Particulate Air Pollution in Mexico City

A Collaborative Research Project

by

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ABSTRACT

PM_{10}, $PM_{2.5}$, precursor gas, and upper-air meteorological measurements were taken in Mexico City from 23 February to 22 March 1997 to understand concentrations and chemical compositions of the city s particulate matter (PM). Average 24-hour PM_{10} concentrations over the period of study at the core sites in the city was 75 g/m^3. The 24-hour standard of 150 g/m^3 was exceeded for seven samples taken during the study period; the maximum 24-hour concentration measured was 542 g/m^3. Nearly half of the PM_{10} was composed of fugitive dust from roadways, construction, and bare land. About 50% of the PM_{10} consisted of $PM_{2.5}$, with higher percentages during the morning hours. Organic and black carbon constituted up to half of the $PM_{2.5}$. Particulate matter concentrations were highest during the early morning and after sunset when the mixed layers were shallow. Meteorological measurements taken during the field campaign show that on most days air was transported out of the Mexico City basin during the afternoon with little day-to-day carryover.

BACKGROUND

Mexico City is one of the world s largest metropolitan areas, containing nearly 20 million inhabitants within the Valle de Mexico (also referred to as the Mexico City basin). The Valle de Mexico occupies ~1,300 km^2 at a nominal elevation of 2,240 m above mean sea level, and is bordered on the east and west by mountains that rise 1,000 m above the valley floor, with low points to the north and south. Although its elevation is high, Mexico City s location at 19 degrees north latitude provides it with a temperate climate throughout the year. The climate is generally dry, but thunderstorms are frequent and intense from June through October. Winters are slightly cooler than summers.

More than 20% of Mexico s entire population lives in the Valle de Mexico, and more than 30% of the country s industrial output is produced within its environs. Though already one of the world s largest cities, the Mexico City metropolitan area is still growing at a rate exceeding 3% annually. More than three million vehicles travel on its streets daily.

As in many large cities, and especially in ones located in valleys with limited ventilation, Mexico City experiences air pollution problems, especially ozone and suspended particles. Stringent controls since 1990 have resulted in major reductions of sulfur dioxide emissions. Sulfur in diesel fuel has been reduced from 0.5% to 0.05%. Only one industrial complex still uses residual oil, and it is slated to soon change to gas. Gasoline-powered vehicles were required to have catalytic converters after 1990, and unleaded fuel was introduced at that time to provide cleaner emissions. Within the Distrito Federal, the central core of Mexico City that has its own government, many old diesel buses and trucks have been replaced with newer vehicles powered by more modern, cleaner engines. Modern pollution controls are required on major industries operating within the Valle de Mexico.

These efforts have attenuated the emissions engendered by growth, but 24-hour PM_{10} (particulate matter with aerodynamic diameter less than 10 m) concentrations exceeding several hundred $\mu g/m^3$ are still measured at many monitoring sites.[1,2] A persistent haze blankets the city, especially during winter, and there is great concern among residents and visitors about the effects of suspended particles on health. Aerosols that contribute to this visibility degradation are usually a combination of primary and secondary particles. Primary particles are directly emitted from different sources, while secondary particles form in the atmosphere from gaseous emissions of sulfur dioxide, oxides of nitrogen, ammonia, and heavy organic gases. Secondary aerosol formation may occur under stagnant air conditions, after gaseous emissions from different sources have mixed and aged, and when pollutants

generated on previous days accumulate or are recycled by winds and are stored overnight in surface-based inversions.

In 1996, the U.S. Department of Energy (DOE) and Mexico s Petr leos Mexicanos (PEMEX) began sponsoring this project to characterize the nature and sources of suspended particulate matter found in the ambient air in Mexico City. This collaborative effort follows another program sponsored by DOE and PEMEX in the early 1990 s to study gas phase pollutants and photochemical oxidants in the Valle de Mexico.[3,4] The high altitude, the year-round sunshine, and the complex atmospheric chemistry characteristic of Mexico City create a challenging laboratory for scientific research. Participants in the research include (1) Instituto Mexicano del Petr leo (IMP); (2) Los Alamos National Laboratory (LANL); (3) Pacific Northwest National Laboratory (PNNL); (4) Argonne National Laboratory (ANL); (5) Desert Research Institute (DRI), University and Community College System of Nevada; (6) Environmental Testing Laboratory, National Oceanic and Atmospheric Administration; and (7) Comisi n Ambiental Metropolitana; and (8) several other research groups from Mexican universities and other research institutes.

This paper describes the goals and objectives of the project, preliminary data results from the field campaign, and a brief summary of ongoing data analyses and modeling efforts.

PROJECT GOALS

The first programmatic goal of the project is to provide additional and more comprehensive information than is currently available to explain the nature and causes of particulate concentrations and visibility impairment in and around Mexico City. This information is needed to better understand the implications of currently planned emission reduction strategies, and to focus future emissions reduction efforts in those areas where they will have the greatest benefit on air quality for the least cost. This goal is being pursued by obtaining and analyzing ambient data acquired during an intensive field campaign carried out in Mexico City in February and March of 1997. This period was selected for the field campaign because historical data suggest that the highest PM concentrations occur in Mexico City in late winter and early spring. Additional information is being generated by emission measurements and by the application of mathematical models and data analysis methods.

The second programmatic goal is to establish the capabilities, in Mexico, to continue aerosol measurements so that proposed emissions controls can be evaluated and their effects can be detected after they are implemented. Measurements made during the intensive field campaign are being used to evaluate the future needs of the comprehensive network of PM_{10} monitors (RAMA- Red Automatica de Monitoreo Atmosferico) established by the Comision

Ambiental Metropolitana to determine compliance with standards and to initiate air quality alerts.

PROJECT OBJECTIVES

Several specific technical objectives of the project that will be discussed in this article include efforts to:

- Characterize the nature and causes of particulate concentrations and visibility impairment in and around Mexico City by obtaining a documented data set of specified precision, accuracy, and validity that supports modeling and data analysis efforts.

- Document the spatial distribution, temporal variation, and intensity of $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 m) and PM_{10} concentrations, and visibility impairment within the Valle de Mexico.

- Measure and characterize the structure and evolution of the boundary layer and the nature of regional circulation patterns that determine the transport and diffusion of atmospheric contaminants in the Valle de Mexico.

- Further characterize the major sources contributing to significant chemical components of PM_{10}, $PM_{2.5}$, and light extinction, including sources that directly emit particles and those that emit precursor gases for secondary aerosol formation.

- Estimate contributions to PM, both with respect to mass concentration and the concentrations of significant chemical components, and relate these contributions to different emissions and meteorological conditions.

