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Atmospheric Environment 35 (2001) 4041–4058

**ATMOSPHERIC
ENVIRONMENT**

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Mexico City air quality: a qualitative review of gas and aerosol measurements (1960–2000)

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Received 2 December 2000; accepted 18 February 2001

Abstract

Mexico City, one of the largest cities in the world, has a major problem with high levels of anthropogenic gases and aerosols. Some facets of this problem have been studied through measurements made during the past 40 years. These measurements are reviewed and evaluated with respect to physical processes that underlie the primary and secondary formation of gases and aerosols, their spatial and temporal evolution as well as their potential impact on the local and regional environment. Past measurements are heavily biased towards certain locations and time periods, and are of limited use for understanding fundamental processes that govern the formation and evolution of the principal pollutants. Recommendations are made whereby the measurement database could be expanded to better represent the characteristics of Mexico City gases and aerosols and to contribute to mitigation strategies that would lessen the environmental impact of these pollutants. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ambient gas and aerosol measurements; Air pollution; Mexico City

1. Introduction

Urban areas produce complex varieties and quantities of gas and particle species whose characteristics depend on a range of factors, including population density, energy consumption, industrial processes, and modes of transportation and usage. These pollutants affect public health, damage agriculture, and alter weather and climate. Many studies have been conducted over the years to better quantify the components of the urban pollution problem, i.e. to identify the sources and magnitudes of pollution and assess its subsequent impact. The majority of these studies were conducted in the United States and Europe where regulations have been implemented to restrict the emission of pollutants. Global “megacities” in developing countries differ in a

number of ways from cities that have been studied in the US and Europe. Less strict regulations allow the production of higher levels and more complex (and possibly more toxic) gases and aerosols. A large fraction of megacities outside of Europe and the US are located in sub-tropical and tropical latitudes where the meteorology and chemistry is quite different than in mid-latitudes. Solar irradiance is higher, winds are lighter and removal processes differ. Another important feature of the megacities in developing countries is the persistence of urban–rural transition zones with unpaved areas, agriculture, cattle, deforested zones, lack of sanitary infrastructure, etc. This close coexistence of rural and urban environments is an important factor that is often overlooked when assessing pollution problems in developing nations. Certainly other polluted cities such as Sao Paulo in Brazil and to a lesser extent, Santiago in Chile, suffer many of the same problems as Mexico City (Kretzschmar, 1994; Cahill et al., 1996).

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Mexico City is a tropical megacity, but unlike many such cities, its pollution problem has been studied for more than 40 years. A moderate set of measurements from these studies have been reported in the open literature while others can be obtained from internal reports. From these we can learn something about underlying physical processes that govern the evolution of those contaminants most harmful to the environment.

The populations of cities continue to increase as well as the amount of pollution produced. According to studies by the United Nation (WHO/UNEP, 1992) more than 50% of the world's population resides in urban areas with an expected increase of 15–20% in the next 30 years. Studies such as those that have been conducted in Mexico City provide valuable information that can provide insight into similar problems in other megacities. The present paper provides a summary of these studies, evaluates their content with respect to some of the principle scientific questions associated with air quality and identifies where additional measurements are needed.

2. Evaluation methodology

The studies of Mexico City air quality involve measurements and modeling of anthropogenic gases and aerosols; however, this paper will only review the observational studies. The purpose of this review is to identify where insufficient data exist to adequately investigate the fundamental physics that govern the production and evolution of gases and aerosols in Mexico City. These processes are complex, involve many chemical reactions and interactions with gaseous and particulate species and are dependent upon meteorology and radiation. We have chosen four general processes to assess the content of the published studies: (1) primary and (2) secondary production of gases, (3) primary and (4) secondary production of aerosols. In addition, we assess how well the measurements represent spatial and temporal variability.

Atmospheric pollution in Mexico City has been a significant problem for more than two decades due to the unrestricted growth of population and industry. The photochemical smog combined with high levels of primary particles is the result of emissions by vehicles (about 3.4 million), industry and two thermoelectric plants located within the elevated basin (2.2 km above sea level), as discussed in PROAIRE (1996). The variation with location, time of the day and time of the year can be seen in a statistical analysis of measurements from the city's pollution monitoring network, Red Automática de Monitoreo Atmosférico (RAMA). This network, established in 1986, now consists of 32 stations that measure CO, O₃, NO_x, SO₂, PM-10, temperature, relative humidity and winds.

Not every station measures all these variables, but all of these variables are measured by at least one station in the central, NE, NW, SE and SW sectors of the city (Fig. 1). The daily, average maximum values of carbon monoxide (CO), ozone (O₃), sulfur dioxide (SO₂) and PM-10 data are shown in Fig. 2, where the four traces in each panel represent measurements from the NE and SW sectors of the city. Figs. 3 and 4 present monthly and yearly averages in the same format as Fig. 2. The general trends are similar but the differences in relative magnitude suggest that the emission and secondary production rates probably vary from sector to sector in the city. The large diurnal and monthly variations also underscore the trends that are likely a result of meteorology, traffic patterns or other factors that affect dispersion of emissions.

Mexico City has taken steps in the past 10 years to address its pollution problem. Table 1 is a chronological history of the different measures that have been implemented. As seen in Fig. 4, CO and SO₂ are decreasing since 1991 when the most significant measures were implemented. Ozone, however, shows no obvious signs of diminishing. The effect of emission reduction strategies on PM-10 cannot be assessed with the RAMA measurements as automatic monitoring of particles was only implemented in 1993. The major difference in CO and SO₂, coupled with the lack of change in O₃, underscores the need to compare measurement studies before and after 1991 to better understand why pollution mitigation strategies have failed to lower ozone levels.

Studies in other large cities, e.g., Los Angeles, have shown that deterioration of air quality can be attributed to primary emissions of gases and particles, followed by secondary production through photochemical processes. The primary gases that are emitted are CO, NO, SO₂ and unburned hydrocarbons. The primary particles emitted are soot, which may contain large significant concentrations of volatile organic compounds (VOCs) formed during combustion of hydrocarbons. Ozone and a large variety of organic compounds are formed through secondary, photochemical reactions. In the absence of VOCs, ozone and NO_x exist in a state of equilibrium during daylight hours whereby NO reacts with O₃ to produce NO₂ and NO is converted back to NO as a result of photolysis, which also leads to the regeneration of O₃ (Seinfeld and Pandis, 1998). In the presence of VOCs, however, excess O₃ is produced because of the removal of NO by organic peroxy radicals (RO₂) that are produced from the photochemical oxidation of VOCs. For this reason, in addition to measurements of NO_x and O₃, there must be measurements of VOCs and RO₂ if we are to understand the processes that produce O₃.

