Air Quality in Mexico City: Spatial and Temporal Variations of Particulate Polycyclic Aromatic Hydrocarbons and Source Apportionment of Gasoline-Versus-Diesel Vehicle Emissions

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Abstract

The Mexico City Metropolitan Area (MCMA) is one of the largest cities in the world, and as with many megacities worldwide, it experiences serious air quality and pollution problems, especially with ozone and particulate matter. Ozone levels exceed the health-based standard, which is equivalent to the U.S. standard, on approximately 80% of all days, and concentrations of particulate matter 10 μm and smaller ($\text{PM}_{10}$) exceed the standard on more than 40% of all days in most years. Particulate polycyclic aromatic hydrocarbons (PAHs) are a class of semi-volatile compounds that are formed during combustion and many of these compounds are known or suspected carcinogens. Recent studies on PAHs in Mexico City indicate that very high concentrations have been observed there and may pose a serious health hazard.

The first part of this thesis describes results from the Megacities Initiative: Local and Regional Observations (MILAGRO) study in Mexico City in March 2006. During this field campaign, we measured PAH and aerosol active surface area (AS) concentrations at six different locations throughout the city using the Aerodyne Mobile Laboratory (AML). The different sites encompassed a mix of residential, commercial, industrial, and undeveloped land use. The goals of this research were to describe spatial and temporal patterns in PAH and AS concentrations, to gain insight into sources of PAHs, and to
quantify the relationships between PAHs and other pollutants. We observed that the highest measurements were generally found at sites with dense traffic networks. Also, PAH concentrations varied considerably in space. An important implication of this result is that for risk assessment studies, a single monitoring site will not adequately represent an individual’s exposure.

Source identification and apportionment are essential for developing effective control strategies to improve air quality and therefore reduce the health impacts associated with fine particulate matter and PAHs. However, very few studies have separated gasoline-versus diesel-powered vehicle emissions under a variety of on-road driving conditions. The second part of this thesis focuses on distinguishing between the two types of engine emissions within the MCMA using positive matrix factorization (PMF) receptor modeling. The Aerodyne Mobile Laboratory drove throughout the MCMA in March 2006 and measured on-road concentrations of a large suite of gaseous and particulate pollutants, including carbon dioxide, carbon monoxide (CO), nitric oxide (NO), benzene (C₆H₆), formaldehyde (HCHO), ammonia (NH₃), fine particulate matter (PM₂.₅), PAHs, and black carbon (BC). These pollutant species served as the input data for the receptor model. Fuel-based emission factors and annual emissions within Mexico City were then calculated from the source profiles of the PMF model and fuel sales data. We found that gasoline-powered vehicles were responsible for 90% of mobile source CO emissions and 85% of VOCs, while diesel-powered vehicles accounted for almost all of NO emissions (99.98%). Furthermore, the annual emissions estimates for CO and VOC were lower than estimated during the MCMA-2003 field campaign.
The number of megacities is expected to grow dramatically in the coming decades. As one of the world’s largest megacities, Mexico City serves as a model for studying air quality problems in highly populated, extremely polluted environments. The results of this work can be used by policy makers to improve air quality and reduce related health risks in Mexico City and other megacities.
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Chapter 1

Literature Review

This research has two main objectives, both of whose ultimate goal is to provide a scientific basis for improving air quality in Mexico City, one of the world’s largest and most polluted megacities. The first objective is to describe temporal and spatial variations in particulate polycyclic aromatic hydrocarbon (PAH) and aerosol active surface area (AS) concentrations in Mexico City. Addressing this objective will produce new knowledge about the sources of PAHs and of the compounds’ evolution as they are transported throughout the megacity atmosphere. The second objective is to apply source-receptor modeling to quantify emissions from gasoline- and diesel-powered vehicles, the largest contributors to much of the gaseous and particulate air pollution in Mexico City.

The literature review presented in this chapter presents essential background information on the sources and health risks of particulate matter (PM) and PAHs. It also contains a section which reviews previous studies of PAHs conducted in Mexico City. Finally, it describes methods of identifying sources of air pollutant emissions based on ambient concentration measurements.

1.1 Mexico City’s air pollution problem

The Mexico City Metropolitan Area (MCMA) has perhaps the most serious air pollution problem in North America (Molina et al., 2002). The environmental dilemmas of the
MCMA result not only from its topographical confinement but are also heavily influenced by social, economic, and demographic changes which have occurred and significantly transformed the region in recent decades. As the world’s second largest megacity, defined as an urban area with a population of at least 10 million, Mexico City may be a model of air pollution problems and solutions to come as the number of megacities in the world grows from 14 in 1995 to 26 by the year 2015 (Lynn et al., 1999).

It is estimated that there are approximately 20 million inhabitants in Mexico City, making it one of the largest metropolises in the world, second only to Tokyo with 26 million inhabitants. In the 1960s, only 5 million people lived in the MCMA; the population has quadrupled over the last 40-50 years. The Mexico City basin is a broad valley which lies 2240 m above sea level. A ring of mountains confines the east, south, and west sides of the basin, leaving openings to the north and to the south-southwest. As a result of the subtropical latitude and high altitude of the MCMA, it is a prime location for high levels of photochemical ozone production and other photochemistry for much of the year.

In the MCMA, the air quality standards most commonly violated are for ozone and PM. Ozone levels exceed the health-based standard, which is equivalent to the U.S. standard, on approximately 80% of all days, and concentrations of PM$_{10}$, particles with aerodynamic diameters smaller than 10 μm, exceed the standard on more than 40% of all days in most years (Molina et al., 2002).

The transportation sector represents a major source of the air pollution problems in the MCMA. In the 1998 emissions inventory, the transportation sector accounted for almost
all of the emissions of carbon monoxide (CO), 35% of PM$_{10}$, and 80% of oxides of nitrogen (NO$_x$) (Comisión Ambiental Metropolitana, 2001). The size of the city’s vehicle fleet was estimated at 3.2 million in 1998 (Comisión Ambiental Metropolitana, 2001), but now it is postulated to be around 5 million vehicles.

The industrial sector has also been shown to contribute significantly to the air pollution problems in Mexico City. Nearly 6300 industries are represented in the 1998 emissions inventory (Comisión Ambiental Metropolitana, 2001). This estimate included large and medium-sized industries and only a tiny portion of the smaller industries, since many of them are not registered. Emissions inventories report that the industrial sector is responsible for 55% of SO$_2$, 16% of PM$_{10}$, and 13% of NO$_x$ emissions (Comisión Ambiental Metropolitana, 2001).

The high levels of particulate matter smaller than 2.5 µm (PM$_{2.5}$) in Mexico City pose an environmental concern because it degrades visibility, and a continuous haze blankets the city, especially during the winter time. High concentrations of PM$_{2.5}$ result from a combination of primary and secondary sources. Primary particles are directly emitted from sources such as vehicular traffic and industry, while secondary particles are formed in the atmosphere from reactions involving gaseous emissions of sulfur dioxide, ammonia, oxides of nitrogen, and heavy organic gases.
1.2 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a class of semi-volatile compounds that are ubiquitous in the atmosphere, and they were among the first atmospheric compounds to be identified as carcinogens (Finlayson-Pitts et al., 1999). PAHs are formed during the incomplete combustion of organic matter such as wood, gasoline, oil, and coal. Thus, some important sources of PAHs include motor vehicles, coal-fired power plants, and wood fires. Because the vapor pressures of individual PAHs span a wide range, smaller PAHs such as naphthalene are found mainly in the gaseous phase, while PAHs with five or more rings, such as benzo[a]pyrene, are found mainly in the particulate phase. Those with two to four rings are found in both the gaseous and particulate phases. PAHs in their condensed form are associated with fine particles (Eiguren-Fernandez et al., 2003), which can infiltrate deep into the lungs and deposit there. Thus, particulate matter acts as a carrier for PAHs.

1.3 Health risks associated with PM and PAHs

Pope et al. (2002) concluded that long-term exposure to PM$_{2.5}$ was a contributory factor in a significant number of early deaths as a result of respiratory and cardiovascular diseases. Additionally, particulate matter that has been inhaled can then migrate into general circulation around the body and be transported to distal organs (Penn et al., 2005).

Many studies have been conducted on the health effects related to PM$_{2.5}$ in Mexico City. Vega et al. (2002) found that the high levels of PM$_{2.5}$ present in different environments of
the MCMA are a cause for concern because of their potentially severe public health effects on the population. Loomis et al. (1999) reported that excess infant mortality in Mexico City is related to exposure to PM$_{2.5}$, with a 10 µm m$^{-3}$ increase in mean concentrations associated with a 7% increase in infant death rates. A study by Sanchez-Carillo et al. (2003) showed that PM$_{10}$ is associated with lower respiratory symptoms in some areas of Mexico City. O’Neill et al. (2004) concluded that exposure to particulate air pollution is associated with an increase in daily mortality. Furthermore, Vallejo et al. (2006) found that acute effects in heart rate variability in normal young adults are related to exposure to PM$_{2.5}$. The consensus of a link between fine particulate air pollution and serious health effects is clearly evident.

While the exact mechanism by which particles cause injury in the lungs remains unknown, some PAHs are known carcinogens; and epidemiologic studies have linked PAH exposure to specific health outcomes. In a study of prenatal exposure to PAHs and its effect on fetal growth, exposure was found to be associated with low birth weights (Choi et al., 2006). In another study of prenatal exposure to PAHs in ambient air and its effects on infants, immunotoxic PAHs were found to weaken a fetus’ immune system and cause respiratory symptoms in newborns and infants (Jedrychowski et al., 2005).

1.4 PAHs in Mexico City

The first study which assessed concentrations of and exposure to PAHs in Mexico City was conducted in 1991 (Salazar et al., 1991). The study was conducted in the northwest portion of the city near an oil refinery in Azcapotzalco. It concluded that the presence of
PAHs caused an increase pulmonary and respiratory illnesses, depreciated air quality, and impacted negatively on the human health of city dwellers due to PAHs’ carcinogenicity. However, this study was conducted at only a single site.

Recent studies have been conducted in other locations throughout the MCMA and have shown it to have some of the highest ambient PAH concentrations ever measured (Marr et al., 2004; Velasco et al., 2004). Baumgardner et al. (2007) assessed the diurnal variability of PAHs and CO in Mexico City in relation to black carbon (BC) in April of 2003 and 2005. CO and BC had similar diurnal trends, and PAHs reached a peak during the morning rush hour period, similar to BC and CO; however PAH concentrations then rapidly decreased within four hours of reaching this peak value.

Dzepina et al. (2007) compared the detection of PAHs in Mexico City during the MCMA-2003 field campaign using an aerosol mass spectrometer (AMS) against two other methods: filter collection with analysis by gas chromatography-mass spectrometry (GC-MS) and aerosol photoionization (Marr et al., 2006). There was a good correlation between the AMS PAH data and aerosol photoionization method in general, with minor differences occurring during periods of fresh traffic emissions in the morning periods. There was more scatter between the GC-MS PAH measurements and the AMS PAH measurements. It was deduced from the measurements of PAHs by the three different techniques that PAH concentrations on the surfaces of particles diminished rapidly during the mid-morning hours due to coating by secondary aerosols in the highly photochemically active environment of Mexico City.
Marr et al. (2004) investigated aerosol surface properties in different environments of the MCMA using a photoelectric aerosol sensor and a diffusion charger, which measured particulate PAHs and aerosol active surface area, respectively. Particle surface properties are important because they have been linked even more strongly than particle mass to health effects. This study found that the median total particulate PAH concentration ranged from 60 to 910 ng m$^{-3}$ along Mexico City’s roadways. These levels were five times higher than those found in the United States and among the highest reported in the literature.