DESCRIPTION OF THE FIELD CAMPAIGN

A major field campaign was carried out in Mexico City from 23 February through 22 March 1997.[5,6] The locations of the primary sampling sites are shown in Figure 1 and their descriptions are found in Table 1.

TABLE 1. Descriptions of the Six Core Sites

Site Name	Site Code	Site Description
La Merced	MER	Central city near heavily traveled, paved and curbed surface streets with light-duty vehicles and modern heavy-duty diesel buses.
Xalostoc	XAL	Northeastern city near light to medium industries. Heavily traveled paved and unpaved roads are nearby with old and new gasoline and diesel vehicles. A dry lake (Lake Texioco) lies approximately 5 km east of the site.
Pedregal	PED	Suburban neighborhood near clean, paved, residential roads. Lightly traveled. No nearby industries.
Tlalnepantla	TLA	Industrial and residential area with nearby electronics manufacturing, corn milling, and metal fabricating facilities.
Nezahuatcoyotl	NET	Near heavily traveled paved and unpaved roads. Directly south of unpaved athletic fields and approximately 10 km south of Lake Texioco.
Cerro de Estrella	CES	Southeastern city near heavily traveled paved and unpaved roads. Several small stonecutting operations (marble monuments) nearby. Heavy old and new vehicle traffic.

Measurements during the field program included:

- PM and ammonia concentrations (24-hour averages) at 25 locations inside and outside the city
- PM_{10} and $PM_{2.5}$ samples four times per day at 3 sites (XAL, MER, and CES) and once per day at an additional 3 sites (TLA, NET, and PED), with analysis for mass, elemental, ion, and carbon concentrations at each site
- Hourly measurements of light scattering and absorption at 2 sites (MER and PED)
- Four 6-hour measurements of nitric acid and ammonia at 1 site (MER)

- Analysis of light hydrocarbon gases at 3 sites (XAL, MER, and PED), and heavy hydrocarbons, polycyclic aromatic hydrocarbons (PAH), and nitro-PAH at 1 site (MER)

- Ozone measurements at the XAL and PED sites and at 17 other sites in the network

- NO_x measurements at the XAL and PED sites and at 14 other sites in the network

- Peroxyacetyl nitrate (PAN), hydrocarbon, and particle impactor measurements at 1 site (IMP)

- Meteorological data, including radar wind profilers, remote acoustic sounding system (RASS) temperature sensors, and temperature and humidity profiles by airsonde at 4 sites (Teotihuacan, Cuautitlan, Chalco, and UNAM), acoustic sodar at 2 sites (Teotihuacan and Chalco), and surface meteorological towers at 3 sites (Teotihuacan, Chalco, and UNAM).

Preliminary findings related to PM mass and chemical measurements are presented in the next section. Results of the meteorological analyses are presented in the following section. In the final section, a brief description is given of the more detailed data analyses currently underway.

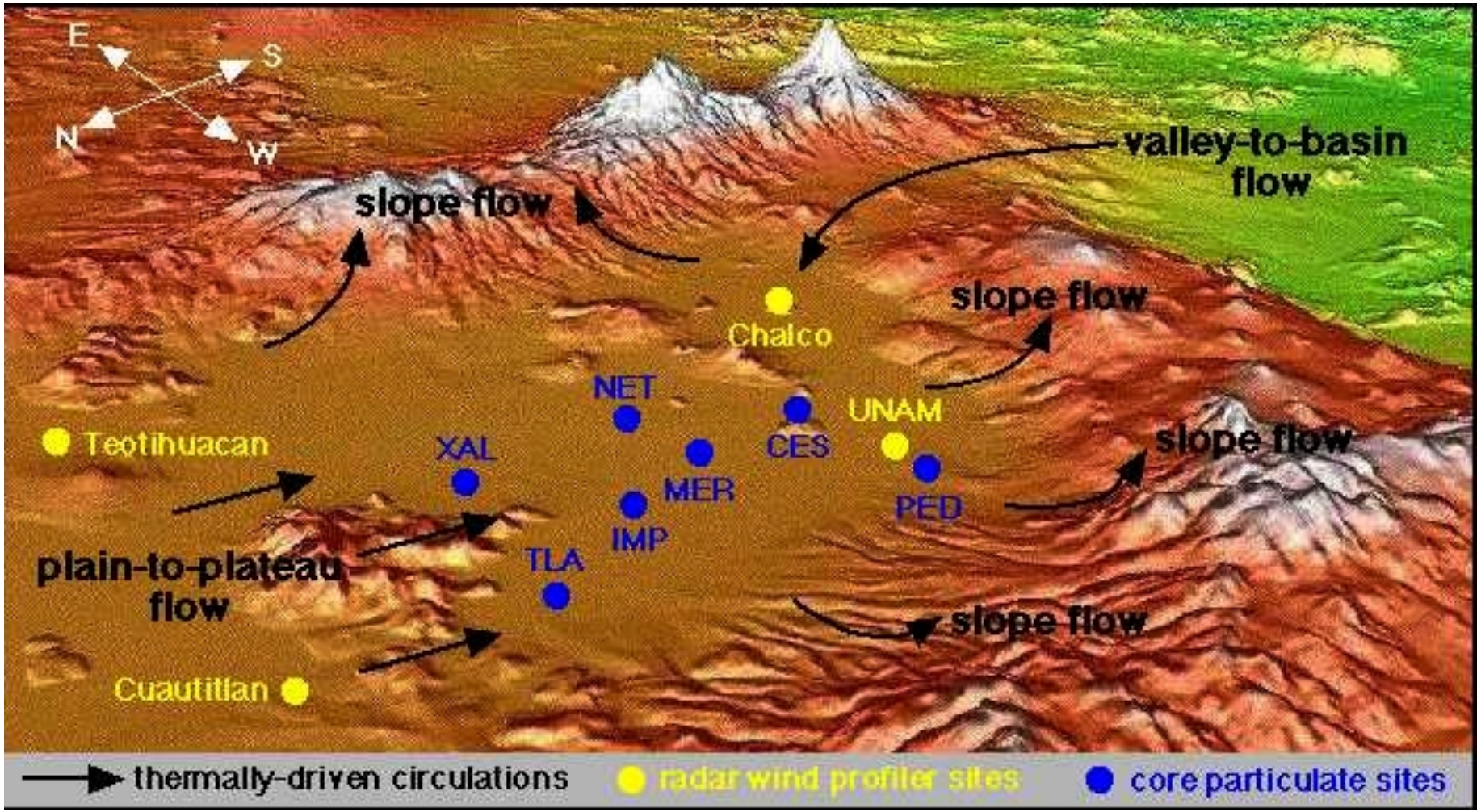

FIGURE 1. Map showing Mexico City basin, measurement sites and predominant flow patterns (see Table 1 for core particulate site names/codes)