A large fraction of the aerosol population is produced from homogeneous and heterogeneous nucleation, and

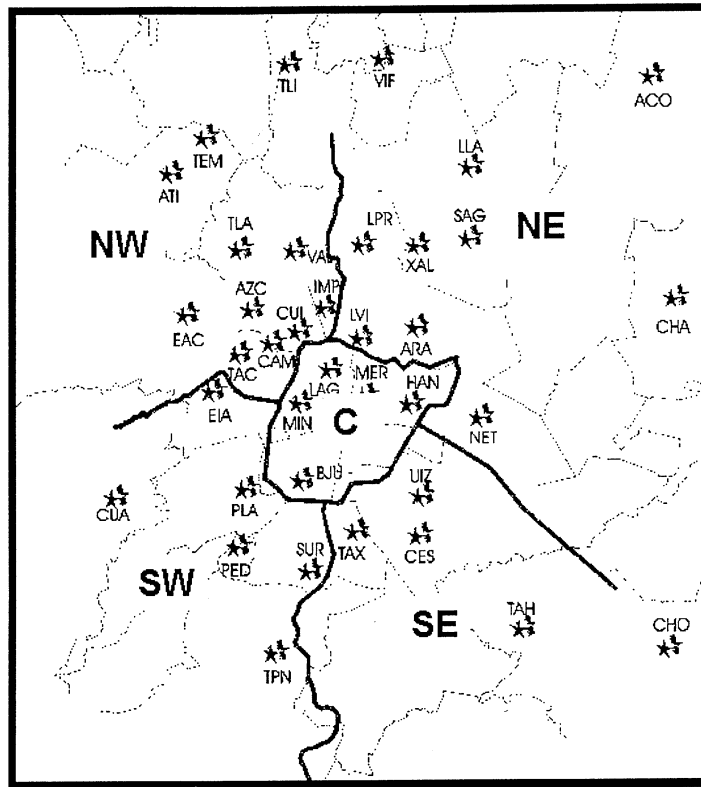


Fig. 1. Map of Mexico City's Metropolitan Region, divided into five sectors for monitoring purposes by Red Automática de Monitoreo Atmosférico (RAMA). The stars show the location of the monitoring stations, with the three-letter acronym that identifies each station.

then grows by condensation and coagulation. These processes can only be understood if size differentiated measurements are made of the chemical composition of these particles. As is well known, aerosols have size distributions that are characterized by three peaks: the nucleation, accumulation, and coarse modes, respectively. The sizes where these modes appear are different for size distributions of number and mass concentration, and will depend upon the composition of the aerosols and the associated environmental conditions. The characteristics of these size distributions provide important information on how the aerosols form and evolve and what their potential impact will be on health and the environment.

The remainder of this presentation will summarize the measurement studies that have been conducted since 1960 and will stratify them according to location, time and the species measured. The principal conclusions that came from these studies are elucidated, followed by a discussion that places these measurements in the context of understanding the processes that govern the primary and secondary production of gases and particles in Mexico City.

3. Gas measurements

There are numerous studies that discuss measurements of gases resulting from anthropogenic activities over the past 40 years. Prior to 1986 when the RAMA was initiated, studies focused primarily on emissions from combustion sources, while more recently, the focus has shifted toward measurements of photochemical pollutants and organic compounds. Table 2 presents a summary of the studies that discuss different aspects of these gases, starting in 1960. Studies can be grouped into those that make their own measurements (Table 2, ref. # 1–3, 5–8, 10–19, 23, 25, 26, 29–31) and those that analyze data from RAMA stations (Table 2, ref. #. 4, 9, 20–22, 24, 27, 28).

3.1. CO , CO_2 , SO_2 , NO_x , and O_3

The main conclusions from the papers that discuss these gases can be summarized as follows:

- (Table 2, ref. # 1, 4, 6, 11, 22, 27, 28) Trends in CO , NO_x and SO_2 are dominated by two daily peaks at

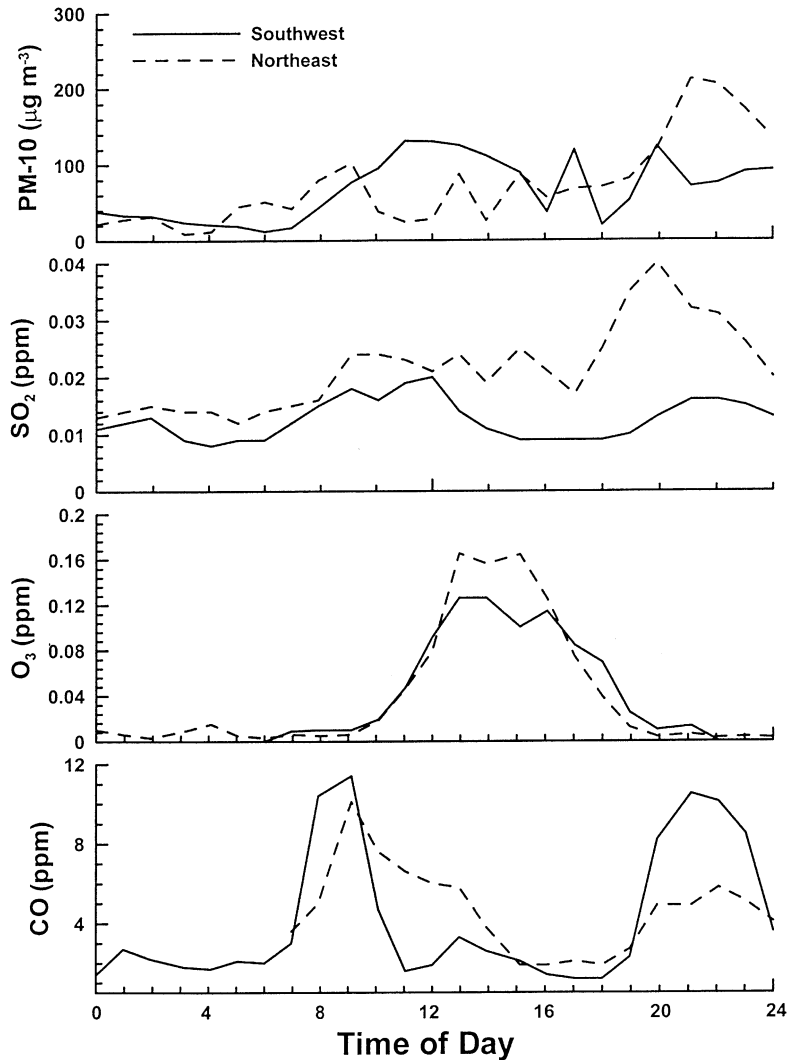


Fig. 2. Time series of PM-10 (top panel), SO₂, O₃ and CO (bottom panel), presenting the hourly average concentrations at two different monitoring stations.

the morning and afternoon rush hours, and a single O₃ peak in the early afternoon.

- (Table 2, ref. # 2) Diurnal trends in CO₂ present three peaks: morning, mid-afternoon and evening.
- (Table 2, ref. # 5, 6, 11, 20, 21, 24, 28, 31) O₃ concentrations increased sharply in 1986 and have only decreased by 20% since 1991.
- (Table 2, ref. # 1, 2, 4, 11) O₃, CO₂ and SO₂ present lower average concentrations during the wet season (May–October).
- (Table 2, ref. # 6) Traffic on primary arteries contributes a significant fraction to the total emissions produced by internal combustion engines.
- (Table 2, ref. # 6, 9, 16) Commuters in public transport are exposed to CO levels well above those in other cities of the world.
- (Table 2, ref. # 6, 13, 17) 1% of the vehicle fleet sampled in 1991 show that average CO emissions are high compared to the US fleet, but more comparable in HC emissions. A possible significant contribution of HC from industry was also noted.
- (Table 2, ref. # 11, 13) Airborne measurements provided vertical profiles of O₃, NO_x, CO and aerosols. Pronounced peaks in O₃ and aerosol concentrations were observed at the top of the mixed layer during the morning hours and decreased during the day.
- (Table 2, ref. # 11) Lidar and tethered sonde measurements confirmed these results and showed that the O₃ persisted as an elevated layer at about 1 km throughout the night.

