



# Title: PMI in outdoor air: sources, ion species content and alkaline properties in the Guadalajara Metropolitan Area, Jalisco-Mexico

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# Introduction

- Outdoor PM
- Secondary and fine particles
- Lack of information of distribution of water-soluble inorganic and organic species
- Air quality
- Health concerns

(Harrison, Jones, & Lawrence, 2004; Whitby, 1978; Tsai, Lin, Yao, & Chiang, 2012, Tsai, Sopajaree, Chotruksa, Wu, & Kuo, 2013).

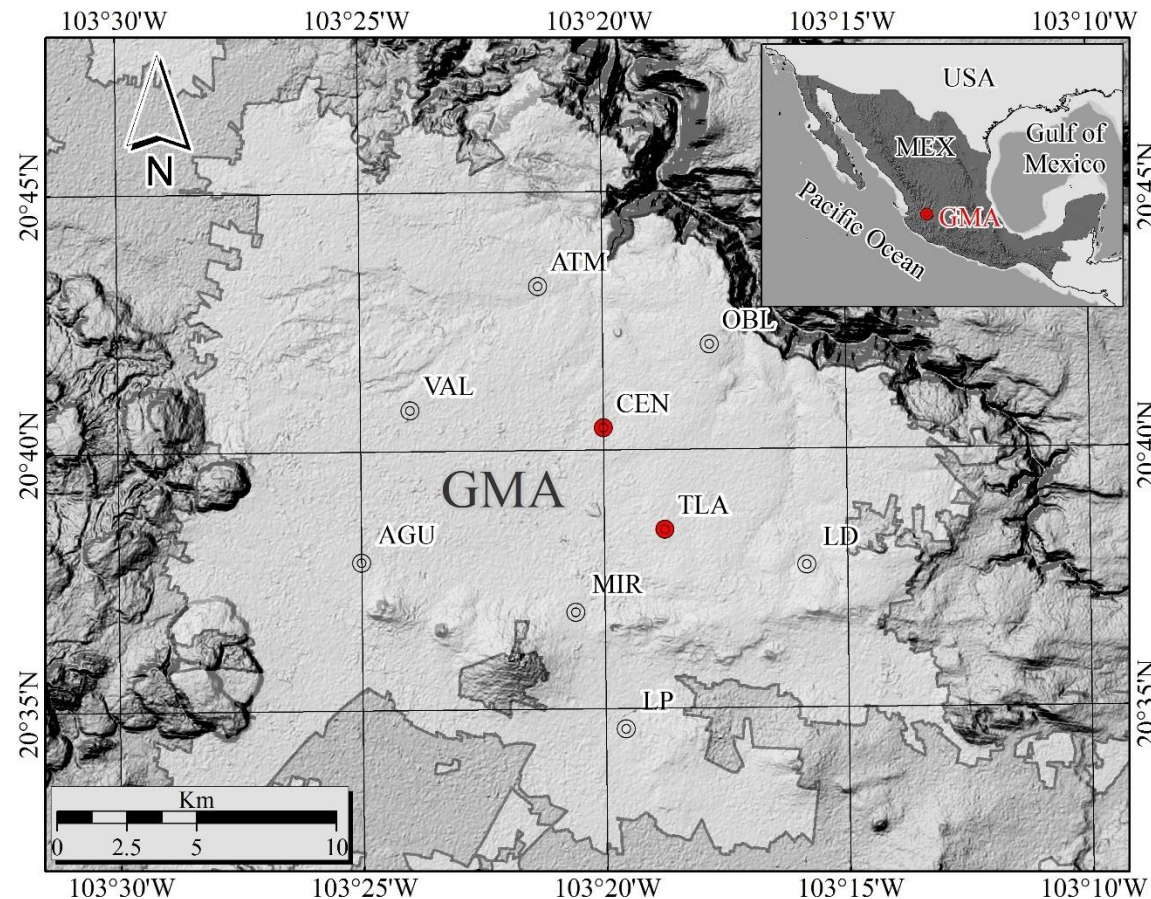
## **Aims**

To determine the chemical composition of inorganic and organic ion species associated with  $PM_{10}$  in the Guadalajara Metropolitan Area (GMA) in Jalisco, Mexico.

