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TEMPORAL AND SPATIAL VARIATIONS OF ATMOSPHERIC RADIOCARBON IN THE MEXICO CITY METROPOLITAN AREA

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ABSTRACT. The Mexico City Metropolitan Area (MCMA) produces a complex mixture of gases and aerosols from diverse sources, including burning of fossil fuels, biomass, and wastes, with a significant biogenic contribution. We present the first results of ongoing projects to study temporal and spatial variations of $^{14}CO_2$ in the area. Temporal variations reconstructed from tree rings of *Taxodium mucronatum* indicate a considerable radiocarbon depletion, in accordance to the vast amount of fossil fuels burnt inside Mexico Valley, with values between 62 and 246‰ lower than background values for the 1962–1968 period, and lower by 51–88‰ for the 1983–2010 period. The lower dilution found for the last decades might indicate an increase in enriched $^{14}CO_2$ sources. Results from the spatial distribution, as revealed from integrated CO_2 samples and grasses from six points within the MCMA collected during the 2013 dry season, show variations between sites and sample types. For integrated CO_2 samples, values range from 35.6‰ to 54.0‰, and for grasses between –86.8‰ and 40.7‰. For three of the sampling points, the grasses are significantly depleted, by up to ~133‰, as compared to the corresponding integrated CO_2 sample. This may result from differences in the carbon assimilation period and exposure to different CO_2 sources. Higher-than-background $\Delta^{14}C$ values were found for all integrated CO_2 samples, presumably resulting from ^{14}C-enriched CO_2 derived from forest fires in the mountains during the sampling period. Results obtained so far confirm the complexity of the ^{14}C cycle in the MCMA.

INTRODUCTION

Radiocarbon in atmospheric CO_2 ($^{14}CO_2$) from urban environments has been used as a direct tracer for fossil-fuel-derived CO_2 to estimate anthropogenic emissions. Because fossil fuels are ^{14}C-free as a result of their age of several million years, the increase in fossil CO_2 emissions has altered the carbon isotopic composition of the atmosphere, more notably in urban and industrial areas, where the $^{14}CO_2$ concentration can be significantly lower than in clean (background) areas (Levin et al. 2003; Turnbull et al. 2006). This approach has been successfully applied for cities in Europe, Asia, and North America with fossil fuel burning as the major source of anthropogenic CO_2, by monitoring atmospheric $^{14}CO_2$ (e.g. Takahashi et al. 2002; Turnbull et al. 2006; Kuc et al. 2007; Levin et al. 2008; Molnár et al. 2010; Zhou et al. 2014). Another important anthropogenic perturbation to atmospheric ^{14}C levels was its significant increase, up to twice the natural levels, derived from the atmospheric nuclear tests performed during the 1950s and 1960s. After the Nuclear Test Ban treaty, signed in October 1963, $^{14}CO_2$ 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 in the last 4 decades. 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), with the possibility of reconstructing ^{14}C levels, with annual resolution, from tree rings (Hua and Barbetti 2004).

Mexico City and its metropolitan area (MCMA) comprise the biggest megacity in North America. The MCMA is located in a high-altitude (~2300 m asl) closed basin surrounded by mountains and

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one active volcano (Popocatepetl, in the eastern MCMA). There are more than 20 million inhabitants, around 30,000 manufacturing industries, and 5.9 million vehicles. Despite being such a big megalopolis, only 65% of the area classifies as urban soil, and the rest corresponds to rural, forest, and shrub-lands (INEGI 2014; SEDEMA 2013). A result of this complexity is the emission of high levels of a complex mixture of gases and aerosols from diverse sources, including burning of fossil fuels, biomass, and wastes, with a significant biogenic contribution. According to the Metropolitan Environmental Commission of Mexico Valley (CAM), the mean daily consumption of energy during 2012 was equivalent to 47 million liters of gasoline, distributed as 44% gasoline, 25% natural gas, 18% liquefied petroleum gas (LPG), and 13% diesel. The consumption by sector was 59% for transport, 25% for industrial activities, 13% for residential combustion, and 3% for other sources including forest fires, gas storage, and landfills (SEDEMA 2013).

Considering the vast amount of fossil fuels consumed in the area, it would be expected to find a significant ^{14}C dilution in the local atmosphere; however, a previous study reported anomalous high levels of atmospheric $^{14}CO_2$ (Vay et al. 2009). In 2006, MCMA and surroundings were the scope of the multinational MILAGRO campaign (Megacity Initiative: Local and Global Research Observations) with the aim of characterizing the sources and processes of emissions as well as to evaluate the impact at regional and global scales (Molina et al. 2010). In this framework, Vay et al. (2009) reported that only 23% of instantaneous air samples had $^{14}CO_2$ levels below the free tropospheric background value (57 ± 2‰, estimated from the INTEX-B transit flight data obtained over the North Pacific for April 2006), indicating a dilution resulting from the addition of fossil CO_2 (^{14}C-free) to the local atmosphere. Surprisingly, the rest of the samples had values up to 75‰ higher than the background values reported for North America, indicating an important contribution from ^{14}C-enriched CO_2 sources, such as burning of biomass with a mean age of 35 yr and $\Delta^{14}C$ of around 500‰, or even other hotter sources including burning of radioactive wastes (Vay et al. 2009).

