THE SCERP MISSION

The Southwest Consortium for Environmental Research and Policy (SCERP) was established by the U.S. Congress in October 1990 to "initiate a comprehensive analysis of possible solutions to the acute air, water quality, and hazardous waste problems that plague the United States-Mexico border region." SCERP is a consortium of five U.S. universities (Arizona State University, New Mexico State University, San Diego State University, University of Texas at El Paso, and University of Utah) and five Mexican universities (Colegio de la Frontera Norte, Instituto Tecnológico de Ciudad Juárez, Instituto Tecnológico y de Estudios Superiores de Monterrey, Universidad Autónoma de Baja California, and Universidad Autónoma de Ciudad Juárez). SCERP carries out its mission through a cooperative agreement with the U.S. Environmental Protection Agency. A permanent administration office is maintained by the consortium in San Diego.

ENVIRONMENTAL PROBLEMS OF THE U.S.-MEXICAN BORDER REGION

The border region lies 100 kilometers, or 60 miles, on each side of the U.S.-Mexican political boundary and encompasses parts of four states in the United States—Texas, New Mexico, Arizona, and California—and six Mexican states—Baja California, Sonora, Chihuahua, Coahuila, Nuevo León, and Tamaulipas. Approximately 13 million people live in the U.S. counties and Mexican *municipios* on the border. The high density of people and increased industrialization since the passage of the North American Free Trade Agreement (NAFTA) have placed an even greater burden on the inadequate infrastructure and environmental resources of the region. Exacerbating the problem is the fact that many U.S. counties along the border are categorized as "economically distressed," and few communities possess the resources needed to address their environmental concerns. Some of the critical border environmental issues include:

- Rapid urbanization and lack of adequate infrastructure
- Air pollution from open burning, vehicle emissions, and industrial operations
- Contamination of surface water and groundwater from open sewers and industrial waste
- Overuse of aquifers and surface streams
- Transportation and illegal dumping of hazardous wastes
- Destruction of natural resources

THE SCERP SOLUTION

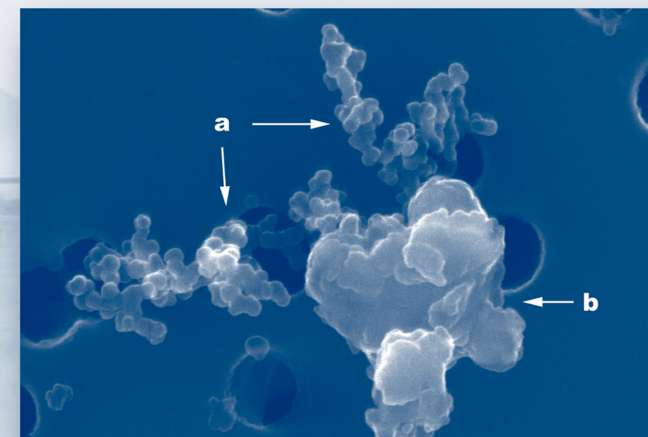
SCERP uses a broad, integrated, multidisciplinary approach to address the issues of the border. SCERP researchers collaborate with the U.S. Environmental Protection Agency (EPA) and Mexico's Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT), as well as local and state governments, tribal nations, business and industry, non-governmental organizations, and communities of the border region. SCERP organizes research, outreach, and training programs devoted to improving environmental conditions and building capacity in the border region for resolving critical environmental problems. SCERP is pioneering a model of binational cooperation that brings U.S. and Mexican researchers together and introduces new skills and perspectives in binational environmental problem solving.

CONSORCIO DE INVESTIGACIÓN Y POLÍTICA AMBIENTAL DEL SUROESTE
SOUTHWEST CONSORTIUM FOR ENVIRONMENTAL RESEARCH & POLICY

THE U.S.–MEXICAN border environment:
Integrated Approach to Defining Particulate Matter Issues in the Paso del Norte Region
SCERP 12

THE U.S.-MEXICAN border environment:

Integrated Approach to Defining Particulate Matter Issues in the Paso del Norte Region



Edited by
Robert C. Currey
Kerry E. Kelly
Henk L. C. Meuzelaar
Adel F. Sarofim

SCERP Monograph Series, no. 12

Southwest Consortium for Environmental Research and Policy

The U.S.-Mexican Border Environment

An Integrated Approach to Defining Particulate Matter Issues in the Paso del Norte Region

SCERP Monograph Series, no. 12

A series edited by Paul Ganster

Contributors

M. A. Amaya	University of Texas at El Paso
J. R. Anderson	Arizona State University
N. S. Arnold	University of Utah
J. Bader	University of Texas at El Paso
J. J. Bang	University of Texas at El Paso
B. E. Barnes	AMEC Earth and Environmental, Inc.
R. R. Chianelli	University of Texas at El Paso
J. C. Chow	Desert Research Institute
J. W. Clague	University of Texas at El Paso
R. M. Currey	University of Texas at El Paso
M. Delgado	University of Texas at El Paso
T. T. Espino	University of Texas at El Paso
H. J. S. Fernando	Arizona State University
P. G. Fields	Eastern Research Group
J. L. Gardea-Torresdey	University of Texas at El Paso
J. C. Greenlee	New Mexico State University
R. Halvey	Western Governors' Association
I. Herrera	University of Texas at El Paso
I. C. Jaramillo	University of Utah
S. Jeon	U.S. Army Corps of Engineers
P. Juárez	University of Texas at El Paso
K. E. Kelly	University of Utah
S.-M. Lee	Arizona State University
W.-W. Li	University of Texas at El Paso
J. S. Lighty	University of Utah
W. P. Mackay	University of Texas at El Paso
P. O. Medina	Private Consultant
G. M. Mejía Velázquez	Instituto Tecnológico y de Estudios Superiores de Monterrey
H. L. C. Meuzelaar	University of Utah
R. Moss	University of Texas at El Paso
B. Nookla	University of Utah
R. Orquiz	University of Texas at El Paso
R. Ortiz	University of Texas at El Paso
N. E. Pingitore Jr.	University of Texas at El Paso
J. J. Reynoso	El Paso City-County Health and Environmental District
C. A. Rincón	Environmental Defense
J. Ramses-Sánchez	Instituto Tecnológico y de Estudios Superiores de Monterrey
A. F. Sarofim	University of Utah

S. A. Sheya	Sierra Research
C. H. Snow	International Emissions Inventories
V. H. Valenzuela	Texas Commission on Environmental Quality
J. G. Watson	Desert Research Institute
M. E. Wolf	Eastern Research Group
M. J. Yacaman	Universidad Nacional Autónoma de Mexico
J. C. Zevallos	National Center for Chronic Disease Prevention and Health Promotion
H. Zhang	University of Utah

The Southwest Consortium for Environmental Research and Policy (SCERP) is a collaboration of U.S. and Mexican universities dedicated to addressing environmental issues of the U.S.-Mexican border region through applied research, outreach, and regional capacity building.

SCERP Universities
Arizona State University
El Colegio de la Frontera Norte
Instituto Tecnológico de Ciudad Juárez
Instituto Tecnológico y de Estudios Superiores de Monterrey
New Mexico State University
San Diego State University
Universidad Autónoma de Baja California
Universidad Autónoma de Ciudad Juárez
University of Texas at El Paso
University of Utah

SCERP website: www.scerp.org

The U.S.-Mexican Border Environment

An Integrated Approach to Defining Particulate Matter Issues in the Paso del Norte Region

Edited by
Robert M. Currey, Kerry E. Kelly,
Henk L. C. Meuzelaar, and Adel F. Sarofim

San Diego State University Press

Published by
San Diego State University Press
5500 Campanile Drive
San Diego, CA 92182-8141
http://sdsupress.sdsu.edu

Cover photos courtesy of J. Anderson, X. Hua, W.-W. Li,
J. J. Bang, R. R. Chianelli, M. J. Yacaman, and R. Ortiz

Printed in the United States of America

ISBN 0-925613-47-9

Previously published volumes in the SCERP Monograph Series,
The U.S.-Mexican Border Environment

No. 1 A Road Map to a Sustainable 2020
No. 2 Water Issues along the U.S.-Mexican Border
No. 3 Economy and Environment for a Sustainable Border Region
No. 4 U.S.-Mexican Border Communities in the NAFTA Era
No. 5 Overcoming Vulnerability: The Southwest Center for Environmental Research and Policy's Research Program (1990–2002) and Future Agenda
No. 6 Air Quality Issues along the U.S.-Mexican Border
No. 7 Trade, Energy, and the Environment: Challenges and Opportunities for the Border Region, Now and in 2020
No. 8 Binational Water Management Planning
No. 9 Tribal Environmental Issues of the Border Region
No. 10 Improving Transboundary Air Quality with Binational Emission Reduction Credit Trading
No. 11 Dynamics of Human-Environment Interactions

About this volume:
All times are local
All monetary figures are US$ unless otherwise specified

Contents

Preface

"I think this is going to be an exciting venture, but not without its share of problems, both technical and political."
–Adel Sarofim, March 8, 1998

During the July 1997 retreat of the Southwest Consortium (then Center) for Environmental Research and Policy (SCERP) Management Committee, the representatives from the consortium's five U.S. universities began an evaluation of the projects completed over the eight years of SCERP's existence, as well as a discussion about the future of the program. The discussions made it abundantly clear that many of the projects completed up to that point had focused on specific areas of environmental concern—water and air quality—and on the same geographic areas—San Diego-Tijuana, and El Paso-Ciudad Juárez. Even more importantly, we recognized that the projects were independent efforts by their primary investigators, that there was little or no coordination among them. That resulted in, for example, an investigator working with high-tech instrumentation just miles away from another investigator who could have benefited from the use of that same equipment.

In an effort to better coordinate projects on similar topics, the Management Committee developed the SCERP Directed Research Program. This program was designed to concentrate SCERP's talent and resources on specific objectives that could benefit from coordinated multi-year, multi-project efforts. A Directed Research Program would be a significant investment, and it would be funded at a level significantly greater than SCERP had heretofore dedicated to individual projects.

Just six months before this meeting, air quality researchers gathered at the SCERP technical conference in Las Cruces, N.M., expressed the need to address the issue of $PM_{2.5}$, or particulates in the air that were 2.5 microns or smaller. The nation's attention had turned only recently to these air pollutants as a result of the U.S.

Environmental Protection Agency (EPA) proposal for new National Ambient Air Quality Standards. EPA and other researchers had determined that these smaller particles were of special concern in terms of impacts on human health. El Paso was the logical place to address $PM_{2.5}$.

Thus the Paso del Norte Air Research Program (PdNARP) became one of the first SCERP Directed Research Projects. This monograph reports some of the results from the several years of activity of that project. Work began in 1999 with the development of a white paper that outlined the objectives for the study. It is important to recognize that the paper was a coordinated effort involving input from both local stakeholders, the Texas Natural Resources Conservation Commission (TNRCC, now the Texas Commission on Environmental Quality [TCEQ]), and EPA's Region 6. The paper asked "What can and should SCERP do?" and answered with five objectives:

- Characterize the nature of particulate matter, both $PM_{2.5}$ and PM_{10}, within the airshed; determine its magnitude, spatial distribution, and chemical composition (organic and inorganic)
- Conduct volatile organic compound (VOC) and semi-volatile organic compound (SVOC) receptor modeling and determine the speciation of VOCs and SVOCs taken from data previously collected by TNRCC, grab samples, and other monitoring stations within the airshed
- Establish a regional information and coordinating center or clearinghouse to coordinate other monitoring and research activities within the airshed
- Conduct and support activities to develop emissions inventories in the airshed
- Coordinate with epidemiologists evaluating the health risks associated with ambient air quality in the airshed

SCERP knew this list outlined an ambitious set of tasks. Upon completion of the white paper, SCERP asked Dr. Wen-Whai Li of University of Texas at El Paso (UTEP) to develop a program proposal. He was instructed to survey the SCERP universities and their researchers and to assemble a program team that could collectively accomplish the mission. The team involved six of the 10 SCERP universities: Arizona State University, New Mexico State University, University of Utah, University of Texas at El Paso, Universidad Autónoma de Ciudad Juárez, and Instituto Tecnológico y de Estudios Superiores de Monterrey.

It is important to note that even with the commitment of resources at a level that was unprecedented for SCERP, not all of the objectives identified above could be addressed. Thus the final objectives for PdNARP were:

- $PM_{2.5}$ characterization (determine the temporal and spatial variability of $PM_{2.5}$ in the airshed) and determine the organic and inorganic chemical composition of the particles
- Perform source characterization and obtain emission inventory information to assist in the next objective
- Determine the sources of PM, hopefully through Chemical Mass Balance
- Establish an information center and clearinghouse
- Develop the capacity of the region to address the issue

Many of these goals were attained, and the research team did make important progress on others. Some of the literature and publications that have resulted from the program are widely recognized as important contributions to the body of knowledge on particulate matter and air pollution. The research of this study has been a springboard to other efforts and has been fundamental to the work now being done by environmental health scientists to answer the key question, What is the effect of this air pollution on the people who live in it?

One of the EPA's fundamental questions—is there anything inherently toxic about El Paso's particulate matter?—has been answered. The PdNARP study has shown that the nature of particulate matter in El Paso, and presumably more of the Southwest region of the United States, is fundamentally different from most areas of the United States, where sulfates or nitrates are the dominant components. Although the particulate matter is not inherently toxic, the hot spots and episodic spikes in concentration at the border are of concern and their impacts need to be studied further.

And, most importantly, we have developed significant capacity and increased our understanding so we now can do more. Many of the students who worked on this program have graduated with advanced degrees and have gone on to work in the air quality field. I firmly believe that the environmental problems of the border region will be solved not by our national and state governments, but by the people who live in the region. And those people attend the universities that comprise SCERP.

As we expand the collective body of knowledge of the various elements of air quality within this airshed and the interactions among them, we become better able to assess and implement more viable control measures, reduce risks, and protect human health and the environment.

Many people, faculty, students, technicians, and administrators, contributed to the Paso del Norte Air Research Program, but I absolutely must recognize Wen-Whai Li, Henk Meuzelaar, Joe Fernando, Jim Anderson, and Rich Arimoto for their central efforts. "Contributions" is not a big enough word to capture the work these scholars invested in the program. I am also unable to adequately describe the tremendous contribution that Adel Sarofim made to this project. He was the intellectual core of the program, and I am proud to thank him for his mentorship and, most importantly, his friendship.

I also recognize the efforts of Guillermo Torres Moye and Alan Torres Páramo at Universidad Autónoma de Baja California and Ma. Gabriela G. Carrillo of SCERP for their work on the Spanish translations that appear here.

Finally, despite the list of editors for this volume, Kerry Kelly at the University of Utah and Amy Conner at SCERP did much of the real work. Inaccessible knowledge is useless; this monograph is one way we are trying to provide access to what we have learned to the reading public. These two remarkable and able women made this volume possible.

Bob Currey
El Paso, Texas
December 2004

Executive Summary

In the Paso del Norte airshed—an area comprised of El Paso County, Tex.; Dona Aña County, N.M.; and Municipio de Ciudad Juárez, Chih.—a greater understanding of air pollution is possible through the development of capacity to monitor particulate air pollution, determination of the sources of ambient particulate matter (PM), and assessment of the effects of elevated particulate levels on human health. In 1999, the Southwest Consortium for Environmental Research and Policy (SCERP) instituted a pilot project to study these aspects of particulate matter. The outcomes of that project are summarized in this monograph.

Several characteristics distinguish Paso del Norte from other airsheds. Its arid climate leads to high concentrations of entrained crustal and resuspended road dust, particularly under high wind conditions. The topography leads to downflows from the surrounding mountains, which in turn contribute to nocturnal spikes in ambient particulate loading. The region has a unique combination of particulate emission sources, including brick kilns, refining, smelting, scrap-metal foundries, maquiladoras, electricity generation, and quarries. Traditional sources of particulate emissions, such as internal combustion engines, have a distinctive local flavor that reflects the mix of vehicles and emission factors at the border, including the hot spots resulting from the high density of idling vehicles at border crossings. Morbidity and mortality in the Paso del Norte area are higher than the U.S. average and are suspected to be related to air pollution. Finally, different air pollution jurisdictions and regulations, as well as a rapidly growing population, particularly on the Mexican side of the border, affect the ability to control negative impacts on air quality. Chapter I describes these and other characteristics of the airshed in detail.

The dynamic nature of air pollution at the border is a consequence of the changing demography and sources of air pollution. These changes underscore the need for monitoring networks that can be used to follow them and for models that can be used to anticipate future problems and guide control strategies. The results in this monograph add to previous studies summarized at the end of Chapter I.

Control of ambient PM concentrations is complicated by the multiplicity of sources of both particles (primary emissions) and particle precursors such as nitrogen oxides (NO_x), sulfur oxides (SO_x), ammonia (NH_3), and volatile organic compounds (VOCs), which undergo atmospheric transformation to form particulate nitrates, sulfates, and condensable organics (secondary particles). Developing inventories of the emissions of primary particles and particle precursors is important because that information can be used to guide emission control strategies. The inventories are also important for the development of air quality models to predict the spatial and temporal variation of airborne particles.

Chapter II provides a discussion of emission inventory studies carried out for the northern areas of Mexico, with emphasis on the 100 kilometers (km) that constitute Mexico's northern border region. These inventories include data for municipalities other than Ciudad Juárez. Table 1 is a guide to the information in Chapter II, much of it summarized from the reports on Mexican emission sources that are difficult to find in the United States. Results for El Paso are documented on the Texas Commission on Environmental Quality (TCEQ) web site (http://www.tceq.state.tx.us/nav/data/), which provides trends in emissions based largely on questionnaires completed by different industries. An emission inventory from 1996 provides estimates of emissions for both El Paso and Ciudad Juárez. These show that the annual particulate emissions for Ciudad Juárez for PM measuring 10 micrometers or less in aerodynamic diameter (PM_{10}) (46,606 tons or 42,300 megagrams [Mg]) are approximately three times those of El Paso (15,510 tons or 14,100 Mg), and that the largest contributors by far for both cities were unpaved roads. Table 2 in Chapter II also provides estimates from 1996 of a number of the anthropogenic sources that are dominated by mobile sources, fuel consumption, and metal processing.

Table 1. Summary of Data on Emission Factors and Emission Inventories in Chapter II

Data Provided	Methodology or Source	Compounds	Location	Comments	Location in Chapter II
Mobile emission factors different vehicle classes	Mobile-Juárez, Mobile 5A	VOCs, NO_x, CO	Ciudad Juárez for different vehicle classes	Emission Factor Ciudad Juárez > U.S.	Figure 2
Fleet average mobile emission factors	Mobile5-Mexico		Ciudad Juárez (J); Aquascalientes (A); Mexico City (M); Denver (D)	Emission Factors J = ~ A > M > D	Figure 3
Potential for emission reduction at border crossings	Mobile5-Juárez	VOC, CO, NO_2, PM	San Diego, Nogales, El Paso, Laredo	Potential Reduction ~ 6 Mg/day (El Paso/Ciudad Juárez)	Figure 5
EI: Point, Area, Mobile, Natural	Regional Air Quality Planning Inventories	NO_x, SO_x, VOC, CO, PM_{10}, NH_3	Monterrey, Ciudad Juárez, Tijuana, Mexicali	PM10 est. Ciudad Juárez ~ 45,100 Mg/year Natural, ~1,500 Anthropogenic	Table 2
EI: Point, Area, Mobile, Biogenic	Inventory of HAPs for ADEQ	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, HAPs	Nogales, Agua Prieta		Table 3
EI: Point, Area, Mobile, Biogenic	1996 Paso del Norte Ozone Study	NO_x, VOC, CO	Paso del Norte	Greater detail Table 2 (Chapter II) including PM	Table 4
EI: Point, Area, Mobile, Natural	SCOS97-NARSTO	NO_x, SO_x, TOG, CO, PM	Northern Baja California	PM sources (Mg/day) ~ 11 point, 376 area, 2 mobile	Table 5
EI: Point, Area, Mobile	BRAVO Study	NO_x, SO_x, VOC, CO, PM_{10}, PM2.5, NH_3	Six northern states	Aggregate Emissions (Mg/year) ~648,000 PM10, ~ 229,000 $PM_{2.5}$	Table 6
EI: Point, Area, Mobile, Natural	TCEQ	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$	Ciudad Juárez	Detailed breakdown of classes of area sources	Table 7
EI: Point, Area, Mobile, Natural	Multiple sources identified in Chapter II	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, NH_3	Six Mexican border states	Estmates for Chihuahua (Mg/year) ~ 135,000 PM_{10}, ~42,000 $PM_{2.5}$	Table 8
EI: Anthropogenic, Point, Area, Mobile	Preliminary Mexico National Emissions Inventory	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, NH_3	Six Mexican border states	Anthropogenic Emissions (Mg/year) ~ 837,000 PM_{10}, ~ 303,000 $PM_{2.5}$	Table 9

Source: Authors

The results for Ciudad Juárez reported in Table 1 support the finding that unpaved roads are the dominant contributor to emissions. It also makes clear the following additional generalizations:

- The emission factors for Mexican cars are higher than those in the United States, reflecting that the mean age of cars on the road is greater and a larger fraction is not registered or maintained
- The potential exists for a significant reduction in automotive emissions through a reduction of traffic congestion at border crossings
- Anthropogenic sources include significant emissions from local sources characteristic of, but not unique to, the border region, such as brick kilns, residential burning of waste, and open burning of agricultural wastes
- The emissions inventories at the border have been obtained for targeted studies related to ozone and visibility

Paso del Norte needs a more systematic approach to the development of PM inventories of the sources affecting its air quality. These inventories should use the boundaries imposed by the region's topography—not political jurisdictions—as their guide for inclusion. Despite differences in regulations and resources across the border, a number of binational agreements addressing environmental problems at the border have helped the progress of information gathering to develop the inventories (see Chapter I).