PRELIMINARY FINDINGS FROM AMBIENT AIR OBSERVATIONS

PM_{10} AND $PM_{2.5}$ MASS MEASUREMENTS

The average 24-hour PM_{10} concentrations over the period of study at the core sites[a] in the city were around 75 g/m^3. The average concentrations measured at the boundary sites at the edges of the Mexico basin were about 30% less. The U.S. and Mexican standard of 150 g/m^3 was exceeded a total of seven times: at the XAL site on 28 February, and 4 and 5 March; at the NET site on 25 February, and 4 and 6 March; and at the CES site on 21 March. The maximum 24-hour concentration measured during the sampling period was 542 g/m^3, measured at the CES site on 21 March 1997. The average 24-hour $PM_{2.5}$ concentration was 36 g/m^3. The maximum 24-hour $PM_{2.5}$ concentration measured during the sampling period was 184 g/m^3, measured at the NET site on 5 March 1997. Although there is no Mexican standard for $PM_{2.5}$, the U.S. 24-hour-average standard of 65 g/m^3 was exceeded four times during the study: at the XAL site on 4 March, at the NET site on 4 and 6 March, and at the CES site on 28 February. The $PM_{2.5}$ fraction generally comprised about 50% of the PM_{10}, with higher ratios during the morning hours. Figure 2 shows the 24-hour-average $PM_{2.5}$ concentrations at the 6 core sites over the experimental period. A summary of the PM_{10} and $PM_{2.5}$ concentrations measured at each site is shown in Table 2.

The highest PM concentrations measured were in the northern and eastern parts of the Valle de Mexico, in contrast to the high ozone concentrations normally found in the southwest. There were large differences (more than a factor of 2) in the PM_{10} and $PM_{2.5}$ concentrations from site to site. High-density sampling around the six core sites indicated that the zone of representation for these long-term monitoring sites was on the order of a few kilometers. Hourly PM_{10} concentrations exhibited diurnal patterns with dual peaks found at mid-morning (~ 0900 CST) and early evening (~ 1900 CST).

[a] Core Sampling Sites: MER=La Merced, XAL=Xalostoc, PED=Pedregal, TLA=Tlalnepantla, NET=Nezahuatcoyotl, CES=Cerro de Estrella

TABLE 2. Summary 24-Hour Average PM Concentrations at the Six Core Sites

Site Code		PM_{10} (g/m^3)	Number in Average	$PM_{2.5}$ (g/m^3)	Number in Average
MER	Minimum	2.37		20.93	
	Maximum	126.69		61.37	
	Average	57.19	28	35.99	28
XAL	Minimum	42.22		24.58	
	Maximum	181.43		66.70	
	Average	103.55	28	44.34	28
PED	Minimum	12.36		9.00	
	Maximum	60.01		33.85	
	Average	39.41	26	21.60	25
TLA	Minimum	26.18		14.78	
	Maximum	77.72		54.83	
	Average	57.92	24	30.53	28
NET	Minimum	15.79		15.85	
	Maximum	267.29		183.70	
	Average	108.27	22	50.01	25
CES	Minimum	21.22		13.16	
	Maximum	541.79		128.52	
	Average	78.68	28	33.23	28

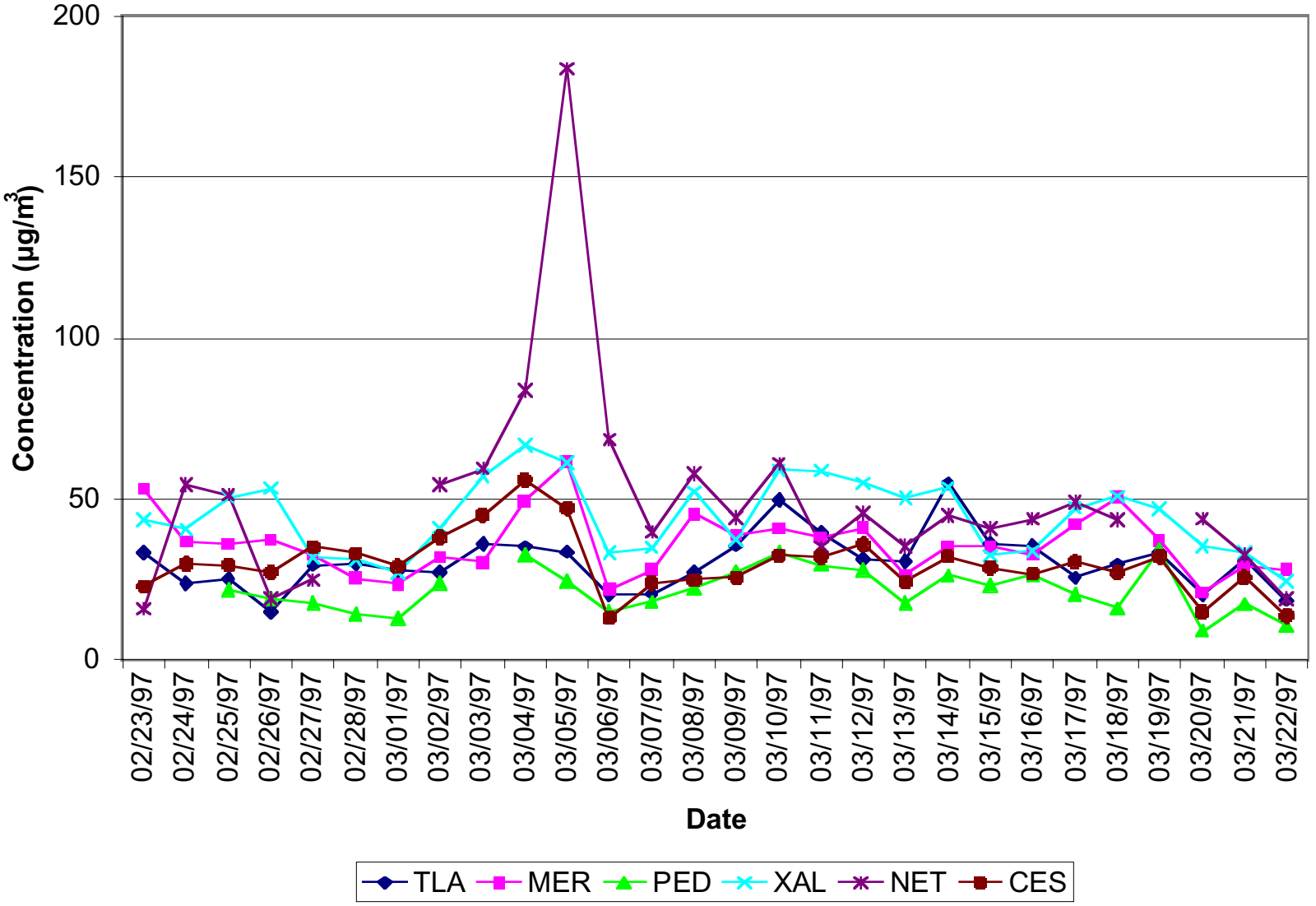

FIGURE 2. Concentrations of $PM_{2.5}$ at the six core sampling sites.

