

Mexico City and the biogeochemistry of global urbanization

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Abstract

Mexico City is far advanced in its urban evolution, and cities in currently developing nations may soon follow a similar course. This paper investigates the strengths and weaknesses of infrastructures for the emerging megacities. The major driving force for infrastructure change in Mexico City is concern over air quality. Air chemistry data from recent field campaigns have been used to calculate fluxes in the atmosphere of the Valley of Mexico, for compounds that are important to biogeochemistry including methane (CH₄), carbon monoxide (CO), nonmethane hydrocarbons (NMHCs), ammonia (NH₃), sulfur dioxide (SO₂), nitrogen oxides (NO_x and NO_y), soot, and dust. Leakage of liquified petroleum gas approached 10% during sampling periods, and automotive pollutant sources in Mexico City were found to match those in developed cities, despite a lower vehicle-to-person ratio of 0.1. Ammonia is released primarily from residential areas, at levels sufficient to titrate pollutant acids into particles across the entire basin. Enhancements of reduced nitrogen and hydrocarbons in the vapor phase skew the distribution of NO_y species towards lower average deposition velocities. Partly as a result, downwind nutrient deposition occurs on a similar scale as nitrogen fixation across Central America, and augments marine nitrate upwelling. Dust suspension from unpaved roads and from the bed of Lake Texcoco was found to be comparable to that occurring on the periphery of the Sahara, Arabian, and Gobi deserts. In addition, sodium chloride (NaCl) in the dust may support heterogeneous chlorine oxide (ClO_x) chemistry. The insights from our Mexico City analysis have been tentatively applied to the upcoming urbanization of Asia. © 2000 Published by Elsevier Science Ltd.

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1. Introduction

The Valley of Mexico contains what is arguably the

world's largest metropolis with 20 million people coexisting in a space of 1000 km² (UN, 1992; Villareal et al., 1996). The confining topography of the basin contributes to pollutant loadings that are among the most severe known (Jauregui, 1971; MARI, 1994).

Recent field campaigns are providing an unprece-

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dented characterization of the composition in the basin atmosphere (Doran et al., 1998; Edgerton et al., 1999). While Mexico City's air environment has been found to resemble peak smog years in cities of the Western United States (Seinfeld, 1989; Finlayson Pitts and Pitts, 1997), pollution extremes have been reached in the Valley of Mexico which may be more relevant to studies of 'megaurban' zones of the developing world. Many new, large cities are expected to emerge across the globe in the near future. For example, whereas just 33% of Asia's population of 3 billion people currently live in urban areas, Organization for Economic Cooperation and Development (OECD) urbanization levels of 75–80% could be attained within two generations (UN, 1992, 1994).

In this work, we investigate Mexico City from a biogeochemical perspective, at a time when cities are becoming increasingly important within the earth system. Emission and ventilation rates are calculated for selected biogeochemically important species (hydrocarbons, carbon monoxide, sulfur dioxide, nitrogen compounds, and particulates) and the results are interpreted in terms of regional to global biogeochemical cycling. Strengths and weaknesses of the megainfrastructure are assessed, and the results are tentatively applied to the industrialization of Asia.

2. Data base and manipulations

Mexico City air quality has been studied in depth by individual groups at both US and Mexican universities and atmospheric science institutions (e.g. Nickerson et al., 1992; Miranda et al., 1994; Blake and Rowland, 1995; Riveros et al., 1995; Vega et al., 1995). Several recent research campaigns in Mexico City have emphasized the coupling of complex meteorological and chemical phenomena (MARI, 1994; Doran et al., 1998; Edgerton et al., 1999). Here, we summarize chemical and meteorological results from the recent campaigns together with our estimates of the burdens, emission rates, and ventilation rates of the key chemical species in the Valley of Mexico. Measurements from the latest international campaign in March, 1997, have been supplemented by results from (1) a standard air quality monitoring system (UN, 1992; Goddard, 1996), (2) earlier measurement intensives (MARI, 1994), and (3) the work of individual Mexican and international atmospheric science groups. The key chemical and meteorological parameters were then manipulated to yield mass fluxes through the Valley system. The analysis reported here has been restricted to the winter–spring season when the data are most abundant.

The data used to generate surface emission and ventilation rates in the Valley of Mexico are given in Table 1. The 'remote concentrations' were drawn from

the literature (e.g. Penner et al., 1991, 1994; Jaffe, 1992; Schlesinger and Hartley, 1992; Benkovitz et al., 1994; Prather et al., 1995; Tegen and Fung, 1995) and are estimates of background concentrations in the local region. The 'urban concentrations' are averages for the mid-afternoon, from samples that were taken over the built-up area of the city. The chemical removal of the gas phase species ('chemistry time constant') was estimated using rate constants from standard tabulations (Atkinson and Lloyd, 1984; Demore et al., 1990). For the reaction rate calculations, concentrations of the chief oxidants were fixed at rough values that have been observed and modeled for daytime polluted atmospheres ($O_3 = 100$ ppbv; $OH = 10^7$ radicals cm^{-3}). The 'scale heights' are those for eddy removal within an analytical one-dimensional framework (Elliott et al., 1997a). Concentrations at the 2 km height ('2 km conc') were constructed from the scale heights, from full photochemical modeling (MARI, 1994; Elliott et al., 1998) and from aircraft measurements (Nickerson et al., 1992; MARI, 1994; Vidal and Raga, 1998). For the short-lived species (NO_x), horizontal distributions across the Valley ('% coverage') were estimated from surface wind speeds and the chemical loss rate. The percent areal coverage for all the longer-lived species is 100% (Table 1). The 'transport time constant' is the residence time for air in the Valley; its value of 0.75 d was derived by applying first order decay kinetics to the Lagrangian parcel export experiments of Fast and Zhong (1998). The overall rate of species removal ($tons\ d^{-1}$) is considered to be a diurnal average of (1) the sum of chemical and meteorological processing during the daytime photoperiod, and (2) transport loss alone at night. The removal time constant ('average time constant') is simply the reciprocal of the average diurnal rate constant. Fractional ventilation from the basin ('% vented' $\div 100$) was characterized as the meteorological removal rate divided by the total loss for each species.