This study is the first to determine the importance of sulfate, nitrate, and ammonium as chemical components of fine particles that can then be used to explore the origins of these components during days with high solar radiation.

# Methodology

## Sampling sites



**Figure 1.1** Location of the PM<sub>1</sub> sampling sites at the CEN and TLA in the Guadalajara Metropolitan Area during the warm-dry period.

- Warm-dry season (April-June 2015) at two sampling sites.
- City center (CEN), located in the downtown area of the GMA (20° 40'25"N 103° 19'59"W), which is characterized by significant vehicular and commercial activity.
- Tlaquepaque (TLA), located in southeastern direction from the CEN (20° 38'27"N -103° 18'45"W), which is characterized by residential areas with major avenues and effects from industrial zones to the southwest.

## Particles collection and gravimetric analysis

- Sets of 14 and 13 samples of PM<sub>1</sub> (CEN and TLA, respectively)
- Partisol Samplers (Model 2300, R & P)

## Aqueous extraction with ultrasonic bath

- Extraction in Ultrasonic bath (Branson 5510) one h and 23 °C
- Filtration through nylon membranes of 0.45 micrometers

## Anions and cations in aqueous extracts from PM<sub>1</sub>

- Ion chromatography coupled conductivity detector and autosampler (Advanced Sample Processor 838, Metrohm)

## Meteorological parameters

- Temperature , relative humidity, wind direction, wind speed, atmospheric pressure, solar radiation, UV radiation were registered (Vantage Pro2 Plus, Davis) every 10 minutes at the two sampling sites