Emission inventories under the best of conditions are subject to significant uncertainties because of the difficulties in obtaining a complete list of sources, emission factors representative of all of the sources, and accurate activity patterns, such as fuel consumption, vehicle miles travelled, and production rates. Emission inventories are complemented by ambient measurements of PM that can be used to refine emission values by comparing ambient particulate concentrations with those calculated from emission inventories and transport models, or by identifying emission sources from the chemical compositions and concentrations of ambient particles using source attribution methodologies. In addition, electron microscopy studies of ambient samples can identify sources from the unique morphological features of many particles and can detect sources that might not otherwise be considered.

Chapters III, IV, and V describe field measurements and selected data on PM_{10}, PM measuring 2.5 micrometers in aerodynamic diameter ($PM_{2.5}$), particle morphology, and composition. These data are useful for establishing compliance with regulations and for showing trends associated with weather patterns and seasons. A major reason, however, for carrying out the concerted studies was to develop models that relate receptor to source (Chapter VI) and human health to exposure to high particle concentrations (Chapter VII).

A sampling network is available for El Paso and Ciudad Juárez that provides historical records of hourly air quality data (http://www.tnrcc.state.tx.us/cgi-bin/monops/particulates). The PM records are more recent and were not yet posted for Ciudad Juárez when this volume was published. In addition, as part of capacity-building efforts at the border, the University of Texas at El Paso (UTEP) has established a sampling network, in parallel with the state, that can be used for targeted studies. Such a study was conducted from January 3 to March 7, 2000, at two sampling sites in El Paso and three in Ciudad Juárez. These measurements, summarized in Chapter III, have been used to provide comparisons between different particulate measurement methods and generalizations of the impact of time of day, season, location, and weather patterns on $PM_{2.5}$ and PM_{10}. The measurements show the following trends:

1. The $PM_{2.5}$:PM_{10} ratio is in the range of 0.16 to 0.36, with the values reflecting changes in location and wind speed; the ratio decreases with increases in suspended crustal or road dust in rural areas, or with increases in wind speed. $PM_{2.5}$ provides a measure of particles of greater importance to negative health impacts and particles dominated by combustion sources. PM_{10} is more a measure of crustal matter suspended by high winds or produced by crushing and grinding operations. A large fraction of PM_{10} consists of particles generated by grinding and mechanical forces on rocks, either natural

processes such as the erosion that has over the ages led to the generation of soils and sands or industrial operations used to comminute ores or rocks.

2. Both $PM_{2.5}$ and PM_{10} show diurnal evening and morning peaks, with the evening peaks being particularly marked. These peaks correspond to periods of relative stagnation and the reversal of flows on the slopes bordering Paso del Norte. The diurnal changes in PM concentration are often reflected with marked changes in visibility.
3. Both $PM_{2.5}$ and PM_{10} exhibit higher values at low wind speeds (<~2m/s) and high wind speeds (>~8 m/s). High PM values at low wind speeds are associated with atmospheric stagnation, during which local emissions accumulate, and dust storms are associated with high wind speeds.
4. Both $PM_{2.5}$ and PM_{10} concentrations are higher in winter than summer (see also Chapter V), correlated to the prevalence of inversions (conditions in which cool air and air pollutants are trapped close to the ground by warmer air above it and the topography of the region) in winter as a consequence of the low surface temperatures.
5. The wide variations in PM concentrations between sites (two in El Paso and three in Ciudad Juárez) underlined the importance of the variability of local sources.
6. Compositions of the coarse ($PM_{2.5\text{-}10}$) and fine ($PM_{2.5}$) particles are presented for the five locations. Compositions of the coarse particle fraction had relatively high concentrations of geologic elements (aluminum, silicon, calcium, iron, titanium, and potassium). By contrast, areas such as the center of Ciudad Juárez, with a low percentage of unpaved roads and located far from exposed crustal matter, showed a relatively low concentration of crustal elements.

Chapter III provides some historical perspective on how the concentrations of trace elements decreased markedly in the period from 1990 to 2000. Arsenic decreased 57-fold and lead 18-fold. Additional information on the long-term trends of toxic elements in airborne particles is provided in Chapter V from the analysis of archived samples dating back to 1977. The chapter shows the dramatic decreases in concentrations and the reasons for these, most notably the phasing out of lead in gasoline starting in 1973 in the United States and in 1998 in Mexico, the decline of the smelter industry, and the increased stringency of air pollution legislation. Currently, ambient concentrations of toxic metals no longer violate U.S. or Mexican air pollution standards.

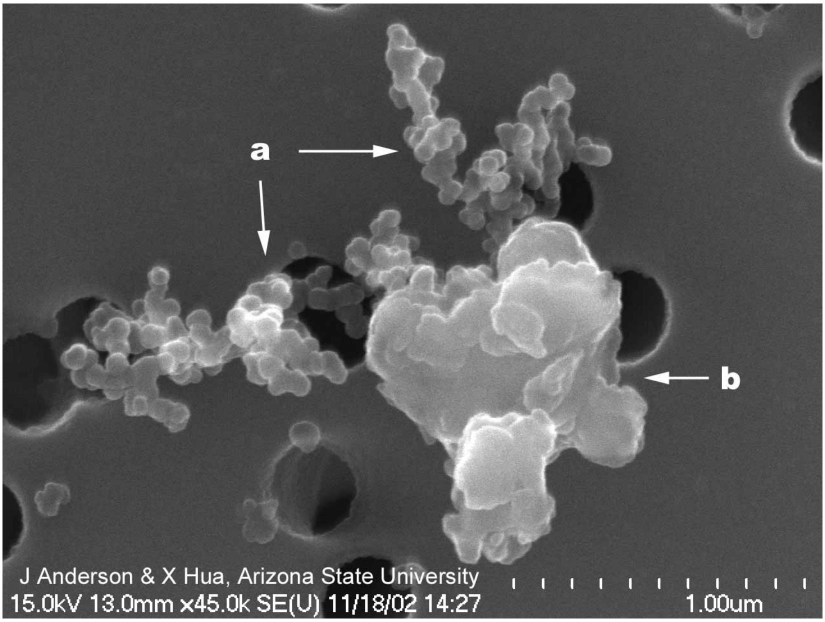
Chapter IV also provides a summary of detailed measurements (at four sites in El Paso and four in Ciudad Juárez) of the spatial and temporal distribution of four trace elements (copper, lead, chromium, and arsenic) in airborne particles for 1994, 1995, and 1996. The data, selected to represent low-wind conditions that emphasize local emissions, show concentrations an order of magnitude higher in the winter and fall compared to the spring and summer; for a given season, up to an order of magnitude variation in concentration between sites was detected. The seasonal trends are attributed to the prevalence of inversions in winter and the differences between sites and local sources.

The concentration of toxic metals in the top layers of soil provide an integration of the historical air deposition patterns, as described in Chapter V. Although current air pollution levels comply with standards, the soil concentrations can reach levels of concern because of the possibility of resuspension, a phenomenon in which settled particulates become airborne again. This is evident in the detailed mapping of the concentrations in top soils proximal to current and former smelting and refining operations. Levels of arsenic and lead in the topsoil exceed 5,000 parts per million (ppm) in several locations. In addition, for purposes of providing data for community studies, detailed mapping of the pollutants covering the cities and surrounding areas of El Paso and Ciudad Juárez are under way. These show, as expected, decays in the concentrations of toxic metals with increasing distance from the heavily populated downtown areas. Two hot spots in outlying areas located northwest and east of downtown El Paso were attributed to local industry and an area of heavy concentration of vehicular and locomotive transportation.

The distribution of the lead, arsenic, copper, and chromium in Paso del Norte shows a historical record of emissions of these metals by the smelting industry and by automotive sources using leaded gasoline. Current ambient concentrations and their temporal and spatial distributions can similarly be related to emission sources. For example, morning PM peaks are attributed to traffic, and evening peaks to wood burning and home cooking. High particulate levels at the Misión air quality monitoring site can be attributed to wood stoves, unpaved roads, and kerosene heaters while those at the Advanced Transformer site can be attributed to the unique mixtures of emission sources in the immediate vicinity (brick kilns, automobiles, unpaved roads, and industrial sources).

Insights on the sources of PM are provided by single particle characterization (Chapter IV). An example of how single particles can be used to show dominant classes of particles is provided in Figure 1, which shows (a) soot particles representative of combustion sources and (b) a clay particle representative of crustal matter. Particle shape and composition also provide signatures for the sources of particles. For example, soot particles form distinct branched chain aggregates of primary, approximately spherical particles 20 nanometers (nm) to 60 nm in size. Soot is produced solely by combustion processes. Trace inorganic constituents in soot can provide an indication of the source of these particles, with calcium and sulfur being indicative of diesel sources and potassium being indicative of biomass, among other sources. Chapter IV categorized PM in Paso del Norte as soot, spherical, cubical, irregularly shaped, or cumulus inorganic. The differences in the relative abundance of these particles were determined at the Chamizal, Sun Metro, and Club 20-30 air quality monitoring sites. Geological elements (aluminum, silicon, calcium, iron, titanium, and potassium) are found in higher concentrations in $PM_{2.5-10}$ than $PM_{2.5}$, as would be expected because larger particles are formed from mechanical operations (such as quarrying) and in base soil while sub-micron sized particles are formed predominantly by the pyrosynthesis processes common to the combustion and smelting processes. A low concentration of particles containing geological elements in the central Ciudad Juárez site is consistent with the remoteness of the site from unpaved roads and crustal matter. Currently, single-particle studies are used to identify classes of particles from dominant sources but are not used in source apportionment studies because of the cost of obtaining the statistically significant numbers of particles that would be needed for quantification.

Figure 1. Scanning Electron Microscopy Images from April 22, 2002, Aerosol Samples



Note: The figure shows (a) soot particles and (b) a clay particle.
Source: James Anderson

Chapter VI provides the results of the scoping studies conducted in 1998 and 2001. The methodology is based on the detailed analysis of the organic compounds in PM samples to identify sources, a methodology that therefore excludes consideration of crustal matter, except where it becomes associated with organic contaminants such as those in road dust. A source pattern library was assembled for 57 compounds from 11 sources—seven obtained from the literature and four from border-characteristic sources (brick kilns, trash burning, a diesel power plant, and a cookout—characterizations obtained by SCERP researchers). Source apportionment was conducted using a chemical mass balance model (CMB) that employs a variance-weighted list of compounds to characterize a source or statistical methods such as principal component regression (PCR) using a wider range of compounds. The statistical methods have the advantage over CMB of being able to identify missing sources. Representative results from the 2001 study are shown in Tables 2 and 3 and were obtained using CMB and PCR. These parallel the 1998 findings. The general trends shown by the results from CMB and PCR are similar but there are significant differences, particularly in the breakdown between gasoline and diesel automotive emissions. Diesel and gasoline contributions are difficult to resolve because of the similarities in their source profiles, and therefore the CMB and PCR models generate such different results. Many of the compounds in diesel and gasoline engine exhaust are the same—the emissions from one can easily be mistakenly characterized as the other. One can, therefore, have a high confidence in their sum but less confidence in their separate contributions. The results from PCR are considered more reliable.

Despite the proximity of the Mexican and U.S. sites, there are some distinct differences in the sources of the PM, with automotive sources being more prevalent at U.S. sites and the burning of unconventional fuels in brick kilns and trash burning more prevalent at Mexican sites. The absence of natural sources in the source apportionment results in Tables 2 and 3 contrasts sharply with the emission inventories referred to in Table 1. This is attributed to two factors. First, the use of organic markers in the source apportionment studies excludes most natural sources. Second, natural sources contribute primarily to the larger particles and do not show up in high concentrations in $PM_{2.5}$. The thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) methodology that has been developed by SCERP researchers permits the chemical analysis of small samples, thus enabling the application of the source apportionment methodologies to samples obtained in a two-hour period. This has resulted in time-resolved measurements (Figure 5, Chapter VI) that show a major increase in tire and road dust during the evening PM peak, proving the utility of TD-GC/MS in identifying the source of the contaminants in the episodic events.

Table 2. Source Apportionment Results Obtained using PCR for Samples from 12 Receptor Sites (see Figure 4, Chapter VI)

Source Category	% Contribution in El Paso	% Contribution in Ciudad Juárez
Automotive, gasoline	16.7	24.7
Automotive, diesel	29.4	3.4
Kilns and trash burning	19.1	30.9
Biomass combustion	11.7	12.5
Cooking	9.1	11.9
Road dust	12.3	12.2
Oil gas	1.7	4.3

Note: Due to number rounding, percentages may not add up to 100.
Source: Authors

Table 3. Source Apportionment Results Obtained from CMB for Samples from 12 Receptor Sites (see Figure 4, Chapter VI)

Source Category	% Contribution in El Paso	% Contribution in Ciudad Juárez
Automotive, gasoline	34.8	12.7
Automotive, diesel	13.7	9.4
Kilns and trash burning	14.5	28.2
Biomass combustion	15.8	28.3
Cooking	7.0	9.2
Road dust	12.1	11.4
Oil gas	2.0	10.8

Note: Due to number rounding, percentages may not add up to 100.
Source: Authors

Finally, Chapter VII brings the data on PM and meteorological monitoring by TCEQ, geographic information system (GIS)-referenced socioeconomic and geographic data, and selected regional mortality and morbidity studies together with the scoping source apportionment and particulate transport models. This provides preliminary conclusions on the health effects of elevated concentrations of PM in the Paso del Norte airshed. A distinguishing feature of border-related particulate problems is transient, primarily evening peaks, with PM_{10} levels sometimes exceeding 1,000 micrograms per cubic meter ($\mu g/m^3$). These episodic peaks are:

- Particularly evident in the periphery of metropolitan areas
- A result of drainage flows that re-aerosolize urban dust
- Distinguishable from crustal matter by the presence of dehydroabietic acid
- Often distinctively visible as a low cloud drifting down slopes (Figure 2)
- Coincident with low winds

Figure 2. Morning Dust Cloud

Notes: This cloud is typical in the winter months when a nocturnal inversion persists into daylight hours. The photo was taken at 9:45 a.m., on November 21, 2002.
Sources: M. Anderson, J. Anderson, and M. Quintero

The leading edge of these clouds is rich in automotive emissions and followed by a heterogeneous mix of resuspended road dust, wood smoke, and products of waste combustion. At the Sodar air quality monitoring site, the low winds are from a south to south-south-west direction, originating in the Ciudad Juárez metropolitan area. These low-wind episodes have been simulated by Arizona State University using the MM5 mesoscale model and occur twice as a result of flow reversal at dusk.

Societal risk to the particulate concentration was evaluated from the GIS data on population distribution for children and adults and PM_{10} concentration distributions resolved to a 1 km x 1 km grid size by mass-balance-based interpolation from the monitored PM data. The maps of social risk in Paso del Norte (Appendix Figures 5a and 5b [pages 309 and 310]) show the highest values in the densely populated regions in south/south-west regions of Ciudad Juárez.

Preliminary studies were conducted to evaluate the literature reports that short-term exposure to high PM levels may be associated with a host of physiological and pathological responses, ranging from minor changes in cardiovascular or pulmonary performance to life-threatening asthma attacks or allergic reactions. Based on these reports, the extreme PM events at the U.S.-Mexican border are of concern. A pilot experiment was conducted in the vicinity of the Sodar site between March 28 and April 23, 2002. The pilot-study involved measurement of PM, measurement and modeling of drainage flows, and time-resolved cardiac (electrocardiography) and pulmonary (spirometry) functions in five relatively healthy young adults. Time-series experiments in which each subject serves as his or her own control were conducted in a manner so that statistically significant results could be obtained with 10 measurements. The subjects were exposed to high and low PM episodes in surroundings where they could not see the changes in ambient conditions. High winds during the test period gave fewer high PM episodes than would have been desired. The data from two time series of a subject were merged to provide at least 17 measurement points. For one of the five subjects (a 25-year overweight male in relatively poor physical condition), the electrocardiograph results showed a strong association (R^2 = 81%, $p < 2.2\%$) with PM_{10} and a strong correlation (R^2 = 90.9%, $p < 0.1\%$) with $PM_{2.5}$. The spirometry data were found to correlate, but less strongly, with $PM_{2.5}$ (R^2 = 83.4%, $p < 0.3\%$) and PM_{10} (R^2 = 60.7%, $p < 12.4\%$). The data further suggest that the physiological responses were rapid (much less than 30 minutes). The results on the other four subjects showed much smaller responses and are still under study.

The episodic high peaks of particulate matter provide opportunities for establishing causality between adverse health effects and particulate matter that are more robust than those determined from epidemiological studies. The pilot study showed the potential health effect of the episodic peak PM events at the border. A much broader study is needed involving both healthy individuals and specific at-risk groups.

SCERP has developed the capacity for measuring and modeling particulate concentrations, determining their principal sources, and determining health risks posed by high particulate levels and concentrated deposits from past emissions on human health. These capabilities can be used to help decision-makers and funding agencies decide on and prioritize strategies for improving air quality by showing which populations are at risk and which sources should be controlled. The model development and source emission inventories can also establish how control strategies will need to be modified in the future to take into account different scenarios for changing demographics, patterns of industrial development, vehicle miles traveled, and pollution-abatement technologies.

Resumen Ejecutivo

En la cuenca atmosférica Paso del Norte y el área compuesta por El Paso, Texas; Ciudad Juárez, Chihuahua; y el condado de Doña Ana, Nuevo México, es posible una mayor comprensión de la contaminación del aire a través del desarrollo de las capacidades para monitorear la contaminación de aire por partículas, la determinación de fuentes de materia particulada (PM), y la valoración en la salud humana de los efectos de niveles elevados de la materia particulada. En 1999, el Consorcio de Investigación y Política Ambiental del Suroeste (CIPAS), un grupo de 10 universidades que estudia el medio ambiente en la frontera México-E.U., instituyó un proyecto piloto para lograr estos resultados. El resultado de ese proyecto comprende esta monografía.

Varias características distinguen al Paso del Norte de otras cuencas atmosféricas. Su clima árido conlleva a altas concentraciones de polvo de carretera resuspendido y de origen rocoso, particularmente bajo condiciones de vientos fuertes. La topografía produce flujos descendentes de las montañas circundantes, lo cual a su vez contribuye con incrementos nocturnos de la carga ambiental de partículas. La región tiene una combinación única de fuentes de emisión de partículas, hornos de ladrillo, refinería, fundición, fundiciones de desechos de metal, maquiladoras, generadoras de electricidad, y excavaciones. Las fuentes tradicionales de emisión de partículas, como los motores de combustión interna, tienen una característica local distintiva que refleja la mezcla de vehículos y factores de emisión en la frontera y los puntos críticos resultantes de la densidad alta de vehículos encendidos y sin movimiento en los cruces fronterizos. La morbilidad y la mortalidad son superiores al promedio de los E.U. y se sospecha que están relacionadas con la contaminación atmosférica. Finalmente, diferentes jurisdicciones y regulaciones de contaminación del aire, así como también una población con crecimiento rápido, particularmente en el lado mexicano de la frontera, afectan la habilidad para controlar los impactos negativos en la calidad de aire. El capítulo I describe en forma detallada estas y otras características de la cuenca atmosférica.

La naturaleza dinámica de la contaminación del aire en la frontera es una consecuencia de la demografía cambiante y las fuentes de contaminación del aire. Estos cambios subrayan la necesidad de redes de monitoreo que pueden usarse para seguirlos y de modelos que pueden utilizarse para anticipar problemas futuros y guiar estrategias de control. Los resultados en esta monografía se suman a los estudios previos resumidos al final de Capítulo I.

El control de las concentraciones ambientales de PM es complicado debido a la multiplicidad de fuentes de ambas partículas (emisiones primarias) y precursores de partículas tales como óxidos de nitrógeno (NO_x), óxidos de azufre (SO_x), amoníaco (NH_3), y compuestos orgánicos volátiles (VOCs), los cuáles experimentan transformaciones atmosféricas para formar nitratos particulados, sulfatos, y orgánicos condensables (partículas secundarias). El desarrollar inventarios de las emisiones de partículas primarias y precursores de partículas es importante porque esa información puede usarse para guiar estrategias de control de emisiones. Los inventarios son también importantes para el desarrollo de modelos de calidad del aire para la predicción de variaciones temporales y espaciales de partículas aerotransportadas.