Analyzing similar parameters and using similar measurement equipment as that used in Marr et al. (2004), Velasco et al. (2004) also investigated PAHs along the roadways of Mexico City. Total particulate PAH concentrations averaged 173 ng m$^{-3}$ among all the roadway locations. This value was lower than observed in Madrid, Paris, Tokyo, and Zurich, but higher than in cities in the United States such as New York and Boston. In Mexico City, higher exposures of PAHs were recorded in locations with denser traffic networks, especially at locations with a greater fraction of diesel-powered vehicles.

A more limited number of studies have estimated emissions of particulate matter in Mexico City. Raga et al. (2001) reported that 5567 tons of PM$_{2.5}$ were emitted in 1998 within the MCMA and approximately 84% of these emissions were related to vehicle emissions. Jiang et al. (2005) sought to provide the first estimates on the emissions of PAHs from motor vehicles in Mexico City. In this study, aerosol photoionization was
used to measure PAHs on board the Aerodyne Mobile Laboratory (AML) during the MCMA-2003 field campaign. The mobile laboratory drove throughout the city and sampled continuously from vehicle exhaust plumes around it. From these measurements, the researchers estimated that motor vehicles in Mexico City emitted $57\pm 6$ metric tons of particulate PAHs per year.

1.5 Source-receptor modeling

Source identification and apportionment are essential for developing effective control strategies to improve air quality and therefore reduce the health impacts associated with fine particulate matter and PAHs. Apportionment is the determination of the relative contribution of each emissions source to ambient pollutant concentrations and is important because it allows identification of the most important sources affecting air pollution at a site. This section describes methods for quantifying the contribution of specific emissions sources to ambient pollutant concentrations using source-receptor modeling.

In this thesis, an approach utilizing receptor-oriented modeling, more specifically, positive matrix factorization (PMF) is applied to data from the Aerodyne Mobile Laboratory (AML) during the MCMA-2006 field campaign. Typically, receptors are fixed points in space, such as stationary monitoring sites, but in the case considered here, the receptor is a mobile platform. PMF of detailed second-by-second concentration data collected on board the AML is used to quantify the relative contribution of each source
type typically encountered on roadways: gasoline-powered vehicles, diesel-powered vehicles, and background ambient air. PMF also derives the source profiles, i.e. the relative amounts of each major pollutant emitted by the pure source.

### 1.6 Source apportionment models

Source-receptor modeling relies on an assumption of mass conservation of emissions from a source and allows the identification of different types of sources and their relative contribution to air pollutant concentrations observed at a receptor. This relationship is demonstrated below in the following equations:

\[
C_T = \sum_i C_i = \sum_j S_j
\]  \hspace{1cm} (1)

where \(C_T\) is the total mass concentration of pollutant \(i\) at a receptor site, and \(S_j\) is the contribution of emission source \(j\) to the total.

\[
C_i = \sum_j a_{ij} S_j, \text{ and } \sum_i a_{ij} = 1
\]  \hspace{1cm} (2)

where \(C_i\) is the mass concentration of species \(i\) at the receptor site and \(a_{ij}\) is the mass fraction of the species \(i\) in the emissions from source \(j\).

A receptor modeling technique frequently encountered throughout the literature is “chemical mass balance,” a linear receptor modeling technique where source profiles must be known for all significant contributors at a receptor. A serious limitation of this method is that in many cases, the source profiles are not readily known.
PMF, however, requires no assumptions about the source profiles but instead derives them as part of the minimization of the object function. It is similar to principal components analysis, except that the source contributions are constrained to be non-negative. PMF is limited by the fact that it does not present explicit information on the specific source profile generated by a particular source category. Rather, this information must be deduced by an informed researcher. The UNMIX model is an alternative to PMF. The main difference between the two is that PMF has no restrictions on the number of factors, while UNMIX is limited to a maximum of seven factors. In studies comparing the two techniques, their common factors correlated quite well (Pekney et al., 2006).

Source-receptor modeling is not without its limitations. Generally, the receptor modeling approach only distinguishes among sources with distinctive fingerprints. Furthermore, there is no internal check with the method which guarantees that all sources have been accounted for; and during analysis of results, there needs to be an objective and informed interpretation of resulting source profiles.

1.7 Highlights of previous work employing receptor modeling

Numerous studies have used the chemical mass balance (CMB) model for source apportionment. Chow et al. (1992) monitored PM$_{10}$ mass concentration at six sites (three urban and three non-urban) in the San Joaquin Valley from 14 June 1988 to 9 June 1989. The CMB receptor model was then applied to the measured concentrations of PM$_{10}$ to determine the relative contributions of major sources. The researchers concluded that
geological sources, i.e. windblown soil, were the largest contributors during the summer and fall months, while secondary ammonium nitrate formation was more significant during the winter months.

Sharma et al. (1994) conducted aerosol sampling in an industrial region of Bombay and employed CMB as a means of source apportionment analysis. The model identified seven distinct sources, but the performance of the model was found to be unsatisfactory at more highly polluted sites in the study area. It was concluded that site-specific source profiles are necessary for the use of CMB in source apportionment.

Robinson et al. (2006) used CMB with molecular markers to apportion ambient organic aerosol to primary sources. The data set used in this study was collected over a 1-year period in Pittsburgh, Pennsylvania. They concluded that the source of elemental carbon and a number of high molecular weight PAHs was metallurgical coke production.

PMF and UNMIX have also been extensively used throughout the literature as a means of source apportionment. Paterson et al. (1999) applied PMF to air quality data from a 1997 summer measurement campaign taken from a tower 31 m above the ground in a rural area of northern Michigan. The researchers were able to identify three factors using the PMF model. These included a local source factor demonstrating weak diurnal signals, a long-range transport factor, and an isoprene-dominated factor showing strong diurnal patterns.
In another study, the sources of PAHs in Baltimore were investigated using three different source apportionment methods (Larsen et al., 2003). These included PMF, UNMIX, and principal components analysis with multiple linear regression. The aim of this research was to compare and contrast the relative strengths and weaknesses of each method. An especially relevant conclusion with respect to the research undertaken in this thesis is that PMF was the only method with the ability to isolate diesel from gasoline sources.

Pekney et al. (2006) compared and contrasted UNMIX and PMF results for daily 24-hour averaged filter-based data collected over a 13-month period beginning in July 2001 in the Pittsburgh region. The UNMIX model determined six factors while the PMF model resolved 10 factors. The four additional factors identified by PMF included primary organic and elemental carbon, lead, a gallium-rich factor, and secondary nitrate. However, the common factors between the models correlated well.

1.8 Study Objectives

This thesis has two main objectives; the first revolves around PAHs and the second around the use of PMF to separate emissions from gasoline-powered motor vehicles versus diesel-powered ones. Both studies use data collected by the author during the MCMA-2006 field campaign. The first goal of the PAH study is to describe the temporal and spatial variations in PAH and AS concentrations in Mexico City. We compare and contrast concentrations in fresh, mixed, and aged emissions by considering a busy downtown location, suburban areas, the city outskirts, and a mountain top location at the
edge of the city. Secondly, we investigate the relationships of ambient PAH concentrations with meteorological parameters and other air pollutants to gain new knowledge about the sources of PAHs and of the compounds’ evolution as they are transported throughout the megacity atmosphere. The results can be used to help develop control strategies for sources of PAHs and to conduct risk assessments of exposure to them in Mexico City.

The main objective of the PMF study is to differentiate between emissions from gasoline- versus diesel-powered mobile sources under real-world driving conditions. We apply PMF to fast measurements of carbon dioxide, CO, NO, volatile organic compounds, and PM$_{2.5}$ to derive source profiles and the relative contribution of each source to roadway pollution on a second-by-second basis. By carbon balance, we then convert the results into emission factors, i.e. the amount of pollutant emitted per unit of fuel consumed, and calculate the total emissions of each pollutant from gasoline and diesel vehicles separately. The ultimate goal of this research is to provide a scientific basis for devising emissions control strategies to improve air quality in Mexico City.

1.9 References


Chapter 2

Spatial and Temporal Variations in Particulate Polycyclic Aromatic Hydrocarbons and Aerosol Active Surface Area in Mexico City

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2.1 Abstract

As part of the Megacities Initiative: Local and Regional Observations (MILAGRO) study in Mexico City in March 2006, we measured particulate polycyclic aromatic hydrocarbon (PAH) and aerosol active surface area (AS) concentrations at six locations throughout the city. The measurements were intended to support the following objectives: to describe spatial and temporal patterns in PAH and AS concentrations, to gain insight into sources of PAHs, and to quantify the relationships between PAHs and other
pollutants. Total particulate PAHs at the Instituto Mexicano del Petróleo (T0 supersite) averaged 50 ng m\(^{-3}\) and reached a maximum value of 3660 ng m\(^{-3}\), the highest observed anywhere during the campaign, while AS averaged 80 mm\(^2\) m\(^{-3}\) and reached a maximum of 760 mm\(^2\) m\(^{-3}\). PAHs and AS were also measured on board the Aerodyne Mobile Lab (AML), which visited five sites encompassing a mix of residential, commercial, industrial, and undeveloped land use. The highest measurements were generally found at sites with dense traffic networks. Weak correlations between PAH and AS suggest that a variety of sources and ages of airborne particles are present in Mexico City, and weak intersite correlations of PAH and AS suggest that exposure to these pollutants cannot be represented by a single regional-scale value. Among carbon monoxide, nitrogen oxides (NO\(_x\)), and carbon dioxide, particulate PAHs are most strongly correlated with NO\(_x\). Finally, Mexico City’s PAH-to-black carbon mass ratio of 0.01 is similar to that found on a freeway loop in the Los Angeles area and approximately 8-30 times higher than that found in other cities.

2.2 Introduction

Mexico City is home to some of the highest measured concentrations of particulate polycyclic aromatic hydrocarbons (PAHs) in the world (Marr et al., 2004; Velasco et al., 2006). PAHs are a class of semi-volatile compounds that are formed during combustion. Many are known or suspected carcinogens. In their condensed form, they are associated mainly with fine particles (Eiguren-Fernandez et al., 2003). PAH exposure has been associated with low birth weights (Choi et al., 2006) and respiratory symptoms in infants
(Jedrychowski et al., 2005). Thus, the extremely high concentrations of PAHs in Mexico City may pose a serious health hazard and demand more complete information about their spatial and temporal patterns, sources, and transformations in the atmosphere.

In April 2003, a multi-national team of scientists conducted an intensive five-week field campaign in the Mexico City Metropolitan Area (MCMA-2003) to contribute to the understanding of air quality problems in megacities (Molina et al., 2007). Measurements of PAHs by three different techniques suggested that aerosol surface PAH concentrations diminish rapidly during the mid-morning hours due to coating by secondary aerosols in the highly photochemically active environment of Mexico City (Dzepina et al., 2007; Marr et al., 2006). However, detailed PAH measurements in 2003 were limited to a single site, so the spatial and temporal variations in their concentrations, which are important from a standpoint of exposure and control, are not known.

