29.86	18	15.03	11.86
s.d.	0.12	6.92	0.47	0.17	0.15	7.52	4.73	3.85	3.92
cv(%)	10.47	24.03	15.72	13.06	48.66	25.2	26.27	25.63	33.05
<b>Gdry Titan</b>									
Min.	2.11	29.5	10.02	11.03	4.49	<LOD	128	11.99	10
Max.	3.37	48.97	25.83	11.03	6.81	<LOD	585	33	12
Mean	2.7	40.61	14.97	7.81	5.5	<LOD	281.82	22.97	8.6
s.d.	0.33	3.96	4.59	1.21	0.56	<LOD	87.24	4.82	1.35
cv(%)	12.11	9.76	30.67	15.43	10.11	<LOD	30.95	20.99	15.75
<b>Mconventional</b>									
Min.	0.59	12.25	2	0.63	0.12	10	5	8.5	55
Max.	1.22	28.75	3.25	1.25	0.46	35	45	18	24
Mean	0.92	23.31	2.52	1.04	0.26	24.14	13.43	14.14	11.8
s.d.	0.12	3.95	0.26	0.15	0.01	6.58	6.73	1.92	4.84
cv(%)	13.46	16.92	10.31	14.65	38.18	25.27	50.09	13.6	41.06
<b>Mdry Titan</b>									
Min.	1.5	34.1	<LOD	3.94	2.38	<LOD	64	18	4
Max.	3.55	61.67	<LOD	7.6	4.8	<LOD	138	31	8
Mean	2.49	50.11	<LOD	5.56	4.07	<LOD	91.03	23	5.2
s.d.	0.43	5.38	<LOD	0.97	0.46	<LOD	20.84	3.06	1.21
cv(%)	17.05	10.751	<LOD	17.51	11.4	<LOD	22.9	22.9	23.23

Min: Minimum, Max: maximum, s.d: standard deviation, cv(%): coefficient of variance and LOD: limit of detection

## 4.2 Comparison Between Methods for Foliar and Fruits Analyzes

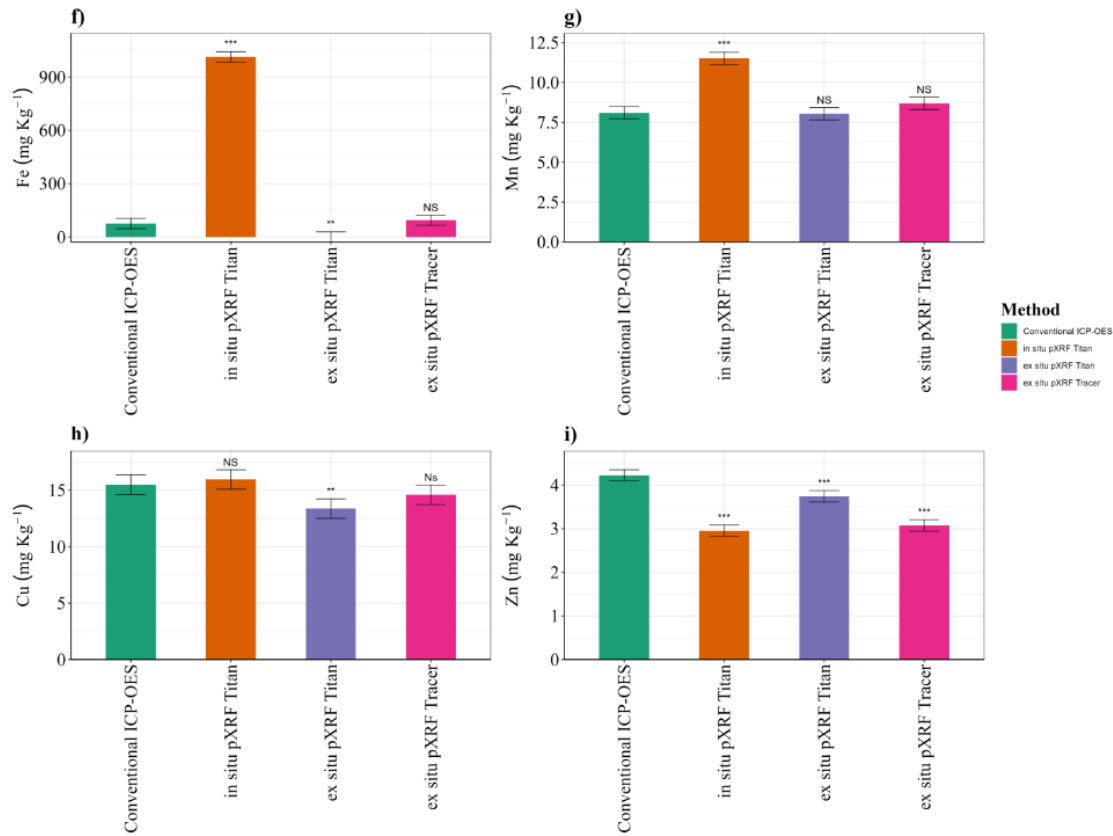
In Figure (Fig. 2), the macronutrient (P, K, Ca, Mg, and S) concentrations obtained after acid digestion followed by ICP-OES quantification, in situ pXRF Titan, ex situ pXRF Titan, and ex situ pXRF Tracer are presented. For K, the concentrations obtained by all conditions were comparable. It is worth mentioning that the K concentrations obtained on intact and fresh coffee leaves were very similar to those obtained by conventional ICP-OES. Similar behaviors were observed for P and Ca. The concentrations obtained via ex situ pXRF conditions using either Titan or Tracer were similar to conventional ICP-OES. The concentrations obtained in situ using pXRF Titan were considerably lower.

This lower significance can be attributed to the effect of the water content of coffee leaves underestimating the results (Silva *et al.*, 2022). A high Mg concentration was observed for in situ pXRF Titan condition. The identification and quantification of light elements like Mg via pXRF is normally hampered (Ribeiro *et al.*, 2021). Herein, the quantification of Mg in situ condition was also influenced by the water content of coffee leaves. However, Mg concentrations obtained via ex situ pXRF Titan were similar to conventional ICP-OES. For S, the concentrations obtained by conventional ICP-OES were lower than those obtained by all pXRF conditions. This result suggests some loss of S during acid digestion procedure, needing further studies to elucidate.



