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Acidic Gases and Nitrate and Sulfate Particles in the Atmosphere in the City of Guadalajara, México

Hugo Saldarriaga-Noreña · Stefan Waliszewski · Mario Murillo-Tovar · Leonel Hernández-Mena · Iliana de la Garza-Rodríguez · Edith Colunga-Urbina · Rosalva Cuevas-Ordaz

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Abstract Atmospheric concentrations of nitrous acid, nitric acid, nitrate and sulfate particles were obtained in this study from April to June 2008 in the center of the city of Guadalajara, while concentrations of ozone, sulfur dioxide, nitrogen dioxide and meteorological parameters (temperature and relative humidity), were acquired by the Secretaría del Medio Ambiente para el Desarrollo Sustentable del Estado de Jalisco (SEMADES). The results showed that nitric acid (2.7 μg m^{-3}) was 2.7 times higher than nitrous acid (1.0 μg m^{-3}). The sulfur dioxide (SO_2) concentration indicated an opposite trend to sulfate (SO_4^{2-}), with the average concentration of SO_2 (6.9 μg m^{-3}) higher in almost the entire period of study. The sulfur conversion ratio *(Fs*, 24.9%*)* and nitrogen conversion ratio *(Fn*, 6.2%*)*, were revealed to be similar to that reported in other urban areas during warm seasons. It is also noted that ozone is not the main oxidizer of nitrogen dioxide and sulfur dioxide. This determination was made by taking into account the slightly positively correlation determined for *Fn* ($r^2 = 0.084$) and *Fs* ($r^2 = 0.092$) with ozone that perhaps suggests there are other oxidizing species such as the radical OH, which are playing an important role in the processes of atmospheric oxidation in this area.

Keywords Conversion ratio · Acid gases · PM2.5

H. Saldarriaga-Noreña (✉) · I. de la Garza-Rodríguez · E. Colunga-Urbina
Facultad de Ciencias Químicas,
Universidad Autónoma de Coahuila, Saltillo, Mexico
e-mail: hugosaldarriaga@uadec.edu.mx

S. Waliszewski
Instituto de Medicina Forense, Universidad Veracruzana, Veracruz, Mexico

M. Murillo-Tovar · L. Hernández-Mena · R. Cuevas-Ordaz
Centro de Investigación y Asistencia en Tecnología y Diseño del Estado de Jalisco, Guadalajara, Mexico

Guadalajara is the city with the second highest population in the Mexican republic with an approximate population of 1,600,894 inhabitants (INEGI 2000, for its acronym in Spanish). It is located in the west of the republic, with a surface area of 187.91 km^2 and an average population density of 9,883 inhabitants km^{-2}. The emissions inventory developed in 2005 (DGMAEG 2008, for its acronym in Spanish) revealed that the principal atmospheric pollution source for the city is traffic emissions, where carbon monoxide was the pollutant with the greatest proportion at 87.4%, followed by total hydrocarbons at 9.8%, oxides of nitrogen at 2.6%, sulfur dioxide at 0.09% and particles less than or equal to 10 μm (PM10) at 0.04%. Some studies have evaluated the inorganic chemical composition of the aerosols in this city (Hernández-Mena et al. 2010, Saldarriaga et al. 2009). Nevertheless, there exists little information about acid species, especially HNO_2 and HNO_3.

The emission of oxides of nitrogen to the atmosphere, NO and NO_2 (NO_x), comes basically from the burning of fossil fuel and biomass, sunlight and biological activity (Mage et al. 1996). The NO_2 reacts with the radical OH to produce HNO_2 and HNO_3 via the route of photochemical reactions. The key mechanism for the formation of HNO_2 and HNO_3 is in the homogeneous reactions.

Nevertheless, an important mechanism for the formation of HNO_2 and HNO_3 during the night is the heterogeneous hydrolysis of N_2O_5 and NO_2 in particles of soot, sulfates and marine salt.

Meanwhile, the oxides of sulfur (SO_2) are emitted to the atmosphere principally by the burning of fossil fuel, volcanism and by photochemical reactions generated from the

oceanic plankton (CH_3S). The reaction of SO_2 with the OH radical produces gaseous H_2SO_4. Once formed, the H_2SO_4 condenses rapidly on the preexisting particles (Huntzicker et al. 1984).

