

Original Research

# Geographical Traceability of *Manilkara huberi* (Ducke) A. Chev. by Chemical Signature

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Received: 10 November 2025

Accepted: 27 February 2026

## Abstract

This study evaluated the potential of Total Reflection X-ray Fluorescence (TXRF) as a geochemical traceability method for wood from *Manilkara huberi* (Ducke) A. Chev., a species of high commercial and ecological value widely exploited in the Legal Amazon. Wood samples were collected in eight locations in the states of Amazonas, Pará, Rondônia, and Roraima, representing different edaphic, geological, and climatic conditions in the context of Amazonian edaphic and geological variability. The multielemental analysis revealed significant variations in trace element and macronutrient concentrations (Fe, Mn, K, Ca, Sr, Rb), reflecting the specific geochemical signatures of each region. Multivariate analyses (PCA and NMDS) showed distinct groupings among the populations, confirming the discriminatory capacity of TXRF in the differentiation of geographical origins. Significant correlations between elements such as  $K \times Rb$  and  $Cr \times Fe$  demonstrated consistent patterns of coaccumulation and antagonism associated with local geochemistry. The results prove the efficiency of TXRF as a non-destructive, sensitive, and low-cost technique for origin authentication and forensic investigation of Amazonian wood, strengthening sustainable management policies and combating illegal exploitation. The proposed methodology is a scientific advance in forest traceability and biodiversity conservation, contributing to the transparency and legality of timber production chains in the Amazon.

**Keywords:** wood geochemistry, forest conservation, massaranduba, X-ray fluorescence, geochemical fingerprinting

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## Introduction

The massaranduba (*Manilkara huberi* (Ducke) A. Chev.), from the family Sapotaceae, is a large tree species widely distributed in the Legal Amazon, occurring in the states of Pará, Amazonas, Rondônia, and Roraima. The tree reaches more than 40 m in height and has a DAP greater than 100 cm. Its wood, dense and reddish-brown, with high latex content, is among the most valued in the international market [1, 2]. Due to its high durability and resistance to decomposition and xylophagous insect attack, it is widely used in civil construction, luxury furniture, and naval structures. Ecologically, it plays an essential role in dense and submontane Ombrophilous Forests, contributing to canopy structure, nutrient cycling, and the diet of fauna through fruits and oilseeds. However, its high commercial value and mechanical resistance have resulted in intense exploitation, placing it among the most heavily exploited species from the Amazon [3].

This has intensified illegal extraction and trade with limited traceability, aggravating deforestation and loss of biodiversity in primary forests. A significant portion of exported Amazonian wood still has an unverified origin, which weakens sustainable management policies and forest certification [4]. In recent decades, the expansion of deforestation and irregular logging has compromised the ecological and socioeconomic integrity of the Amazon, since a significant portion of the timber traded in the country comes from unauthorized sources [5].

Although official traceability systems, such as the Document of Forest Origin (DOF), have been implemented, failures in monitoring and verification of origin still allow the insertion of illegal products into the production chain [5, 6]. Traditional botanical identification, based on morphological characteristics of leaves, flowers, and bark, is not always sufficient to determine the geographical origin of processed wood, since its visual properties can be easily changed. In this context, scientific methods of independent verification of the geographical origin of wood have emerged as promising forensic tools to combat illegal logging. Among them, geochemical traceability emerges as an innovative tool for controlling the forest production chain, allowing the distinction of woods from different regions based on their elemental chemical signatures [5, 6].

The principle of traceability is based on the premise that each forest environment has a unique geochemical signature, resulting from the interaction between soil mineral composition, climatic conditions, and weathering processes. These factors influence the absorption and accumulation of chemical elements in trees, generating specific multielemental patterns that function as origin “geochemical codes” [7, 8]. The multielemental analysis of wood, based on the quantification of trace elements and macronutrients incorporated into woody tissue, has proven to be

an effective tool to authenticate the geographical origin and combat the illegal exploitation of tropical timber. This approach presents high discriminatory power between populations and regions of occurrence, reflecting the local geochemical, edaphic, and climatic conditions [3, 4].

Recent studies have extended this perspective by integrating isotopic analyses, such as the ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{18}\text{O}$ , to the elemental profiles of multiple tropical species, demonstrating the efficiency of these markers in the differentiation of materials from the Amazon and the Atlantic [6, 8]. The integration of chemical, isotopic, and anatomical approaches emerges as a multidisciplinary frontier of forest forensic geochemistry, able to support the authenticity and traceability of timber products of high economic and ecological value. Recent evidence reinforces that the chemical composition of wood reflects regional variations related to geology, soil fertility, and microclimatic conditions, highlighting the importance of elemental signatures for traceability studies in species of high commercial value, such as the massaranduba [4].