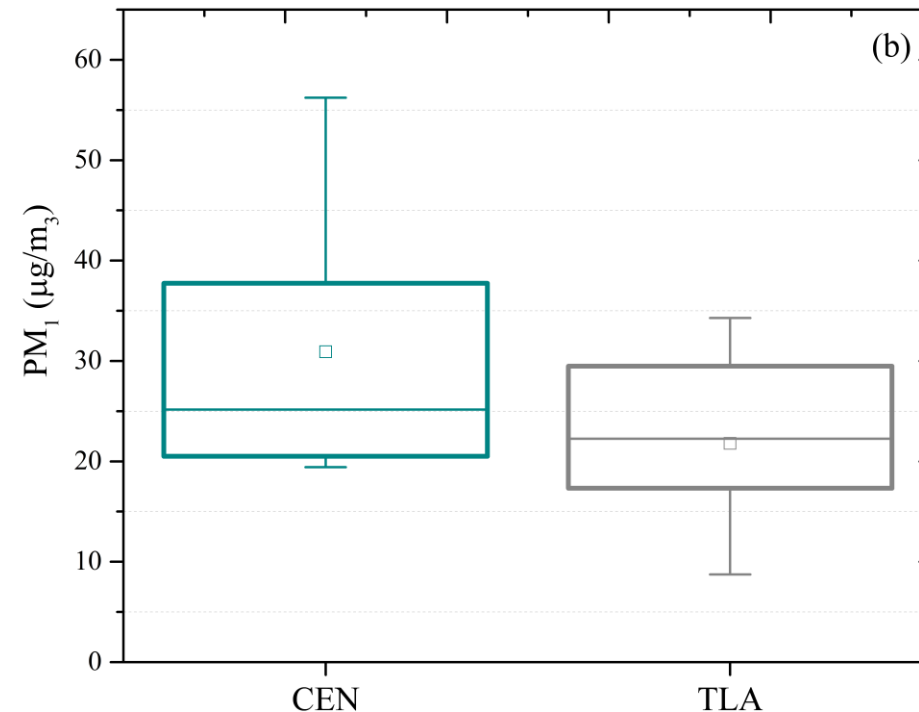
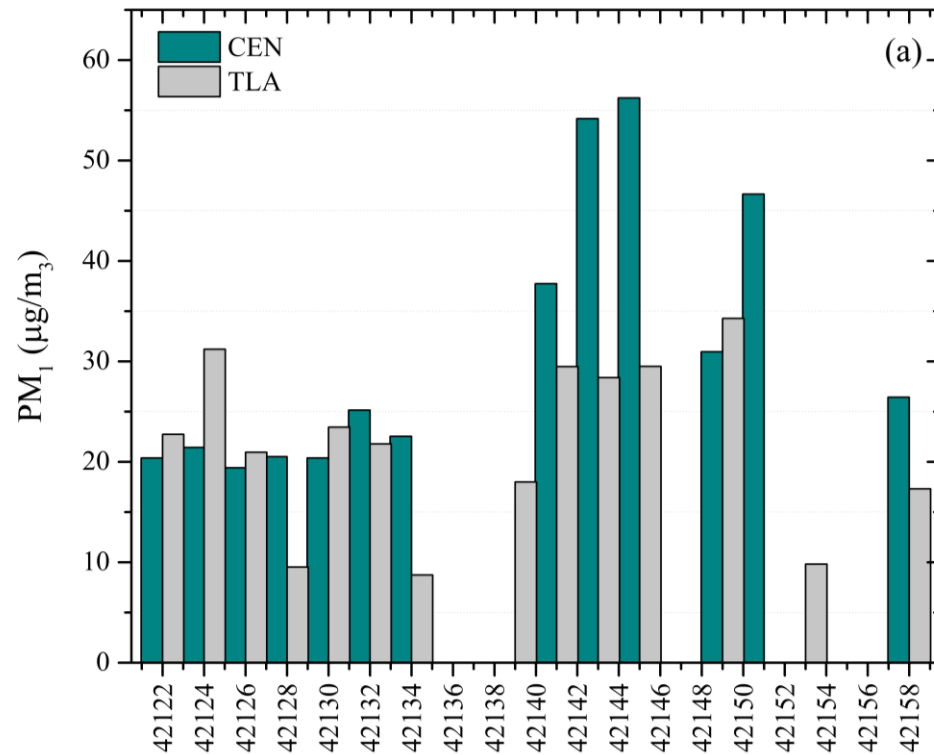
## Statistics analysis

- *Shapiro-Wilk* normality test , *Mann-Whitney* test, *Kruskal-Wallis* test, Linear regression análisis, *Spearman* correlation analysis

# Results

## Variations of the particle matter

- There were some increases in particles between days 42,141 and 42,158 in the CEN, there were no *intersite* differences ( $p>0.18$ ), probably because a higher variation of  $PM_{10}$  in the CEN.



**Graphic 1.1(a)** Concentration of  $PM_{10}$  sample collected over 24 h in the CEN and TLA show higher levels during 42,141 and 42,151 days at the first site; **(b)** Particle concentration without differences between sites ( $p>0.05$ ).

