DENDROCHRONOLOGICAL POTENTIAL OF *FRAXINUS UHDEI* AND ITS USE AS BIOINDICATOR OF FOSSIL CO_2 EMISSIONS DEDUCED FROM RADIOCARBON CONCENTRATIONS IN TREE RINGS

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ABSTRACT. Dendrochronological studies are limited in tropical regions because not many tree species form annual growth rings. This work reports an evaluation of the dendrochronological potential of tropical ash (*Fraxinus uhdei*) and its use as a bioindicator of fossil CO_2 concentration in urban areas by means of radiocarbon analysis on growth rings. We analyzed a cross-section of a tree that grew during the period 1932–2007 in San Luis Potosí, one of the most industrialized cities in Mexico. The $\Delta^{14}C$ values obtained follow the same variation pattern as the calibration curve of the Northern Hemisphere (NH) zone 2 (Hua and Barbetti 2004), with the peak centered in 1964, but they are lower by up to 124‰. The high correlation coefficient ($r = 0.990$, $p < 0.001$) between the variation patterns indicates that this species does form annual growth rings, and the lower values can be attributed to the ^{14}C dilution caused by fossil CO_2 emissions. The magnitude of the Suess effect varied between –6.9% and –0.5%, equivalent to fossil CO_2 concentrations ranging between 21.9 and 1.5 ppmv. The Suess effect and fossil CO_2 values have significant variations with no apparent monotone increasing trend, suggesting that the CO_2 emissions during the studied period have diverse sources. It is concluded that *F. uhdei* has potential for dendrochronological studies in tropical areas because its growth rings are formed annually and, furthermore, it can be used as a bioindicator of atmospheric ^{14}C variations and fossil CO_2 concentration in urban areas.

INTRODUCTION

It is commonly assumed that tropical tree species do not form annual growth rings due to the lack of seasonality of the temperature, limiting dendrochronological studies in the tropics. However, several works have reported the annual nature of growth rings for numerous tropical species, generally resulting from the annual variation of either precipitation or flooding (Worbes 2002; Rozendaal and Zuidema 2011 and references therein). One of the methodologies used for demonstrating the annual nature of growth rings in tropical species is by means of radiocarbon analysis, and comparison with the atmospheric ^{14}C levels registered since the nuclear tests period (Worbes and Junk 1989).

^{14}C levels increased significantly during the late 1950s and early 1960s as a result of the atmospheric nuclear tests, reaching concentrations in the atmosphere up to twice as high as the pre-bomb era. After the Nuclear Test Ban Treaty in 1963, the atmospheric ^{14}C concentration started to decrease due to carbon exchange with other reservoirs, mainly the biosphere and oceans, and the important increase in anthropogenic fossil CO_2 emissions since the mid-1970s. The pulsed input of excess ^{14}C makes it a potential tracer to study the carbon dynamics between and within the different reservoirs of the carbon cycle (Levin and Hesshaimer 2000). Some of the applications of excess ^{14}C levels are to study the growth rate of tropical tree species, to evaluate the annual nature of tree rings, and to reconstruct the fossil CO_2 concentration in urban areas.

Because fossil fuels are ^{14}C-free, the increase in fossil CO_2 emissions since the late 19th century has altered the carbon isotopic composition of the atmosphere, more notably in urban and industrial

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areas, where the ^{14}C concentration as carbon dioxide ($^{14}CO_2$) can be significantly lower than in clean areas. The first to notice the $^{14}CO_2$ dilution due to fossil fuel burning was Suess (1955), thus this phenomenon is known as the Suess effect. By comparing the $^{14}CO_2$ concentration in an urban or industrial area to that of clean air from an area isolated from anthropogenic CO_2 sources, it is possible to estimate the Suess effect and the fossil CO_2 concentration in the urban/industrial atmosphere. This can be done either by directly monitoring the $^{14}CO_2$ in the atmosphere (Levin et al. 2003) or by analyzing the ^{14}C of plant material, mainly tree rings (Rakowski et al. 2001).

In this work, we report an evaluation of the annual nature of growth rings of tropical ash (*Fraxinus uhdei*) as revealed by ^{14}C, as well as a reconstruction of atmospheric ^{14}C levels for the growing season during the 1950–1970 period (presumably from March to October), and the estimates of the fossil CO_2 concentration for one of the most important urban and industrial areas in Mexico.

