

## Evidence for Volcanic Influence on Mexico City Aerosols

G. B. Raga<sup>1</sup>, G. L. Kok<sup>2</sup>, D. Baumgardner<sup>1,2</sup>, A. Báez<sup>1</sup> and I. Rosas<sup>1</sup>

**Abstract.** In situ measurements of sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO) and sulfate mass provide evidence that aerosol composition in Mexico City is affected by emissions from the neighboring volcano, Popocatepetl. The data collected over a two-week period in November 1997 suggest that there are two distinct pathways by which SO<sub>2</sub> is incorporated into particulates. Periods of high humidity, fog, and rain are accompanied by elevated sulfate mixing ratios, attributed to aqueous chemistry. Similarly, elevated sulfate concentrations in low humidity periods appear to be a result of adsorption onto existing particles. These two mechanisms are important for understanding the processes associated with particle formation in this highly polluted urban area. Under the influence of volcanic emissions, SO<sub>2</sub> concentration can reach more than four times the monthly mean daily average (20ppbv) and particulate sulfate can be a factor of 2 larger.

### Overview

High levels of ozone (O<sub>3</sub>), carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), volatile organic compounds (VOC), and particulates dominate pollution in the Mexico City Basin. Until 1992, SO<sub>2</sub> was also present in high concentrations (yearly averages greater than 100 ppbv). Since then, as a result of vigorous mitigation strategies that reduced industrial emissions, the average levels fell to daily concentrations of approximately 20 ppbv. Current emission inventories [PROAIRE, 1996] estimate that SO<sub>2</sub> emissions are approximately 45 ktons per year, primarily from industrial processes and vehicular traffic. These emission inventories, however, do not account for natural sources of SO<sub>2</sub>. This is an environmentally important omission, considering that a nearby volcano, Popocatepetl, has been venting 10–40 ktons per day since late 1993 [Delgado et al., 1998; Goff et al., 1998]. Because of the elevation and location of the volcanic cone (3000 m above and 60 km SE of Mexico City) these volcanic emissions might affect the urban area. Recirculating flows [Bossert, 1997; Fast and Zhong, 1998] are a frequent feature of the local dynamics and would provide the mechanism for transporting air from upper levels into the city. The generally light winds and boundary layer growth would also act to entrain SO<sub>2</sub> enriched air from aloft.

Recent measurements show that SO<sub>2</sub> concentrations frequently exceed the monthly averages by more than a factor of three and sulfate mass also exceeds pre-volcanic [e.g., Aldape et al., 1991

a, b; Miranda et al., 1992; Paredes-Gutierrez et al., 1997] values of 11–14  $\mu\text{g m}^{-3}$  in particles with mean aerodynamic diameter below 2.5 $\mu\text{m}$ , by more than a factor of two. The objective of this paper is to show the link between elevated SO<sub>2</sub> and sulfate mass and the relationship with transport of volcanic SO<sub>2</sub> from upper levels.

### Measurement Program

A measurement campaign was conducted in Mexico City from 4 to 18 November, 1997, near the end of the rainy season. The research site is located in the SW quadrant of the basin at an elevation of 440 m above the mean city level of 2240m and is located above the polluted layer during the night and early morning. The hills where the research site is located reach 1.5 km above the mean basin level. Of interest to this study were measurements of CO, SO<sub>2</sub> and O<sub>3</sub>. The instrumentation used for gas phase measurements was similar to that used by Kok et al. [1997]. The particle mass was derived from filter samples (a 6-stage Andersen impactor with fiberglass filters and a flow rate of 28 l min<sup>-1</sup>) and some inorganic ions were determined by ion chromatography. Basic meteorological parameters were also measured. The sampling strategy consisted of 24-hour gas measurements and the cascade impactors were exposed for 7-hour periods from 10am to 5pm, to include only samples from the polluted mixed layer. Figure 1 shows the location of the research site and Popocatepetl, as well as the basin monitoring station Pedregal.

### Results

Figure 2 shows the time series of SO<sub>2</sub>, relative humidity (RH) and O<sub>3</sub> at the research site for the 2-week sampling period. Several peaks in SO<sub>2</sub> concentrations are evident at the beginning and end of the time period, separated by days of high RH when clouds, fog, and some rain were present. The monthly SO<sub>2</sub> average concentration of 20 ppbv (40  $\mu\text{g m}^{-3}$ , based on the average temperature and pressure at the research site of 293°K and 745 hPa), measured by the city's monitoring network, is clearly exceeded several times in the two weeks presented here. Moreover, the large peaks are observed at nighttime and the site is relatively far away from local anthropogenic sources. Particle sulfate mass was determined by the analysis of filter samples from six days. The O<sub>3</sub> measured at the research site (Fig. 2c) has high values at both ends of the sampling period, separated by relatively low values (lower than the Mexican standard of 110 ppbv per hour) when clouds were present. November 15<sup>th</sup> and 18<sup>th</sup> (dates for which sulfate data will be discussed) indicate elevated O<sub>3</sub> levels, characteristic of sunny and relatively calm days.