PM_{10} AND $PM_{2.5}$ CHEMICAL MEASUREMENTS

Three specific episodes of high pollution were observed during the measurement period and the chemical constituents in these samples were analyzed in more detail. Although there has been some prior chemical analysis of particulate matter in Mexico City,[7-9] this project included the most comprehensive chemical analysis of particulate matter in that city to date. Sample analyses included sulfate and nitrate analyses by ion chromatography,[10] elemental analyses by x-ray fluorescence,[11] water soluble sodium and potassium analyses by atomic absorption spectroscopy,[12] ammonium analysis by automated colorimetry,[13] and organic and elemental carbon (black carbon or soot) by thermal/optical reflectance.[14]

Secondary ammonium nitrate and ammonium sulfate were distributed relatively homogeneously throughout the valley and constituted approximately 10%-20% of the PM_{10} and 15%-30% of the $PM_{2.5}$. Areawide average sulfate concentrations were 5-6 g/m^3 and average nitrate and ammonium concentrations were 2-3 g/m^3. While sulfate levels were relatively low compared to that found in the Eastern United States, they were higher than expected given recent emission reductions of sulfur dioxide in Mexico City. There was sufficient ammonia and nitric acid present to favor the formation of particle-phase ammonium nitrate. Figures 3 and 4 show the sulfate/nitrate/ammonium concentrations and the organic and elemental carbon concentrations respectively at the downtown MER site. Valley-wide, carbon-containing aerosols accounted for about 20%-35% of the PM_{10} and 25%-50% of the $PM_{2.5}$.

Geological material (estimated using chemical concentrations of the abundant crustal species Al, Si, Fe, Mg, and Ca) was the major contributor to PM10, especially at the NET and XAL sites, accounting for 40%-55% of the PM10 mass across the city. For PM2.5, the NET site shows a substantially larger contribution from the geological component than do the other sites, consistent with the windblown dust emissions observed at the site. The NET site also shows substantially less contribution from organic and elemental carbon than the other sites.

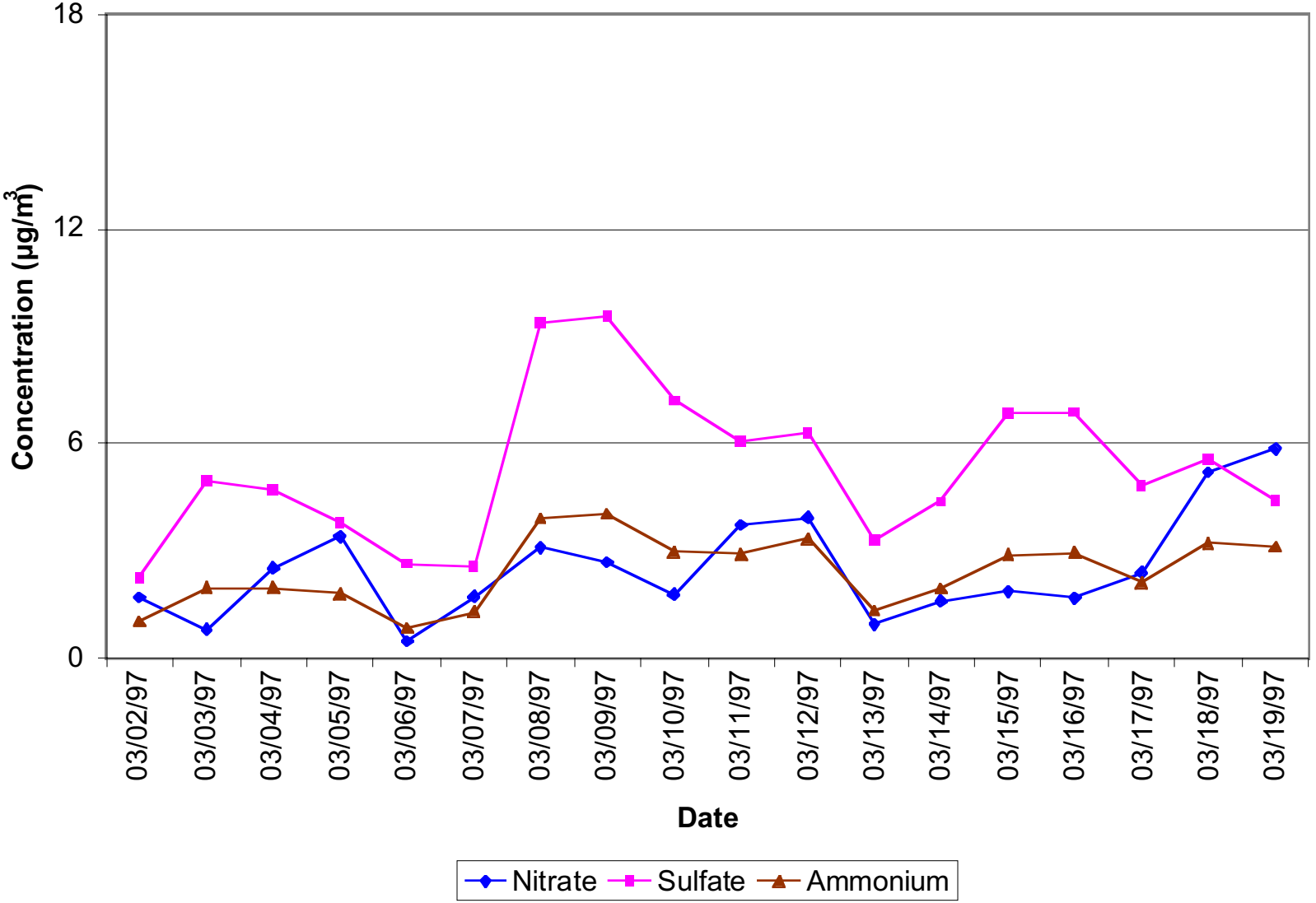

FIGURE 3. Concentration (g/m^3) of secondary $PM_{2.5}$ inorganic aerosols at La Merced, an urban sampling site in downtown Mexico City.