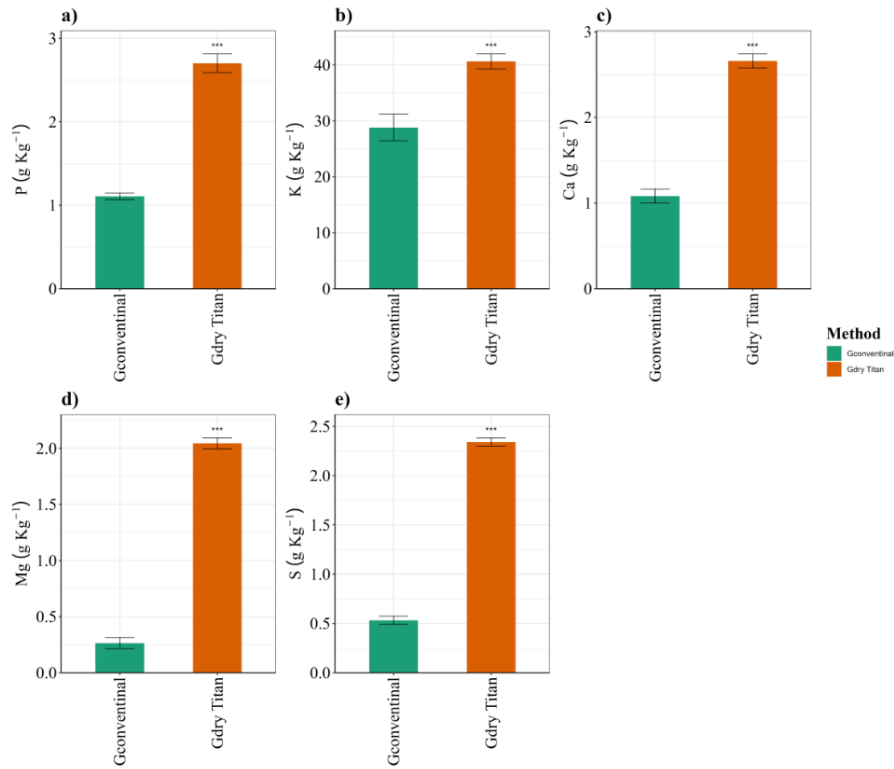
**Figure 2:** Conventional ICP-OES method and pXRF sensor on oven-dried coffee leaves of macronutrients (P, K, Ca, Mg and S).

Regarding the micronutrients (Fig. 3), the Mn concentrations obtained by pXRF in ex situ conditions were comparable to conventional ICP-OES. For Cu, its direct determination in the field was completely comparable to the conventional ICP-OES method. For Zn, despite a statistical difference was observed between methods, the maximum difference was only  $\sim 1.0$  mg kg<sup>-1</sup>. For Fe, the concentration obtained via ex situ pXRF Tracer was equal to the conventional ICP-OES method. A complete anomalous result was observed for in situ pXRF Titan. This can be attributed to a nonspecific calibration (Geoexploration) in the pXRF Titan. All analyzes using pXRF Tracer were conducted using a plant-manufactured calibration.

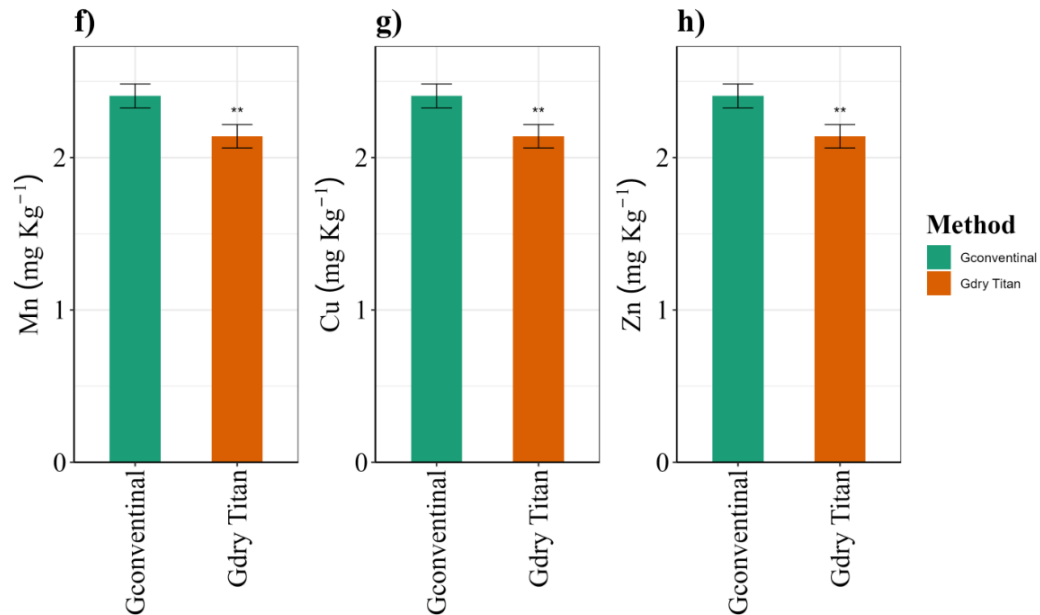


**Figure 3:** Conventional ICP-OES method and pXRF sensor on oven-dried coffee leaves of micronutrients (Fe, Mn, Cu, and Zn).

