

Chapter

The Use of Stable Isotopes to Identify Carbon and Nitrogen Sources in Mexico City PM_{2.5} During the Dry Season

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Abstract

Stable nitrogen and carbon isotopes were used to trace the interaction between atmospheric particles < 2.5 mm in diameter (PM_{2.5}) with atmospheric physical variables and atmospheric chemical species in an urban environment. PM_{2.5} were collected daily at two sites in Mexico City during three dry seasons during two-week periods. PM_{2.5} varied between 10 and 70 µg/m³, with the highest concentrations occurring during low-speed southerly winds and the lowest during high-speed easterly winds. Stable carbon isotope composition (δ¹³C) showed that the main carbon source of PM_{2.5} included emissions from fossil fuel combustion, along with low-molecular-weight carbon emissions and suspended dust. Stable nitrogen isotope values (δ¹⁵N) in PM varied between -9.9 and 21.6‰. The most ¹⁵N-enriched particles generally occurred during low wind speeds and correlated significantly with hourly averaged ambient NO_x and NO₂ concentrations. Simultaneous samples from MER (commercial site) and XAL (industrial site) showed that PM_{2.5} mass concentration was generally lighter and the carbon and nitrogen isotopic compositions were heavier at the commercial site relative to the industrial site. The δ¹⁵N of PM_{2.5} increased with the %N in PM_{2.5} concordant with an isotopic fractionation during gas-to-particle condensation. Results suggest that wind speed, along with the nitrogen emission source, determines the nitrogen isotopic composition of PM_{2.5}.

Keywords: PM_{2.5}, δ¹³C, δ¹⁵N, Mexico City, ambient air

1. Introduction

Two major atmospheric contaminants are airborne particulate matter (PM) and nitrogen oxides (NO_x). PM from both natural and anthropogenic sources affect human health and air quality and, although they are size-regulated by national and international environmental standards, its control remains a challenge. PM has been associated with cardiovascular and respiratory diseases and life-expectancy reduction [1]. Because of its small size, PM_{2.5} (PM < 2.5 mm in diameter) enter deep into the lungs and produce short- and long-time effects on the respiratory system,

generating oxidative stress, systemic inflammation, and neuroinflammation, among other ailments [1, 2]. In contrast to PM₁₀ (PM < 10 mm in diameter), which is usually composed of resuspended dust from unpaved roads, industrial emissions, agricultural activity, pollen, and bacteria, PM_{2.5} is formed by combustion processes and the accretion of very small particles and/or condensation of gases on the surfaces of small particles [3]. PM_{2.5} and PM₁₀ contain numerous chemical compounds, such as carbon, sulfates, nitrates, and ammonium, among others, depending on the emission location. Primary particles are emitted directly from sources and can be formed through gas-to-particle conversion known as secondary particles. The secondary inorganic PM fraction is mainly composed of ammonium nitrate and ammonium sulfate whose precursors are emitted as NO_x, SO₂, and NH₃ and then converted to solids through chemical reactions (e.g., [4]).

In turn, nitrogen oxides (NO_x), especially nitrogen dioxide (NO₂), are strong atmospheric oxidants that enhance low atmospheric visibility, play a role in climate change, and are precursors of secondary contaminants [3]. As a result of anthropogenic activities, atmospheric nitrogen species and fluxes in urban environments far outweigh biogenic sources. For example, over 80% of nitrogen oxides (NO_x) are originated by the combustion of fossil fuels for transportation, electricity generation, and industrial activities. This contrasts with the 4% emissions by agricultural and biogenic sources [5]. Other nitrogen species also occur as gases or in particles in the atmosphere. NH₄⁺ salts contribute to the long-range transport of acidic pollutants due to day-scale atmospheric lifetime and after deposition, they can contribute to forest decline and soil acidification. Ammonia and nitric acid are the main precursors of nitrate aerosols. Nitric acid is produced in the atmosphere as an additional reaction product of NO₂, from fossil fuel combustion, biomass burning, or from soil. NO₂ can oxidize and also react to form HNO₃ by pathways relied on the formation of NO₃⁻.

Mexico City Metropolitan Area is characterized by being one of the largest megacities in the world. In addition to its more than 20 million inhabitants and a fleet of over 6 million vehicles, the air quality of the metropolitan area (which includes Mexico City and adjacent municipalities of the States of Hidalgo and Mexico) is affected by industrial and vehicular activity in the north and northeast sectors of the city and by biomass burning from a nearby agricultural activity, which is then transported into the urban area (e.g., [6]). The city lies on a high-altitude plateau (2240 m above sea level) and, except for the NE and SE sectors, is surrounded by mountain chains, which preclude an efficient pollutant dispersion (**Figure 1**). As such, in 2010, the PM_{2.5} annual average concentration of 25 µg/m³ was over two times higher than the recommended annual average of 10 µg/m³ established by the World Health Organization (WHO), which clearly underscores the difficulty to reach the PM regulations [7]. Likewise, in 2010, the NO₂ annual average of 55 µg/m³ was clearly greater than WHO's 40 µg/m³. As a result of control enforcement policies during 2004–2008, PM_{2.5} average concentration decreased by 27% [7], and in 2014, there was a decrease in PM of 11% with respect to 2013. Control measures, such as banning lead from gasoline, the use of natural gas, and mandatory vehicle emission inspection, have consistently decreased PM emissions.