## Anions and cations from PM<sub>1</sub> aqueous extracts

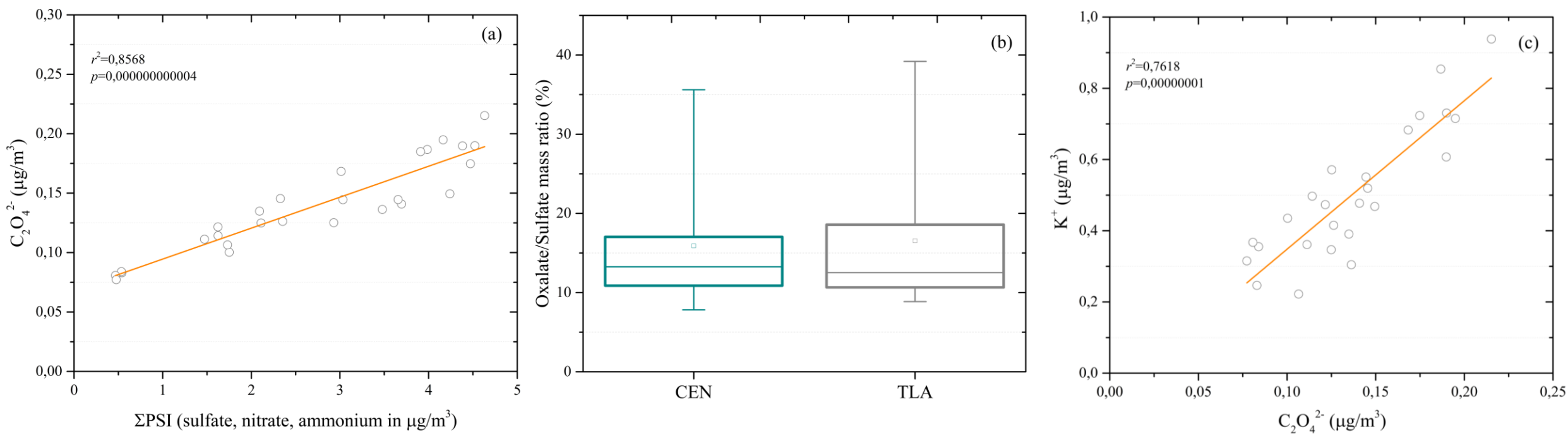
**Table 1.1** Regression analysis parameters of PM<sub>1</sub> and anions and cations at the *study area*.

Study Area	Equation	r <sup>2</sup>	p-value
∑Anions	$y = 1.92 + 8.43x$	0.30	<0.002
∑Cations	$y = 9.14 + 6.19x$	<b>0.39</b>	<0.0007
∑PSI	$y = 14.22 + 4.41x$	0.26	<0.006
∑TI	$y = 9.26 + 3.70x$	0.31	<0.002
NO <sub>3</sub> <sup>-</sup>	$y = 14.36 + 21.22x$	0.27	<0.006
SO <sub>4</sub> <sup>2-</sup>	$y = 13.75 + 11.18x$	0.29	<0.003
NH <sub>4</sub> <sup>+</sup>	$y = 16.39 + 8.50x$	0.23	<0.01
Na <sup>+</sup>	$y = -0.99 + 44.16x$	0.22	<0.02
K <sup>+</sup>	$y = 10.09 + 28.84x$	<b>0.49</b>	<0.00004
∑oxalate+formate	$y = -3.9 + 119.90x$	<b>0.40</b>	<0.0004

∑Ani: sum anions; ∑Cat: sum cations; ∑PSI: sum principal secondary ions; ∑TI: sum Total Ions. Higher values in bold. Source: own elaboration.

- The results give specific evidence of the effect of some of the most abundant species of ions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>) on the variation of PM<sub>1</sub>.
- These results suggest that the origins of these species are the likely sources of the concentration of fine particles in the *study area*.