Burdens of the individual substances were computed by treating the Valley of Mexico as a $50 \times 50 \times 2$ km vessel containing 750 mb pressure. The concentration of each substance was assumed to decrease linearly with height in the enclosure, unless the scale height for the species was less than 2 km (see Table 1). The 2 km basin depth was determined by the height of a chimney effect blocking upper level flow over the surrounding ridgetops during the daytime (Bossert, 1997). At night, purging can occur down to the average ridge altitude of about 1 km AGL. Valley-wide ventilation and chemical loss rates were calculated from the burden and generalized removal constants for each species. Top down emissions are those required to balance the Valley-wide ventilation and chemical loss. Bottom up emissions are estimated from the accumulation of each species under the low nocturnal to morning inversion,

but only when the time resolution of the data is sufficient. The inversion altitude was set at 200 m AGL (MARI, 1994; Elliott et al., 1997a).

The calculated emissions compared favorably with Mexican and international tabulations (PICCA, 1990; TUV, 1992; MARI, 1994), although the discrepancy between the bottom up and top down fluxes was a factor of two in either direction. The error in the downwind deposition calculations includes error propagation and is therefore larger. We note that the averaged concentrations, burdens, and ventilation rates presented here have been constructed very indirectly, and that the chemical transformations and flow within the Valley have been handled using only first order kinetics and simple transport models. Because the analysis was based on data primarily from surface measurements, our interpretations of Mexico City air chemistry could be significantly improved in future studies by placing more emphasis on aircraft platforms and on regional chemistry/aerosol transport modeling. In addition, geostationary satellites will soon provide 10 km resolution for several components of urban effluent (Fishman, 1991).

3. Local air chemistry

The ozone and particulate levels that were measured in Mexico City are comparable to values from the inland Los Angeles area during the peak years of the 1970s. For example, Stage 1 ozone episodes (O_3 exceeding 200 ppbv over a 1-h averaging period) were customary for many dozens of days per year in the Los Angeles of the 1970s, over much of its basin area (NRC, 1991). On heavy smog days in Los Angeles,

total suspended particulate (TSP) aerosol masses greater than $100 \mu\text{g m}^{-3}$ were often measured. In March 1997, O_3 exceeded 150 ppb over most of the urban area in the Valley of Mexico on half of the sampling days, and particulate matter of less than $2.5 \mu\text{m}$ (PM-2.5) averaged $40 \mu\text{g m}^{-3}$ overall.

By analogy with megaurban zones of the developed world (see Sillman et al., 1990a,b; Russell and Odman, 1993), we expect that the Mexico City effluent will be augmented by neighboring plumes. In particular, Puebla, Toluca, and Cuernavaca are nearby cities of population greater than 1 million. In air exchanging with upper levels at the 2 km chimney height, the concentrations of reactive escaping photochemicals such as NMHCs, NO_y , O_3 and sulfur oxides (SO_x) were found to be orders of magnitude greater than tropospheric background levels (Table 1). For example, at the transition to geostrophic winds, O_3 approached 300 ppb on winter afternoons (MARI, 1994; Vidal and Raga, 1998). Within the basin, NMHC losses balance O_3 production at the usual yields with a NO_x efficiency of 5–10 (Liu et al., 1987; NRC, 1991; Jacob et al., 1993a,b). Volatile organics remaining in the air carry ppm-level potential ozone production capacity. Nitrogen oxides and SO_2 also have well-established effects on oxidant and cloud condensation nucleus (CCN) fields as they dilute into remote air masses (Liu et al., 1987; Crutzen, 1988; Benkovitz et al., 1994; Schwartz and Andreae, 1996). An upper limit O_3 flux of 5000 tons d^{-1} was established over the photoperiod, for the eddy ventilation piston velocity of 10 cm s^{-1} and over the $50 \times 50 \text{ km}$ area. Indeed, the O_3 emanating directly from the Valley of Mexico adds 30–50 Dobsons to the tropospheric column density, and the high levels of O_3

Table 1

For selected substances within the Valley of Mexico atmosphere: concentrations ('conc.', ppb for individual gases, ppbC for NMHC, $\mu\text{g m}^{-3}$ for fine particles), removal time constants (τ , days), scale distances (km), areal coverages (%), ventilation fractions (%), burdens (tons for individual gases and for particles in the fine mode, tons C for NMHC, tons NO for NO_x , tons N for NO_y) and fluxes (tons day^{-1}). The methane burden is effective over background