Some studies on Mexico City's atmosphere have reported that PM_{2.5} is mainly composed of 50% carbonaceous aerosol, suggesting an origin from incomplete combustion of fossil fuels and biomass burning, followed by sulfates, nitrates, ammonium, and geological material among others [8, 9]. The main secondary inorganic aerosol components in PM_{2.5} mainly occurred as ammonium sulfate [(NH₄)₂SO₄] and ammonium nitrate [NH₄NO₃] due to the neutralization of atmospheric acids with gaseous

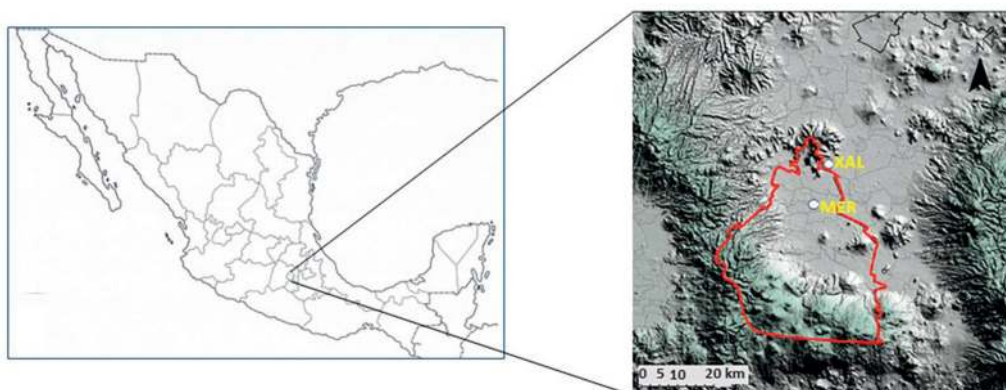


Figure 1.
Study zone where depicting XAL and MER sampling sites in Mexico City Metropolitan Area.

ammonia from agriculture, landfills, industries, biomass burning, and motor vehicles. In Mexico City, measurements made inside roadway tunnels showed a contribution of 8% of NH_4^+ emissions from on-road vehicles [10].

Stable nitrogen (^{15}N and ^{14}N) isotopes are valuable tools to trace the sources and transformations of airborne PM. Examples include tracing the sources of primary and secondary nitrogen in PM_{10} [11], nitrate accumulation in $\text{PM}_{2.5}$ [12], and NO_x contribution in nitrogen dry deposition [13]. On the other hand, stable carbon isotopes (^{13}C and ^{12}C) have been used in urban atmospheres to trace diesel and gasoline combustion, dust, soil and industrial emissions since these have distinct isotopic signatures [14–16]. Here, we use stable carbon isotopes and stable nitrogen isotopes of $\text{PM}_{2.5}$ from a data set to elucidate sources and chemical processes between the nitrogen in particles and several species of atmospheric nitrogen at two contrasting sites during three dry season periods in Mexico City. The sources of $\text{PM}_{2.5}$ are further studied using stable carbon isotopes. This chapter provides a baseline for $\delta^{15}\text{N}$ in Mexico City atmospheric particles as no previous data on N isotopes have been previously published.

2. Methodology

2.1 Sampling

During three two-week sampling campaigns (November 2003 and 2004, and March 2004), $\text{PM}_{2.5}$ samples were collected at two sites with different land use. **Figure 1** shows the two sampling sites, along with the orographic characteristics of the Mexico City Metropolitan Area. La Merced (MER) is an important commercial site with a major food market, located approximately 0.2 km west of downtown; the site is near to moderately traveled paved streets. Xalostoc (XAL) is located in the northeast of the city, adjacent to heavily traveled paved and unpaved roads where old and new gasoline and diesel vehicles transit in an industrialized area; this site is 5 km west of the dry Lake Texcoco, thus resuspended dust from the dry lake bed may affect this site.

Particle samples were collected with battery-powered MiniVol portable $\text{PM}_{2.5}$ samplers (Airmetrics) operating with a volume intake of air of 5 L/min for 24 h. Before sampling, the filtration volume of the samplers was previously calibrated at standard conditions of temperature and pressure. Teflon membranes were used to measure

mass by gravimetry. Details of the equipment and sampling procedures can be found elsewhere [9].

2.2 PM_{2.5} concentration and composition measurements

PM_{2.5} mass was determined by duplicate samples collected on 47 mm Teflon filters, which were weighted in a microbalance prior to and after sampling.

Ions were collected on quartz filters and extracted in deionized water by sonication. Ions were analyzed by high-performance liquid chromatography. Nitrate, sulfate, and ammonium were analyzed by ion exchange chromatography. Organic carbon and elemental carbon were analyzed by thermal-optical reflectance.

2.3 Stable nitrogen and carbon isotopes measurements

Stable carbon and nitrogen isotopes of PM_{2.5} were collected in pre-combusted GF/F filters, which were placed in the MiniVol samplers. After sampling, filters were freeze-dried to remove any water or humidity in the sample, placed in aluminum vials, and inserted into a combustion column. Generated gases (CO₂ and N₂) were analyzed in a MAT-Finnigan 252 stable isotope mass spectrometer to quantify the ¹³C/¹²C and ¹⁵N/¹⁴N isotopes in each sample. Standards used for instrument calibration were acetanilide, methionine, and urea, all with a known isotopic value. An acetanilide substandard was run for every 10 samples. Carbon and nitrogen isotopes are referred to as VPDB and Vienna air nitrogen standards, respectively.

2.4 Meteorological and ambient air data

Ancillary ambient data were obtained from the RAMA and REDMET data sets. RAMA (Spanish acronym for automatic ambient monitoring network; [17]) measures criteria atmospheric pollutants (PM₁₀, CO, CO₂, NO_x, NO₂, SO₂, and O₃) at 15 locations within Mexico City on an hourly basis. At MER, PM_{2.5} hourly data are also measured by RAMA. Wind velocity and direction, relative humidity, and temperature measured on an hourly basis were obtained from the REDMET (meteorological network) database [17]. For each sampling period, the hourly data were averaged, except for wind direction where the hourly mode was used.

