Dendrochronologia

Volcanic activity signals in tree-rings at the treeline of the Popocatépetl, Mexico

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Abstract

The Popocatépetl volcano resumed its eruptive activity in 1994 and is still active. The largest eruption recorded during this new stage of activity occurred in December 2000. We traced the volcanic activity signal in tree-rings from *Pinus hartwegii* trees located in the north slope of the volcano, located at ~3km from the volcanic cone. Annually resolved tree-ring widths, elemental and stable $\delta^{13}C$ and $\delta^{18}O$ isotope composition were measured during the period 1989-2014 to study the effects of the volcanic activity on trees. Our results indicate a high increase in the concentration of metal elements (Co, Cr, Cu, Fe, Li, Mo, Ni, Pb, Rb, Sr, Ti, Zn) in tree rings following the major 2000 volcanic eruption, compared to the pre-eruption period from 1989 to 1993. Other chemical elements such as Al, K and S peaked 2 years later, in the 2003 tree ring, that matched with the formation of a very narrow ring that year. This sharp reduction of growth was probably driven by a combination of harsh climatic conditions (drought) with the lagged negative effects of the 2000 eruption. Carbon isotope discrimination ($\Delta^{13}C$) and $\delta^{18}O$ increased from 1995 to 2006, suggesting reduced stomatal conductance, photosynthetic activity and water use efficiency due to the large dust veil covering the study zone. The variation of relevant elements (Ca, Mn) showing significant correlations with tree growth, $\Delta^{13}C$ and $\delta^{18}O$ can be attributed to the selective availability of elements following the soil acidification caused by the volcanic activity. Our findings suggest that the recent activity of the Popocatépetl might have increased tree vulnerability, as reflected in the sharp reduction of growth following the drought recorded 2 years after the large eruption of December 2000. Our results warn about the cumulative negative effects of volcanic activity and harsh climatic conditions on tree growth and functioning.

Keywords

Tree-rings, *Pinus hartwegii*, dendrochemistry, carbon isotope discrimination, oxygen isotopes.

Introduction

Dendrochronological studies have provided evidence of the impact of volcanic eruptions on forest ecosystems located hundreds of kilometers away from the volcano or situated near the volcanic cone (e.g., Biondi et al., 2003; Yamaguchi and Lawrence, 1993). Large-scale effects due to the injections of aerosols into the stratosphere cause surface cooling such as the 1815 Tambora eruption, which was followed by one of the coldest years recorded in the northern Hemisphere, often referred to as 'the year without summer' (Luterbacher and Pfister, 2015). These large-scale effects have been profusely recorded on temperature-sensitive tree-ring records worldwide, with reductions of tree-ring width or maximum density (e.g. Briffa et al., 1998; D'Arrigo et al., 2001; Wilson et al., 2016) and formation of frost rings (LaMarche and Hirschboeck, 1984). However, local effects of volcanic eruptions on forest ecosystems are understudied mainly because the chances of trees surviving large volcanic eruptions in the nearby habitats are low (Rodríguez Martín et al., 2013). Surviving trees living close to the eruptive vent record effects on tree functioning following large eruptions, such as mechanical damage to foliage or wood from the direct impact of the tephra fallout or dust layers that reduce the photosynthetic rate and tree growth (Watt et al., 2007).

Previous studies have also reported that volcanic eruptions induce increases of the concentrations of some chemical elements in tree-ring wood, such as S, Na, Zn, Fe, Cl, Ca, Ba, Cu, Hg and other rare elements (Hall et al., 1990; Padilla and Anderson, 2002; Sheppard et al., 2008, 2009; Rodríguez Martín et al., 2013; Hevia et al., 2018). The increase in the concentrations of certain chemical elements following volcanic eruptions has been associated to dry fumes and a decrease in soil pH due to the volcanic induced acid rain or from tephra deposition (Sheppard et al., 2008, 2009). However, to archive the depositional signal of persistent volcanic activity, the combination of dendrochronology and dendrochemistry methods is not enough (Watt et al., 2007). In this sense, the use of carbon and oxygen stable isotopes in tree rings, in order to infer changes in photosynthetic and stomatal conductance rates (Grams et al., 2007; Scheidegger et al., 2000), might help with reconstructing the impact on tree physiology following volcanic eruptions (Battipaglia et al., 2007).

Here we used several proxies, such as tree-ring widths, chemical element concentrations and carbon and oxygen isotope ratios to investigate the knowledge gaps relating volcanic eruptions and their impact on trees. For this study we tracked the impact of the recent activity of the Popocatépetl volcano (Mexico) on *Pinus hartwegii* trees growing near the volcanic cone. Since the most recent awakening of the Popocatépetl in 1994, it has been among the strongest permanent emitters of volcanic gases, mainly SO_2, HCl, CO_2 and HF, with an average SO_2 emission rate ~4,800 t day^{-1} and a peak emission rate that reached the extraordinary value of ~150,000 t day^{-1} in December 2000 (Campion et al., 2018; Global Volcanism Program, 2019). This peak SO_2 emission amounts to twice as much as the Pinatubo eruption of 1991 (Campion et al., 2018). Despite the permanent activity of the Popocatépetl since 1994, in this study we focus on the impacts following the more recent large eruption which occurred in December 2000. By using a combination of tree-ring records and dendrochemical and stable isotopes analyses, we aim to understand the impacts of this large eruption on the growth and ecophysiological functioning of affected trees and its interaction with climate. We hypothesized that the permanent emission of volcanic gases by the Popocatépetl since 1994, could have increased the vulnerability to drought of the *P. hartwegii* trees standing near the volcanic cone by reducing their photosynthetic capacity.

Methodology

Volcanic activity

The Popocatépetl (5426 m a.s.l.) is a stravolcano that is part of the Iztaccíhuatl-Popocatépetl National Park, located in the eastern half of the Trans-Mexican volcanic belt, 70 km southeast of Mexico City. Geological records of the eruptive history of Popocatépetl show several plinian eruptions in the last 10,000 years (Siebe et al., 1996). The last plinian eruption occurred at 800 A.D, and relatively mild eruptions followed until the large eruption recorded in 1663 (Delgado-Granados et al., 2001). The next severe eruption of the Popocatépetl occurred in 1920 and lasted 7 years. The volcano followed a dormancy period of about 70 years until ~1989 when it resumed its seismic and fumarolic activity, starting a new eruptive period on 21 December 1994 that is still going on at the time of writing (Campion et al., 2018).

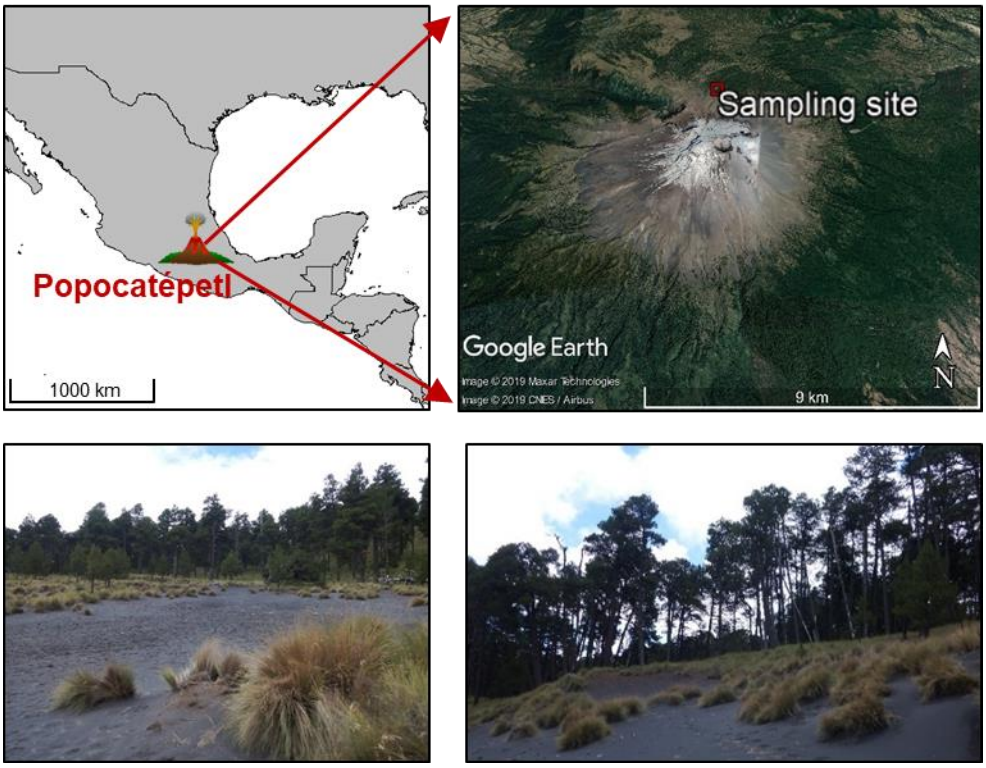
Information regarding the sulfur dioxide (SO_2) emissions of the Popocatépetl volcano is scarce and not available before 2006. For this study we compiled all daily and monthly information from several open sources (e.g. http://www.wovodat.org/) and published papers (e.g. Delgado-

Granados et al., 2001), to obtain a rough summary of the Popocatépetl SO_2 emissions since 1994.