Among the techniques available to determine the elemental composition of wood, Total Reflection X-ray Fluorescence (TXRF) stands out for its high sensitivity, reproducibility, and non-destructive character. This methodology allows simultaneous detection of macro and microelements, including heavy metals and trace elements, even at very low concentrations [9, 10]. The method is based on the excitation of the atoms of the sample by an X-ray beam, causing the emission of secondary radiation characteristic of the specific “signature” of each chemical element. Compared to conventional methods such as ICP-MS, TXRF requires minimal sample preparation, reduces the risk of contamination, and presents low operational cost, which makes it a promising tool for forest traceability studies [3, 4].

When applied to wood, TXRF yields accurate information on the elemental composition of heartwood and sapwood, reflecting interactions between plant physiological processes and soil conditions of the surrounding environment. Recent research has shown that the technique allows us to differentiate wood samples from various Amazonian regions by analyzing the relative concentrations of elements such as Fe, Mn, Ca, K, Sr, and Rb [4, 11]. These results reinforce the applicability of TXRF in forensic verification and legal timber certification programs [12]. The method presents additional advantages, including using small sample volumes, eliminating complex acid digestion procedures, and high reproducibility. Such features make it particularly suitable for forensic and environmental analyses that require preservation of samples [13, 14].

In addition to its importance for traceability, Total Reflection X-ray Fluorescence (TXRF) has been extensively applied in environmental biomonitoring, enabling the evaluation of industrial pollution, atmospheric deposition, and trace element mobility

in ecosystems under anthropic pressure [14, 15]. In the forensic field, advances in spectral comparison algorithms and machine learning models have improved differentiation between samples with similar chemical signatures [16]. The combination of high sensitivity, low cost, and analytical speed consolidates TXRF as a strategic tool for traceability studies and origin authentication of tropical species such as *Manilkara huberi*, contributing to sustainable policies and the fight against illegal logging. Despite advances in forensic geochemistry, few studies have applied TXRF specifically to Amazonian hardwoods, integrating multielement signatures and multivariate modeling.

Therefore, this study aimed to assess the potential of Total Reflection X-ray Fluorescence (TXRF) for the geochemical discrimination of populations of *Manilkara huberi* in the Legal Amazon, contributing to the development of precise analytical tools for the conservation and traceability of timber species of high ecological value.

## Materials and Methods

The present study focused on *Manilkara huberi*, commercially known as massaranduba. The objective was to evaluate the potential for tracing the geographical origin of massaranduba through X-ray fluorescence analysis by total reflection (TXRF) in wood samples from living trees. This approach has been effective in authenticating the origin of forest products and combating illegal exploitation, as demonstrated in previous studies with tropical species [3, 4].

The botanical identification in the field was conducted by parobotanists and forest engineers, using identification keys based on diagnostic morphological characteristics such as leaves, flowers, fruits, and stem morphology, complemented by the analysis of organoleptic characteristics and the observation of the presence and consistency of latex, a striking attribute of the species [1, 2].

### Study Areas and Sampling

The collections were carried out in four states of the Legal Amazon: Pará (PA), Amazonas (AM), Roraima (RR), and Rondônia (RO), selected for presenting the highest rates of cumulative deforestation [17]. Within each state, priority was given to areas under the forest concession regime to ensure the representativeness of the typical ecological and management conditions of commercially exploited forest formations.

In Pará, the collections were carried out in the municipality of Juruti (1 area); in Amazonas, in Humaitá (1), Parintins (1), and Silves (1); in Roraima, in the municipalities of Rorainópolis (1) and Caracaraí (1); and in Rondônia, in the localities of Candeias do Jamari – National Forest of Jamari (FNJD, 1 area) and Itapuã do Oeste - Jacundá National Forest (FNJM, 1 area).

The environmental conditions of the sampling areas were characterized considering the meteorological, phytophysiological, geological, and pedological information obtained from official bases and field observations. Climate data were used, including annual average temperature, precipitation, relative humidity, and rainfall patterns [18, 19], allowing the microclimatic characterization of each locality.

The forest typology was defined based on official classifications [20] and complemented by in situ observations, considering canopy structure, floristic composition, and succession stage of plant formations. The evaluated areas include formations of Dense Ombrophilous Forest, Semi-deciduous Seasonal Forest, and Dry Land Forest, with variations associated with local altitude gradients and water availability.

The geological and pedological characteristics were obtained from [21] and the Brazilian Soil Classification system [22]. The predominant soils are Yellow Latosols, Red-Yellow Argisols, and Fulvic Neosols, reflecting different degrees of weathering and natural fertility.

### Collection and Georeferencing

A total of 80 live trees of *Manilkara huberi* were sampled, with ten individuals per locality, between August 2022 and July 2023. The selected individuals presented a minimum diameter at chest height (DBH) of 50 cm, ensuring the representativeness of adult and physiologically stable trees. The minimum distance between trees ranged from 80 to 100 m, avoiding pseudo-spatial repetition and ensuring sampling independence [4].

Each tree was georeferenced with a high-precision GPS receiver, recording coordinates in degrees, minutes, and seconds (DMS). The structure of the database will allow future applications in systems for forensic traceability and production chain control [12].

### Wood Sampling Procedures

For each individual of *Manilkara huberi*, three collection points were defined along the trunk, at a height of 1.30 m (DAP), following methodological recommendations widely adopted in dendrochemical studies [5].