3. Results and discussion

3.1 Meteorological characterization

Table 1 gives the basic statistics of meteorological variables during the three periods of study. On average, November 2003 was colder than the other sampling periods. In turn, March 2004 was drier and had the highest wind speeds. November 2004 was characterized by low wind speeds. During the first two sampling periods, the most frequent wind direction was from the NW-NE sectors. In November 2004, both XAL and MER sites were affected by E-SE winds

The diurnal variation of the meteorological parameters during the study is shown in **Figure 2**. The hourly data at each sampling period and site is an average of 14 days. In all three sampling periods and the two sites, early morning was characterized by low temperatures at 6 h, which increased consistently to a maximum at 16 h to then

Date	Site	Temperature (°C)			Humidity (%)			Wind speed (m/s)			Wind direction (°)	
		Average	Min	Max	Average	Min	Max	Average	Min	Max	Max	Mode
Nov 2003	MER	13.96	3.40	24.50	54.27	24.00	90.00	1.18	0.04	3.86	30-60	0-30
	XAL	13.90	4.00	24.00	55.62	21.00	84.00	1.65	0.07	6.52	30-60	0-30
Mar 2004	MER	17.75	8.80	29.1	46.83	19.00	80.00	1.61	0.15	5.07	0-30	330-360
	XAL	16.87	8.60	27.10	53.74	25.00	84.00	2.18	0.02	7.49	0-30	30-60
Nov 2004	MER	17.02	8.60	26.10	54.26	18.00	94.00	1.14	0.17	3.69	60-90	90-120, 30-60
	XAL	16.40	8.80	25.20	53.52	20.00	84.00	0.92	0.04	4.80	120-150	330-360

Table 1.
 Basic statistics of meteorological variables during the three periods of study.

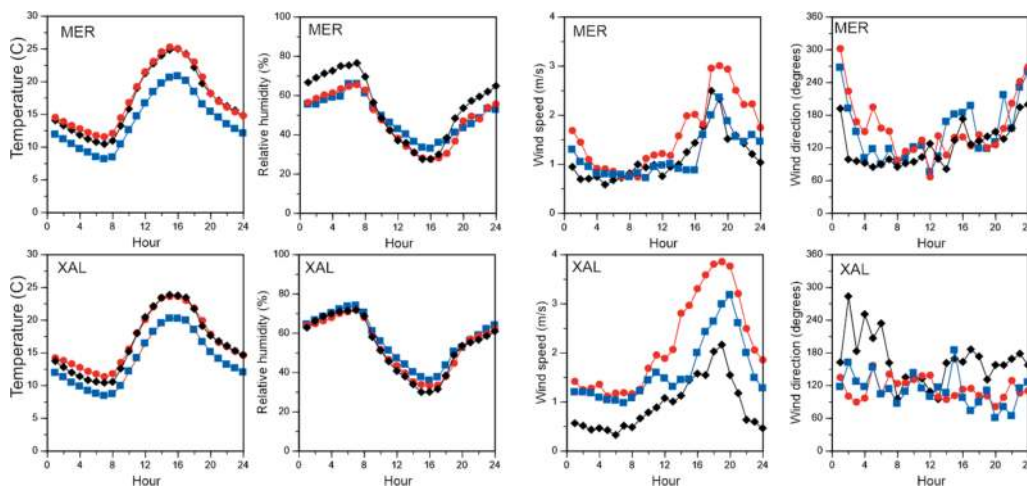


Figure 2. Hourly average of temperature, relative humidity, wind speed, and wind direction at MER and XAL during November 2003 (blue squares), March 2004 (red dots), and November 2004 (black diamonds). Each symbol is the hourly average of 14 days at each sampling site from the Mexico City Meteorological Network (REDMET).

decrease again. In turn, the most humid conditions were present at 6 h and decreased to a minimum of 30% at 16 h. Wind speeds were usually low during the morning hours and increased to a maximum around 18 h, which favors contaminant dispersion from the valley. At MER, low wind speeds were consistently slow until 14 h, in contrast to speeds at XAL where wind speed increased from 6 h to maximum speeds at 18 h. The lowest daily average wind speeds were significantly lower at XAL during November 2004. In general, westerly winds were present at MER between 22 h and the next day 2 h. On average, easterly winds were dominant throughout the rest of the day at both locations.

3.2 PM_{2.5} concentrations

Scatterplots of the daily PM_{2.5} concentrations collected with the MiniVol samplers were compared with the respective average daily PM₁₀ concentrations from hourly measurements from the RAMA stations at XAL and MER (**Figure 3**). At MER, hourly measurements of the MiniVol PM_{2.5} data were also compared with RAMA PM_{2.5} data. The scatterplots show a high correlation ($R^2 > 0.9$) between PM_{2.5} from our MiniVols and the RAMA data and show that our daily samples are representative of the average daily PM_{2.5} concentrations [18]. The high correlation between PM_{2.5} and PM₁₀ further suggests a common source or formation mechanism of these particles. López-Veneroni [14] showed similar correlations in concentrations and carbon isotope compositions for simultaneous PM_{2.5} and PM₁₀ samples in Mexico City.

The average diurnal variations of PM₁₀ at XAL and MER, and of PM_{2.5} at MER from the RAMA stations during the period of study are shown in **Figure 4**. These data provide insight into the time of the major particle accumulation throughout the day. Morning PM_{2.5} concentrations were around 30 $\mu\text{g}/\text{m}^3$ and peaked to 70 $\mu\text{g}/\text{m}^3$ at 10 h. Concentrations then decreased until 18 h and remained constant at 30 $\mu\text{g}/\text{m}^3$ throughout the night and early morning. In contrast, the diurnal variation of PM₁₀ showed two major peaks at 8 h and 18 h, which probably result in particle accumulation during traffic rush hours. During the afternoon, the increase in wind speeds dispersed these pollutants.

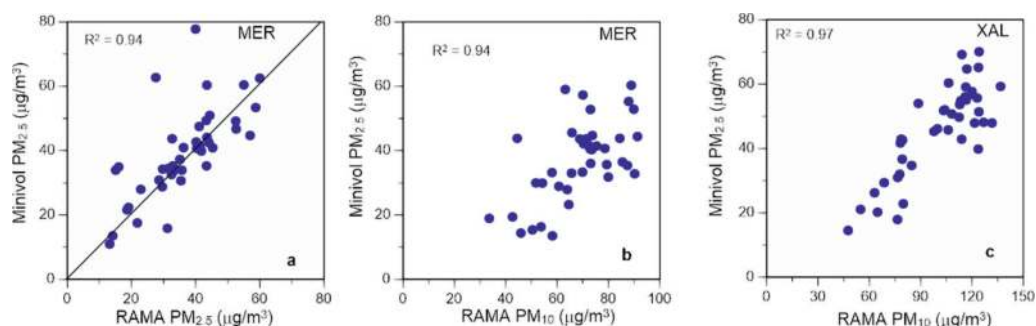


Figure 3. Scatterplots of (a): PM_{2.5} samples collected daily by MiniVol samplers vs. 24 h averaged PM_{2.5} samples from Mexico City atmospheric monitoring automatic network (RAMA) at MER. (b): PM_{2.5} samples collected daily by MiniVol samplers vs. 24 h averaged PM₁₀ from RAMA at MER. (c): PM_{2.5} samples collected daily by MiniVol samplers vs. 24 h averaged PM₁₀ from RAMA at XAL.