Biomass burning as a source of CO_2 in the MCMA is further supported by previous works reporting the presence of retene (1-methyl-7-isopropyl phenanthrene) in the southwestern MCMA (Bravo et al. 2006; Amador-Muñoz et al. 2013). Retene is a polycyclic aromatic hydrocarbon marker of softwood combustion generated from the burning of vegetation (Ramdahl 1983). High concentrations have been reported for the dry warm season (March-April), with especially high levels in 1998 due to the presence of many fires around the valley caused by severe dry conditions associated with the El Niño phenomenon (Amador-Muñoz et al. 2013). Up to 40% of the total seasonal variability in rainfall for Mexico may be explained by the El Niño–Southern Oscillation (ENSO) (Magaña et al. 2003).

With the aim of gaining a better understanding of the ^{14}C cycle in such a complex area, we are conducting three projects to establish temporal and spatial variations of $^{14}CO_2$ as revealed from tree rings, grasses, and integrated CO_2 samples. This article presents the first results of annual variations reconstructed from annual growth rings of *Taxodium mucronatum* sampled in the central area of MCMA, and results of a study of the spatial variations, as revealed from integrated CO_2 and grasses at six points with different traffic regimes, population density, and CO_2 sources with a seasonal resolution since April 2013.

METHODOLOGY

Study Area

The MCMA is located in a high-altitude (~2300 m asl) volcano-tectonic basin, surrounded by mountains to the south, east, and west, and almost completely open on the north side. It comprises Mexico City and 88 municipalities, covering an area of about 1800 km^2. The MCMA can be divided into urban areas (65.5%) and conservation areas (34.5%, including rural soils, forests, and shrub-

lands). The industrial activity is mainly concentrated in the northern and eastern parts of Mexico City, mixed with highly populated areas. The central, southern, and western zones are dominated by residential, commercial, and conservation areas (SEDEMA 2013).

The Mexico City Basin is located in tropical-subtropical latitudes (19°36′ to 19°20′N) with climate tempered by altitude and influenced by tropical air masses during summer (May to October) and mid-latitude cold air masses from North America during winter (Jauregui 2004). The mean annual temperature is 16°C and the annual precipitation, concentrated in summer months, is 400–500 mm in the northern part of the basin and 700–1200 mm in the central and southern parts (Jauregui 2004; INEGI 2014).

The population has grown considerably in the last decades, though since 1990, the growth has been mainly in the metropolitan area. In 1950, there were around 3 million inhabitants in Mexico City, with the metropolitan area dominated by small rural communities. In 1970, there were 6.87 million inhabitants in Mexico City and 2.19 million in the metropolitan area; by contrast, in 2010, Mexico City had around 8.85 million inhabitants, whereas the metropolitan area had more than 11.7 million inhabitants (Escamilla-Herrera and Santos-Cerquera 2012; INEGI 2014).

Sampling and Sample Preparation

Tree Rings

The sampling site for the annual reconstruction was Chapultepec Forest, the largest park in the MCMA. It is an urban forest located in northwest Mexico City in the downtown district (from 19°23′40″ to 19°25′45″N and 99°10′40″ to 99°14′15″W). This sampling site was selected because this location has been inside the urban area for centuries and a master dendrochronology has been previously reported (Villanueva-Diaz et al. 2003). Three specimens of *Taxodium mucronatum*, the most common native species present in this park, were sampled using a 12-mm Pressler incremental borer at about 1.5 m height, taking three ring cores from each tree. To establish the ^{14}C background values for Mexico City's latitude, a tree of the same species was sampled in the same way at Barranca de Amealco (20°21′50″N, 100°06′22″W), a steep gorge located in an uncontaminated area away from the influence of urban areas, 140 km to the NW from Mexico City. This site was selected because a *T. mucronatum* master dendrochronology has already been reported (Stahle et al. 2011).

Samples were dried for 48 hr at 60°C, mounted on wooded core mounts, and sanded with increasing grit number sandpaper (400–1500) to expose cell structures. To avoid cross-ring contamination, the generated dust was removed with a brush and vacuum. The annual rings were counted under stereoscopic microscopes and the chronologies were established by comparison with the master dendrochronologies already reported for this species in both sampling sites (Villanueva et al. 2003; Stahle et al. 2011).

Integrated Atmospheric CO_2

Sampling points correspond to five stations of the Atmospheric Monitoring Network of Mexico City's environmental authority (SIMAT in Spanish), where criteria pollutants (CO, NO_X, O_3, SO_2, $PM_{2.5}$, PM_{10}) have been monitored since the late 1980s. Meteorological parameters (temperature, pressure, relative humidity, and wind speed and direction) are also monitored at some of the stations. The five stations (out of 44 in the network) were selected as representative of the different areas of the valley, with diverse traffic regimes, commercial activities, population density, and CO_2 sources and wind regimes (Figures 1, 2; Table 1). Tlalnepantla (referred to as NW) is located to the northwest in a mainly industrial area; San Agustín (referred to as NE) is located to the northeast and characterized as an industrial and densely populated area; Merced (referred to as C), located in the central district