El capítulo II provee un compendio de estudios de inventarios de emisiones realizados para las áreas del norte de México, con énfasis en los 100 kilómetros (km) que constituyen la región fronteriza del norte de México. Estos inventarios incluyen datos para otras ciudades y municipios aparte de Ciudad Juárez. La Tabla 1 es una guía para la información del Capítulo II, gran parte de ella resumida de los reportes de fuentes mexicanas de emisión que son difíciles de encontrar en los Estados Unidos. Los resultados para El Paso están documentados en el sitio Web de la Comisión de Texas para Calidad Ambiental (TCEQ) (http://www.tceq.state.tx.us/nav/data/) la cual provee información de las tendencias en emisiones basándose principalmente en encuestas respondidas por diferentes industrias. Un inventario de emisiones de 1996 provee estimaciones de emisiones para ambos El Paso y Ciudad Juárez. Estos muestran que las emisiones anuales de partículas para Ciudad Juárez de PM midiendo 10

Tabla 1. Resumen de Datos de Factores de Emisión e Inventarios de Emisión en el Capítulo II

Información Proporcionada	Metodología o Fuente	Compuesto	Ubicación	Comentarios	Ubicación en el Capítulo II
Factores de emisiones móviles diferentes clases de vehículos	Móvil-Juárez, Móvil 5A	VOCs, NO_x, CO	Ciudad Juárez por diferentes clases de vehículos	Factor de Emisión en Ciudad Juárez > U.S.	Figura 2
Porcentaje promedio de factores de emisiones móviles de flotas	Móvil5-México		Ciudad Juárez (J); Aguascalientes (A); Ciudad de México (M); Denver (D)	Factores de Emisión J = ~ A > M > D	Figura 3
Potencial para la reducción de emisiones en los cruces fronterizos	Móvil5-Juárez	VOC, CO, NO_2, PM	San Diego, Nogales, El Paso, Laredo	Reducción Potencial ~ 6 Mg/día (El Paso/Ciudad Juárez)	Figura 5
EI: Punto, Área, Móvil, Natural	Inventarios Regionales de Planeación de la Calidad del Aire	NO_x, SO_x, VOC, CO, PM_{10}, NH_3	Monterrey, Ciudad Juárez, Tijuana, Mexicali	PM10 est. Ciudad Juárez ~ 45,100 Mg/año Natural, ~ 1,500 Antropogénica	Tabla 2
EI: Punto, Área, Móvil, Biogénico	Inventario de HAPs para ADEQ	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, HAPs	Nogales, Agua Prieta		Tabla 3
EI: Punto, Área, Móvil, Biogénico	Estudio de Ozono del Paso del Norte de 1996	NO_x, VOC, CO	Paso del Norte	Tabla 2 a mayor detalle (Capítulo II) incluyendo PM	Tabla 4
EI: Punto, Área, Móvil, Natural	SCOS97-NARSTO	NO_x, SO_x, TOG, CO, PM	Norte de Baja California	Fuentes de PM (Mg/día) ~ 11 puntos, 376 área, 2 móvil	Tabla 5
EI: Punto, Área, Móvil	Estudio BRAVO	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, NH_3	Seis estados del norte	Emisiones Agregadas (Mg/año) ~648,000 PM_{10}, ~ 229,000 $PM_{2.5}$	Tabla 6
EI: Point, Área, Móvil, Natural	TCEQ	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$	Ciudad Juárez	Desglose detallado de clases de fuentes de área	Tabla 7
EI: Punto, Área, Móvil, Natural	Fuentes múltiples identificadas en el Capítulo II	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, NH3	Seis estados mexicanos fronterizos	Estimaciones para Chihuahua (Mg/año) ~ 135,000 PM_{10}, ~42,000 $PM_{2.5}$	Tabla 8
EI: Antropogénico, Punto, Área, Móvil	Inventario Nacional Mexicano Preliminar de Emisiones	NO_x, SO_x, VOC, CO, PM_{10}, $PM_{2.5}$, NH_3	Seis estados mexicanos fronterizos	Emisiones Antropogénicas (Mg/año) ~ 837,000 PM_{10}, ~ 303,000 $PM_{2.5}$	Tabla 9

Fuente: Los autores

micras o menos de diámetro aerodinámico (PM_{10}) (46,606 toneladas o 42,300 mega gramos [Mg]) es aproximadamente tres veces que las de El Paso (15,510 toneladas o 14,100 Mg), y que los contribuyentes principales por mucho para ambas ciudades fueron las carreteras sin pavimento. La Tabla 2 en el Capítulo II también provee estimaciones de 1996 de un número de fuentes antropogénicas que están dominadas por fuentes móviles, consumo de gasolina y proceso de metales.

Los resultados para Ciudad Juárez reportados en la Tabla 1 apoyan el hallazgo de que las carreteras sin pavimento son el contribuyente dominante de las emisiones. También hace claras las siguientes generalizaciones adicionales:

- Los factores de emisión para automóviles mexicanos son más altos que los de Estados Unidos, reflejando que la edad promedio de carros en circulación es mas grande y que una proporción alta de ellos no están registrados o con mantenimiento
- Existe potencial para una reducción significativa en emisiones automotoras a través de una reducción de la congestión del tráfico en cruces fronterizos
- Fuentes Antropogénicas incluyen emisiones significativas de fuentes específicas de la frontera como hornos de ladrillo, quema de basura residencial y quemas de desechos agrícolas a cielo abierto
- Los inventarios de emisiones en la frontera han sido obtenidos para estudios específicos relacionados con el ozono y la visibilidad

La región necesita un enfoque más sistemático de las fuentes afectando su calidad de aire para el desarrollo de inventarios de PM. Estos inventarios deberán usar los límites impuestos por la topografía de la región –no así los de jurisdicciones políticas- como guía para su inclusión. A pesar de las diferencias en las normas y recursos a través de la frontera, un número de acuerdos binacionales relacionados con los problemas ambientales en la frontera, han ayudado al progreso en la recopilación de información para el desarrollo de los inventarios (ver Capítulo I).

Los inventarios de emisiones en condiciones ideales están sujetos a incertidumbres significativas debido a las dificultades para obtener una lista completa de fuentes, factores de emisiones representativos de todas las fuentes, y patrones precisos de las actividades. Los inventarios de emisiones son complementados por medidas ambientales de PM que pueden usarse para refinar los valores de emisión comparando las concentraciones de partículas ambientales con aquellas calculadas de inventarios de emisiones y modelos de transporte, o identificando fuentes de emisión a partir de las concentraciones y composiciones químicas de partículas ambientales usando metodologías de identificación de fuentes. Además, los estudios de microscopía electrónica de muestras ambientales pueden identificar fuentes a partir de las características morfológicas únicas de muchas partículas y puede detectar fuentes que de otra manera podrían no ser consideradas.

Los Capítulos III, IV, y V describen medidas de campo y datos seleccionados en PM_{10}, PM midiendo 2.5 micrómetros en diámetro aerodinámico ($PM_{2.5}$), morfología de partículas y composición. Estos datos son útiles para establecer el cumplimiento con normas y para mostrar tendencias asociadas con patrones climáticos y estacionales. Sin embargo, una razón fundamental para llevar a cabo los estudios, fue el desarrollar modelos que relacionan los receptores con las fuentes (Capítulo VI) y la salud humana con la exposición a concentraciones altas de partículas (Capítulo VII).

Una red de muestreo está disponible para El Paso y Ciudad Juárez que provee datos históricos de calidad de aire para cada hora (http://www.tnrcc.state.tx.us/cgi-bin/monops/particulates). Los registros de PM son más recientes y no se encontraban aún publicados para Ciudad Juárez cuándo este volumen fue publicado. Además, como parte de los esfuerzos de construcción de capacidades en la frontera, la Universidad de Texas en El Paso (UTEP) ha establecido una red para tomar muestras, en paralelo con el estado, que pueden utilizarse para estudios puntuales. Tal estudio fue realizado del 3 de enero al 7 de marzo, 2000, en dos sitios de muestreo en El Paso y tres en Ciudad Juárez. Estos resultados, resumidos en el Capítulo III, han sido usados para realizar comparaciones entre diferentes métodos de medición de partículas y generalizaciones del impacto de la hora del día, la estación, ubicación, y patrones climáticos en $PM_{2.5}$ y PM_{10}. Los resultados muestran las tendencias siguientes:

1. La proporción de $PM_{2.5}$:PM_{10} está en el rango de 0.16 a 0.36, con los valores reflejando cambios en la localidad y velocidad del viento; La proporción decrece con incrementos de polvo rocoso suspendido o polvo de la carretera en áreas rurales, o con incrementos en la velocidad del viento. $PM_{2.5}$ provee una medida de partículas de importancia mayor para los impactos en la salud y partículas dominadas por fuentes de combustión. El PM_{10} es más una medida de material rocoso fragmentado suspendido por vientos fuertes o producido por operaciones de trituración y molido.
2. Ambos $PM_{2.5}$ y PM_{10} muestran valores máximos diurnos matutinos y vespertinos, siendo los picos de la noche particularmente marcados. Estos picos corresponden a periodos de estancamiento relativo y la inversión de flujos en las pendientes que rodean el Paso del Norte. Los cambios diurnos en la concentración de PM se reflejan a menudo con variaciones marcadas en la visibilidad.
3. Ambos $PM_{2.5}$ y PM_{10} exhiben valores mayores en velocidades de viento bajas (<~2m/s) y altas (>~8 m/s). Los valores altos de PM en velocidades de viento bajas, están asociados con el estancamiento atmosférico, durante el cual las emisiones locales se acumulan, y las tormentas de polvo están relacionadas con velocidades altas de viento.
4. Ambas concentraciones $PM_{2.5}$ y PM_{10} son superiores en el invierno que en verano (ver también el Capítulo V), correlacionadas con el predominio de las inversiones en invierno como consecuencia de las bajas temperaturas superficiales.
5. Las amplias variaciones en concentraciones de PM entre sitios (dos en El Paso y tres en Ciudad Juárez) destacaron la importancia de la variabilidad de las fuentes locales.
6. Las composiciones de las partículas gruesas ($PM_{2.5\text{-}10}$) y finas ($PM_{2.5}$) son presentadas para las cinco localidades. Las composiciones de la fracción de partícula gruesa tuvieron concentraciones relativamente altas de elementos geológicos (aluminio, silicio, calcio, hierro, titanio, y potasio). En con-

traste, las áreas como el centro de Ciudad Juárez, con una fracción baja de carreteras si pavimentar y localizada lejos de material rocoso expuesto, mostraron una concentración relativamente baja de elementos rocosos.

El capítulo III provee una perspectiva histórica de cómo las concentraciones de elementos traza disminuyeron notablemente en el período de 1990 al 2000. El arsénico disminuyo 57 veces y el plomo 18 veces. Información adicional sobre las tendencias de largo plazo de elementos tóxicos en partículas aerotransportadas es proporcionada en el Capítulo V a partir del análisis de muestras archivadas desde el año 1977. El capítulo muestra las disminuciones dramáticas en concentraciones y las razones para estas, de manera más notable el control de plomo en la gasolina empezando en los Estados Unidos en 1973 y en 1998 en México, el declive de la industria de fundición, y el aumento restrictivo de la legislación de contaminación del aire. Las concentraciones ambientales de metales tóxicos ya no violan normas actuales de contaminación del aire.

El Capítulo V también provee un resumen de mediciones detalladas (en cuatro sitios en El Paso y cuatro en Ciudad Juárez) de la distribución espacial y temporal de cuatro elementos traza (cobre, plomo, cromo, y arsénico) en partículas aerotransportadas para los años 1994, 1995, y 1996. Los datos, seleccionados para representar condiciones de viento escaso que enfatizan emisiones locales, muestran a las concentraciones un orden de magnitud más alto en el invierno y otoño en comparación con la primavera y el verano; para una estación determinada del año, fue detectado hasta un orden de magnitud en la variación de la concentración entre sitios. Las tendencias estacionales son atribuidas al predominio de inversiones (las condiciones en las cuales el aire frió y los contaminantes de aire son atrapados cerca de la tierra por aire superior más caliente) en el invierno y las diferencias entre sitios y fuentes locales.

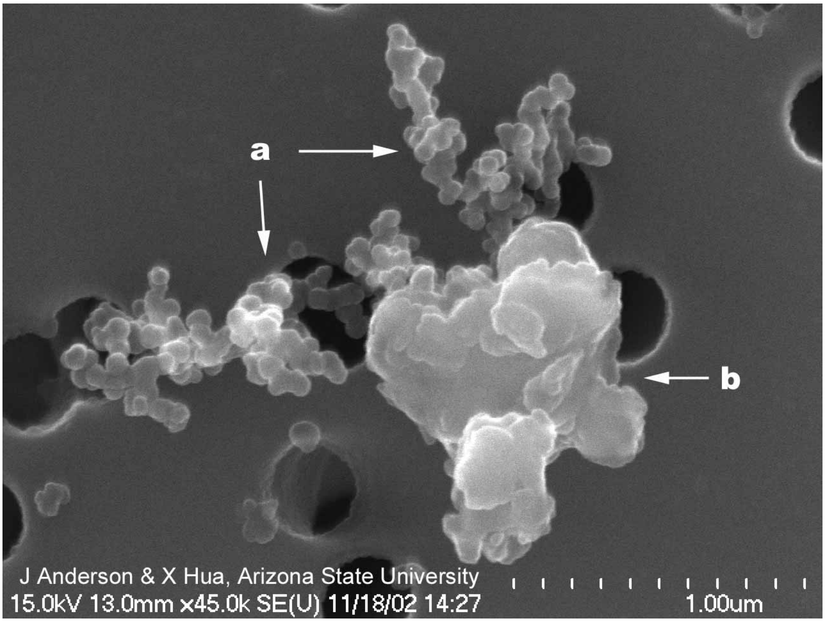
La concentración de metales tóxicos en los estratos superiores del suelo provee una integración de los patrones históricos de depositación, como se describen en el Capítulo V. Aunque los niveles actuales de contaminación del aire cumplen con las normas, las concentraciones del suelo pueden alcanzar niveles preocupantes por la posibilidad de resuspensión. Esto es evidente en el mapeo detallado de las concentraciones en los suelos superficiales próximos a terrenos con actividades históricas o presentes de fundición y procesamiento. Los niveles de arsénico y plomo en la capa superior del suelo exceden las 5,000 partes por millón (ppm) en varias localidades. Además, para el propósito de proveer datos para los estudios de la comunidad, un mapeo detallado de los contaminantes cubriendo las ciudades y los contornos de El Paso y Ciudad Juárez está en proceso. Estos muestran, como era esperado, disminución en las concentraciones de metales tóxicos a distancias mayores de las áreas altamente contaminadas del centro urbano. Dos puntos críticos en áreas alejadas del centro localizadas al Este y Noroeste del centro de la ciudad de El Paso fueron atribuidos a la industria local y a un área de alta concentración de transporte vehicular y de locomotores.

La distribución de plomo, arsénico, cobre, y cromo en el Paso del Norte muestra un record histórico de emisiones de estos metales por fuentes automotoras que usan gasolina y por la industria pirometalúrgica. Concentraciones ambientales actuales, y sus distribuciones temporales y espaciales, pueden estar relacionadas de modo semejante a las fuentes de emisión. Por ejemplo, los picos matutinos de PM están relacionados con el tráfico y los de la tarde a la quema de madera y cocina casera. Los altos niveles de partículas en el sitio de monitoreo de calidad de aire en la Misión pueden ser atribuidos a estufas de madera, carreteras sin pavimentar, y calentadores de petroleo, mientras que aquellos en el sitio del Transformador Avanzado pueden ser atribuidos a las mezclas especiales de fuentes de emisión en las afueras inmediatas (hornos de ladrillo, automóviles, carreteras sin pavimentar, y fuentes de industriales).

Información sobre las fuentes de PM es proporcionada en la caracterización por partículas (Capítulo IV). Un ejemplo de cómo partículas individuales pueden usarse para mostrar clases dominantes de partículas es provisto en la Figura 1, la cual muestra (a) partículas de hollín representativas de fuentes de combustión y (b) una partícula de arcilla representativa de material rocoso. La forma de la partícula y su composición también proporcionan señales sobre las fuentes de las partículas. Por ejemplo, las partículas de hollín forman agregados de cadenas de partículas primarias aproximadamente esféricas de 20 nanómetros (nm) a 60 nm en tamaño. El hollín es producido solamente por procesos de combustión. Componentes de rastros inorgánicos en el hollín pueden proveer una indicación de la fuente de estas partículas, con calcio y azufre siendo indicativos de fuentes de diesel y el potasio indicativo de biomasa, etc. El capítulo IV ha clasificado la PM observada en el Paso del Norte en categorías de hollín, esférico, cúbico, de forma irregular, y cúmulos inorgánicos. Las diferencias en la abundancia relativa de estas partículas fueron determinadas en los sitios de control de calidad del aire en El Chamizal, Sun Metro, y Club 20-30. Los elementos geológicos (el aluminio, silicón, calcio, hierro, titanio, y potasio) son encontrados en concentraciones superiores en $PM_{2.5-10}$ que en $PM_{2.5}$, como se esperaría debido a que las partículas mayores son formadas de operaciones mecánicas (como excavar) y en terreno bajo mientras que las partículas de tamaño sub-micrón se forman predominantemente por los procesos de pirosíntesis comunes para la combustión y los procesos pirometalúrgicos. Una concentración baja de partículas conteniendo elementos geológicos en el sitio central de Ciudad Juárez es consistente con la lejanía del sitio de carreteras sin pavimentar y materia rocosa. Actualmente, el estudio de partículas aisladas es usado para identificar clases de partículas de fuentes dominantes pero no son usados en los estudios de prorrateo de fuentes debido al costo de obtención de números estadísticamente significativos de partículas que serían necesarias para la cuantificación.

El capítulo VI provee los resultados de los estudios de sondeo llevadas a cabo en 1998 y 2001. La metodología se basa en el análisis detallado de los compuestos orgánicos en muestras de PM para identificar fuentes, una metodología que por consiguiente excluye la consideración de la materia rocosa, excepto donde se asocia con contaminantes orgánicos como los del polvo de la carretera. Una biblioteca de patrones de fuentes fue creada para 57 compuestos de 11 fuentes -siete obtenidas de la literatura, y cuatro de fuentes relacionadas con la frontera (hornos de ladrillo, quema de basura, una planta eléctrica diesel, y una cocina al aire libre- obtenidas por investigadores CIPAS). El prorrateo de las fuentes fue dirigido usando un modelo químico de balance de masas (CMB) que utiliza una lista de varianza ponderada de compuestos para caracterizar una fuente o métodos estadísticos como la regresión de componentes

Figura 1. Imágenes Microscopio Electrónico de Barrido de Abríl 22, 2002, Muestras de Aerosol



Notas: El sitio se encuentra 200 metros al norte de la frontera México-E.U. La figura muestra (a) partículas de hollín y (b) una partícula de arcilla.
Fuente: James Anderson

principales (PCR) usando un rango más amplio de compuestos. Los métodos estadísticos tienen la ventaja sobre el balance químico de masas por ser capaces de identificar fuentes faltantes. Resultados representativos del estudio 2001 son presentados en las Tablas 2 y 3 y fueron obtenidos usando CMB y PCR. Estos son paralelos a los descubrimientos de 1998. Las tendencias generales mostradas por los resultados de CMB y PCR son similares pero hay diferencias significativas, particularmente en la separación de las emisiones automotoras de gasolina y diesel. Las contribuciones de diesel y gasolina son difíciles de resolver debido a las similitudes en sus perfiles de fuentes, y por consiguiente los modelos CMB y PCR generan resultados tan diferentes. Los resultados de RCP son considerados más confiables.

A pesar de la proximidad de los sitios en la frontera México-E.U. existen algunas diferencias distintivas en las fuentes de PM, siendo las fuentes automotoras más importantes en sitios de E.U. y la quema de combustibles poco convencionales en hornos de ladrillo y la quema de basura más importantes en sitios mexicanos. La ausencia de fuentes naturales en el prorrateo resultante de fuentes mostrados en las Tablas 2 y 3 está fuertemente contrastada con los inventarios de emisiones a las que se hace referencia en la Tabla 1. Esto es atribuido a dos factores: El uso de marcadores orgánicos en los estudios de prorrateo de fuentes excluye la mayoría de las fuentes naturales, y las fuentes naturales contribuyen primordialmente con partículas mayores y no aparecen en concentraciones altas de $PM_{2.5}$. La metodología de desorción termal-cromatografía de gases/espectrometría de masas (TD-GC/MS) que ha sido desarrollada por investigadores CIPAS permite el análisis químico de muestras pequeñas, permitiendo el uso de las metodologías de prorrateo de fuentes para muestras obtenidas en un período de dos horas. Esto ha resultado en medidas resueltas temporalmente (Figura 5, Capítulo VI) que muestran un incremento mayor de polvo durante el pico de PM de la tarde, probando la utilidad de TD-GC/MS en la identificación de fuentes de contaminantes en los eventos episódicos.

Finalmente, el Capítulo VII proporciona los datos de monitoreo meteorológico por TCEQ y de PM, el sistema de información geográfico (GIS) con referencias de datos socioeconómicos y geográficos, y estudios seleccionados de mortalidad y morbilidad conjuntamente con los modelos de sondeo de fuentes prorrateadas y de transporte de partículas. Esto aporta conclusiones preliminares de los efectos en la salud de las concentraciones elevadas de PM en la cuenca atmosférica del Paso del Norte. Un rasgo distintivo de problemas relacionados con partículas en la frontera es el de los valores altos al atardecer, con niveles del PM_{10} algunas veces excediendo los 1,000 microgramos por metro cúbico ($\mu g/m^3$). Estos picos episódicos son:

- Particularmente evidentes en la periferia de las áreas metropolitanas
- Resultado de flujos de drenaje que re-aerosolizan el polvo urbano

Tabla 2. Resultados de prorrateo de fuentes obtenidas usando PCR para muestras de 12 sitios receptores (ver figura 4, Capítulo VI)

Categoría de la Fuenta	% Contribución en El Paso	% Contribución en Ciudad Juárez
Automovilístico, gasolina	16.7	24.7
Automovilístico, diesel	29.4	3.4
Hornos y quemado de basura	19.1	30.9
Combustión de Biomasa	11.7	12.5
Cocina	9.1	11.9
Polvo de la calle	12.3	12.2
Gasolina de petróleo	1.7	4.3

Nota: Debido a cómo estaban redondeados los números, los porcentajes pueden no sumar hasta 100.
Fuente: Los autores

Tabla 3. Resultados de prorrateo de fuentes obtenidas de muestras CMB de 12 sitios receptores. (ver a Figura 4, Capítulo VI)

Categoría de la Fuenta	% Contribución en El Paso	% Contribución en Ciudad Juárez
Automovilístico, gasolina	34.8	12.7
Automovilístico, diesel	13.7	9.4
Hornos y quemado de basura	14.5	28.2
Combustión de Biomasa	15.8	18.3
Cocina	7.0	9.2
Polvo de la calle	12.1	11.4
Gasolina de petróleo	2.0	10.8

Nota: Debido a cómo estaban redondeados los números, los porcentajes pueden no sumar hasta 100.
Fuente: Los autores

- Distinguibles de la materia rocosa por la presencia de ácido dihidroabietico
- A menudo distinguibles visualmente como una nube baja deslizándose cuesta abajo (Figura 2)
- Coincidentes con vientos bajos

Figura 2. Nube Matutina de Polvo

Notas: Esta nube es típica en los meses de invierno cuando una inversión nocturna persiste hasta horas del día. La foto fue tomada a las 9:45 a.m., el 21 de noviembre, 2002, mirando al este-sureste del Cochise Collage hacia Douglas-Agua Prieta.
Fuentes: M. Anderson, J. Anderson, y M. Quintero

El filo delantero de estas nubes es rico en emisiones automotoras y seguidas por una mezcla heterogénea de polvo de carretera resuspendido, humo de madera, y productos de combustión de desechos. En la estación de monitoreo de calidad del aire Sodar, los vientos bajos son de una dirección sur a sur-sur-oeste, originándose en el área metropolitana de Ciudad Juárez. Estos episodios de vientos bajos han sido simulados por la Universidad del Estado de Arizona usando el modelo mesoescala MM5 y ocurren dos veces como resultado del cambio del sentido del flujo al atardecer.