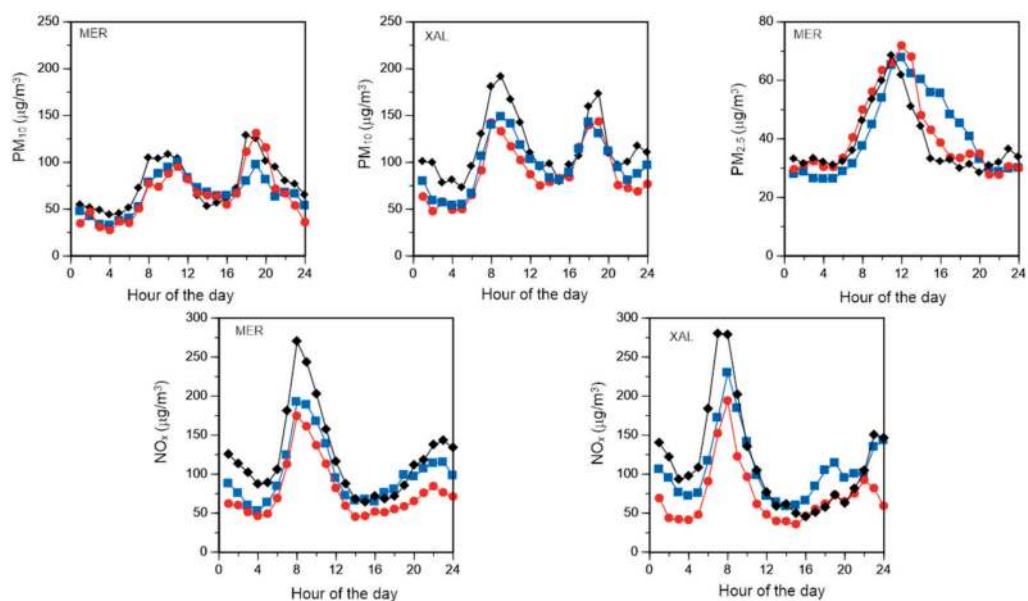


Figure 4. Average diurnal variations of PM₁₀ concentrations and NO_x concentrations at MER and XAL from Mexico City atmospheric monitoring automatic network (RAMA), and PM_{2.5} diurnal variations at MER from RAMA, during November 2003 (blue squares), March 2004 (red dots), and November 2004 (black diamonds).

Average PM_{2.5} concentrations for the two sites and three sampling periods are given in **Table 2**. In November 2003 and May 2004, concentrations were similar in both sites. In November 2004, PM_{2.5} concentrations were significantly lower at MER relative to XAL, in accordance with the industrial activity of this site [9, 10] and low wind speeds, which preclude pollutant dispersion. Average concentrations were below 65 µg/m³ (the Mexican Health Standard Norm at the time of the study) at all sampling stations and dates (the current allowable maximum is 41 µg/m³, [7]). In the two sites, PM_{2.5} concentrations were highest during weekdays (Monday to Friday) relative to the weekends (*t*-test, *p* < 0.01).

Average concentrations of total carbon, nitrate, and ammonium for each sampling period were also similar at MER and XAL. **Figure 5** shows that wind speed is

Date	Site	PM2.5 ($\mu\text{g}/\text{m}^3$)		$\delta^{13}\text{C}$ (‰)		$\delta^{15}\text{N}$ (‰)		NH4 ($\mu\text{g}/\text{m}^3$)		NO3 ($\mu\text{g}/\text{m}^3$)		Total carbon ($\mu\text{g}/\text{m}^3$)	
		Ave (stdev)	Range	Ave (stdev)	Range	Ave (stdev)	Range	Ave (stdev)	Range	Ave (stdev)	Range	Ave (stdev)	Range
Nov 2003	MER	39.40 (12.93)	18.69 to 60.07	-25.69 (1.93)	-27.43 to -21.98	9.84 (5.32)	-2.27 to 18.26	3.49 (2.07)	1.23 to 8.94	5.60 (4.14)	1.75 to 17.18	13.47 (4.23)	7.83 to 21.00
		46.89 (15.16)	20.93 to 69.90	-25.28 (1.46)	-27.00 to -23.09	10.02 (6.83)	-2.72 to 21.64	3.68 (2.28)	0.85 to 9.39	5.62 (3.88)	1.13 to 15.49	20.68 (7.17)	10.59 to 35.13
March 2004	MER	28.96 (11.44)	13.33 to 43.61	-27.02 (0.53)	-27.95 to -26.28	5.45 (4.56)	-2.19 to 15.43	2.89 (1.67)	0.96 to 6.17	3.37 (2.43)	1.09 to 9.54	12.70 (3.45)	7.01 to 18.41
		37.14 (14.89)	14.29 to 60.17	-28.95 (5.56)	-41.26 to -24.02	0.93 (5.41)	-7.51 to 10.50	2.77 (1.77)	0.53 to 5.99	3.66 (2.66)	0.42 to 8.66	16.26 (5.83)	5.70 to 23.76
Nov 2004	MER	39.60 (9.96)	23.01 to 58.84	-20.62 (3.11)	-25.65 to -15.31	5.97 (8.47)	-9.90 to 19.43	3.42 (2.12)	1.55 to 9.65	5.11 (2.24)	1.99 to 9.22	20.11 (3.89)	13.89 to 28.11
		52.89 (6.94)	42.43 to 64.99	-22.76 (0.90)	-23.89 to -20.40	2.67 (2.23)	-0.61 to 8.51	3.23 (1.61)	1.59 to 7.97	5.37 (1.81)	3.56 to 10.57	21.99 (3.59)	14.09 to 28.46

Significant differences between sites for each sampling season are given in bold (*t*-test < 0.05).