Study area and sampling protocols

The study area corresponds to the alpine treeline ecotone of the Popocatépetl volcano, going from the upper forest limit of *Pinus hartwegii* Lindl. to the upper treeline located near alpine communities (3950-4500 m a.s.l.; Almeida-Lenero et al., 2007; Fig. 1). Above 3500 m, *P. hartwegii* colonizes and represents the climax species due to the low temperatures and lower water availability (Rodríguez-Trejo, 2015). During the eruptive activity of the Popocatépetl, the forest limit and treeline situated closer to the volcanic cone regularly experience burns due to the incandescent bombs ejected by the volcano, that ignite wildfires in contact with the forest cover (Rodríguez-Trejo, 2015).

Figure 1. Location and views of the sampling site situated in the northern slope of the Popocatépetl Volcano, central Mexico.



During summer 2015 (August-September), 17 *P. hartwegii* trees were randomly selected from the northern slope of the Popocatépetl timberline. We avoided sampling individuals with visible scars or severe damages from the volcanic activity whose tree-ring sequences could be too distorted for reconstructing changes in radial growth. From each tree we collected 3 cores at 1.3 m above ground using Pressler increment borers (Haglöf, Sweden). Two of the three cores were used for dendrochronological analyses. To avoid contamination, we only used the third core sampled per tree for chemical and stable isotope analyses. Diameter at breast height (DBH), total height of the trees and basic stand characteristics were also recorded (Table 1).

Table 1. Forest structure and tree-ring width statistics.

Latitude N	19.0529°
Longitude W	98.625°
Elevation (m a.s.l.)	3967
Tree density (trees ha^{-1})	375
DBH ± SD (cm)	48 ± 13
Height ± SD (m)	16 ± 5
No. trees (No. cores)	17 (31)
Period of tree-ring data	1904-2014
Period EPS>0.85	1946-2014
Tree-ring width ± SD (mm)	1.0 ± 0.3
Interseries correlation	0.50

DBH: Diameter at breast height; EPS: Expressed Population signal

Dendrochronology

The two cores assigned for the dendrochronological analyses were air-dried, glued and sanded until the tree-ring boundaries became clearly visible. The cores from the same tree were visually cross-dated with a stereomicroscope, i.e, synchronized to assign the year of formation. We verified the visual cross-dating with the program COFECHA (Holmes, 1983). All the cores were scanned at high resolution using a flatbed scanner, and tree-ring widths were measured with a 0.01 mm resolution using the program CooRecorder v9.3 (Cybis Elektronik, 2018). Measured tree-ring width series were individually detrended using a negative exponential function to remove age-related trends and they were averaged using a bi-weight robust mean (Cook and Kairiukstis, 1990). In this way, we built a standard chronology of tree-ring width indices (TRWi) using the dplR package (Bunn, 2008).

Chemical and stable isotopes analyses

The extra third wood core extracted per tree was prepared with a core microtome. We selected the nine best preserved cores for subsequent chemical and stable isotope ($\delta^{13}C$ and $\delta^{18}O$) analyses. Pooling wood material from those nine trees, allowed us to have enough wood material to carry out annually resolved chemical and stable isotope analyses with the same sample. For each core, we separated annual tree rings from 1989 to 2014 using scalpels and pooled the wood material of all sampled trees by year. This particular period, 1989-2014, allowed us to study the chemical and isotopic composition variation on *P. hartwegii* individuals before the Popocatépetl resumed its volcanic activity.

All the wood samples were milled to a fine powder using a ball mill (Retsch MM301, Haan, Germany). Elemental concentrations were measured by ICP-OES (Thermo Elemental Iris Intrepid II XDL, Franklin, MA, USA) after a microwave-assisted digestion with HNO_3:H_2O_2 (4:1, v:v). Elemental concentration series were converted to z-scores for subsequent analyses (i.e. the mean was subtracted from each value and divided by the standard deviation). With the remaining wood material, we measured $\delta^{13}C$ and $\delta^{18}O$ in each pooled, annual sample. For $\delta^{13}C$ ratios, 0.50–0.70 mg of dry wood was weighed into tin foil capsules and analyzed after combustion using a Finnigan MAT Delta C isotope ratio mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). For $\delta^{18}O$ ratios, 0.50–0.70 mg of dry wood was weighed into silver foil capsules and analyzed with a Finnigan Deltaplus XP isotope ratio mass spectrometer (Thermo Fisher Scientific Inc., Bremen, Germany). C and O isotope ratios were expressed as per mil deviations using the δ notation relative to Vienna Pee Dee Belemnite and Vienna Standard Mean Ocean Water standards, respectively. The accuracy of $\delta^{13}C$ and $\delta^{18}O$ analyses was 0.1-0.3‰, respectively. In the case of $\delta^{13}C$, results were converted to isotopic discrimination between the carbon of atmospheric CO_2 and wood carbon ($\Delta^{13}C$; see Farquhar and Richards, 1984). The combined analysis of both $\delta^{18}O$ and $\mathit{\Delta}^{13}C$ in tree rings provides complementary information, as $\delta^{18}O$ is related to stomatal conductance (g_s) and cumulative transpiration but is unaffected by photosynthetic rate (A_N), and can thus help separate the independent effects of A_N and g_s on $\Delta^{13}C$ (Scheidegger et al., 2000; Barbour, 2007; Grams et al., 2007; Moreno-Gutiérrez et al., 2012).

Climate-growth and climate-isotope analyses

Monthly precipitation, mean temperature and cloud cover data were obtained from the CRU dataset CRU TS 4.02 (Harris et al., 2014) available on a 0.5º grid at the KNMI Climate Explorer webpage (http://climexp.knmi.nl/). Climate-growth and climate-isotope analyses (Pearson correlations) were developed for the common period between monthly and seasonal Precipitation, temperature and cloud cover variables with TRWi and $\Delta^{13}C$ and $\delta^{18}O$ series, i.e, considering the 1950–2014 and 1989-2014 periods, respectively. These analyses were done considering the temporal window from previous October to current September based on previous dendrochronological studies in the same species (Villanueva-Díaz et al., 2015).

Statistical analyses

We calculated the percentage of variation in the 23 chemical elements during the year 2001, after the large eruption of December 2000, and during the year 2003, the first dry year following this large eruption, with respect to the pre-eruption period (see Results section).

We ran Pearson correlations and 10-year running correlations between the TRWi, $\Delta^{13}C$ and $\delta^{18}O$ series for the common period from 1989 to 2014 (significance level assessed at $P < 0.05$). We also ran Pearson correlations between all the chemical elements series and the TRWi, $\Delta^{13}C$ and $\delta^{18}O$ series for the same common period (Appendix, Fig. A.1). The elements showing significant correlations with the TRWi series were included in a Principal components analyses (PCA) calculated on a covariance matrix. The first PCA axis was used for subsequent analyses as predictor variable in Linear Mixed-Effects Models (hereafter PCA Axis 1).