Three years later in March 2006, a multi-national team of researchers in Mexico City undertook one of the largest studies ever conducted in atmospheric science: Megacity Initiative: Local and Global Research Observations (MILAGRO). As part of the MCMA-2006 ground-based component of MILAGRO, we measured particulate PAHs, aerosol active surface area (AS), and other gaseous, particulate, and meteorological parameters at six locations throughout Mexico City. PAH and AS measurements were situated at the Instituto Mexicano del Petróleo (supersite T0) just north of the city center and on board the Aerodyne Mobile Laboratory (AML). In addition to visiting the T0 supersite, the
AML also traveled to five other suburban, exurban, and rural sites (Figure 2.1.) that encompassed residential, industrial, commercial, undeveloped, and mixed settings.

The objectives of this study are to describe the temporal and spatial variations in PAH and AS concentrations in Mexico City. We compare and contrast concentrations in fresh, mixed, and aged emissions by considering a busy downtown location, suburban areas, the city outskirts, and a mountain top location at the edge of the city. Furthermore, we investigate the relationships of ambient PAH concentrations with other pollutants to gain new knowledge about the sources of PAHs and of the compounds’ evolution as they are transported throughout the megacity atmosphere. The results can be used to help develop control strategies for sources of PAHs and to conduct risk assessments of exposure to them in Mexico City.

2.3 Experimental

2.3.1 Particle surface characterization

PAHs were measured using real-time sensors (EcoChem PAS 2000 CE) that photoionize particle-bound PAHs by exposing the aerosol to ultraviolet light at a wavelength of 254 nm, which is specific to condensed-phase PAHs. The current generated by the flow of charged particles is then measured. The analyzer produces a semi-quantitative estimate of total PAHs adsorbed on particles’ surfaces at 10-s resolution with a detection limit of 1 ng m$^{-3}$. Although the technique does not provide speciation information, its strengths are
its sensitivity and high time resolution, both of which are limitations of traditional filter-based methods.

Aerosol active surface area, or Fuchs surface, is defined as that which is accessible to a molecule that might diffuse to a particle’s surface. It was measured by diffusion charging (EcoChem DC 2000 CE). The DC analyzer generates a corona discharge, which produces a cascade of electrons and ions that can attach to particles. As with the photoemission aerosol sensor for PAHs, a sensitive electrometer is then used to measure the current generated by the charged particles. The analyzer reports aerosol surface area of particles smaller than ~100 nm at 10-s resolution with a detection limit of 1 mm² m⁻³. The simultaneous measurement of particle surface properties with the PAS and DC sensors has been described as a technique for fingerprinting different types of combustion particles (Bukowiecki et al., 2002).

All the PAH and AS analyzers were factory calibrated three months prior to the field campaign. At the beginning of the field campaign, we co-located and cross-calibrated the instruments against each other while measuring ambient air in Mexico City and then applied the resulting correction factors to all data. To facilitate analysis using diagnostic ratios and multivariate statistics, we averaged all data over a common interval, 2 or 10 min, to produce uniform time series. Black carbon (BC), operationally defined as the light-absorbing component of particles, was measured at 2-min intervals using an aethalometer (Magee Scientific AE-3) at 880 nm.
2.3.2 Measurement sites

During the month-long MCMA field campaign in March 2006, we conducted measurements at Instituto Mexicano del Petróleo (T0 supersite) and on board the Aerodyne Mobile Laboratory (AML), which visited six sites including the T0 supersite (Fig. 2.1). The supersite is located 10 km north of downtown Mexico City in the midst of a residential, commercial, and services area. It is surrounded by streets that are heavily traveled by light-duty vehicles and modern heavy-duty diesel buses. The PAH and AS analyzers were situated on a building rooftop, approximately 15 m above ground level. The nearest major roads were 40 m away.

The AML was designed and built by Aerodyne Research Inc. (Kolb et al., 2004) and had been previously deployed in the MCMA-2003 field campaign. It was equipped with a comprehensive suite of gas and particle analyzers that measure carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NOₓ), speciated volatile organic compounds (VOCs), PAHs, and AS, among others. The AML hosted a second pair of PAH and AS analyzers identical to those used at T0. During MCMA-2006, the AML drove to six sites and remained parked for 1-7 days at each location (Table 2.1). These sites encompassed varying environments, including residential, downtown, industrial, undeveloped, and mixed land use areas.

The AML visited the T0 and T1 (Universidad Tecnológica de Tecámac) supersites, Pedregal, Picos Tres Padres, Santa Ana, and PEMEX (Fig. 2.1). Intended to represent the partially aged Mexico City plume as it drifts downwind under certain meteorological
conditions, the T1 supersite is located ~30 km northeast of T0. T1 is in a suburban city in
the State of Mexico and has a mixture of commercial and residential areas. The site is
within 2 km of the town center, and the nearest road is several hundred meters away.
Pedregal is located ~25 km southwest of downtown Mexico City in a suburban
residential area whose roads are lightly traveled. The sampling site was the JFK
Elementary School, which is also a routine air quality monitoring site for Mexico’s
environmental agency. Picos Tres Padres is an isolated mountain ~15 km north-northeast
of T0 and 2900 m above sea-level, or 700 m above the valley floor. A single, mostly
unused road runs up the mountain, and the surrounding area is not well traveled. Santa
Ana is located in a residential area at the southern tip of the city, ~40 km southeast of T0.
Its roads are lightly traveled. Under certain meteorological conditions, Santa Ana
represents an outflow receptor for air pollution coming from the city center. Located in
the extreme north of the city, the PEMEX site is in a highly industrialized area closely
situated to a major oil refinery (5 km away), cement plants, other chemical factories,
agricultural activities, and a thermo-electric station.

During the MCMA-2006 field campaign, air flow trajectories within the Mexico City
basin and the fate of the urban plume were simulated, and five types of wind circulation
patterns were identified (de Foy et al., 2005; de Foy et al., 2006): O$_3$-South, O$_3$-North,
Gulf, Cold Surge and Convection. O$_3$-South events have winds from the north/northeast
aloft, which lead to ozone peaks in the southern part of the city. O$_3$-North events have
high ozone levels in the northern part of the city and occur when winds are aloft from the
southwest. Gulf events are similar to O$_3$-North days in the morning, but during the
afternoon, the incoming wind from the Gulf of Mexico dominates. On Cold Surge days, cold winds flow from the Gulf of Mexico and reach the MCMA in the late afternoon hours, producing strong winds and precipitation. Finally, as a result of increased humidity and weak winds following Cold Surge events, there is horizontal wind convergence in the basin along with afternoon showers, described as Convection events. During the 31 days of the MCMA-2006 field campaign in March, eight were O₃-South (1ˢᵗ - 7ᵗʰ, 1³ᵗʰ), seven were O₃-North (8ᵗʰ-1⁰ᵗʰ, 1⁷ᵗʰ-2⁰ᵗʰ), two were Gulf (1¹ᵗʰ, 1²ᵗʰ), three were Cold Surge (1⁴ᵗʰ, 2¹ˢᵗ, 2³ʳᵈ), and 11 were Convection (1⁵ᵗʰ, 1⁶ᵗʰ, 2²ⁿᵈ, and 2⁴ᵗʰ-3¹ˢᵗ). The prevailing meteorological conditions strongly influence ambient pollutant concentrations for given emission levels and also determine the regional impacts of the urban plume (de Foy et al., 2006).

2.4 Results

Figure 2.2 displays time series of AS and total particulate PAH concentrations at the T0 supersite. The raw 1-min measurements are shown by colored lines, whose color indicates the wind transport episode defined for each day. The black lines in Fig. 2.2 represent 1-hr averages and are intended to highlight diurnal patterns in the measurements. In terms of absolute concentrations, at T0 the highest AS concentrations occurred on Gulf and O₃-North days, while the highest average PAH concentrations occurred on Convection and Cold Surge days. However, a comparison of PAH versus AS concentrations and temporal differences, as a function of wind circulation patterns, yielded no relationship.
AS concentrations at T0 averaged 80 mm$^2$ m$^{-3}$ during the campaign, with a maximum value of 760 mm$^2$ m$^{-3}$ on 30 March at 9:58. Typically, concentrations rose to ~180 mm$^2$ m$^{-3}$ between 6:30-8:30 and then decreased throughout the remainder of the morning and afternoon to ~40 mm$^2$ m$^{-3}$. Like with AS, diurnal patterns in PAHs were also evident. PAH concentrations averaged 50 ng m$^{-3}$ throughout the campaign with a maximum value of 3660 ng m$^{-3}$ on 30 March at 10:02, within minutes of the maximum AS observation. During the morning rush hour, PAH concentrations generally rose to a maximum of ~250 ng m$^{-3}$ between 6:30-8:30 and then decreased throughout the remainder of the morning and afternoon to ~50 ng m$^{-3}$. Overnight concentrations rose as high as 75 ng m$^{-3}$.

Figure 2.3 shows PAHs and AS at each site visited by the AML in chronological order. At Pedregal, PAH concentrations were most elevated, over 140 ng m$^{-3}$, just before noon on Saturday 4 March and between 6:00-8:00 on Monday 6 March. They were slightly elevated in the hours before midnight on the evening of 4 March. These periods probably correspond to the times of greatest traffic. AS showed no obvious diurnal pattern; concentrations were higher, nearly 80 mm$^2$ m$^{-3}$, at the beginning of the measurement period, on 4 March at 9:00. At T0, there was an early evening (19:00-20:30) peak in PAH concentrations on 6 March. During the morning rush hour period between 6:00-8:00 on 7 March, PAH concentrations were elevated and approximately four times higher than at Pedregal. High concentrations persisted until late morning. AS concentrations at T0 also rose during the morning rush hour on 7 March, but the increase lagged PAH by 20 min, for reasons that are unknown.
At Picos Tres Padres, PAH concentrations remained below 10 ng m$^{-3}$ except on two occasions: 13 March at 15:00, when they reached 200 ng m$^{-3}$ and 14 March at 7:40, when they reached 120 ng m$^{-3}$. Diurnal patterns were apparent in AS concentrations at Picos Tres Padres. They usually peaked during mid-morning, between 9:30-11:30. On 13 and 16 March, we also observed mid-afternoon peaks (14:30-16:30) in AS. At T1, PAH concentrations increased to 100-200 ng m$^{-3}$ during the morning rush hour. They also increased to nearly 500 ng m$^{-3}$ on 22 March around noon. The largest peaks in AS occurred during the early evening, before midnight. At Santa Ana, PAH concentrations were near zero most of the time, although they rose above 400 ng m$^{-3}$ on 23 March around noon and to 1200 ng m$^{-3}$ on 25 March in the early evening at 17:10. AS concentrations remained below 10 mm$^2$ m$^{-3}$ except on 23 March, when they approached 20 mm$^2$ m$^{-3}$. At PEMEX, where the AS analyzer failed, PAH concentrations increased above 200 ng m$^{-3}$ during the morning rush hour on Thursday and Friday 28 and 29 March, but not on 26 or 27 March.