Table 2. Average and standard deviation of carbon and nitrogen parameters of PM_{2.5} in XAL and MER during November 2003, March 2004, and November 2004.

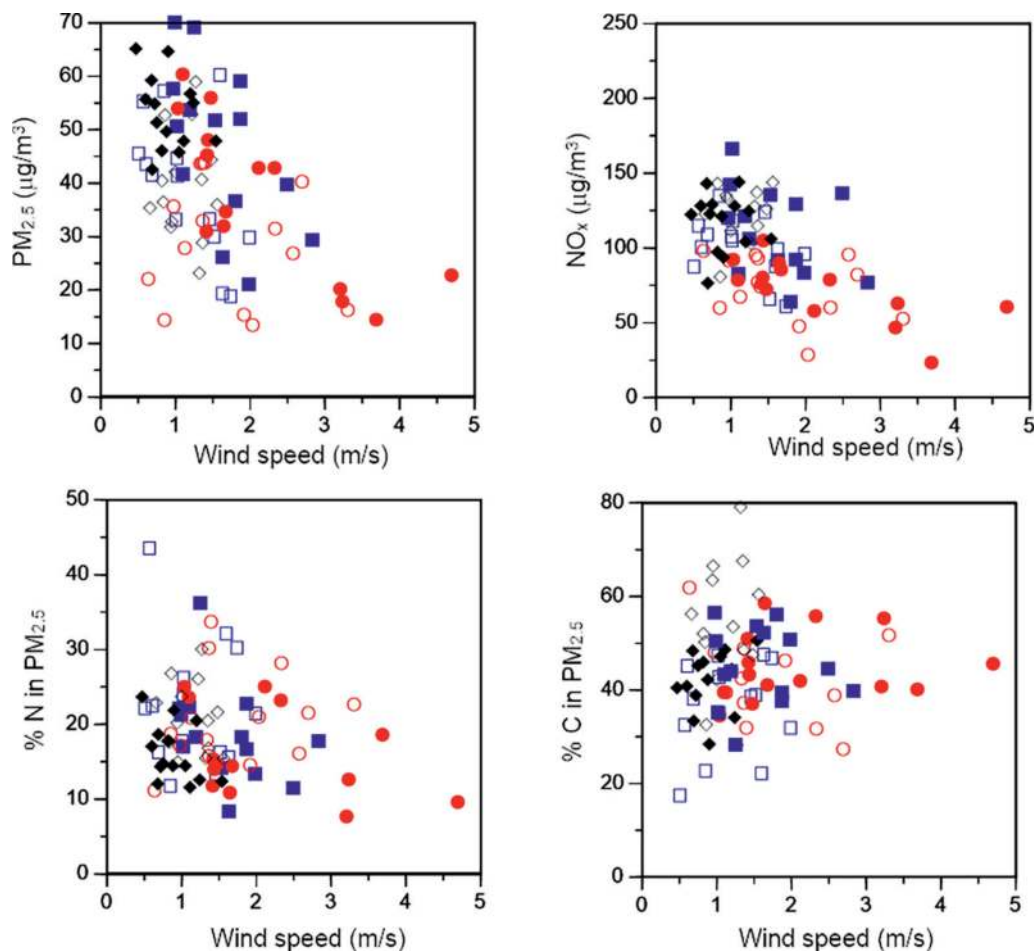


Figure 5. Scatterplots of wind speed vs. PM_{2.5} concentrations, averaged NO_x concentrations from Mexico City atmospheric monitoring automatic network (RAMA), % N in PM_{2.5}, and % C in PM_{2.5}, for samples collected at MER (closed symbols) and XAL (open symbols) during November 2003 (blue symbols), March 2004 (red symbols), and November 2004 (black symbols).

important in determining the PM_{2.5} concentration and carbon and nitrogen composition. As wind speeds decrease, particle concentrations increase and suggest that the emitted (primary) or coalesced (secondary) particles increase when no mechanism disperses them. Likewise, the percentage of N and NO₃⁻ concentration in PM_{2.5} also increased at low wind speeds, in accordance to the gas-to-particle conversion of nitrogen compounds [4]. By contrast, the percentage of the total carbon is increased along with an increase in wind speeds and a decrease in particle concentrations, and this suggests that at high wind speeds low particle concentrations appear to be primarily composed of direct carbon emissions.

3.3 Stable carbon and nitrogen isotopes of PM_{2.5}

Figure 6 gives the frequency histograms of stable carbon and nitrogen isotopes in PM_{2.5} collected at MER and XAL during the three sampling campaigns. Averages and ranges are given in **Table 2**.

The majority of δ¹³C values fell in the -27 to -25‰ range, with an important number of data points skewed to more positive values (-24 to -15‰). A few samples