We ran a Linear Mixed-Effects Model (LMEM) to determine the effect of climate on the TRWi (hereafter *Climatic* LMEM) for two different calibration periods, but using similar time series length of 26 years to facilitate comparisons between models, i.e. the periods 1963-1988 and 1989-2014. The predictive variables in the *Climatic* LMEM were the seasonal precipitation, temperature and cloud cover variables displaying the highest climate-growth associations (see Results section).

Similarly, we ran a LMEM to determine the interaction between climatic variability and the Popocatépetl volcanic activity on the TRWi for the period 1989-2014 (hereafter *Climatic* × *Chemical* LMEM), considering as predictive variables the previously mentioned climatic variables and the chemical elements (PCA Axis 1) showing significant relations with the TRWi.

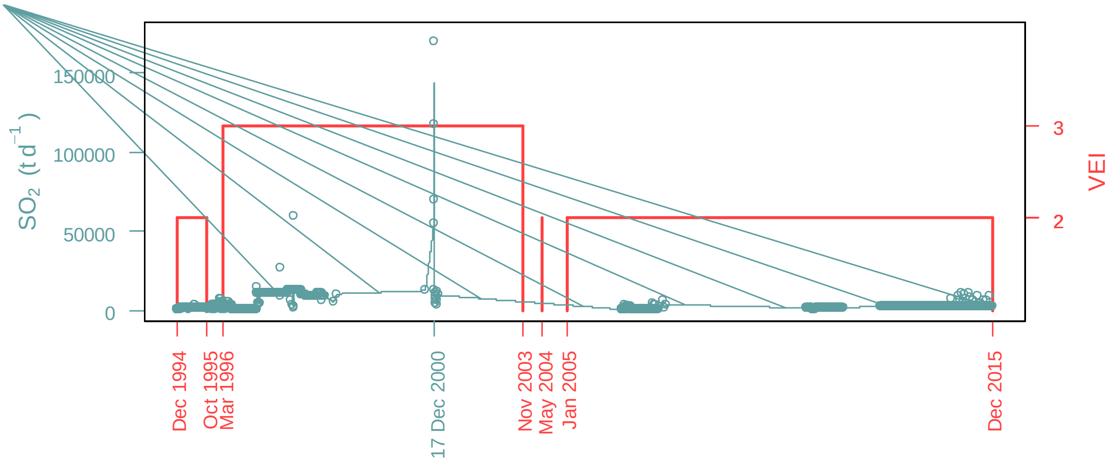
The year was included as random effect in all the LMEMs. A first-order autocorrelation structure (AR1) was considered in all the LMEMs to control for the temporal autocorrelation of TRWi by using the function ‘lme’ from the ‘nlme’ package (Pinheiro et al., 2018). The best model was chosen by selecting the LMEM with the lowest Akaike Information Criterion (AIC) among sets of alternative models obtained with the dredge function in the ‘MuMIn’ R package (Barton, 2018). We calculated marginal R^2 (the proportion of variance explained by fixed effects; R^2_m) and conditional R^2 (the proportion of variance explained by fixed and random effects; R^2c) for the LMEMs following Nakagawa and Schielzeth (2013) and using the ‘MuMIn’ R package (Barton, 2018).

We predicted TRWi for the period 1989-2014 from the three LMEMs above-mentioned, i.e, the *Climatic* LMEMs for the calibration periods 1963-1988 and 1989-2014 and the *Climatic* × *Chemical* LMEM for the calibration period 1989-2014. We compared the percentage of variation explained by the three predictions of TRWi with the observed values following the large eruption of December 2000, particularly during the year 2003, when a sharp reduction in growth was detected (see Results section).

Results

After several years of increasing seismic and fumarolic unrest, the Popocatépetl volcano resumed its eruptive activity in 1994. Since 1994, the Popocatépetl eruptions rated from 2 to 3 on the Volcanic Explosivity Index (VEI; https://volcano.si.edu/, Fig. 2). The maximum SO_2 emissions were recorded in December 2000, when more than 150,000 t day^{-1} were exhaled during that event (Fig. 2).

Figure 2. Sulfur dioxide (SO_2) emissions in the Popocatépetl volcano from 1994 to 2016. Data obtained from http://www.wovodat.org/ and Volcanic Explosivity Index (VEI) categories (red lines) obtained from https://volcano.si.edu/.



Popocatépetl activity signals on tree-rings following the eruption of December 2000

After the large eruption of December 2000 we detected an increase in the concentration of several elements such as Co, Cr, Cu, Fe, Li, Mo, Ni, Pb, Rb, Se, Ti, Zn in the 2001 tree ring as compared to the pre-eruption period (1989-1993). Such increase ranged from +7% for Sr to +88% for Li. Other chemical elements such as Al, Ca, Mg and Si showed decreases after the 2000 eruption, compared to the pre-eruption period, that ranged from -5% for Ca to -119% for Si (Table 2, Fig. A2, Fig. 3).

Table 2. Averaged elemental concentrations in tree-rings from nine trees for the pre-eruption period 1989-1993, the year 2001 (following the large eruption of December 2000), the drought year 2003 and the percentage of variation during the years 2001 and 2003 with respect to the pre-eruption period. The negative % values indicate a negative % change. Grey shaded rows indicate significant correlations between TRWi (*), $\Delta^{13}C$ (†) or $\delta^{18}O$ (‡) and trace elements for the period 1989-2014 (See Fig. A.1 in the Appendix).

	1989-1993 (Mean ± SD)	2001	2003	% Variation 2001	% Variation 2003
*Al (mg Kg^{-1})	21 ± 4	15	44	-44	52
†B (mg Kg^{-1})	2 ± 1	<0.001	1	n.d.	-184
‡Ca (g 100g^{-1})	0.042 ± 0.007	0.040	0.029	-5	-43
Cd (mg Kg^{-1})	0.031 ± 0.013	<0.001	<0.001	n.d.	n.d.
Co (mg Kg^{-1})	0.09 ± 0.04	0.189	0.026	54	-232
Cr (mg Kg^{-1})	44 ± 3	86	39	49	-12
Cu (mg Kg^{-1})	1.34 ± 0.12	2	1.64	37	18
Fe (mg Kg^{-1})	299 ± 13	523	317	43	6
*K (g 100g^{-1})	0.053 ± 0.003	0.053	0.104	1	49
Li (mg Kg^{-1})	0.02 ± 0.03	0.19	0.05	88	58
Mg (g 100g^{-1})	0.018 ± 0.003	0.017	0.016	-8	-14
‡Mn (mg Kg^{-1})	37 ± 5	40	21	8	-75
Mo (mg Kg^{-1})	0.82 ± 0.09	1.14	0.73	28	-13
Na (g 100g^{-1})	0.006 ± 0.001	0.009	0.006	28	-5
Ni (mg Kg^{-1})	2.1 ± 0.6	4.5	1.7	55	-22

*Pb (mg Kg^{-1})	0.12 ± 0.06	0.57	0.44	80	74
*P (g $100g^{-1}$)	0.0083 ± 0.0004	0.0087	0.0189	5	56
*Rb (mg Kg^{-1})	1.11 ± 0.08	1.23	1.92	10	42
Se (mg Kg^{-1})	5.8 ± 0.3	11.4	4.7	50	-23
Si (mg Kg^{-1})	87 ± 95	40	59	-119	-48
*S (g $100g^{-1}$)	0.013 ± 0.003	0.014	0.017	8	22
Sr (mg Kg^{-1})	3.6 ± 0.3	3.8	2.8	7	-27
Ti (mg Kg^{-1})	2.2 ± 0.5	5.4	2.6	59	15
Zn (mg Kg^{-1})	11 ± 4	15	11	26	2

n.d.: below detection limits.