METHODS

Study Area

San Luis Potosí (22.11°N, 101°W; 1890 m asl) is one of the most industrialized cities in Mexico. It is a semi-arid region with annual mean temperature of 17.3 °C and average rainfall of 387 mm/yr, mainly during June–October. Vegetation is dominated by shrubs and grasses, with some introduced tree species such as *Eucalyptus globulus*, *Fraxinus uhdei*, and *Casuarina equisetifolia* in parks and gardens (INEGI 2005).

The city of San Luis Potosí (SLP) has grown considerably from a population of 155,238 inhabitants in 1950 to 267,951 inhabitants in 1970. In 2005, the population had grown to more than 950,000 inhabitants, with more than 3000 industries and 230,000 vehicles (INEGI 2005). The industrial activity has been mainly concentrated in 2 areas, one located on the northwest side of SLP, including a copper smelting facility that was in operation from 1925 to 2010; the other industrial area is an industrial park district established in 1963 on the southeastern side of the city, which mainly comprises steel, iron, and non-ferrous metal processing; auto-part manufacturing; foundries; and chemical industries (rubber, plastic, and pharmaceutical products) (Carranza-Alvarez et al. 2008).

Sampling and Sample Preparation

A cross-section of a tropical ash (*Fraxinus uhdei*) was collected at the Morales Park, located in the western part of SLP, in April 2008 (Figure 1). A 10-cm-tall section was cut with a chain saw at 1.30 m from the roots of a tree that was felled 1 week prior to sampling due to strong winds in the area. The growing season is not well defined for *Fraxinus uhdei*; however, it drops leaves in late autumn and by late winter (February) the new season's leave buds are already formed.

The cross-section was sliced into 8 parts to facilitate handling; each slice was sanded with increasing grit number sandpaper (400–1500), first using a belt sander and then manually, to expose cell structures, and cleaned with a brush and vacuum in order to eliminate dust generated during sanding to avoid cross-ring contamination. The rings were counted using stereoscopic microscopes with 20× and 30× lenses, and pictures were taken with an Olympus SZ-STF microscope in order to corroborate the counting, detect false rings, and assign the estimated year of growth. The criterion for the identification of growth rings was the variation in vessel density, and bands not associated to changes in vessel density were marked as false rings (Figure 2). Rings presumably corresponding to the 1954–1967 period were separated with a stainless steel chisel and cleaned in a Soxhlet with an ethanol:toluene (1:2) mixture for 48 hr. Samples presumably corresponding to the years 1955, 1956, and 1960 did not yield enough sample quantity to be analyzed by liquid scintillation spectrometry.

Dried samples were milled in an agate ball micro-mill. After sample homogenization, a subsample of each milled ring was separated for $\delta^{13}C$ analysis.