Table 2.1 summarizes PAH and AS concentrations measured by the AML at different sites throughout Mexico City. The highest average PAH concentration was observed at T0 (73 ng m$^{-3}$) and the lowest at Pico Tres Padres (3 ng m$^{-3}$). However, the maximum PAH concentration throughout the entire campaign was observed at PEMEX (1675 ng m$^{-3}$). This table does not include continuous measurements at T0, which were already described. The highest average AS concentration was also observed at T0 (25 mm$^2$ m$^{-3}$) and the lowest at Santa Ana (3 mm$^2$ m$^{-3}$).
The relationships between PAH concentrations and carbon monoxide (CO), carbon dioxide (CO₂), and nitrogen oxides (NOₓ) measured by the AML are displayed in Table 2.2. The slope (e.g. PAH/CO) and standard error of the least-squares linear regression and correlation coefficient (R²) are displayed in the table. For CO, the correlations are weak at all sites with PAHs being most strongly correlated at T0 (R²=0.38). PAH concentrations are strongly correlated with NOₓ at T0 and T1, and weakly correlated with NOₓ at Pedregal, Pico Tres Padres, Santa Ana and PEMEX. For CO₂, the correlations are fair to weak at all sites except for Pico Tres Padres, where the correlation is very weak (R²=0.04). Of the three pollutants, NOₓ is most strongly correlated with PAHs with R²=0.86 at T1. PAH concentrations at Santa Ana are weakly correlated with NOₓ (R²=0.34), with CO₂ (R²=0.36) and with CO (R²=0.08). Similar observations arise at PEMEX, where PAHs are weakly correlated with NOₓ (R²=0.37), with CO₂ (R²=0.42), and with CO (R²=0.05). Correlation factors are relatively weak at Pico Tres Padres (R²≤0.3). At each site visited by the AML, the PAH correlation with NOₓ was higher than with CO or CO₂, except for Santa Ana and PEMEX, where in both cases the R² value for PAH/CO₂ is slightly higher.

The simultaneous measurement of PAHs and AS at T0 and other sites allows examination of their spatial variability in the MCMA. Table 2.3 presents the Pearson correlation coefficients (r) of 10-min PAH and AS concentrations at various sites visited by the AML against those measured continuously at the T0 supersite during periods of simultaneous measurements. A correlation factor could not be calculated for Pedregal because monitoring at T0 had not yet begun. The correlations between all sites and T0 are
weak ($|r|<0.3$). Of the combinations shown, AS at T0 and PEMEX are most strongly correlated.

The relationship between PAH and AS has been shown to be related to the source type and aging of the particles (Siegmann et al., 1999; Bukowiecki et al., 2002; Marr et al., 2004). Figure 2.4 illustrates the relationship between PAH and AS concentrations (10-min averages) at the T0 supersite throughout the field campaign. The color indicates the time of day of each measurement. The correlation between PAH and AS at T0 throughout the field campaign is fair, with $R^2=0.44$. For the subset of data between 6:00-9:00, the equation of the line is $\text{PAH} = 0.80\text{AS} + 6.75$ with $R^2 = 0.44$. For the subset of data between 12:00-15:00, the equation of the line is $\text{PAH} = 0.03\text{AS} + 16.6$ with $R^2 = 0.02$. Figure 2.4 suggests that higher PAH/AS ratios, i.e. those points falling above the solid regression line, and those with high absolute PAH and AS values, tend to occur during the early morning hours. The slope of the line is 27 times higher in the morning compared to the afternoon.

Figure 2.5 shows PAH versus AS concentrations (10-min averages) at the sites visited by the AML. Although correlations are weak at all sites, some sites exhibit distinguishing characteristics. Santa Ana is notable for its bimodal relationship. There are two distinct regimes of PAH/AS: one with a very steep slope and one with a very shallow, near-zero slope. Pico Tres Padres has one of the lowest slopes; PAH concentrations here rarely exceed 40 ng m$^{-3}$. The T1 supersite tends to have higher PAH and lower AS concentrations compared to the other sites.
PAHs and BC are expected to be correlated since both originate from combustion sources. Figure 2.6 shows PAH versus BC at T0 throughout the field campaign and then specifically between 6:00-9:00 and 12:00-15:00, classified by the time of day. As with Figure 2.4, this figure also shows that higher PAH/BC ratios tend to occur during the morning rush hour period. The equation of the line between 6:00-9:00 is $PAH = 0.01BC - 20.2$ with a goodness of fit value of $R^2 = 0.73$. As the day proceeds and PAH concentrations dissipate more than BC, we tend to observe lower PAH/BC ratios. The equation of the line between 12:00-15:00 is $PAH = 0.0003BC + 18.072$ with a goodness of fit value of $R^2 = 0.002$. The correlation between the two throughout the field campaign is fairly strong ($R^2 = 0.77$), and the slope of the line, $0.0116 \pm 0.0001$, indicates that PAHs are 1% of BC by mass. Table 2.4 contrasts PAH/BC ratios in Mexico City with those measured in three other cities, where the same aerosol photoionization method was used to measure PAHs. The mass ratio of PAHs to BC in Mexico City is similar to that measured along a freeway loop in the Los Angeles area and approximately 8-30 times higher than in diluted vehicle exhaust in Utah and ambient air in Fresno, California, and the correlation factors between PAHs and BC are similar in all cities.

2.5 Discussion

2.5.1 PAH and AS concentrations, sources, and aging

PAH concentrations may vary considerably between cities due to differences in emission sources and meteorological conditions. Mexico City’s PAH concentrations are substantially higher than those measured in other large cities. PAH concentrations in rural
and urban areas of Los Angeles are 0.5 ng m$^{-3}$ and 2 ng m$^{-3}$, respectively (Eiguren-Fernandez et al., 2004). In contrast, concentrations in urban and rural areas of Mexico City are nearly 25 times higher. In Hong Kong, particulate PAHs concentrations range from 0.41 ng m$^{-3}$ to 48 ng m$^{-3}$ in rural to urban areas (Zheng et al., 1998). These values compare more closely with Mexico City; however, PAH concentrations in Mexico City are still higher. PAHs have also been measured in different environments of Greece (Mantis et al., 2005), where concentrations range from 2 ng m$^{-3}$ to 52 ng m$^{-3}$ in rural to urban areas. Again, these values compare more closely with the results seen in Mexico City, but the values for Mexico City are higher yet.

Vehicular traffic has been recognized as the major contributor to PAH emissions in urban areas (Kittleson et al., 2004; Lee et al., 1995), and therefore it is not surprising that the highest average PAH and AS concentrations are found at T0, where traffic is heaviest. High PAH values are also observed at PEMEX, which is a highly industrialized area surrounded by a major oil-refinery and a thermo-electric station. Furthermore, the timing of PAH peaks at the more urban locations corresponds to periods of rush hour traffic.

At some locations, including Pedregal, T1, and PEMEX, increases in PAH concentrations occur at nighttime around midnight (Fig. 2.3). The increase in PAHs may be due to transport of particles emitted earlier in the evening during times of high traffic density, or it may indicate the presence of other nighttime sources. The impact of emissions at nighttime can be magnified because of stable atmospheric conditions. Some industries are thought to switch to using dirtier fuels and processes at night, when enforcement of
regulations is less likely. Furthermore, at T1 during the first two weeks of the field campaign, Doran et al. (2006) observed increased organic and elemental carbon during nighttime hours with peak values attained in the morning hours near sunrise. We observe a similar pattern in PAH and AS at T1 on 21 March. The temporal variations imply that at night a buildup of pollution from nearby urban sources is occurring, followed by a subsequent dilution during the next morning as the boundary layer expands.

Spatial and temporal patterns in concentrations indicate not only potential sources of PAHs but also the degree of atmospheric processing the particles undergo. As emissions are transported, there are subject to dilution, and other transformations. PAHs as detected by the surface-specific photoemission method may diminish due to coating by secondary aerosol (Marr et al., 2006), and AS may be reduced by coagulation and growth into sizes no longer detected by the diffusion charger. This behavior is supported by Fig. 2.3, which shows that in general, higher PAH and AS concentrations occur at T0 and PEMEX, which are dominated by fresh emissions; lower concentrations, aside from transient spikes, occur at Picos Tres Padres and Santa Ana, which are remote sites where emissions have aged by the time they reach these receptors; and intermediate concentrations occur at T1 and Pedregal, which lie between the two extremes. Furthermore, the aging of aerosol appears to diminish PAH concentrations to below 10 ng m$^{-3}$ most of the time at Picos Tres Padres and Santa Ana, despite the presence of particle surface area. At T1, the increase in AS between 18:00 and midnight may be due to evening sources or the arrival of particles transported from the urban area.
Figures 2.4 and 2.6 also support the hypothesis that primary particles are rapidly coated by secondary aerosol. In Fig. 2.4 which shows the relationship between PAH and AS concentrations, the slope changes from 0.801±0.046 during the 6:00-9:00 morning period, to 0.032±16.59 for the 12:00-15:00 afternoon period. Similarly for Fig. 2.6, which shows the PAH/BC relationship, the slope changes from 0.0131±0.0004 between the 6:00-9:00 morning period, to 0.0003±0.0003 for the 12:00-15:00 afternoon period. Over the course of the day, the highest PAH/AS and PAH/BC ratios occur during the morning rush hour between 6:00-9:00, when emissions are freshest, and the ratios decrease over the course of the day as the particles age and the surface PAH signal diminishes. While rising ambient temperatures and volatilization of condensed-phase PAHs from particles throughout the day could cause the decrease in ratios, our previous work suggests that coating of the particles by secondary aerosol is occurring. Coating would diminish the ability of the PAS to detect PAHs on the particles’ surfaces. Volkamer et al. (2006) reported that secondary organic aerosol formation in the polluted urban atmosphere is higher and more rapid than previously thought. This finding could explain the temporal patterns observed in PAH/AS and PAH/BC ratios. The loss of PAHs due to heterogeneous reactions is another possible, though less likely, explanation (Marr et al., 2006).

Picos Tres Padres is of special interest because it sits 700 m above the valley floor, and during the morning hours, it is above the mixing (boundary) layer that contains freshly emitted pollutants. Its diurnal patterns of AS concentrations are more pronounced than at the other sites, but they do not follow the traditional urban pattern of higher
concentrations during the morning rush hour (Fig. 2.3). Rather, AS increases around 10:00 each day, coinciding with the initial rising of the boundary layer up to the AML’s location on the mountain. Throughout the morning and early afternoon, the boundary layer continues to grow and fully encompasses the sampling site on top of the mountain around 16:00. At this time, the initially fresh morning emissions from the valley below would have undergone dilution and photochemical reactions, resulting in a reduction in the concentration of PAHs.