El riesgo de la sociedad a la concentración de partículas fue evaluado de los datos GIS de la distribución poblacional para niños y adultos y las distribuciones de concentración PM_{10} resueltas para una cuadrícula de 1 km x 1 km de tamaño por interpolación de balance de masas basada de los datos monitoreados de PM. Los mapas de riesgo social en el Paso del Norte (Apéndice Figuras 5a y 5b [paginas 309 y 310]) muestran los valores más altos en las regiones altamente pobladas en el sur/sur-oeste de Ciudad Juárez.

Estudios preliminares fueron dirigidos para evaluar los reportes de literatura que demuestran que la exposición de corto plazo para niveles PM altos puede ser asociada con gran cantidad de respuestas fisiológicas y patológicas, yendo desde cambios menores en rendimiento cardiovascular o pulmonar hasta ataques de asma o reacciones alérgicas que podrían amenazar la vida. Basado en estos reportes, los acontecimientos extremos de PM en la frontera México-E.U. son de preocupación. Un experimento piloto fue dirigido en la vecindad del sitio Sodar entre el 28 de marzo y 23 de abril, 2002. El estudio piloto implicó la medición de PM, modelado y medición de flujos de drenaje, y funciones cardiacas (electrocardiografía) y pulmonares (espirometría) en cinco adultos jóvenes relativamente saludables. Los experimentos de las series de tiempo en los cuales cada sujeto sirve como su propio control, fueron dirigidos de tal manera que los resultados estadísticamente significativos pudieran ser obtenidos con 10 mediciones. Los sujetos fueron expuestos a episodios altos y bajos de PM en localidades en donde no podían ver los cambios en las condiciones ambientales. Vientos altos durante el periodo de pruebas dieron menos episodios altos de PM que los que se hubieran deseado. Los datos de dos series de tiempo fueron unidos para proporcionar al menos 17 puntos de medición. Para uno de los 5 sujetos (un varón de 25 años pasado de peso, en condición física relativamente pobre), los resultados del electrocardiógrafo mostraron una fuerte asociación (R^2 = 81%, p<2.2%) con PM_{10} y una fuerte correlación (R^2 = 90.9%, p<0.1%) con $PM_{2.5}$. Se encontró que los datos de espirometría correlacionan, pero menos fuertemente, con $PM_{2.5}$ (R^2 = 83.4%, p<0.3%) y PM_{10} (R^2 = 60.7%, p<12.4%). Los datos sugieren además que las respuestas fisiológicas fueron rápidas (mucho menos de 30 minutos). Los resultados en los otros cuatro sujetos mostraron respuestas mucho más pequeñas y se encuentran todavía bajo estudio.

Los altos valores episódicos de materia particulada proveen oportunidades para el establecimiento de causalidad entre efectos adversos de salud y materia particulada que son más robustos que los determinados de estudios epidemiológicos. El estudio piloto mostró el efecto potencial en la salud de los eventos episódicos de valores altos de PM en la frontera. Es necesario un estudio mucho más amplio involucrando a ambas personas físicas saludables y grupos específicos de riesgo.

CIPAS ha desarrollado la capacidad para medir y modelar concentraciones de partículas, determinando sus fuentes principales, y determinando riesgos para la salud humana debidos a niveles altos de partículas y depósitos con concentración histórica de emisiones. Estas capacidades pueden usarse para ayudar a los tomadores de decisiones y las agencias financiadoras a decidir y priorizar las estrategias para limpiar el aire mostrando cuales poblaciones están en riesgo y cuáles fuentes deben controlar. El desarrollo de modelos y los inventarios de fuentes de emisiones también pueden establecer como las medidas de control necesitarán ser modificadas en el futuro para tomar en consideración diferentes escenarios para las características demográficas cambiantes, los patrones de desarrollo industrial, las millas vehiculares viajadas, y las tecnologías de disminución de contaminación del medio ambiente.

List of Abbreviations

µA	microampere
µm	micrometers
ADEQ	Arizona Department of Environmental Quality
Al	aluminum
As	arsenic
Asarco	American Smelting and Refining Company
BAM	Beta Attenuation Monitor
BEIS-II	Biogenic Emission Inventory System Version 2
BELD	Biogenic Emissions Landcover Database
BER	Basic emission rate
BRAVO	Big Bend Regional Aerosol and Visibility Observational Study
Ca	calcium
CAMS	Continuous Air Monitoring Station
CCA	canonical correlation analysis
Cd	cadmium
CEC	Commission for Environmental Cooperation
CENRAP	Central Regional Air Planning Association
CERM	Center for Environmental Resource Management at UTEP
CMB	chemical mass balance
CO	carbon monoxide
CO_2	carbon dioxide
COAs	Cédulas de Operación (Annual Operating Reports)
COI	compounds of interest
Cr	chromium
Cu	copper
DCP	direct current plasma
DGEPC	Ciudad Juárez General Directorate of Ecology and Public Safety
DRI	Desert Research Institute
ECG	electrocardiogram
EDCJ	Environmental Department of Ciudad Juárez
EDX	energy dispersive x-ray spectrometer
EIIP	Emissions Inventory Improvement Program
EPA	U.S. Environmental Protection Agency
EPCCHED	El Paso City-County Health and Environmental District
ev	electron volts
Fe	iron
FFT	Fast Fourier Transform
FRM	Federal Reference Method
GC	gas chromatography

GC/MS	gas chromatography/mass spectrometry
GCVTC	Grand Canyon Visibility Transport Commission
GIS	geographic information system
GloBEIS3	Global Biosphere Emissions and Interactions System Version 3
GPS	global positioning system
HAPs	hazardous air pollutants
HC	hazard coefficient
HC	hydrocarbon
HDDV	heavy-duty diesel vehicle
Hg	mercury
HRV	heart rate variability
I/M	inspection and maintenance
ICP-MS	inductively coupled plasma-mass spectrometry
IDL	instrument detection limits
IMECA	Indice Metropolitano de Calidad del Aire (Air Quality Metropolitan Index)
IMIP	Instituto Mexicano de Investigación y Planeación
INE	Instituto Nacional de Ecología (National Institute of Ecology)
INEGI	Instituto Nacional de Estadística, Geografía e Informática
IRIS	Integrated Risk Information System
ITESM	Instituto Tecnológico y de Estudios Superiores de Monterrey
K	potassium
kV	kilovolts
LDGV	light-duty gas vehicles
LGEEPA	Ley General del Equilibrio Ecológico y la Protección al Ambiente (General Law of Ecological Balance and Environmental Protection)
LIDAR	Light Detection and Ranging System
LPG	liquefied petroleum gas
MDA	multivariate data analysis
Mg	megagrams
MLR	multilinear regression
MMA	Monterrey Metropolitan Area
MS	mass spectrometry
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NAFTA	North American Free Trade Agreement
NEI	Mexico National Emissions Inventory
ng/m^3	nanograms per cubic meter
NH_3	ammonia
NIST	National Institutes of Standards and Technology

nm	nanometers
NMED	New Mexico Environment Department
NOM	Norma Oficial Mexicana
NO_x	nitrogen oxides
O_3	ozone
PAHs	polycyclic aromatic hydrocarbons
Pb	lead
PCA	principal component analysis
PCR	principal component regression
PdNARP	Paso del Norte Air Research Program
Pemex	Petróleos Mexicanos
PIXE	particle induced X-ray emission
PLS	partial least squares
PM	particulate matter
$\{PM\}^2$	peri-metropolitan particulate matter episodes
PM_{10}	PM measuring 10 micrometers or less in aerodynamic diameter
$PM_{2.5}$	PM measuring 2.5 micrometers or less in aerodynamic diameter
PMF	positive matrix factorization
PNAHs	polynuclear aromatic hydrocarbons
ppm	parts per million
PROFEPA	Procuraduría Federal de Protección al Ambiente (Federal Attorney General for Environmental Protection)
QA/QC	quality assurance/quality control
QF	quartz fiber
RETC	Registro de Emissions y Transferencia de Contaminantes (Pollutant Releases and Transfers Register)
RSD	remote sensing device
SCERP	Southwest Consortium for Environmental Research and Policy
SCOS97-NARSTO	1997 Southern California Ozone Study-North American Research Strategy for Tropospheric Ozone
SEAs	state environmental agencies
SEM	scanning electron microscopy
SEMARNAT	Secretaría de Medio Ambiente y Recursos Naturales
SENER	Secretaría de Energía (Secretariat of Energy)
Si	silicon
SNOKE	Sparse Matrix Operator Kernel Emissions modeling system
SO_x	sulfur oxides
STP	standard temperature and pressure
SX	solvent extraction

TAC	Technical Advisory Committee
TACB	Texas Air Control Board
TCEQ	Texas Commission on Environmental Quality
TCLP	Toxicity Characteristic Leaching Procedure
TD	thermal desorption
TD-GC/MS	thermal desorption-gas chromatography/mass spectrometry
TEM	transmission electron microscopy
TEOM	tapered element oscillating microbalance
THC	total hydrocarbon
Ti	titanium
TNRCC	Texas Natural Resource Conservation Commission
TOG	total organic gases
TSP	total suspended particulates
UNMIX	Named for its function, which is to "unmix" the concentrations of chemical species measured in the ambient air to arrive at the magnitudes of the underlying sources
UTEP	University of Texas at El Paso
VIFs	variance inflation factors
VKT	vehicle kilometers traveled
VOCs	volatile organic compounds
WEG	wind erodibility groups
WGA	Western Governors' Association
WRAP	Western Regional Air Partnership
XRF	x-ray fluorescence

I

Background and Recent Research on Particulate Matter in the Paso del Norte Border Region

C. A. Rincón, J. R. Anderson, J. J. Bang, J. C. Greenlee, K. E. Kelly, and W.-W. Li

Abstract

The Paso del Norte region is located midway along the U.S.-Mexican border where the Rio Grande/Río Bravo cuts through the Franklin Mountains to the north and the Sierra de Juárez to the south. The region encompasses the communities of Doña Ana County, N.M.; El Paso County, Tex.; and Municipio de Ciudad Juárez, Chih., which are separated by the river at the point where Ciudad Juárez, El Paso, and Sunland Park, N.M., meet. Paso del Norte, like most U.S.-Mexican border communities, is experiencing rapid urban growth in a semi-arid climate, where topography, meteorology, economic, and population pressures all combine to influence the air quality of the region.

Several locations in Paso del Norte currently do not meet their country's air quality standards for pollutants, including particulate matter (PM). Elevated PM concentrations have been associated with increased mortality rates and other adverse health effects (Pope, et al. 1991; Dockery, et al. 1993; Maynard and Maynard 2002; Peters, et al. 2001). In Ciudad Juárez, Romieu, et al. (2003) found associa-

tions between PM_{10} (matter with an aerodynamic diameter less than 10 micrometers [μm]) concentrations and mortality for children in the lowest socioeconomic class. Because the region's air resources are shared across several political boundaries, understanding and managing PM emissions is a challenge.

Antecedentes e Investigaciones Recientes de Materia Particulada en la Región Fronteriza Paso del Norte

C. A. Rincón, J. R. Anderson, J. J. Bang, J. C. Greenlee, K. E. Kelly, y W.-W. Li

Resumen

La región Paso del Norte está ubicada medio camino a lo largo de la frontera México-E.U. donde el Río Grande/Río Bravo corta a través de las Montañas Franklin hacia el norte y las Montañas de Sierra de Juárez hacia el sur. La región abarca a las comunidades del condado de Doña Ana, Nuevo México; El Paso, Texas; y Ciudad Juárez, Chihuahua, las cuáles se encuentran separadas por el río en el punto en donde Ciudad Juárez, El Paso, y Sunland Park, Nuevo México, convergen. El Paso del Norte, como la mayoría de las comunidades fronterizas de México-E.U, está experimentando un crecimiento urbano rápido en un clima semiárido, donde la topografía, meteorología, y las presiones económicas, y demográficas se combinan para influenciar la calidad de aire de la región.

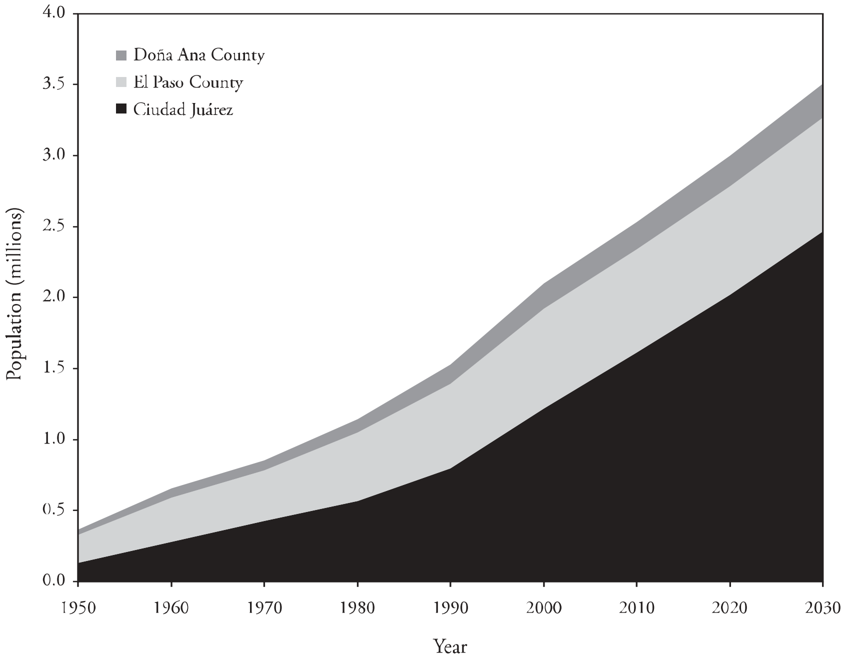
Varias áreas en Paso del Norte actualmente no cumplen las normas de calidad de aire para contaminantes de su país, incluyendo materia particulada (PM). Concentraciones elevadas de PM han sido asociadas con aumento en tasas de mortalidad y otros efectos adversos para la salud (Pope, et al. 1991; Dockery, et al. 1993; Maynard

y Maynard 2002; Peters, et al. 2001). En Ciudad Juárez, Romieu, et al. (2003) encontraron asociaciones entre concentraciones PM_{10} (materia con un diámetro aerodinámico inferior a 10 micras [μm]) y la mortalidad para niños en la clase socioeconómica mas baja. Debido a que los recursos atmosféricos de la región son compartidos a través de varias fronteras políticas, entender y administrar las emisiones PM es un reto.

Population

Population in the Paso del Norte region is increasing; the vast majority of growth is concentrated in the cities of El Paso, Tex.; Ciudad Juárez, Chih.; and Las Cruces, N.M. Unlike El Paso and Ciudad Juárez, which comprise the majority of the population in their respective county and municipality, the city of Las Cruces represents about half the population of Doña Ana County, N.M. Population growth in the region is the result of a combination of many factors, including the local and national economies, the work force, and constraints on available space. From 1990 through 2000, the growth rate for Ciudad Juárez averaged 4.36% annually—more than double that of its twin city, El Paso. The underlying reasons for this difference must be taken into account when predicting future growth rates. According to the 2000 census, approximately 2.25 million people reside in Paso del Norte, 1,257,926 of them in Ciudad Juárez. The El Paso County census reported 704,318 inhabitants, with a 1.45% annual growth rate throughout the 1990s; Doña Ana County reported 174,682 inhabitants. Figure 1 illustrates the historic and projected population growth for Paso del Norte from 1950 through 2030.

Figure 1. Population Data for Doña Ana County, El Paso County, and Municipio de Ciudad Juárez



Source: Paso del Norte Water Task Force

Geographic and Meteorological Characteristics

Climate and topography are important factors in the formation and transport of air pollution in this region. The local topography is classified as complex terrain because of the moderately sized mountain ranges that lie north, south, and west of the central Ciudad Juárez urban area (Appendix Figure 1 [page 305]). Local elevations range from 1,150 meters (m) (3,773 feet) at the Rio Grande bed to 1,850 m (6,070 feet) at Range Peak, located in the Franklin Mountains. The Franklin Mountains run north-south and divide the urban areas of west and north central/northeast El Paso. Downtown El Paso lies just beyond the southern end of the Franklin

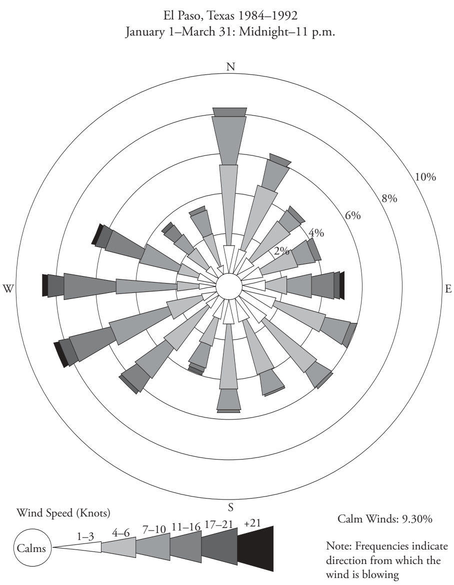
Mountains. The Rio Grande flows south out of central New Mexico through the Mesilla Valley on the west side of the Franklin Mountains. A large igneous intrusion known as Sierra de Cristo Rey lies directly in the path of the river's southward course at the southern end of this valley. The river bends around Cristo Rey, cuts through the pass between the Franklin Mountains and Sierra de Juárez, flowing in a general southeasterly direction between the downtown districts of El Paso and Ciudad Juárez, and finally flows into the Brad Valley to the southeast.

To the southwest of Ciudad Juárez lies the Sierra de Juárez, rising to 1,650 m (5,413 feet) above the valley floor. The Chihuahua Plateau lies to the south of Ciudad Juárez; it is characterized by relatively flat terrain, gradually increasing in altitude above the valley floor moving south. Northeast of downtown El Paso lies the extreme southern portion of the Tularosa Basin, bordered on the east by the Sacramento Mountains and on the west by the northern reaches of the Franklin Mountains. Much of the recent urban growth in El Paso is occurring in the northeast and northwest sections at the foot of the Franklin Mountains.

The weather in this region is mostly sunny and dry; it receives approximately 20 centimeters (cm) of rainfall annually, which occurs mostly during brief thunderstorms from July through September. The Paso del Norte region enjoys a wide range of seasonal conditions. Snow falls almost every year, but quickly melts due to the generally mild conditions that prevail during winter. Spring quickly fades into summer as temperatures usually reach the mid-80s to mid-90s (°F). From June to September, daily high temperatures are in the 90s and can stay close to or above 100°F for several consecutive days. Given that Paso del Norte is also a high desert region, the low for most nights will drop to the mid-60s and the relative humidity ranges between 10% and 35% for most of the year. Diurnal temperatures oscillate between 30°F and 40°F.

The region's arid conditions, land cover, and periodic high-wind episodes combine to produce high crustal contributions to particulate matter (PM) levels. Figures 2a, 2b, 2c, and 2d are wind roses for the four seasons, which show that wind speed and direction vary by season. In the rural areas of Paso del Norte, the most common land cover is shrub and brush rangeland, and most of this soil is highly

Figure 2. Wind Roses for El Paso Showing the Average Wind Speed and Direction for January–March (a), April–June (b), July–September (c), and October–December (d) for 1984 to 1992



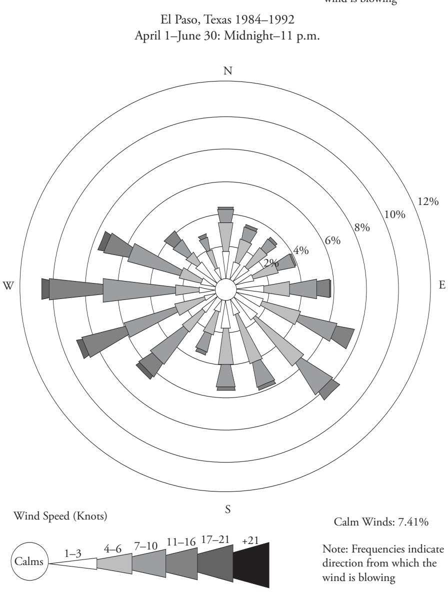
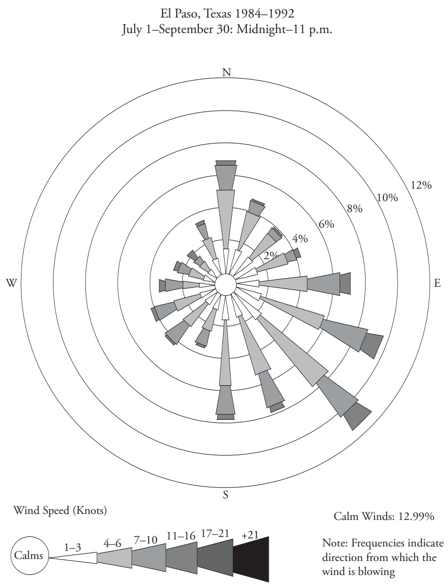


Figure 2. continued



Source: Authors

susceptible to wind erosion (Okrasinski and Greenlee 2000). For example, Appendix Figure 2 (page 306) shows a map of Doña Ana County's wind erodibility. The nine wind erodibility groups, in order of progressively greater erodibility, are designated 1, 2, 3, 4, 4L, 5, 6, 7, and 8, and are detailed in Table 1.