Before drilling, the stem surface was cleaned by scraping off the bark and removing adhering residues from the surface to prevent external contamination. The extraction of wood was conducted with the aid of a portable battery drill (model Makita 40V Li-Ion 140 Nm), equipped with ¼-inch steel drills, sterilized between samples to prevent cross-contamination. During drilling, the material corresponding to the first 5-7 cm of depth was discarded, allowing the wood shavings collected to represent exclusively the sapwood and the wood core, regions that reflect the composition of the tree metabolism [6].

The samples were packaged in Kraft paper bags, properly labeled with the matrix code and the geographical identification of the tree, ensuring traceability during the laboratory steps at LABGEMVEG-UFAM. The wounds caused by the perforation were promptly sealed with neutral silicone gel, inhibiting moisture infiltration and microbial growth, while adopting minimal impact management protocols [5].

Still in the field, the samples were pre-dried in artisanal greenhouses maintained between 40 and 50°C. After this stage, the material was transported to the Forensic Laboratory of Stable Isotopes and X-ray Fluorescence of the Regional Superintendence of the Federal Police in Amazonas.

#### Preparation for X-Ray Fluorescence Analysis by Total Reflection (TXRF)

The wood samples were dried in a forced air circulation oven at 40°C. The grinding of the wood was carried out using a bench-top vibratory mill (MM 400 - Retsch, GmbH, Germany) for 2 min, operating at 30 s<sup>-1</sup>. Grinding jars with a volume of 50 cm<sup>3</sup>, made of stainless steel AISI 304-, and 25-mm-diameter balls were used. The samples were again dried for a period of 2 h at 60°C, to complete the grinding of the wood. The resulting powder was transferred to 2 mL microtubes. Each microtube was identified according to the number of the master tree, the sample number, and the place of origin.

About 20-50 mg of each pulverized sample were used and weighed in 2.5 mL microtubes. In each microtube, 1.5 mL of Triton X-100 aqueous solution was added at 1%, promoting the suspension and homogenization of the material by vortex stirring. Subsequently, 10 µL of the iridium (Ir) internal standard was added, an element absent in the wood matrix, used for the calculation of relative sensitivities and correction of instrumental variations, as described by [11, 23, 24].

The quartz discs were previously cleaned in a laboratory sequence (rapid immersion in 5% HNO<sub>3</sub>,

rinse with ultrapure water, and drying) and additionally subjected to low-temperature treatment for elimination of organic traces [9]. The center of each disc received a microdrop of PVC (polyvinyl chloride) solution and was dried (at room temperature); then 10 µL of the suspension was added to the center of each disc and again dried until a homogeneous thin film formed [11, 23, 24].

The readings were performed in an S4 T-STAR benchtop spectrometer (Bruker, Billerica, MA, USA), equipped with a Mo tube (17.5 keV) and a W cathode, operated for excitation up to 35 kV, according to the protocol adopted in the studies of [11, 23]. The counting time of ~600 s per point ensured an adequate signal-to-noise ratio. The multielemental quantification was performed utilizing the internal standard method, with calculation of relative sensitivities based on the ratio of the peak areas of the elements to that of the Ir.

#### Statistical Analysis

The similarity dendrogram and non-metric multidimensional scaling (NMDS) ordination were elaborated in R software [25], using specific packages for multivariate analysis and data visualization, such as *vegan*, *ggplot2*, and *cluster*. The principal component analysis (PCA) was conducted in the integrated RStudio environment [26], which allowed reducing the dimensionality of the data and identifying the variables that most contributed to the total variance observed [27]. The correlations between the chemical elements and the evaluated parameters were determined in the program *Genes* [28], widely used in genetic and environmental analysis, while the graphical representations of these correlations were generated in RStudio [26].

## Results and Discussion

The Western Amazon (Silves, Parintins, Humaitá) has a humid tropical climate with high rainfall, especially between December and May. The relative

Table 1. Regional climatic characteristics in different municipalities of the Amazon, based on historical data of annual precipitation (mm), relative humidity (%), and average temperature (°C).

Municipality	State	Precipitation (annual)	Relative humidity	Average temperature
Silves	Amazonas	2.841	80-85	26.5 (24-30)
Parintins	Amazonas	2.801	75-85	26.5 (24-30)
Humaitá	Amazonas	2.459	80-85	26.5 (23-31)
Juruti	Pará	3.023	80-85	26.5 (24-31)
Rorainópolis	Roraima	2.742	75-80	27.0 (22-30)
Caracaráí	Roraima	2.960	78-85	27.0 (22-32)
Itapuã do Oeste	Rondônia	2.209	70-85	26.5 (22-33)
Candeias do Jamari	Rondônia	2.509	56-98	26.5 (22-33)

humidity remains high throughout the year, between 80 and 85% (Table 1). Among the municipalities analyzed in the Transition region (Juruti, Rorainópolis, and Caracaraí), Juruti stands out with the highest average annual precipitation (3,023 mm), while the localities of Roraima have characteristics of transition between the Amazon and the Cerrado (Table 1).