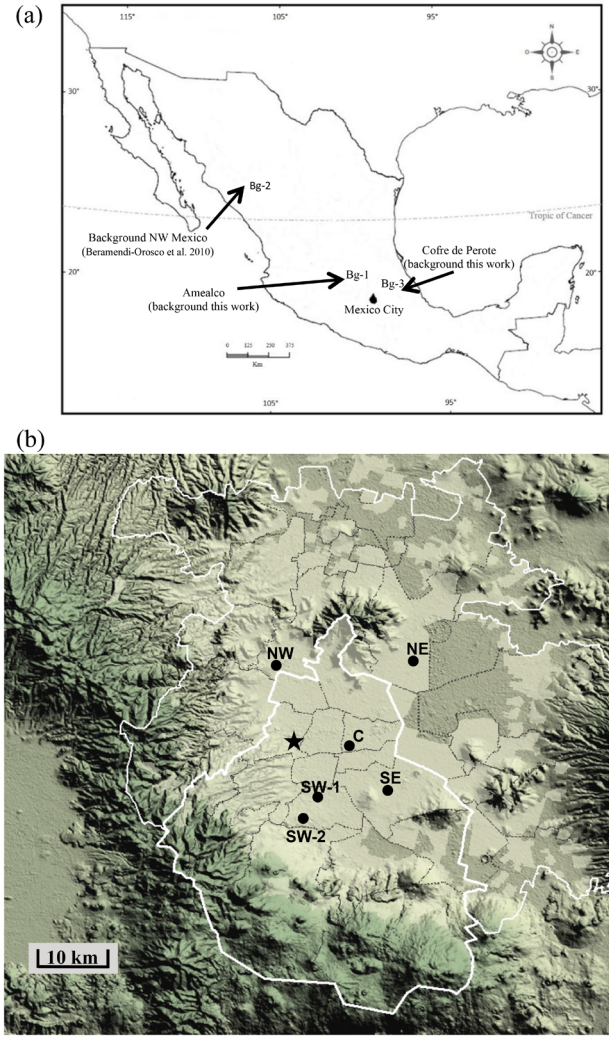

Figure 1 (a) Map of Mexico showing location of Mexico City (black dot) and the background sampling sites. (b) Map of MCMA showing sampling sites for tree-ring samples (black star) and for CO_2 and grass samples (black circles). Maps modified from INEGI (http://cuentame.inegi.org.mx/mapas/).

of Mexico City, represents a commercial and residential area; Coyoacán in southwest Mexico City (referred to as SW-1) is located in a residential area with lower population density; and Iztapalapa (referred to as SE) is located inside the campus of the Universidad Autónoma Metropolitana in an industrial, commercial, and residential area. The sixth sampling point corresponds to the rooftop of a 3-story building inside the main campus of the Universidad Nacional Autónoma de México (referred to as SW-2) located at the southern end of the urban area of Mexico City, adjacent to the place where a monthly $^{13}CO_2$ and $^{14}CO_2$ monitoring program has been performed by our research group since 2009.

Integrated samples were collected by pumping air (20 mL min^{-1}) continuously through a column with 1 L of a 0.7M NaOH solution (carbonate-free, Sigma-Aldrich Mexico) for 30 days, at a height between 4 and 10 m from ground level. Immediately after sampling, CO_3^{2-} was precipitated as $BaCO_3$ by adding an excess of $BaCl_2$, dried at 50°C, and stored in glass flasks inside a vacuum desiccator until analysis. The sampling procedure was adapted from Levin et al. (1980) and Povinec et al. (1986), setting the flow rate of air through the NaOH solution after potentiometric titration of the final solution, in order to have an excess of OH^- anions to guarantee a quantitative CO_2 retention.

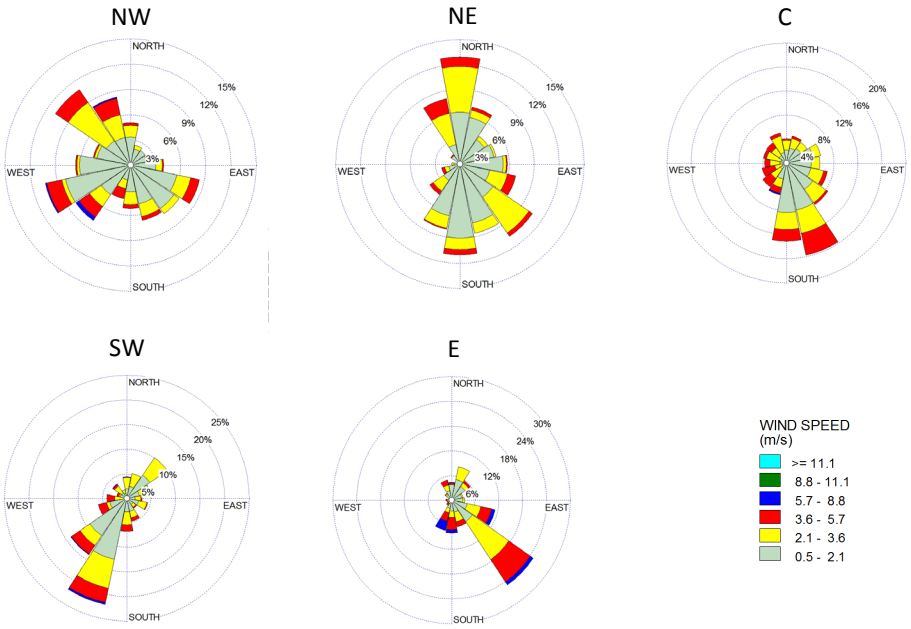

Figure 2 Wind roses for the sampling period (5 April–6 May 2013) with data registered at SIMAT stations Tlalnepantla (NW), San Agustín (NE), Merced (C), Pedregal (SW, nearest meteorological station to SW-2 and SW-1 sampling points), and Nezahualcóyotl (E, nearest meteorological station to SE sampling point). Calm wind conditions (wind speed <0.5 m s^{-1}) were lower than 3.54% of the sampled period. Data taken from SIMAT (http://www.aire.df.gob.mx/default.php?opc=%27aKBhnmI=%27&opcion=Zw).