During winter, atmospheric stagnation conditions marked by stable air masses and low wind speeds are often encountered in the region. These calm conditions result in pollutant buildup over time in the stable air mass. The region's complex topography (mountains) also serves as a dispersion barrier, trapping the local air pollution in the air basin (Appendix Figure 1 [page 305]). Pollutant dilution is further minimized during the evening and early morning hours by the formation of radiation inversions, which are stagnation events. Meteorological data taken during short-term PM_{10} (PM with an aerodynamic diameter of 10 micrometers [µm] of less) studies confirm the presence of very shallow vertical mixing heights in the evening and early morning hours of the winter season. During these stagnant conditions, high PM levels are frequently observed (Chapter III).

Regulatory Status

Ciudad Juárez and El Paso exceed their country's ambient air quality standards. With the enacting of the U.S. Clean Air Act and its 1990 amendments, El Paso was classified as a non-attainment area for three of the six criteria pollutants—ozone (O_3), carbon monoxide (CO), and PM_{10}—throughout most of the 1990s. In addition, portions of Doña Ana County exceed the National Ambient Air Quality Standards (NAAQS) for ozone and PM_{10}. Ciudad Juárez air quality exceeds the Mexican ambient air quality standards known as the Norma Oficial Mexicana (NOM) (SEMARNAT 1998) for PM_{10}, ozone, and carbon monoxide.

Under the provisions of the U.S. Clean Air Act, a non-attainment area is subject to stringent cleanup requirements and may be penalized for failure to meet the requirements specified by NAAQS. However, a border city such as El Paso may not be penalized if it can demonstrate it has taken all necessary measures to control sources within the region and its failure to meet NAAQS is due to emissions generated outside the United States (EPA 1990).

Table 1. Wind Erodibility Groups

WEG	Properties of Soil Surface Layer	Wind Erodibility Tons/Acre/Year
1	Very fine sand, fine sand, sand, or coarse sand	310
2	Loamy very fine sand, loamy fine sand, loamy sand, loamy coarse sand, or sapric organic soil materials	134
3	Very fine sandy loam, fine sandy loam, sandy loam, or coarse sandy loam	86
4	Clay, silty clay, noncalcareous clay loam, or silty clay loam with >35% clay content	86
4L	Calcareous loam, silt loam, clay loam, or silty clay loam	86
5	Noncalcareous loam and silt loam with <20% clay content, or sandy clay loam, sandy clay, and hemic organic soil materials	56
6	Noncalcareous loam and silt loam with >20% clay content, or noncalcareous clay loam with <35% clay content	48
7	Silt, noncalcareous silty clay loam with >35% clay content, and fibric organic soil material	38
8	Soils not suitable for cultivation due to coarse fragments or wetness	Wind erosion not a problem

Source: Okrasinski and Greenlee 2000

Although air quality in El Paso has improved gradually since 1990, it is still classified as non-attainment for ozone, carbon monoxide, and PM_{10} (TNRCC 1999a, 1999b, 1999c). According to data collected by the state and local environmental agencies on both sides of the border, PM concentrations are higher near:

- South-central El Paso, near the University of Texas at El Paso (UTEP) campus at Vilas Elementary School (Appendix Figure 1 [page 305], UTEP site)
- The Sun Metro public transit terminal (Appendix Figure 1 [page 305], Sun Metro site)

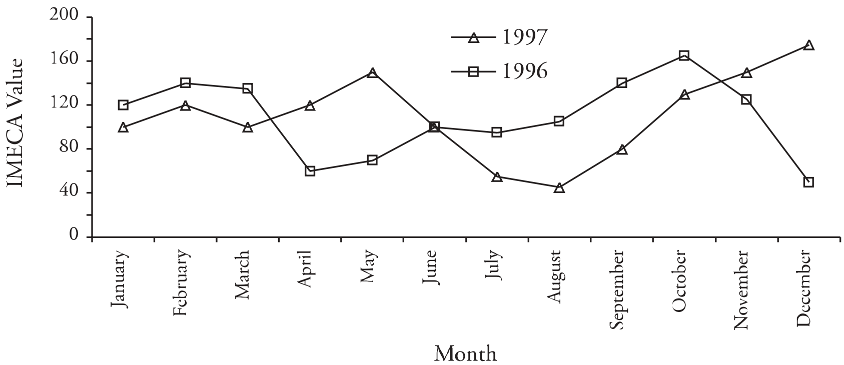
- The brick-making community in central Ciudad Juárez (Appendix Figure 1 [page 305], Advanced Transformer site)

All of these sites regularly report PM concentrations at or above the PM NAAQS for their respective country. For example, during the last quarter of 1998, the 24-hour average PM_{10} standard was exceeded at least five times in Ciudad Juárez (EPCCHED 1999).

As the population in Paso del Norte continues to expand, meeting ambient standards for PM will remain a challenge. Average annual concentrations in Ciudad Juárez are increasing. The Ciudad Juárez Air Quality Management Plan for 1998 through 2002, a plan similar to the U.S. State Implementation Plans, reports that 23% of the PM_{10} measurements exceeded 100 Indice Metropolitano de Calidad del Aire (Air Quality Metropolitan Index, in Spanish IMECA) points during 1996; in 1997 the percentage decreased to 18%. However, PM_{10} monitoring in Ciudad Juárez is conducted with hand-operated equipment, taking, on average, 24-hour samples once every six days. Therefore, approximately 61 measurements are collected annually. In terms of the number of standard exceedances, PM is similar to ozone; however, the percentages are much higher for PM_{10} (around 20%). For this reason, it will be important to incorporate continuous PM_{10} monitoring equipment into the monitoring stations because this pollutant could be the most relevant for Ciudad Juárez. In addition, although Mexico does not have an air quality standard for particulates smaller than 2.5 µm ($PM_{2.5}$), the initiation of its monitoring is highly recommended in the Paso del Norte airbasin.

Figure 3 indicates that the maximum monthly PM_{10} levels occasionally reach nearly 200 IMECA points. Most months had values exceeding 100 IMECA points.

Figure 3. Maximum Monthly IMECA of PM_{10} in Ciudad Juárez, 1996–1997



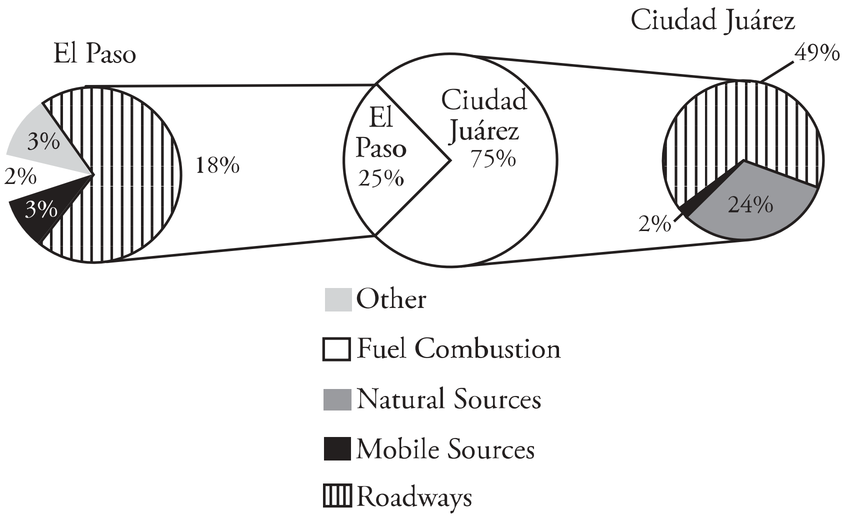
Source: Ciudad Juarez Air Quality Management Plan 1998–2000

Major Sources of Particulate Matter

According to the most recent emissions inventory (1996) for El Paso-Ciudad Juárez, Ciudad Juárez contributes 75% of the PM_{10} emissions; the largest contributors are road dust, followed by wind erosion of soil (Figure 4). It is estimated that 50% of the urban roads in Ciudad Juárez are unpaved (Gonzalez 1998). In El Paso, the majority of its PM_{10} emissions also come from road dust, followed by mobile sources. El Paso County has approximately 800 miles of unpaved roads, but these roads see very little vehicle traffic and are generally in undeveloped areas. It is worthwhile to note that in El Paso, PM emissions from paved roads far outweigh those from unpaved roads (TNRCC 1996). In Doña Ana County, PM_{10} is dominated by wind erosion of soil.

In addition, vehicles and other combustion sources contribute to PM_{10} concentrations and are more significant contributors to $PM_{2.5}$ levels. Approximately 333,000 vehicles are registered in El Paso and 420,000 vehicles are registered in Ciudad Juárez. An average of approximately 40,000 vehicles cross the U.S.-Mexican border into El Paso each day (EPMPO 1998). On average, Mexican vehicles have higher emissions than U.S. vehicles but are driven less often. In addition, the low per capita income in the region manifests itself in

Figure 4. 1996 PM_{10} Emissions Inventory for the Paso del Norte



Source: Authors

the burning of scrap wood and refuse material for home heating and cooking in the more economically disadvantaged regions of Ciudad Juárez, El Paso, and Sunland Park. These activities can have a significant effect on PM levels, particularly during the winter season because of its stagnant air conditions. Finally, small amounts of PM come from commercial and industrial activities such as refining, smelting, scrap-metal foundries, agricultural activities, open-burning batch-type brick making, maquiladoras in Ciudad Juárez, and quarry operations and electric generation in El Paso. Some of these activities, such as smelting, can have a significant effect on PM composition (as discussed in Chapter V).

Chapter II provides an extensive inventory of emission sources along the U.S.-Mexican border. Chapter VI discusses important organic contributors to PM and identifies several sources that are characteristic of the border region, including refuse burning and brick kilns. Chapter V discusses sources of metal emissions in the Paso del Norte airshed.

Collecting an integrated emission inventory for an airbasin such as Paso del Norte's is a challenge. In the United States, emission sources are divided into three categories: mobile, point, and area. Yet in Mexico, emission sources are categorized by economic sector: industrial, commercial and service, transportation, and natural sources. As in all emissions inventories, there are levels of uncertainty in emissions estimation that influence an inventory's overall accuracy. In Paso del Norte, there are uncertainties associated with the estimation methodologies themselves, in addition to the fact that there are source categories for which emissions estimates are currently unavailable.

Size and Composition of Particulate Matter

The composition of PM in Paso del Norte differs from the PM found in other regions of the United States because of the significant contribution from geologic sources. For example, along the East Coast sulfates are significant, and in the Los Angeles basin nitrates are significant (Tropp, et al. 1998; Dattner 1994). The geologic contribution to PM is predominantly found in the coarser fraction of PM ($PM_{2.5}$ to PM_{10}) (Chapter III).

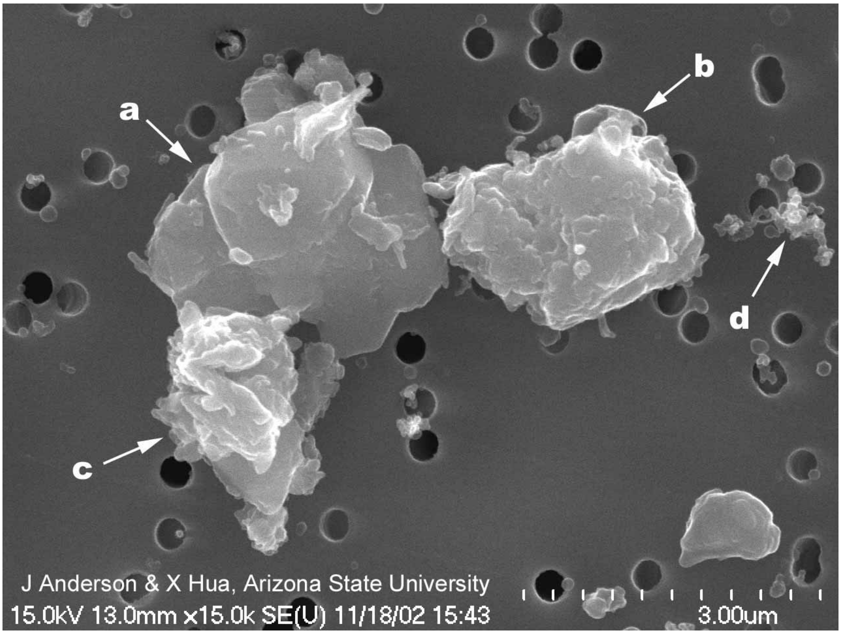
In the 1970s, the Paso del Norte airshed had high levels of airborne lead (see Chapter V for additional details on historical levels of airborne metals). During that time, 12 sampling sites regularly exceeded the U.S. Environmental Protection Agency's (EPA) quarterly average lead standard of 1.5 micrograms per cubic meter ($\mu g/m^3$), with one location reporting a quarterly average lead concentration of 15.5 $\mu g/m^3$ (Dattner 1996). Because of concerns over the health effects of lead, the U.S. and Mexican governments successfully implemented measures to reduce ambient lead concentrations. These included the elimination of leaded fuel used in motor vehicles and more stringent controls on the American Smelting and Refining Company (Asarco) metal smelter in El Paso (Appendix Figure 1 [page 305]). Starting in 1972, some U.S. vehicles could not use leaded fuel, and by 1980 very few new cars could use leaded fuel. By 1990, most Texas gas stations stopped selling leaded fuels. Mexico adopted similar regulations and also dramatically reduced the use of leaded fuel. In the late 1970s, the American Smelting and Refining Company (Asarco) modernized its lead plant, and between 1984 and 1992 closed its arsenic, lead, antimony, and cadmium processes.

Between 1972 and 1995, airborne lead concentrations in the Paso del Norte airshed decreased by approximately 90%. Currently, the concentrations of metals-associated anthropogenic sources, such as smelters (arsenic, copper, chromium, and lead), are highest in ambient PM and surface soil samples collected in the urban core of El Paso-Ciudad Juárez and near the Asarco smelter (for additional details on this, see Chapter V).

As the levels of lead and other toxic metals have declined, attention has shifted to reducing the contributions of geologic sources to PM levels and to reducing contributions from combustion sources such as brick kilns and residential burning. Chapter VI provides details about organic contributions to PM in the Paso del Norte airshed. The source apportionment techniques discussed in Chapter VI provide a measure of the different contributions in different locations as a function of time.

Advanced techniques are also helping improve the understanding of the composition and sources of PM in the region. Chapter IV presents microscopy results of various types of PM identified in the region. Figure 5 shows an example of several types of particles common to the U.S.-Mexican border.

Figure 5. Scanning Electron Microscopy Images of Aerosol Samples



Notes: (a) calcium sulfate, (b) calcium carbonate with minor aggregated aluminosilicate, (c) aluminosilicate (clay), (d) black carbon (soot and small carbon cenospheres). Many other small black carbon particles are unlabeled (15,000X). These are reasonably representative of particles within the twin cities of Douglas-Agua Prieta, although the complexity in the variety of particle types (especially black carbon) and their aggregation cannot be represented in just a few images. Phase identifications are made from energy dispersive x-ray spectra. Samples were collected through the PM_{10} inlet onto polycarbonate membrane filters with 0.4 µm pores. Images were taken with the Hitachi S-4700 scanning electron microscope, with 15 kV accelerating voltage.
Source: J. Anderson and X. Hua

Air Quality Monitoring

Air quality monitoring networks have been deployed throughout the air basin to measure population exposure to PM_{10}, $PM_{2.5}$, carbon monoxide, and ozone (Appendix Figure 1 [page 305]). There are nine monitoring sites operated by the Texas Commission on Environmental Quality (TCEQ) in El Paso, 11 stations in Doña Ana County operated by the New Mexico Environment Department (NMED), and six monitoring sites in El Paso operated by El Paso City-County Health and Environmental District (EPCCHED). The Ciudad Juárez General Directorate of Ecology and Public Safety (in Spanish DGEPC) obtains daily air quality data from equipment at five Ciudad Juárez air quality monitoring sites. EPCCHED provides maintenance, quality control, and technical support for these stations.

Because new monitors are required to measure $PM_{2.5}$ under the new U.S. fine particle standard, TCEQ has established a $PM_{2.5}$ monitoring site for El Paso. EPA and the Mexican Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT) are working on a proposal to deploy $PM_{2.5}$ monitors in Ciudad Juárez.

Chapters III, IV, V, and VI present PM measurements and analysis of PM collected at several of the monitoring sites shown in Appendix Figure 1 (page 305). The following paragraphs describe a few of the key monitoring sites in more detail.

United States

The Chamizal site is located in south El Paso, west of the Cordova International Bridge. It is in an enclosed area set aside for air monitoring at Chamizal National Park. It is a designated EPA State and Local Air Monitoring Site and Photochemical Air Monitoring Station network where daily, 24-hour Federal Reference Method $PM_{2.5}$ samples are collected. It is also a TCEQ Continuous Air Monitoring Station (CAMS 41) where hourly Beta Attenuation Monitor (BAM) PM_{10} and meteorological data are continuously recorded. The area is classified as a mixed residential and semi-industrial area. This site is subject to vehicular traffic sitting idle during rush hour at the international border crossing.

The Sun Metro site is an urban commercial/industrial site approximately four kilometers (km) from Chamizal. It is located in southwest El Paso just north of the Rio Grande and south of Interstate 10. The site is collocated to TCEQ's CAMS 40, where hourly BAM PM_{10} and meteorological data are continuously recorded. This site is subject to the effects of vehicular traffic during rush hour from Interstate 10 in El Paso and the effects of unpaved roads in Ciudad Juárez. Additionally, it is subjected to the effects of heavy wood and cardboard burning for home heating from Ciudad Juárez homes.

Mexico

The Club 20-30 site is located east of downtown Ciudad Juárez. The site contains a high-volume PM_{10} sampler co-managed by the Environmental Department of Ciudad Juárez (EDCJ) and EPCCHED. The surrounding area is heavily populated and close to a major road with heavy vehicle traffic during rush hour.

The Advanced Transformer site is located in the maquiladora industry district. The brick kiln district is located just south of the site, and heavy burning occurs daily. The site contains a high volume PM_{10} sampler co-managed by EDCJ and EPCCHED.

The Misión site is located at the foothills of the Sierra de Juárez, in the southwest portion of the air basin. The surrounding area is heavily populated and the site is located in a community with unpaved roads where residents burn materials during winter months. Located to the south of this site is a cement factory. The site represents a typical residential location on the outskirts of Ciudad Juárez.

Previous Studies

This section summarizes results from studies conducted in the last several years to characterize the sources of pollution and the state of air quality in Paso del Norte. Special attention is given to studies aimed at achieving a better understanding of the physical and chemical processes that lead to high concentrations of fine particulates and ozone. Similarly, a brief description is made of studies currently being conducted and those completed, the results of which will be forthcoming.

El Paso/Juárez Saturation PM_{10} Study (Kemp 1990)

Given that the city of El Paso has exceeded the U.S. air quality standard for PM_{10} since the standard's promulgation in 1987, the Texas Air Control Board (TACB) was required to design a State Implementation Plan to control this pollutant in the area. In response, this study was conducted in December 1989 and represents the first formal opportunity for conducting joint work on both sides of the border. The study's general objectives were to:

- Characterize the PM_{10} levels in the area and determine what the PM_{10} concentrations are in areas of the basin not sampled regularly and whether the current monitoring system for PM_{10} adequately characterizes the atmospheric environment
- Develop parameters and protocols for handling portable monitoring equipment for PM_{10} in future short-term studies

One of the study's most significant results is that according to three-and-a-half-hour samples taken during the first two weeks of December 1989, the PM_{10} concentrations varied between 24 $\mu g/m^3$ (in Sunland Park, near the border between Texas and New Mexico) and 745 $\mu g/m^3$ (in Ciudad Juárez's west side). The levels of PM_{10} on the eastern side of the basin were approximately 90 $\mu g/m^3$.

The 22-hour samples taken on December 11, 1989, were used to interpolate data and generate a map of contours to estimate basin-wide concentrations. According to these estimations, the greatest PM_{10} levels were observed toward the south of the junction between the borders of New Mexico, Texas, and Chihuahua.

The study's general conclusions indicate two points. First, the highest levels were regularly found along both sides of the border in the regions not covered by the local monitoring system. Second, the PM_{10} monitoring system has proved to be of little value for its characterization of the distribution of PM_{10} in the basin.

LIDAR-Observed Wind Patterns in the Mexico-New Mexico-Texas Border Region (Barr, et al. 1994)

In collaboration with the Physical Sciences Laboratory at New Mexico State University and other institutions, Los Alamos National Laboratory participated in a short but intense field campaign during the first two weeks of September 1994. Its intent was to study the patterns of wind circulation that contribute to the presence of high ozone levels in the region.

Some of the principal results indicate that the growth in the mixing layer during the days analyzed can be described in three stages: slow growth, almost uniform (200 meters per hour [m/h]) from 8:00 am until after midday; intermediate growth (approximately 400 m/h) with convective heterogeneity until the beginning of the afternoon when the humid convection begins; and vigorous growth, whose quickness is governed by the magnitude of the humid convection.

The data generated by the Light Detection and Ranging (LIDAR) system allowed the visualization of some of the characteristics of the transport and dispersion patterns. For example, it was found, at least during the days analyzed, that the dominant winds in Sunland Park generally flow from the southeast.

From the previous results, the authors concluded that the shallowness of the mixing layer, combined with southern and eastern winds, are probably the source of the brown cloud observed toward the north near Las Cruces. As such, they have concluded that when considering Sunland Park's ozone problems, the area analyzed should be extended several kilometers to the south and east because ozone is a product of photochemical reactions with pollutants transported from distant locations in the south and east, and air in Sunland Park is generally not at a standstill.

Winter Season Air Pollution in El Paso-Ciudad Juárez (Einfeld and Hugh 1995)

This report summarizes numerous research efforts conducted since the 1980s in the Paso del Norte area, highlighting the work sponsored by the U.S. Congress and administered by EPA. The summary outlines aspects such as spatial and seasonal distribution of the pollutants and the polluting potential from both mobile and stationary sources located on both sides of the border.