Nitrates (NO_3^-) and sulfates (SO_4^{2-}) react with the ammonia forming ammonium nitrate (NH_4NO_3) and ammonium sulfate $(NH_4)_2SO_4$, respectively. Ammonium nitrate is one of the principal constituents of atmospheric aerosols with approximately 10%–20% of the total mass of the small particles. Often it coexists with ammonium sulfate; these two compounds together affect the visibility in urban atmospheres, radiative forcing and climate change (Seinfeld and Pandis 1998).

The exposure to high levels of concentration of atmospheric pollutants, or long periods to low concentrations, has attracted the attention of the community due to the negative impacts on health and ecosystems (Dockery et al. 1993). In the specific case of acid pollutants, Speizer (1989) found a correlation between the hydrogen ion concentrations in particles with chronic bronchitis in children between 10 and 12 years. Meanwhile, Bates and Sizto (1987) observed a correlation between the concentration of SO_4^{2-} and the number of admissions to the hospital for respiratory diseases in the south of Ontario. Dockery et al. (1993) found a positive correlation between the concentration of atmospheric particles, including SO_4^{2-}, with death from lung cancer.

With the above results providing motivation, the intention of this study was to acquire quantitative information for acid species and particles of nitrate and ammonium in the downtown of Guadalajara.

Materials and Methods

The samplings were made at the Centro station of the Network of Atmospheric Monitoring operated by the Secretaría del Medio Ambiente para el Desarrollo Sustentable del Estado de Jalisco (SEMADES, for its acronym in Spanish). The Centro station is located in an area that is characterized by high commercial and vehicular activity, both petrol and diesel. A Partisol equipment model 2300 (Rupprecht and Patashnick Co., Inc.) was used for collecting suspended particles less or equal to 2.5 μm (PM2.5), operated at a gaseous flow rate of 16.4 L min^{-1}. The equipment possesses two honeycomb denuders, which are used for the collection of gaseous species (acid and/or alkaline). To collect the acid species, one of the denuders was impregnated with Na_2CO_3 (1% w/v glycerol, in a solution 1:1 methanol/water). The particles of nitrate and sulfate were collected using a 47 mm nylon filter. Filters and denuders were extracted with deionized water in an ultrasonic bath (BRANSON 5510) for 30 min. The extracts were filtered trough nylon membrane (0.22 μm) and stored at 4°C until analysis.

Table 1 Mean ozone concentration, temperature and relative humidity from April to June 2008

Parameter (N = 12)	Range	Mean	SD
Ozone (ppm)	0.03–0.12	0.05	0.03
Temperature (°C)	21.8–26.6	24.2	1.5
Relative humidity (%)	22.3–72.1	47.4	18.2

N number of daily samples, *SD* standard deviation

The analyses were performed using an ion chromatograph (CI, Metrohm model 861 Advanced Compact with conductivity detector). The limit of detection (LD) was calculated for each species, and the values obtained were: 0.277, 0.255 and 0.248 μg mL^{-1} for NO_3^-, SO_4^{2-} and NO_2^-, respectively. Recovery percentages were determined by spiking a standard solution into one out of every 10 samples, and they were estimated to be between 91.0% and 99.2% for all species.

Results and Discussion

A total of 12 samples were collected from April to June 2008 at the Centro station. Table 1 shows the mean, ranges and standard deviation values for the concentration of ozone and meteorological parameters (temperature and relative humidity). The average concentration of ozone during the period of study was 0.05 ppm, the average temperature was 24.2°C and the average relative humidity was 47.4%. The mean concentration for the nitric and nitrous acids, sulfur dioxide, nitrogen dioxide, nitrate and sulfate particulates, as well as the conversion ratios of nitrogen and sulfur, are summarized in Table 2.

The mean concentration of HNO_2 was 1.0 μg m^{-3}. It is important to mention that April to June is a season of warm climate in the city of Guadalajara, where the solar radiation is significant, therefore it is expected that the concentrations of HNO_2 would be less than that in the cold season (November–January). In this respect, Harrison et al. (1996) indicated that in the summer season low concentrations of HNO_2 are present due to photolytic reactions. The average concentration of HNO_3 was 2.7 times higher than HNO_2. The major concentration of HNO_3 can be explained by the high volatility of the ammonium nitrate (NH_4NO_3) particles at the average temperature of 24.2°C during the period of study and the reaction between the NO_2 and the OH radicals in warm seasons (Danalatos and Glavas, 1999).