Table 1 Description of sampling sites within the MCMA.

Site name	Position within MCMA	Coordinates	Main characteristics
Tlalnepantla	Northwest, NW	19°31′42″N, 99°12′15″W	Commercial/residential/industrial area. Medium traffic.
San Agustín	Northeast, NE	19°31′56″N, 99°01′48″W	Commercial/residential/industrial area. High traffic.
Merced	Central, C	19°25′28″N, 99°07′09″W	Commercial/residential area. High traffic.
Iztapalapa	Southeast, SE	19°21′45″N, 99°04′16″W	Universidad Autónoma Metropolitana Commercial/industrial area. High traffic.
Coyoacán	Southwest, SW-1	19°20′58″N, 99°09′26″W	Commercial/residential area. Medium traffic.
UNAM	Southwest, SW-2	19°19′19″N, 99°10′37″W	Surrounded by buildings and ecological reserve. Commercial/residential areas nearby. Medium traffic.

[a]Information taken from INECC (2012).

Grass Samples

Grasses that were already growing close to the sampling stations at ground level (except for NW) were trimmed with stainless steel scissors the same day the atmospheric CO_2 capture systems were installed, leaving 1.5 cm for regrowth. Sampling was performed on the same day the CO_2 capture

systems were removed. In this way, the sampled grasses fixed C during the same CO_2 sampling period. At the NW sampling point, it was not possible to obtain a grass sample. Immediately after trimming, samples were packed in aluminum foil and, once in the laboratory, were washed with deionized water, dried at 50°C, and stored in aluminum foil until analysis. Sampled species, identified by a botanical expert at the Faculty of Sciences-UNAM, were *Cynodon dactilon* (C_4 metabolism species) in NE; *Bromus catharticus* (C_3 species) in C; *Pennisetum clandestinum* (C_4 species) in SW-1 and SE; and *Bouteloua gracilis* (C_4 species) in SW-2. We acknowledge that sampling different grass species makes the interpretation of the $\Delta^{14}C$ data a difficult task, as differences in CO_2 uptake and growth can result in $\Delta^{14}C$ significantly different between plants growing at the same conditions, and thus could be misinterpreted as different contribution of fossil CO_2 (Bozhinova et al. 2013).

Annual Plants

To establish a ^{14}C background for 2013, leaves from annual plants (*Senecio cinerariodes* and *Lupinus montanus*) were sampled during May 2013 at Cofre de Perote Mountain (19°29′30″N, 97°09′13″W), ~200 km away from the MCMA. Leaves were collected with stainless steel scissors and packed in aluminum foil. Once in the laboratory, samples were washed with deionized water, dried at 50°C, and stored in aluminum foil until analysis. These samples were used as the background for 2013 as the tree-ring sequence from the other background site (Amealco) did not cover this year, and it was not possible to organize a field trip to Amealco during 2013. Despite its different location and that care should be taken with the interpretation of $\Delta^{14}C$ from annual plants, in terms of different plant parts and growth periods (Bozhinova et al. 2013; Turnbull et al. 2014), this sample was analyzed to provide a reference value for the ^{14}C levels in clean air, as it has been demonstrated that the gradient in background ^{14}C distribution is only a few per mil (Levin et al. 2010; Graven et al. 2012).

Sample Analysis

Tree Rings

Individual tree rings were analyzed by accelerator mass spectrometry (AMS) at the Centro Nacional de Aceleradores (CNA), Seville, Spain. Prior to measurement, previously cleaned samples were graphitized using the AGE system (Wacker et al. 2010a). This system couples an elemental analyzer (EA) to the graphitization unit. Approximately 3 mg of wood was wrapped in tin foil and loaded in the EA, where it was combusted. The columns inside the EA separate the gases produced in the combustion, loading the reactor of the graphitization unit with the CO_2, and releasing to air the other components. H_2 is added to the reactor with Fe used as a catalyst to reduce CO_2 to graphite. Ovens are used to heat the part of the reactor where the reducing reaction takes place, and Peltier coolers are used to freeze the water produced in the reaction. The system prepares samples of ~1 mg C, and allows the preparation of seven samples in parallel, fully automatized.

Once graphitized, samples were measured in the MICADAS system (Synal et al. 2007). This ^{14}C detection system works at 200 kV and selects charge state 1+ after the stripping process for a total ion energy of 440 keV. Ions are counted in an ionization chamber. The major interference in the identification of ^{14}C is the molecular fragment ^{13}C coming from the ^{13}CH molecule. A special Faraday cup measures the current of this molecular fragment at the high-energy side and the number of counts in the detector is corrected correspondingly. $\delta^{13}C$ is measured simultaneously in the graphite for a proper correction of the results.