The municipalities of Rondônia (Itapuã do Oeste and Candeias do Jamari) have characteristics of a tropical climate transition. Itapuã do Oeste records the lowest annual precipitation (2,209 mm), while Candeias do Jamari has a higher relative humidity amplitude (56-98%) (Table 1).

All municipalities have two well-defined seasons: a rainy season (October to May) and a dry season (June to September), with variations in relative air humidity following this seasonal pattern (Table 1).

In the municipalities of Silves, Parintins, and Juruti, dense ombrophilous lowland forests predominate and are associated with dystrophic yellow latosols (DYL) and flat to gently undulating terrain, with altitudes ranging from 74 to 104 m (Table 2). In Humaitá, the Alluvial Open Ombrophilous Forest occurs on Dystrophic Red-Yellow Argisol (DRYA) in flat relief and at an average altitude of 63 m (Table 2), indicating strong fluvial and depositional influence. Rorainópolis and Caracaraí present Submontane Dense Ombrophilous Forests, located in transition zones between the Amazon and the Cerrado, with Argisols and Haplic Dystrophic Gleysols (AYD and GXbd) soils and gentle undulating and flat relief, between 100 and 105 m in altitude (Table 2).

In the localities of Itapuã do Oeste and Candeias do Jamari, Submontane Open Ombrophilous Forests and Lowlands predominate over Dystrophic Yellow Latosols (DYL) in flat to gently undulating relief, with altitudes between 103 and 121 m (Table 2).

Partial clustering was observed among the samples, suggesting that *M. huberi* populations present

phenotypic differentiation associated with regional environmental conditions (Fig. 1). Silves and Parintins samples are closer to each other (Fig. 1), indicating morphological similarity and possible influence of terrestrial forest environments with similar edaphic and climatic characteristics. A different behavior was observed for the samples from Juruti, which were distributed in a more distant position on the Dim1 axis (Fig. 1), indicating greater internal variability and humid environmental conditions, consistent with the Dense Ombrophilous Forest of the Lowlands. The samples from Rorainópolis and Caracaraí, located in transition environments between the Amazon and the Cerrado, grouped in the positive portion of Dim1 (Fig. 1), reflecting phenotypic adaptations to less humid soils and greater thermal amplitude. The samples of Itapuã do Oeste and Candeias do Jamari are more dispersed (Fig. 1). The samples from Humaitá, grouped and isolated from all others, have their own characteristics, requiring complementary analysis to highlight the factors that promoted individualization.

### Principal Component Analysis

The Principal Component Analysis (PCA) revealed the phenotypic variability among wood samples collected from different municipalities of the Amazon (Fig. 2). The first two dimensions explained 34.37% of the total variance of the data, showing distinct patterns of clustering between the localities (Fig. 2).

The formation of well-defined clusters is observed, indicating intra-regional similarity and different characteristics between the regions (Fig. 2). There was a clear separation between the Humaitá samples (Dim 2 axis) (Fig. 2), suggesting particular phenotypic characteristics and low overlap with other groups. The municipalities of Juruti, Silves, Itapuã do Oeste, and Parintins presented partial overlap of their

Table 2. Regional characteristics among municipalities of the Amazon analyzed, based on forest types, soil classes, relief, and mean altitude.

Municipality	Type of forest	Type of soil	Relief	Altitude
Silves	Dense Lowland Ombrophilous Forest	DYL - Dystrophic yellow latosols	Flat and smooth wavy	104
Parintins	Dense Lowland Ombrophilous Forest	DYL - Dystrophic yellow latosols	Soft wavy	74
Humaitá	Open Alluvial Ombrophilous Forest	DRYA- Dystrophic Red-Yellow Argisol	Plan	63
Juruti	Dense Lowland Ombrophilous Forest	DYL - Dystrophic yellow latosols	Flat and smooth wavy	101
Rorainópolis	Dense Submontane Ombrophilous Forest	AYD - Argisol Yellow Dystrophic	Soft wavy	105
Caracaraí	Dense Submontane Ombrophilous Forest	GXbd - Haplic Tb Dystrophic Gleysol	Plan	100
Itapuã do Oeste	Open Ombrophilous Submontane Forest	DYL - Dystrophic yellow latosols	Flat and smooth wavy	121
Candeias do Jamari	Open Lowland Ombrophilous Forest	DYL - Dystrophic yellow latosols	Flat and smooth wavy	103

confidence ellipses (Fig. 2), which indicates certain similarity between samples, possibly related to intermediate soil and climate conditions.

Samples collected from the localities of Candeias do Jamari and Caracarái formed close clusters, with partially overlapping ellipses (Fig. 2), reflecting shared phenotypic patterns resulting from transition environments between the Amazon and the Cerrado biomes. Notably, the Rorainópolis samples showed intermediate dispersion, without well-defined clustering, indicating higher internal variability (Fig. 2).