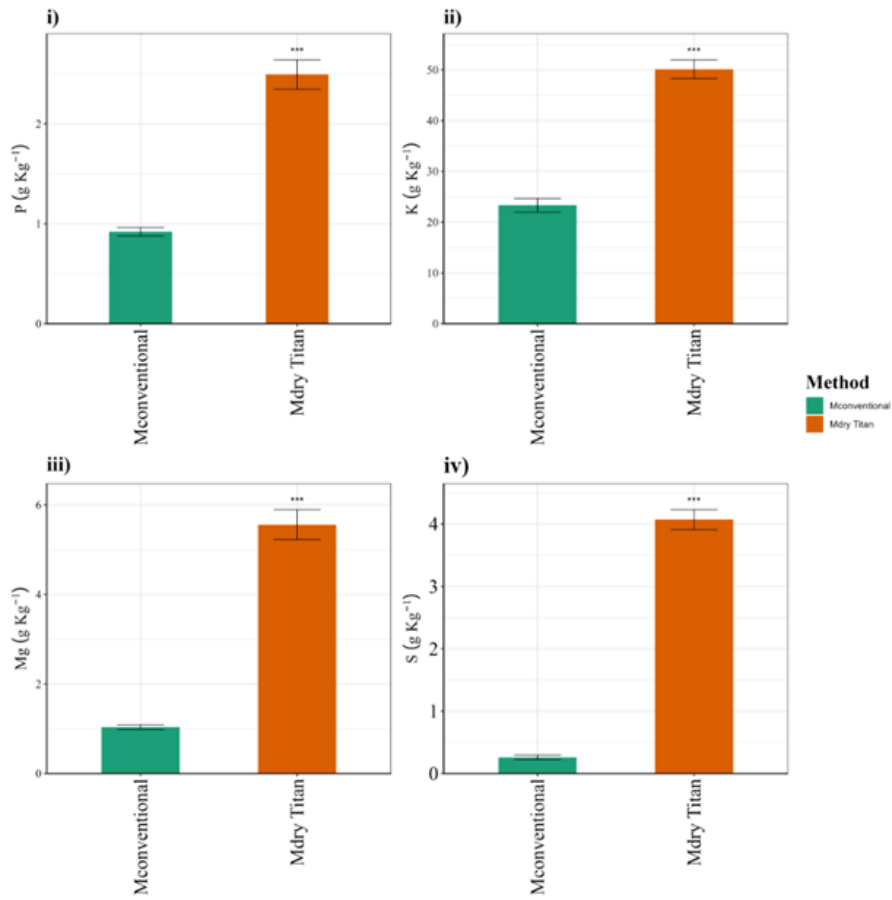
Regarding fruits (Fig. 4, 5, 6 and 7) the macro- and micronutrients between conventional ICP-OES and ex situ pXRF Titan were compared. The concentrations obtained via pXRF were significantly superior to those obtained by conventional ICP-OES for all macronutrients. However, Mn and Cu concentrations were comparable in micronutrients. And the underestimation of Zn observed can be attributed to Fe, Mn, and Cu antagonism (Bueno, 2008; Kachinski *et al.*, 2020). The equipment provided accurate results and a reliable tool for assessing the elemental composition of coffee nutrition for most of the variables (Lima *et al.*, 2019).



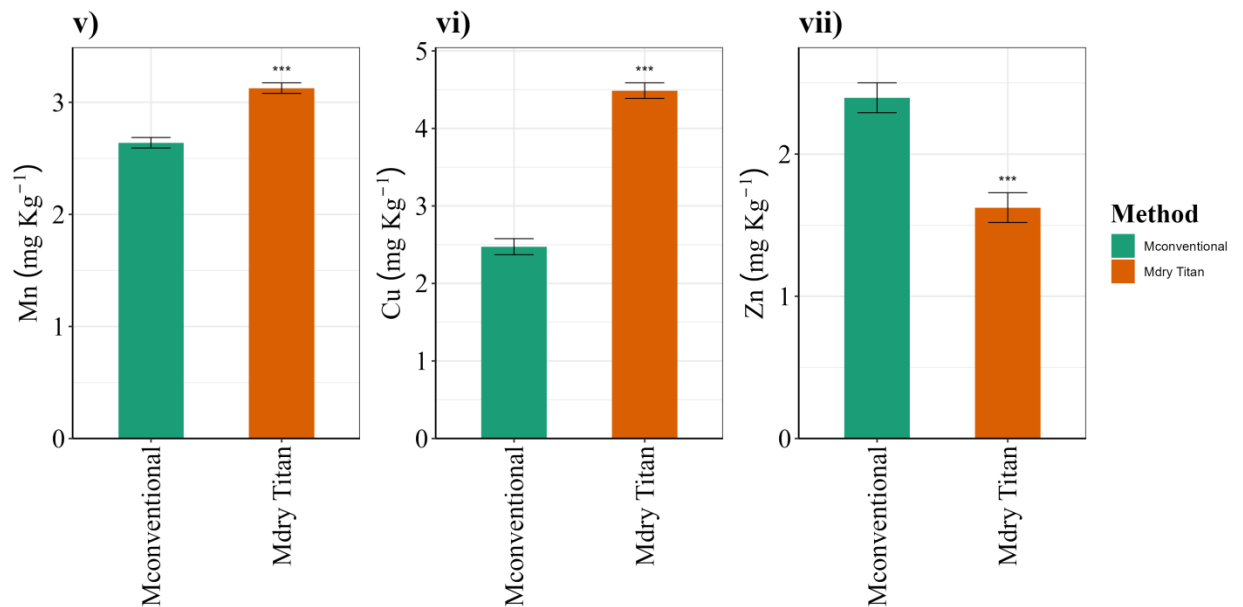
**Figure 4:** Conventional ICP-OES method and pXRF sensor on oven-dried green fruits of macronutrients (P, K, Ca, Mg and S).



**Figure 5:** Conventional ICP-OES method and pXRF sensor on oven-dried green fruits of micronutrients (Mn, Cu and Zn).



**Figure 6:** Conventional ICP-OES method and pXRF sensor on oven-dried mature coffee fruits of macronutrients (P, K, Mg and S).