Samples were measured for 1 hr and data were analyzed using the BATS software (Wacker et al. 2010b). Oxalic acid II (SRM 4990C) was used as the normalization standard. The mean analytical

relative uncertainty of the reported data was 0.42%. The ^{14}C results are reported as $F^{14}C$ and $\Delta^{14}C$ corrected for both isotopic fractionation and decay (Stuiver and Polach 1977; Reimer et al. 2004).

Integrated Atmospheric CO_2, Grass, and Plant Samples

^{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, clean samples were transformed to benzene (1.5 mL) in a vacuum synthesis line and mixed with 0.5 mL of scintillation cocktail (PPO + POPOP dissolved in dead spectrophotometric-grade benzene) in 3-mL Teflon® vials. Analyses were performed in a Quantulus™ 1220 ultra-low-level liquid scintillation spectrometer as detailed in Beramendi-Orosco et al. (2006). Each sample was analyzed for 2500 min distributed in 50 cycles, alternating sample vials with oxalic acid II (SRM 4990C) standard and background vials. The counting window was set to optimize the figure of merit [defined as the ratio (counting efficiency)^2/background], with a ^{14}C counting efficiency higher than 65% and the background less than 0.2 counts per minute g^{-1} C. The ^{14}C results are reported as $F^{14}C$ and $\Delta^{14}C$ corrected for both isotopic fractionation and decay (Stuiver and Polach 1977; Reimer et al. 2004).

To correct $\Delta^{14}C$ values for isotopic fractionation, $\delta^{13}C$ analyses were performed at the Laboratory of Stable Isotopes Spectrometry at the Institute of Geology UNAM. Results are reported as $\delta^{13}C$ relative to the Vienna Pee-Dee Belemnite (VPDB) standard, with a precision of 0.2‰ and normalized with NIST and IAEA standard reference materials (NBS 22, PEF1, IAEA CH6, USGS 40, and USGS 41).

RESULTS AND DISCUSSION

Tree Rings – Temporal Trend

Results obtained so far for tree-ring samples from Chapultepec (urban) and Amealco (background) are presented in Table 2, and compared to reported background values in Figure 3. ^{14}C values obtained for Amealco are in agreement with previously reported background values for the Northern Hemisphere (NH) zone 2, confirming that this area can be considered as background. When compared to the international curve for NH zone 2 (Hua et al. 2013), considered as the background values for the latitudes corresponding for all Mexico, the differences between the two data sets, for rings 1970–2007, are within 1σ, except for 2007, which is within 2σ. For the pre-1970 period, despite that only two samples have been analyzed, the difference between the data sets seems to be significant. For 1964, the difference is ~70‰ as compared to the NH zone 2 curve, and ~23‰ as compared to the previously reported data for NW Mexico (Beramendi-Orosco et al. 2010).

Values obtained for tree rings from Chapultepec (Mexico City) follow a similar increasing trend as the background values for the period 1953–1960, being closer to those reported for NW Mexico than to those of the NH zone 2 curve. For samples post-1962, the values obtained for tree rings from Chapultepec are significantly ^{14}C depleted with respect to all the background data sets, indicating a significant ^{14}C dilution by fossil CO_2 in the urban atmosphere. This depletion was expected considering the vast amount of fossil fuels burned inside the valley; however, the magnitude of dilution seems bigger in the mid-1960s than in more recent decades. For years 1962.5–1965.5, the confidence intervals (95% level) are lower than the confidence intervals for NH zone 2 by between 113 and 205‰; whereas for years 1983.5, 1990.5, and 2010.5, the confidence intervals are lower than the NH zone 2 confidence intervals by 65, 43, and 37‰, respectively. This is somehow unexpected considering the significant growth in the consumption of fossil fuels associated with the increase in population and extension of MCMA since 1970, with a population increase from 9.06 million inhabitants in the valley to more than 20.55 inhabitants in 2010, and an increase of 245% in the number of registered vehicles from 1990 to 2010 (Escamilla-Herrera and Santos-Cerquera 2012; INEGI 2014).

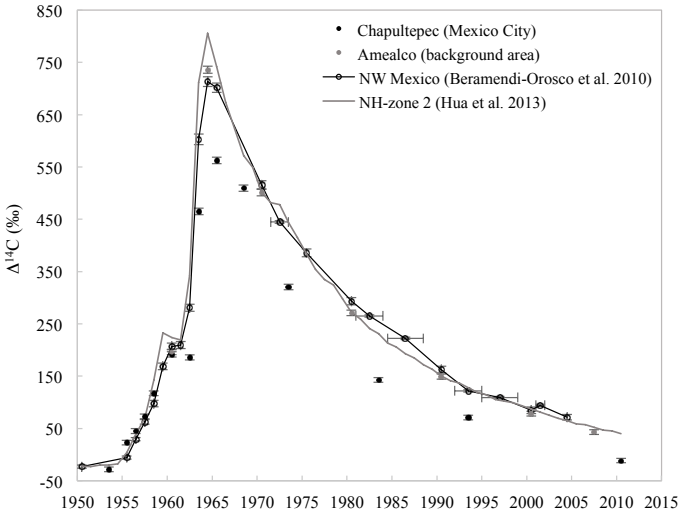

Figure 3 $\Delta^{14}C$ values for tree rings from Chapultepec Park, Mexico City (black circles), and tree rings from Amealco (background area, gray diamonds). Vertical error bars correspond to ±1σ. Background values from NH zone 2 (Hua et al. 2013, gray line) and from tree rings from NW Mexico (Beramendi-Orosco et al. 2010, black line) are plotted for comparison. Horizontal error bars reflect the number of years comprising samples analyzed by liquid scintillation in the data set from NW Mexico.