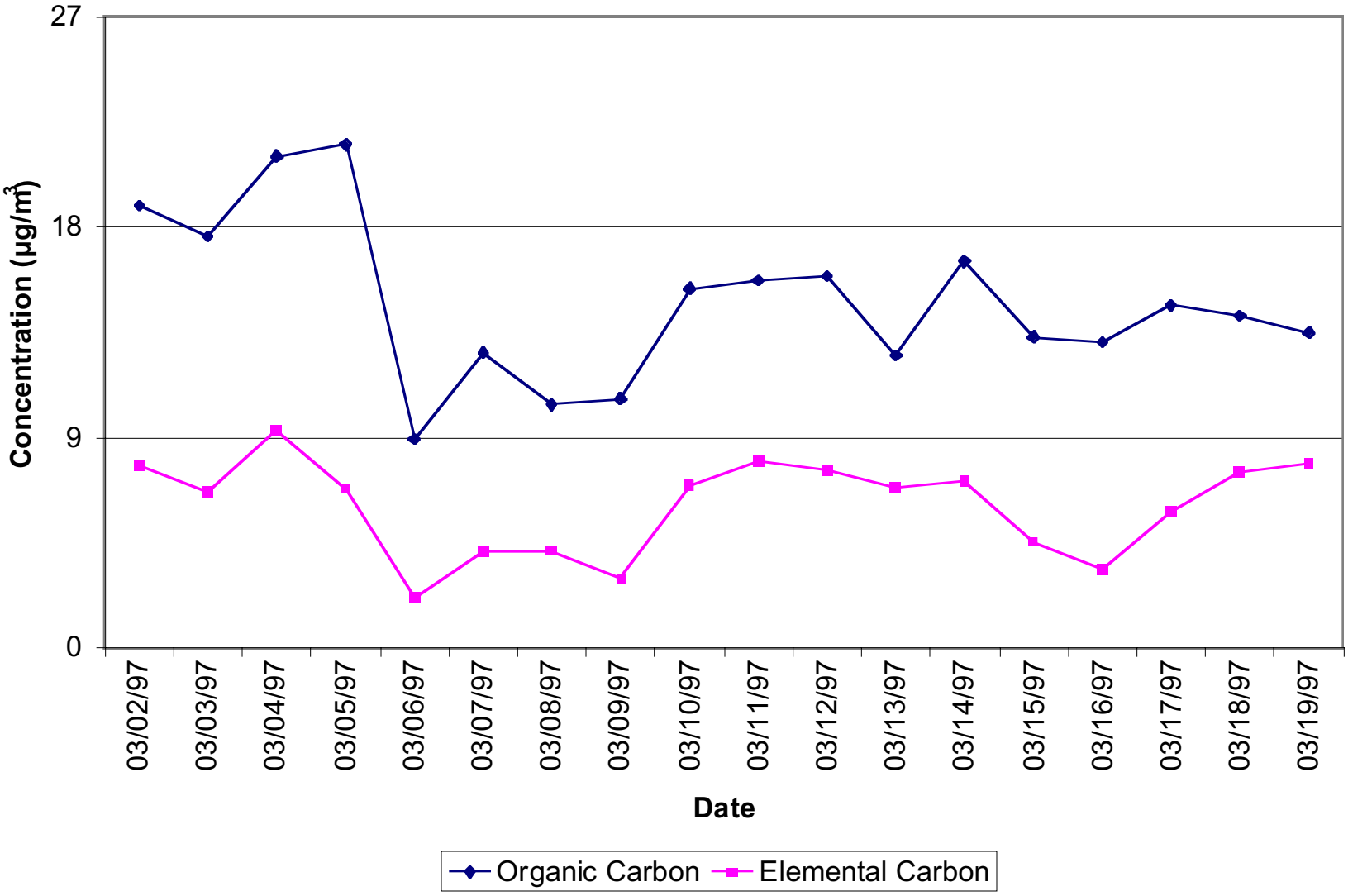

FIGURE 4. Concentrations of $PM_{2.5}$ carbonaceous aerosols at La Merced, an urban sampling site in downtown Mexico City.

VISIBILITY MEASUREMENTS

Hourly nephelometer and aethalometer measurements of light scattering and absorption at the downtown MER and suburban PED sites showed a high correlation with $PM_{2.5}$ concentrations and reduced visibility at both sites, particularly during the morning hours (0800-1100 CST). The relationship between $PM_{2.5}$ and the light absorption coefficient (B_{abs}) for MER is shown in Figure 5. Black carbon aerosol is likely responsible for much of the light absorption.

VOLATILE ORGANIC MEASUREMENTS

Volatile organic compounds (VOC) concentrations were measured in canisters over 3- and 6-hour periods at 3 sites (MER, XAL, PED) and are shown in Figure 6. The highest concentrations measured at all sites occurred during the morning hours (0600-0900 CST), and these were often 3 times the concentrations measured later in the day. The concentrations at La Merced were the highest, averaging about 4,106 ppbC, followed by XAL at 3,130 ppbC and PED at 1,136 ppbC. Higher concentrations of VOC were measured at MER, whereas in the past, the higher concentrations have been measured at XAL. VOC concentrations at the PED site were only 25-35% of the levels measured at the MER and XAL sites.

PEROXYACYL NITRATES (PANS)

Peroxyacyl nitrate (PAN) concentrations measured at a commercial site approximately 7 km north of the La Merced site were similar to those found in Los Angeles during the early 1970s.[16] PAN levels exceeded 30 ppb on five of the days sampled and exceeded 10 ppb on all but a few days of the study.[17] Although there is no air quality standard for PAN, high PAN concentrations are a good indicator of the organic oxidizing capacity of the urban air mass, since they are directly connected to organic peroxy radical formation and nitrogen dioxide (both ozone-forming precursors).

PAN concentrations measured near the city center from 20 February to 23 March 1997 are shown in Figure 7. PAN was typically 90% of the total PANs observed, with the rest of the PANS being approximately 9% peroxypropionyl nitrate (PPN), and approximately 1% peroxybutyrl nitrate (PPB). Maximum values for PAN, PPN, and PPB were 35, 6, and 1 ppb, respectively. These high levels of PANS reserve an appreciable amount of the nitrogen dioxide, thus slowing the reaction of OH with NO_2 to form nitric acid and subsequently ammonium nitrate aerosols. Relatively low levels of inorganic nitrates were found in the $PM_{2.5}$ measured at La Merced, as compared to the high

NO_y[b] levels in the air.[18,19] This is consistent with the high levels of PANS measured nearby acting as a reservoir for nitrogen dioxide and lowering the formation of ammonium nitrate in Mexico City during the daytime. These PAN concentrations are often accompanied by organic aerosols, including nitrophenols and nitro-PAH, formed from oxidation reactions.[19,20]

As shown in Figure 7, PAN concentrations exhibit a strong diurnal variation, consistent with a complete venting of the air mass during the late afternoon and early evening as observed in the meteorological data. Exceptions occurred on 6 March, when wind speeds were high, and during the night of 11-12 March, where some carryover was observed. These data support the finding that the polluted air is often transported out of the Mexico City air basin and carried aloft into the regional air masses downwind of the city.