### Pearson's Correlation

The Pearson correlation matrix showed significant interrelationships between the chemical elements detected in *M. huberi* wood samples, indicating consistent patterns of accumulation and elemental antagonism. The most significant positive correlations ( $p < 0.01$ ) were observed between elements associated with structural and nutritional processes, such as  $K \times Rb$  ( $r = 0.93$ ),  $Cr \times Fe$  ( $r = 0.75$ ),  $Co \times Cu$  ( $r = 0.77$ ), and  $Ni \times Yb$  ( $r = 0.77$ ) (Fig. 3). Other relevant groupings include

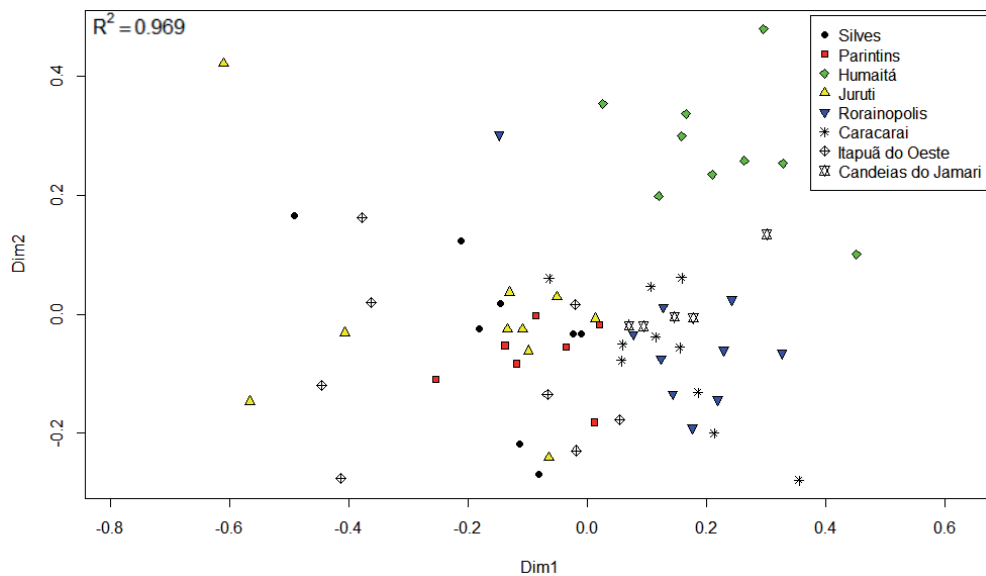


Fig. 1. Analysis of multidimensional non-metric scaling (NMDS) of phenotypic distances between wood samples from *Manilkara huberi*, in different municipalities of the Amazon. The adjustment value ( $R^2 = 0.969$ ) indicates high representativeness of two-dimensional ordering.

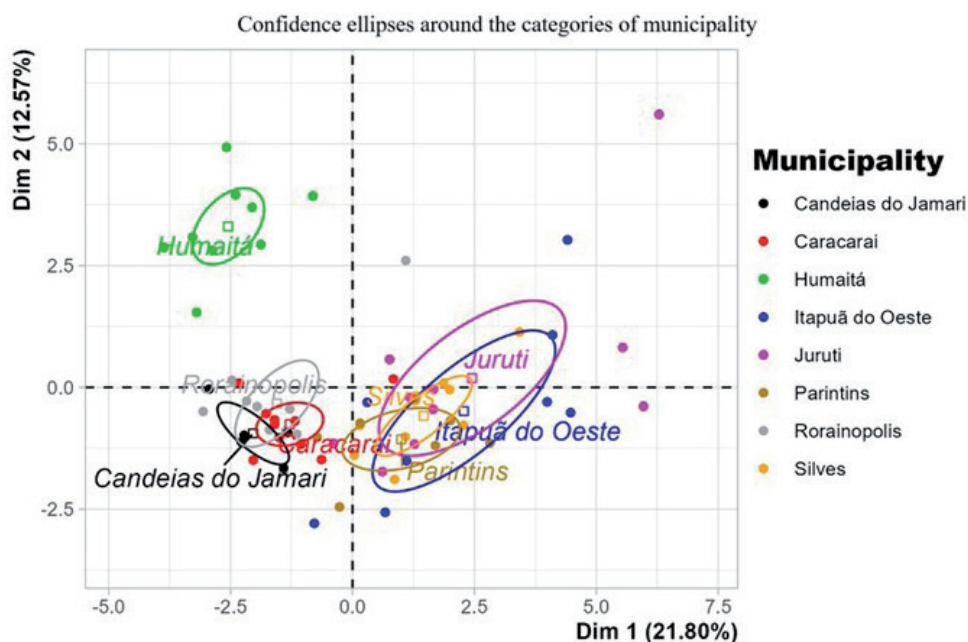


Fig. 2. Principal Component Analysis (PCA) among wood samples of *Manilkara huberi*.

positive correlations between Ca × S (r = 0.52), Mg × S (r = 0.34), and Mn × S (r = 0.31) (Fig. 3). An association was also observed between trace elements such as Fe × Yb (r = 0.40) and Ce × Cr (r = 0.44) (Fig. 3). In contrast, negative correlations were recorded between Fe × K (r = -0.43), Cl × Rb (r = -0.47), and Ce × K (r = -0.36) (Fig. 3).