Figure 1 shows the correlations of NO_2 with HNO_2, HNO_3 and [HNO_2 + HNO_3]. Although significant correlations were not observed in any of the cases (NO_2 and HNO_2,

Table 2 Mean gaseous nitric and nitrous acid, sulfur dioxide, nitrogen dioxide, particulate nitrate and sulfate concentration, nitrogen (*Fn*) and sulfur (*Fs*) ratio conversion during from April to June 2008

	G-HNO_3 ($\mu g\ m^{-3}$)	G-HNO_2 ($\mu g\ m^{-3}$)	G-SO_2 ($\mu g\ m^{-3}$)	G-NO_2 ($\mu g\ m^{-3}$)	P-NO_3^- ($\mu g\ m^{-3}$)	P-SO_4^{2-} ($\mu g\ m^{-3}$)	*Fn* %	*Fs* %
(N = 12)								
Mean	2.7	1.0	6.9	52.5	2.0	3.2	6.2	24.9
SD	1.4	0.6	4.0	8.9	1.2	1.4	2.2	12.2
Min	0.7	0.1	2.4	43.3	0.7	1.0	2.8	7.5
Max	6.3	2.0	18.0	71.8	4.9	6.3	10.7	47.6

N number of daily samples, *SD* standard deviation

$r^2 = 0.116$), (NO2 and HNO3, $r^2 = 0.001$), (NO2 and HNO2 + HNO_3, $r^2 = 0.009$), it is important to mention that for the case of NO_2 with HNO_2, a slight positive trend was observed. Similar behavior was observed by Harrison et al. 1996. They indicated in their study that the HNO_2 correlated with the NO_2 in suburban and rural areas, but not as well in urban areas. This probably could be explained by the fact that the HNO_2 also can be produced by the reaction:

$$2NO_2 + H_2O \overset{\text{Surface}}{\rightarrow} HNO_2 + HNO_3 \quad (1)$$

The HNO_3 produced by this reaction is not equivalent to the quantity of HNO_2, due to surface adsorption (Finlayson-Pitts and Pitts, 2000). Gerecke et al. (1998), proposed an alternate route for the formation of HNO_2 for the following heterogeneous reaction:

$$NO_2 + \text{surface reduced site} + H_2O \rightarrow HNO_2 + \text{surface oxidized site} + OH^- \quad (2)$$

Both reactions can occur simultaneously in urban atmospheres, as well as in the presence of particles of soot from aircrafts (Finlayson-Pitts and Pitts, 2000). For this reason, the positive trend that was observed between the NO_2 and the HNO_2 might be explained partly by Eq. 1, although it is important to note that the HNO_2 also forms from the reaction between NO and the OH radical (Harrison et al. 1996).

In general, for almost all days sampled during April and June the average daily concentrations of SO_2 were greater than those of SO_4^{2-}. This possibly indicates that during this period the process of oxidation of SO_2 was not so significant, and that there were long periods of oxidation, due to the periods of meteorological stagnation.

Grosjean and Friendlander (1975) established the conversion ratios for sulfur (*Fs*) and for nitrogen (*Fn*) in the modified forms of the gas–particle distribution factors.

$$F_s = \frac{SO_4^{2-}}{SO_4^{2-} + SO_2} \quad (3)$$

Where SO_4^{2-} is the concentration of sulfate in particles, expressed as SO_2 ($\mu g\ m^{-3}$) and SO_2 is the concentration of dioxide of sulfur in the gaseous phase ($\mu g\ m^{-3}$).

$$F_n = \frac{GNO_3^- + PNO_3^-}{NO_2 + GNO_3^- + PNO_3^-} \quad (4)$$

Where PNO_3^- represents the concentration of particles of nitrate as $\mu g\ m^{-3}$ of NO_2, GNO_3^- is the concentration of gaseous nitrate as $\mu g\ m^{-3}$ of NO_2 and NO_2 is the concentration of NO_2 in the gaseous phase.

These equations were used for evaluating the process of oxidation of NO_2 to nitrate and SO_2 to sulfate, respectively.

The conversion ratio for the nitrogen (*Fn*) ranged between 2.8% and 10.7% with an average of 6.2%. This value is lower than that reported by Khoder (2002) from the summer station in Giza, Egypt (8.48%) and that observed by Lin et al. (2006) in the urban zone of Taiwan (17.4%). Meanwhile the conversion ratio of sulfur (*Fs*) ranged between 7.5% and 47.6%, with an average of 24.9%. This value was higher than that registered for Khoder (2002) (12.22%), but lower than that reported for Cheng et al. 2007 in the urban zone of Taiwan (37%). Studies conducted in other urban zones have revealed that during the summer and spring, stations report that the conversion percentages of nitrogen and sulfur are higher than in autumn and winter. This phenomenon is explained partly by the conversion of NO_2 to HNO_3 and SO_2 to H_2SO_4, due to the high concentrations of OH radical that are present at high temperatures, which is in agreement with the results obtained in this study, considering that the average temperature during the period of study was 24.2°C.