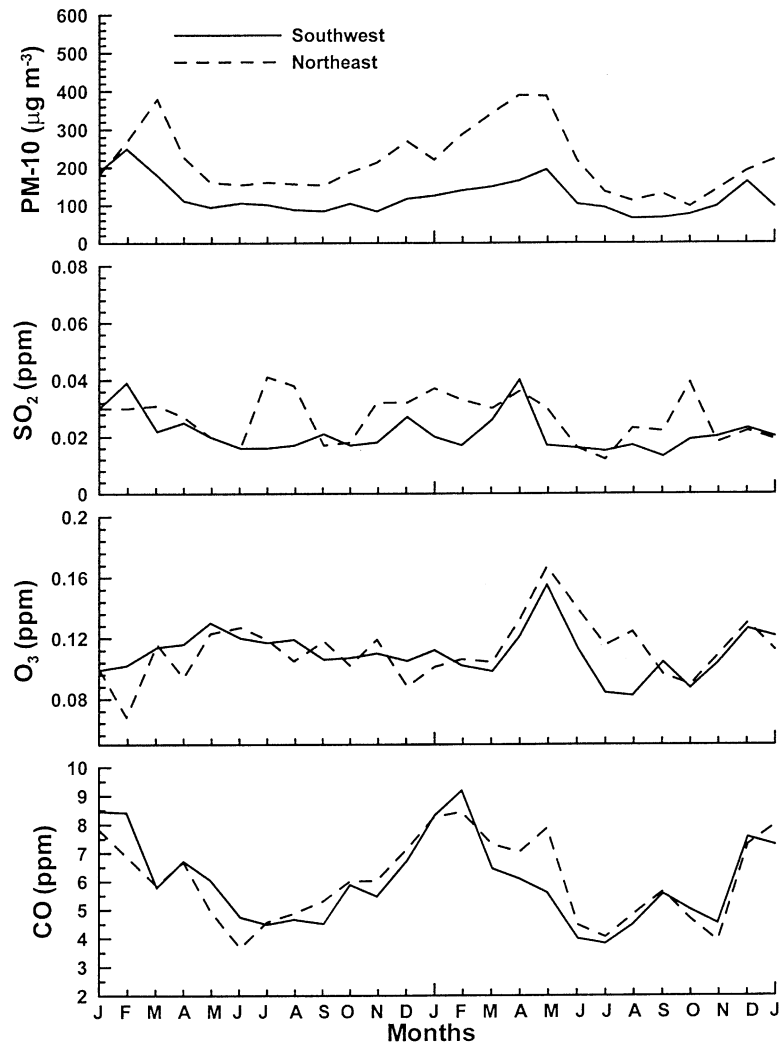


Fig. 3. Time series of PM-10 (top panel), SO_2 , O_3 and CO (bottom panel), presenting the monthly average concentrations at two different monitoring stations.

- (Table 2, ref. # 15) The contribution of ozone to the total column in the urban area of Mexico City is about 20 DU.
- (Table 2, ref. # 18) Direct measurements of NO_2 photolysis rates in Mexico City, using a flow reactor, show the importance of providing local resolution for photolysis rate by considering different local conditions and a better characterization of aerosols properties.

3.2. Hydrocarbons and volatile organic compounds

The main conclusions of the papers discussing hydrocarbons (Table 2, ref. # 6, 8, 10, 12, 13, 17, 21,

23, 26, 29) and organic compounds (Table 2, ref. # 3, 12, 13, 19, 25, 30) can be summarized as follows:

- (Table 2, ref. # 12, 13) The ratio of non-methane hydrocarbons to NO_x in Mexico City is larger than 20.
- (Table 2, ref. # 23, 25, 26, 29) The concentration of more than 200 identified hydrocarbons decreases significantly from north to south and the ambient composition showed 56% alkanes, 17% aromatics, 11% alkenes and 4% alkynes.
- (Table 2, ref. # 3, 12, 14, 19) Measurements of formaldehyde and acetaldehyde showed no significant variation between monthly mean values and are among the highest reported in the literature—similar

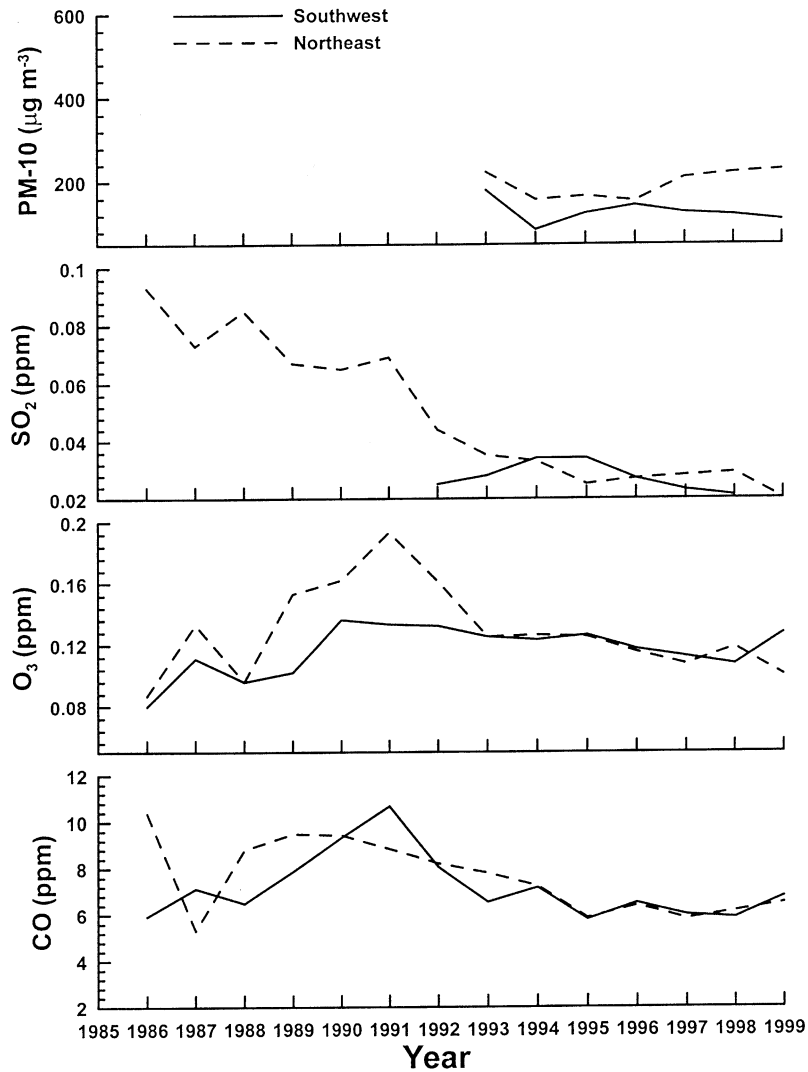


Fig. 4. Time series of PM-10 (top panel), SO₂, O₃ and CO (bottom panel), presenting the yearly average concentrations at two different monitoring stations.

to those measured for Los Angeles during severe photochemical pollution conditions in the 1960s and 1970s.