Popocatépetl activity signals on tree-rings during the dry year 2003

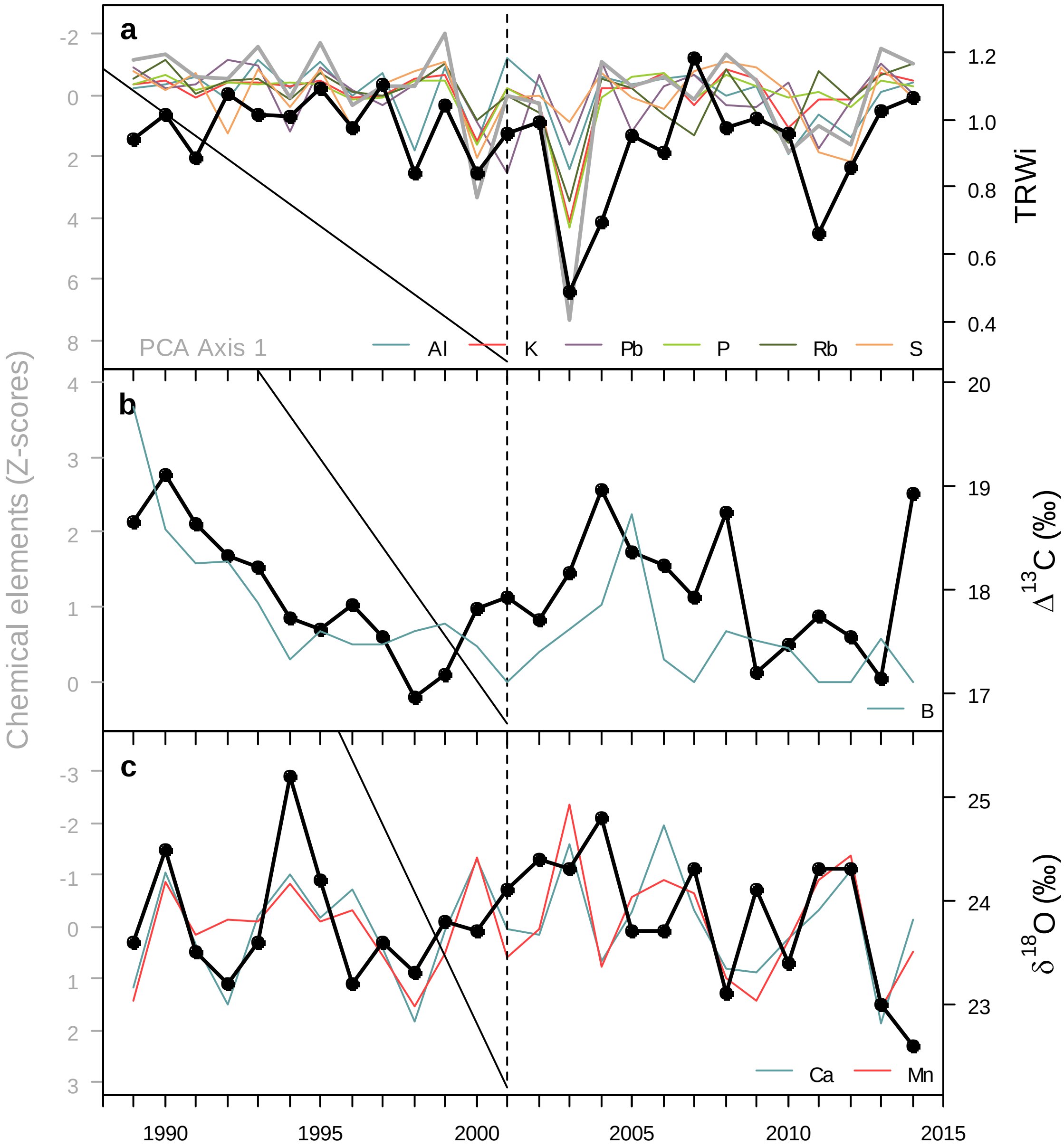
In 2003, the first dry year following the eruption of December 2000, we found a decrease in the concentration of the elements Co, Cr, Mo and Sr compared to the pre-eruption period, whereas the concentration of other elements such as Cu, Fe, Li, Ti and Zn remained above pre-eruption values. Pb and Rb concentrations remained very high in the 2003 tree ring, i.e. +74% and +42% compared to the pre-eruption period, respectively. Interestingly, other elements such as Al, K and S, that showed reductions (Al) or a very small increase (K, S) in their concentrations in the 2001 tree ring, peaked 2 years later in the 2003 tree ring, with variations of +52%, +49% and +22% compared to the pre-eruption period, respectively. There was also a reduction in the concentration of B (-184%), Ca (-43%) and Mn (-75%) in the 2003 tree ring, compared to pre-eruption values (Table 2, Fig. A2, Fig. 3).

Correlations between ring-width indices, stable isotopes and chemical elements from 1989 to 2014

Significant negative associations were found between TRWi and Al, K, Pb, P, Rb and S concentrations for the period 1989-2014 (range from r= - 0.40 to r= -0.62; $P < 0.05$; Fig. A.1, Fig. 3a). For the same period, the $\Delta^{13}C$ series showed significant positive associations with B concentrations (r = 0.46, $P < 0.05$; Fig. A.1, Fig. 3b), whereas the $\delta^{18}O$ series showed significant ($P < 0.05$) negative associations with Ca and Mn (r = -0.41 and r = - 0.42, respectively; Fig. A.1, Fig. 3c). Note that Ca and Mn concentrations were highly correlated (Fig. A.1). No significant correlations were found between TRWi, $\Delta^{13}C$ and $\delta^{18}O$ for the period from 1989 to 2014.

Figure 3. Tree-ring width indices (TRWi) (**a**) and $\Delta^{13}C$ (**b**) and $\delta^{18}O$ (**c**) series showing significant correlations with annual chemical elements (Z-scores values; see Fig. A.1) from 1989 to 2016.

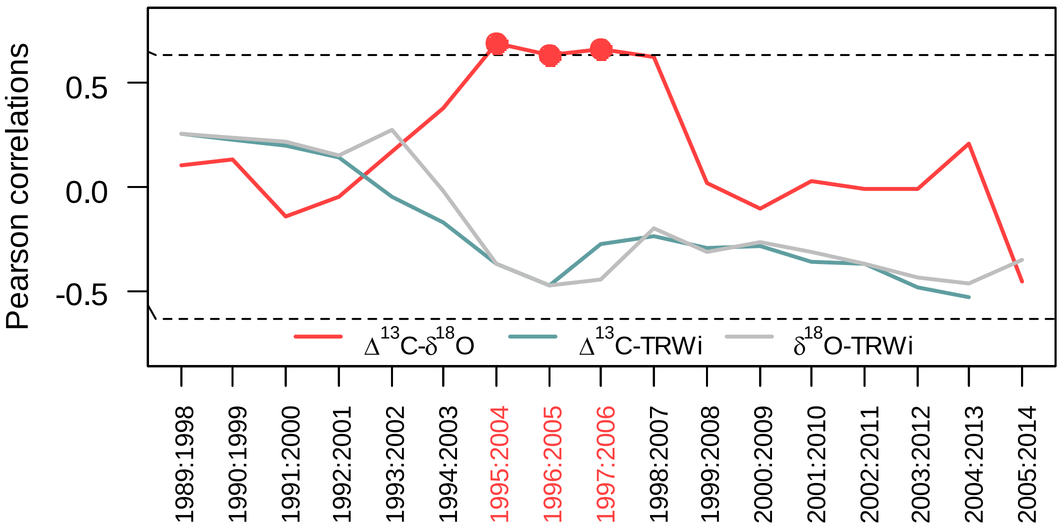
Chemical elements and PCA axis 1 are reversed in panels (**a**) and (**c**). PCA Axis 1 obtained from Al, K, Pb, P, Rb and S tree-ring concentrations is also plotted (reversed) in panel (**a**) as a grey line. The vertical dashed line indicates the large volcanic eruption recorded on December 2000.



Running correlations between ring-width indices and stable isotopes from 1989 to 2014

The 10-yr running correlations between $\Delta^{13}C$ and $\delta^{18}O$ series showed significant positive associations during the most active period of the Popocatépetl, i.e. from 1995 to 2006 (Fig. 4). This indicates that decreases in the stomatal conductance rate and transpiration are linked to concurrent decreases in water-use efficiency, which necessarily implies large reductions in photosynthetic rates as well during the most active period of the volcano. Running correlations between TRWi and Δ^{13}C and between TRWi and δ^{18}O series showed negative (but non significant) associations during the same period (Fig. 4).