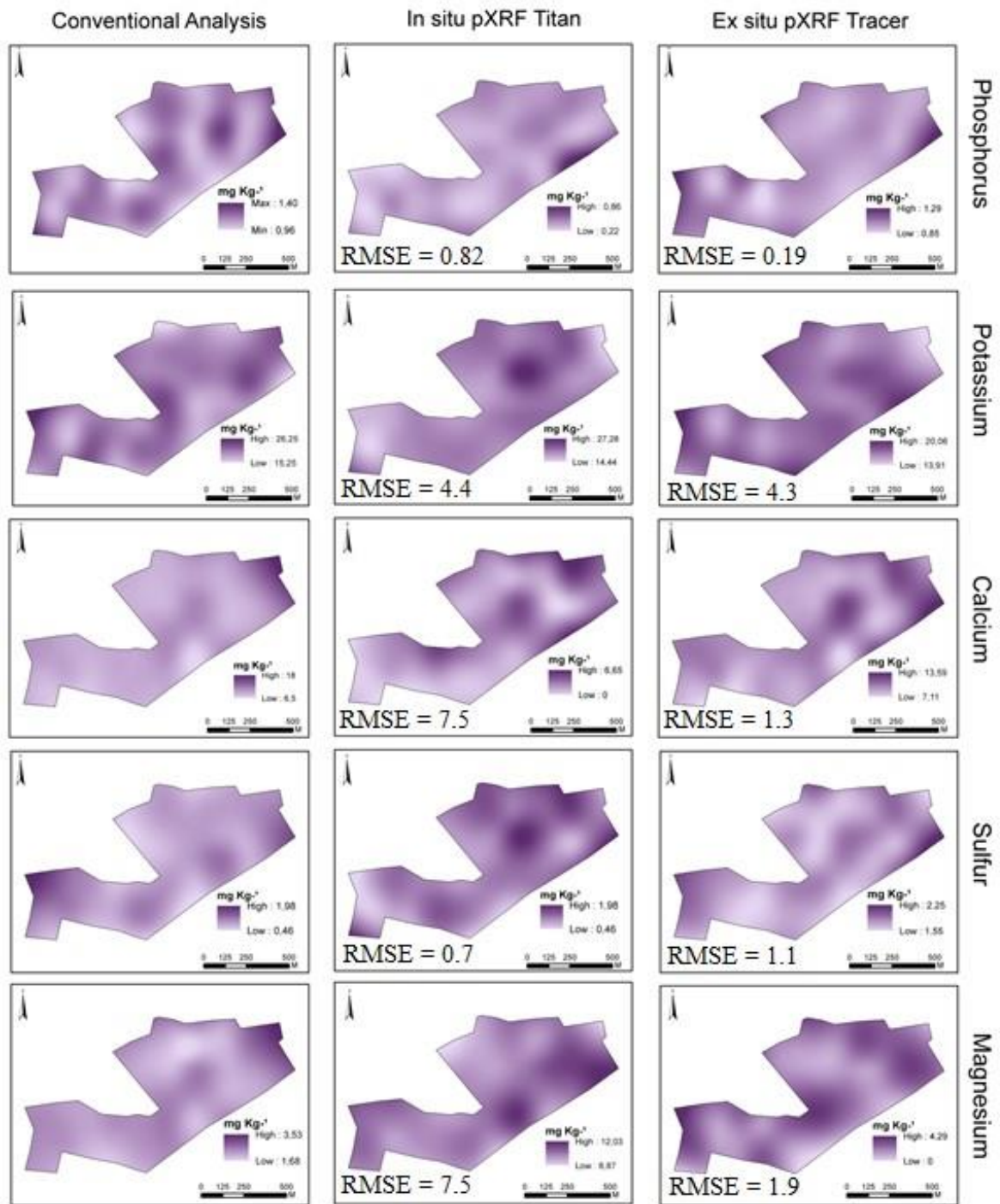
**Figure 7:** Conventional ICP-OES method and pXRF sensor on oven-dried mature coffee fruits of micronutrients (Mn, Cu and Zn).

## 5.0 Spatial Distribution of Coffee Leaves Elemental Composition

The spatial distribution variables exhibited minor differences in interpolated spline maps, reflecting spatial similarity levels. The spatial distribution for macronutrients (Fig. 8), P on in situ pXRF Titan, showed slight similarity with conventional ICP-OES analyze. High consistent similarity distribution on ex situ pXRF Tracer revealed comparing with the conventional analyzes spatial map.

For K on in situ pXRF Titan and ex situ Tracer, indicated higher significance and uniform spatial distribution aligning closely with conventional analyzes, thus, in situ pXRF Titan was slightly shifted. The Mg and Ca elements, on in situ pXRF Titan were consistent and matched the conventional ICP-OES analyze.

While on ex situ pXRF Tracer for Ca and Mg showed strong spatial distribution, with noticeable high concentrations but more diffused overall. The S results, on in situ pXRF Titan aligned closely with conventional analyze. And more uniform distribution, with high concentrations, spread evenly across the map on ex situ pXRF Tracer.

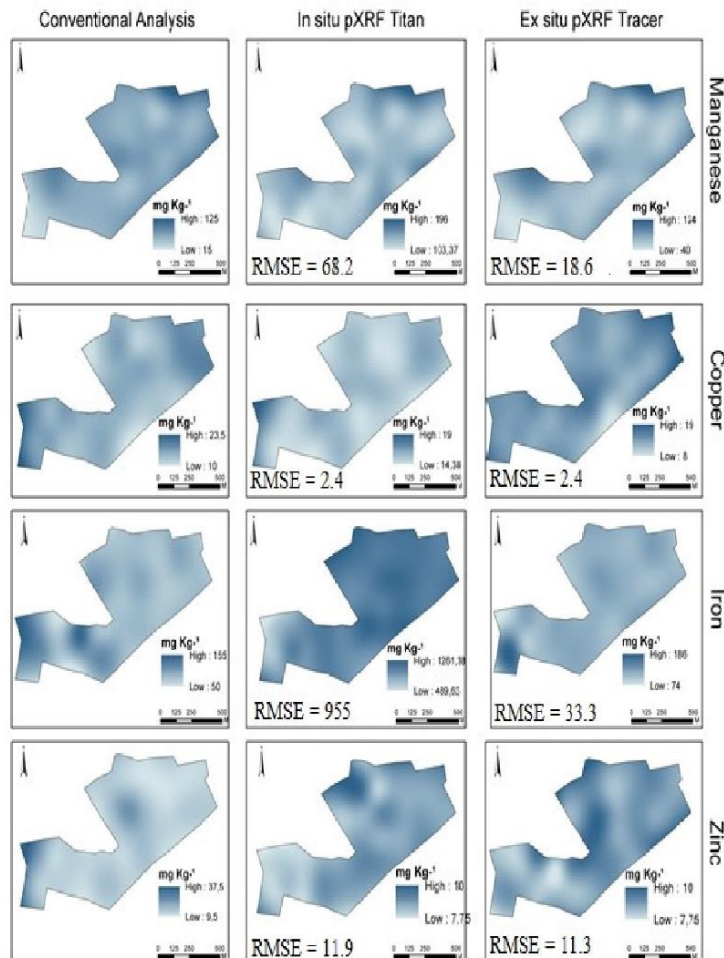


**Figure 8:** Spatial Distribution of Macronutrients on oven-dried leaves in Conventional ICP-OES and pXRF Sensor Analyzes

Concerning micronutrients (Fig. 9), Fe, on in situ pXRF Titan demonstrated higher distribution than conventional ICP-OES and ex situ pXRF Tracer showed similarity. Comparable was Mn on conventional ICP-OES analyzes with in situ pXRF Titan and ex situ pXRF Tracer.

The elements Cu and Zn, on in situ pXRF Titan presented a similar pattern with slight diffusion with conventional analyzes. While ex situ pXRF Tracer displayed a smoother, more homogeneous distribution.