[b] NO_y includes NO, NO_2, HNO_3, N_2O_5, $RONO_2$, and other nitrogen species.

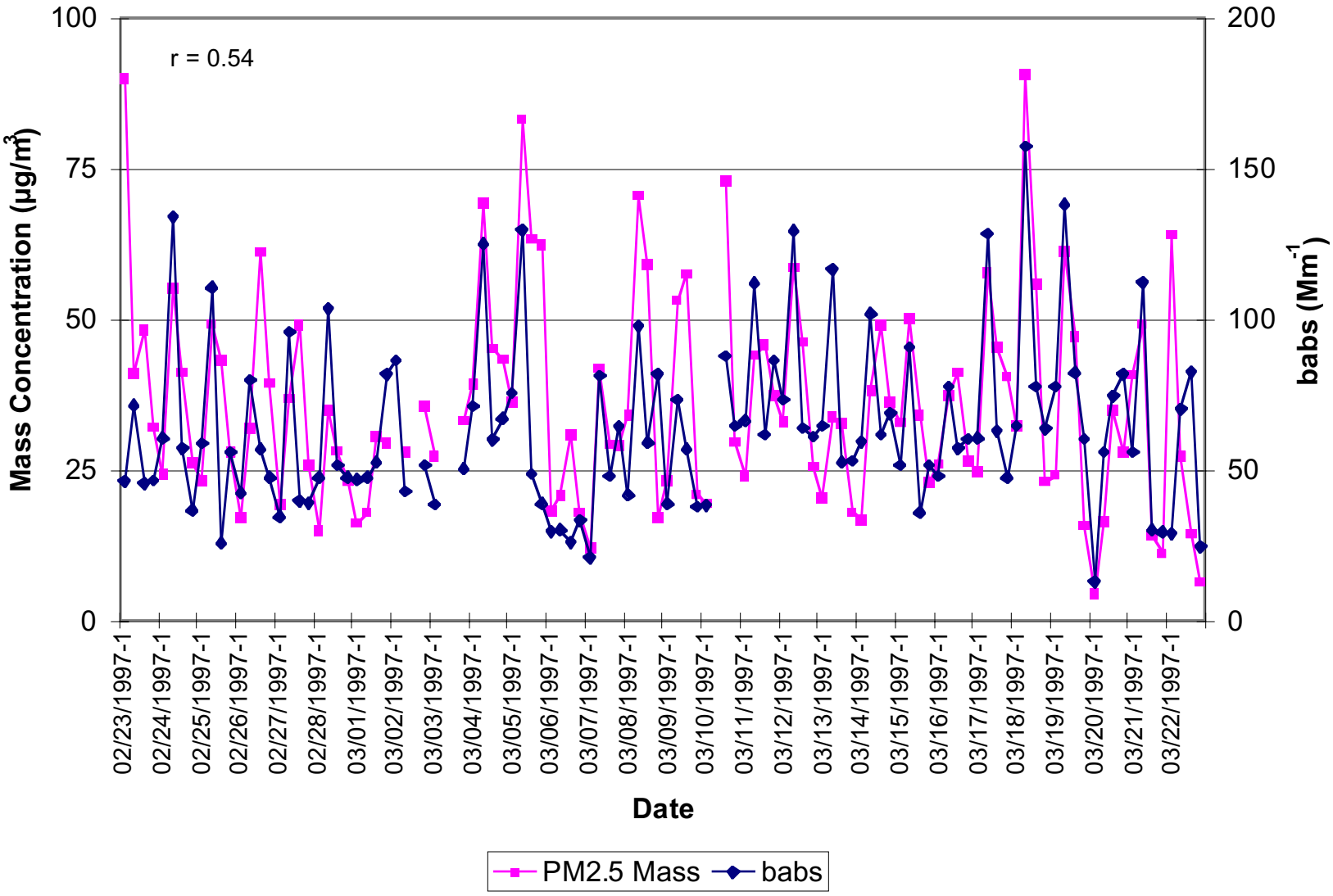

FIGURE 5. $PM_{2.5}$ mass and light absorption (b_{abs}) at La Merced for six-hour averages.