	CH_4	CO	C_3H_8	NMHC	NH_3	SO_2	NO_x	NO_y	Soot	Dust
Remote conc.	1800	100	0.2	30	0.01	< 1	< 1	< 1	0.1	0.1
Urban conc.	1950	3000	25	700	20	50	75	100	5	5
Chemistry τ	long	> 10	1.0	0.4	10	1.0	0.1	long	long	long
Scale height	large	> 10	3	2	10	3	1	large	large	large
2 km conc.	1850	1000	8	250	7	16		35	1.5	1.5
% Coverage	100	100	100	100	100	100	50	100	100	100
Transport τ	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Average τ	0.75	0.75	0.55	0.39	0.75	0.55	0.16	0.75	0.75	0.75
% Vented	100	100	73	51	100	73	20	100	100	100
Burden	270	10,000	120	1000	40	350	90	175	15	15
Emissions (bottom up)	750	11,000	130	1500		300	300	230		
Emissions (top down)	360	13,000	220	2500	50	650	600	230	20	20
Venting (bottom up)	750	11,000	100	750		220	60	230		
Venting (top down)	360	13,000	160	1250	50	475	120	230	20	20

may be detectable in the Total Ozone Mapping Spectrometer (TOMS) data stream.

Extrema in the Mexico City measurements suggest that nonstandard oxidation and removal mechanisms exist for species including NMHCs, peroxyacetyl nitrate (PAN), NH_3 , nitrates, particulates, and ClO_x . Half of the NMHCs emitted within the basin are also degraded there, because of the combination of high oxidant concentrations with a relatively long three-quarter day residence time for air in the Valley of Mexico. In this special, relative sense Mexico City is cleaner than counterparts such as Los Angeles, which ventilates in half a day. The local air in Mexico City is nonetheless rich in hydrocarbons. Total organic matter in the gas phase was found to average nearly 1 ppmC through the urban zone, with a morning maximum of 4 ppmC at many sites (Fig. 1). In addition, the concentrations of organic nitrates (which are hydrocarbon oxidation products) are enhanced by kinetic and mass action effects.

Total ammonia emissions within the Valley of Mexico (Table 1) appear to be comparable to those of greater Los Angeles of the 1970s, despite a different source distribution for the two cities. In Southern California, half of the airborne reduced nitrogen is volatilized from feedlots, with a few percent from domestic animals (Cass et al., 1982; Russell et al., 1983). By contrast, the two fractions are reversed in the Valley

of Mexico, and domestic animals rather than feedlots make a larger contribution to NH_3 volatilization.

The latest NH_3 inventories in the Valley attribute 75% of the emissions to dogs, cats, and rats in residential areas, together with partially treated human waste (Osnaya Ruiz, 1998). Because human and domestic animal inputs dominate the NH_3 emissions, the source of ammonia is necessarily connected with areas of intense human activity. The baseline of NH_3 lies at 20 ppb across the urban zone (Table 1), and falls off only slowly towards the foothills. The concentration of NH_3 is sufficient to titrate photochemically generated acids ubiquitously into fine mode (PM-2.5) aerosols (Russell et al., 1983, 1985, 1993).

Taken together, the NMHCs and NH_3 shift the odd nitrogen (NO_y) from a traditional nitric acid (HNO_3) reservoir towards species that deposit more slowly, including fine particles and PAN (McRae and Russell, 1984; Russell et al., 1985, 1993). Peroxyacetyl nitrate concentrations regularly reached 30 ppb on the grounds of the Mexican Petroleum Institute, located in the north-center of the city (Fig. 2). PAN has exhibited rapid afternoon declines in Mexico City that may be heterogeneous in nature and may rely on surfactant coatings (Ravishankara, 1997). Such surface chemistry would return carbon and nitrogen to aerosol accessibility. Nitrates also withhold carbon from the secondary