Paso del Norte Pilot Border Study of Ozone Precursors and Air Toxins

EPA designed this pilot study to plan the development of an intense study monitoring ozone precursors and air toxins for the summer of 1996. The pilot study, conducted in 1995, was aimed at obtaining preliminary information on pollutant concentrations and to test sampling and analysis methods that would be used in the principal study, scheduled to be conducted during the summer of 1996.

In developing this study, two sites were selected—one in Ciudad Juárez and the other in El Paso. The El Paso site was located at the Sun Metro monitoring station and the Ciudad Juárez site was located at the Tecnológico monitoring station. The final results identified sampling and analysis methods for the chemical species in the international air basin.

Operating Plan for Ozone Modeling Data Collection in El Paso-Ciudad Juárez-Sunland Park (Roberts, et al. 1996)

Considering the need to better address the tropospheric ozone problems in the El Paso-Ciudad Juárez-Sunland Park area and that the majority of studies conducted to date had focused on collecting PM_{10} and carbon monoxide data, EPA sponsored a field study for the collection of sufficient data to support the region's ozone modeling activities. The final objective was to develop an air quality model validated for a variety of meteorological conditions that could be used to evaluate the potential effect of future scenarios.

The design of the operating plan for the data collection was located within this context. One of the most important tasks in developing the design was reviewing all the information generated by previous studies in the area. The review allowed a statistical characterization of the high ozone concentration, a general description of the air quality (including basic statistics on how, when, and how frequently ozone episodes occur), a preliminary characterization of meteorological and air quality phenomena associated with ozone episodes, and a preliminary characterization of volatile organic compounds (VOCs) in the area.

Some of the principal conclusions drawn from analyzing the information were:

- The majority of ozone standard exceedances are from June to October; the greatest concentrations are in August
- The accumulation of pollutants in high areas plays an important role in high ozone concentration events
- The surface area wind patterns vary significantly
- The daily profiles of the mixing layer heights probably play an important role in high ozone concentrations
- The monitoring system requires modification or amplification to adequately characterize the volatile organic compounds and the carbonyls in the region's air

Analysis of Meteorological and Air Quality Data for the 1996 Paso del Norte Ozone Study (Roberts, et al. 1997)

This study analyzes the meteorological and air quality data collected in Paso del Norte during the summer of 1996. Its objective was to characterize the meteorological and air quality processes that influence the formation and transport of ozone precursors and ozone itself within the study area. The study also aimed to provide information on the initial and border conditions that should be used during the later meteorological and photochemical modeling of the atmospheric basin.

As a result of this analysis, a simple conceptual model of the episodes of high ozone concentration in the area was developed. A conceptual model is a description of the most important phenomena and characteristics that produce ozone episodes. An ozone episode is a day in which the air quality standard for this pollutant is exceeded at minimally one of the sampling sites.

The following highlights the principal characteristics of the conceptual model as well as some other important conclusions from this study. Table 2 indicates the work considered in this study, as well as the institutions that conducted it. According to the authors, some of the primary conclusions reported are:

- Industrial sources are not a significant source of particulates in Paso del Norte
- Winter levels of PM_{10} are greater in the central areas of Ciudad Juárez and El Paso; in general, there is a concentration gradient that tends to increase toward Ciudad Juárez
- Average emissions of vehicles in Ciudad Juárez are three times greater than those of vehicles in El Paso
- The number of kilometers that vehicles in El Paso travel is three times greater than those of vehicles in Ciudad Juárez
- Atmospheric stability during winter and complex topography significantly limit the dilution of pollutants in the region
- During the winter season, PM_{10} concentrations in Paso del Norte reach levels that exceed the U.S. air quality standard for this pollutant

Table 2. Ambient Air Quality Studies Conducted in Paso del Norte from 1983 to 1994

Title of Study	Participating Institutions
Carbon monoxide studies	University of Texas at El Paso, 1983
Inhaleable fraction particulates evaluation	Environmental Research and Technology, Inc. 1983
Air quality database	Radian Corporation, 1983
Quantitative microscopic study in El Paso	Energy Technology Consultants, 1983
LIDAR study	Environmental Monitoring Systems Laboratory, 1989
Visibility and high wind study	University of Texas at El Paso, 1989
PM_{10} saturation study	EPA Region 6, 1989
Gasoline vapor pressure study in Ciudad Juárez	SEDESOL and others, 1990
Research on emissions control device tampering	Colorado State University, 1990
Ciudad Juárez emissions inventory	Alliance Technologies and others, 1990
Short-term winter particulate study	Texas Air Control Board, Sandia National Laboratories, 1990
Evaluation and recommendations of the PM_{10} modeling plan	Systems Application International, 1991
Development of State Implementation Plan for PM_{10}	Texas Natural Resource Conservation Commission, 1991
Ciudad Juárez industrial emissions study	EPA-SEDESOL, 1992-93
Vehicle emissions remote sensing study	University of Denver, 1993
MOBILE5 reviews	Energy and Environmental Analysis Inc., 1993
Characterization of Ciudad Juárez's vehicle fleet	Texas Transportation Institute, 1993
Ciudad Juárez brick kiln study	El Paso Natural Gas Co./FEMAP, 1993
Pollution emissions from residential heating systems	University of Utah, 1993
Temperature and high wind data collection	University of Texas at El Paso, 1993
Use of oxygenated fuels in Ciudad Juárez-El Paso	SEDESOL and others, 1993
Other activities	Paso del Norte Air Quality Task Force, 1993
Comparison of inspection and maintenance programs in Ciudad Juárez and El Paso	Paso del Norte Air Quality Task Force, 1994
Technology transfer session with inspection and maintenance technicians	Colorado State University, 1994

Source: Authors

References

Barr, S., W. G. Buttler, D. A. Clark, W. B. Cottingame, and W. E. Eichinger. 1994. *Lidar-Observed Wind Patterns in the Mexico-New Mexico-Texas Border Region.* Los Alamos, N.M.: Los Alamos National Laboratory.

Dattner, S. L. 1994. *El Paso/Juárez 1990 PM_{10} Receptor Modeling Feasibility Study* AS-43. Austin, Tex: TNRCC.

Dattner, S. L. 1996. *Airborne Lead in the PdN Airshed: A Success Story.* Austin, Tex.: TNRCC.

Dockery, D. W., A. C. Pope, X. Xiping, J. D. Spengler, J. H. Ware, M. E. Fay, B. G. Ferris, and F. E. Speizer. 1993. "An Association between Air Pollution and Mortality in Six U.S. Cities." *New England Journal of Medicine* 329(24): 1753–1759.

Einfeld, W., and H. W. Church. 1995. "Winter Season Air in El Paso-Ciudad Juarez." Sandia National Laboratories Report No. SAND95-0273 (March).

El Paso City-County Health and Environmental District. 1999. *Quarterly Air Quality Data.* Paper presented at the 10th meeting of the Joint Advisory Committee for the Improvement of Air Quality in the Ciudad Juárez/El Paso/Doña Ana County Air Basin. 25 February.

El Paso Metropolitan Planning Organization. 1998. *El Paso Metropolitan Transportation Plan 2020.* El Paso: El Paso Metropolitan Planning Organization.

Gonzalez, S. 1998. *Integrated Transportation Plan.* Ciudad Juárez: Instituto Municipal de Investigación y Planeacion de Ciudad Juárez.

Kemp, M. 1990. *El Paso/Juárez Saturation PM-10 Study: December 8, 1989–December 18, 1989.* EPA Document No. 906-R-92-001. Washington, D.C.: EPA.

Maynard, A. D., and R. L. Maynard 2002. "A Derived Association between Ambient Aerosol Surface Area and Excess Mortality Using Historic Time Series Data." *Atmospheric Environment* 36: 5561–5567.

Okrasinski R., and J. Greenlee 2000. *Correlation of High Particulate Matter Concentration in Doña Ana County, New Mexico, with Atmospheric and Geographical Characteristics.* Southwest Center for Environmental Research and Policy Report A00-6. http://www.scerp.org.

Peach, J., and J. Williams. 2004. "Population Dynamics of the U.S.-Mexican Border Region." Forthcoming SCERP Monograph. San Diego: SDSU Press.

Peters, A., D. Dockery, J. E. Muller, and M. A. Mittleman. 2001. "Increased Particulate Air Pollution and the Triggering of Myocardial Infarction." *Circulation* 103: 2810–2815.

Pope, C. A., D. W. Dockery, J. D. Spengler, and M. E. Raizenne. 1991. "Respiratory Health and PM_{10} Pollution. A Daily Time Series Analysis." *American Review of Respiratory Disease* 144(3 Pt. 1): 668–674.

Roberts P. T., H. H. Main, and M. A. Yocke. 1996. "Operating Plan for Ozone Modeling Data Collection in El Paso-Ciudad Juarez-Sunland Park." Draft final report prepared for EPA under subcontract to SAIC by Sonoma Technology, Inc. SAIC Project No. 01-1030-07-3823-xxx.

Roberts P. T., C. P. MacDonald, H. H. Main, T. S. Dye, D. Coe, and T. L. Haste. 1997. "Analysis of Meteorological and Air Quality Data for the 1996 Paso del Norte Ozone Study." Final report prepared for EPA under subcontract to SAIC by Sonoma Technology, Inc.

Romieue, I., M. R. Aguilar, H. M. Macias, A. B. Villarreal, L. H. Cadena, and L. C. Arroya. 2003. *Health Impacts of Air Pollution on Morbidity and Mortality among Children of Ciudad Juárez, Chihuahua, Mexico.* Montréal: Commission for Environmental Cooperation.

Secretaría de Medio Ambiente y Recursos Naturales. 1998. *Cd. Juárez Air Quality Management Plan.* Mexico City: SEMARNAT.

Texas Natural Resources Conservation Commission. 1996. *Revision to the Texas State Implementation Plan for PM_{10} for El Paso, TX.* Austin, Tex.: TNRCC.

Texas Natural Resource Conservation Commission. 1999a. "Air Pollution Trends in Texas, Nonattainment Areas." http://www.tnrcc.state.tx.us/air/monops/eloz.html.

Texas Natural Resource Conservation Commission. 1999b. "El Paso Annual Average Respirable Particulate Matter of 10 Microns or Less* 1988-1997." http://www.tnrcc.state.tx.us/air/monops/elppm10.html.

Texas Natural Resource Conservation Commission. 1999c. "El Paso Second Highest Eight-Hour Maximum Carbon Monoxide Concentrations* 1988-1997." http://www.tnrcc.state.tx.us/air/monops/elpco.html.

Tropp, R. J., S. D. Kohl, J. C. Chow, and C. A. Frazier. 1998. *Final Report for the Texas $PM_{2.5}$ Sampling and Analysis Study.* Desert Research Institute Document No. 6570-685-7770.1F. http://www.dri.edu.

U.S. Environmental Protection Agency. 1990. "Clean Air Act Amendments." Section 179b; 42.U.S.C. 7509a. http://www.epa.gov/oar/oaq_caa.html/.

II

Emissions Inventories for Northern Mexico

P. G. Fields, R. Halvey, G. M. Mejía Velázquez, C. H. Snow, and M. E. Wolf

Abstract

Early emissions inventory development efforts in Mexico focused on building the technical capacity of the Mexican government staff and academics. Sponsorship of training and methodology reference manuals by government agencies on both sides of the border have helped meet capacity-building objectives. Since the mid-1970s, projects sponsored by many Mexican, U.S., and Canadian environmental entities have resulted in the development of emissions inventories of criteria and toxic air pollutants for various states, municipalities, cities, and rural areas in Northern Mexico and throughout the country.

The focus of this chapter is on emissions inventories that have been developed for Northern Mexico. Several of these studies focus on emissions of particulate matter 10 micrometers (μm) and 2.5 μm in aerodynamic diameter (PM_{10} and $PM_{2.5}$), as well as the PM precursors nitrogen oxides (NO_x), sulfur oxides (SO_x), volatile organic compounds (VOC), and ammonia (NH_3). Some of the inventories presented in this chapter were developed to provide input into air quality models that analyze ozone levels, while others address haz-

ardous air pollutants (HAPs). This chapter provides a comprehensive summary of the most current emissions inventory studies reported in the available literature; thus, all pollutants included in each inventory are presented and discussed. Also, special projects related to the development of on-road motor vehicle emissions are discussed, including results from several projects related to the development of the MOBILE-Juárez, MOBILE5-Mexico, and MOBILE6-Mexico emissions factor models.

The Mexico National Emissions Inventory will include state- and municipality-level emissions for the entire country; preliminary results from this project for the northern states are presented in this chapter. Finalization of the national inventory for the border states in 2004 will immediately stimulate additional planning activities on the recently adopted Border 2012 plan. The future of emissions inventory development in Mexico is hopeful. In this era of unprecedented cooperation between Mexico and the United States, Mexico can take advantage of the efforts of Regional Planning Organizations and the governments of the United States and Canada to standardize emissions inventory reporting formats and develop a North American system of inventory reporting.

Inventario de Emisiones para el Norte de México

P. G. Fields, R. Halvey, G. M. Mejía Velázquez, C. H. Snow, y M. E. Wolf

Resumen

Los esfuerzos iniciales hacia el desarrollo de un inventario de emisiones en México se concentraron en construir la capacidad técnica del personal del gobierno de México y de académicos. El patrocinio

de entrenamiento y manuales de referencia metodológica por organismos gubernamentales en ambos lados de la frontera han ayudado a alcanzar los objetivos de construcción de capacidades. Desde mediados de los 1970s, los proyectos patrocinados por varias entidades ambientales de México, E.U. y Canadá han resultado en el desarrollo de inventarios de emisiones y criterios de contaminantes tóxicos de aire para varios estados, municipios, y áreas rurales en el Norte de México y a lo largo del país.

El enfoque de este capítulo es en los inventarios de emisiones que han sido desarrollados para el Norte de México. Varios de estos estudios se enfocan en emisiones de materia del particulada 10 micras (µm) y 2.5 µm de diámetro aerodinámico (PM_{10} y $PM_{2.5}$), así como precursores de PM óxido de nitrógeno (NO_x), óxidos de azufre (SO_x), compuestos orgánicos volátiles (VOC), y amoníaco (NH_3). Algunos de los inventarios presentados en este capítulo fueron desarrollados para proveer información para los modelos de calidad de aire que analizan niveles de ozono, mientras otros se dirigen a contaminantes atmosféricos riesgosos (HAPs). Este capítulo provee un resumen comprensivo de los estudios mas actuales de inventarios de emisiones reportados en la literatura disponible; así, todos los contaminantes incluidos en cada inventario son presentados y discutidos. También son discutidos, proyectos especiales relacionados con el desarrollo de las emisiones de vehículos en tránsito, incluyendo resultados de varios proyectos relacionados con el desarrollo de los modelos de factores de emisiones de MOBILE-Juárez, MOBILE5-México, y MOBILE6-México.

El inventario Nacional de Emisiones de México incluirá las emisiones a nivel estatal y municipal para el país entero; en este capítulo se presentan resultados preliminares de este proyecto para los estados del norte. La finalización del inventario nacional para los estados de la frontera en el 2004 inmediatamente estimulará actividades adicionales de planificación en el recientemente adoptado Plan Fronterizo 2012. El futuro del desarrollo de inventario de emisiones en México es esperanzador. En esta era de cooperación sin precedentes entre México y los Estados Unidos, México puede aprovechar los esfuerzos de Organizaciones de Planeación Regional y los gobiernos de los Estados Unidos y Canadá para estandarizar formatos para el reporte de inventarios de emisiones y desarrollar un sistema norteamericano de inventarios.

INTRODUCTION

Emissions inventory development in Mexico began with the efforts by Mexican and U.S. government agencies to increase the technical capacity within Mexico for developing inventories. In the summer of 1974, the Texas Air Control Board (TACB), now the Texas Commission on Environmental Quality (TCEQ), sponsored a training program for Mexican engineers in the major operations of the agency, including permitting and compliance activities, source sampling, and emissions inventory development. The 1983 La Paz Agreement enabled the United States and Mexico to share resources to continue to expand these capacity-building efforts.

Air quality agencies in the United States representing areas along the U.S.-Mexican border that had been designated as non-attainment for criteria air pollutants under the U.S. Clean Air Act Amendments were concerned about emissions impacts from Mexico, thus increasing the need to develop emissions inventories for Mexican sources. Then, in 1991, the U.S. Congress created the Grand Canyon Visibility Transport Commission (GCVTC) to advise the U.S. Environmental Protection Agency (EPA) on strategies for protecting visual air quality at national parks and wilderness areas on the Colorado Plateau. The GCVTC, organized as a special program within the Western Governors' Association (WGA), began a series of studies designed to focus on the origin of the pollutants that may contribute to or cause regional haze.

In 1994, GCVTC and Mexico's Instituto Nacional de Ecología (National Institute of Ecology, INE in Spanish) of the Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT) initiated a project to develop a national emissions inventory methodology and increase the technical capacity of emissions inventory professionals in Mexico (Fields, et al. 1998). Some important products of this project were the Mexico Emissions Inventory Manuals (Radian 1996a, 1996b, 1997a, 1997b, 1997c, and 2000a; ERG 2002, 2003a).

In the 1990s and continuing until today, efforts of the governments of the United States and Mexico have resulted in the development of inventory tools and methodologies specifically for Mexican sources. Emissions inventories have been developed for the major metropolitan areas in Mexico bordering the United States, and projects are underway to improve those inventories over time.

Compendium of Emissions Inventory Data for Northern Mexico

This chapter presents a compendium of emissions inventory studies conducted or being conducted for Northern Mexico. Several of these studies focus on emissions of particulate matter 10 micrometers (μm) in aerodynamic diameter and smaller (PM_{10}) and particulate matter 2.5 μm in aerodynamic diameter and smaller ($PM_{2.5}$). Some studies also address PM precursors, including nitrogen oxides (NO_x), sulfur oxides (SO_x), volatile organic compounds (VOCs), and ammonia (NH_3). Some inventories presented in this chapter were developed to provide input into air quality models for analyzing ozone levels; thus, they include emissions estimates for VOCs, NO_x, and carbon monoxide (CO). Others address hazardous air pollutants (HAPs). This chapter provides a comprehensive summary of the most current emissions inventory studies reported in the available literature; thus, all pollutants included in each inventory are presented and discussed.

This chapter does not compare or judge the relative quality of these inventories, but rather provides information necessary for the reader to discern whether these inventories would be useful to other studies or as the basis for future inventory development in a particular region. In most cases, a detailed quality analysis of the emissions data and inventory results discussed in this chapter would require significant additional research; however, evaluations are discussed where quality was assessed and reported in the literature.

Figure 1 shows the various locations covered by the emissions inventories conducted to date in Northern Mexico, including associated U.S. border cities and some cities within the interior of Mexico where data were developed for use in Northern Mexico. These inventory studies have various geographic domains, ranging from specific cities to the 100-kilometer (km) border zone, as defined by the La Paz Agreement, to the entire six-state region.

Figure 1. Locations of Emissions Inventories Developed in Northern Mexico

Notes: The dashed line indicates the 100-km border zone. Some locations within the interior of Mexico are shown where studies were conducted to develop data for use in Northern Mexico.
Source: Authors

The source types addressed by these emissions inventories include the following:

- Point (stationary sources, mainly industrial facilities)
- Area (non-point sources, such as residential combustion of fuel, fugitive dust, and non-road vehicles [e.g., aircraft, locomotives, non-road mobile equipment])
- Mobile (on-road motor vehicles, including gasoline-powered automobiles and heavy-duty diesel trucks)
- Natural sources (non-man-made sources of pollution, such as vegetation and soils [from microbial nitrogen processing])

Any exceptions to these source-type classifications within the emissions inventories discussed in this chapter are noted. All emissions summaries are given in metric units, since most were developed on a megagrams per year (Mg/year) or Mg per day (Mg/day) basis. Some emissions summaries were converted from English to metric units for consistency; these are noted accordingly.

Mobile Source Emissions Inventory Studies

The number of special studies devoted to motor vehicles are evidence of their importance in the emissions inventories for Northern Mexico. Equally important is the development of emission factor models representative of Mexican vehicles. This section discusses the use and development of mobile emission factor models for Mexico as well as other special studies conducted in Northern Mexico focusing on motor vehicle emissions and their impacts.

MOBILE-Juárez Emission Factor Model

Historically, estimating mobile emissions in Mexico involved the use of EPA's MOBILE5a emission factor model. However, EPA developed this model through extensive testing of U.S. vehicles in U.S. cities and it was intended for use by U.S. federal and state environmental agencies. The model was not designed to estimate tailpipe emissions on vehicles outside the United States and therefore its use in Mexico was not appropriate. A model for use in Mexico had to be developed that would represent the Mexican vehicle fleet of light-duty gas vehicles (LDGV).

In 1995, tailpipe testing of 200 vehicles in Ciudad Juárez, Chihuahua, was conducted using EPA's portable dynamometer. These data were used to modify the MOBILE5a model and develop the MOBILE-Juárez emissions factor model (Radian 1996c). Figure 2 shows the comparison of NO_x, VOC, and CO emissions estimated with MOBILE-Juárez and MOBILE5a (Snow, et al. 1997). (PM emissions are not available with these models; however more recent versions of the model do predict PM emission factors. See the discussion on MOBILE6-Mexico.) This figure shows that the MOBILE-Juárez model predicts higher emissions for most pollutant/vehicle category combinations as compared to MOBILE5a.

