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Nutrient concentrations of 17- year-old *Pinus taeda* annual tree-rings analyzed by X-ray fluorescence microanalysis

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ABSTRACT

Tree-rings are sensitive indicators of soil chemical changes. X-ray fluorescence microanalysis (μ-XRF) can reveal the elemental distribution pattern along these rings. However, reports on quantitative μ-XRF methods targeted to wood analysis are scarce. This study aimed to analyze iron (Fe), manganese (Mn), calcium (Ca), potassium (K), sulfur (S) and phosphorus (P) in annual tree-rings of wood cores cut from 24 trees of 17 year-old *Pinus taeda* planted in soil amended with six doses of composted pulp-mill sludge (CPMS). The nutrient concentrations were accessed using calibration curves built with spiked *P. taeda* wood pellets. Calcium and Mn content decreased from the pith to bark direction; K and S decreased from the pith up to 3rd tree-ring and, then, increased to the bark. Iron and P slight decreased from the pith up to the 13–14th tree-ring. Calcium, K and S presented strong and positive correlation with the rainier and hotter season ($r > 0.4$, $p < 0.05$). The CPMS increased the Ca, K, Fe and S and decreased Mn and P concentration in *P. taeda* wood in the 2nd–5th years. Furthermore, the *P. taeda* annual tree-ring molar ratios of Ca/Mn and K/Ca were good indicators of soil-pH and wood cambium activity. The μ-XRF methodology, as non-destructive method of nutrient concentration analysis in tree-rings, revealed potential uses in monitoring soil fertilizer treatments.

1. Introduction

Nutrients are uptaken and loaded in tree species xylem tissues, the main contributor to mass productivity (Rubilar et al., 2005; Garcia Villacorta et al., 2015). They are translocated by apoplastic and symplastic processes (Meerts, 2002). These physiological mechanisms depend on the element nature, solubility and ionic radius ratio; and also on the tree xylem matrix, sap pH and sapwood-heartwood relation; varying within and among species and site conditions (Cutter and Guyette, 1993; Peterson and Anderson, 1990; Smith and Shortle, 1996; Hevia et al., 2018). Considering the seasonality activity of the cambial meristem the resulting annual tree-rings are considered a precise tool that stores information on the element variability inside the xylem (Balouet et al., 2009).

Dendrochronology has been extensively applied to record environmental variables (Dobbertin and Grissino-Mayer, 2004). Dendrochemistry, a branch of dendrochronology, monitors the chemical composition of annual tree-rings yielding information on the soil and water chemistry (Watmough, 1997). For example, one could uncover environmental contamination of soil and groundwater (Balouet et al., 2009, 2012; Balouet and Chalot, 2015). Some industrial environmental changes are related to tree-growth responses due to the incorporation of nutrients (e.g., P, S and Cl) in the soil and their absorption is detected in wood tissues (e.g., MaClauchlan et al., 1987; McClenahen et al., 1989; Vroblesky and Yanosky, 1990; Vroblesky et al., 1992; Kashuba-Hockenberry and DeWalle, 1994; Beauregard et al., 2010; Smith et al., 2014; Balouet and Chalot, 2015). Conversely, dendrochemistry application to evaluate fertilizer and nutritional treatment effectiveness is a less common approach, as it is little-known to forest managers (Watmough, 1997; Hevia et al., 2018).

Concerning the *Pinus taeda*, it is the most planted conifer species in southern Brazil (Vasques et al., 2007) due to its higher growth rates, 35 m^3 ha^{-1} $year^{-1}$ in 18 year rotation (Cubbage et al., 2007). Furthermore, their silviculture has been developed on nutrient-poor soils characterized as Yellow Red Latosols, affected by different intensitivy agricultural crops or forest plantations rotations, and consequently, fertilization treatments have been required (Gonçalves, 1995; Silva et al., 2013; IBA, 2016). Therefore, temporal and spatial tree-nutrition monitoring has also been necessary due to the relationship of the fertilizer with forest productivity and production costs (Moro et al., 2014;

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Ferraz et al., 2016).

The nutrient detection methodologies to determine the tree-elements concentrations comprises the application of atomic absorption and plasma emission spectroscopy as a standard method (Malavolta et al., 1989; Welz and Sperling, 1999; Rubilar et al., 2005; Ferraz et al., 2014; Garcia Villacorta et al., 2015). However, it is limited to smaller temporal precision and sensitivity to identify certain inter-annual element trends and analyze their mobilization inside the xylem (MaClauchlan et al., 1987). Actually, the X-ray methods have been applied to avoid this aspect and are able to monitor the chemical elements with inter-annual sensitivity (Balouet et al., 2009). Several studies report an X-ray Fluorescence (XRF) advantage in investigating the trace elements contained in tree-rings in relation to analytical techniques such as Neutron Activation Analysis (NAA) or Proton-Induced X-ray Fluorescence (PIXE) (Maclauchlan et al., 1987; Vives et al., 2005; Scharnweber et al., 2016).

The main advantages offered by X-ray fluorescence microanalysis are: i) the straightforward preparation, since sample grinding and digestion are not required and the sample is preserved; ii) high lateral spatial resolution, since the X-ray spot size varies from tens of micrometers to the millimeter range; iii) all chemical elements with atomic number > 11 (sodium) can be simultaneously evaluated; iv) the analysis does not require gases or chemical reactants which makes it relatively cheap and certainly environmentally friendly (Maclauchlan et al., 1987; Smith et al., 2008; Balouet et al., 2012; Hevia et al., 2018). A disadvantage of the technique lies in its detection limits, typically few mg kg^{-1} for direct analysis, which is higher than those exhibited by destructive methods such as AAS in the range of tens of μg kg^{-1} (MacDonald et al., 2011).