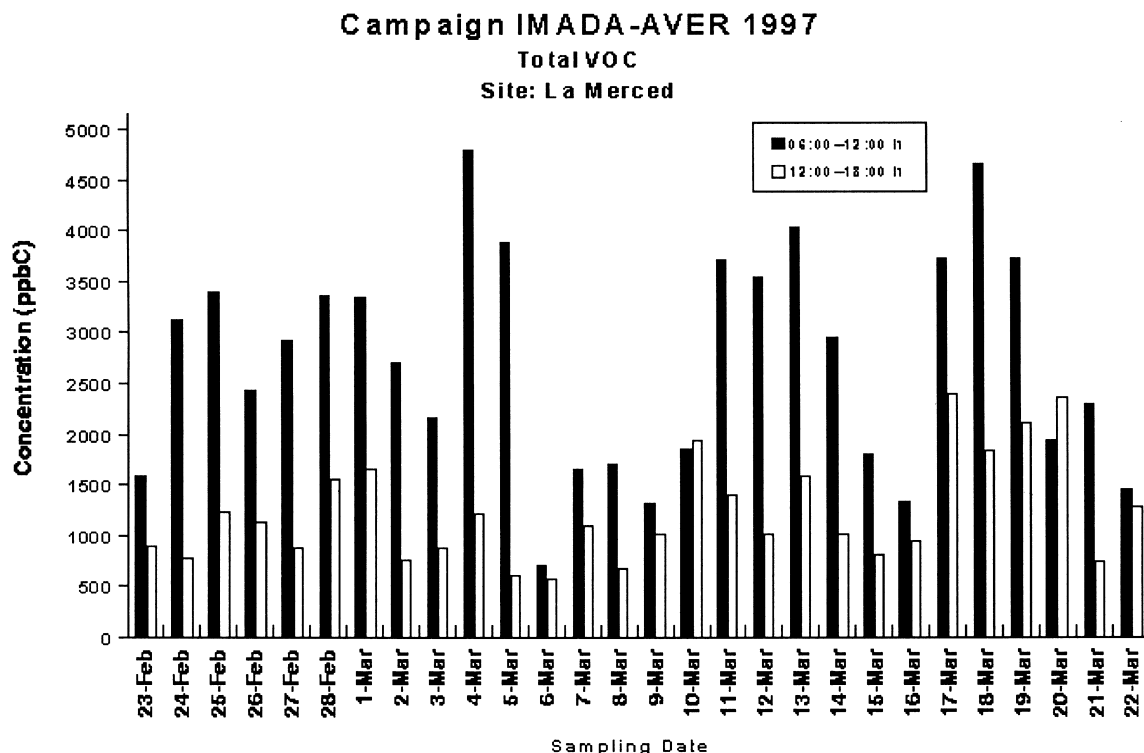


Fig. 1. Total nonmethane hydrocarbon (NMHC) as a volatile organic carbon mixing ratio, at a downtown site in Mexico City (La Merced) during the spring 1997 intensive.

organic aerosol, which accounts for one third of the fine mass aerosol.

In Mexico City, PM-10 contains a high concentration of chloride, ranging from 1 to 10 $\mu\text{g m}^{-3}$ in the Xalostoc and Nezahualcoyotl neighborhoods (Fig. 3). The bed of Lake Texcoco has tentatively been identified as the chloride source. Dry sediment covers much of the eastern half of the Valley of Mexico, as a result of hydrological reengineering during centuries of European rule (Ezcurra, 1991). At night, NO_x reacts with NaCl to give photosensitive ClNO_2 , and ultimately ClO_x (Finlayson Pitts, 1993; Abbatt and Waschewsky, 1998). By contrast with marine environments, however, the Mexican chlorine chemistry will not be nitrogen limited.

4. Biogeochemical considerations

Several of the substances we have investigated couple major biogeochemical cycles to the Mexico City infrastructure. The cycling of substances within Mexico City has been studied often, but has not been interpreted from a biogeochemical perspective. Here, we use urban air measurements to quantify the release of

pollutants from the Valley of Mexico and to investigate their influence on regional and global biogeochemical cycling.

Methane (CH_4) is a prime example of a species whose release from Mexico City can influence larger scale biogeochemical cycles. Methane is a strong greenhouse gas and it regulates the tropospheric oxidizing capacity (Cicerone and Oremland, 1988; Crutzen, 1988). The CH_4 that is emitted into the atmosphere of Mexico City is exported to the free troposphere. The metropolis of Mexico City consumes approximately 500 PJ of energy per year, of which 20% is derived from natural gas (UN, 1992; Villareal et al., 1996). Usage is 5000 metric tons of CH_4 per day. If the average of the top down and bottom up emission estimates in Table 1 were entirely attributable to losses from the natural gas infrastructure, the leak rate would be 10%. The figure constitutes an upper limit because the local source distribution of CH_4 (including contributions from landfills, sewers and automobiles) has yet to be determined. It is nevertheless of interest to contrast the leak rate with loss estimates of CH_4 along its global industrial life cycle. Leakage for overall gas production is only 1% from venting and flaring at extraction sites, and 0.1–0.3% along most pipelines (Muller, 1992).