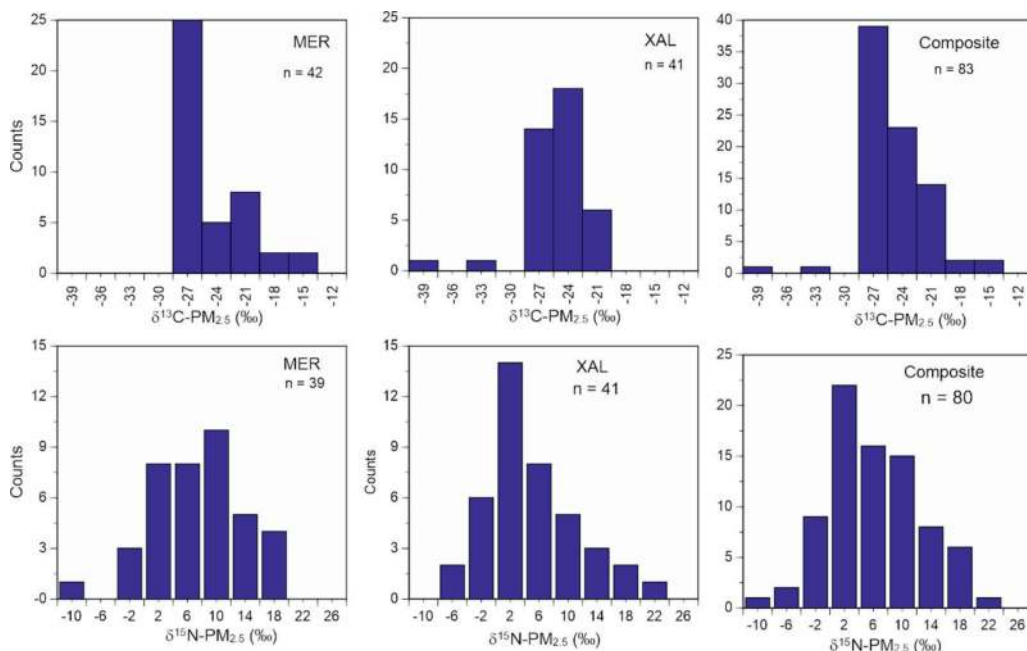


Figure 6.

Upper panel: histograms of $\delta^{13}\text{C-PM}_{2.5}$ (‰) at MER, XAL, and all data. Lower panel: histograms of $\delta^{15}\text{N-PM}_{2.5}$ (‰) at MER, XAL, and all data.

at XAL were lighter than -28‰ . In contrast, during November 2004 at MER, most $\delta^{13}\text{C}$ values were heavier than -22‰ . This range of isotopic compositions for bulk carbon contrasts with data from a previous study in Mexico City, where most $\delta^{13}\text{C}$ in $\text{PM}_{2.5}$ ranged between -26 and -24‰ [14]. According to the carbon isotope composition of the different potential sources in Mexico City, the predominant carbon source in $\text{PM}_{2.5}$ is the emissions of fossil fuels [14]. The extreme isotopic values at XAL show

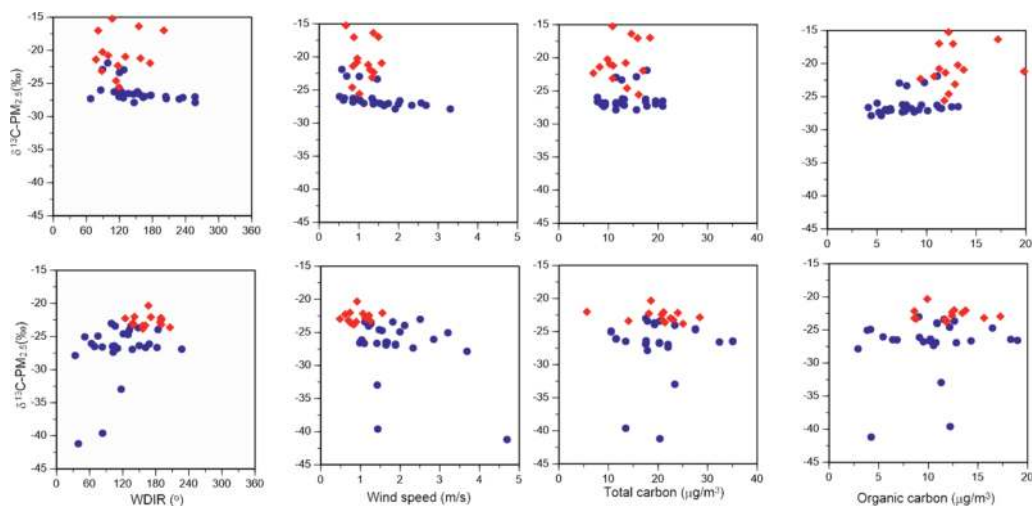


Figure 7.

Upper panel: scatterplots of $\delta^{13}\text{C-PM}_{2.5}$ vs. wind direction, wind speed, total carbon, and organic carbon at MER. Lower panel: scatterplots of $\delta^{13}\text{C-PM}_{2.5}$ vs. wind direction, wind speed, total carbon, and organic carbon at XAL. Blue symbols denote samples collected during November 2003 and March 2004. Red symbols denote samples collected during November 2004.

that during March 2004, light hydrocarbons (such as methane and propane) were the predominant emissions. In contrast, the relatively enriched $\delta^{13}\text{C}$ values at MER during November 2004 reflect the emission of particles of geological origin.

Scatterplots of $\delta^{13}\text{C}$ values vs. wind direction, wind speed, organic carbon, and total carbon are depicted in **Figure 7**. The enriched ^{13}C values during November 2004 are associated with low-speed E-SE winds and suggest organic-rich, soil-derived carbon. In contrast, the carbon content of PM_{2.5} in the other two sampling periods at MER is related to emissions from fuel combustion. At XAL, the heaviest $\delta^{13}\text{C}$ values are associated with low-speed winds and organic carbon-enriched particles. The ^{13}C -depleted samples apparently originate from SE winds.