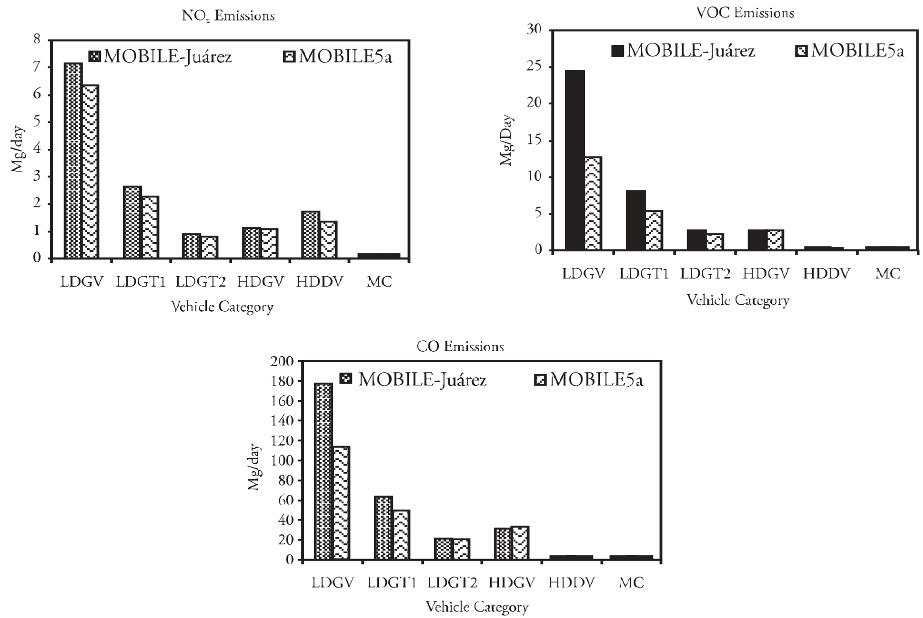
MOBILE-Juárez was revised in 1999 to include the ability to estimate tailpipe exhaust PM emissions. The methodologies and procedures to collect the data required for the revision were similar to the 1995 testing program, with the exception that the dynamometer was equipped with a sampling train to measure exhaust PM (ERG 2001a, 2001b).

MOBILE5-Mexico Emission Factor Model

Although MOBILE-Juárez was originally designed for use in Ciudad Juárez and there was no intention to use it in other Mexican cities, it proved suitable for use in other Mexican border cities with some minor modifications. However, extensive modifications were required for the model to generate accurate emission factors for non-border cities. The need for a "national" model led to the development of MOBILE5-Mexico.

The development of the MOBILE5-Mexico model was the next logical development step following MOBILE-Juárez. The MOBILE5-Mexico model was based on EPA's MOBILE5a model and incorporated data from various regions within Mexico to more accurately represent the Mexican vehicle fleet (ERG 2000). MOBILE5-Mexico was divided into five modules that were then used to model five different regions that had distinct fleet characteristics and reg-

Figure 2. On-Road Mobile Source Emissions in Ciudad Juárez, Estimated Using MOBILE-Juárez and MOBILE5a



Notes: LDGV = light-duty gasoline vehicle; LDGT1 = light-duty gasoline truck with gross vehicle weight under 6,000 lbs; LDGT2 = light-duty gasoline truck with gross vehicle weight between 6,000 lbs. and 8,500 lbs.; HDGV = heavy-duty gasoline vehicle; HDDV = heavy-duty diesel vehicle; MC = motorcycle.
Source: Snow, et al. 1997

ulatory structures. The MOBILE5-Mexico model used existing testing data from Mexico City and Ciudad Juárez, as well as new testing data from Aguascalientes.

The main differences between MOBILE5-Mexico and MOBILE5a were:

- Specific region types (i.e., Mexico City, border urban, border rural, interior urban, and interior rural) can be selected
- The effects of the U.S. regulations (such as the U.S. Clean Air Act Amendments) should always be disabled in MOBILE5-Mexico
- Metric units should be used for input vehicle speeds (kilometers per hour [km/hr]) and temperatures (degrees Celsius [°C])
- Output emission factors are given in units of grams per kilometer (g/km)

Unlike MOBILE5a, some MOBILE5-Mexico data are contained in external data files that can be modified by the model users, including:

- Registration fractions
- Mileage accumulation rates
- Number of vehicles
- Fraction of Mexico-registered vehicles
- Local Inspection and Maintenance (I/M) program information
- Basic emission rate (BER) information

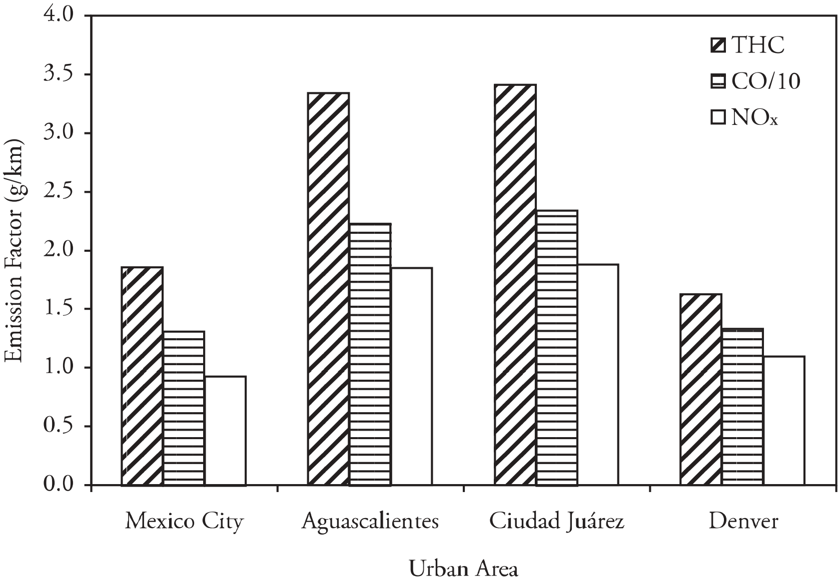
A key advance found in the development of the MOBILE5-Mexico model was the inclusion of the first Mexico-specific BERs. These Mexico-specific BERs were directly developed for the interior urban module using emissions testing data collected in the city of Aguascalientes in central Mexico. These testing data were collected in 1998 on a portable dynamometer using appropriate testing protocols for more than 200 Aguascalientes vehicles. Although BERs used for the Mexico City and border urban modules were also based on emissions testing data from Mexico City and Ciudad Juárez, BERs for these areas were estimated using an emission control "technology equivalence matrix" that mapped MOBILE5a BERs to equivalent Mexican vehicles, based on emissions testing data (for example, a 1996 model year Mexico vehicle might be equivalent to a 1990 model year U.S. vehicle for exhaust emissions). However, these BERs (for Mexico City and Ciudad Juárez) were approximations rather than actual calculated values. It should be noted that only exhaust BERs were directly calculated for the interior urban module. Other BERs were still estimated using the "technology equivalence matrix."

The use of the MOBILE5-Mexico modules is shown in the output results presented in Figure 3 (Burnette, Kishan, and Wolf 2001). The Mexico City, interior urban, and border urban modules were used to model Mexico City, Aguascalientes, and Ciudad Juárez. Mexico City is an extremely large metropolitan area with a diverse fleet and road network that has a large fraction of intensive-use vehicles. Aguascalientes is the capital of the state of Aguascalientes in central Mexico and has a relatively new vehicle fleet and a somewhat congested roadway system consisting of an old city center, peripheral "ring" roads, and few stretches of real "freeway." Ciudad Juárez is across the U.S.-Mexican border from El Paso, Tex. It has some of the heaviest crossing traffic in the border region, including a large fraction of commercial trucks and vehicles registered in El Paso.

Figure 3 graphically compares 2010 fleet average emission factors (in g/km) for these three Mexican metropolitan areas, along with Denver, Colo. (The carbon monoxide emission factors shown in Figure 3 were scaled down by a factor of 10 to facilitate clearer presentation of the results.) Mexico City was predicted to have the cleanest fleet average vehicle of the three Mexican urban areas, probably due to a relatively new fleet and the existence of an I/M program. Aguascalientes has a marginally cleaner fleet average vehicle than Ciudad Juárez, probably because the Aguascalientes fleet is somewhat newer. The difference between Aguascalientes and Ciudad Juárez is expected to be more pronounced, but it is possible that the effect of Aguascalientes' newer fleet is largely offset by the relatively large fraction of cleaner U.S.-registered vehicles assumed to be driving in Ciudad Juárez.

Figure 3 also includes 2010 motor vehicle emission factors for Denver. A comparison of Denver and Mexico City shows that emission estimates for both cities are comparable in magnitude for all

Figure 3. 2010 Fleet Average Vehicle Emission Factors for Four Urban Areas



Source: Burnette, Kishan, and Wolf 2001

pollutants. Both of these areas have relatively sophisticated I/M programs and are located at high altitudes. The total hydrocarbon (THC) emission factor for Denver is slightly lower than for Mexico City, while the NO_x emission factor for Mexico City is lower than Denver's. Predicted carbon monoxide emission factors for the two cities are essentially the same. These results appear to validate that, for two large North American cities with similar vehicle standards (which Denver and Mexico City will have in 2010) and similar pollution control programs (as modeled), the outputs of the two models yield similar results. The observed differences are probably due to the fact that Denver was assumed to have a higher proportion (on a basis of vehicle kilometers traveled) of heavy-duty diesel vehicles than Mexico City, and these tend to emit less hydrocarbon (HC) and carbon monoxide but more NO_x than gasoline vehicles.

MOBILE6-Mexico Emission Factor Model

One goal of the Commission for Environmental Cooperation (CEC) is to standardize emissions estimation methodologies among the three countries of North America. In 2000, EPA had replaced MOBILE5a with MOBILE6 as the regulatory mobile model for estimating mobile source emissions by state environmental regulatory agencies.

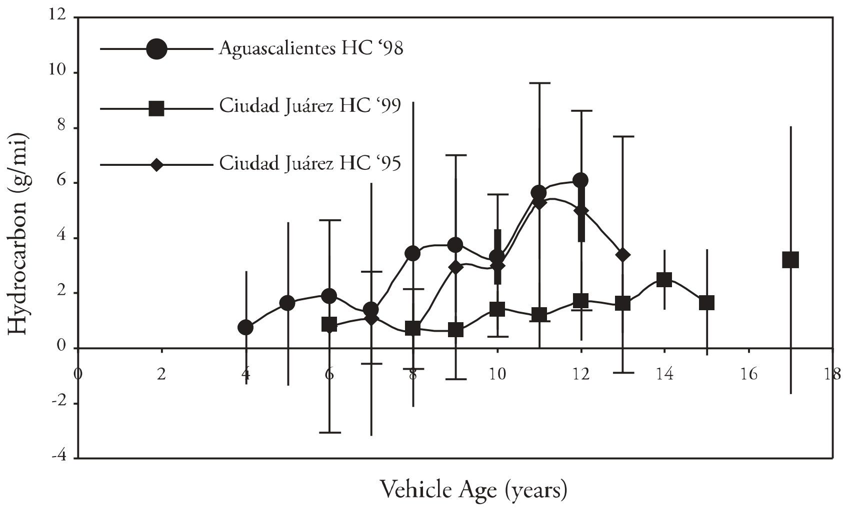
To be consistent with CEC's goals, MOBILE5-Mexico was replaced with MOBILE6-Mexico (ERG 2003b). MOBILE6-Mexico has more flexibility and can predict emissions for more pollutant types than the previous MOBILE5-Mexico emission factor model. It also has more up-to-date assumptions about how quickly vehicle emission control systems deteriorate and about how much lower the emissions levels of future vehicles will be when compared to current vehicles.

The basic structure of the MOBILE6-Mexico model is based on EPA's MOBILE6 emission factor model (EPA 2002). MOBILE6-Mexico estimates hydrocarbon, carbon monoxide, NO_x, PM, and carbon dioxide (CO_2) emission factors for 28 gasoline- and diesel-powered on-road motor vehicle types. The specific emission factor estimates depend on various conditions such as ambient temperatures, average travel speed, vehicle operating modes, fuel volatility, and mileage accumulation rates. Nearly all the required input variables can be specified by the user; however, the provided default values should be appropriate for most areas of the country. MOBILE6-Mexico can be used to estimate emission factors for any calendar year between 1952 and 2050. For each calendar year, the overall vehicle fleet consists of the 25 most recent vehicle model years.

Based on recent data collection, it has been determined that the previous model was unnecessarily complicated. MOBILE5-Mexico assumed that Mexico should be modeled using five different regional types (i.e., Mexico City, interior urban, interior rural, border urban, and border rural) because the vehicles in each region were thought to be significantly different from each other. MOBILE6-Mexico no longer makes this assumption. The model now assumes that vehicles in different parts of Mexico exhibit similar emissions characteristics. This assumption has proved reasonable. Analysis of actual emissions data collected in different areas of Mexico has shown that regardless of the part of Mexico in which they are driven, vehicles of similar age, type, and model have similar emissions.

Figure 4 compares hydrocarbon emissions in grams/mile (g/mi) of vehicles in Aguascalientes to vehicles in Ciudad Juárez. Although these emissions are for different years, similar vehicles from each city and measurement date had median emissions that were not significantly different. In other words, emission rates for a given age fall within the 1-standard deviation error bar for that given age. This was also true for average emissions and for all pollutants measured. Considering the uncertainties of modeling vehicle emissions and the similarity of emissions from different regions of Mexico, modeling each region separately (based on previous practice using MOBILE5-Mexico) was determined to be unnecessary.

Figure 4. Median Hydrocarbon Emissions Using MOBILE6-Mexico (for Vehicle Standard Group 3)



Source: ERG 2003b (for Vehicle Standard Group 3)

The basic structure of the MOBILE6-Mexico model is based on the MOBILE6 emission factor model. The model was expanded to allow adaptation to local conditions in Mexico. Data from previously developed models and from various vehicle studies in Mexico were assembled to help develop the necessary assumptions to adapt the model to Mexico. Wherever possible, data collected in Mexico were used to develop the new assumptions. If no appropriate Mexican data existed, then the results of recent studies in Mexico, engineering judgment, and default MOBILE6 values were used to adapt the assumptions to the Mexican situation. The model adaptation used the following vehicle fleet demographic data:

- Registration data from municipal authorities in Ciudad Juárez (ERG 2001a, 2001b)
- Vehicle fleet demographic data collected during the most recent Mexico City emissions inventory (GDF, et al. 2002)
- I/M data from district authorities in the Mexico City area (Perrusquía-Máximo 2003)
- National vehicle sales data from a report compiled for the World Bank (Grupo Trafalgar 2000)
- On-road fleet information from a recent study in Mexico City using vehicle remote sensing device (RSD) technology (Schifter, et al. 2003)

The first use of the MOBILE6-Mexico emission factor model in Mexico will be for the development of on-road motor vehicle emission estimates for the Mexico National Emissions Inventory (NEI) (ERG 2003c). The MOBILE6-Mexico emission factor model provides the most up-to-date, Mexico-specific motor vehicle emission factors for inclusion in the Mexico NEI.

Heavy-Duty Diesel Vehicle Study in Ciudad Juárez

Until 2001, extensive testing and analysis of mobile source emissions in Ciudad Juárez had been performed only on LDGV vehicles. No information existed about emissions from the commercial diesel truck and bus operations in the city.

TCEQ sponsored a study conducted by the Universidad Autónoma de Ciudad Juárez in 2001 that focused on determining the commercial truck and bus population in Ciudad Juárez and the volume of heavy-duty diesel vehicle (HDDV) traffic passing through the three international border crossings linking Ciudad Juárez with El Paso (Snow, Velasquez, and Hardison 2002). A survey was designed to gather actual HDDV (truck and bus) activity data throughout Ciudad Juárez by asking questions of the truck companies and their truck operators about the size of their truck fleet, where they drove within the city, and where they crossed the international border.

In order to estimate traffic volume (i.e., vehicle kilometers traveled [VKT]), the route for each trip reported in the driver's survey was plotted on a geographic information system (GIS) map of the roadway network for Ciudad Juárez. This was performed using the information for the origin and destination of each trip and the shortest route between those points along the truck routes and major arterials of the roadway network. Then, a GIS utility within the software program ArcView was used to calculate the length of each trip. The daily VKT was obtained for each truck or bus by adding all the individual trips for a 24-hour period. The VKT for each vehicle ranged from 7.36 km (4.57 miles) to 148.07 km (92.02 miles), with an average of 53.21 km (33.07 miles) for all trucks and buses.

Table 1 shows the total number of trucks and buses operating in Ciudad Juárez, including the types of fuel used (Snow, Velasquez, and Hardison 2002). This table shows that diesel is the predominant fuel used in Ciudad Juárez by HDDVs. These data can be used in the future to update the Ciudad Júarez mobile sources inventory.

Unregistered Vehicles Study in the Monterrey Metropolitan Area

The mobile source emissions inventory for Monterrey, Nuevo León, (for 1995) is based on the available data of vehicles registered in Monterrey (GNL, et al. 1997). In some Mexican cities, the fraction of unregistered vehicles may represent an important contribution of vehicle emissions. In the case of the Monterrey Metropolitan Area

Table 1. Total Number of Heavy-Duty Vehicles Operating in Ciudad Juárez

Heavy-Duty Vehicle Type	Type of Fuel Used			
	Diesel	Gasoline	Natural Gas and Propane	Total
Trucks	4,947	127	241	5,315
Buses	2,341	0	1,445	3,786
Total	7,288	127	1,686	9,101

Source: Snow, Velasquez, and Hardison 2002

(MMA), there are a significant number of vehicles circulating with out-of-state or non-Mexican license plates. There are also many old U.S. vehicles operating in the MMA, both registered and unregistered. These vehicles represent an important contribution to mobile source emissions.

As part of the Mexico National Emissions Inventory Program, the Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM) performed a study to determine the fraction of unregistered vehicles in the MMA (Mejía, et al. 2003). This study was strongly supported by local authorities of the Nuevo León state government.

Vehicles throughout Mexico are identified using two license plates, one in the front and one in the rear. A sticker is also used with the same plate number that must be displayed on the rear window; however, many owners of vehicles do not always comply with this requirement, making it difficult to determine whether or not a vehicle is registered. Another identifier of vehicles is the payment of a federal tax called *tenencia*. This tax is paid every year and the owner receives a sticker that must be placed on the rear plate; however, as with the vehicle identification sticker, not all drivers comply with this requirement.

Because of this noncompliance, it was not possible for this study to identify registered and non-registered vehicles based on the stickers. Therefore, the fraction of unregistered vehicles was determined by comparing the vehicle's plate data with the database of registered vehicles in Nuevo León. The database includes data on the type of vehicle, color, and plates, among other characteristics necessary to compare with sample data of the number of vehicles in the MMA. The vehicles considered in this study included private vehicles, taxis, sport utility vehicles, light trucks, and government vehicles with special plates.

Data from 3,758 vehicles, including the vehicle manufacturer, brand, year, color, and plate, were collected between February 14, 2002, and February 26, 2002, in 14 parking lots of supermarkets and shopping malls in the MMA. Data from 3,149 pictures of vehicles collected during six emission remote sensing campaigns between November 5, 2002, and February 21, 2003, were also used in the study. These data were compared with the data from the state's April 2003 vehicle registration file. The vehicles were classified as unregistered if they did not appear in the vehicle registration file. Unclassified vehicles were further divided as non-registered, out-of-state, another country (usually from the United States), or vehicles with special characteristics such as for police or governmental use. Finally, resampling of the data collected was performed for quality assurance. The vehicles sampled (6,907) represent 0.77% of the registered vehicle fleet in the MMA. For quality assurance, 5.3% of the data was recorded on forms where pictures were not available and were selected at random and reviewed.

The results of the study show that the fraction of registered vehicles in the MMA is approximately 88.5%. Of the total vehicles with Nuevo León plates, only 1.0% were classified as unregistered; this value is small compared with data for other cities. Possible explanations of this small value are that vehicles in Nuevo León were required to change plates in 2002. After a few months, vehicle owners were fined if plates were not changed and the owner continued to operate the vehicle. Under these conditions, it is expected that a high percentage of vehicles with the new plates will be registered and only a small amount would not be registered and continue to operate illegally with new plates. The fraction of other-state vehicles was 8.8%, other country vehicles totaled 0.9%, and 0.74% had special plates.

The results of this study show that a significant percentage of unregistered vehicles continue to operate in the MMA. These vehicles should be considered as they impact the vehicle registration data used to update the mobile source emissions inventory for the MMA in the future.

Border Congestion, Air Quality, and Commerce

The U.S.-Mexican border region, typically defined as a 100-km band (approximately 62.5 miles) that extends on each side of the nearly 2,000-mile international boundary, includes 10 U.S. and Mexican states and a combined population of more than 11.9 million people, a number that is expected to double by 2030 (Peach and Williams 2004). International (crossborder) transportation is critical to the support of this regional economy and to the economic growth of both nations. Traffic congestion and delays at the border crossings have increased in many locations due in part to increasing binational trade and manufacturing, the implementation of the North American Free Trade Agreement (NAFTA), and the associated regional population growth.

There have been two important negative consequences associated with the increase in traffic and congestion. First, vehicles idling in long queues emit harmful pollutants into the air, thus negatively affecting air quality that is already below acceptable standards in some locations. Second, at many larger crossings, substantial delays in the passage of commercial vehicles have been documented. Clearly, such delays have an economic cost associated with them. While it is an important goal to increase international trade and tourism, it is equally important that progress take place while considering the local and regional environment, as well as the need to engage in commerce successfully.

In 1999, WGA initiated a study to examine reasons for border congestion, understand the relationship between various factors that contribute to border congestion and delays, and propose opportunities to alleviate that congestion and the resulting impacts on air quality and commerce (Halvey 2002). An important advantage of this study was that it combined field research and scientific modeling with the perceptions and experiences of those familiar with border congestion. At the public forums there was open discussion about problems, needs, and causes, followed by identification of potential opportunities. Participants were urged to identify the problems and needs most important to their businesses and other activities and to reach agreement on the problems, needs, and most beneficial and acceptable improvements to be pursued.