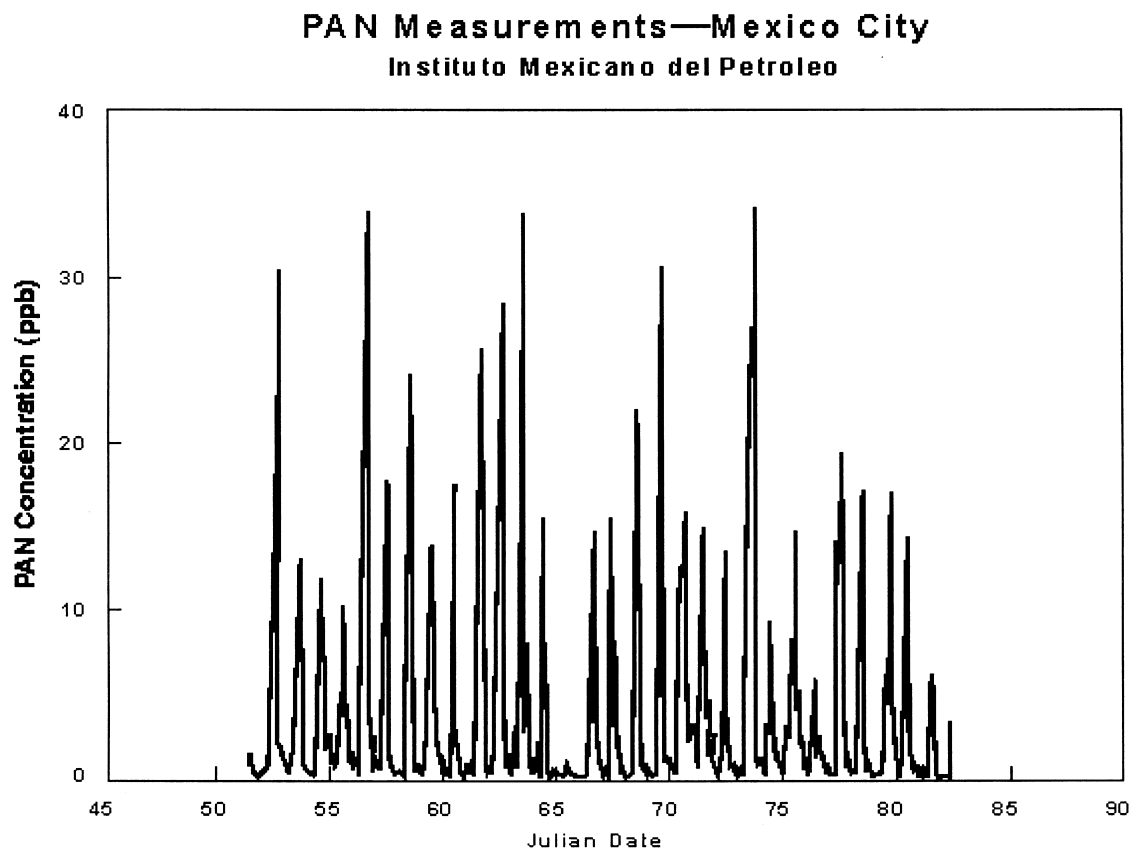


Fig. 2. Peroxyacetyl nitrate (PAN) mixing ratios at the Mexican Petroleum Institute, during the spring 1997 intensive.

Only in former Eastern Block countries are the percentage loss figures believed to approach double digits. Direct human inputs of CH_4 associated with the natural gas industry (50 Mton yr^{-1}) represent about a tenth of the world sources of 500 Mton yr^{-1} (Khalil and Rasmussen, 1983; Cicerone and Oremland, 1988). Losses from megacities that rely heavily upon natural gas thus have the potential to add significantly to the planet's CH_4 inventory.

The various governments administering Mexico City have emphasized the implementation of liquefied petroleum gas (LPG) systems in residential areas (MARI, 1994; Blake and Rowland, 1995; Villareal et al., 1996). LPG was deemed a safe domestic fuel because it can be transported by truck through the earthquake prone

basin. The Mexican LPG is half butane (iso and normal; C_4H_{10}) and half propane (C_3H_8) by moles (Blake and Rowland, 1995). LPG comprises another 20% of energy use in Mexico City, with 5400 metric tons consumed daily. Source profiling demonstrates that LPG is the dominant propane source. By contrast, automobiles make only small contributions to the concentrations of C_3 – C_4 alkanes. The propane emissions (Table 1) indicate that the liquefied gases show a substantial leakage which is consistent with handling losses of almost 10%. However, because photochemistry in the Valley of Mexico is NO_x -limited rather than hydrocarbon limited, minimizing the leakage of hydrocarbons from LPG will have only a minimal effect on local O_3 levels.