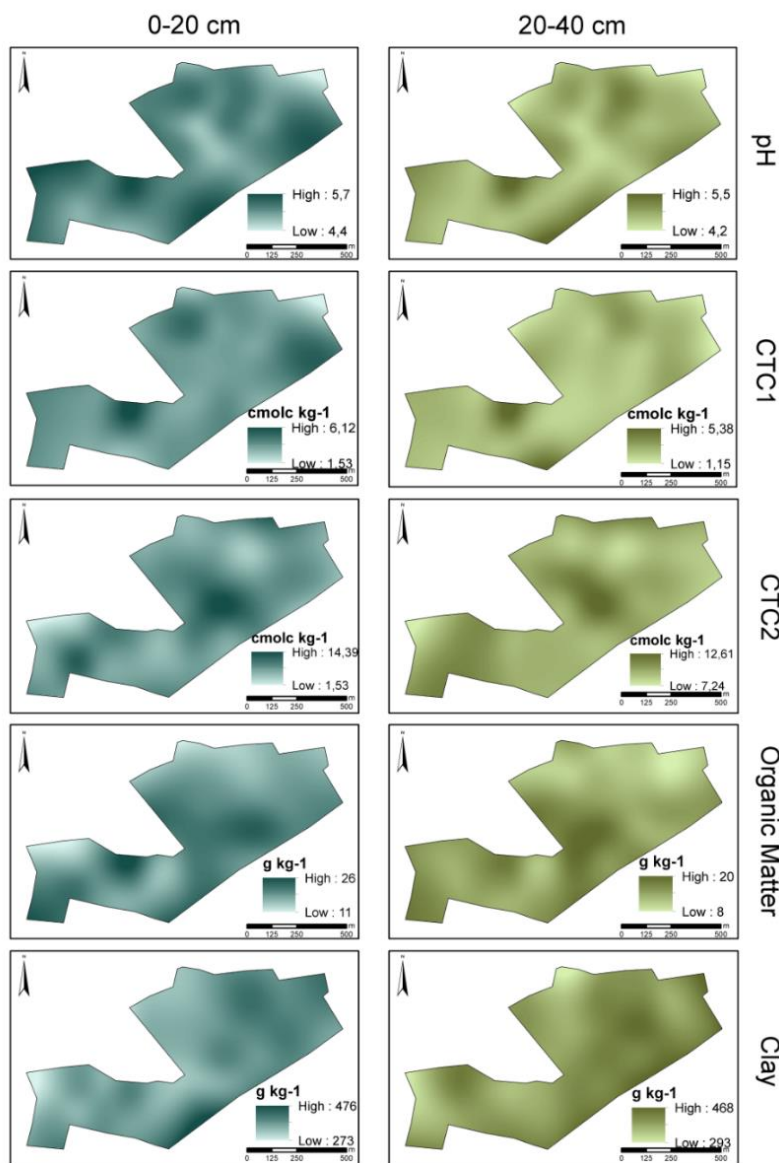
Overall, pXRF methods (both Titan and Tracer) generally offered more uniform distributions spatial compared to conventional ICP-OES across most elements. This suggests that pXRF methods may provide a more consistent and spatially stable assessment of elemental concentrations (Yuan *et al.*, 2014).



**Figure 9:** Spatial Distribution of Micronutrients on oven-dried leaves in Conventional ICP-OES and pXRF Sensor Analyzes

### 5.1.0 Spatial Distribution of Soil Attributes

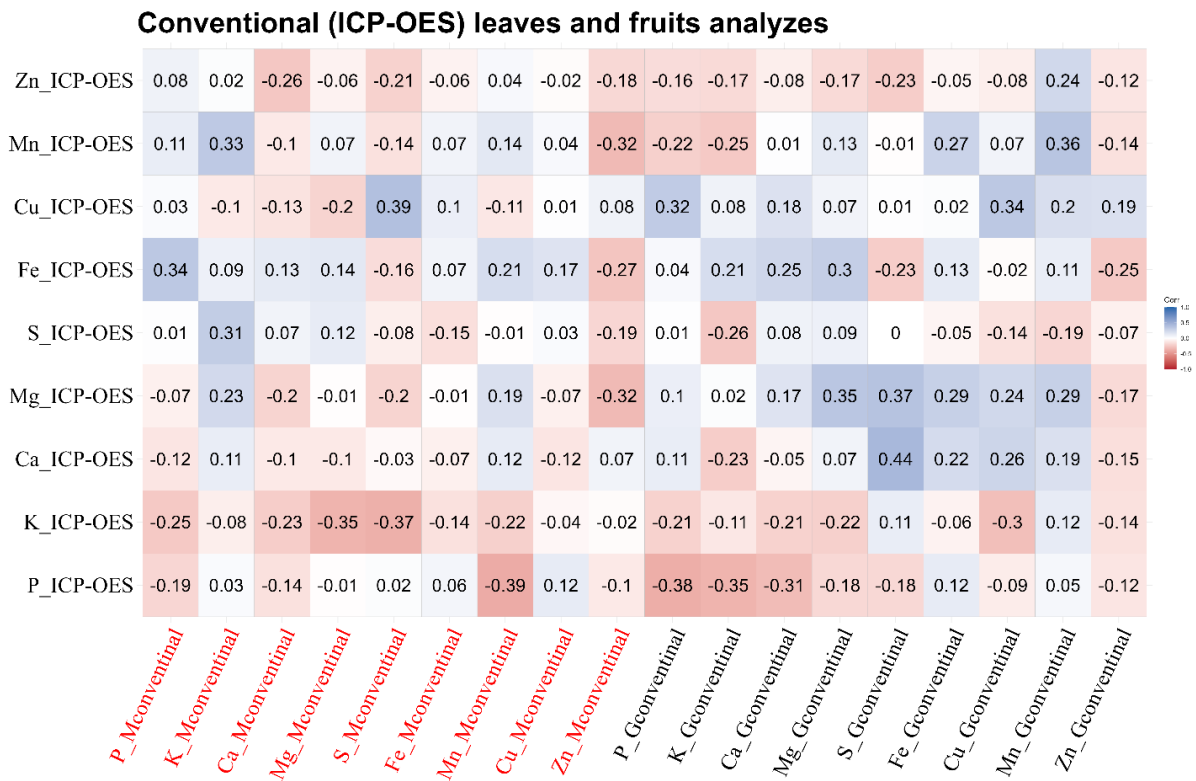
The spatial soil attributes distributions (Fig. 10), displayed among the area significant similarity pH, OM, and Clay from 20-40 cm layers levels over 0-20 cm. Regarding CEC<sup>1</sup> and CEC<sup>2</sup> on 20-40 cm, were slightly lower across 0-20 cm. However, Soil pH management and equilibrating balanced inputs fertilizer are important to elevate soil fertility attributes (SELIM, 2020) and maintain the nutritional coffee crops to speed up productivity with a better nutritional composition (Netsere & Takala, 2021). The spline interpolation was a potential tool for obtaining interpolated maps (Borghetti *et al.*, 2008).