Figure 4. 10-yr running correlations of carbon discrimination (Δ^{13}C) and oxygen (δ^{18}O) isotopes (red line), Δ^{13}C and tree-ring width indices (TRWi) (blue line) and δ^{18}O and TRWi (grey line). Red circles indicate significant correlations between Δ^{13}C and δ^{18}O during three 10-yr periods corresponding to the most active period of the Popocatépetl volcano (from 1995 to 2006). Horizontal dashed lines indicate the confidence intervals at 95 %.



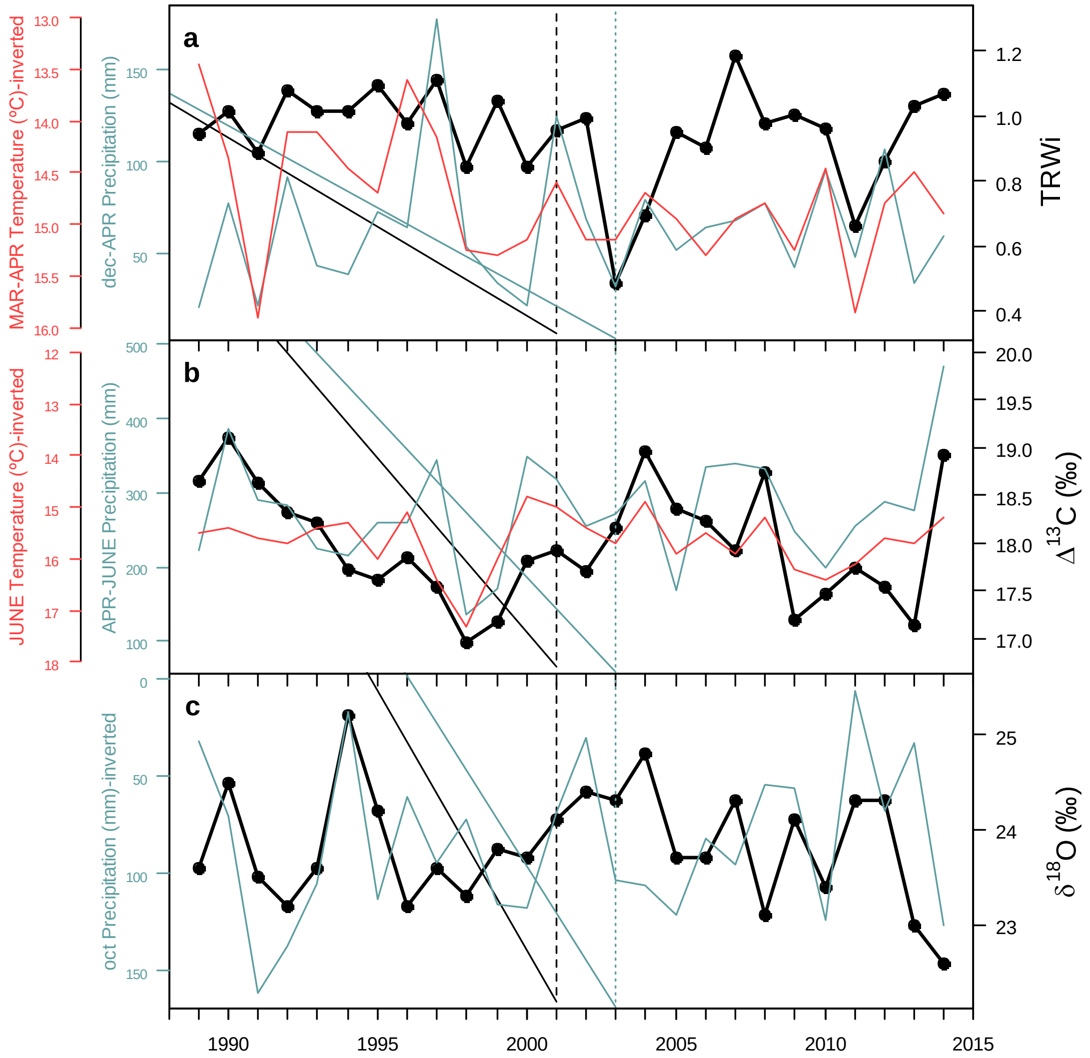
Relationships between climate variables, ring-width indices and stable isotopes

Climate-growth associations computed for the period 1950-2016, revealed that radial growth was mainly enhanced by wet winter to spring conditions (from the previous December until current April, r = 0.36, P < 0.05), and cool and cloudy early-spring conditions (March-April r = -0.31 and February-March r = 0.31, respectively, P < 0.05; Appendix, Fig. A.3). Similar climate relationships computed for the period 1989-2014 for the Δ^{13}C and δ^{18}O series showed that Δ^{13}C was enhanced by wet spring and early summer conditions (April-June, r = 0.60, P < 0.05) and cool and cloudy June conditions (r = -0.57 and r = 0.48, respectively, P < 0.05, Appendix, Fig. A.4), whereas δ^{18}O was negatively related to the precipitation of the previous October (r = -0.43, P < 0.05; Fig. A.5). No significant influence of temperature or cloud cover was found on the δ^{18}O time series.

Climate interactions with the Popocatépetl activity effect on ring-width indices and stable isotopes

TRWi showed a sharp decrease during the year 2003, the first year recording a severe drought after the large eruption of December 2000 (Fig. 5). The sharp decrease in TRWi recorded in 2003 was followed by sharp increases in both $\delta^{18}O$ and $\Delta^{13}C$ in the following year (2004). We also found another previous large peak in $\delta^{18}O$ values in 1994 (a dry year), just before the Popocatépetl resumed its activity, but this peak was not accompanied by any large $\Delta^{13}C$ increases or TRWi reductions in the same, preceding or following years (Fig. 5).

Figure 5. Mean series (chronology) of tree-ring width indices (TRWi) related to the seasonal maximum correlation obtained in climate-growth analyses (see Fig. A.3), i.e. sum precipitation from prior December to current April and mean temperature from March to April (*a*), Carbon discrimination ($\Delta^{13}C$) and oxygen ($\delta^{18}O$) isotopes related to seasonal maximum correlation obtained in climate-isotopes analyses, i.e. sum April-June precipitation and mean June temperature (see Fig. A.4, *b*) and precipitation of the previous October (see Fig. A.5, *c*), respectively. Note that y-axes for temperatures in panels *a* and *b* are inverted. The vertical black dashed line indicates the large volcanic eruption recorded on December 2000. The vertical dotted blue line indicates the year with the maximum decrease in tree growth after the December 2000 eruption.



We found that the TRWi for the period 1989-2014 was more accurately predicted by the LMEM that included climatic variables and the PCA Axis 1 of the peak chemical concentrations (*Climatic* x *Chemical* LMEM) as predictive variables, compared to the LMEMs that only considered the climatic drivers as predictive variables (*Climatic* LMEMs, Table 3, Fig. 6). The *Climatic* x *Chemical* LMEM resulted in the lowest AIC and twice as high R^2_m values when compared to the two *Climatic* LMEMs regardless of the calibration period; Table 3). The *Climatic* x *Chemical* LMEM also showed a more accurate prediction of the TRWi value recorded during the dry year 2003, compared to the prediction of the *Climatic* LMEMs, i.e. 5% of variation *vs* 76-91% of variation, respectively (Fig. 6).