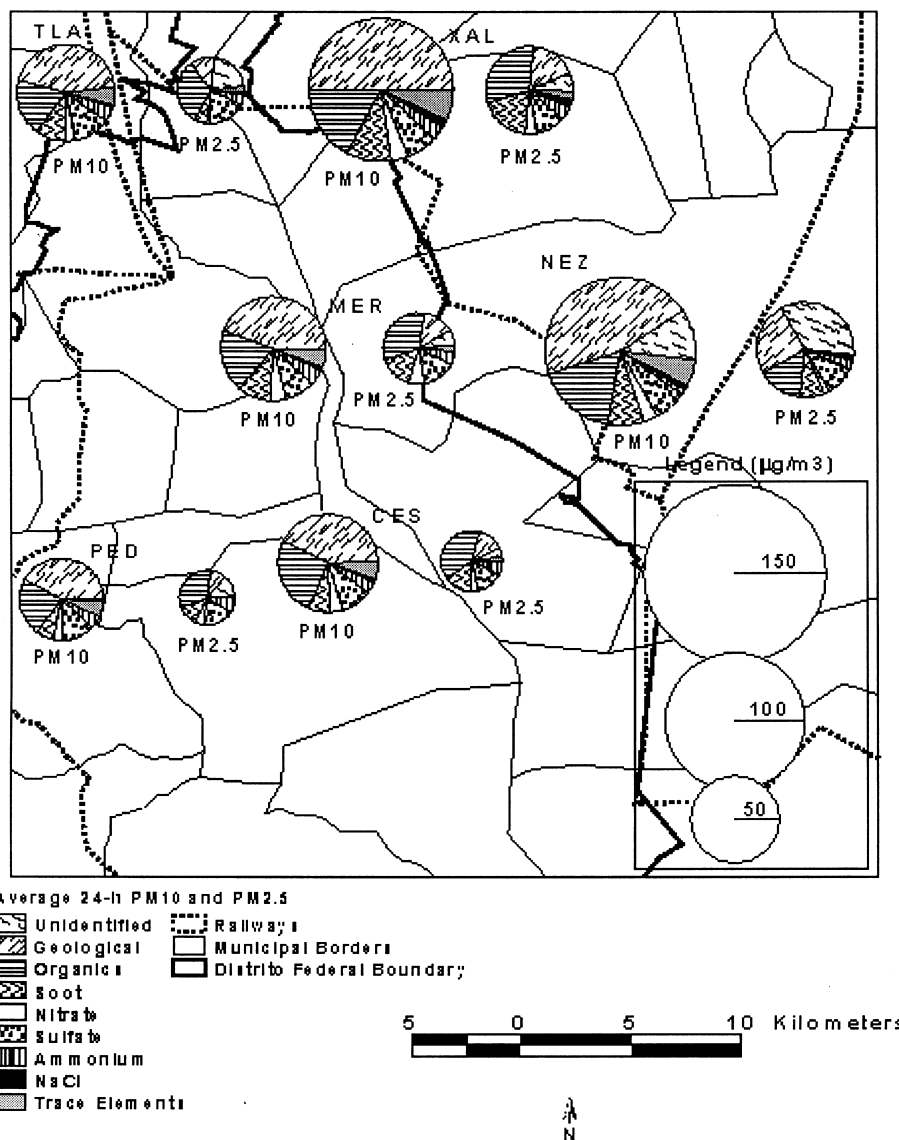


Fig. 3. Particulate matter (PM-10 and PM-2.5) composition in the Mexico City area for spring, 1997. The site codes are Tlalnepantla (TLA), Xalostoc (XAL), La Merced (MER), Nezahualcoyotl (NEZ), Cerro de Estrella (CES) and Pedregal (PED).

Carbon monoxide, NO_x , and a subset of the NMHCs are among the gas phase vehicular pollutants with biogeochemical significance. As with O_3 and aerosols, the concentrations of CO, NO_x and NMHCs in Mexico City resemble those from peak pollution years in Los Angeles. The similarity may be crudely explained by two factors: the population density of Mexico City is several times that of Los Angeles, while the auto-to-person ratio is correspondingly lower (UN, 1992; MARI, 1994). Low incomes and efficient public transportation are continuing to keep the auto-to-person ratio low.

The global nitrogen cycle is second only to the carbon cycle in terms of influence on the climate (Jaffe, 1992). Here, we consider Mexico City in terms of its contribution toward nutrient transport to ecosystems throughout the region. In Los Angeles, nitrogen deposition is attributable mainly to HNO_3 (McRae and Russell, 1984; Russell et al., 1985). By contrast, the depositional depletion of airborne nitrogen is expected to be less in the Valley of Mexico than in Los Angeles. This is partially because of reaction of nitric acid with an ample supply of NH_3 to create ammonium nitrate aerosol. Unlike HNO_3 , ammonium nitrate does not readily deposit and thereby enables nitrogen to be transported out of the Valley of Mexico. The gas phase organic nitrates also sequester nitrogen atoms.

Ammonia injections into the Mexico basin are traceable to the local food supply. Emissions and venting ($50 \text{ metric tons d}^{-1}$; Table 1) are roughly comparable to NH_3 losses from fertilizer application in the agricultural region associated with Mexico City (Schlesinger and Hartley, 1992; Matson et al., 1997, 1998). Because local and international agronomists are working to cut production costs by maximizing fertilizer use efficiency during intensive wheat farming in the central and northern portions of the country (Matson et al., 1998), the urban volatilization pathway will increase in relative magnitude. The urban waste treatment infrastructure in Mexico City appears to lie in between developed and rural analogs in its effectiveness. For example, waste treatment in Mexico is less effective than in US cities, but NH_3 fluxes are nevertheless low compared to the emissions from rural areas (Dentener and Crutzen, 1994).

Oxidized nitrogen emissions from Mexico City figure quite differently from ammonia/reduced nitrogen in regional to global budgets. Even at the low urban vehicle-to-person ratio in Mexico City, the per capita release of NO_y surpasses the global average (Jaffe, 1992; Prather et al., 1995). The NO_y concentration in the basin ventilate (2 km height) is five times higher than that of NH_3 (Table 1). During the daytime, the NO_y concentration is about 35 ppbv at the transition into the upper level flow. The mobilization of nitrogen in Mexico City is thus leading to significant export

from the Valley. Nearby cities also contribute to a plume of urban effluent which is perhaps 100 km in breadth and dilutes slowly in the horizontal (Gifford, 1982). Given standard tropospheric eddy diffusivities (Thompson and Cicerone, 1982; Liu et al., 1984), 20 ppb of NO_y may contact the surface downwind. At a generalized deposition velocity of 1 cm s^{-1} (McRae and Russell, 1984), $5 \times 10^{11} \text{ N atoms cm}^{-2} \text{ s}^{-1}$ could enter regional soils. By contrast, nitrogen fixation in central Mexico is on the order of $1 \times 10^{11} \text{ N atoms cm}^{-2} \text{ s}^{-1}$ (Schlesinger, 1997), and the sum of background NH_3 and NO_y deposition is similar (Penner et al., 1991; Schlesinger and Hartley, 1992; Dentener and Crutzen, 1994). Our simple analysis of the Mexico City plume chemistry suggests that it is likely to alter regional soil nitrogen cycling. The impact of NO_y on regional soil chemistry will become increasingly important in the future if the vehicle-to-person ratio in Mexico City increases.