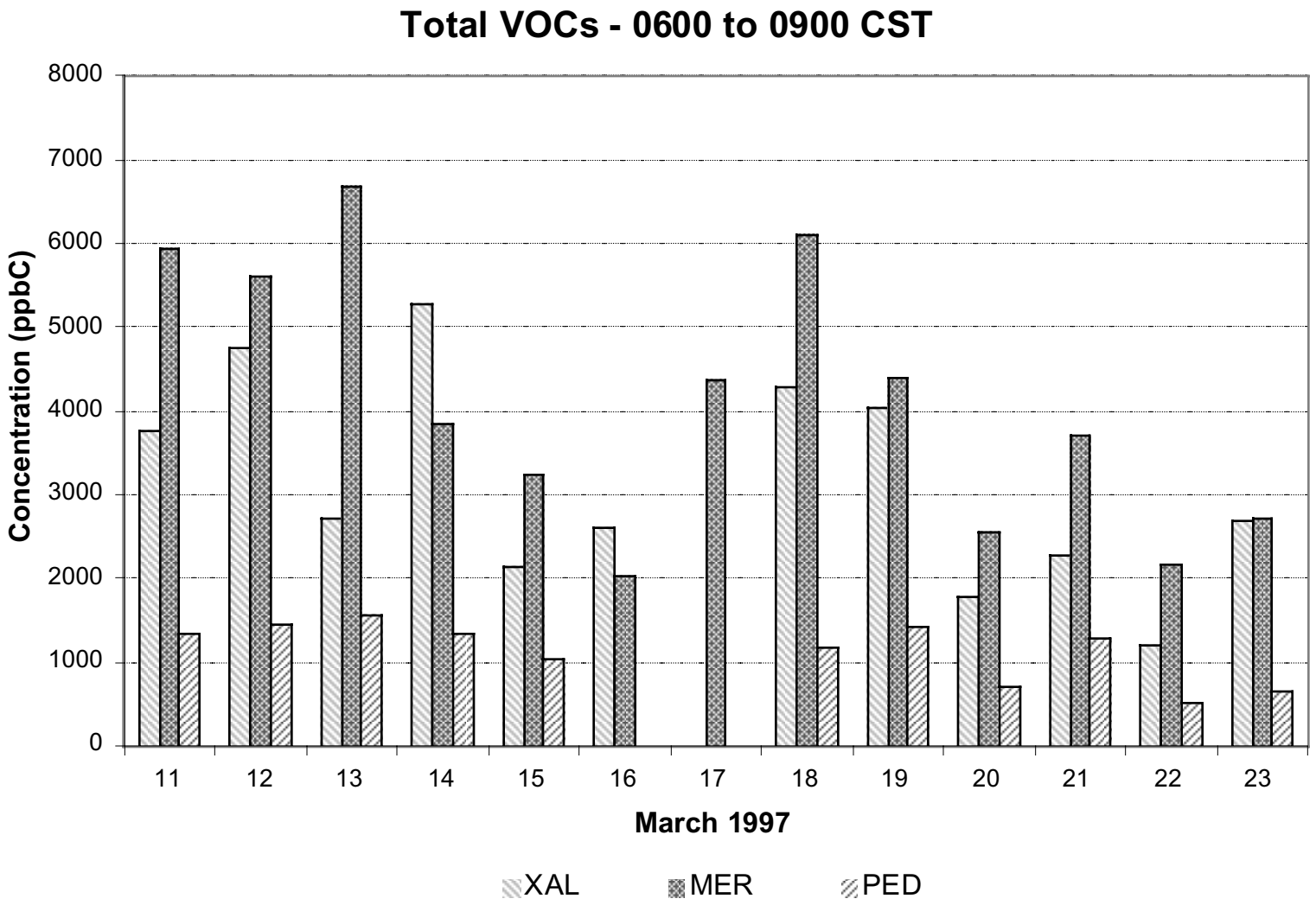

FIGURE 6. Concentrations of volatile organic compounds at 3 sites.

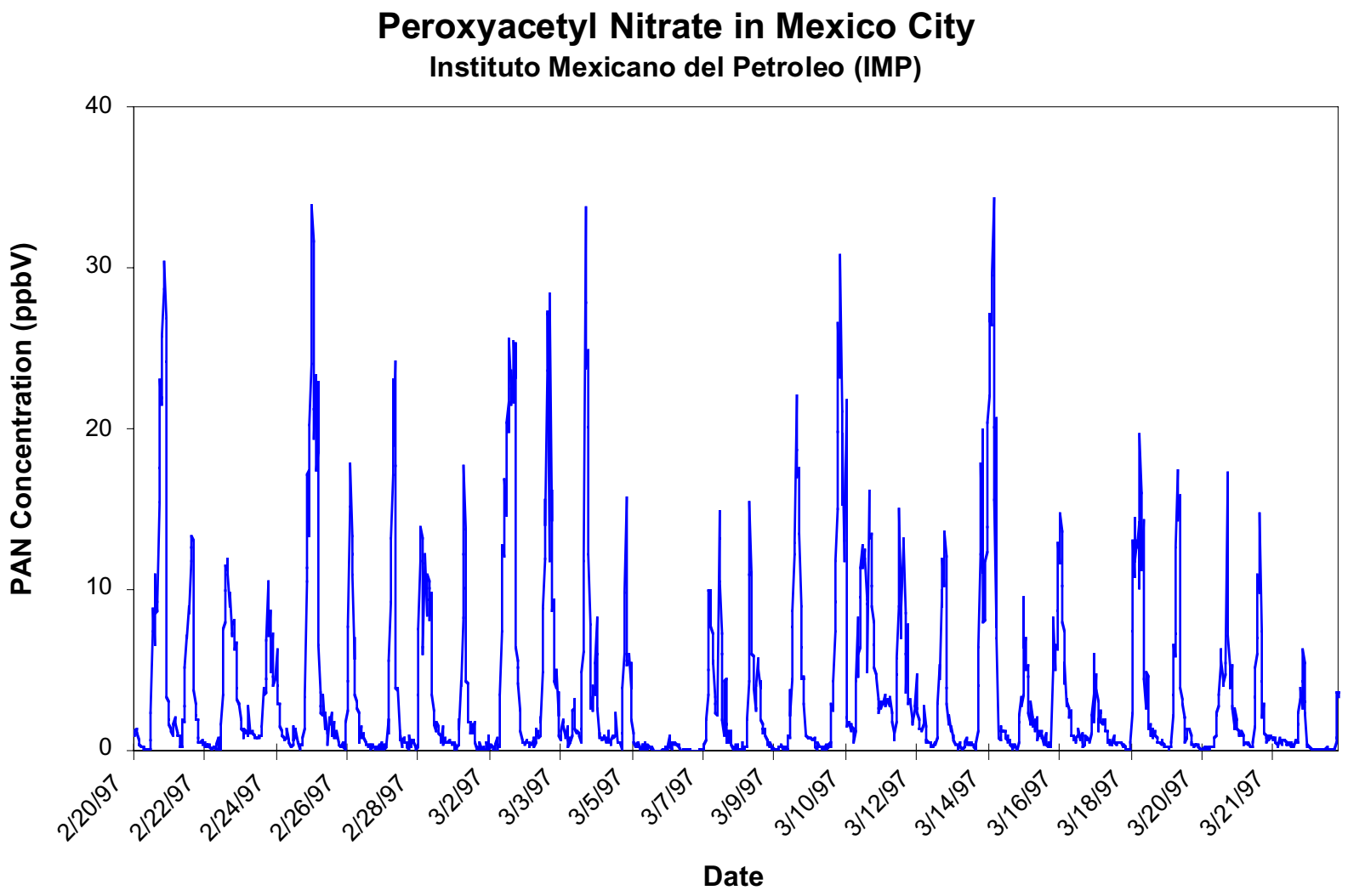

FIGURE 7. Plot of peroxyacetyl nitrate (PAN) measurements at the IMP site.

METEOROLOGICAL FINDINGS

Because of the topographic setting of the city, the moderately strong insolation associated with its tropical latitude and high elevation, and weak prevailing synoptic winds, Mexico City is strongly affected by thermally and topographically induced circulation patterns. Three daytime flow patterns were observed during February and much of March 1997:[21-23] (1) a regional plain-to-plateau flow of air from the lower lying areas to the north and east into the basin from the north in the late afternoon, driven by the heating of the elevated terrain in central Mexico; (2) local valley-to-basin flow in which southerly winds would develop and propagate through the gap in the mountains to the southeast and over the ridge forming the southern boundary of the Mexico City basin; and (3) local upslope flows driven by the heating of the sidewalls of the mountains. Figure 8 shows schematic diagrams illustrating important meteorological processes contributing to pollutant transport.[24-28]

The southeasterly wind pattern measured at Chalco was the most consistent flow feature measured during the experimental period. These winds developed in the mid-afternoon in a layer up to 1 km deep and continued for several hours. The local upslope flows evident in the early afternoon in the southwestern part of the basin were weaker and shallower than anticipated. These flows have been associated with the prevalence of high ozone concentrations in this area of the valley. On about half of the days studied, late afternoon drainage flows from the northeast, beginning at about 1800 CST and persisting for several hours, ventilated the valley.