$\delta^{15}\text{N}$ -PM_{2.5} values spanned between -9.9 and $+21.6\text{‰}$ (**Table 2**). Although the average $\delta^{15}\text{N}$ composition between sites for a given sampling period was similar (except for March 2004), the frequency histogram of $\delta^{15}\text{N}$ in PM_{2.5} shows a different distribution. At XAL, most $\delta^{15}\text{N}$ values fell in the 2‰ bin, with over 50% of the

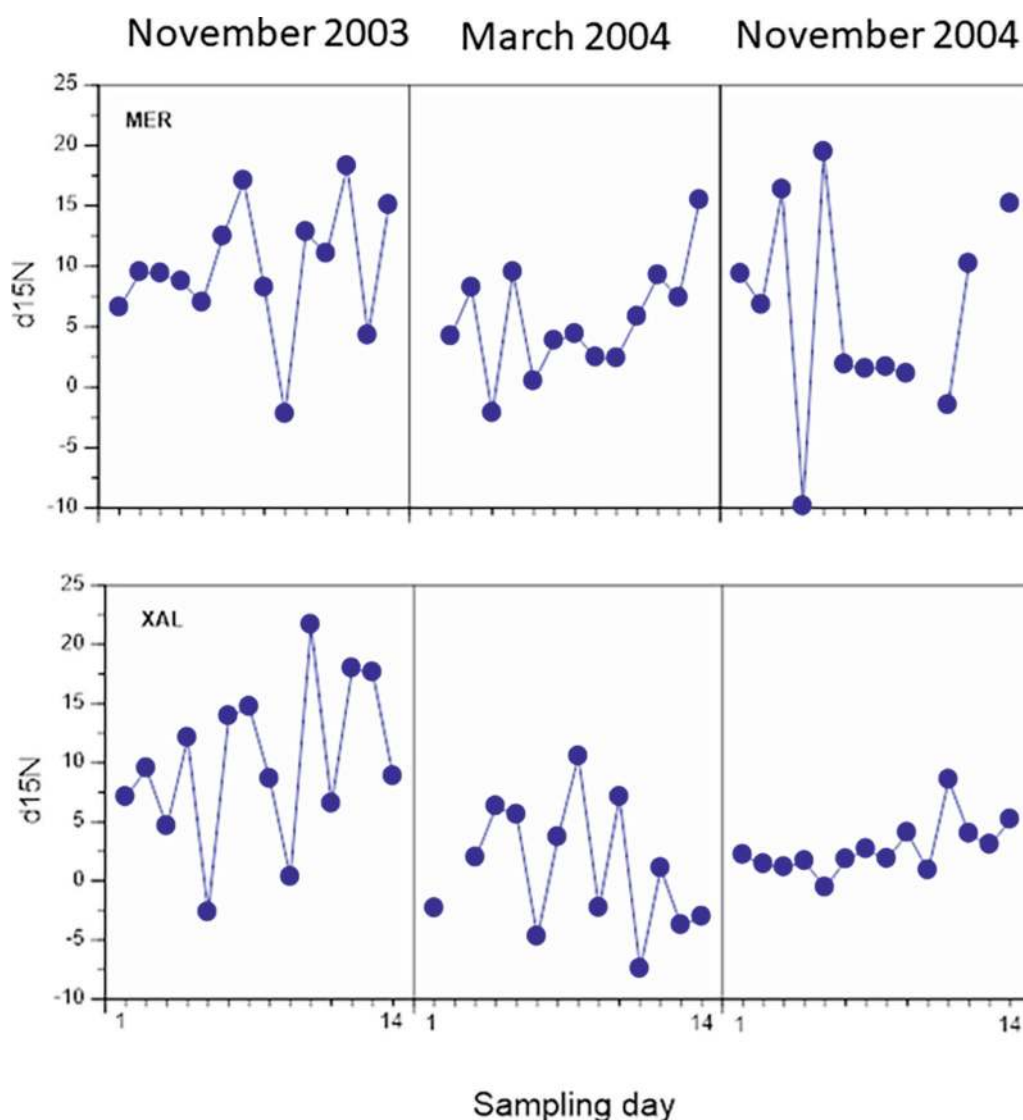


Figure 8. Time series of $\delta^{15}\text{N}$ -PM_{2.5} values at MER (upper panel) and XAL (lower panel).

data points between -2 and 6‰ . In contrast, the $\delta^{15}\text{N-PM}_{2.5}$ distribution at MER had a wider distribution, with most values between 2 and 10‰ . The time series of $\delta^{15}\text{N-PM}_{2.5}$ at the two sites shows that at XAL, values were always lower than at

Location	Particle size	Season	Average + std. deviation	Range	Comments	Reference
Paris, France	PM10	winter	10.0 ± 3.4	5.3 to 15.9		[15]
Paris, France	PM10	summer	10.8 ± 3.4	5.9 to 16.1		[15]
Cienfuegos, Cuba	PM10	urban	9.2 ± 4.4	1.5 to 19.1		[19]
Seoul Korea	PM2.5 NH4	warm	16.4 ± 2.8			[20]
Seoul Korea	PM2.5 NH4	cold	4.0 ± 6.1			[20]
Seoul Korea	PM2.5 NO3	summer	-0.7 ± 3.3			[21]
Seoul Korea	PM2.5 NO3	winter	3.8 ± 3.7			[21]
Shijiazhuang, China	PM2.5 NO3	warm months		-11.8 to 13.8	No differences in $\delta^{15}\text{N-NO}_3$ between polluted and non-polluted days	[12]
Shijiazhuang, China	PM2.5 NO3	cold months		-0.7 to 22.6		[12]
Northeast cities, USA	PM2.5 NO3					[13]
New Delhi, India	PM2.5 bulk	Spring summer	12.3 ± 4.6			[22]
New Delhi, India	PM2.5 bulk	Post- monsoon	7.7 ± 4.1			[22]
New Delhi, India	PM2.5 bulk	winter	7.3 ± 6.6			[22]
Beijing, China	PM2.5 bulk	winter	11.97 ± 1.79	8.68 to 14.50	Sampling in haze and non-haze conditions	[23]
Chennai, India	PM2.5 bulk	summer	22.2 ± 4.3	19.3 to 25.2		[24]
Chennai, India	PM2.5 bulk	winter	25.5 ± 2.4	18.0 to 27.8		[24]
Mexico City, Mexico	PM2.5 bulk	dry cold	4.6 ± 6.4	-7.5 to 21.6	XAL-industrial site	This study
Mexico City, Mexico	PM2.5 bulk	dry cold	7.2 ± 6.4	-9.9 to 19.4	MER-residential/ commercial site	This study

Table 3.
 $\delta^{15}\text{N}$ values in $\text{PM}_{2.5}$ and PM_{10} in megacities.