The marine effects of Valley ventilation are difficult to gauge because of the intervening overland distance between Mexico City and the ocean. The Caribbean Sea behaves oligotrophically (Berger and Wefer, 1991), and at oceanic Redfield ratios (Redfield, 1963; Takahashi et al., 1985) $1 \times 10^{11} \text{ new N cm}^{-2} \text{ s}^{-1}$ enter the euphotic zone from deeper waters below. The plume emanating from the urban highlands of Mexico could well augment the input of nitrogen into the Caribbean. The Gulf of Mexico is five times more productive than the Caribbean (Berger and Wefer, 1991), and it often lies along the dispersion trajectory from Mexico City (Bossert, 1997). As a result, nitrogen emissions from the Valley of Mexico may also impact the Gulf of Mexico.

Primary aerosol has been inventoried only for the fine mode (PM-2.5) in Table 1, in order to facilitate comparisons with the ammonium salts and organics. For dust, the PM-10 mass concentration is 5 times higher than the fine mode dust value that is shown in Table 1. A mode radius of $4 \mu\text{m}$ is applicable for PM-10 dust (Tegen and Fung, 1995), and sedimentation is minimal. The PM-10 dust may be considered inert within the basin, and an emission of $0.015 \text{ kg m}^{-2} \text{ yr}^{-1}$ is calculated. This emission rate is comparable to (1) natural suspension from the Mexican plateau, (2) contributions from local land use change, and (3) peripheral suspension from the belt of dry soils running from the Sahara through the Middle East to Central Asia (Penner et al., 1994; Tegen and Fung, 1995). In Mexico City, the source of the PM-10 dust may be purely mechanical as a result of urbanization. New neighborhoods regularly arise in the form of squatter communities lacking in government-sponsored roads or sanitation (Frieden, 1965; Varley, 1987). Throughways in Xalostoc and Nezahualcoyotl have remained unpaved as township populations move into the

millions. These suburbs record TSP levels in the hundreds of $\mu\text{g m}^{-3}$ (Jauregui, 1989; UN, 1992; Villareal et al., 1996). Effects of the dry lake bed which supplies ClO_x have yet to be quantified. The Mexico City atmosphere is quite basic so that an assessment of metal solubilization may be needed. For example, much of the literature on photodissolution of iron from dust assumes an acid coating (Zhuang et al., 1992a,b). Soot particles are confined to the fine mode (Penner et al., 1994; Cooke and Wilson, 1996), and concentrations in the Valley and its effluent are sufficient to lower extinction lengths in the visible range. Indeed, black carbon and the urban haze in general already compromise the strength of the Mexican tourist industry (Bravo et al., 1988; Vasilyev et al., 1995).

There are several areas in which progress has been made in controlling pollution in the Valley of Mexico. Sources of sulfur dioxide and of liquefied petroleum gas leaks have been identified, and removal/rehabilitation efforts have been made (MARI, 1994; Blake and Rowland, 1995). A strong motivator for controlling pollutant levels lies outside any earth system issue, and may be as basic as visibility: the perception of haze may be the most likely motivating factor for the tightening of urban infrastructures. Indeed, climatologists have pointed out that the global aerosol may be controlled early simply because it is tangible and fleeting (Rind, 1998).

5. The urbanization of Asia

We now discuss the implications of these findings in a global context. The next burst of urbanization is predicted in Eastern Asia and is expected to involve almost half of the earth's population (UN, 1992, 1994; OSTP, 1997). In the People's Republic of China (PRC), a strong intranational economic gradient is driving a migration towards the coast. As urban incomes rise along the seaboard, the demand for readily available coal is declining while imports of cleaner petroleum gases rise. Increased global anthropogenic inputs of CH_4 and certain NMHCs could occur if the 10% leakages of LPG that were estimated in Mexico City applied to commercial gas infrastructures across coastal Asian cities.

The Chinese vehicle fleet is expanding exponentially, particularly in the cities (WB and CMC, 1994; Sathaye et al., 1994; Elliott et al., 1997b). Vehicle-to-person ratios are currently negligible but are projected to reach the Mexican value of 0.1 in 2020, based on estimates of gross domestic product (GDP) evolution within China. The release of combustion products will rise accordingly, and dust suspension may occur in dry areas of the coastal plains, as has been found in Western China (Zhou et al., 1994). Not only in Latin

America but globally as well, automobiles have typically entered new and developing markets before highways can be built to accommodate them (Sathaye et al., 1994; Smith et al., 1994), thereby leading to increased levels of dust suspension. The Chinese atmosphere of the next century is likely to be rich in both ammonia and acids, so that the pH of its aerosol cannot easily be predicted.

In the Valley of Mexico, the interplay of gases in a pollutant-rich atmosphere stabilizes against nitrogen deposition, thereby facilitating long-range transport. As megacities in China begin to mobilize nitrogen on an unprecedented scale, Asian ecosystems are also expected to be placed at risk (Galloway, 1996). Managed ecosystems of Asia must feed the coming megapopulation, and it is clear that they will be severely taxed. While harvests must increment at 1% per year to keep pace with a growing population, leaf damage by O_3 and SO_2 is likely to lower crop yields on the order of 10% (Chameides et al., 1994). Further, aerosols may be sufficiently reflective and adsorptive to limit crop growth by affecting photosynthetically available radiation (Parungo et al., 1994; Zhou et al., 1994). Clearly, the magnitude of these problems will be largest in the vicinity of the Asian population corridor. Because the economic gradient leads eastward in the PRC, regions such as Japan, the North Pacific, and even Western North America lie downwind and also may be affected by pollution originating from Eastern China (Elliott et al., 1997b,c).