- (Table 2, ref. # 3, 12, 14, 19) Formaldehyde levels were consistently higher than those of acetaldehyde during the sampling period and the highest levels of carbonyl compounds were found in the morning hours. Formaldehyde was higher during sunny days, but acetaldehyde showed no difference.
- (Table 2, ref. # 3) Formaldehyde mixing ratios in rainwater are very high. Scavenging by rainfall below cloud base is more active during the earlier portions of rain development.
- (Table 2, ref. # 30) Peroxyacyl nitrates (PANs) were very high, purportedly the highest ever reported in

the US. A very strong diurnal variation was observed, with maximum concentrations during the early afternoon. It is likely that the introduction of MTBE in gasolines in the 1990s has contributed to the high levels of isobutene and formaldehyde observed in ambient air.

- (Table 2, ref. # 8) Natural hydrocarbons may represent between 10% and 25% of the total hydrocarbon emissions within the basin.

4. Aerosol measurements

Different samplers are used to determine the concentration of particulate matter and the subsequent analysis

Table 1
Air pollution mitigation measures

| Year | Type of action taken |
|-----------|--|
| 1986 | Partial introduction of natural gas in power plants and some industries |
| 1986 | RAMA begins making measurements to monitor air quality |
| 1987 | PEMEX ^a begins program to gradually remove lead from gasoline |
| 1988–1989 | A group of non-government environmental scientists initiates a program “Hoy No Circula” in which motorists are asked to voluntarily not drive 1 day each week |
| 1988–1989 | A pilot program is initiated to inspect and maintain private vehicles |
| 1990 | The federal government officially acknowledges that there is an air quality problem in Mexico City and launches a plan whose principal components were (1) introduction of gas without lead and diesel with lower SO ₂ , (2) oxygenated compounds in gasoline, (3) SO ₂ emissions control in the oil refineries, (4) control of evaporative emissions in storage facilities for combustible liquids, (5) implementation of a mandatory “Hoy No Circula”, (6) use of liquid petroleum (LP) in commercial vehicles, (7) use of natural gas in power plants, and (8) mandatory, yearly inspections of all vehicles registered in the city |
| 1991 | Replacement of older public buses with newer minibuses with catalytic converters begins |

^a Petróleos Mexicanos (PEMEX), the Mexican national oil company.

of the mass in the exposed filters provides information on their composition. Total suspended particles (TSP) were sampled using high volume (HV) samplers, while stacked filter units (SFU) were used to separate particles into two size categories: 2.5–15 µm (coarse fraction) and less than 2.5 µm (fine fraction). Some studies used HV samplers for PM₁₀ and PM_{2.5} and cascade impactors were used in other studies to determine mass size distributions in a range of sizes, depending on the number of stages.

4.1. Composition

The majority of the particle composition utilized elemental analyses, based on the following techniques: proton induced X-ray emission (PIXE), proton elastic scattering analysis (PESA) and laser integrating plate method (LIPM). Eleven papers (published between 1984 and 2000) present elemental composition of TSP, coarse and fine fraction determined from PIXE and PESA

analyses and sampled at different locations throughout the city over different sampling periods (see Table 3a, ref. # 3, 6, 7, 9, 10, 12, 15, 16, 17, 19 and 21). Several of the studies used other techniques or multiple techniques to determine composition, as also listed in Table 3a (ref. # 1, 4, 8, 14, 18 and 20). Only four studies (Table 3a, ref. # 2, 5, 11 and 18) report mass size distributions and two of them provide information on composition as a function of particle size.

The main conclusions with respect to the elemental composition can be summarized as follows:

- *TSP*. The highest diurnal concentrations are observed between 6 a.m. and noon, with a tendency for maximum concentrations in the winter season (for 23 elements from sodium to lead).
- *Coarse and fine fractions*. Fine mass concentrations of sulfur are more abundant than coarse mass concentrations. Day versus night variability, for metals such as copper, zinc and lead shows that they are present at all times, indicative of uninterrupted industrial activity. Daytime samples show higher concentrations during the rainy period, while dry season concentrations show no difference between day and night. Three dominant sources are identified for the measured elements in the fine mass: (a) ammonium sulfate or sulfuric acid; (b) automotive emissions; (c) industrial emissions. In contrast, the coarse mass shows soil as their principal components, with also some contribution from industrial and vehicle sources. Even though lead concentrations in PM-10 samples have decreased in concentration with time, high lead levels were found in the blood samples of children and women living close to the sites where airborne particles were sampled.

Regarding ionic composition, mineral content, organic carbon and black carbon content of particles, the conclusions are as follows:

- *TSP*. (Table 3a, ref. # 1, 4, 8) Maximum concentrations of sulfates and nitrates occur during the dry season. Minerals composed primarily of quartz, tridimite, cristobalite, feldspar, calcite and iron oxides constitute 25% of TSP mass. The fraction of organics soluble in benzene, presents maximum concentrations in December and January and minimum concentrations during June–August.
- *Coarse fraction and fine fractions*. (Table 3a, ref. # 8, 20) PM-2.5 mass is highest in the northern and Eastern parts of Mexico City. Secondary ammonium nitrate and ammonium sulfate were distributed homogeneously and constituted 10–20% of PM-10 and 15–30% of PM-2.5. Carbon containing aerosols accounted for 20–35% of PM-10 and 25–50% of PM-2.5.