2.5.2 Intersite correlations of PAH and AS concentrations

Table 2.3 shows that intersite correlation coefficients calculated for AML sites versus T0 are quite weak. While strong intersite correlations would indicate spatially uniform emission patterns and sources, and regional-scale mixing of pollutants, the results for Mexico City suggest that PAHs and AS vary considerably in space. Concentrations at individual sites are largely independent of one another and are instead dominated by local sources. Conversely, Mantis et al. (2005) and Siegmann et al. (1999) reported higher correlation coefficients for their intersite comparisons during studies of PAHs in Greece and Switzerland, respectively. The study in the Greater Athens area of Greece found an intersite correlation of \( r = 0.61 \) between two urban locations, \( r = 0.76 \) between an urban location and a background location, and \( r = 0.57 \) between an urban location and a mixed-urban industrial location. An important implication for risk assessment studies is that a single monitoring site in Mexico City will not adequately represent the population’s exposure.
2.5.3 Correlation of PAH with AS

The ratio of PAH to AS measurements has been described as a fingerprint for different types of combustion particles (Bukowiecki et al., 2002; Matter et al., 1999; Siegmann et al., 1999). The relationship between these parameters provides qualitative means of identifying different sources and describing the physical and chemical properties of particles. In contrast to previous studies which have shown tighter relationships between PAHs and AS for specific sources such as diesel exhaust, roadway vehicle emissions, candles, fires, and cigarettes (Bukowiecki et al., 2002; Marr et al., 2004; Siegmann et al., 1999), the relationships shown here contain significantly more scatter. The PAH/AS relationships shown in Fig. 2.5 indicate the presence of different sources or different aerosol mixing states at each sampling site. For a single source, the relationship between PAHs and AS is expected to be linear with a characteristic slope. The spread of the data indicates that the aerosol represents a mixture of different sources and particles of different ages and from different locations. Ambient measurements in complex environments are expected to produce such results.

PAH/AS ratios vary considerably across sites (Figs. 2.4 and 2.5). Only at T0, with a slope of 1.80 ng mm\(^{-2}\) measured near ground level by the AMS (Fig. 2.5), does the value compare to a slope of 1.28-1.83 ng mm\(^{-2}\) measured near a roadway in Switzerland (Siegmann et al., 1999). However, the slope at Santa Ana is even higher than at T0. At this site there seems to be a bimodal relationship with two distinct slopes of PAH/AS: one with a very steep slope and one with a very shallow, near-zero slope. The measurements comprising the higher slope all stem from a few hours on 25 March and
are probably due to an unusual emissions event in the area. Sites with lower slopes and \( R^2 \) values, such as Pico Tres Padres and Pedregal, represent sites where emissions are mixed and/or aged (not fresh), and thus are more strongly influenced by transport and chemistry.

2.5.4 Correlation of PAHs with NO\(_x\), CO\(_2\), CO, and BC

The stronger correlation of PAHs with NO\(_x\) rather than with CO and CO\(_2\), probably reflects the importance of diesel engines as sources of both PAH and NO\(_x\) emissions. CO is emitted mainly by gasoline-powered vehicles, which do not typically emit high levels of PAHs. Weak positive correlations between PAHs and NO\(_x\) have also been reported for Brisbane, Australia (Muller et al., 1998).

The correlation of PAH with BC in the MCMA is fairly strong. While a similar mass concentration ratio of PAH/BC is observed along a freeway loop in the Los Angeles area (Westerdahl et al., 2005), lower ratios are observed in ambient air in Fresno, California and diluted vehicle exhaust in Ogden, Utah (Arnott et al., 2005). The differences may be due to different PAH content of fuels, as this is known to affect emissions (Marr et al., 1999); different ratios of gasoline-to-diesel-powered vehicles on the road; and/or the presence of other combustion sources such as biomass burning and garbage burning that may produce sooty particles with higher PAH content in Mexico City or lower PAH content in Fresno and Ogden.

Pollutant ratios can be useful for estimating emissions and for describing the evolution of the relative emissions of different pollutants over decadal time scales (Marr et al., 2002).
The mass ratio of particulate PAH/NO\textsubscript{x} from the MCMA-2003 field campaign was 4.74×10\textsuperscript{-4} (Jiang et al., 2005). During the MCMA-2006 field campaign, this ratio ranged from 7.86×10\textsuperscript{-4} to 8.07×10\textsuperscript{-4} across all the urban sites. The increase in PAH/NO\textsubscript{x} ratio suggests that PAH emissions increased and/or NO\textsubscript{x} emissions decreased between 2003 and 2006.

2.6 Conclusion

It is apparent that PAH pollution is a major problem throughout the entire Mexico City. The highest PAH and AS concentrations were found near sites with the densest traffic (T0) or major industrial sources (PEMEX). PAH concentrations at T0 exhibit a consistent diurnal pattern and routinely exceed 200 ng m\textsuperscript{-3} during the morning rush hour. Weak correlations between PAH and AS are indicative of the wide variety of sources and ages of particles present in Mexico City. PAH concentrations are poorly correlated in space and time, and therefore PAHs cannot be treated as a regional-scale pollutant. An important implication of this result is that for risk assessment studies, a single monitoring site will not adequately represent an individual’s exposure. The stronger correlation of PAHs with NO\textsubscript{x}, rather than with CO and CO\textsubscript{2}, probably reflects the importance of diesel engines as sources of both PAH and NO\textsubscript{x} emissions. Mexico City’s PAH/BC ratio is similar to that found along freeways in Los Angeles and 8-30 times higher than that found in two other cities. Aging of primary combustion particles by coating with secondary aerosol appears to result in a decrease in surface PAH/AS and PAH/BC ratios over the course of the day.
2.7 Acknowledgments

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2.8 References


Tables

Table 2.1. Statistics of AS and PAH at different sites, measured on board the Aerodyne Mobile Laboratory.

<table>
<thead>
<tr>
<th>Site (Dates in March)</th>
<th>PAH (ng m$^{-3}$)</th>
<th>AS (mm$^2$ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Maximum$^a$</td>
</tr>
<tr>
<td>Pedregal (4th-6th)</td>
<td>9±18</td>
<td>145</td>
</tr>
<tr>
<td>T0 (6th-7th, 29th-30th)</td>
<td>73±98</td>
<td>560</td>
</tr>
<tr>
<td>Pico Tres Padres (7th-19th)</td>
<td>3±9</td>
<td>206</td>
</tr>
<tr>
<td>T1 (19th-22nd)</td>
<td>26±48</td>
<td>473</td>
</tr>
<tr>
<td>Santa Ana (22nd-25th)</td>
<td>17±82</td>
<td>1220</td>
</tr>
<tr>
<td>PEMEX (25th-29th)</td>
<td>68±132</td>
<td>1675</td>
</tr>
</tbody>
</table>

$^a$Maximum of 1-min concentrations.
Table 2.2. Least-squares linear regression slope and $R^2$ between PAHs and gaseous pollutants.

<table>
<thead>
<tr>
<th>Site</th>
<th>PAH/CO (ng m$^{-3}$ ppb$^{-1}$)</th>
<th>$R^2$</th>
<th>PAH/NO$_y$ (ng m$^{-3}$ ppb$^{-1}$)</th>
<th>$R^2$</th>
<th>PAH/CO$_2$ (ng m$^{-3}$ ppm$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pedregal</td>
<td>0.003±0.001</td>
<td>0.10</td>
<td>0.09±0.02</td>
<td>0.14</td>
<td>0.40±0.03</td>
<td>0.35</td>
</tr>
<tr>
<td>T0</td>
<td>0.060±0.009</td>
<td>0.38</td>
<td>1.09±0.05</td>
<td>0.81</td>
<td>2.36±0.68</td>
<td>0.55</td>
</tr>
<tr>
<td>Picos Tres</td>
<td>0.003±0.002</td>
<td>0.03</td>
<td>0.060±0.003</td>
<td>0.26</td>
<td>0.32±0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Padres</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>0.020±0.002</td>
<td>0.20</td>
<td>1.10±0.02</td>
<td>0.86</td>
<td>2.28±0.13</td>
<td>0.50</td>
</tr>
<tr>
<td>Santa Ana</td>
<td>0.016±0.003</td>
<td>0.08</td>
<td>0.22±0.02</td>
<td>0.34</td>
<td>3.13±0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>PEMEX</td>
<td>0.017±0.003</td>
<td>0.05</td>
<td>1.14±0.06</td>
<td>0.37</td>
<td>0.119±0.006</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Table 2.3. Pearson correlation coefficient ($r$) for pairwise comparisons between 10-min AS and PAH concentrations measured at different sites v. T0.

<table>
<thead>
<tr>
<th></th>
<th>T1</th>
<th>Pico Tres Padres</th>
<th>Santa Ana</th>
<th>PEMEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH</td>
<td>0.02</td>
<td>-0.17</td>
<td>-0.29</td>
<td>0.17</td>
</tr>
<tr>
<td>AS</td>
<td>-0.11</td>
<td>0.14</td>
<td>-0.07</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.4. Total particulate PAH-to-BC mass ratios in Mexico City compared to other locations.

<table>
<thead>
<tr>
<th>Location</th>
<th>PAH/BC (mass ratio)</th>
<th>$R^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mexico City</td>
<td>$1 \times 10^{-2}$</td>
<td>0.77</td>
<td>This study</td>
</tr>
<tr>
<td>Ogden, UT$^a$</td>
<td>$1.25 \times 10^{-3}$</td>
<td>0.75</td>
<td>Arnott et al., 2005</td>
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<tr>
<td>Fresno, CA (Winter)</td>
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<td>0.78</td>
<td>Arnott et al., 2005</td>
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<tr>
<td>Fresno, CA (Summer)</td>
<td>$3.3 \times 10^{-4}$</td>
<td>0.75</td>
<td>Arnott et al., 2005</td>
</tr>
<tr>
<td>Los Angeles, CA</td>
<td>$1 \times 10^{-2}$</td>
<td>0.82</td>
<td>Westerdahl et al., 2005</td>
</tr>
</tbody>
</table>

$^a$ Diluted vehicle exhaust, not ambient air.
**Figures**

![Map showing measurement sites in the MCMA during the MILAGRO field campaign. Supersites are indicated by circles, mobile lab sites by diamonds. The black line traces the boundary of Mexico City’s Federal District.](image)

**Source:** Dr. Linsey Marr

**Fig. 2.1.** Map showing measurement sites in the MCMA during the MILAGRO field campaign. Supersites are indicated by circles, mobile lab sites by diamonds. The black line traces the boundary of Mexico City’s Federal District.
**Fig. 2.2.** AS and PAH concentrations at T0 during the entire field campaign. Raw 1-min measurements are shown by the colored lines, where color indicates the wind transport episode, and 1-hr averages are shown in black.
Fig. 2.3. 10-min averages of PAH and AS at sites visited by the AML.
Fig. 2.4. PAH v. AS concentrations at T0 colored by the time of day. The solid line is the linear regression between PAH and AS at all times, and its equation is shown in the box. The dotted lines labeled 6:00-9:00 and 12:00-15:00 represent a subset of data showing the relationship specific to these time periods. The equations of these lines are given in the text.
Fig. 2.5. PAH v. AS concentrations at sites visited by the AML.
Fig. 2.6. PAH v. BC concentrations at T0 colored by time of day. The solid line is the linear regression between PAH and BC at all times, and its equation is shown in the box. The dotted lines labeled 6:00-9:00 and 12:00-15:00 represent a subset of data showing the relationship specific to these time periods. The equations of these lines are given in the text.
Chapter 3

Application of Positive Matrix Factorization to On-Road Gaseous and Particulate Measurements for Source Apportionment of Diesel and Gasoline Emissions in Mexico City