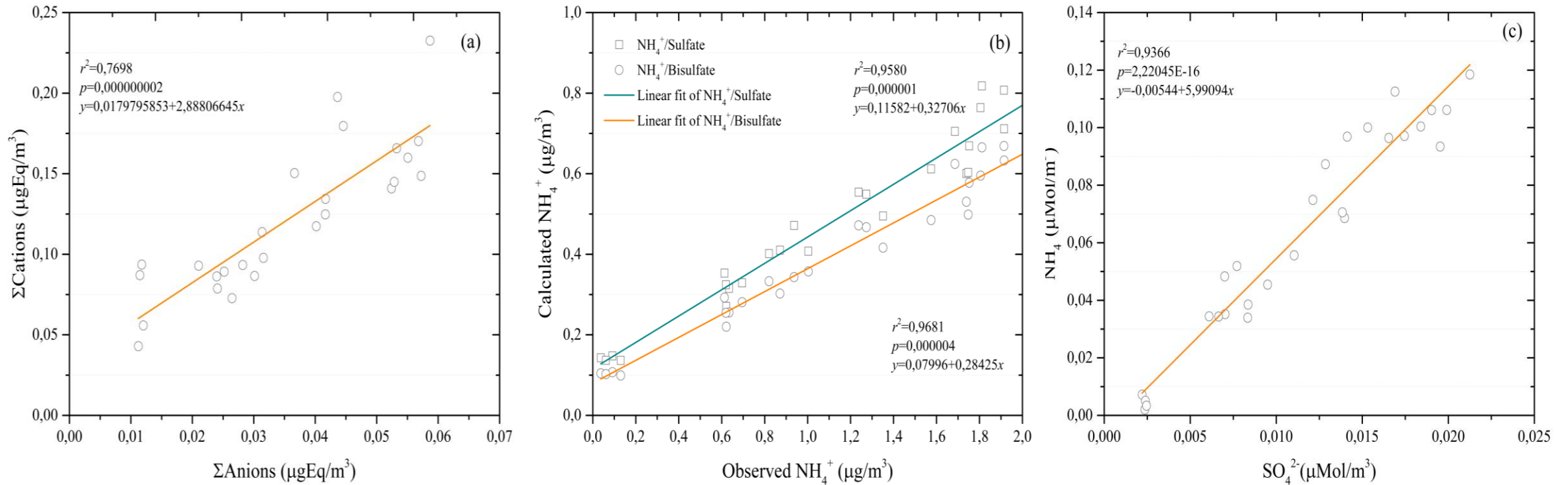
# Anions and Cations sources



**Graphic 1.2** (a) The linear fitted curve between oxalate and  $\Sigma$ PSI concentration (sulfate, nitrate, and ammonium) at the *study area* ( $r^2=0.86$ ) suggests that oxalate is attributable to a secondary formation; (b) the  $\text{C}_2\text{O}_4^{2-}/\text{SO}_4^{2-}$  ratio (in mass) suggests similar levels between the sites ( $p>0.05$ ) with a low ratio (<13.2%) of oxalate by secondary formation; (c) The linear fitted curve between concentrations of oxalate and  $\text{K}^+$  (of biomass burning origin) shows that a part of the  $\text{C}_2\text{O}_4^{2-}$  has the same source ( $r^2=0.76$ ).



# Neutralization process in PM<sub>1</sub>



**Graphic 1.3 (a)** Ion balance of  $\Sigma\text{Cat}$  and  $\Sigma\text{Ani}$  with data from *study area*; the slope value (2.86) suggests that the anion deficit of PM<sub>1</sub> neutralizes scarcely the cations present and that this condition contributes to the alkaline character of the particles; **(b)** Comparison between calculated and observed ammonium in fine particles at the *study area* ( $(\text{NH}_4)_2\text{SO}_4$ : calculated  $\text{NH}_4^+ = 0.38 * [\text{SO}_4^{2-}] + 0.29 * [\text{NO}_3^-]$  and  $\text{NH}_4\text{HSO}_4$ : calculated  $\text{NH}_4^+ = 0.192 * [\text{SO}_4^{2-}] + 0.29 * [\text{NO}_3^-]$ ); **(c)** the total ammonium/total sulfate (TA/TS>6) ratio of the *study area* is indicative of rich ammonium conditions.