Table 2 $F^{14}C$ and $\Delta^{14}C$ values for tree-ring samples from Chapultepec Park in Mexico City and Amealco (background site).

Sample code	Year	$F^{14}C$ ±1σ	$\Delta^{14}C$ ±1σ (‰)	Difference from mean NH zone 2 (‰)
Chapultepec Park, Mexico City				
CNA-2647.1.1	1953.5	0.9793 ± 0.0044	–28.3 ± 4.3	–8
CNA-2645.1.1	1955.5	1.0311 ± 0.0046	23.1 ± 4.5	19
CNA-2644.1.1	1956.5	1.0531 ± 0.0047	45.0 ± 4.6	6
CNA-2646.1.1	1957.5	1.0813 ± 0.0048	73.0 ± 4.8	3
CNA-2814.1.1	1958.5	1.1258 ± 0.0047	117.2 ± 4.7	–26
CNA-2643.1.1	1960.5	1.2011 ± 0.0052	191.8 ± 5.2	–32
CNA-2813.1.1	1962.5	1.1949 ± 0.0049	185.7 ± 4.9	–156
CNA-2642.1.1	1963.5	1.4765 ± 0.0064	465.1 ± 6.3	–246
CNA-2815.1.1	1965.5	1.5749 ± 0.0064	562.7 ± 6.4	–179
CNA-2816.1.1	1968.5	1.5213 ± 0.0062	509.6 ± 6.2	–62
CNA-2641.1.1	1973.5	1.3306 ± 0.0053	320.3 ± 5.3	–124
CNA-2640.1.1	1983.5	1.1518 ± 0.0046	142.9 ± 4.6	–88
CNA-2638.1.1	1993.5	1.0791 ± 0.0043	70.8 ± 4.3	–57
CNA-2638.1.1	2010.5	0.9962 ± 0.0041	–11.5 ± 4.1	–51
Amealco (background)				
CNA-2637.2.1	1960.5	1.2056 ± 0.0052	196.3 ± 5.2	–28
CNA-2636.2.1	1964.5	1.7495 ± 0.0071	736.0 ± 7.0	–70
CNA-2635.2.1	1970.5	1.5128 ± 0.0063	501.1 ± 6.3	0
CNA-2634.2.1	1980.5	1.2811 ± 0.0055	271.2 ± 5.4	–1
CNA-2633.2.1	1990.5	1.1581 ± 0.0050	149.2 ± 4.9	–1
CNA-2632.2.1	2000.5	1.0868 ± 0.0048	78.4 ± 4.7	–9
CNA-2631.2.1	2007.5	1.0509 ± 0.0046	42.8 ± 4.5	–9

A possible explanation for the higher ^{14}C dilution in the 1960s than in the following 3 decades could be an increase in ^{14}C-enriched CO_2 emissions from biomass burning, deforestation, and land-use change associated with the growth of the urban area. Some other highly enriched sources, such as incineration of radioactive hospital wastes, cannot be ruled out. However, we consider that emissions from the nuclear power plant Laguna Verde, which began operations in 1990 and is located on the coast of the Gulf of Mexico, are unlikely because it is located 300 km to the east of Mexico City at sea level, with the Sierra Madre Oriental mountain range in between. Before estimating the annual variations of the concentration of fossil CO_2 (C_{fossil}) in the urban region, it is important to analyze both tree-ring sequences (Amealco and Chapultepec) with a higher resolution, as this background area seems to be more representative of the variation during the initial years of the ^{14}C bomb perturbation in the latitude corresponding to Mexico City, in agreement with the previously reported ^{14}C data for NW Mexico (Beramendi-Orosco et al. 2010).

Integrated Atmospheric CO_2 and Grasses – Spatial Variations

Results for the integrated CO_2 samples (six sampling points) and grasses (five sampling points) collected during April 2013 are plotted in Figure 4 and tabulated in Table 3. Results show variations, both between sites and between sample types. For integrated CO_2 samples, $\Delta^{14}C$ values range from 35.6‰ to 54.0‰. For grasses, the variation between sites is higher, with $\Delta^{14}C$ values ranging between –86.82‰ and 40.71‰. For three of the sampling points, the grasses are significantly depleted, by up to ~133‰, compared to the corresponding CO_2 sample. For sampling points SW-1 and C, the values for both sample types are within 1σ and 2σ, respectively. The big difference between the $\Delta^{14}C$ values recorded by the grass samples and the corresponding CO_2 sample may be associated