**Figure 10:** Spatial Distribution Soil Attributes on Conventional ICP-OES Analyzes

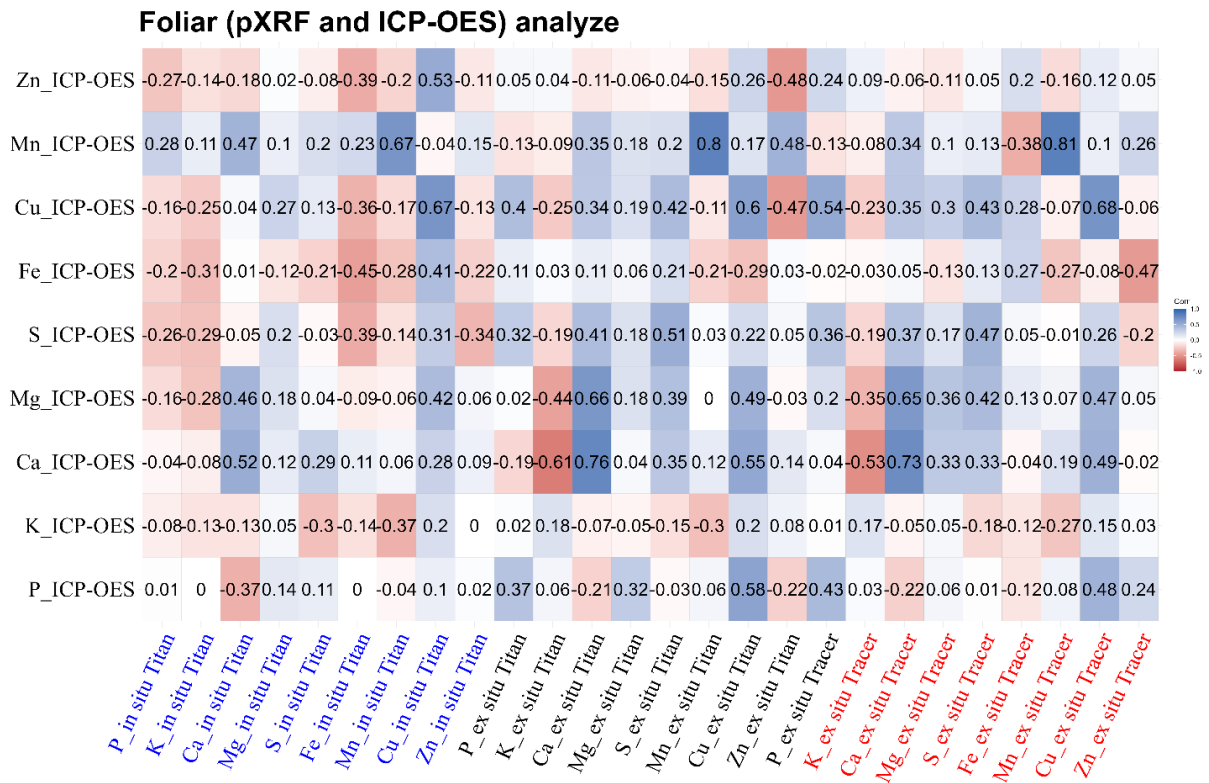
## 6.0 Correlations of Plant Materials

The oven-dried leaves, green (Gconventional), and mature (Mconventional) fruits analyzes (Fig. 11). Macro- P, Mg, S (32-44%), and micronutrients Cu and Mn (34-36%), demonstrated moderate correlations between Gconventional fruits within conventional ICP-OES leaves analyzes. An insignificant correlation was observed for Mconventional fruits. Additionally, suboptimal digestion during ICP-OES analyzes could potentially impact the results if the acid employed did not adhere to the recommended laboratory conditions for the digestion of solid materials (Matias, 2008).



**Figure 11:** Correlation of Macronutrients (P, K, Ca, Mg, and S) and Micronutrients (Mn, Cu, and Zn) in plant Materials using the Conventional ICP-OES Method.

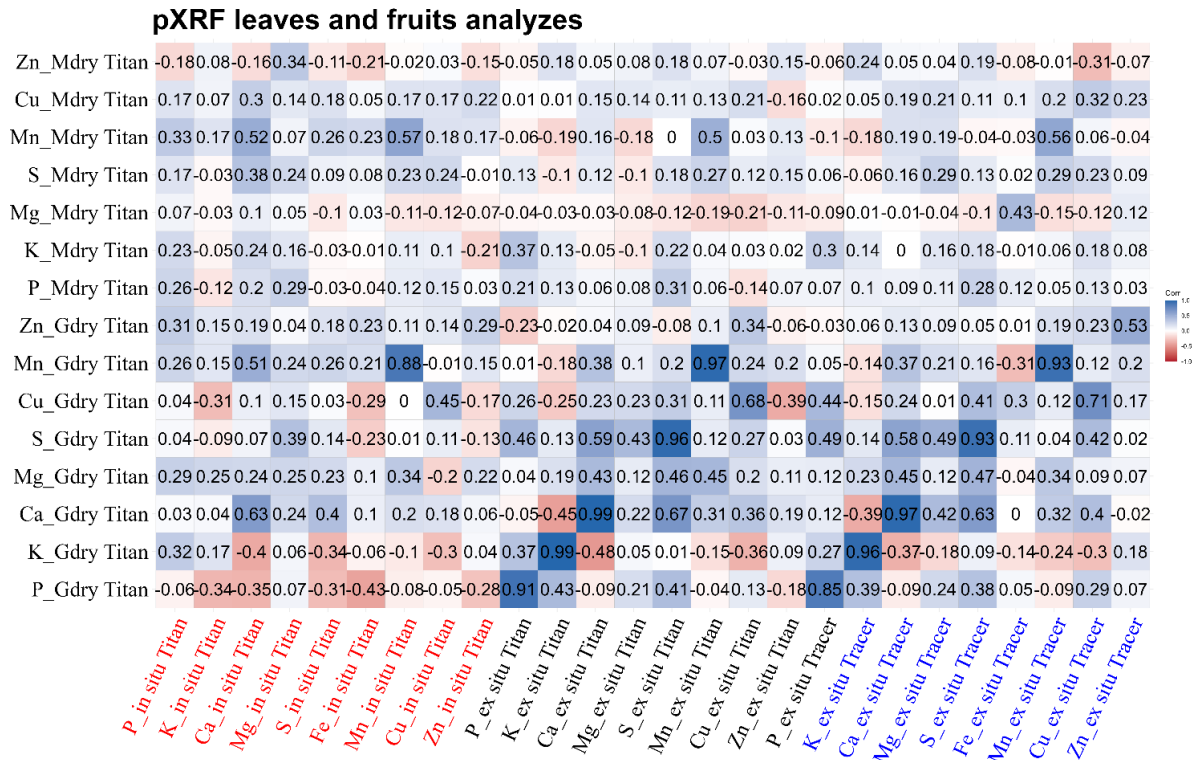
A contrast was observed in the pXRF equipment over conventional ICP-OES analyzes on oven-dried leaves (Fig. 12), Ca, Cu, and Mn (52-67%) obtained on in situ pXRF Titan exhibited higher correlations. In the ex situ pXRF Titan and Tracer methods, significant correlations were noted for Ca and S (51-76%), then, Cu and Mn (60-81%) among the micronutrients. Additionally, Ca showed a high correlation over Mg in the ex-situ pXRF Titan and Tracer methods that can be explained by the synergism effect (Costa et al., 2024) these elements can compete for the same absorption sites in the plant.