Table 2
Gas measurement summary

| Reference | Species | Technique | Sites | Measurement dates |
|--|--|---|---|-------------------------------------|
| 1 Bravo (1960) | Particles | High volume sampler (fine fiber glass filter) | S, NW | Sep. 1959 |
| | Smoke | Smoke sampler (filter paper) | | Dec. 1959 |
| 2 Báez et al. (1988) | SO ₂ | Fluorescent SO ₂ analyzer | | Jan.–Jul. 1959 (6 months) |
| 3 Báez et al. (1989) | CO ₂ | GC | S, NW, C | 1981–1982 |
| | Aldehydes and ketones | Visible spectroscopy | SW | Jul.–Dec. 1985 |
| 4 Bravo et al. (1990) | SO ₂ | Fluorescent SO ₂ analyzer | RAMA | 1986–1988 |
| 5 Garcia et al. (1991) | O ₃ | Chemoluminescence | SW | 1985, 1987–1998 |
| 6 Beaton et al. (1992), Tejeda and Aquino (1993), MARI (1994), Streit and Guzmán (1996) | CO, CO ₂ and HC | FEAT unit (collimated infrared light, detector with specific filter for CO, CO ₂ and HC) | Vehicular fleet (32,000 vehicles), N, SE, SW | Feb. 1991 |
| 7 Nickerson et al. (1992, 1993), Perez Vidal and Raga (1998) | SO ₂ , O ₃ , CO | Fluorescent SO ₂ analyzer, Chemoluminescence O ₃ analyser, GFC | Research aircraft over entire city, airport soundings | 13 and 19, Feb. 1991 |
| 8 Ruiz-Suárez et al. (1993) | Natural HCs | Experimental emission factor | All sectors | Prior to 1993 |
| 9 González et al. (1993) | CO | GFC | RAMA | Jan., Apr., July, Oct. 1988–1990 |
| 10 Seila and Lonneman (1993) | HC | GC | All sectors | Mar. 1992 |
| 11 Streit and Guzmán (1993, 1996), MARI (1994) | O ₃ , SO ₂ , NO _x | Tethersonde and ozonesonde Chemoluminescence | SE, NE | Sep. 1990 (2 weeks) |
| 12 MARI (1994) | HC, aldehydes and ketones | GC/GC–MS and portable photoionization monitor, HPLC | All sectors | Feb. 1991, Mar. 1992, 1993 |
| 13 MARI (1994) Streit and Guzmán (1996), | CO, CH ₄ , NMHC and speciated HC | Portable photoionization detector and canisters | NW, SE, SW | Feb. 11–Feb. 21, 1991 |
| 14 Báez et al. (1995a, b) | Aldehydes and ketones | HPLC | SW | Mar.–May 1993 |
| 15 Juárez et al. (1995) | Ozone column | Dobson's spectrophotometer | SW | 1986–1989 |
| 16 Fernández and Ashore (1995) | CO | Infrared absorption | Inside motor vehicles | Mid-Jan. and Mid-Mar. 1991 |
| 17 Blake and Rowland (1995) | HC | GC | NE, C, SW | Feb. 1993 |
| 18 Castro et al. (1995, 1997) | NO _x | Chemoluminescence | NW, C, SW | Feb., Mar., Apr. 1994 |
| 19 Báez and Belmont (1996) | Aldehydes and ketones | Visible spectroscopy and HPLC | SW | Jun.–Sep. 1982, 1983 |
| 20 Nava et al. (1996) | O ₃ | Chemoluminescence | RAMA | Winter/spring 1987–1994 |
| 21 Riveros (1996) | O ₃ , NO _x , HC (benzene, toluene, formaldehyde, <i>p</i> -xylene) | Chemoluminescence, canister analysis | RAMA | Dec. 28–31, 1992 Mar. 1–15, 1993 |
| 22 Raga and LeMoyné (1996) | O ₃ , SO ₂ | Chemoluminescence Fluorescent SO ₂ analyzer | All sectors RAMA | 1993 |
| 23 Arriaga et al. (1996, 1997a, b) | HC | GC | All sectors | Mar., Nov., 1992–1996 |
| 24 Nava et al. (1997) | O ₃ | Chemoluminescence | RAMA | Jan.–Feb., Apr. –May. 1988–1996 |
| 25 Ruiz-Suárez and Andraca-Ayala (1997) | Aldehydes and ketones | HPLC | SW, NW | Jan.–Mar., 1996 |
| 26 Arriaga et al. (1997b) | HC | GC | C | Feb.–Mar. 1997 |

Table 2 (continued)

| Reference | Species | Technique | Sites | Measurement dates |
|--|--|---|-------------|----------------------|
| 27 Riveros et al. (1998a) | CO | GFC | RAMA | 1987–1995 |
| 28 Riveros et al. (1998b) | O ₃ , NO _x , SO ₂ and CO | Chemoluminescence and GFC, canisters GFC | RAMA | Mar. 1992 |
| 29 Mugica et al. (1998) Gamas et al. (1999) | HC | GC | All sectors | May, 1996 |
| 30 Gaffney et al. (1999) | Peroxyacyl nitrates | GC | NE | Feb.–Mar. 1997 |
| 31 Bravo and Torres (2000) | O ₃ , reformulated gasoline | Chemoluminescence | SW | Jul. 27– Aug. 2 1998 |

- *Size distributions.* (Table 3a, ref. # 5, 11, 18) Measurements have only been made in the SW, at the university campus and 400 m above the average city level. The fine fraction (defined as particles with aerodynamic diameter between 0.49 and 3 µm) constituted between 40% and 60% of the total mass from 32 samples throughout the year, and shows a seasonal pattern of somewhat lower concentration of the fine fraction during the rainy months. CCN and Aitken nuclei are correlated with vehicular and industrial activities. High resolution, time-dependent size distributions show a clear diurnal pattern, related to the development and growth of the polluted layer, as well as to the local meteorology. The presence of sulfates in small particles has been linked to volcanic emissions and to increased efficiency of gas to particle conversion in cloudy and rainy conditions.

A separate category of particles is considered to discuss the results of biological measurements regarding both free organisms in the atmosphere (as particles) and the biogenic elements associated to airborne particles. Bacteria, fungi, algae and protozoa, as well as proteins, carbohydrates and other biogenic compounds, have been sampled, classified and counted in several studies. Work has also been done on the characterization of biological airborne material, their viability and those characteristics that could be used as environmental quality indicators. These types of aerosols can cover a size range from less than 1 µm to greater than 30 µm. Table 3b presents the details of these studies.

The main conclusions for the different types of bioaerosols can be summarized as follows:

- *Bacteria.* (Table 3b, ref. # 7, 11) A great heterogeneity in viable bacteria abundance (from 14 to 13 000 CFU m⁻³) showed larger amounts during the dry season coinciding with the pattern observed for PM₁₀.
- *Algae.* (Table 3b, ref. # 1, 2) Ten species were identified and variations in algal counts were related with wind speed and direction, with maximum variety observed during the dry season.

- *Fungi.* (Table 3b, ref. # 4, 5, 8, 10) Total fungal colonies present the highest average concentration at night and the lowest at noon without a definite seasonal trend. In contrast, *Aspergillus* (14 species isolated) presents a seasonal pattern with maximum concentrations in the dry season and more abundance in morning samples. Eight species of *Penicillium* were observed, but no seasonality was present. Basidiomycete spores constitute 32% and 28% of the total airborne fungal spore load in south and central areas, respectively. The largest concentrations are observed in the wet season and greatest abundance in the early morning (2:00–6:00 h). Deuteromycete conidia constitute 52% of the spores trapped in the SW and 65% in the Central area and its abundance is correlated with maximum temperature and relative humidity of the previous day.
- *Protozoa.* (Table 3b, ref. # 3, 6) Out of 63 strains of protozoa belonging to 18 free-living species of flagellates, amoeboflagellates and ciliates that were isolated, the highest diversity was recorded in the NE and NW. Species of the genera *Bodo*, *Monas*, *Cercobodo* and *Colpoda* were the most abundant, and all species isolated were small and cyst formers.
- *Proteins.* (Table 3b, ref. # 9) Protein presence does not show a geographical pattern but has a clear seasonal one, with highest concentrations in the dry season positively correlated with airborne PM₁₀.