<sup>1</sup> Centro de Ciencias de la Atmósfera, UNAM, México

<sup>2</sup> National Center for Atmospheric Research, Boulder, CO, USA

Copyright 1999 by the American Geophysical Union.

Paper number 1999GL900154.  
0094-8276/99/1999GL900154\$05.00

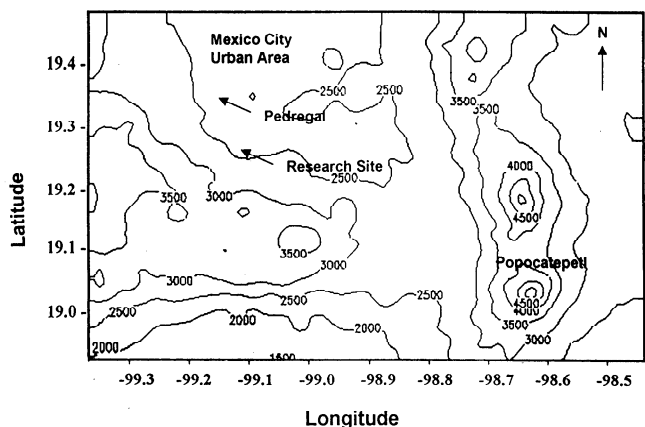


Figure 1. Topographical map of measurement region.

Evidence that the high  $\text{SO}_2$  concentrations observed during the evenings were not the result of anthropogenic activities is found by relating them to simultaneously measured CO concentrations, as seen in Figure 3 for one of the polluted periods (16-18 November) and for the rainy period (10-12 November), at the research site and one of the basin sites (Pedregal). The data presented are 30 minute averages and the different symbols correspond to different periods during the day, as discussed by Raga et al. [1999]. Figures 3a and b indicate a distinct separation between the polluted layer and the afternoon transition and nighttime values (when the downslope flow was dominant). Within the polluted layer there is a close relationship between CO and  $\text{SO}_2$ , indicative of a common source for these pollutants. In contrast, during the late afternoon and night (corresponding to

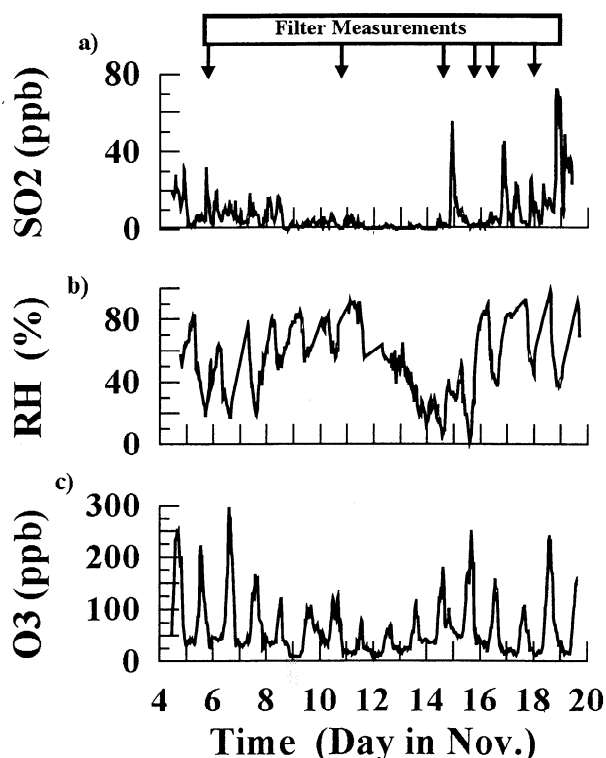


Figure 2. Time series of: a)  $\text{SO}_2$ , b) RH and c)  $\text{O}_3$  (30 minute data for all traces). Days when filter samples were taken are indicated by arrows.