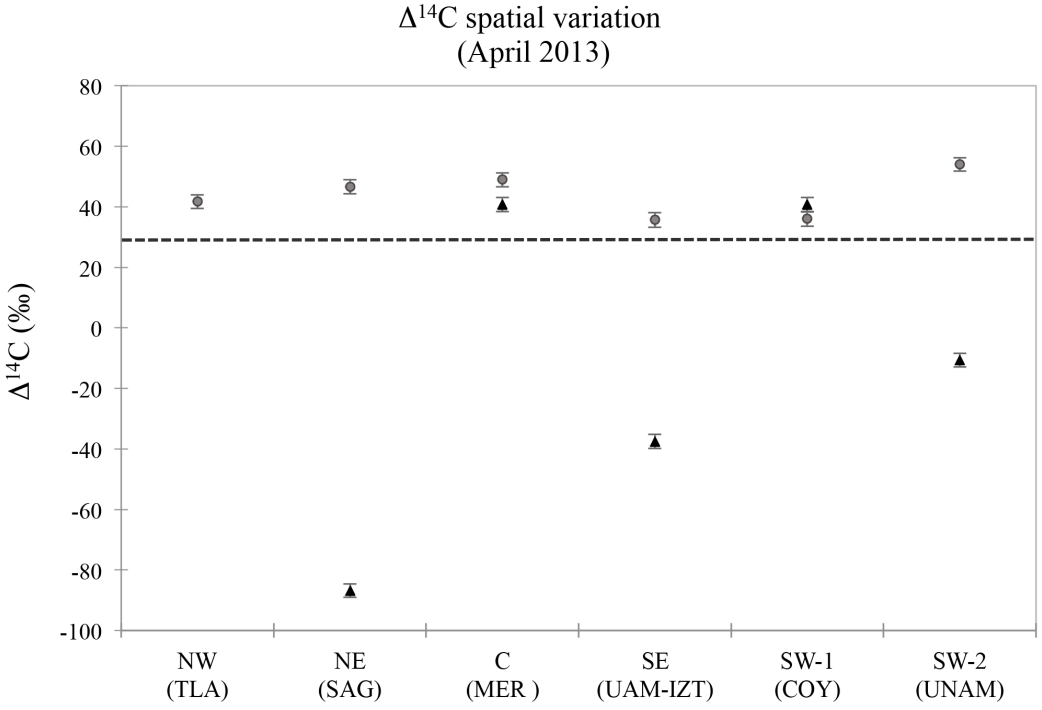

Figure 4 $\Delta^{14}C$ values for integrated CO_2 samples (gray circles) and grasses (black triangles) from six sampling points within Mexico City Metropolitan Area. Horizontal dotted line represents the mean $\Delta^{14}C$ background value from annual plants collected at Cofre de Perote, located 200 km east of Mexico City (see text for details).

with three factors. First, $\Delta^{14}C$ values of grass samples correspond to daytime integrated samples, as C is fixed through photosynthesis. Second, $\Delta^{14}C$ can be related to the residence time of C in grass, which could result in grass samples reflecting $\Delta^{14}C$ values not representative of the same sampling period as the CO_2 samples, which has been described as uncertainties in the CO_2 assimilation period represented by the grass sample (Turnbull et al. 2014). The other factor may be the difference in sampling position and height; grass samples were collected at ground level in open spaces, some of them close to roads and exposed, almost directly, to fossil CO_2 from vehicle exhaust; whereas CO_2 samples were collected on rooftops between 4 and 10 m from ground level, suggesting that at these heights the CO_2 from the different sources has mixed, and thus is more representative of the local atmosphere. The facts that for sampling sites SE and SW-1, with grass samples of the same species (*Pennisetum clandestinum*), there is a big difference (74.14‰) between the $\Delta^{14}C$ values of the grass-integrated CO_2 pair from SE, while $\Delta^{14}C$ values for SW-1 are statistically the same, suggesting that the position of the sample has a larger influence, at least for this grass species. The grass sample from the SW-1 site was collected inside an elementary school, in a courtyard behind a 4-story building approximately 50 m away from the road, whereas the grass sample from the SE site was collected 12 m away from the road in an open area.

Table 3 Radiocarbon levels for CO_2 and grass samples collected at six points within the Mexico City Metropolitan Area.

	Sampling site					
	NW (TLA)	NE (SAG)	C (MER)	SE (UAM-Izt)	SW-1 (COY)	SW-2 (UNAM)
Sampling period (2013)	05/04-07/05	05/04-07/05	08/04-06/05	08/04-06/05	08/04-06/05	08/04-07/05
	Integrated CO_2 samples					
Sampling height (m)	6	5	4	10	10	6
Sample code (UNAM-)	1324	1325	1326	1328	1327	1329
$\delta^{13}C$ (‰)[a]	–13.5	–13.0	–15.1	–17.6	–15.1	–14.9
$F^{14}C$[b]	1.0498	1.0547	1.0571	1.0436	1.0439	1.0622
$\Delta^{14}C$ (‰)[c]	41.68	46.60	48.92	35.60	35.95	54.00
	Grass samples					
Species	n.a.	*Cynodon dactilon*	*Bromus catharticus*	*Pennisetum clandestinum*	*Pennisetum clandestinum*	*Bouteloua gracilis*
Sample code (UNAM-)	n.a.	1356	1358	1353	1352	1331
$\delta^{13}C$ (‰)[a]	n.a.	–17.7	–27.2	–14.1	–14.4	–15.6
$F^{14}C$[b]	n.a.	0.9203	1.0488	0.9699	1.0488	0.9970
$\Delta^{14}C$ (‰)[c]	n.a.	–86.82	40.70	–37.54	40.71	–10.65

[a] $\delta^{13}C$ error ($\pm 1\sigma$) was 0.2‰.
[b] $F^{14}C$ error ($\pm 1\sigma$) was between 0.0022 and 0.0024 for all the samples.
[c] $\Delta^{14}C$ error ($\pm 1\sigma$) was between 2.2‰ and 2.4‰ for all the samples.