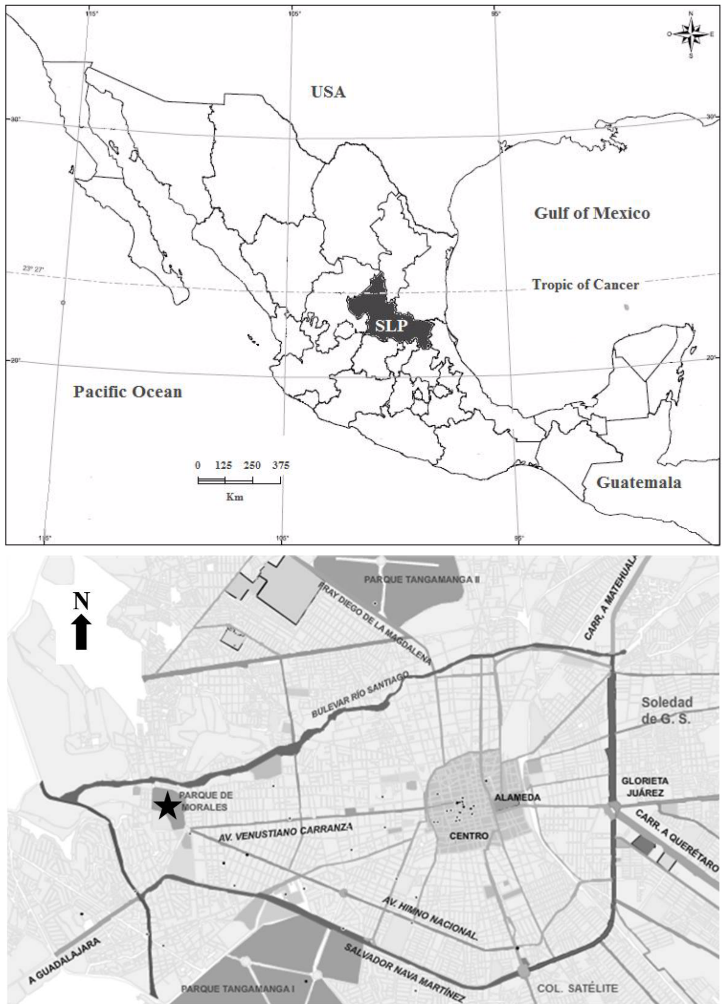

Figure 1 Map of Mexico showing location of San Luis Potosí State (top) and sampling site (black star) within San Luis Potosí City (bottom).

Analysis

^{14}C analyses were performed at the Radiocarbon Laboratory at the National Autonomous University of Mexico (UNAM) by ultra-low level liquid scintillation spectrometry. Prior to analysis, samples were transformed to benzene (1.5 mL) in a vacuum synthesis line and mixed with 0.5 mL of scintillation cocktail (2,5-diphenyloxazole [PPO] + 1,4-Bis(5-phenyl-2-oxazolyl)benzene [POPOP] dissolved in dead spectrophotometric-grade benzene) in 3-mL Teflon® vials. Analysis was performed in a Quantulus™ 1220 ultra-low level liquid scintillation spectrometer as detailed elsewhere (Beramendi-Orosco et al. 2006). Each sample was analyzed for 2500 min, distributed in 50 cycles, alternating sample vials with oxalic acid SRM 4990C standard and background vials. The counting window was set to optimize the figure of merit with a ^{14}C counting efficiency higher than 65% and the background <0.2 CPM/g C. The ^{14}C results are reported as $\Delta^{14}C$ corrected for isotopic fractionation and decay (Stuiver and Polach 1977).

Stable ^{13}C isotope analyses were performed at the Laboratory of Stable Isotopes Spectrometry at the Institute of Geology, UNAM. Measurements were made using a Finnigan DELTAplus XL mass spectrometer with dual inlet and elemental analyzer Flash 1112EA and ConFloIII as interface. Results are reported as $\delta^{13}C$ relative to the Vienna Pee Dee belemnite standard (VPDB) with a precision of 0.2‰ and normalized with NBS-19 (calcite standard reference material) and LSVEC (lithium carbonate standard reference material) scale according to Coplen et al. (2006).

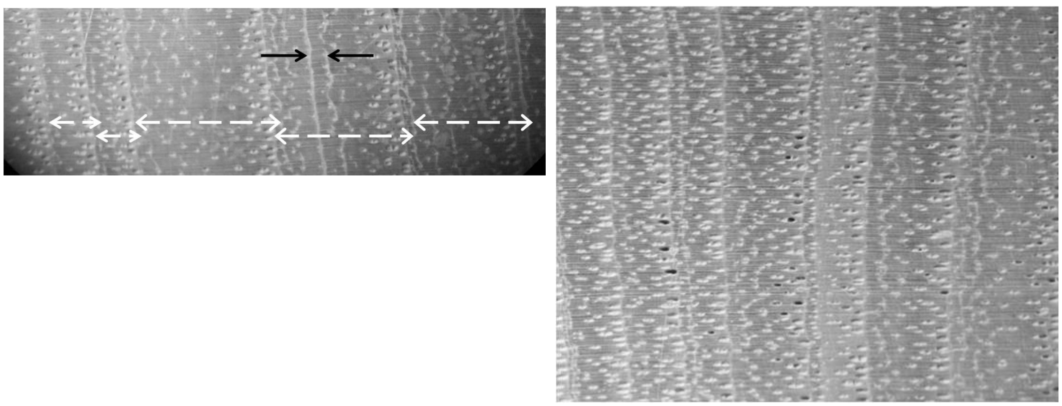

Figure 2 Photographs of *Fraxinus uhdei* growth rings under the microscope. Tree rings are marked by white arrows and black arrows indicate the presence of a false ring (left).