The multielemental analysis of the wood of *Manilkara huberi* presents strong potential for the objective of geographical traceability among the populations analyzed in the Legal Amazon. The use of Total Reflection X-ray Fluorescence (TXRF) allowed for the detection of trace elements and macronutrients in different concentrations between localities, reflecting the edaphic, climatic, and geological variations that characterize the different Amazonian ecosystems. Mineral elements associated with multivariate statistical analyses allow distinguishing with high precision the geographical origin of organisms across different regions, showing that multielemental signatures are sensitive to edaphic and climatic conditions [29]. Thus, the elemental and isotopic profiles are important markers in provenance, extending the effectiveness of traceability systems [30].

The order obtained by Principal Component Analysis (PCA) and the Pearson correlation matrix indicated that chemical differences in wood are strongly associated

with local environmental conditions. Municipalities such as Humaitá and Juruti presented characteristic elementary profiles, related to river influence and higher soil moisture, while Rorainópolis and Caracarái exhibited distinct patterns associated with clay soils and transition environments between the Amazon and the Cerrado, with higher levels of Fe and Mn. These regional variations corroborate the hypothesis that the chemical composition of wood reflects the geochemical signature of the original environment, as observed in research with other tropical species [3, 4, 6]. These results confirm what was observed by [7], who identified specific multielemental profiles among *Handroanthus* (ipês) species in the Amazon, highlighting the importance of elements such as Sr, Ba, La, and Ce in the differentiation between origins.

The correlation analysis between the chemical elements confirmed the presence of co-accumulation and antagonistic patterns associated with *M. huberi* physiology and soil geochemistry. Expressive positive correlations, such as K × Rb, Co × Cu, and Cr × Fe, and negative correlations (Fe × K; Cl × Rb) were observed. This chemical dynamic is in line with the observations of [5], which highlighted the relevance of trace elements in the geochemical differentiation of wood in contrasting environments within the Amazon basin. The results

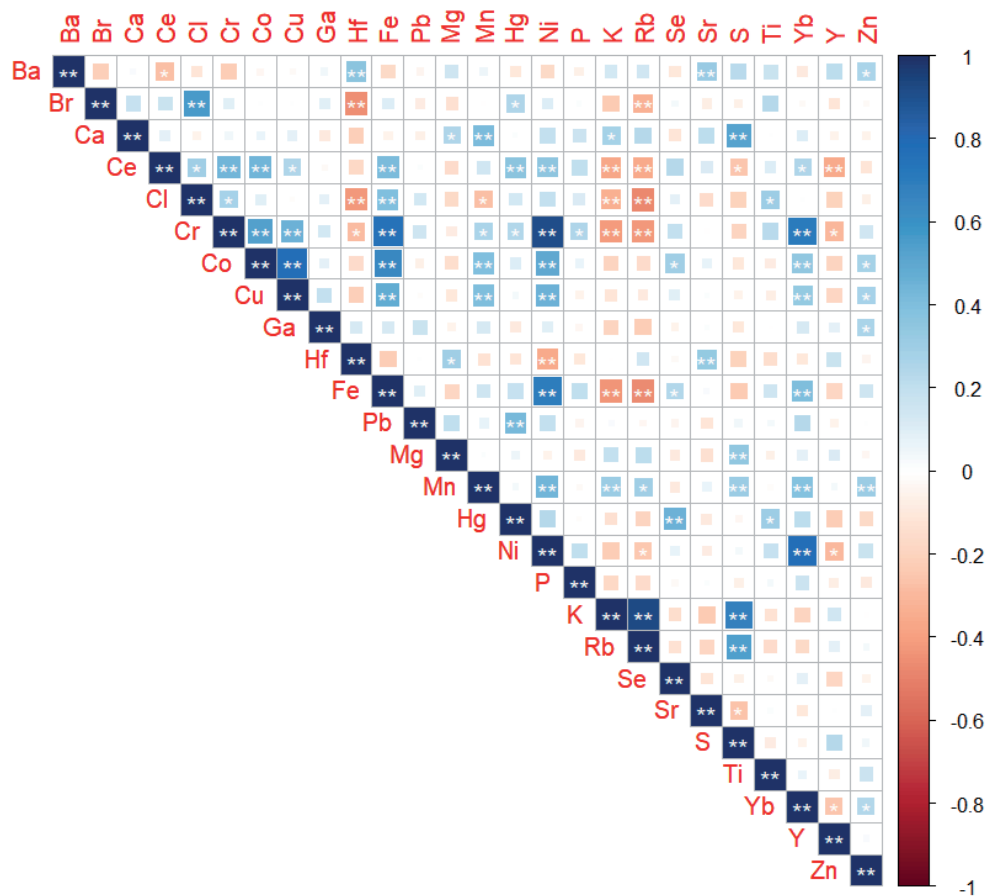


Fig. 3. Phenotypic correlation between chemical elements present in wood samples of *Manilkara huberi*. \*\*, \*, p<0.01, p<0.05, respectively, by the t-test.

also align with the isotopic evidence presented by [6], which mapped the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in Amazonian woods and demonstrated that the strontium isotope signature is highly dependent on the base geology, allowing for the distinction of forests over crystalline shields and recent sedimentary areas. Similarly, [8] demonstrated the effectiveness of Sr isotopes as a tool for authentication in economically valuable species, highlighting the relevance of integrating isotopic and multielemental analyses to strengthen traceability reliability. The combination of elemental and isotopic signatures can enhance the discriminant power of origin models, especially in regions with strong geological contrast [30].