Contrary to expectations, the $\Delta^{14}C$ value for the CO_2 sample from SW-1 is significantly lower (95% confidence interval) than those found for samples from areas where the industrial and population densities are higher (NE, NW), suggesting that the fossil CO_2 contribution is higher in SW-1, despite being characterized as a residential area with no industrial activities. Another relevant result is the fact that CO_2 samples were ^{14}C enriched as compared to background values, estimated from $\Delta^{14}C$ analyses of two annual plants, collected during May 2013 at Cofre de Perote Mountain (19°29′30″N, 97°09′13″W), with values of 24.74 ± 2.35‰ and 27.65 ± 2.34‰ (mean 26.20‰,

dotted line in Figure 4). This background value is in agreement with the values reported for the last months of 2012 for North America (between 25 and 32‰, Niwot Ridge, Colorado; data from http://www.esrl.noaa.gov/gmd/dv/iadv/). As mentioned in the Introduction, this is not the first time $\Delta^{14}C$ values higher than background are found for atmospheric CO_2 in Mexico City (Vay et al. 2009). This previous work reported values up to 75‰ higher than the background values, and attributed the ^{14}C enrichment mainly to CO_2 emissions resulting from biomass burning, especially during the dry season, when forest fires are frequent (Vay et al. 2009).

A possible explanation for the high $\Delta^{14}C$ values reported here for the integrated CO_2 samples is also the occurrence of forest fires during the sampling period. According to the National Forestry Commission, there were 1157 fires in the mountains surrounding the valley between January and May 2013 (CONAFOR 2014), with four big forest fires during 13–14 April, two in the southern mountains, one in the mountains between the NW and NE sampling points, and the other fire in the western mountains. Although most of the fires affected mainly shrub-lands dominated by annual species (having a $\Delta^{14}C$ value similar to that of the atmosphere), the organic matter in the burned top-soils, having an age of some decades, could be an enriched source of $^{14}CO_2$ to the atmosphere, with $\Delta^{14}C$ values of up to 500–600‰. The enriched $^{14}CO_2$ produced in the mountains could be transported to the valley by the dominant wind directions (Figure 2), and mixed, at heights were integrated samples were taken, with the CO_2 from the different sources (mainly respiration, fossil fuels, wastes, and biomass incineration), canceling out the ^{14}C dilution resulting from the vast amount of fossil fuels burned in the area. The higher ^{14}C enrichment (significant at 95% confidence level) found for the CO_2 sample from SW-2 could be explained because it is closer to the southern mountains, with the dominant wind direction coming from the SSW during the sampling period (Figure 2). These results are in agreement with the high concentrations of retene previously found for this area (Amador-Muñoz et al. 2013).

CONCLUSIONS

The Mexico City Metropolitan Area is a complex environment, with diverse emission sources, some having high $\Delta^{14}C$ values, thus making the direct use of ^{14}C to estimate fossil CO_2 concentrations in the local atmosphere a difficult task. Temporal variations with annual resolution, as revealed from tree rings, show a significant ^{14}C depletion, with values up to 246‰ lower than background ^{14}C, in accordance with the vast amount of fossil fuels consumed in the area. On the other hand, $\Delta^{14}C$ levels for integrated CO_2 samples, collected during a warm dry month with frequent forest fires in the mountains surrounding the valley, were up to 27‰ higher than the value obtained for a background area for the same sampling year. These results are in agreement with a previous report finding high atmospheric ^{14}C levels for a dry warm period in this complex megacity (Vay et al. 2009).

We believe it is important to continue studying the ^{14}C cycle in this complex urban environment. It is necessary to complete the analyses of tree-ring sequences from both areas to reconstruct annual changes in $\Delta^{14}C$ and calculate accurately the magnitude of ^{14}C dilution, thus being able to estimate an historical trend of emissions, and find a possible explanation for the lower ^{14}C dilution observed for the last decades. Regarding the $\Delta^{14}C$ spatial variations, we are currently analyzing samples for the other sampling campaigns, and in the second stage of this project, we are including other tracers, isotopes, and sample types, such as CO_2 concentration, soil respiration, and analyses of airborne particulate matter (PM). The analysis, both the isotopic and chemical composition, of PM can help to confirm the influence of biomass burning to the higher-than-background values found for the different areas sampled within the MCMA during April 2013.

Finally, because biomonitoring is an inexpensive and easy way to study temporal and spatial $\Delta^{14}C$

variations, it is important to gain a better knowledge of the C dynamics in grasses, which would help in establishing an adequate monitoring resolution and the time correspondence to atmospheric $^{14}CO_2$ concentrations, despite the fact that the plants are daytime-only integrated samples.

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