**Figure 12:** Correlation of Macronutrients (P, K, Ca, Mg, and S) and Micronutrients (Mn, Cu, and Zn) in coffee leaves using pXRF Sensor and ICP-OES.

A significant correlation in green (Gdry Titan) fruits (Fig. 13) and leaves, was shown on ex situ pXRF Titan and Tracer analyzes for P, K, Ca, and S (85-99%). Moreover, in situ pXRF Titan for Ca showed a high correlation (63%). Regarding micronutrients, Mn and Cu (68-97%), demonstrated consistent correlations. Lower correlations were demonstrated (Fig. 13), in mature fruits (Mdry Titan), though, significant correlations were observed in Mn (50-57%) in all parameters of pXRF methods.

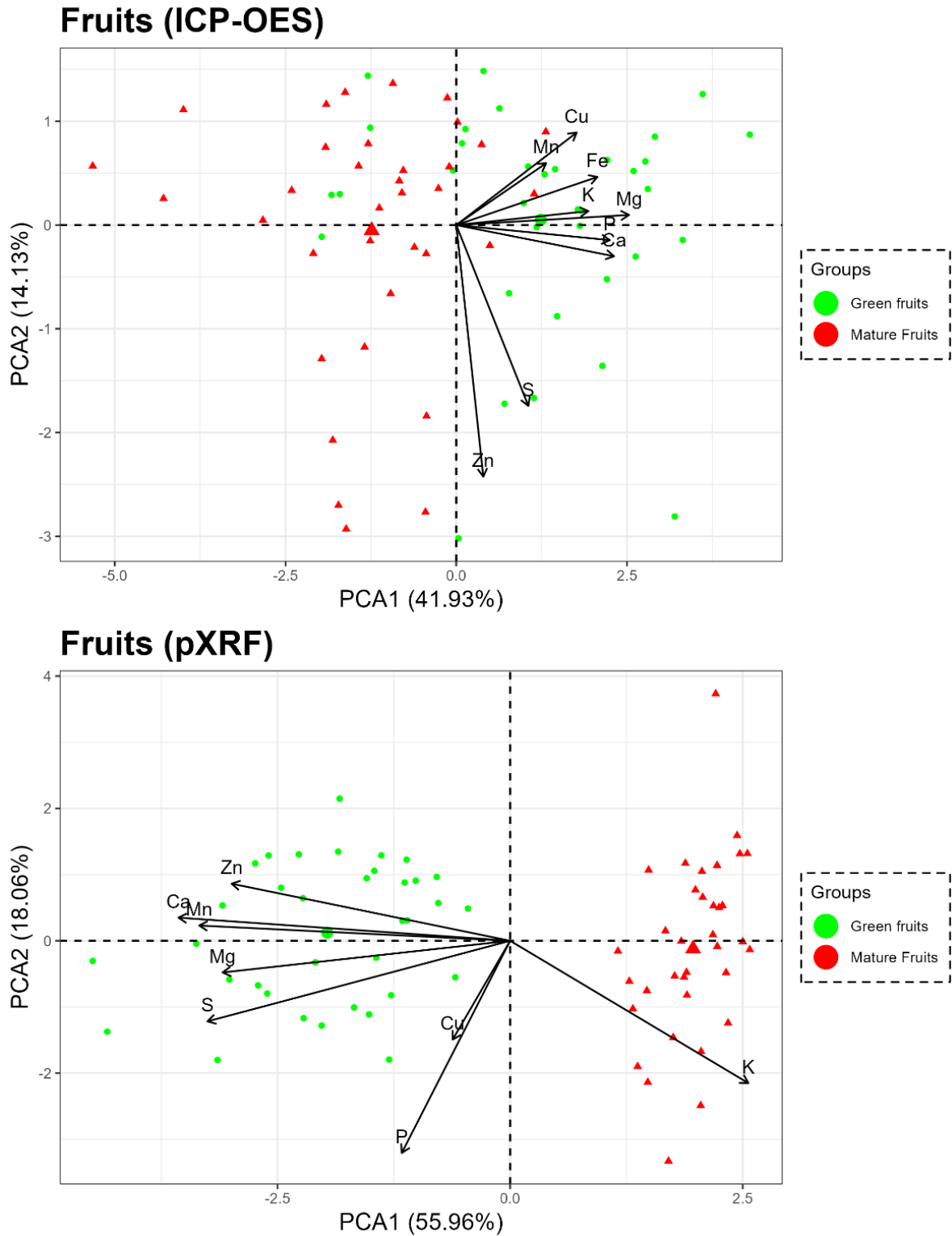
The higher correlation significance between ex situ pXRF analyzes and green fruits associated both samples being collected simultaneously and the nutritional distribution in coffee plants during their plant stage (Laviola *et al.*, 2007; Ferreira *et al.*, 2021). The pXRF sensor exhibited a superior correlation for elemental composition compared to conventional ICP-OES analyze, particularly for macronutrients and micronutrients in coffee leaves and green fruits. The higher correlation observed with pXRF methods underscores their effectiveness in analyzing coffee plant nutrition (Dalazen *et al.*, 2022).