The spatial distinction observed in *M. huberi* follows the trend identified by [31], who applied mass spectrometry (DART-TOFMS) on *Cedrela* species in Bolivia, achieving success in chemical differentiation between species and localities, albeit with limited effectiveness over short distances. The studies reinforce that the spatial scale and the geological context are determinants for the discriminant power of chemical signatures. In addition, the combination of multiple analytical methods, such as isotopic, genetic, and elemental, increases the reliability of origin attribution [32]. The integration of chemical approaches (TXRF) with isotopic and genomic analyses can strengthen the systems of provenance verification of *M. huberi*.

The distinction between geographical groupings identified by multivariate analyses reinforces the forensic applicability of the method. The elemental composition, acting as a “geochemical code”, makes it possible to trace the origin of wood according to unique patterns of concentration and correlation between elements [4]. This approach, integrated with spatial and morphometric data, can be incorporated into legality verification and forest certification [12]. Highly complex discriminant models can identify subtle geochemical patterns with high precision, reinforcing the forensic potential of elemental signatures [33].

The chemical signature of *M. huberi* wood consistently reflects the geoenvironmental heterogeneity of the Amazon, confirming that TXRF is an efficient, non-destructive, and high-resolution technique for geographic traceability studies [10]. The adoption of this methodology in monitoring and control programs of the production chain of massaranduba represents significant progress in sustainable forest management, combating illegal exploitation, and economic valuation of native Amazonian species [13]. Forest degradation alters the functional sensitivity of trees to climatic extremes, thereby altering nutrients and trace element absorption patterns [34]. The loss of ecosystem services affects key biochemical processes, reinforcing the importance of monitoring chemical signatures associated with the degree of ecological integrity [35].

The application of Total Reflection X-ray Fluorescence spectrometry (TXRF) goes beyond the field of forest traceability, assuming a central role also in evaluating and monitoring environmental contamination

[16]. Considered a multielemental, sensitive, and non-destructive technique, TXRF allows the simultaneous detection of macro and microelements, including heavy metals and trace elements associated with industrial and urban pollution, such as Fe, Pb, Cr, Ni, and Co, even at low concentrations [14]. TXRF is highly effective in detecting environmental contamination in biological matrices, allowing the identification of heavy metals with high sensitivity [36]. In addition, it is suitable for biomonitoring of impacted areas, including environments under urban and industrial pressure [37].

The distinction between anthropogenic areas and forest fragments was explained by the variation in concentrations of heavy metals and trace elements in soil and leaves of *Stryphnodendron pulcherrimum* [11]. In anthropogenic areas, there was an accumulation of Fe, Pb, and Co, while in forest fragments, Yb, Cr, and S predominated. This behavior is similar to that observed in *M. huberi*, whose elemental composition also reflects the condition of environmental integrity: preserved regions presented a greater balance between essential elements and a lower presence of metals associated with anthropic activity. Degraded forests show significant changes in physiological and biogeochemical dynamics [34]. Degradation compromises hydrological and nutrient cycling, directly reflecting on the chemical signature of tree species [35].

Studies such as that of [11] showed its potential in the identification of toxic elements accumulated in plant tissues of *S. pulcherrimum* in degraded areas, confirming its efficiency in differentiating contaminated environments from forest fragments. In the context of *M. huberi*, the technique was equally effective in verifying the influence of edaphic and anthropic gradients on the chemical composition of wood, which reinforces its use as an integrated tool for both geographical traceability and environmental quality diagnosis, contributing to conservation actions, sustainable management, and mitigation of the impacts of pollutants in Amazonian ecosystems [14, 15].

The present study confirms that the TXRF technique has high sensitivity and reproducibility in the simultaneous detection of multiple chemical elements, being effective in characterizing the elemental variability between plant samples and in distinguishing geographical origins, as observed by [23]. In the study with *Coffea canephora*, TXRF proved crucial in discriminating among clones based on the differential absorption of elements such as Rb, Hf, Zn, and Fe, in addition to facilitating the estimation of genetic variance and heritability. Similarly, in *M. huberi*, the elements Fe, Mn, K, and Ca were also highly discriminant between localities, indicating the potential of the technique for analysis of geochemical signatures and environmental adaptability. TXRF was applied to the species *Stryphnodendron pulcherrimum*, identifying the ability of this Amazonian tree to accumulate trace elements such as Cr, Y, Yb, Pb, and Co, demonstrating its applicability as a bioindicator of contaminated

areas and as an environmental biomonitoring tool [11]. The present study extends this use to the context of forest traceability and conservation, indicating that the elementary variations of *M. huberi* also reflect local environmental conditions such as fertility, hydrology, and geology, which allows us to infer the ecological integrity of the Amazonian environments. Complex multivariate analyses amplify the ability to recognize elementary patterns associated with both origin and environmental adaptation, strengthening interpretations about geochemical variation [33].