MER (**Figure 8**). Furthermore, $\delta^{15}\text{N}$ for PM_{2.5} at XAL during the low wind speeds of November 2004, was nearly constant during the sampling period.

A comparison between $\delta^{15}\text{N}$ for PM_{2.5} in Mexico City with those of other megacities is shown in **Table 3**. The average values for XAL and MER are similar to the averages of New Delhi [22] and several months in Shijiazhuang [12], but lighter than for Paris [11], Beijing [23], and the warm months of New Delhi [22] and Seoul [21]. These differences can be attributed to different sources of NO_x emissions [13, 23].

Scatterplots of XAL and MER $\delta^{15}\text{N}$ values of PM_{2.5} samples vs. wind speed and averaged air quality data are given in **Figure 9**. The figure shows that as windspeed increases, the nitrogen isotopic composition becomes ¹⁵N-depleted, while at low wind speeds, PM_{2.5} particles are isotopically enriched. In turn, $\delta^{15}\text{N}$ values are positively correlated with average daily NO_x ambient concentrations. At low wind speeds, particles are dispersed and the isotopic composition should reflect primary emissions. This is consistent with low $\delta^{15}\text{N}$ values of fossil fuels. In turn, the NO_x- $\delta^{15}\text{N}$ -PM_{2.5} positive correlation shows that the gas-to-particle condensation fractionates the condensed nitrogen, leaving isotopically enriched N in the particles.

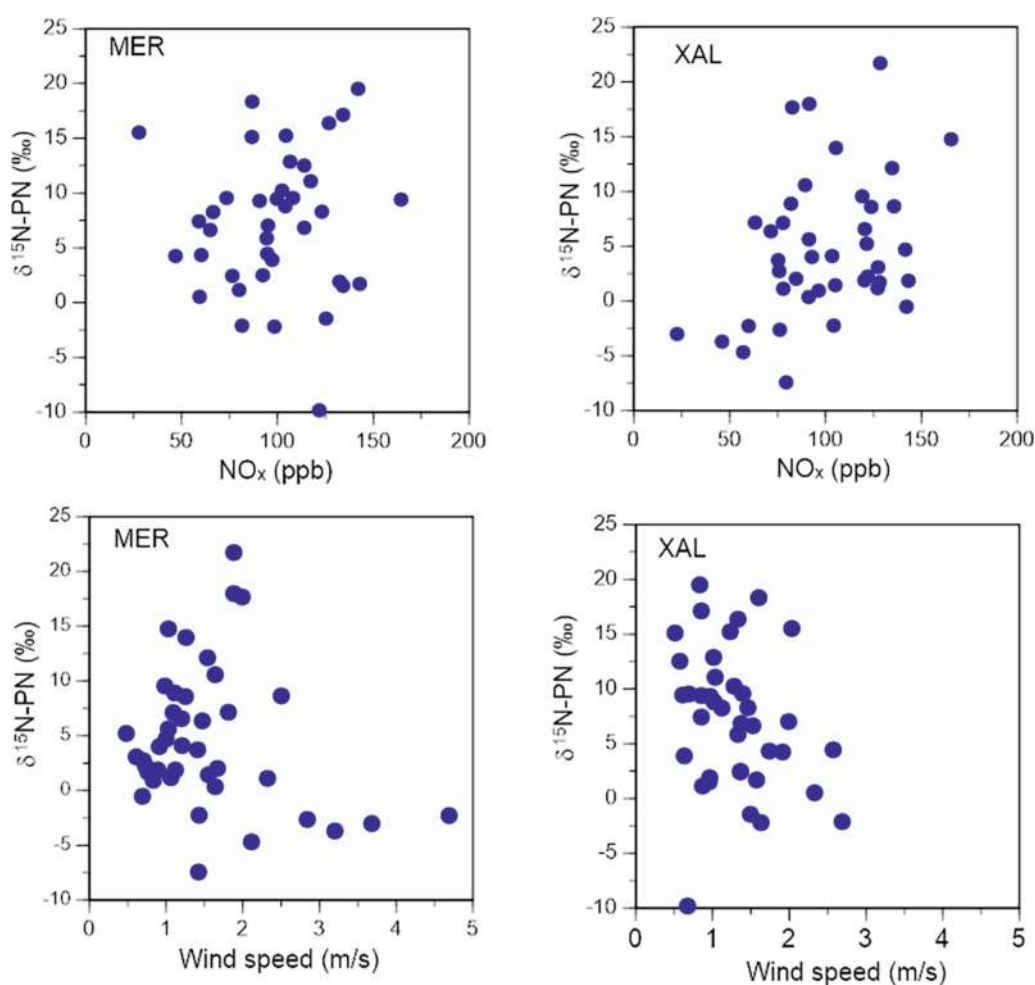


Figure 9. Scatterplots of $\delta^{15}\text{N}$ -PM_{2.5} values vs. NO_x (upper panel) and wind speeds (lower panel) at MER and XAL.

4. Conclusions

Potential N and C sources of PM_{2.5} in an industrial sector and a commercial/residential zone of Mexico City were evaluated during three dry season periods (March and November) using stable nitrogen and carbon isotopes. Daily PM_{2.5} concentrations ranged between 10 and 70 µg/m³ and were inversely correlated to wind speed. The percentage of N in PM_{2.5} also increased at low wind speeds and suggests gas-to-particle conversion of nitrogen compounds. In contrast, the % C increased with high wind speeds and low PM_{2.5} concentrations reflecting direct carbon emissions. Based on δ¹³C values, the principal carbon sources of PM_{2.5} are fossil fuel emissions, although geological material is an important component when easterly winds resuspend dust from the nearby Texcoco dry lakebed. δ¹⁵N-PM_{2.5} values ranged between -9.9 and 21.6 ‰, similar to values from other megacities. δ¹⁵N values were consistently lower at the industrial site and suggest isotopic fractionation of NO_x emissions during particle accretion. The δ¹⁵N-PM_{2.5} values presented here provide a nitrogen isotope baseline for Mexico City airborne fine particles as no previous data have been collected for this megacity.

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Conflict of interest

The authors declare no conflict of interest.

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