Mixed layers grew to depths of 2,500 to 4,000 meters, with a rapid period of growth beginning shortly before noon and lasting for several hours. Significant differences between the mixed-layer temperatures in the basin and outside the basin were observed. Data analyses and models provide evidence that the circulations are highly complex and that relatively weak upper-level synoptic systems had an impact on the local and regional thermally driven flows in the area.[29-32]

Despite recurring flow patterns, the structure and evolution of the boundary layer and the circulation patterns in the basin varied considerably on a day-to-day basis. Wind flows measured during the field campaign were very light, and their patterns were dependent on interactions among several complex meteorological mechanisms. Winds in the well-mixed boundary layers showed significant changes in direction, and therefore the use of surface wind data alone to determine pollutant dispersion patterns may be very misleading. Although recirculation of pollutants within the course of a day appeared to be important, recirculation over several days did not result in pollutant buildup during the period of study.

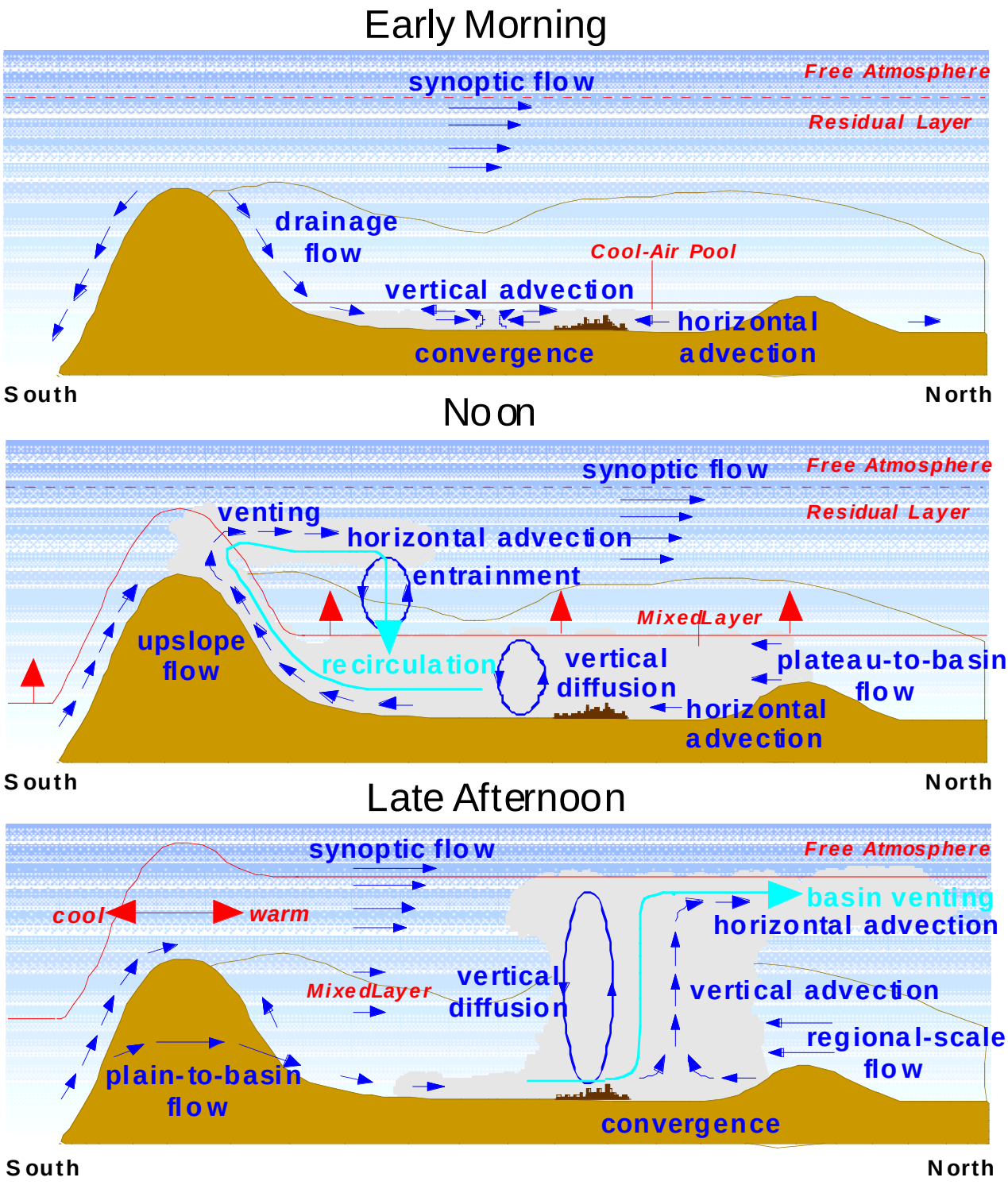

FIGURE 8. Important meteorological processes contributing to pollutant transport in the Valle de Mexico.

ONGOING DATA ANALYSES AND MODELING EFFORTS

Field data are being integrated into well-developed and tested models to better understand and characterize aerosol pollution in Mexico City. The spatial, temporal, size, and chemical characteristics of specific emissions sources are needed to allow their contributions to PM concentrations to be distinguished from each other and to provide accurate inputs to air quality models. Source samples for motor vehicle exhaust, cooking and food preparation activities, and geological material are being characterized for chemical profiles (of both gaseous and particulate matter emissions) that will be used to estimate source contributions to PM_{10} and $PM_{2.5}$ at receptors.

Source and receptor-oriented models will be used, both together and independently, to identify and quantify contributions to average and elevated PM levels. Data analysis and modeling activities will help determine where and when different sources are significant contributors, what their zones of influence are under different meteorological conditions, and what characteristics allow the contributions from one emitter to be differentiated from other emitters. The major and minor contributors will be identified, with the intent that further research and control efforts focus on the major contributors.

Some of the data analysis efforts underway include the following:

- Wind rose, wind vector, and streakline plots to determine transport
- Time-height plots of temperature, relative humidity, and winds to determine mixed layers, shears, slope flow, and pollutant carryover
- Diagnostic and prognostic wind models
- Photochemical models for the formation of ozone and other end-products of photochemical reactions
- Time series and spatial variation plots and correlations
- Advanced multivariate analysis, including time series, principal components analysis, cluster analysis, factor analysis, and empirical orthogonal functions
- Chemical equilibrium models for sulfates, nitrates, and ammonium

- Chemical mass balance receptor models for volatile organic compounds and particulate chemical composition.

Though much understanding will be gained from this project, it will not provide the final solution to the complex pollution problem in Mexico City. The experience gained, and the infrastructure created for Mexico City will remain, however, for continued application to questions that remain after the project is completed.

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