4.2. Optical properties

Aerosol optical properties (combining their size and composition) have a direct impact on atmospheric visibility, particularly in regions of high pollution. Table 3c lists the details of the studies that have been carried out linking radiation measurements to aerosol pollution in Mexico City. The main conclusions can be summarized as follows.

- No correlation is found between TSP and visibility, but a significant one exists between fine particles and visibility. Particles with diameters in the range

Table 3

| Reference | Aerosol property measured | Instrumentation and sample rate | Analysis technique | Location | Measurement dates |
|---|---|---|---|--------------------|--|
| (a) Non-biogenic particle measurement summary | | | | | |
| 1 Salazar et al. (1981), Bravo and Salazar (1982, 1984), Salazar and Bravo (1986), Salazar et al. (1989) | TSP; mineral, metals and soluble organics, SO ₄ ²⁻ , NO ₃ ⁻ | Hi-vol, 24 h samples | Gravimetric; XRF for soil elements; organics extracted with benzene and ion chromatography | SW | 7/79–8/80 (179 days) |
| 2 Bravo et al. (1982) | TSP and FSP mass | Hi-vol and 5-stage impactor 24 h samples | Gravimetric | Two sites in SW | 5/80– 8/80 (123 days) |
| 3 Barfoot et al. (1984) | TSP elemental composition | Hi-vol, 24 h samples | PIXE | SW | 15/11/80–15/02/81 (51 days) |
| 4 Bravo et al. (1989) | TSP; SO ₄ ²⁻ , NO ₃ ⁻ | Hi-vol, 24 h samples | Gravimetric, ion chromatography | Two sites in SW | 1/81–3/88 (912 days) |
| 5 Salazar et al. (1992) | PSD (0.49 to > 7.2 μm) | 5-stage impactor | Gravimetric | SW | 1986 (32 days) |
| 6 Aldape et al. (1991a) | TSP elemental composition and BC | Hi-vol, 6 h samples | PIXE and LIMP | NW | One week in 04/88, 07/88, 11/88 and 01/89 (28 days) |
| 7 Aldape et al. (1991b) | TSP elemental composition and BC | Hi-vol, 4 h samples | PIXE and LIMP | NW | Once per week, 3/88–2/90 (49 days) |
| 8 Barbiaux et al. (1991), Vega et al. (1997) | TSP; PM2.5, SO ₄ ²⁻ , NO ₃ ⁻ ; EC; OC | Hi-vol, single and dual filter packs 12 h samples | Gravimetric, PIXE, ion chromatography, and thermal optical | SW | 12/89–2/90 (33 days) |
| 9 Miranda et al. (1992) | PM(15–2.5) and PM2.5 analysis of elements heavier than neon, C, H | SFU 6 h samples | PIXE, LIMP and PESA | NW | 22–28/08/90 (7 days) |
| 10 Aldape et al. (1993) | TSP elemental composition. | Hi-vol, 6 h samples | PIXE | NW | 18–25/04/88 (7 days) |
| 11 Montañez and García-García, (1993) | PSD, CCN | Aerosol size analyzer, CCN counter | | SW | 22/07–9/08/85 (19 days) |
| 12 Miranda et al. (1994) | PM(15–2.5) and PM2.5 analysis of elements heavier than neon, C, H | SFU 6 h samples | PIXE, LIMP and PESA | Two sites in NW | 12–25/09/90 (14days) 12/02–1/03/91 (18 days) |
| 13 Díaz-Francés et al. (1994) Nickerson et al. (1992) | PSD; CN | OPC; CN Counter | | Aircraft | 2/22/91 (14 days) |
| 14 Rosas et al. (1995b) | PM10 | Hi-vol 24 h samples | Atomic absorption | NW C SW | 4 days per week Jan.–Dec. 1991 (208 days) |

Table 3 (continued)

| Reference | Aerosol property measured | Instrumentation and sample rate | Analysis technique | Location | Measurement dates |
|--|--|---|--|--|---|
| 15 Aldape et al. (1996a) | PM(15–2.5) and PM2.5, elemental composition | SFU 7–11 a.m. and 11 a.m.–3 p.m. | PIXE | NW | 1 day per week Jan.–Dec. 1990 |
| 16 Miranda et al. (1996) | PM(15–2.5) and PM2.5, elemental composition | SFU 6 h samples | Gravimetric, PIXE, PESA and XRF | SW | (52 days) 16/10/93–10/12/93 |
| 17 Aldape et al. (1996b) | PM(15–2.5) and PM2.5, elemental composition | SFU 6 h samples | PIXE | C Two sites in SW | (51 days) 7 alternate days, between 25/11/93 and 5/12/93 |
| 18 Raga et al. (1999), Baumgardner et al. (2000) | PSD (0.05–0.7 µm); TC, OC, BC and SO ₄ ²⁻ ; Scattering and absorption coefficients | 10-stage and six-stage impactors 24 h samples | DMA; EGA; Ion chromatography; nephelometer and soot photometer | SW | 11/97 (14 days) |
| 19 Flores et al. (1999) | PM(15–2.5) and PM2.5, elemental composition | SFU 12 h samples | PIXE | NE | 26/07–23/08/96 (29 days) 14/02–14/03/97 (29 days) |
| 20 Edgerton et al. (1999) | PM10 and PM2.5 elemental analysis for SO ₄ ²⁻ , NO ₃ ⁻ ; Na, K, NH ₄ ⁺ , OC and EC | Hi-vol 6 h samples at three sites; 24 h samples at three sites | X-ray fluorescence, ion chromatography, atomic absorption, thermal/optical reflectance | Two sites in NE NW C SW SE | 23/02–22/03/97 (29 days) |
| 21 Miranda et al. (2000) | PM(15–2.5) and PM2.5 analysis of elements heavier than neon | SFU 6 h samples | PIXE | SW | 14/08–15/09/95 (22 days) |
| (b) Biological particle measurement summary | | | | | |
| 1 Rosas et al. (1987) | Airborne algae | Bubble flasks with Bold's basal medium One sample per day | Culture, isolation and identification | SW | 7/82–8/82 7/85–12/85 (31 days) |
| 2 Rosas et al. (1989) | Airborne algae | Bubble flasks with Bold's basal medium (1/day) | Culture, isolation and identification | SW | 1/85–10/85 (46 days) |
| 3 Rivera et al. (1992) | Isolated total protozoa | Impaction in impinger with Bold's basal medium Once per day (11:00–13:30) | Incubation and culture in several media. Identification and counting | NE, NW, SE SW | 2/88–1/89 (260 days) |
| 4 Rosas et al. (1992) | <i>Aspergillus</i> spores and | Two-stage Andersen, 3 | Cultured by plates incubation. | SW | 1/90–12/90 |