Although the correlations between *Fn* ($r^2 = 0.084$) and *Fs* ($r^2 = 0.092$) and the concentration of ozone are not significant, a slight relationship was observed, which indicates that ozone is not the only species that it is affecting to the conversion ratios of NO_2 to nitrate and SO_2 to sulfate. Likewise, it is possible to say that to improve the conversion ratio, high concentrations of ozone are needed.

In summary, during the period of study the meteorological conditions favored the formation of nitric acid, which was 2.7 times higher than nitrous acid, which is understandable, taking in account that in hot seasons photolytic reactions are present with greater frequency. Likewise, it is known that salts such as ammonium nitrate

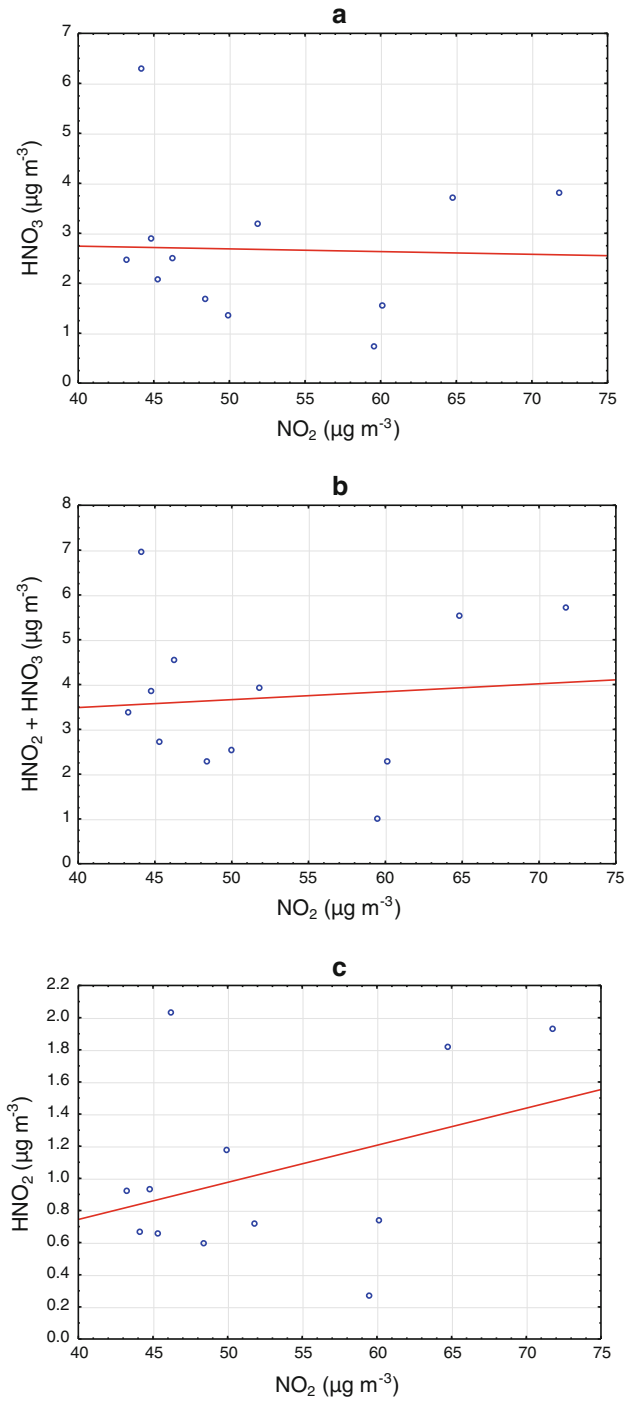

Fig. 1 Correlation between **a** HNO_3 and NO_2, **b** $HNO_2 + HNO_3$ and NO_2 and **c** HNO_2 and NO_2

volatilizes in the atmosphere, giving nitric acid as a product. Meanwhile the conversion ratios of nitrogen and of sulfur revealed that in the downtown area of Guadalajara, the ozone there is not the only factor influencing the generation of nitrates and sulfates by the oxidation of nitrogen dioxide and of sulfur. For this reason, it is expected that the radical OH is favoring the transformation of sulfur dioxide to sulfuric acid and of nitrogen dioxide to nitric acid.

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