Calculation

The magnitude of the local Suess effect (^{14}S) was calculated with Equation 1 (Rakowski et al. 2001), where $\Delta^{14}C$ is the local atmospheric ^{14}C concentration, obtained from the corresponding *Fraxinus uhdei* growth ring, and $\Delta^{14}C_{Bkg}$ is the ^{14}C concentration of the background atmosphere (clean air) corresponding to the NH zone 2 data (Hua and Barbetti 2004):

$$^{14}S = \frac{\Delta^{14}C - \Delta^{14}C_{Bkg}}{1000 + \Delta^{14}C_{Bkg}} \times 100 \tag{1}$$

The concentration of fossil CO_2 (C_{fossil}) was estimated with Equation 2, considering that fossil fuels do not contain ^{14}C and that the biospheric contribution has a $\Delta^{14}C$ equal to that of the background atmosphere (Levin et al. 2003).

$$C_{fossil} = C_{Bkg}\left[\frac{\Delta^{14}C_{Bkg} - \Delta^{14}C}{\Delta^{14}C_{Bkg} + 1000}\right] \tag{2}$$

where C_{Bkg} is the CO_2 concentration of clean air and corresponds to mean values between data reported for Mauna Loa station (Keeling et al. 2009) and reconstructed from Antarctic ice cores (Etheridge et al. 1996).

RESULTS AND DISCUSSION

The ^{14}C results are plotted in Figure 3 and tabulated in Table 1. Samples presumably corresponding to the years 1955, 1956, and 1960 did not yield enough sample quantity to be analyzed by liquid scintillation spectrometry. The obtained $\Delta^{14}C$ values for *Fraxinus uhdei* growth rings follow the same pattern as the Northern Hemisphere zone 2 calibration curve (Hua and Barbetti 2004), with a high correlation coefficient (r = 0.990, p < 0.001) and a peak centered in 1964 with a value of 680.02 ± 2.33‰. Although the value for the peak year is lower than the mean value of the NH zone 2 calibration curve by 124‰, these results indicate that the estimated years correspond to the real year of growth, confirming the annual nature of the rings, and also prove that the bands not associated to a change in vessel density are indeed false rings. The fact that the rings are formed annually, and that there are few false rings in the studied sequence (only 4 in 69 growth rings), suggest that *F. uhdei* has potential for dendrochronological studies, as was previously reported by Miranda-Aviles et al. (2009). In that study, it was possible to generate a 160-yr-long standard chronology from crossdating 28 increment cores from 10 trees sampled in Queretaro State, central Mexico.

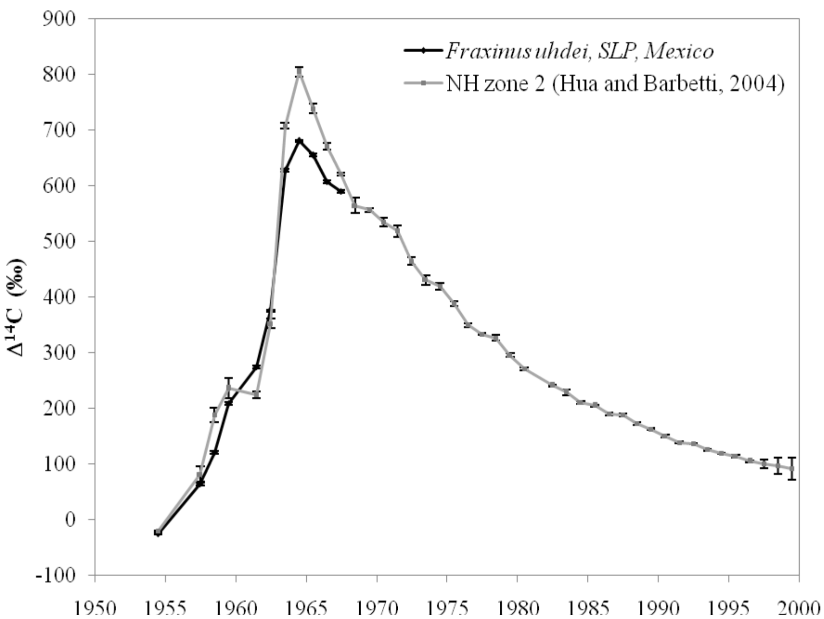

Figure 3. Comparison between obtained $\Delta^{14}C$ values for *Fraxinus uhdei* growth rings from San Luis Potosí City, México, and NH zone 2 values reported by Hua and Barbetti (2004). Note that rings corresponding to the years 1955, 1956, and 1960 were not analyzed (see text for details).