As the urbanization of the PRC progresses, China may leapfrog certain aspects of Western development. For example, Chinese society has traditionally relied on the bicycle-rail combination for mass transit, and still has the option to retain the strategy (Zhihao, 1990). Similarly, the efficient metro of Mexico City has been credited in part for stabilizing its auto-to-person quotient. However, pressure for a rapid update of the transportation system in China is tremendous, and Japanese/Western auto manufacturers are aggressively seeking to fill the vacuum (WB and CMC, 1994; Elliott et al., 1997b,c). By contrast, because returns in oil exploration are diminishing, the total recoverable reserves may be insufficient to supply a large Asian fleet of vehicles (Kerr, 1998).

6. Summary

The Valley of Mexico is arguably the world's most populated and heavily polluted urban zone, and it may serve as a partial model for the growth of megacities in other areas of the developing world. The air chemistry of Mexico City is relatively well studied, and we have used local air quality surveys to estimate the

emissions, processing, and ventilation of major carrier species.

The air in the Valley of Mexico resembles peak smog episodes in cities of the Western United States during the 1970s. However, the Mexico City pollution is considered to be extreme in several senses. Leakage rates of 10% were calculated for the NMHC components of LPG. Losses may also be high from the natural gas system, but individual CH₄ sources need to be quantified for the situation to be properly assessed. Automotive emissions of CO, NO_x, and some NMHCs are already comparable to the most polluted parts of the US and Europe, despite a lower vehicle-to-person ratio in Mexico City. Further, the emissions will rise if the vehicle fleet expands. The release of ammonia in the Valley of Mexico occurs from dispersed sources because domestic animals make a much larger contribution to NH₃ volatilization than emissions from feedlots. An excess of NH₃ forces photochemically generated acids into fine mode particles. Together, the NMHCs and NH₃ shift the nitrogen reservoir (NO_y) towards species which deposit more slowly, such as fine particles and PAN. Partly as a result, there is a mobilization of the urban nitrogen whereby the concentration of NO_y at 2 km is about 35 ppb (vs < 1 ppb in remote areas), and significant export from the Valley occurs. Finally, chloride originating from dry sediments of the former Lake Texcoco coexists with concentrations of 100 ppb of NO_y in Mexico City, raising the possibility of inland ClO_x photochemistry.

The export of pollutants from the Valley of Mexico is expected to impact local, regional and global biogeochemical cycles. If the LPG leakage rates in Mexico City apply to commercial gas infrastructures in newer megacities of the developing world, the next generation megacities taken as a group may add significantly to the planet's CH₄ inventory. In addition, O₃ emanating directly from the Valley of Mexico adds 30–50 Dobsons to the tropospheric column density, and the enhancement may be detectable in the TOMS data stream. The mobilization of oxidized nitrogen may lead to a downwind deposition that is several times larger than nitrogen fixation or the background atmospheric source in Central America. Emissions from Mexico City are therefore likely to affect regional soil nitrogen cycling. Similarly, sizeable nitrogen deposition into the Caribbean Sea and Gulf of Mexico appears likely. Massive mineral dust suspension from the Valley floor is a result of reliance on unpaved roads in suburbs such as Xalostoc and Nezahualcoyotl. The dust generation on an areal basis is similar to rates on the edges of the Sahara, Arabian, and Gobi deserts.

Over the next few generations, Asia is expected to dominate the human dimension of geochemical change. Rising incomes in the coastal zone of China will lead to the demand for fossil fuels that are cleaner

than coal. The transport and use of natural and liquefied petroleum gases is therefore likely to occur, though the leak rates in the Valley of Mexico indicate that caution should be applied. The Asian vehicle-to-person quotient is rising rapidly and should reach 0.1 within a few decades. As a result, per capita NMHC and NO_x emissions may surpass Latin American levels if vehicle maintenance is not established as a priority. Nitrogen mobilization from Eastern China is expected to impact both continental and oceanic ecosystems that lie downwind in the North Pacific (Japan, the central gyre, and North America). The recent economic difficulties in Asia may lead its next generation of megacities along a high-impact biogeochemical pathway, similar to that of Mexico City. However, it is also possible that Asia will improve on certain aspects of Western city design by centralizing energy consumption and minimizing reliance on the automobile. As in Mexico City, infrastructure improvements in Asia will likely be driven by popular concerns over health and visibility.

Any success in our approach as it has been applied to Mexico City is due in part to the very basin which creates the local pollution problem. Analyses such as the one offered here for Mexico City may be successfully conducted in other such metropolitan areas, and the approach could be extended to create a statistically useful earth system data base. For example, populous, confined cities are found throughout Latin America and Asia, and include Sao Paulo (Brazil) and Chongqing (PRC). Further, the infrastructure deductions we compile may apply across the developing world, regardless of topography. Coordination with local air quality studies is recommended as a way to bootstrap biogeochemical research to other developing megacities.

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