Thus, this study aimed to develop a non-destructive procedure using μ-XRF to quantify Iron (Fe), Manganese (Mn), Calcium (Ca), Potassium (K), Sulfur (S) and Phosphorus (P) in annual tree-rings of *P. taeda* planted in soil amended with six doses of composted pulp-mill sludge (CPMS). We also explored annual nutrient concentrations linked to precipitation and temperature variables. Furthermore, the study also aims to provide information regarding the CPMS soil application effect on tree-ring radial nutrient concentration trends and Ca/Mn, K/Ca molar ratio variations.

2. Material and methods

2.1. Study area and stand characteristics

A 17-year-old *Pinus taeda* plantation with 3.5 ha located on the Matarazzo Farm, Jaguariaíva, Paraná state (50°43′W; 25°15′S; 872 m a.s.l.; slope 3–8%) was selected. The area is characterized by a subtropical moist mesothermic climate (Cfb) according to the Köppen classification. The mean annual rainfall is 1323 mm, with a dry season between July and August and the temperature is moderate, with an annual mean of 18.1 °C (Fig. 1A). The soil is classified as dystrophic Red-Yellow Latossol, medium texture, less than 35% clay, more than 15% sand, strongly drained and extremely acidic (pH < 4.3), poor in macronutrients, low organic matter content and with a low cation exchange capacity (Table 1).

The experiment was planted in June 1996 in a complete randomized block design with six treatments and four replicates (24 blocks of 400 m^2; 7 rows; 13 plants each). Each treatment consisted of six different doses of CPMS applied at the time of plantation establishment as input for the chemical soil preparation (Table 2). Five internal lines/block were selected to avoid the edge effect (12 trees/line/block and 60 trees/replicate). After the establishment of *P. taeda* trees, a mortality index of 1.1% (19 trees) was registered. Then, a selective thinning of 54.5% of the stand density (940 smaller trees) was conducted in the 9th year (June 2005). The final harvest was carried out in the 17th year (December 2013).

2.2. Sample collection, preparation and measurements

Twenty-four trees (4 trees/treatment) classified as dominant were selected from the plots of 6 CPMS soil treatments. The selection criteria was based on the mean volume inventoried (Table 2) and on the higher tree-ring width chronology correlation with the master chronology of 60 trees previously analyzed ($r > 0.6$, $p < 0.05$) (acoording to Hevia et al., 2018). The trees were felled, wood disc cross sections cut at 1.30 m (DBH); a thin wood sample (1.5 mm, thickness) cut transversely with a parallel double circular saw and conditioned (60 °C, 24 h in a climatic chamber).

The transverse surface wood of slices were scanned (pith-bark direction) following a line scan area (spots of 1 mm in wide) in an X-ray fluorescence microanalysis spectrometer (μ-XRF), Orbis PC model, EDAX, Rh tube, silicon drift chamber detector - SDD detector (30 keV, 600 μA), vacuum condition and 20 s/measurement point (Fig. 1B). The tree-ring chemistry profiles of the trees were built with the X-ray transmission intensity values and chemical elements were selected for dendrochemistry analysis.

2.3. Elements selection

The selected elements were the macronutrients: Ca, involved in the cell wall formation; P, structural component of plant compounds; K, involved in the cambial activity; S, essential in redox state regulation, and the micronutrients: Fe, most required plant micronutrient; Mn, involved in respiratory process (Peterson and Anderson, 1990; Fairchild et al., 2009). Calcium, P and K were selected based on the significant nutrients concentrations observed in the wood of 7 year-*P. taeda* trees in a previous study (Rodrigues et al., 2005). Sulfur, Fe and Mn were also selected based on convincing reports of nutrient detection in other tree-species using similar X-ray fluorescence systems (Scharnweber et al., 2016; Hevia et al., 2018). Furthermore, the ecologically meaningful molar ratios Ca/Mn, related to soil pH indicator (Kuang et al., 2008) and K/Ca, related to the wood formation (Fromm, 2010), were explored.

2.4. Quantitative analysis

The intensity counts of Ca, Fe, K, Mn, P and S were analyzed to distinguish the detected signal from the background with a reasonable certainty for an analytical quantification process. A quantification threshold (Function 1) was used to assign an intensity threshold below which the elemental peak from quantification calculations are removed (EDAX Insight, 2017). Also the statistical intensity threshold value for each element was considered as their limit of quantification.

$$N_{Threshold} = \sigma\sqrt{2\frac{BG}{s}} \quad (1)$$

where: $N_{Threshold}$ = Statistical intensity threshold (cps); σ = sigma factor, set to 6 as default from Orbis software; BG = background (cps); and s = time at each measurement point.

Thus, the elements with peak intensity above the applicable threshold (Ca > 4.84, Fe > 10.96, K > 4.47, Mn > 10.02, P > 2.14 and S > 2.99 cps) were quantified using multi-elemental standard solutions (Geraldo et al., 2014).

Intending to build the calibration curves, wood powder was spiked with the elements of interest and then pelletized. A quarter of each *P. taeda* DBH wood disc was dried (60 °C, air circulation), ground (Retsch ZM200 mill, 0.2 mm mesh), with five 0.5 g portions of wood powder separated to apply to pure elements solution, dried (60 °C air circulation fan) and pressed (X-Press 3624B) thus manufacturing the wood pellets (~0.93 g cm^{-3}, density) (Table 3). Five measurements per pellet were obtained by the μ-XRF spectrometer applying the same condition as for wood samples, following the determination of the mean intensity