An important feature of the obtained $\Delta^{14}C$ values is that most of them are lower than those reported for the NH zone 2 curve (Hua and Barbetti 2004), with only 2 yr (1961 and 1962) having values higher than the calibration curve. The lower values differ from the NH zone 2 curve by between 4.77 and 124‰, and can be attributed to the ^{14}C dilution caused by fossil CO_2 emissions in the studied area. The 2 samples with $\Delta^{14}C$ values higher than the NH zone 2 data correspond to the years of the sharp increase in the global ^{14}C atmospheric concentration, and thus the difference between the obtained data and the mean values for the NH zone 2 curve can be attributed to a lag in the distribution of the excess ^{14}C produced, mainly in high latitudes of the Northern Hemisphere, during these years. The value for 1961 in San Luis Potosí is even higher than the values reported for areas covered by the NH zone 1 (mean 232 ± 4‰) and comparable to the values reported for the small peak registered at the NH zone 1 during 1959, further suggesting a lag in bomb-produced ^{14}C distribution towards the south. Moreover, for these years there are just 2 data sets available for constructing the NH zone 2 curve, neither from the American continent. For 1961, the value of the NH zone 2 curve corresponds to only 1 reported value from Agematsu, Japan (222.7 ± 5.8‰); and for 1962, the curve value corresponds to the mean of 2 reported values, one from Agematsu, Japan (349.5 ± 3.7‰) and the other from Mts Chiak and Kyeryong, Korea (381.0 ± 12.7‰).

The magnitude of the Suess effect (^{14}S) and the concentration of fossil CO_2 (C_{fossil}) estimated for the studied area are given in Table 1 and plotted in Figure 4. The 2 yr with values higher than the NH zone 2 curve were excluded from the calculations because they do not fit the assumption of a ^{14}C dilution resulting from fossil fuel burning; however, it is important to stress that this does not mean that during these years there was no emission of fossil-fuel-derived CO_2 in the studied area. The ^{14}S varied between –6.9% and –0.5% (mean of –3.6%), corresponding to C_{fossil} concentrations ranging between 21.9 and 1.5 ppmv (mean 7.6 ppmv).

Table 1 $\Delta^{14}C$ values obtained for *Fraxinus uhdei* growth rings, estimation of Suess effect, and fossil CO_2 concentration for San Luis Potosí (SLP).

Year[a]	$\Delta^{14}C$ (‰ ±1σ)	Suess effect ^{14}S (%)	Background CO_2 (ppmv)[b]	Fossil CO_2 SLP (ppmv)
1954.5	–25.77 ± 2.32	–0.49	312.4	1.50
1957.5	63.44 ± 2.32	–1.62	314.2	5.10
1958.5	120.24 ± 2.38	–5.62	314.9	17.71
1959.5	208.31 ± 2.34	–2.16	315.8	6.82
1961.5	273.22 ± 2.35	—	—	—
1962.5	374.66 ± 2.35	—	—	—
1963.5	626.56 ± 2.39	–4.71	318.7	15.02
1964.5	680.02 ± 2.33	–6.87	319.3	21.95
1965.5	654.31 ± 2.33	–4.82	320.0	15.41
1966.5	606.44 ± 2.32	–3.86	321.1	12.41
1967.5	589.81 ± 2.39	–1.86	321.9	6.00

[a] 1955, 1956, and 1960 were not analyzed due to small sample size.

[b] Background CO_2 concentrations correspond to mean values reported for Mauna Loa station (Keeling et al. 2009) and reconstructed from Antarctic ice cores (Etheridge et al. 1996).