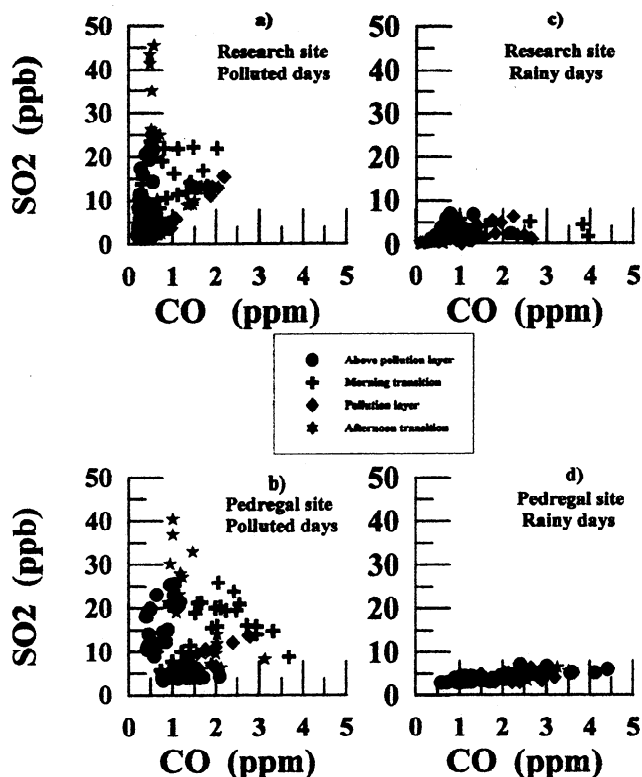


Figure 3. Scatter diagrams of CO vs.  $\text{SO}_2$  for: a) polluted days at the research site, b) polluted days at the basin site Pedregal, c) rainy days at the research site and d) rainy days at Pedregal site. The four symbols correspond to the different periods in which the day was divided. The label 'above pollution layer' corresponds to the nighttime period (9pm to 7am) dominated by downslope flow at the research site. The morning transition corresponds to the period when upslope flow started in the morning, but before the actual top of the mixed layer reached the site. Data labeled as pollution layer, correspond to the period when the site was fully within the mixed layer. The afternoon transition starts when the wind shifted in the afternoon and the downslope flow became established.

datapoints labeled 'afternoon transition' and 'above pollution layer' in Figure 3), low CO values (less than 1.0 ppm) are observed, but  $\text{SO}_2$  values are much higher than those measured when the city emissions reach the research site, indicating that the source of the  $\text{SO}_2$  is not anthropogenic. The only other source close to the basin is the active volcano. Predominant easterly winds observed in the local sounding at 500 hPa (corresponding to the height of the volcano rim) also support the hypothesis that the elevated  $\text{SO}_2$  concentrations have been transported from the volcano to the research site. In contrast, data for the cloudy/rainy days (Figs. 3 c and d) show no evident bifurcation between day and night, and the overall  $\text{SO}_2$  concentration is much lower than in Figs. 3 a and b.

Figure 4 presents sulfate mass for three of the six days for which filter samples were available, and  $\text{SO}_2$  concentrations, both from the previous night and obtained during the same period as the filter samples. The two polluted days show large  $\text{SO}_2$  concentrations during the previous night, but only one of them has a large daytime value which is clearly related to the enhanced particle sulfate mass. This large daytime  $\text{SO}_2$  concentration is evidence that the nighttime volcanic emissions have been entrained into the following day's polluted mixed layer. The

filter samples collected the other 3 days show similar values to November 15<sup>th</sup>, when there was no influence of volcanic emissions reaching the city.

## Discussion

Two of the six days for which filter samples were analyzed for sulfate mass, showed greatly enhanced values above those previously reported from observations before the volcanic activity began [e.g. Aldape et al., 1991 a, b ; Miranda et al., 1992]. These days vary significantly in the meteorological conditions. The first event of enhanced particle sulfate (Fig. 4) corresponds to the day (18 November 1997) in which the elevated SO<sub>2</sub> concentrations from volcanic origin reach the basin. It was characterized by a somewhat suppressed boundary layer growth, evidenced by a fairly low dilution (~13%) from the basin to the research site, at 440m above the basin. Dilution is calculated from the ratio of CO measured at the research site to that in the basin [Raga et al., 1999]. Based on this dilution rate and the emissions from the city (assumed to be 40  $\mu\text{g m}^{-3}$ ), it is estimated that about 35  $\mu\text{g m}^{-3}$  of SO<sub>2</sub> would be transported up to the research site. It is assumed that no SO<sub>2</sub> is transported out of the basin before it reaches the research site. This assumption is justified since the mountain passes in the ranges that surround the basin are located at higher elevations than the research site. The total SO<sub>2</sub> at the research site would be  $\approx 59 \mu\text{g m}^{-3}$  when the mass transported up from the city is combined with the amount observed at the site due to volcanic emissions during the previous night. From this available SO<sub>2</sub>, 34  $\mu\text{g m}^{-3}$  were converted into sulfate mass (57.6%), with a residual SO<sub>2</sub> concentration at the site of about 26.7  $\mu\text{g m}^{-3}$ , which results in an approximate mass balance. The RH was very low on this day, and the mechanism for conversion from SO<sub>2</sub> to sulfate is likely the gas adsorption onto existing particles [Seinfeld and Pandis, 1997].