**Figure 13:** Correlation on oven-dried leaves, green (Gdry Titan) and mature (Mdry Titan) fruit concentrations using pXRF sensor

## 6.1 PCA for Plant Materials Analyzes

Analyzes obtained from conventional ICP-OES (Fig. 14), P, Ca, Mg, Fe, Cu, and Mn showed lower significance correlations per mature and higher for green fruits. PC1 captured 41.93% of the correlation; however, it could not distinguish the status of the fruits (green and mature), thereby complicating the identification of noticeable correlation components. Nevertheless, the pXRF sensor demonstrated enhanced correlation for Mg, Ca, and S, Mn, and Zn in green fruits, with the PC1 capturing 55.96% of the correlation. For P and Cu showed only a slight correlation. For K, the PC2 captured 18.06% in mature fruits with a moderate correlation. Despite this, the pXRF sensor was able to differentiate between green and mature fruits, a distinction not observed in the conventional ICP-OES analyze. Mature fruits tend to accumulate more K to support critical physiological processes, such as the formation of sugars and other compounds essential for coffee quality (E. *et al.*, 2010; Dalazen *et al.*, 2022).



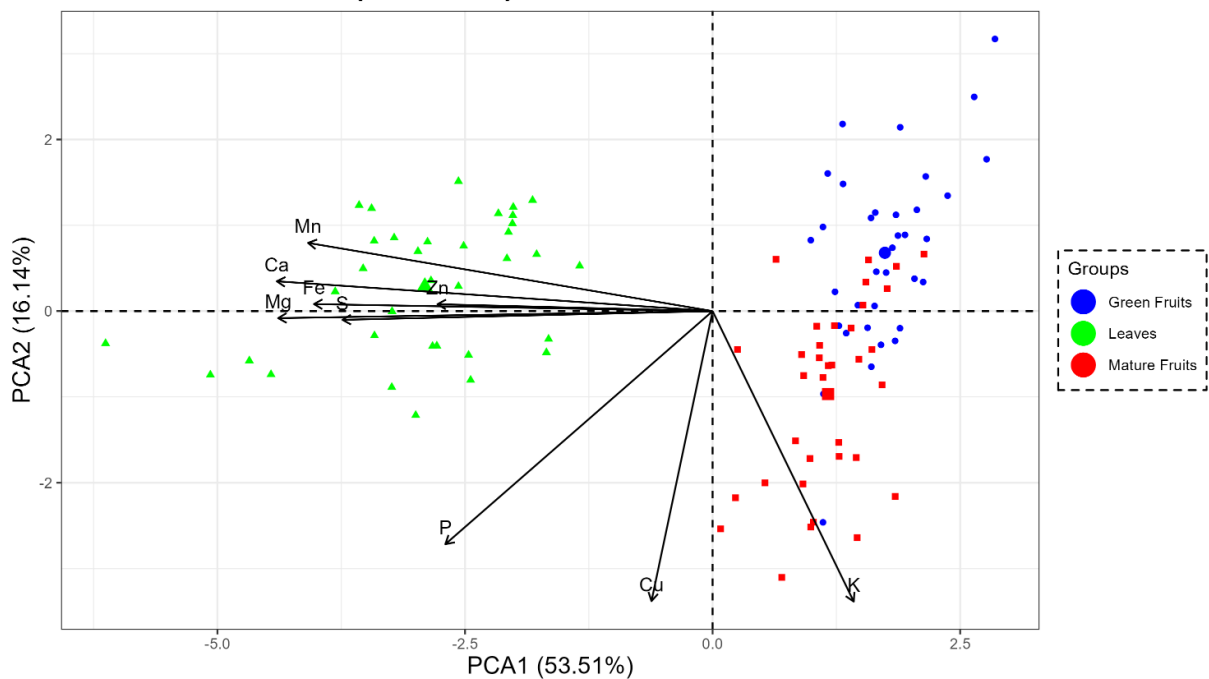
**Figure 14:** PCA of macronutrients (P, K, Ca, Mg and S) and micronutrients (Mn, Cu, and Zn) on oven-dried green and mature fruits concentrations using conventional ICP-OES and pXRF Titan sensor.

In the PCA analyze of leaves and fruits (Fig. 15), PC1 captured 53.51%, and higher correlations were observed for Ca, Mg, S, Mn, and Zn in oven-dried leaves obtained by

conventional ICP-OES analyzes and significantly lower in green and mature fruits. Consequently, the same merging of green and mature fruits observed in (Fig. 14) in ICP-OES analyze, was verified again, indicating an inability to distinguish the status of the fruits.

These findings enhance the accuracy, reliability, and applicability of the pXRF sensor for analyzing and monitoring the nutritional content of coffee (Costa *et al.*, 2024). The pXRF sensor performs better in correlating macronutrient and micronutrient data than conventional ICP-OES, particularly in differentiating between green and mature coffee fruits. This improvement highlights the pXRF sensor's potential for more accurate and reliable nutritional analyze in coffee production (Ferreira & Santos, 2022).

### Leaves and fruits (ICP-OES)



**Figure 15:** Plant materials PCA of macronutrients (P, K, Ca, Mg and S) and micronutrients (Mn, Cu and Zn) on oven-dried leaves, green and mature fruits concentrations using conventional ICP-OES.

## 7.0 Conclusion

The data obtained via pXRF and conventional ICP-OEs analyzes were successfully characterized by a statistical GLS model except for Fe and Zn on coffee leaves. The pXRF equipment analyzes (in situ Titan, ex situ Titan and ex situ Tracer), significantly monitored higher levels of macronutrients and micronutrients over the conventional ICP-OES in coffee leaves and green fruits. These, ensure that pXRF sensor analyzes even on in situ applicability can be reliable and give accurate results.

Regarding K was significantly comparable with the conventional ICP-OES and similarities were seen in P and Ca on in situ pXRF Titan. Concerning Mn was emphasized in all pXRF analyzes on leaves and fruits. Though, mature fruits the significance was lower, likely due to differences in sample collection times. About in situ pXRF Titan analyzes were influenced by water content showing malicious for P and Cu that light elements are more vulnerable to water effect.

A strong differentiating between green and mature coffee fruits was shown in PCA (Fig. 11). Best correlations were observed between leaves and green fruits using conventional and pXRF methods. Regarding soil spatial distribution fertility, slight significance was observed on CEC<sup>1</sup> and CEC<sup>2</sup> between 0-20 cm and 20-40 cm showing equilibrate soil management and balanced fertilizers area. For soil classification, the area was classified by Dystrophic Red-Yellow Latosol, Eutrophic Red-Yellow Argisol, Gleysolic Eutrophic Red-Yellow Argisol, and Dystrophic Red-Yellow Argisol.

The pXRF mapping of elemental composition displayed similarities and high spatial distribution comparable to conventional analyses. Portable X-ray Fluorescence (pXRF) was an excellent tool for assessing and mapping the elemental composition of coffee leaves and fruits, potentially overcoming the delays of traditional analysis protocols.

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