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Towards a better understanding of long-term wood-chemistry variations in old-growth forests: A case study on ancient *Pinus uncinata* trees from the Pyrenees

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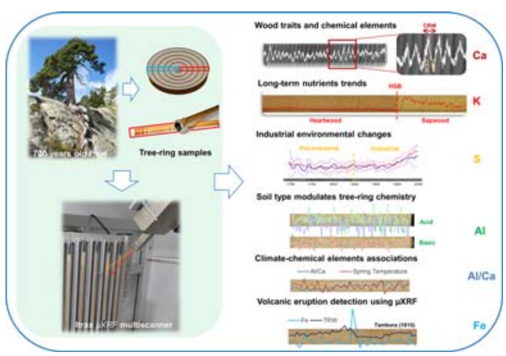
HIGHLIGHTS

- 300-year long series of wood-chemistry were reconstructed using micro X-ray fluorescence.
- Common long-term centennial trends for Ca, K and Zn were found.
- Cl, P and S increased after 1850.
- Peaks in S, Fe, Cl, Zn and Ca were linked to volcanic eruptions.

GRAPHICAL ABSTRACT



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ABSTRACT

Dendrochemical studies in old forests are still underdeveloped. Old trees growing in remote high-elevation areas far from direct human influence constitute a promising biological proxy for the long-term reconstructions of environmental changes using tree-rings. Furthermore, centennial-long chronologies of multi-elemental chemistry at inter- and intra-annual resolution are scarce. Here, we use a novel non-destructive method by applying Micro X-ray fluorescence (*µXRF*) to wood samples of old *Pinus uncinata* trees from two Pyrenean high-elevation forests growing on acidic and basic soils. To disentangle ontogenetic (changes in tree age and diameter) from environmental influences (e.g., climate warming) we compared element patterns in sapwood (SW) and heartwood (HW) during the pre-industrial (1700–1849) and industrial (1850–2008) periods. We quantified tree-ring growth, wood density and relative element concentrations at annual (TRW, tree-ring) to seasonal resolution (EW, earlywood; LW, latewood) and related them to climate variables (temperature and precipitation) and volcanic eruptions in the 18th and 19th centuries. We detected differences for most studied elements between SW and HW along the stem and also between EW and LW within rings. Long-term positive and negative trends were observed for Ca and K, respectively. Cl, P and S showed positive trends during the industrial period. However, differences between sites were also notable. Higher values of Mg, Al, Si and the Ca/Mn ratio were observed at the site

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with acidic soil. Growing-season temperatures were positively related to growth, maximum wood density and to the concentration of most elements. Peaks in S, Fe, Cl, Zn and Ca were linked to major volcanic eruptions (e.g., Tambora in 1815). Our results reveal the potential of long-term wood-chemistry studies based on the *μXRF* non-destructive technique to reconstruct environmental changes.

1. Introduction

During the last decades, a global increase in chemical pollution has been observed, growing into an international problem that affects forest ecosystems worldwide (EEA, 2015). Since trees are natural proxies of environmental conditions (Balouet et al., 2007, 2009), temporal atmospheric changes in the course of climate change may be registered in annual tree-rings as well (e.g., Cutter and Guyette, 1993; Smith and Shortle, 1996). As a consequence, tree-ring variables are used as temporal proxies of human impact during the industrial period (i.e., after 1850) on tree functioning (e.g., Battipaglia et al., 2010; Granda et al., 2017), forest health (e.g., Kuang et al., 2007; St. Clair et al., 2008), changes in soil chemistry (e.g., Augustin et al., 2005; Kuang et al., 2008) and cascade effects on tree-soil interactions (e.g., Panyushkina et al., 2016). In this context, related processes like soil acidification have been investigated using tree-rings to assess the changes in the soil ability to hold and supply nutrients (Augustin et al., 2005). In cold environments, deposition of acidic anions (e.g., SO_4 and NO_3^-) affects tree uptake of important macronutrients such as Ca, P, Mn and K (Agren et al., 2012). Consequently, long-term environmental alterations in forest growth can influence the exchange of elements between soil and trees (Panyushkina et al., 2016; Sheppard et al., 2001). However, the responses of old trees to changing environmental conditions are still understudied and a better understanding of long-term wood-chemistry is needed (e.g., Pearson et al., 2009a, 2009b; Vaganov et al., 2013).

Mineral nutrients are limiting resources to forest growth (Meerts, 2002), and mechanisms of allocation and translocation of nutrients occur among different tree organs to enhance nutrient-use efficiency (e.g., Aerts and Chapin, 2000; Nambiar and Fife, 1991). Nutrients translocations have been documented from senescing sapwood during heartwood formation to functional sapwood in different tree species (e.g., Andrews et al., 1999; Meerts, 2002). Secondary compounds tend to accumulate in heartwood, while storage products (starch), soluble sugars, amino-acids and mineral elements are more abundant in sapwood rings (e.g., Colin-Belgrand et al., 1996). Furthermore, sapwood production has been shown to influence tree growth rates in cold-limited forests (Galván et al., 2012).