Table 3 (continued)

| Reference | Aerosol property measured | Instrumentation and sample rate | Analysis technique | Location | Measurement dates |
|---|--------------------------------------|---|---|---|---|
| 5 | Rosas et al. (1993) | isolated fungal propagules <i>Penicillium</i> spores | times per day; 5 days per week Two-stage Andersen, 22 mornings | Counting and identification Cultured by plates incubation. | NE, C, SW 2/90–10/90 (22 days) |
| 6 | Rivera et al. (1994) | <i>Amoebae</i> | Impaction in impinger with Bold's basal medium Once per day (11:00–13:30) | Incubation and culture in appropriate media Identification and counting | NE NW SE SW 2/88–1/89 (260 days) |
| 7 | Rosas et al. (1994) | Total airborne bacteria | Six-stage impactor 3 times per week at noon | Plates incubation, isolation, counting and identification | SW 1/89–12/89 (150 days) |
| 8 | Calderón et al. (1995) | Basidiomycete spores | Volumetric spore trap Burkard collected on tapes, 7-day samples | Tapes cut for 24 h exposure analysis and identification on microscope | C SW 1/91–12/91 (358 days) |
| 9 | Rosas et al. (1995a) | Proteins | Hi-vol, 24 h samples | Extraction from filters, MW and concentration determined | NE, C, SW 1/91–12/91 (50 days) |
| 10 | Calderón et al. (1997) | Deuteromycete spores | Volumetric spore trap Burkard 7-day samples | Tapes cut for 24 h exposure analysis and identification on microscope | C SW 1/91–12/91 (365 days) |
| 11 | Rosas et al. (1997) | <i>Escherichia coli</i> | Two-stage Andersen 2 samples per week | Incubation, isolation from gram-negative, identification and plasmid analysis | SW 4/96–05/1996 (16 days) |
| (c) Particle measurement summary radiative properties | | | | | |
| 1 | Galindo and Muhlia (1970) | Turbidity | Pyrheliometer | | SW 1912, 1913, 1927, 1957 |
| 2 | Galindo and Bravo (1975) | Turbidity | Pyrheliometer | | SW 11/74–2/75 |
| 3 | Muhlia et al. (1989) | Column integrated aerosols | Actinometer (hourly) | | SW 5/84–3/85 (11 days) |
| 4 | Vasilyev et al. (1992, 1995a, 1995b) | Spectral optical depth | Spectrophotometer (1 h after sunrise, sampling for 2 h) | | SW MC 4/92–6/92 (24 days) |
| 5 | Galindo et al. (1995) | UV irradiance | Photometer (hourly) | | SW (880 days) |
| 6 | Jáuregui and Luyando (1999) | Global radiation | Pyranometer (hourly) | | C NE 1/94–12/98 (1825 days) |

Table 4
Sampling days for aerosols

| | Location | Condition | Elemental analysis | OC/EC analysis | SO ₄ /NO ₃ analysis | Size distribution | Coarse mass | Fine mass | Optical properties | Bio-aerosols |
|-------------|----------|-----------|--------------------|----------------|---|-------------------|-------------|-----------|--------------------|--------------|
| Before 1992 | NE | Wet | | | | | | | | 296 |
| | | Dry | | | | | | | | 296 |
| | NW | Wet | 54 | 55 | | | 28 | 47 | | 260 |
| | | Dry | 72 | 70 | | | 46 | 44 | | 260 |
| | C | Wet | | | | | | | | 397 |
| | | Dry | | | | | | | | 397 |
| | SW | Wet | | 90 | 546 | 10 | 669 | 123 | | 911 |
| | | Dry | 51 | 123 | 579 | 22 | 630 | 33 | | 880 |
| | SE | Wet | | | | | | | | 260 |
| | | Dry | | | | | | | | 260 |
| After 1992 | NE | Wet | 29 | | | | 29 | 29 | | |
| | | Dry | 87 | 58 | 58 | | 87 | 87 | | |
| | NW | Wet | | | | | | | | |
| | | Dry | 146 | 72 | 72 | 14 | 146 | 146 | 14 | |
| | C | Wet | | | | | | | | |
| | | Dry | 65 | 58 | 58 | | 65 | 65 | | |
| | SW | Wet | | | | | | | | |
| | | Dry | 146 | 72 | 72 | 14 | 146 | 146 | 14 | 16 |
| | SE | Wet | | | | | | | | |
| | | Dry | 58 | 58 | 58 | | 58 | 58 | | |

0.4–0.59 μm are responsible for most of the light scattering.

- A high correlation is found between sulfate and nitrate concentrations and turbidity.
- Derived optical thickness is found between 0.6–1.2 and 0.5–0.8 in UV and visible wavelengths, respectively, and single scattering albedos of 0.7–0.9 and 0.6–0.8 for UV and visible wavelengths, respectively. Direct measurements of the scattering and absorption coefficients at visible wavelengths by Baumgardner et al. (2000) agree well with the derived estimates by Vasilyev et al. (1995a).
- Large diurnal variations in UV irradiance are observed and a significant impact on solar radiation is due to volcanic emissions. An increase in optical depth of 3% is estimated when volcanic aerosols are transported over the city.
- Annual temperatures near city edges are declining, attributed to the smog layer transported from the city.

5. Discussion

Tables 2 and 3 summarize the majority of observational studies that have been conducted over the past 40 years. The measurements are listed chronologically and are briefly described by the publications that discuss

them, the species measured, the techniques used to make the measurement, and the locations and dates of the samples. A number of observations can be made, based on these tables and concerning the current state of our knowledge about gases and aerosols in Mexico City.

In the second section of this paper the diurnal, seasonal and year to year variations with respect to location were demonstrated with a sample of RAMA data. Aside from the gas and PM-10 measurements made at the RAMA sites there are no speciated HC measurements that can adequately characterize diurnal or geographical variations and the seasonal information is limited in its scope. The same is true for aerosols over virtually all space and temporal scales. An attempt has been made to obtain representative samples of some of the major gas species and the mass and elemental composition of aerosols from the five sectors of the city in both wet and dry seasons. There have been very few measurements made close to major sources of pollution, however, in order to measure the components of primary emission, e.g., more information is needed at locations directly next to major highways, concentration points of public transports, cottage industries using biomass burning (adobe brick, tile making, etc.) or other industries producing large quantities of combustion products. Secondly, the dispersion of pollutants and their interaction with the environment is clearly a three-dimensional problem; however, with the exception of a

limited set of balloon and aircraft measurements there is very little information on gases and particles in the vertical dimension.

Also discussed in the second section was the need to address the primary scientific issues that concern the processes that govern the formation and development of anthropogenic gases and aerosols, primarily those of photochemical production of secondary gases and aerosols. In general, the measurements of gases and aerosols have served to track trends in statistical quantities, i.e. minimum, maximum, and average, but there has been practically no analysis of the measurements with respect to physical processes behind these trends. There are some exceptions, such as the study of Raga and LeMoyne (1996), who analyzed O_3 and SO_2 data and put forward the hypothesis of an existing horizontal vortex (with anticlockwise rotation) within the basin. Such a vortex has been inferred from profiler data and has been modeled by regional meteorological models (Doran, Whiteman, and Banchett, pers. comm.). Also, with the exception of measurements of NO_2 photolysis rates (Castro et al., 1995), there is no information about photolysis rates of other photochemically important gases like O_3 or VOCs. Riveros (1996) ventured a guess that O_3 production is more sensitive to NO_x than to HCs. However, the measurement database is inadequate to make such speculations until much more is known about the chemical nature of both the primary and secondary HCs. A recent study (Molina, 2000) confirmed that the ratio VOC/NO_x ranges between 19 : 1 and 34 : 1 ppbC/ppb, and indicates that O_3 concentrations seem to be more sensitive to NO_x levels. The study also proposes that additional measurements of PAN, nitric acid and hydrogen peroxide are needed in order to better assess the photochemical situation in Mexico City.