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3.1 Abstract

Very few studies have separated gasoline-powered vehicle emissions from diesel-powered emissions under a variety of on-road driving conditions. The main goal of this research is to quantify diesel- and gasoline-powered motor vehicle emissions within the Mexico City Metropolitan Area (MCMA) using positive matrix factorization (PMF) receptor modeling. During the MILAGRO field campaign in 2006, the Aerodyne Mobile Laboratory drove throughout the MCMA and measured on-road concentrations of a large suite of gaseous and particulate pollutants, including carbon dioxide, carbon monoxide (CO), nitric oxide (NO), benzene (C₆H₆), formaldehyde (HCHO), ammonia (NH₃), fine particulate matter (PM₂.₅), particulate polycyclic aromatic hydrocarbons (PAHs), and black carbon (BC). These served as the input data for the receptor model. The source profiles derived by PMF in conjunction with knowledge of emission markers allowed the apportionment of gasoline and diesel emissions. Fuel-based emission factors and annual emissions within Mexico City were then calculated from the source profiles and fuel sales data. The annual emissions inventory for motor vehicles in the MCMA is estimated at 465,000 (metric) tons of CO, 130,000 tons of volatile organic compounds (VOC), 49,010 tons of NO, 3700 tons of PM₂.₅, 620 tons of NH₃, 1800 tons of HCHO, 3200 tons of BC, and 35 tons of PAHs. Gasoline-powered vehicles are responsible for 90% of mobile source CO, 85% of VOC, 0.02% of NO, 30% of PM₂.₅, 65% of NH₃, and 56% of HCHO emissions. Diesel-powered vehicles account for the remaining percentages. The estimates for CO and VOC were lower than emissions estimates from 2003 that were also derived using data collected by the Aerodyne Mobile Laboratory but that did not apportion emissions between the two engine/fuel types.
3.2 Introduction

With the rapid growth and development of the Mexico City Metropolitan Area (MCMA) over the past 30-40 years, there has been a commensurate increase in sources within the transportation sector that has significantly impacted air pollution in the region. Within the MCMA, the transportation sector is a major air pollution source (Molina et al., 2002). Emissions from the vehicle fleet include pollutants such as carbon dioxide (CO$_2$), carbon monoxide (CO), oxides of nitrogen (NO$_x$), volatile organic compounds (VOC), fine particulate matter (PM$_{2.5}$), and sulfur dioxide (SO$_2$) (Molina et al., 2002).

There has been a major effort by the government authorities of the MCMA to curb mobile source emissions. In 1985, 99.5% of cars in the MCMA lacked catalytic converters, and by 1999, this fraction had dropped to 34.7% (Molina et al., 2002) as a direct result of a law which required two-way catalytic converters beginning with model-year 1991 vehicles and three-way catalytic converters beginning with model-year 1993 vehicles. There have also been stringent and significant improvements to the inspection and maintenance of vehicles throughout the MCMA. Many studies have demonstrated the benefits of the introduction of stringent emission control standards and technological advancements in fuels and vehicles (Kirchstetter et al., 1999a, 1996, Sawyer et al., 2000). Such improvements have been responsible for reducing mobile source emissions, or at least preventing them from growing in the face of an increased number of vehicles on the road and distances driven. Despite its efforts, the MCMA still has serious air pollution problems with many pollutants regularly exceeding air quality standards.
Motor vehicles are the dominant source of emissions of many of the problematic pollutants in the MCMA. Table 3.1 summarizes the emissions of CO, NO\textsubscript{x}, VOCs, coarse particulate matter (PM\textsubscript{10}), and SO\textsubscript{2} from mobile sources in 1998 (Comisión Ambiental Metropolitana, 2001) and 2003 (Jiang et al., 2005), and their percentage contribution to total emissions from all sources in the MCMA for 1998 emissions data only. A comparison between the two years reveals that CO, NO\textsubscript{x}, and VOC emissions are 31\% lower, 28\% lower, and 31\% higher, respectively, in the more recent year. Differences in the methodologies used to construct the 1998 and 2003 inventories may account for some of the changes seen over the five-year period. According to the 1998 emissions inventory, even though diesel-powered engines only accounted for 10\% of all vehicles, they were responsible for 83\% of PM\textsubscript{10} and 47\% of mobile source NO\textsubscript{x} emissions (Comisión Ambiental Metropolitana, 2001).

An important distinction in examining mobile source emissions is that gasoline- and diesel-powered vehicle emissions differ enormously by pollutant. CO and VOC are mainly associated with gasoline-powered engines, PM\textsubscript{2.5} with diesel-powered engines, and NO\textsubscript{x} with both. Differences in operating conditions between the Otto and Diesel cycles and between the two types of fuels are the primary cause for the distinction. A second reason for the difference is that at present, there are more stringent controls on light-duty gasoline-powered cars than on heavy-duty diesel-powered trucks. As a result, the development of effective control strategies focusing on mobile sources must accurately distinguish between the two major engine types and their associated emissions.
A comprehensive review of mobile source emissions summarized results from on-road measurements of light- and heavy-duty vehicles in tunnels throughout the United States (Sawyer et al., 2000). Generally, the light-duty vehicles (nearly all gasoline-powered) emitted at least three times more CO per unit mass of fuel burned. This quantity is known as an emission factor or an emission index. The VOC emission index was also higher for the light-duty vehicles. However, the NO\textsubscript{x} emission index was at least four times higher for heavy-duty vehicles (>70% diesel-powered) than for light-duty vehicles in the tunnel studies. In one particular set of studies along a northern California roadway tunnel, Kirchstetter et al. (1999) investigated the emissions from light-duty vehicles (98% gasoline-powered) and heavy-duty diesel trucks. They reported that the heavy-duty diesel trucks’ PM\textsubscript{2.5} emission factor was 24 times higher compared to light-duty gasoline vehicles. Furthermore, the NO\textsubscript{x} emission factor was almost five times higher with heavy-duty diesel trucks. Heavy-duty vehicles accounted for almost half of total NO\textsubscript{x} emissions from on-road motor vehicles in California (Kirchstetter et al., 1999; Harley et al., 2005). Comparable results were also observed in the MCMA’s 1998 emissions inventory (Comisión Ambiental Metropolitana, 2001).

Emissions of minor pollutants such as black carbon (BC) and particulate polycyclic aromatic hydrocarbons (PAHs) also differ by engine technology. A comparative assessment of on-road studies of emission factors was reported in Jiang et al. (2005). They reviewed tunnel experiments in Oakland, California (Kirchstetter et al., 1999), and Zurich, Switzerland (Weingartner et al., 1997) and found that both studies reported higher emission factors for BC and particulate PAHs in heavy-duty (mainly diesel-powered) versus light-duty (mainly gasoline-powered) vehicles. Miguel et al. (1998)
reported different PAH speciation profiles between diesel engines and light-duty gasoline engines. Emissions of low-molecular weight PAHs were larger from diesel engines as compared to high-molecular weight PAHs, which predominated in light-duty gasoline engine emissions (Marr et al., 1999; Miguel et al., 1998).

Total emissions are the product of an emission factor and an activity level, or in this case, the amount of fuel consumed. Diesel fuel sales by volume are generally much lower than that of gasoline. Jiang et al. (2005) reported that the MCMA’s diesel fuel sales were 1.50 billion liters, while gasoline sales were 6.82 billion liters in 2003 (Instituto Mexicano del Petróleo, 2001). The most recent fuel sales report for the MCMA indicated diesel sales rose to 2.08 billion liters and gasoline sales to 7.25 billion liters in 2004 (Comisión Ambiental Metropolitana, 2006).

When measuring ambient pollutant concentrations that are impacted by both diesel and gasoline emissions from vehicles plus other sources, separation of diesel and gasoline emissions can be accomplished using source apportionment methods, including statistical models such as positive matrix factorization (PMF). PMF has been used extensively as a means of source apportionment (Lee et al., 2006; Pekney et al., 2006; Kim et al., 2004; Paterson et al., 1999), which is the quantification of the air quality impacts of specific emissions sources at a certain location. These studies assessed the source apportionment of fine particulate matter by examining speciation profiles of the particles. In fact, Larsen et al. (2003) identified PMF as the only effective modeling method with the ability to isolate diesel from gasoline sources in their study on PAHs. Detailed compositional data
is essential in order to effectively distribute combustion sources into diesel and gasoline vehicles (Kim et al., 2004a).

The objectives of this study are to differentiate between gasoline- versus diesel-powered sources in an effort to provide a scientific basis for estimating motor vehicle emissions in Mexico City and then ultimately for devising emissions control strategies to improve air quality. A key advantage of this study versus others is it uses a mobile platform to conduct measurements. Measurements are not confined to a laboratory or a single site along a roadway but instead can take place anywhere a vehicle can go. A mobile laboratory therefore allows sampling of the complete range of driving conditions. To separate gasoline- and diesel-engine emissions from background air pollution, we apply PMF to data collected by the Aerodyne Mobile Laboratory as it drove along the streets of Mexico City. From the source profiles, we then calculate fuel-based emission factors and the total motor vehicle emissions inventory for the MCMA.

3.3 Methodology

Measurements were conducted along the MCMA’s roadways using a mobile laboratory. The Aerodyne Mobile Lab (AML) was designed and built by Aerodyne Research Inc. (Kolb et al., 2004) and had been previously deployed in the MCMA-2003 field campaign. It was equipped with a comprehensive suite of gas and particle analyzers that measure CO, CO$_2$, NO$_x$, speciated VOCs, PM$_{2.5}$, BC, and particulate PAHs, among others (Jiang et al., 2005; Kolb et al., 2004; Zavala et al., 2006). In contrast to the MCMA-2003 field
campaign where the AML was more regularly deployed in a chasing mode, during the MCMA-2006 field campaign experiments focused on stationary site measurements with the AML parked at a fixed site location for several days. However, in driving between sites during the 2006 field campaign, the van was operated in chasing mode and was continuously sampling the exhaust emissions from surrounding vehicles. A video camera recorded the view ahead, providing a record of surrounding traffic conditions, types of vehicles, and possible emission sources.

Most of the AML’s instrumentation had fast response times, varying from 1 to 10 s. For CO₂ measurements at 1-s time response, a nondispersive infrared (NDIR) unit (Licor LI-6262) was used. A quantum cascade laser (QCL) with a 1-s time response was used to measure CO. This method is different from the one which was employed in the MCMA-2003 field campaign, when a slower NDIR analyzer with a 10-s response time was used. There were two chemiluminescent analyzers on board the AML to measure NOₓ: one single-channel (EcoPhysics CLD-88y) and one dual-channel (Thermo 42C). These instruments were operated in the 1-s measurement mode. Similarly as in the 2003 field campaign, an aerosol photometer (TSI DustTrak 8250) was used to measure PM₂.₅. A dual tunable infrared laser differential absorption spectroscopy (TILDAS) monitor was used to measure ammonia (NH₃) and formaldehyde (HCHO), among other compounds. A multi-angle absorption photometer (MAAP-Model 5012) was used for BC. A photoemission aerosol sensor and diffusion charger (EcoChem PAS 2000CE and EcoChem DC 2000CE) were used to measure particulate PAHs and aerosol active surface area, respectively. A proton transfer reaction mass spectrometer (PTR-MS) was used to measure selected VOCs, including benzene (C₆H₆). Standard environmental
parameters such as wind speed, pressure, temperature, and relative humidity were also measured continuously.