Although wood usually presents a low mineral nutrient concentration (Meerts, 2002), the extent to which nutrients are stored in stemwood has been demonstrated to reflect changes in environmental factors such as soil chemistry (e.g., Andrews et al., 1999; Augustin et al., 2005; Kuang et al., 2008), pollution (e.g., Ferretti et al., 2002; Nabais et al., 1999; Shcherbenko et al., 2008; Smith et al., 2008), climate (Poussart et al., 2006; St. Clair et al., 2008; Witt et al., 2017) or volcanic eruptions (e.g., Pearson et al., 2005, 2006, 2009a, 2009b; Sheppard et al., 2008, 2009). In this sense, trees from high-elevations, i.e., close to the treeline, are expected to be especially sensitive to ongoing environmental changes and rising temperatures (Galván et al., 2014). Moreover, little is known about the changes in wood chemical elements of multi-centennial old trees (Pearson et al., 2006, 2009b; Vaganov et al., 2013).

In the last years, the emergence of dendrochemistry, i.e., the chemical analysis of annually resolved tree-rings, has provided new data on several element concentrations in stemwood (e.g., Smith et al., 2014). The major confounding factor in dendrochemical analysis is the potential radial translocation of elements across rings, which is based on the mobility of the elements within the xylem (Wagner et al., 2012). However, dendrochemical analyses allow identifying patterns of tree responses to environmental conditions over time (Cutter and Guyette, 1993). Although mineral element concentrations across rings within an individual tree are variable (Scharnweber et al., 2016; Wagner et al., 2012), similar patterns of elements may indicate a common environmental influence (Penninckx et al., 2001). For instance, using molar ratios of elements (e.g., Ca/Mn or Al/Ca) was found to be more diagnostic for environmental effects than assessing xylem elemental concentrations alone (DeWalle et al., 1999; Kuang et al., 2008). Thus, the comparison of chemical element profiles from several individuals under similar soil conditions allows evaluation of the ability of chemical-element tree-ring series (chronologies) to reflect common environmental signals. Moreover, determining the nature of the responses of nutrient cycling to climate warming is essential to forecast the impacts of rising temperatures on soil-nutrient availability, and hence their potential influences on forest functioning (Yuan et al., 2017).

Destructive dendrochemical methods (e.g., Inductively Coupled Plasma Mass Spectroscopy) have limitations to analyze annual changes in tree-ring chemical elements in old trees and are highly time consuming (e.g., Panyushkina et al., 2016; Pearson et al., 2009b; Sheppard et al., 2008). In addition, extremely narrow tree-rings are often formed by old and slow-growing tree species which limit the analysis of wood samples using aforementioned techniques (Pearson et al., 2009b). However, micro X-ray fluorescence (*μXRF*) offers the opportunity to overcome these analytical restrictions (e.g., Scharnweber et al., 2016; Smith et al., 2008, 2014). Here, we use *μXRF* to study the inter- and intra-annual concentrations of multiple chemical elements in tree-rings of old trees considering two Mountain pine (*Pinus uncinata*) high-elevation sites with different soil properties (alkaline vs. acidic soils). Our objectives were: (i) to assess the variation and mean concentrations of chemical elements in the heartwood and sapwood; (ii) to investigate long-term trends and relationships among different elements, (iii) to test whether the long-term patterns in chemical elements change depending on soil properties and anthropogenic effects (e.g., by comparing pre-industrial and industrial periods with different warming rates); and (iv) to test if some of those elements (e.g., Ca, Fe, S, Cl, Zn) may serve as proxies of volcano eruptions. We expected elemental concentrations to be generally higher in trees inhabiting sites with acidic than on alkaline soils which may buffer anthropogenic effects as acid rain, and that tree features as sapwood production affect the inter- and intra-annual tree-ring chemical element composition. In this study we only consider selected elements that are considered the most informative, although the method allowed us to determine the concentration of a wider range of elements.

2. Material and methods

2.1. Study area and species

We sampled two old-growth and high-elevation Mountain pine (*Pinus uncinata* Ram.) forests located in protected areas of the Spanish Pyrenees that have not been disturbed by logging during the 20th century (Table 1): 'Ordesa y Monte Perdido' National Park (hereafter, ORD site) and 'Aigüestortes i Estany de Sant Maurici' National Park area (hereafter, AIG site) (Galván et al., 2015). In ORD, soil of the study site was alkaline (Entisol, mean pH is 7.8), whereas soil in AIG was acidic (umbril leptosol, mean pH is 5.1) (Granda et al., 2017). Mean annual temperature and total precipitation in the studied sites ranged from