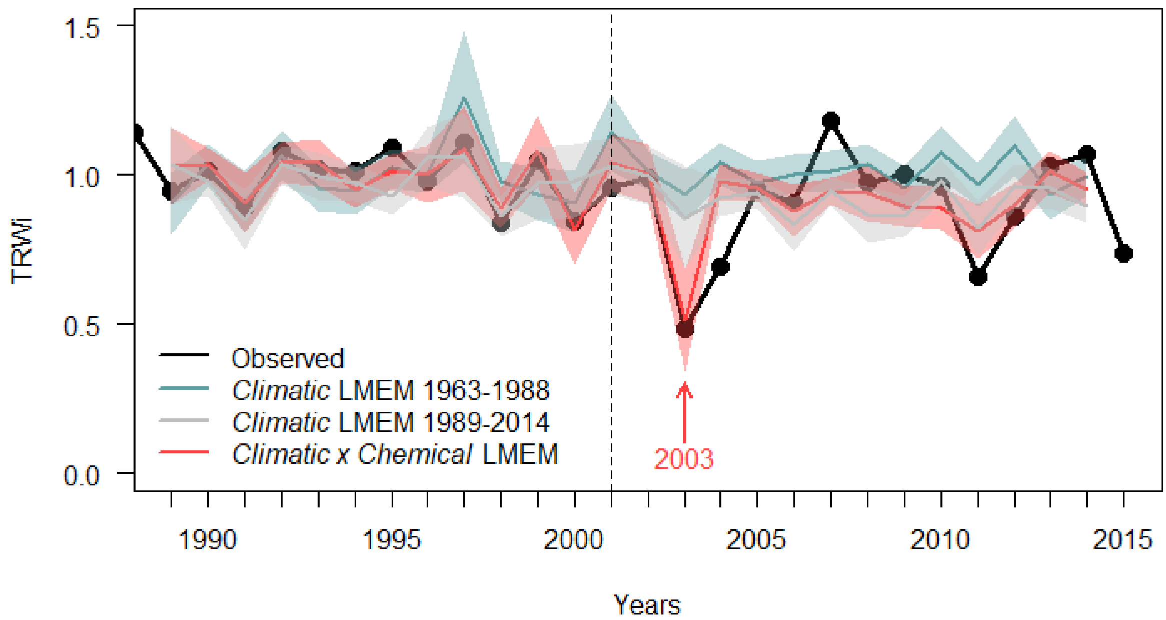
Table 3. Coefficients of LMEMs for the tree-ring width indices (TRWi) for the calibration periods 1963-1988 and 1989-2014, only including climatic variables as predictors, and the TRWi for the

calibration period 1989-2014, including climatic variables and the chemical components (PCA axis 1 of Al, K, Pb, P, Rb, and S) as predictors. Predictive variables were scaled.

	Climatic 1963-1988			*Climatic* 1989-2014			*Climatic × Chemical* 1989-2014		
Fixed effects	Estimate	SE	*P*	Estimate	SE	*P*	Estimate	SE	*P*
Intercept	1.04	0.03	<0.001	0.946	0.027	<0.001	0.946	0.020	<0.001
March-April T				-0.040	0.029	0.187	-0.020	0.022	0.386
February-March CC				0.047	0.029	0.122	0.051	0.022	<0.05
dec-April Prec	0.08	0.03	<0.05						
PCA Axis 1-Al,K,Pb,P,Rb,S	n.a			n.a			-0.048	0.011	<0.001
Random effects	SD			SD			SD		
Years	0.06			0.05			0.04		
R^2_m	0.18			0.22			0.56		
R^2c	0.90			0.90			0.95		
AIC	-1.75			-4.43			-9.85		

n.a.: not applied; T: Temperature; CC: Cloud cover; Prec: Precipitation; SE: Standard error; SD; Standard deviation; R^2_m: marginal R^2 or proportion of variance explained by fixed effects; R^2c: conditional R^2 or proportion of variance explained by fixed and random effects; AIC: Akaike Information Criterion.

Figure 6. Mean series of tree-ring width indices (TRWi, black line) and predicted values for the period 1989-2014 obtained from the *Climatic* LMEMs -calibration period 1963-1988 (blue line) or 1989-2014 (grey line)- and from the *Climatic × chemical* LMEM (red line). The vertical black dashed line indicates the large volcanic eruption recorded on December 2000. The arrow indicates the drought year (2003) with the maximum decrease in tree growth after the December 2000 eruption.



Discussion

After decades of dormancy, the Popocatépetl volcano resumed its activity in 1994, recording the most violent explosions from December 2000 to January 2001 (Fig. 2). Up-to-date, the volcano remains active, with multiple steam, gas and ash emissions and incandescent bombs ejections (Global Volcanism Program, 2019). Tree-ring proxies (TRWi, chemical elemental concentrations, $\Delta^{13}C$ and $\delta^{18}O$) from *P. hartwegii* trees located at the treeline near the Popocatépetl volcanic cone were studied to unravel how the recent volcanic activity affected tree growth and functioning.

Immediate responses of tree-rings to volcanic activity

Multi-elemental analyses of tree rings revealed higher concentrations of some metal elements (Co, Cr, Cu, Fe, Li, Mo, Ni, Pb, Rb, Se, Ti and Zn) in the 2001 tree ring, which was formed just a few months after the large eruption of December 2000, that were not accompanied by abrupt growth reductions. Torres-Alvarado et al. (2011) confirmed the presence of some of these elements (e.g. Fe, Cu and Zn) in samples of ashes and rock fragment exhalations from the Popocatépetl volcano during the activity period registered in December 2000. Previous dendrochemistry studies also detected an increment in the concentration of Fe and Cu (Cruz-Muñoz et al., 2008) and Zn (Calva-Vázquez et al. 2006) in tree rings from forests surrounding the Popocatépetl volcano, during the three years following the December 2000 eruption. Immediate increases in ring S and P content were also reported in pines growing near the cinder cone of Parícutin volcano in Michoacán, Mexico, following the eruption of 1943 (Sheppard et al., 2008). Metal elements can be incorporated in tree rings through roots, leaves or bark absorption (Lepp, 1975). The rapid accumulation of metal elements in the 2001 wood ring after the December 2000 eruption, suggests that metals deposited on trees were absorbed directly through bark or foliage, and were translocated from the phloem to the cambium to be deposited in the outer, most recently formed ring (Watmough, 1999). This should have happened during or after the acid rain that followed the eruptions.

Lagged response to volcanic activity in tree rings

Despite the rapid bark or foliage absorption of metal elements in trees growing nearby the volcano cone, root uptake is still considered the major pathway of entry for most elements in tree-ring wood (Lepp, 1975). In the Popocatépetl, volcanic fumes incorporate chemical elements in the ecosystem mainly through the water melted from the glaciers on top of the volcano (Cruz-Muñoz et al., 2008). When root uptake predominates, a time lag is expected between metal deposition on soils and their translocation from roots to the cambium and their deposition in tree-ring wood (Lukaszewski et al., 1993). In addition, drought can also alter the uptake of chemical elements and affect their concentrations in the xylem (Schachtman and Goodger, 2008), resulting in lagged responses. Thus, the 2-year delayed peak in wood concentrations of Al, K, P, S, Pb and Rb suggests a delayed root uptake for these chemical elements (Pearson et al., 2005), that may be exacerbated or prompted by the drier conditions reported during the year 2003.

Annually resolved tree-ring records unveiled a large reduction in growth in 2003 (two years after the large eruption of December 2000, Fig. 6). For trees growing nearby the volcano cone, a lag between volcanic eruptions and the tree-ring response for one year or more has been previously reported. For instance, Biondi et al. (2003) found a 2-year growth reduction in *P. hartwegii* trees growing on the treeline of Nevado de Colima after the eruption of the nearby Volcán de Fuego, in 1913. In Southern Italy, a mixed stand of *Fagus sylvatica* and *Acer pseudoplatanus* growing in the area of the Vesuvius volcanic complex also showed a significant decrease in ring width during the years following volcano eruptions (Battipaglia et al., 2007).

Interestingly, the large reduction in growth recorded during 2003 matched with the first severe drought episode after the December 2000 eruption. Previous studies reported that growth reductions in *Pinus nigra* trees caused by intense air pollution in Turkey were exacerbated during long drought periods (Tolunay, 2003). In this study, the lagged tree-ring width reduction observed in 2003 could be explained by the use of carbohydrate reserves and the mild climate conditions recorded in the two years following the large eruption of December 2000 (Fig. 5). *P. hartwegii* individuals may have relied on stored carbohydrates for needle and earlywood production for up to two years until the 2003 drastic growth reduction. Therefore, this sharp decrease in wood production was probably caused by the combined negative effects of the two years of reduced photosynthetic capacity after the large dust layer covering the study zone and the increase in concentration of potentially toxic elements such as Al, Pb and Rb following the December 2000 eruption and harsh climatic conditions related to the 2003 drought (Fig. 5a). This interpretation was supported by our LMEMs. The predictive power of the 2003 growth reduction significantly increased when the LMEM included as predictive variable the time series of the chemical elements concentrations (PCA Axis 1 of Al, K, P, Pb, Rb and S). Consequently, we corroborate our initial hypothesis that the high recent activity of the Popocatépetl could have enhanced the vulnerability to drought of *P. hartwegii* trees growing nearby the volcano cone.