In order to assess the importance of the volcanic emissions in particulate mass, a case characterized by high SO<sub>2</sub> concentrations the previous night, but which do not influence sulfate production within the polluted layer, is also presented in Fig. 4 (15 November 1997). Even though SO<sub>2</sub> concentrations at nighttime were elevated on this day, there was no evidence of high concentrations during the day. The dilution rate based on the ratio of SO<sub>2</sub> at the basin during the day to that at the research site was 31%, and implies that 27.6  $\mu\text{g m}^{-3}$  would have reached the research site. Fifty percent of this was converted into sulfate while the rest remained as SO<sub>2</sub>. Even though the conversion efficiency from SO<sub>2</sub> to sulfate this day was only marginally lower than in the previous one (50 vs 57.6 %), the resulting sulfate fraction was a factor of 2 lower, where the sulfate fraction is the ratio of the sulfate mass to the total mass.

The final case for comparison (10 November 1997) does not include volcanic emissions but provides insight into the SO<sub>2</sub> to sulfate conversion in the presence of clouds, fog and rain. There was no elevated SO<sub>2</sub> observed during the night, consistent with mainly westerly winds that day. A 50% dilution from the basin to the research site was observed, based on the ratio of measured CO at these two locations. This suggests that  $\approx 20 \mu\text{g m}^{-3}$  of SO<sub>2</sub> would have been available at the research site for conversion to sulfate during the period in which particles were collected. The combined measurement of sulfate and SO<sub>2</sub> however, was 38.7  $\mu\text{g m}^{-3}$  and implies that another source is needed to account for the observed sulfate. Additional sulfate produced within clouds

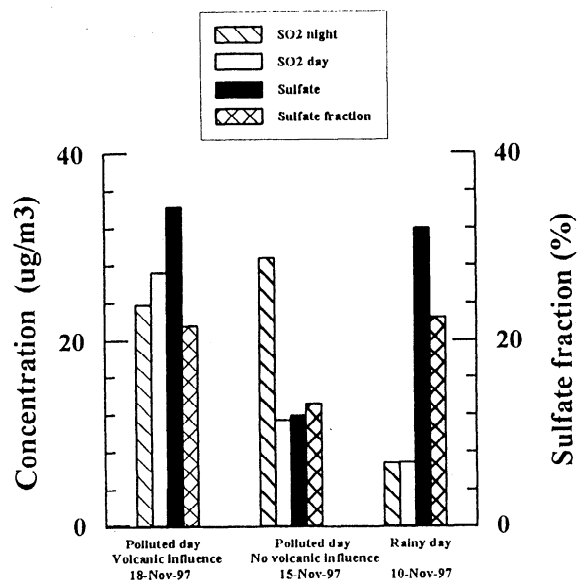


Figure 4. Concentration of SO<sub>2</sub> from 7pm to 10am (gray), from 10am to 5pm (white) and particle sulfate (black) for the 3 cases discussed in text.

could be transported downwards by droplet sedimentation and sulfate aerosols would remain after evaporation. There are 2 pathways by which SO<sub>2</sub> can be incorporated into fog or cloud droplets and, upon evaporation, result in particulate sulfate [Pruppacher and Klett, 1997]. On this day the fraction of particle sulfate to the total mass measured (also shown in Fig. 4) was about 22%, compared to about 15% reported under dry conditions and no volcanic influence [Edgerton et al, 1998]

## Summary

The evaluation of sulfate on aerosol particles shows that enhancements occur under conditions of elevated SO<sub>2</sub> (due to volcanic emissions) or high humidity in the presence of fog or clouds. These two mechanisms are particularly important for understanding particle formation processes in the highly polluted region of Mexico City. Steps have been taken by the local government to significantly lower anthropogenic SO<sub>2</sub> emissions, but the influx of SO<sub>2</sub> from the neighboring volcano offsets these mitigation strategies through increased sulfate production by adsorption onto existing particulates. Secondly, and perhaps just as important, the amount of sulfate produced by wet deposition during days of no volcanic influence was almost the same as when SO<sub>2</sub> was a factor of two or more higher. This suggests that sulfate production under conditions of high humidity and volcanic influence will lead to even more particulate sulfate in the Mexico City Basin.