These estimates are similar to values reported for other urban areas. For example, Rakowski et al. (2001) reported ^{14}S values between –8.7% and 1.4% estimated from ^{14}C in tree rings from forests in urban areas in southern Poland for the period 1965–1995. In another study Rakowski et al. (2008) reported yearly mean C_{fossil} values, derived from tree-ring $\Delta^{14}C$ data, of 12.6 and 3.6 ppmv for Nagoya, Japan (1967–2002), of 5.9 ppmv for Kraków, Poland (1983–2003), and 4.56 ppmv for Arequipa, Peru (1986–1992). Furthermore, for Heidelberg, Germany, a mean C_{fossil} value of 10.96 ppmv for the period 1986–2006, with values ranging from ~5 ppmv in summer to 20 ppmv in winter, has been estimated from comparing monthly $\Delta^{14}CO_2$ observations at Heidelberg and Jungfraujoch (Levin et al. 2008). In a more recent study based on tree rings, Djuricin et al. (2012) estimated fossil fuel CO_2 mixing ratios between 3 and 23 μmol mol^{-1} for the period 1980–2008 for 6 sites within the Los Angeles basin, demonstrating also that tree-ring $\Delta^{14}C$ data can be useful to resolve local and temporal variability in fossil-fuel-derived CO_2 emissions.

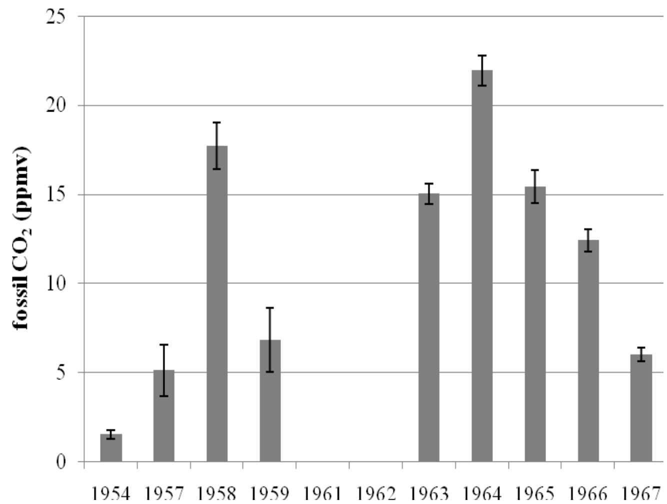

Figure 4 Estimates of fossil CO_2 concentration (in parts per million in volume [ppmv]) for the urban area of San Luis Potosí, México.

As there was a significant growth in SLP's population during the studied period, it would be reasonable to expect finding an increase in fossil-fuel-derived CO_2. However, the estimated fossil CO_2 concentrations have significant variations with no apparent monotone increasing trend. This could be explained by CO_2 emissions from diverse sources, including those containing ^{14}C. Possible CO_2 sources enriched in ^{14}C are related to biomass combustion, either from its use as fuel, mainly for cooking and heating during the winter months, or from agricultural burning to prepare the land (still a common practice in Mexico). Respiration-derived CO_2 could also be a significant source of $^{14}CO_2$ as it has been reported that aboveground respiration in urban areas could contribute even more CO_2 than other emission sources during spring (Djuricin et al. 2010).

CONCLUSIONS

Based on the results presented, tropical ash (*Fraxinus uhdei*) in the San Luis Potosí (SLP) area forms annual growth rings, and due to the low number of false rings, it appears to be a tropical species with potential for dendrochronological studies. This is relevant because it is a native species to tropical areas between 500 and 2600 m asl, where other tree species commonly used for dendrochronological studies may not be present. Furthermore, the annual nature of the growth rings makes it possible to use this species as a bioindicator of $^{14}CO_2$, aiding in the reconstruction of atmospheric ^{14}C variability. Because *F. uhdei* is widely distributed in Mexico, especially in urban areas, it can be used to reconstruct fossil CO_2 concentrations.

The high $\Delta^{14}C$ variability and lack of clear trend suggest multiple sources of CO_2 emissions for the studied period. It is important to analyze the rest of the tree-ring sequence from SLP in order to evaluate if there is a long-term trend in fossil CO_2 emissions in the area. Finally, it is important to continue generating more $\Delta^{14}C$ data sets from clean areas, especially from the American continent, in order to construct a more representative calibration curve for the NH zone 2. This would yield more accurate estimates of fossil-fuel-derived CO_2 in urban areas.

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