Stable isotopes response to volcanic activity

Significant positive associations were found between B concentrations in tree rings and $\Delta^{13}C$ (Fig. 3b). The role of B in forests ecosystems was reviewed by Lehto et al. (2010). These authors pointed that, particularly under environmental stress, B-deficient trees can show disorders in the structural development of organs and whole plant due to impaired development of the primary cell wall, ultimately affecting wood quality and productivity. Ca and Mn concentrations in tree rings were negatively associated to $\delta^{18}O$ (Fig. 3c), indicating that a reduced stomatal conductance and cumulative transpiration was associated to lower concentration of Ca and Mn in tree rings. The depletion of B, Ca and Mn in tree rings reported here could have been exacerbated by soil acidification after the volcanic acid rain deposition (Lehto et al., 2010), such as that caused by SO_2 emission produced by the Popocatépetl eruptions. This could have occurred following the eruption of December 2000, as denoted by the sharp reduction of Ca and Mn concentrations in the 2003 tree ring. In addition, the acid rain increases the concentrations of elements such as K and Rb in tree rings (Häsänen and Huttunen, 1989), making also ions such as Al more available (Cronan and Grigal, 1995), and ultimately causing tree stress and reducing Ca and P availability (Lawrence et al., 1995), which are essential elements for basic plant processes of wood formation and growth (Fromm, 2010).

The influence of volcanic eruptions on photosynthetic rate and stomatal conductance, assessed using as proxies $\Delta^{13}C$ and $\delta^{18}O$, has been scarcely studied (but see Battipaglia et al., 2007; Churakova (Sidorova) et al., 2014). In this study, TRWi and $\Delta^{13}C$ and $\delta^{18}O$ were not significantly associated during the period from 1989 to 2014. However, 10-yr running correlations indicated a positive association between $\Delta^{13}C$ and $\delta^{18}O$ for the most recent period of volcanic activity of the Popocatépetl (Fig. 4). Positive trends in both $\Delta^{13}C$ and $\delta^{18}O$ values during this period of high volcanic activity (1995-2006, Figs. 4-5) could be explained by reduced stomatal conductance and photosynthetic activity as a consequence of reduced light intensity caused by volcanic dust veils (Churakova (Sidorova) et al., 2014). This reduced light intensity and photosynthesis activity may lead to an increase in the leaf intercellular concentration thereby increasing $\Delta^{13}C$ (Farquhar et al., 1989), that can indicate stressful conditions for gas exchange (Churakova (Sidorova) et al., 2014). This interpretation is further supported by the negative sign found for TRWi-$\Delta^{13}C$ and TRWi-$\delta^{18}O$ 10-yr running correlations, displaying (non-significant) negative trends during this period (Fig. 4).

Based on climate-TRWi and climate-isotope analysis ($\Delta^{13}C$ and $\delta^{18}O$), $\Delta^{13}C$ was the proxy recording the strongest climatic signal, showing a strong association with wet and cool spring and early summer conditions. After the December 2000 eruption, mild wet and cool conditions during 2001 and 2002 should have prompted higher $\Delta^{13}C$ values. In particular, June temperatures recorded during the years 2000 and 2001 were among the coolest recorded from 1989 to 2014 (below the 10th percentile of the time series, Fig. 5b). However, we found relatively lower $\Delta^{13}C$ during the year 2002, which could be linked to stomatal closure caused by the volcanic dust as suggested by the relatively high $\delta^{18}O$ values and strong decrease in growth detected during the year 2003 (Fig. 5a). In contrast to our findings, Battipaglia et al. (2007) reported no significant responses of $\Delta^{13}C$ to volcanic activity, but a decrease in $\delta^{18}O$ linked to an increase in relative humidity and a decrease in temperature following eruptions of the Vesuvius, Italy. However, the sampling site in the study of Battipaglia et al. (2007) was located 40 km away from the volcano whereas our sampling site was located only 3 km away from the volcano cone, suggesting major differences in acid or tephra deposition on nearby forests.

Conclusions

This study highlights the importance of using tree-ring multi-proxy chronologies, i.e. TRWi, chemical elements, carbon and oxygen isotopes, to assess the volcanic activity impact on trees growing close to an active volcanic cone. In particular, our results confirmed the effectiveness of combining chemical and carbon-oxygen isotope analyses for assessing volcanic activity impacts on leaf gas exchange characteristics. The significant positive association found between $\Delta^{13}C$ and $\delta^{18}O$ for the most active period of volcanic activity reveals reduced stomatal conductance and photosynthetic rates and water use efficiency that was reflected in lower growth during the same period. The increased concentration of some metal elements in the wood after the large 2000 eruption may have increased tree vulnerability to drought, as reflected by the sharp growth reduction recorded in the dry year 2003. Lagged responses in soil nutrient availability and uptake after volcanic eruptions and interactions with climate stress should be taken into account to assess volcanic effects on forests and to accurately date past volcanic eruptions using tree rings.

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Appendix

Figure A.1. Pearson correlations calculated between TRWi, Δ[13]C, δ[18]O and chemical elements for the period 1989-2014. Only significant associations are plotted.

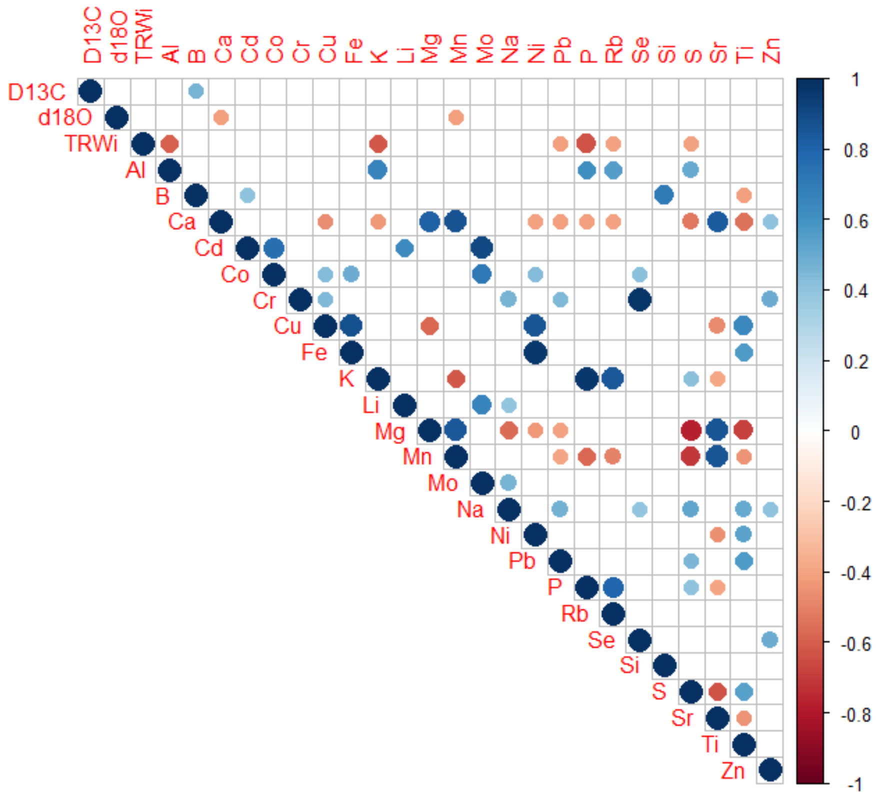

Figure A.2. Annual chemical elements (Z-scores values) series (non-plotted in Figure 3) from 1989 to 2016. The vertical black dashed line indicates the large volcanic eruption recorded on December 2000. The vertical dotted blue line indicates the year with the maximum decrease in tree growth after the December 2000 eruption.