This study underscores the importance of advancing research focused on the geochemical traceability of *M. huberi* wood as a scientific and strategic instrument for the conservation of Amazonian forests. Identifying specific chemical signatures associated with different environments and soil conditions demonstrates that *M. huberi* accurately reflects the geoenvironmental characteristics of its origin, allowing verification of provenance and contributing to the fight against illegal exploitation. In addition to ensuring transparency in forest production chains, the application of techniques such as TXRF strengthens sustainable management policies, certification, and supervision, ensuring that the use of Amazonian wood occurs in an ethical and environmentally responsible way. Thus, the traceability of massaranduba goes beyond the technological aspect, representing a tool for protecting biodiversity, maintaining ecosystem services, and promoting forest conservation. The sensitivity of the Amazon to climatic disturbances and extremes reinforces the relevance of chemical tools for ecological monitoring [34]. The maintenance of ecosystem services depends directly on effective traceability and origin verification strategies [35].

### Conclusions

Total Reflection X-ray Fluorescence (TXRF) demonstrated high efficiency in the geochemical discrimination of populations of *Manilkara huberi* in the Legal Amazon, showing that the elemental wood composition accurately mirrors local soil, geological, and climatic conditions. The differentiation observed between localities validates the technique's potential as a precise and non-destructive tool for wood forensic traceability, allowing for the identification of regional geochemical patterns that function as unique signatures of origin. These results corroborate the hypothesis that trace elements and macronutrients act as efficient environmental markers, able to distinguish materials from different ecological and geographical contexts.

Furthermore, given its methodological value, the study reinforces the strategic relevance of TXRF in consolidating public policies aimed at sustainable forest management and control of illegal logging in the Amazon. The implementation of this approach in certification and monitoring programs can strengthen the transparency

of production chains, ensuring biodiversity conservation and ethical use of forest resources. Thus, the geochemical traceability of *M. huberi* constitutes an essential scientific and technological advance for the protection of tropical forests and for the improvement of environmental governance mechanisms in the Amazon region.

### Author Contributions

Conceptualization, A.C.L.S., M.T.G.L., J.S.T., C.S.B., M.S.F.V., H.L.V.C., S.L.F.R., and R.L.; methodology, A.C.L.S., M.T.G.L., J.S.T., C.S.B., and R.L.S.M.; software, M.S.F.V., M.T.G.L., R.L.S.M., and A.M.P.; validation, A.C.L.S., M.T.G.L., J.S.T., C.S.B., R.L.S.M., and R.L.; formal analysis, A.C.L.S., M.T.G.L., J.S.T., C.S.B., and M.S.F.V.; resources, M.T.G.L.; R.L., R.L.S.M., A.M.P., and S.L.F.R.; writing – original draft preparation, A.C.L.S., M.T.G.L., J.S.T., C.S.B., H.L.V.C., R.L., A.M.P., and S.L.F.R.; writing – review and editing, A.C.L.S., M.T.G.L., J.S.T., C.S.B., H.L.V.C., R.L.S.M., R.L., A.M.P., M.S.F.V., and S.L.F.R.; funding acquisition, M.T.G.L., A.M.P. and All authors have read and agreed to the published version of the manuscript.

### Acknowledgments

The authors would like to thank the Coordenação de Melhoria do Pessoal de Ensino Superior Brasil (CAPES) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for providing the research productivity grant that allowed this research to be completed: Santiago Linorio Ferreyra Ramos (Process no. 305280/2022-8), Ricardo Lopes (Process No. 308815/2023-8), Maria Teresa Gomes Lopes (Process no. 306943/2025-5) and Caroline de Souza Bezerra (Post-doctoral Junior - PDJ 2024, Process no.153747/2025-0). The authors thank the Polícia Federal do Amazonas for their support in carrying out this research and the Fundação de Amparo à Pesquisa do Estado do Amazonas (FAPEAM): Jennifer Souza Tomaz (Process No. 01.02.016301.01271/2025-82).

### Funding

This study was financed by the Coordenação de Melhoria do Pessoal de Ensino Superior Brasil (CAPES) – No. 16/2020 – PROCAD-SPCF, Process Number: 88881.516217/2020-01, and No. 16/2022 – Postgraduate Development Program (CAPES-PDPG) Strategic Post-Doc, Process Number: 88887.692247/2022-00 and (FUNBIO, Call No. 05/2021, contract No.034/2022).

### Conflict of Interest

The authors declare no conflict of interest.

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