This study focuses on a drive between the Universidad Tecnológica de Tecámac (T1) and Santa Ana. The distance between the two sites is approximately 75 km from T1 in the northeastern part of the MCMA to Santa Ana south of the city. The chase-mode experiment took place on March 22, 2006, from 11:00 until 14:30.

Quality assurance and control of the measurements included calibration with zero-air every five minutes, removal of potential self-sampling data points when the wind was originating from the rear of the van, and precise alignment of all pollutant time series by visual inspection. After screening, 4038 data points of each pollutant time series remained and were used as the input matrix data for the PMF model. The species CO₂, CO, PM₂.₅, C₆H₆, and NO were used as inputs into the PMF model.

The United States Environmental Protection Agency’s (EPA) PMF 1.1 receptor model was used to conduct the source apportionment modeling. With the use of constrained, weighted least squares, EPA PMF 1.1 allows the user to specify a certain number of factors (sources) which impact a receptor site and assumes that linear combinations of these factors result in the measured concentrations of pollutants. The model does not account for reactivity. For each species measured and inserted into the PMF modeling engine, an uncertainty file which specified the method detection limit and its percentage uncertainty was constructed. Furthermore, the weighting of a factor could be adjusted if necessary and represents another mechanism by which the model accounts for uncertainty.
The EPA PMF 1.1 model documentation suggests that a range of 2-18 factors be considered. In this study, we varied the number of factors between three and five, with 20 repeat solutions for each factor. The factor identities depend on markers for these factors and the modeled source profiles (Larsen et al., 2003). The optimal number of factors seemed to be three, as analysis of the modeled source profiles for both four and five factors did not provide distinctive time series assignments but only appeared to separate out individual pollutants.

For other species of interest which were not strong markers in the separation of gasoline versus diesel emissions, we calculated their source profiles using multiple linear regression. The regression model was constructed in MINITAB by using the factor contributions time series obtained from the PMF model in conjunction with the pollutant concentrations at similar instances in time. We applied this method to NH₃, HCHO, BC and PAHs.

### 3.4 Results

Figure 3.1 displays a five-minute time series of pollutant concentrations measured by the AML in chasing mode. It depicts the rapid temporal variation in the concentrations of pollutants over ranges much broader than typically seen at stationary monitoring sites. Concentrations of different pollutants are roughly correlated in time. Peaks correspond to periods when the AML intercepted less diluted exhaust plumes from the surrounding areas.
traffic. The straight lines in the figure skip over zero-air calibration periods, missing data from one or more pollutants, or self-sampling from the AML.

The species shown in the upper section of this figure were used as inputs into the PMF model. These included CO₂, CO, PM₂.₅, C₆H₆, and NO. The four species shown in the lower section of the figure were not used as PMF inputs, but their source profiles were derived using the PMF output together with multiple linear regression. During the initial stages of the PMF analysis, ammonia and formaldehyde were also tested as input data. However, we concluded from the output data that both of these species were not strong markers in the separation of gasoline versus diesel emissions, and thus, we disregarded them as inputs.

Figure 3.2 depicts the source profiles derived by PMF. Three factors had been specified for the data set. In the figure, the solid bars indicate the amount of each pollutant species allocated to the factor (left axis), while the dots reflect the percentage of the species distributed to each factor (right axis). In the Discussion section, we suggest that Factor 1 represents gasoline-engine emissions, Factor 2 represents the background air, and Factor 3 represents diesel-engine emissions. Factor 1 is comprised of 69 ppm of CO₂, 2836 ppb of CO, 0.4 ppb of NO, 3.9 ppb of C₆H₆, and 6.4 µg m⁻³ of PM₂.₅. From the percentage apportionment scale, nearly 90% of the CO, 80% of the C₆H₆, and just under 20% of the CO₂ are associated with Factor 1. Much smaller percentages of PM₂.₅ and NO are associated with this factor. Factor 2 shows considerably higher concentrations of CO₂ (329 ppm), PM₂.₅ (95 µg m⁻³), and NO (22 ppb) than for Factor 1. In contrast, the mass apportionment factors for CO and C₆H₆ decreased. Approximately 85% of the PM₂.₅ and
80% of the CO₂ are attributed to Factor 2, with much smaller contributions (<10%) from the other pollutants. For Factor 3, there is a noticeable increase in NO mass and percentage apportionments as compared to the other two factors. Nearly 90% of the NO and 192 ppb of this species are associated with Factor 3. For C₆H₆, there is very little difference in either concentration or percentage apportionment between Factors 2 and 3. For PM₂.₅, the Factor 3 results closely resemble those of Factor 1. There is some mass and percentage apportionment attributed to Factor 3 for CO, with both these parameters larger than with Factor 2 but significantly dwarfed by of the assignment to Factor 1. CO₂ has an apportionment of 15 ppm and <5% percent to Factor 3. These values are less than for Factor 1.

Figure 3.3 displays the time series of the factor contributions associated with the entire driving period. A factor contribution value of one represents an average contribution to a receptor at a particular point in time. Thus, a value greater than one means that the factor is contributing an above-average amount to the receptor site at that point in time, and vice versa. Factor 2’s contribution (blue line) hovers around one most of the time, while the contributions from Factors 1 (red) and 3 (green) have a wider range and larger variance.

Figure 3.4 displays the correlation between the results of PMF and analysis of the video recorded by the AML. At discrete times throughout the period, the relative contributions of Factors 1 and 3, assumed to represent gasoline- and diesel-engine emissions, respectively, were compared to the ratio of numbers of heavy-duty diesel trucks and buses to light-duty gasoline-powered cars visible in the video record. The visual assignments were based on a recent study investigating vehicle emissions in the MCMA.
A correlation factor ($R^2$) of 0.72 was observed between the PMF model results and the results from the video recording, suggesting that the assignment of Factors 1 and 3 to gasoline- and diesel-engine emissions is reasonable.

Table 3.2 shows some properties of gasoline and diesel fuels used to compute emission factors and the emissions inventory, and Tables 3.3-3.5 summarize emission factors and annual emissions estimates for pollutant species in the MCMA and other cities worldwide. Emission factors, in units of mass of pollutant emitted per mass of fuel burned, are calculated by carbon balance involving all carbon-containing species in exhaust—CO$_2$, CO, and VOCs—and the weight fractions of carbon in gasoline and diesel fuel. The underlying assumptions and equations were previously described by Kirchstetter et al. (1999) and Jiang et al. (2005).

Table 3.3 presents emission factors of particulate species, including PM$_{2.5}$, BC, and PAHs, in Mexico City compared to two other tunnel studies in the U.S. and Europe. Mexico City’s emission factors for BC and PAHs in diesel vehicles were the highest among studies in Oakland, California (Kirchstetter et al., 1999) and Zurich, Switzerland (Weingartner et al., 1997). While the PM$_{2.5}$ emission factor for heavy-duty vehicles in Mexico City was lower than in the Oakland study, the emission factor was higher for gasoline vehicles in Mexico City compared to Oakland. The emission factor of BC from diesel vehicles in Mexico City was just over six times higher than that in Zurich, and about one-and-a-half times higher than that in Oakland. For PAHs, diesel vehicles in Mexico City emitted almost nine times more of this pollutant per kilogram of fuel than in Oakland and about three times more than in Zurich. For gasoline vehicles in the MCMA,
we report an emission factor of zero for both BC and PAHs. The multiple linear regression reported negative values for the source profiles related to gasoline emissions, probably due to uncertainties in the modeling, although it is possible that the exhaust from gasoline-powered cars contains less BC and PAHs than the intake air, which is polluted by the surrounding traffic.

Table 3.4 presents emission factors of gaseous species, including CO, NO, VOC, NH₃, and HCHO. For light-duty vehicles, CO and VOC rank highest among the pollutants, while for heavy duty vehicles, NO ranks highest. The emission factors related to NH₃ and HCHO are relatively small compared to the above mentioned species.

Table 3.5 presents annual emissions from gasoline- and diesel-powered vehicles in Mexico City in 2006 compared to 2003. Gasoline-powered vehicles are responsible for 90% of mobile source CO, 85% of VOC, 0.02% of NO, 30% of PM₂.₅, 65% of NH₃, and 56% of HCHO emissions. Diesel-powered vehicles account for the remaining percentages of the pollutant species. The emissions estimate of CO in this study is 58% less than that computed in Jiang et al. (2005) for the year 2003. PM₂.₅ estimates are much closer; however the estimate in this study is slightly lower and falls outside the range of one standard error of the 2003 value. For VOCs, again our estimate is about 45% lower than that reported in Jiang et al. (2005). For BC, our estimate is about 100% higher, and for PAHs, it is 60% lower. Annual emissions of NH₃ from gasoline vehicles are estimated at 400 metric tons yr⁻¹ and from diesel vehicles, 220 metric tons yr⁻¹. The table compares these estimates to Zavala et al. (2006), whose assessment considers gasoline vehicles only. The value for gasoline vehicles falls within range of the estimate reported in Zavala
et al. (2006). For HCHO, we estimated that gasoline vehicles emit 1000 metric tons yr\(^{-1}\) and diesel vehicles about 800 metric tons yr\(^{-1}\). The estimate in this study for annual emissions of HCHO is about 66% lower than that reported in Zavala et al. (2006).

### 3.5 Discussion

#### 3.5.1 Compositional profiles of the PMF model

Based on analysis of the PMF factors shown in Figure 3.2 and their associated time series shown in Figure 3.3, we hypothesize that Factor 1 represents gasoline-powered vehicles, Factor 2 represents background air on roadways, and Factor 3 represents diesel-powered vehicles. Gasoline-powered vehicles are mainly associated with CO and VOC (Sawyer et al., 2000; Weingartner et al., 1997), and this was exemplified with the highest CO and benzene mass and percentage apportionment factors associated with Factor 1. With gasoline emissions, we expect to see some NO also. With Factor 2, the high mass and percentage apportionment factors of CO\(_2\) and PM\(_{2.5}\) may suggest diesel-powered engines as the source. However, on closer inspection of the time series associated with this factor and its contributions (blue line in Figure 3.3), it is evident that the contribution of Factor 2 is relatively constant in time, which is indicative of a background source rather than transient plumes from vehicles. With mobile sources, the factor contributions would fluctuate depending on variables such as traffic conditions and meteorological parameters. Factor 3 contains a very high mass contribution and percentage apportionment of NO. As discussed in Sawyer et al. (2000), we would expect higher NO\(_x\)
emissions from diesel vehicles than from gasoline vehicles purely on a fuel-consumption basis. With diesel-powered engines, we expect relatively high PM$_{2.5}$ emissions with some NO$_x$ (Kirchstetter et al., 1999). This knowledge combined with the factor contribution data (green line in Figure 3.3), which shows that Factor 3 fluctuates over a wide range, suggests assignment of this factor to diesel-powered vehicles.

The main basis for the identification of diesel versus gasoline emissions of pollutant species is rooted in the fundamental differences in engine operating conditions and fuel types. Gasoline engines tend to operate around an equivalence ratio of one, but can also run fuel-rich in some situations, especially in the reduced oxygen atmosphere of Mexico City. In the absence of a functioning catalytic converter, fuel-rich conditions lead to high emissions of CO and VOCs due to incomplete combustion. In contrast, diesel engines operate under fuel-lean conditions, which maximize NO$_x$ emissions, and lack catalytic converters. The heavier diesel fuel produces greater amounts of soot and less evaporative emissions.