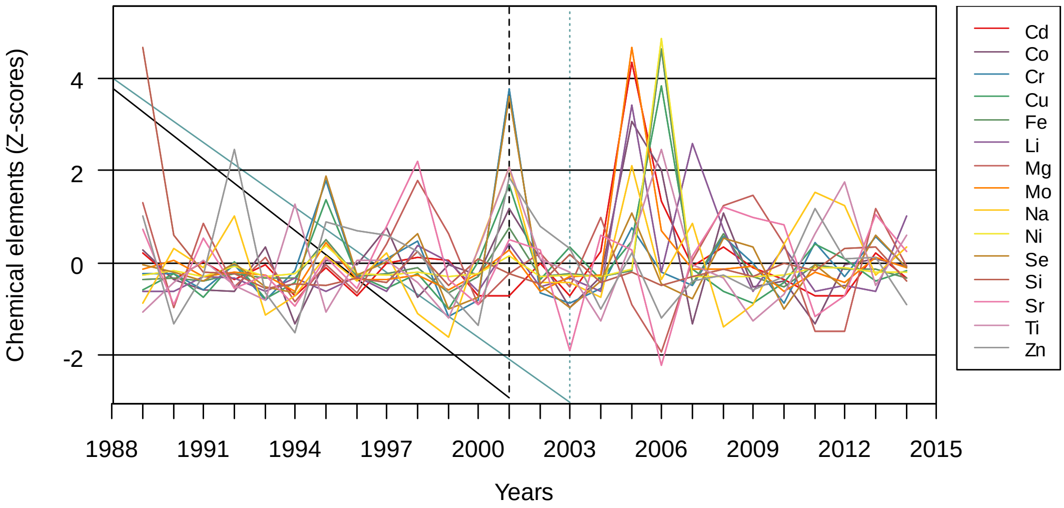

Figure A.3. Climate-growth correlations considering the associations between the mean series (chronology) of ring-width indices, monthly precipitation, temperature and cloud cover for the period 1950-2016. Filled bars indicate significant correlations at $P < 0.05$.

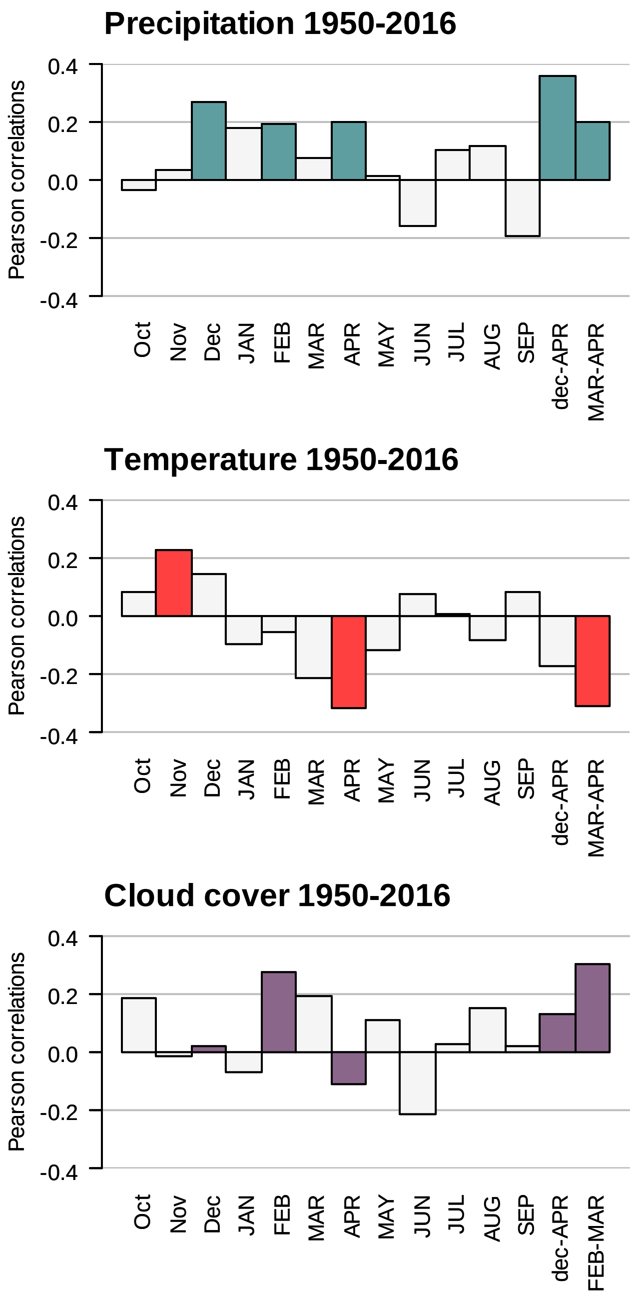

Figure A.4. Climate- $\Delta^{13}C$ correlations after processing with a 10-year high-pass filter to isolate interannual variability, and considering monthly precipitation, temperature and cloud cover for the period 1989-2016. Filled bars indicate significant correlations at $P < 0.05$.

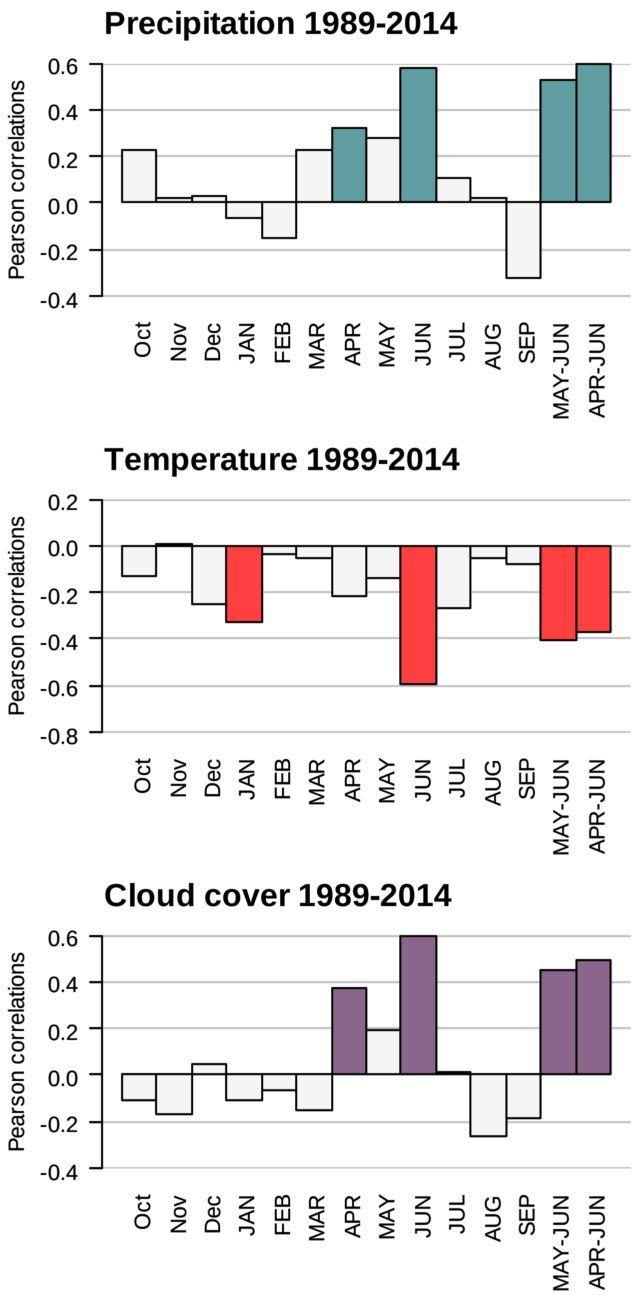

Figure A.5. Climate-$\delta^{18}O$ correlations after processing with a 10-year high-pass filter to isolate interannual variability, and considering monthly precipitation, temperature and cloud cover for the period 1989-2016. Filled bars indicate significant correlations at *P* < 0.05.