# Meteorological parameters and their relationship with the ionic species

- Medians of the daily, maximum, and minimum temperatures and RH did not have *intersite* differences ( $p > 0.05$ , all cases).
- The wind speed (WS) and maximum wind speed (MWS) in general were  $< 3.1$  m/s without significant differences ( $p > 0.05$ , in both cases).
- For TLA, both the WS and MWS directions come from the west. Atmospheric pressure, UV radiation, and MaxUV radiation had higher levels at the CEN ( $p < 0.00001$ ,  $p < 0.005$ , and  $p < 0.00031$ , respectively). The SR and MaxSR did not show the *intersite* differences ( $p > 0.05$ , in both cases).

**Table 1.4** Descriptive statistics of the meteorological parameters at the Centro (CEN) and Tlaquepaque (TLA) sites during the warm-dry period.

CEN						
	n	Mean	S.D.	Median	Maximum	Minimum
AT (°C)	15	24.30	1.46	24.92	25.81	21.03
MT (°C)	15	24.41	1.46	25.01	25.92	21.16
mT (°C)	15	24.18	1.46	24.82	25.70	20.90
RH (%)	15	46.33	9.35	47.45	69.55	34.40
WS (m/s)**	15	0.9	--	0.90	2.70	0.00
WD**	15	W (10)	--	--	--	--
MWS (m/s)**	15	2.2	--	3.10	6.30	0.90
WDMWS **	15	WNW (4)-N (4)	--	--	--	--
AP (mmHg)	15	842.08	1.20	842.35	844.06	839.33
SR (W/h)	15	255.47	27.36	263.08	288.04	204.19
MaxSR (W/h)	15	987.67	60.98	966.00	1111.00	897.00
UV	15	2.38	0.29	2.44	2.76	1.83
MaxUV	15	10.89	1.20	11.10	8.60	12.90
TLA						
	n	Mean	S.D.	Median	Maximum	Minimum
AT (°C)	14	24.61	1.306	25.01	25.94	20.79
MT (°C)	14	24.73	1.30	25.13	26.06	20.91
mT (°C)	14	24.49	1.31	24.89	25.82	20.66
RH (%)	14	45.33	10.46	45.22	70.76	33.99
WS (m/s)**	14	0.40	--	1.10	2.20	0.40
WD**	14	W (8)	--	--	--	--
MWS (m/s)**	14	3.10	--	3.10	4.90	0.90
WDMS**	14	W (8)	--	--	--	--
AP (mmHg)	14	835.57	1.21	835.76	837.55	832.82
SR (W/h)	14	262.50	26.70	263.83	308.78	217.66
MaxSR (W/h)	14	969.43	49.17	960.50	1049.00	871.00
UV	14	2.05	0.21	2.06	2.45	1.72

# Conclusions

- Fine particles ( $PM_{10}$ ) at two study sites in the GMA suggest homogeneity in their concentrations in ambient air.
- Meteorological parameters showed similar values between sites (except atmospheric pressure and UV radiation) and temperature was identified as the variable with the most influence on the particle's concentration levels.
- Low or absent correlations with other meteorological parameters suggest that local emission sources better explain the variations in the particle's nature.
- Sulfate, nitrate, and ammonium were found to be the principal secondary ions (PSI) highlighting the crucial role of atmospheric transformation processes (and the sodium and potassium from direct emissions) on the formation of fine particles at the CEN and TLA.

- In relation to oxalate, a significant correlation with  $K^+$ —which is a marker of biomass burning—and with PSI (sulfate, nitrate, and ammonium) was observed, which suggests two different origins.
- The PSI values also had equal levels at both sampling sites (like fine particles) under the sampling conditions tested.
- The ion balance between  $\sum \text{Anions}$  and  $\sum \text{Cations}$  indicated fine particles with alkaline properties in the CEN and TLA, resulting from a higher amount of cations.
- Ion species showed positive correlation coefficients, mainly with RH and MWS, and negative correlations with MaxSR and UV radiation.
- Based on the high *intersite* similarity of the meteorological parameters and the moderate variability that explains the variation in ion species, we recommend that studies should be conducted during other seasons of the year and with more samples collected.

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