There have been a number of measurements of HCs using GC, but these measurements have only identified a very limited number of species. There is a strong need for more spectral (infrared and mass fragmentation pattern) analysis of GC measurements, in particular the identification of less recognizable peaks in the GC chromatogram that represent compounds in small quantities yet of toxicological importance. A prime example of these are the pesticide compounds that have recently been identified in urban areas (Cortes and Hites, 2000) that are hazardous to health and can be transported on regional or synoptic scales.

Table 4 summarizes all the aerosol measurements that have been made in Mexico City and presents the number of days of samples taken and analyzed for different aerosol characteristics. It is evident that there are almost no measurements of either size distributions or optical properties and yet, as discussed in Section 2, the evolution of aerosols and their impact on other environmental properties cannot be understood without

a knowledge of these properties. There are a fair number of measurements of aerosol SO_4^{2-} , NO_3^- , OC and EC composition, but these were all from the result of a single, 1 month measurement campaign in 1997 (Edgerton et al., 1999) during the dry season. Rain and high humidity have a significant affect on aerosol composition (Raga et al., 1999; Baumgardner et al., 2000); thus, more size differentiated measurements are needed of the inorganic, organic carbon and soot content of aerosols in both the wet and dry seasons.

There were a large number of measurements made prior to 1992, of TSP and, to a lesser extent, FSP; however, they were primarily made in the SW sector of the city. A similar situation occurs after 1992 where the majority of the mass measurements are biased towards locations in the SW. In addition, although a fair amount of elemental analysis has been made of aerosols, most has been done on aerosols collected on either PM10 or PM2.5 filters. In the case of PM10, coarse mode aerosols will dominate the aerosol mass and elements identified may not be particularly important for health or the environment. Analyses of PM2.5 aerosols are important for health considerations, but lack of size differentiation diminishes our ability to understand the relative importance of the physical processes that formed these aerosols, e.g., nucleation and growth by condensation and coagulation. Although theoretical studies suggest that a large fraction of environmentally important aerosols form from secondary photochemical reactions of VOCs, without a size-differentiated analysis of the inorganic and organic composition, the importance of these formation processes cannot be evaluated.

The measurement of mass has been the primary focus of almost every one of the published studies. It is the surface area of particles, however, that is the critical characteristic in many of the processes in which aerosols are involved, i.e. transport of respirable particles, heterogeneous chemistry, and optical properties. In addition, the hygroscopicity of Mexico City aerosols has never been measured; however, it is this property that governs the ability of a particle to grow as it is inhaled or to form cloud droplets.

The biogenic properties of aerosols are characteristics of particles that require a much more in-depth study, regarding physical processes of transport and biochemical interactions with gases and inorganic aerosols, as well as the environmental triggers for their emission and behavior.

As seen in Table 4, a great deal of sampling was done in all five sectors of the city, but most of it prior to 1992. There have been few measurements in the past 8 years, even as the population continues to grow along with land development and increased stress on sewage treatment facilities, two of the major contributors to the biogenic aerosol population. In spite of the recognized importance of biogenic aerosols on human

health, there is far too little information about their size and composition of biogenic aerosols, particularly those biological aspects closely linked to land use in the vicinity of human activity. Many biogenic materials use non-biogenic aerosols as their carrier, but this aspect of aerosol properties has not been explored enough in Mexico City.

6. Recommendations

In light of the large variations in gas and aerosol emissions and their subsequent evolution and interaction with their environment, dependent upon location, time of day and season, more frequent and widespread measurements are clearly needed. The quality of the measurements is as important as the quantity, specifically in obtaining a much broader range of organic gas and particulate species. Mobile ground stations can measure pollutants close to their source. The measurement platforms and techniques should utilize state-of-the-art advances, particularly for obtaining vertical profiles of gas and aerosol species. Aircraft provide an important means of obtaining these measurements but balloons and passive and active remote sensing hold promise for measuring time varying vertical structure of ozone, some hydrocarbons, water vapor and aerosols. Wind profilers are essentials for understanding complex circulation that contributes to the transport of urban pollutants.

Modeling studies of Mexico City meteorology and photochemistry that have been published in the open literature will be the subject of another review currently under way, that will complement the present paper. Very few models have been developed, however, to investigate gas, aerosol, and radiative processes in Mexico City. Models, coupled with observations, are valuable tools for evaluating these processes and more effort should be devoted to developing these models.

There have been limited laboratory studies that look at gas and particle formation and evolution under controlled conditions. A key to understanding such processes in their natural environment is an evaluation of the complex components that contribute to these processes. Well-designed laboratory studies play an important role in unraveling these processes.

There is a wealth of data that has been accumulated in the past 40 years in Mexico City, yet very little evaluation of this database has been undertaken to understand the physical processes that are most important in ozone production and aerosol formation and evolution. A part of the problem is the lack of trained personnel who can work on all aspects of air quality studies. Human resources are needed at all levels—student, technician, engineering and scientific, to

design and conduct experiments and to evaluate and document the observations.

An understanding of the processes that underlie the degradation of air quality in Mexico City is essential before effective mitigation strategies can be implemented by government and health officials. Limited progress can be made, however, until a substantial investment in material and human resources is made to develop measurement programs and the associated infrastructure that systematically address the most critical aspects of the problem.

Acknowledgements

This work was partially supported by a grant from the Massachusetts Institute of Technology and the Comisión Ambiental Metropolitana through funds from the Fideicomiso Ambiental del Valle de México (MIT-FUMEC-UNAM-2.4). The authors gratefully acknowledge discussions with Drs. Luisa Molina and Mario Molina. Thanks are also due to Ing. Pedroza and his team at the Red Automática de Monitoreo Atmosférico (RAMA), who provided data from the monitoring network sites. DB, TC and GR acknowledge the support of Consejo Nacional de Ciencia y Tecnología de Mexico through grants 27528-T and 27529-T.

Appendix A. Terminology

| | |
|--------|--|
| BC | black carbon |
| CCN | cloud condensation nuclei |
| CN | condensation nuclei |
| DMA | differential mobility analyzer |
| EC | elemental carbon |
| EGA | evolved gas analysis |
| FSP | fine suspended particles |
| GC | gas chromatography |
| GFC | gas filter correlation |
| Hi-Vol | high volume sampler |
| HPLC | high performance liquid chromatography |
| LIPM | laser integrating plate method |
| MCMA | Mexico City metropolitan area |
| MOUDI | micro-orifice uniform deposit impactor |
| MS | mass spectrometry |
| MW | molecular weight |
| PESA | proton elastic scattering analysis |
| PIXE | proton induced X-ray emission |
| PSD | particle size distribution |
| OC | organic carbon |
| RP | respirable particles |
| SFU | stacked filter unit |
| TC | total carbon |
| TSP | total suspended particles |
| VOC | volatile organic carbon |
| XRF | X-ray fluorescence |

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