**Acknowledgments.** The experimental site was generously provided by J. Soberón and A. Hernández (Instituto de Ecología, UNAM) and L.G. Ruiz Suárez and F. García García (Centro de Ciencias de la Atmósfera, UNAM) are also acknowledged for their efforts in arranging for the use of the site. The authors are indebted to W. Luke, for the loan of the sulfur dioxide analyzer and to H. Padilla and M.C. Torres for their collaboration in the HPLC analysis of inorganic ions. The authors thank Ing. Pedroza and his team at the Red Automática de Monitoreo

Atmosférico (RAMA), who provided data from the monitoring network sites. Partial support for the field campaign was provided by Academia Mexicana de Ciencias and by the UNAM-CRAY program (SC007597).

## References

- Aldape, F., J. Flores, and R.V. Diaz, Seasonal study of the composition of atmospheric aerosols in Mexico City, *Int. J. PIXE*, 1, 355-371, 1991a.
- Aldape, F., J. Flores, and R.V. Diaz, Two year study of elemental composition of atmospheric aerosols in Mexico City, *Int. J. PIXE*, 1, 373-388, 1991b.
- Bossert, J.E., An investigation of flow regimes affecting the Mexico City region, *J. Appl. Met.*, 36, 119-140, 1997.
- Delgado, H.G., L.G. Cardenas, and N.S. Piedad, Sulfur dioxide emissions from Popocatepetl volcano (Mexico): Case study of a high flux, passively degassing, erupting volcano, *J. Volcan. and Geothermal Res.*, Submitted, 1998.
- Edgerton, S., et al., Particle chemistry and spatial variability in Mexico City paper presented at AGU Spring Meeting, Boston, 26-29 May, 1998.
- Fast, J.D. and S. Zhong, Meteorological factors associated with inhomogeneous ozone concentrations within the Mexico City Basin, *J. Geophys. Res.*, 103, 18,927-18,946, 1998.
- Jáuregui, E. and E. Romales, Urban effects on convective precipitation in Mexico City. *Atmos. Environ.*, 30, 3383-3389, 1996.
- Kok, G.L., J.A. Lind, and M. Fang, An airborne study of air quality around the Hong Kong territory. *J. Geophys. Res.*, 102, 19,043-19,057, 1997.
- Goff, F., et al., Geothermal surveillance of magmatic volatiles at Popocatepetl volcano, Mexico, *GSA Bulletin*, 110, 695-710, 1998.
- Miranda, J., J.R. Morales, T.A. Cahill, F. Aldape, and J. Flores, A study of elemental contents in atmospheric aerosols in Mexico City, *Atmosfera*, 5, 95-108, 1992.
- Paredes-Gutierrez, R., A. Lopez-Suarez, J. Miranda, E. Andrade and J.A. Gonzalez, Comparative study of elemental contents in atmospheric aerosols from three sites in Mexico City using PIXE, *Rev. Int. Contam. Ambient.*, 13, 81-85, 1997.
- PROAIRE, Programa para Mejorar la Calidad del Aire en el Valle de Mexico 1995-2000, Departamento del Distrito Federal, 213 pp., 1996.
- Pruppacher, H. and J. Klett, *Microphysics of clouds and precipitation*, 2nd ed., 954 pp, Kluwer Academic Publishers, London, 1997.
- Raga, G.B., D. Baumgardner, G. Kok and I. Rosas, Some aspects of boundary layer evolution in Mexico City. *Atmos. Environ.*, Accepted, 1999.
- Seinfeld, J., and S. Pandis, *Atmospheric Chemistry and Physics. From air pollution to climate change*, 1326 pp. John Wiley and Sons, Inc., New York, 1997.

---

A. Báez, D. Baumgardner, G. Raga, and I. Rosas, Centro de Ciencias de la Atmósfera, UNAM, Ciudad Universitaria, 04510, DF México. (e-mail: barmando@ccaunam.atmosfcu.unam.mx; darrel@servidor.unam.mx; raga@servidor.unam.mx; iarp@ccaunam.atmosfcu.unam.mx)

G. L. Kok, National Center for Atmospheric Research, Boulder, CO, USA

(Received October 29, 1998; revised January 26, 1999; accepted February 2, 1999)