Results of the visual inspection of traffic conditions during the chase-mode experiment strongly corroborate the assignment of PMF factors (Figure 3.4). A correlation factor of 0.72 is fair and suggests the separation of factors into diesel versus gasoline emissions by the PMF model is consistent with observed traffic conditions.
3.5.2 Emission factors and inventory

Studies worldwide have shown that PM$_{2.5}$, BC, and PAH emissions from motor vehicles are dominated by heavy-duty diesel vehicles. However, in Mexico City the emission factors are generally higher than in other cities. A major difference in emission factors may result from the fact that studies done in the other cities were tunnel studies restricted to a single site as compared to the mobile laboratory experiment conducted in Mexico City, where the measurement platform could drive around and capture a larger distribution of driving conditions and on-road vehicles. Furthermore, the age of the vehicle fleet and general maintenance and inspection standards may also result in the differences seen in the emission factors. In Oakland and Zurich, the vehicle fleet is likely to be newer than it is in Mexico City, and newer vehicles have technological improvements in engine design and emissions control systems that lead to more efficient operation and reduced emissions. Also, more stringent emission standards in these cities may result in lower emission factors.

The total emissions calculated for 2006 are lower than the estimates obtained in Jiang et al. (2005), especially for CO and VOC. The emissions result shown in Table 3.5 exemplify a key significance of distinguishing gasoline versus diesel emissions in on-road vehicles. We can determine which type of vehicle contributes more significantly to pollutant emissions and thus, where we should focus emission control strategies. A limitation of our estimates is that we rely on fuel sales from 2004, the most recent data available, to compute the emissions inventory for 2006. Another limitation of this study
is that the PMF model does not report standard deviations on the results. This prohibits calculation of uncertainty in our emission factors and inventory estimates.

3.6 Conclusion

In this study, we have measured pollutant concentrations along Mexico City’s roadways using fast-response instruments aboard the AML and then have applied PMF to the data to separate diesel and gasoline emissions. We have also estimated emission factors and the total motor vehicle emissions inventory for CO, NO, VOCs, NH₃, HCHO, PM₂.₅, BC, and PAHs throughout the MCMA. The emission factors for both CO and VOC computed in 2006 are not significantly different from those measured by the AML in 2003. We estimate that gasoline-powered vehicles are responsible for 90% of mobile source CO, 85% of VOC, 0.02% of NO, 30% of PM₂.₅, 65% of NH₃, and 56% of HCHO emissions. Diesel-powered vehicles account for the remaining percentages. The annual emissions inventory for motor vehicles in the MCMA is estimated at 465,000 metric tons for CO, 49,010 metric tons for NO, 130,000 metric tons for VOC, 620 metric tons for NH₃, 1800 metric tons for HCHO, 3700 metric tons for PM₂.₅, 3200 metric tons for BC, and 35 metric tons for PAHs. The estimates for CO and VOC were lower than estimated during the MCMA-2003 field campaign. In future work, we suggest analysis of additional chase-mode experiments, so that a more representative sample might be used as the basis for fleet-wide emissions.
3.7 Acknowledgments

We thank E. Deustúa for his assistance during the field campaign and C. Kolb for the use of the ARI Mobile Laboratory. We acknowledge financial support from the U.S. National Science Foundation, the U.S. Department of Energy, and the National Aeronautics and Space Administration. This study was also supported by the Molina Center for Strategic Studies in Energy and the Environment. D. Thornhill is supported by a Fulbright Fellowship.

3.8 References


measured by a mobile laboratory in Mexico City. Atmospheric Chemistry and Physics, 5, 3377-3387.


### Table 3.1. MCMA emissions inventory for mobile sources in 1998 and 2003.

<table>
<thead>
<tr>
<th>Pollutant (metric tons per year)</th>
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<th>2003(^b)</th>
</tr>
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<tr>
<td>CO</td>
<td></td>
<td>1,733,000 (98.0%)(^c)</td>
<td>1,190,000±40,000</td>
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<tr>
<td>NO(_x)</td>
<td></td>
<td>166,000 (80.5%)</td>
<td>120,000±3000</td>
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<tr>
<td>VOCs</td>
<td></td>
<td>188,000 (39.5%)</td>
<td>240,000±50,000</td>
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<tr>
<td>PM(_{10})</td>
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<td>7000 (35.9%)</td>
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</tr>
<tr>
<td>SO(_2)</td>
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<td>5000 (20.8%)</td>
<td>NA</td>
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\(^a\) Comisión Ambiental Metropolitana, 2001; 1998 emissions inventory.  
\(^b\) Jiang et al. (2005).  
\(^c\) The numbers in parentheses indicate the percentage contribution of mobile sources to total emissions in the MCMA. These data are available for 1998 only.
Table 3.2. Properties of gasoline and diesel fuels used in calculating emissions factors and annual emissions estimates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gasoline</th>
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<tbody>
<tr>
<td>Mass fraction of carbon, $w_c^a$</td>
<td>0.85</td>
<td>0.87</td>
</tr>
<tr>
<td>Fuel density$^d$ (kg L$^{-1}$)</td>
<td>0.74</td>
<td>0.84</td>
</tr>
<tr>
<td>VOC/C$_6$H$_6$ ratio by mass$^b$</td>
<td>65±28</td>
<td>65±28</td>
</tr>
<tr>
<td>Fuel sales$^c$ (L)</td>
<td>7.25×10$^9$</td>
<td>2.08×10$^9$</td>
</tr>
</tbody>
</table>

$^a$Kirchstetter et al. (1999).
$^b$Velasco et al. (2007).
$^c$Comisión Ambiental Metropolitana (2006); 2004 emissions inventory.
Table 3.3. Particulate matter emission factors reported separately for gasoline (LD) and diesel (HD) vehicles for PM$_{2.5}$, BC, and PAHs in Mexico City and other studies

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>PM$_{2.5}$ (g kg$^{-1}$)</th>
<th>BC (g kg$^{-1}$)</th>
<th>PAHs (g kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Mobile laboratory</td>
<td>LD:0.20</td>
<td>LD:0$^a$</td>
<td>LD:0$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HD:1.48</td>
<td>HD:1.84</td>
<td>HD:0.02</td>
</tr>
<tr>
<td>Kirchstetter et al. (1999)</td>
<td>Tunnel study</td>
<td>LD:0.11±0.01</td>
<td>LD:0.035±0.003</td>
<td>LD:9.0×10$^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HD:2.5±0.2</td>
<td>HD:1.3±0.3</td>
<td>HD:0.0023</td>
</tr>
<tr>
<td>Weingartner et al. (1997)$^b$</td>
<td>Tunnel study</td>
<td>NA</td>
<td>LD:0.02</td>
<td>LD:0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HD:0.3</td>
<td>HD:0.007</td>
</tr>
</tbody>
</table>

$^a$The multiple linear regression produced negative values for the source profiles related to gasoline emissions. We have elected to report these emission factors as zero.

$^b$The emission factors in units of g kg$^{-1}$ are reported from Jiang et al. (2005), but the original results were reported in units of mg km$^{-1}$. 
Table 3.4. Comparison of fuel-based emission factors (g kg\(^{-1}\)) from motor vehicles in Mexico City.

<table>
<thead>
<tr>
<th>Location</th>
<th>Vehicle types</th>
<th>CO</th>
<th>NO</th>
<th>VOC</th>
<th>NH(_3)</th>
<th>HCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mexico City, 2006(^{a})</td>
<td>LD(^{c})</td>
<td>77</td>
<td>0.001</td>
<td>19</td>
<td>0.07</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>HD(^{d})</td>
<td>25</td>
<td>28</td>
<td>10</td>
<td>0.12</td>
<td>0.45</td>
</tr>
<tr>
<td>Mexico City, 2003(^{b})</td>
<td>All</td>
<td>190±160</td>
<td>NA</td>
<td>38±27</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(^{a}\)This study.
\(^{b}\)Jiang et al. (2005).
\(^{c}\)Light-duty (gasoline) vehicles.
\(^{d}\)Heavy-duty (diesel) vehicles.
Table 3.5. Comparison of annual emissions estimates (metric tons yr\(^{-1}\)) from motor vehicles from the most recent studies in Mexico City.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>This study</th>
<th>Zavala et al. (2006)(^b)</th>
<th>Jiang et al. (2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gasoline</td>
<td>Diesel</td>
<td>Total</td>
</tr>
<tr>
<td>CO</td>
<td>420,000</td>
<td>45,000</td>
<td>465,000</td>
</tr>
<tr>
<td>VOC</td>
<td>110,000</td>
<td>20,000</td>
<td>130,000</td>
</tr>
<tr>
<td>NO</td>
<td>10</td>
<td>49,000</td>
<td>49,010</td>
</tr>
<tr>
<td>PM(_{2.5})</td>
<td>1100</td>
<td>2600</td>
<td>3700</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>400</td>
<td>220</td>
<td>620</td>
</tr>
<tr>
<td>HCHO</td>
<td>1000</td>
<td>800</td>
<td>1800</td>
</tr>
<tr>
<td>BC</td>
<td>0(^a)</td>
<td>3200</td>
<td>3200</td>
</tr>
<tr>
<td>PAHs</td>
<td>0(^a)</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^a\) The multiple linear regression produced negative values for the source profiles related to gasoline emissions. We have elected to report these emission factors as zero.

\(^b\) Emissions estimates based on gasoline vehicles only.
Figure 3.1. Time series of pollutant concentrations measured by the AML during an example five-minute period. The top panel shows pollutants used in the PMF analysis, and the bottom panel shows pollutants whose source profiles were derived by multiple linear regression.
Figure 3.2. Factor profiles showing concentration (left axis) and percentage (right axis) apportionment of five species. The concentration units vary by pollutant: CO$_2$ is in ppm; CO, NO, and C$_6$H$_6$ are in ppb, and PM$_{2.5}$ is in $\mu$g m$^{-3}$. 
Figure 3.3. Time series of PMF factor contributions.

Figure 3.4. Correlation between PMF results and video analysis.
Chapter 4

Conclusions

The analysis of spatial and temporal variations of PAH and AS concentrations in Mexico City during the MCMA-2006 field campaign had led to the following deductions:

- The highest measurements of PAHs and AS were generally found at sites with dense traffic networks.
- PAH concentrations vary considerably in space, and therefore PAHs cannot be treated as a regional-scale pollutant.
- For risk assessment studies, a single monitoring site will not adequately represent an individual’s exposure.
- Aging of primary combustion particles by coating with secondary aerosol appears to result in a decrease in surface PAH/AS and PAH/BC ratios over the course of the day.

From the source apportionment of on-road measurements of a suite of gaseous and particulate pollutants, we concluded that:

- PMF can be applied to fast on-road measurements of CO₂, CO, NO, VOC, and PM₂.₅ to separate gasoline from diesel engine emissions.
- Gasoline-powered vehicles are responsible for 90% of mobile source CO, 85% of VOC, 0.02% of NO, 30% of PM₂.₅, 65% of NH₃, and 56% of HCHO.
emissions with diesel-powered vehicles accounting for the remaining percentages.

➢ The emission factors for both CO and VOC computed in 2006 are within one standard deviation and not significantly different from those measured by the AML in 2003.