A number of problems were identified. The highest priority issues were that:

- Many vehicles crossing the border pollute excessively
- Unnecessary delays occur in queues at border station primary inspection booths
- "Dead heading" (traveling to a destination with a load and returning to the origin with no load) trucks produce additional congestion and exhaust emissions
- Border crossing demands exceed capacity, resulting in congestion
- No single agency has primary responsibility for coordinating the inspection process
- Congestion and delays result from inefficient or circuitous access
- Inspection and transportation agencies do not always have the budget to make broad operational and infrastructure changes
- There is no long-range planning for international trade corridors and facilities serving border crossings

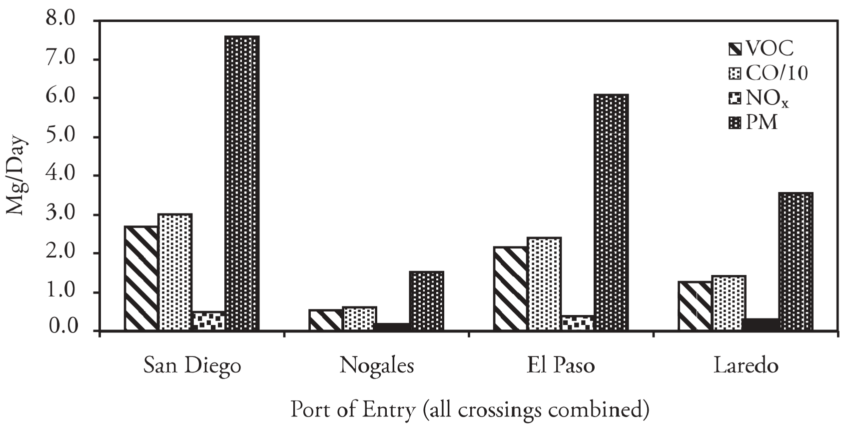
After identifying and characterizing problems, the study proposed a number of opportunities, including enforcing existing emissions standards, ensuring sufficient staffing at the border crossings, expediting full implementation of NAFTA, and considering a unified binational port of entry system. These potential opportunities were examined for their effects on border congestion and air quality through a series of surveys conducted at seven ports of entry along the U.S.-Mexican Border: San Diego-Tijuana (San Ysidro and Otay Mesa), Ambos Nogales (Nogales I), El Paso-Ciudad Juárez (Bridge of the Americas and Ysleta-Zaragosa), and Laredo-Nuevo Laredo (Laredo I and II). Each opportunity was prioritized as high, medium, or low based on its likelihood of implementation or performance by a driver. The high and medium opportunities were put into a delay model to estimate the average avoidable delay in minutes per vehicle at each port of entry. Then the MOBILE5-Juárez emission factor model was used to estimate potential emission reductions based on the avoidable delays at each port of entry. The results are shown in Figure 5 for VOCs, carbon monoxide, NO_x, and PM emissions.

An important finding of this project was that regardless of the solutions adopted, there is nearly universal agreement that alleviating border congestion will have positive effects on the economies of both countries and environmental quality along the U.S.-Mexican border.

Regional Emissions Inventories for Northern Mexico

In Northern Mexico, regional inventories for industrial, area, mobile, and natural sources are an important part of the air quality plans for Tijuana, Mexicali, Ciudad Júarez, and Monterrey. Other U.S.-Mexican border inventories support development of transborder air quality plans and health risk assessments, as well as improving data for specific area sources and toxic sources of air pollution.

Figure 5. Estimated Potential Emissions Reductions from Avoidable Delay for VOCs, Carbon Monoxide, NO_x, and PM Emissions



Source: Halvey 2002

Emissions Inventories for Air Quality Planning

Table 2 summarizes the results (in Mg/year) of the air quality planning inventories conducted for regions located in Northern Mexico. The table includes criteria pollutants and ammonia for Mexicali and Tijuana.

Monterrey, Nuevo León

Monterrey is the largest city in any of the Mexican states bordering the United States. Although technically outside the 100-km border zone (thus removing it from Border 2012 control strategies), air emissions sources located within the MMA can contribute to air pollution within the U.S.-Mexican border area.

The initial 1995 base year inventory (summarized in Table 2) was developed for the Monterrey Air Quality Plan (GNL, et al. 1997). The quantity of annual PM_{10} emissions from natural sources (763,725 Mg) comes mostly from wind erosion of disturbed lands. The absence of area source SO_x emissions indicates that emissions from fuel combustion in the industrial, commercial, and residential sectors are not accounted for in this inventory.

Ciudad Juárez, Chihuahua

Ciudad Juárez lies directly across the U.S.-Mexican border south of El Paso. It is the largest metropolitan area directly adjacent to the border and has been an area of focus for many regional air quality studies related to impacts on criteria pollutant air quality standards, visibility, and public health in the Paso del Norte region (which includes Ciudad Juárez, El Paso County, and Doña Ana County, N.M.) (Turner, et al. 1998; Yocke, et al. 2001; Parks, et al. 2003).

The initial 1996 base year inventory (summarized in Table 2) was developed for the Ciudad Juárez Air Quality Plan (GCh, et al. 1998). These results indicate a significant contribution to the overall inventory by mobile sources for every pollutant except PM_{10}. Based on known significant activity by industrial sources, particularly the maquiladora industry in Ciudad Juárez during 1996, the point source emissions in this inventory are surprisingly low relative to area source SO_x emissions, indicating that point source fuel com-

Table 2. Summary of Air Quality Planning Emissions Inventories for Northern Mexico

Inventory Area, Year	Source Types	Emissions Estimates (Mg/year)					
		NO_x	SO_x	VOC[a]	CO	PM_{10}	NH_3
Monterry, Nuevo León, 1995	Point	18,549	27,997	5,578	3,281	45,946	nd
	Area	458	nd	36,660	8	16	nd
	Mobile	34,268	2,469	83,137	904,473	5,941	nd
	Natural	nd	nd	nd	nd	763,725	nd
	Total	53,275	30,466	125,375	907,762	815,628[b]	nd
Ciudad Júarez, Chihuahua, 1996	Point	1,393	716	2,395	861	210	nd
	Area	802	1,834	19,244	2,055	281	nd
	Mobile	23,920	1,596	54,493	449,844	1,020	nd
	Natural	nd	nd	nd	nd	45,096	nd
	Total	26,115	4,146	76,132	452,760	46,607[b]	nd
Mexicali, Baja California, 1996	Point	1,537	2,849	1,407	4,721	1,994	nd
	Area	735	11	15,379	18,944	61,932	4,749
	Mobile	14,927	937	31,184	243,073	515	nd
	Natural	1,348	nd	3,441	nd	20,548	nd
	Total	18,547	3,797	51,411	266,073	84,989	4,749
Tijuana, Baja California, 1998	Point	4,243	22,838	8,783	629	3,388	nd
	Area	2,009	8,204	33,083	22,980	22,724	4,556
	Mobile	25,356	984	38,610	294,378	1,371	nd
	Natural	149	nd	1,458	nd	nd	nd
	Total	31,757	32,026	81,934	317,987	27,483	4,556

Notes: [a]Emissions are reported as hydrocarbon except for Tijuana, which are reported as total organic gases (TOG); [b]Emissions are reported as total suspended particulates (TSP); nd = no data.

Sources: Monterrey (GNL, et al. 1997), Ciudad Júarez (GCh, et al. 1998), Mexicali (GBC, et al. 1999), Tijuana (GBC, et al. 2000) bustion may be under-reported. Also, recent projects sponsored by TCEQ have focused on improving the area sources inventory (ERG 2003d).

Mexicali, Baja California

Mexicali lies directly across the U.S.-Mexican border south of Imperial County, Calif. It is the capital of the state of Baja California and has considerable amounts of agricultural activity. There has been significant recent construction of natural gas-fired power plants in the Mexicali area, triggering new air quality concerns (Johnson and Alvarez 2003).

The initial 1996 base year inventory (summarized in Table 2) was developed for the Mexicali Air Quality Plan (GBC, et al. 1999). The inventory was developed as a special task under the Mexico Emissions Inventory Program sponsored by WGA, EPA, and INE (Radian 2000b). The inventory results for Mexicali show that motor vehicles generate the majority of the NO_x, VOC, and carbon monoxide emissions. Area sources (mainly paved and unpaved road reentrainment) and natural sources (wind erosion) generate the majority of PM_{10}. The most significant PM_{10} area source categories are paved and unpaved road reentrainment and wind erosion from disturbed areas (considered as a “natural source” in this inventory). The metallic and non-metallic mineral industries generate the majority of point source emissions of all pollutants (Radian 2000b).

Tijuana, Baja California

Tijuana lies directly across the U.S.-Mexican border south of San Diego, Calif. After Ciudad Juárez, it is the largest metropolitan area directly adjacent to the border. This area’s impact on ozone levels in Southern California has been studied for more than a decade as part of the Southern California Ozone Study-North American Research Strategy for Tropospheric Ozone (SCOS-NARSTO) (discussed below).

A preliminary annual emissions inventory for 1998 was developed for the Tijuana Air Quality Plan (GBC, et al. 2000). The cities of Rosarito and Tecate were also included in the inventory domain. As with the Mexicali inventory, the Tijuana inventory was developed as a special task under the Mexico Emissions Inventory Program sponsored by WGA, EPA, and INE. Subsequent to the publication of the preliminary inventory in the Tijuana Air Quality Plan, the inventory was reviewed and revised (ERG 2003e). The revised inventory is summarized in Table 2. As in Mexicali, motor vehicles generate the majority of NO_x, VOCs, and carbon monoxide emissions, while paved and unpaved road reentrainment and wind erosion are responsible for the majority of the PM_{10} emissions (ERG 2003e).

Hazardous Air Pollutant Emissions Inventories

Table 3 summarizes the results (in Mg/year) of the HAP emissions inventories developed for areas in Northern Mexico.

Nogales, Sonora

The Ambos Nogales HAP emissions inventory (Radian 1997d) followed the development of HAP emissions inventories for four regions of Arizona under the Arizona Hazardous Air Pollution Research Program. The inventory was developed for 1994. The inventory domain measured 12 km by 19 km and was equally divided between Nogales, Ariz., and Nogales, Son. The inventory included 113 individual HAPs drawn from the Arizona HAP Research Program list, as well as PM_{10} and $PM_{2.5}$. Reporting focused on 25 compounds of interest (COI) that were initially identified as having the greatest potential impact on human health within the inventory domain.

The total HAP (25 COI) emissions for the Nogales, Son., portion of the Ambos Nogales HAP emissions inventory are shown in Table 3. The Nogales, Son., portion of the inventory included 49 point sources (primarily maquiladoras). Emissions were estimated for 21 different area source categories, including some unique source categories such as residential biomass combustion, wire reclamation, and produce fumigation. On-road motor vehicle emissions were estimated using MOBILE-Juárez (Radian 1996c). Non-road mobile source and biogenic emissions were not estimated.

Table 3. Summary of Hazardous Air Pollutant Emissions Inventories for Northern Mexico

Inventory Area, Year	Source Types	Emissions Estimates (Mg/year)[a]						
		NO_x	SO_x	VOC	CO	PM_{10}	$PM_{2.5}$	HAPs
Nogales, Sonora, 1994	Point	nd	nd	nd	nd	nd	nd	443
	Area	nd	nd	nd	nd	7,980	3,864	105
	Mobile	nd	nd	nd	nd	81	39	426
	Non-Road	nd	nd	nd	nd	nd	nd	nd
	Biogenic	nd	nd	nd	nd	nd	nd	nd
	Total	nd	nd	nd	nd	8,061	3,903	974
Agua Prieta, Sonora, 1999	Point	366	1,925	727	1,747	431	366	80
	Area	146	nd	322	28	96,967	17,732	29
	Mobile	1,757	51	2,008	20,744	54	46	622
	Non-Road	100	23	49	556	10	10	12
	Biogenic[b]	3	nd	1,077	nd	nd	nd	nd
	Total	2,372	1,999	4,183	23,075	97,463	18,155	743
Northern States, 1999[c]	Gold mining/ Refining	nd	nd	nd	nd	nd	nd	5.341
	Chlor-Alkali plants	nd	nd	nd	nd	nd	nd	0.863
	Power plants	nd	nd	nd	nd	nd	nd	0.819
	Ferrous and non-ferrous smelters	nd	nd	nd	nd	nd	nd	0.701
	Refineries	nd	nd	nd	nd	nd	nd	0.143
	Other manufacturing	nd	nd	nd	nd	nd	nd	0.010
	Hazardous/ Medical waste incineration	nd	nd	nd	nd	nd	nd	0.001
	Total	nd	nd	nd	nd	nd	nd	7.878

Notes: [a]nd (no data) indicates that emissions were not estimated or are not applicable for that pollutant/source type; [b]Biogenic emissions are reported for the entire domain of Agua Prieta and Douglas; [c]HAP emissions are reported for mercury only.
Sources: Nogales (Radian 1997d), Agua Prieta (Meszler, et al. 2002), Northern States' Mercury Inventory (Acosta-Ruiz and Powers 2003)

Agua Prieta, Sonora

Under the Arizona Hazardous Air Pollution Research Program, the Arizona Department of Environmental Quality (ADEQ) conducted an air quality monitoring program for Douglas-Agua Prieta (Meszler, et al. 2002). The inventory was developed in 1999. The inventory domain is identified by Meszler, et al. (2002) as including Douglas and Agua Prieta, but the exact domain definition is not clear. The inventory included NO_x, SO_x, VOCs, carbon monoxide, PM_{10}, $PM_{2.5}$, and HAPs (343 compounds from EPA's HAP list and 740 compounds from EPA's Integrated Risk Information System [IRIS]).

The total HAP emissions for the Agua Prieta portion of the emissions inventory are shown in Table 3. The Agua Prieta portion of the inventory included 71 point sources (including maquiladoras, brick kilns, dry cleaners, a lime kiln, and a landfill). Emissions were estimated for only 11 area source categories (including paved and unpaved road dust, degreasing, pesticide and consumer product use, residential butane combustion, residential wood combustion, printing operations, structural fires, automobile fires, trash fires, and charbroiling). On-road motor vehicle emissions were estimated with EPA's MOBILE6 emission factor model. Non-road mobile source and biogenic emissions were also estimated.

Northern States' Mercury Inventory

A national mercury (Hg) inventory was developed for Mexico under the sponsorship of CEC (Acosta-Ruiz and Powers 2003). The objectives of this inventory were to develop a comprehensive list of potential stationary sources of atmospheric mercury emissions in Mexico, provide annual process throughputs for these sources, and estimate mercury emissions using indirect approaches (such as emission factors). This inventory included only stationary industrial sources of mercury.

The most significant sources of mercury within the six northern states, as shown in Table 3, were determined to be gold mining and refining, chloro-alkali plants, power plants, and ferrous and non-ferrous (i.e., copper, zinc, and lead) smelters. Mercury is a by-product of gold refining and ferrous/non-ferrous smelting, used to produce chlorine gas in chloro-alkali plants, and a component of the Maya crude oil used as feedstock to produce *combustóleo*, which is used in thermal power plants and industrial/commercial boilers.

Other Criteria Air Pollutant Emission Inventories

Other regional inventories for criteria air pollutants in Northern Mexico were developed for input to models for assessing impacts on ozone levels in the U.S.-Mexican border region and visibility impacts across the United States and into Canada.

Paso del Norte Study

The Paso del Norte includes the area around the cities of El Paso and Ciudad Juárez. The Paso del Norte Ozone Study was conducted during the summer of 1996 to assist EPA, TCEQ (then the Texas Natural Resource Conservation Commission [TNRCC]), and others to collect the data needed to perform reliable ozone modeling (Roberts, Main, and Yocke 1996). The resulting ozone modeling protocol included specification for a gridded base-case emissions inventory, as well as procedures for modeling base-case and future-year applications of the ozone model (Yocke 1997). The Paso del Norte modeling domain was selected to include all of El Paso County, parts of Doña Ana and Otero Counties in New Mexico, part of Hudspeth County in Texas, and the metropolitan area of Ciudad Juárez.

The annual 1996 Paso del Norte emissions inventory (in Mg/day) is shown in Table 4 (Haste, et al. 1998). The emissions inventory for the modeling domain was developed (mainly) from existing emissions inventory data for point, area, mobile, and biogenic sources. The exception was that EPA's Biogenic Emission Inventory System Version 2 (BEIS-II) was used to estimate the biogenic emissions.

For the U.S. portion of the domain, the inventory values were provided by a number of sources, including TCEQ, the EPA Emission Trends Database for 1995, and the Sunland Park State Implementation Plan. A quality assurance (QA) review of these emissions determined they were reasonable and no adjustments were made.

Table 4. 1996 Paso del Norte Study Emissions Inventory

Source Types	Emissions Estimates (Mg/day)		
	NO_x	VOC	CO
U.S. Counties within Modeling Domain			
Point	79	18	48
Area	43	59	186
Mobile	49	43	440
Biogenic	16	95	nd
Total	187	215	674
Ciudad Juárez Metropolitan Area			
Point	39	5	11
Area	3	42	16
Mobile	63	142	1,201
Biogenic	11	30	nd
Total	115	219	1,228

Note: [a]Emissions were converted from short tons/day to Mg/day for this table. nd = no data.
Source: Haste, et al. 1998

For Ciudad Juárez, 25 point sources, 32 major area sources, mobile sources, and biogenic sources were included in the inventory. Emissions for point, area, and mobile sources were provided by the Instituto Mexicano de Investigación y Planeación (IMIP) in Ciudad Juárez. The biogenic emissions were estimated using BEIS-II. A QA review of the VOC and NO_x emissions from approximately one-half of the industrial sources in the Ciudad Juárez inventory revealed some problems with the emissions as provided by IMIP, such as unexpectedly small VOC emissions from a pharmaceutical production facility and unexpectedly large VOC emissions from an electrical accessory fabrication plant. Mobile source emissions were found to be consistent with gasoline sales data; however, heavy-duty diesel truck NO_x emissions may be underestimated.

SCOS97-NARSTO

The 1997 Southern California Ozone Study-North American Research Strategy for Tropospheric Ozone (SCOS97-NARSTO) was organized as a follow-up study to the Southern California Air Quality Study completed more than a decade earlier (Shah, et al. 1998). The SCOS97-NARSTO emissions inventory was developed for use as input to photochemical air quality models for assessing the contributions of and interactions among air pollution sources in the region, and for developing, implementing, and tracking the progress of control strategies. This modeling region for SCOS97-NARSTO contains a portion of northern Baja California, including Tijuana, Tecate, and Mexicali.

The SCOS97-NARSTO emissions inventory for northern Baja California (in Mg/day) is shown in Table 5 (Funk, Coe, and Chinkin 2001). This inventory was developed using per capita scaling factors and other inventories conducted in 1990 for northern Baja California (SAI 1997) and in 1996 for Mexicali (Radian 2000b). The scaling factors provide a reasonable method to scale emissions that are highly uncertain and of unknown quality.

Table 5. 1997 SCOS97-NARSTO Emissions Inventory for Northern Baja California

Source Types	Emissions Estimates (Mg/day)				
	NO_x	SO_x	TOG	CO	PM
Point	9	17	9	28	11
Area	5	nd	92	114	376
Mobile	56	5	115	904	2
Total	70	22	216	1,046	389

Note: [a]Emissions were converted from short tons/day to Mg/day for this table. nd = no data.
Source: Funk, Coe, and Chinkin 2001

BRAVO Study

The Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study examined visibility impairment at Big Bend National Park in Southwest Texas. To support BRAVO, an emissions inventory for 1999 was developed for visibility pollutants and precursors of sources located within seven U.S. states (Texas, New Mexico, Colorado, Kansas, Oklahoma, Louisiana, and Arkansas) and 10 Mexican states (Baja California, Sonora, Chihuahua, Coahuila, Nuevo León, Tamaulipas, Sinaloa, Durango, Zacatecas, and San Luis Potosí) (Kuhns, Green, and Etyemezian 2001). It also included emissions from the three municipalities of Tula, Vito, and Apaxco—the largest industrial grouping of sulfur dioxide (SO_2) sources in Mexico. Further, it detailed power plant emissions and the Popocateptl volcano (located in the Mexican state of Puebla). The BRAVO inventory was used as input into the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system (Kuhns and Vukovich 2003). SMOKE supported various modeling applications used to simulate air quality over the entire United States and most of Mexico for specified time periods.

The BRAVO emissions inventory for the six northern Mexican states is summarized in Table 6 (Kuhns, Green, and Etyemezian 2001). Emissions in this table are for the six northern Mexican states only, although the BRAVO study emissions inventory includes 10 Mexican states.

The Mexican portion of the BRAVO study emissions inventory relied on the previous inventories for Mexico, including the Monterrey, Ciudad Juárez, Mexicali, and Tijuana Air Quality Planning inventories. Area and mobile emission factors were calculated for these four cities based on five activity indicators: population, number of households, total number of registered vehicles, agricultural acreage, and head of cattle (Kuhns and Vukovich 2003). Activity data from Mexico's Instituto Nacional de Estadística, Geografía e Informática (INEGI) was used to estimate emissions from the uninventoried areas in Mexico. Point source emissions were estimated using data contained in the National Mercury Inventory (Acosta-Ruiz and Powers 2003) and fuel consumption data provided by CEC.

Table 6. 1999 BRAVO Emissions Inventory for the Six Northern Mexican States

Source Types	Emissions Estimates (Mg/day)						
	NO_x	SO_x	VOC	CO	PM_{10}	$PM_{2.5}$	NH_3
Point	114,410	490,873	612	10,974	29,121	14,445	nd
Area	23,395	28,322	434,128	431,072	602,422	197,787	88,049
Mobile	250,349	14,479	512,559	4,602,774	16,995	16,506	nd
Total	388,154	533,675	947,299	5,044,820	648,537	228,739	88,049

Note: nd = no data
Source: Kuhns, Green, and Etyemezian 2001

Ciudad Juárez Area Sources Emissions Inventory

For many years, emissions data have been collected by both Mexican and U.S. authorities related to large industrial sources and on-road motor vehicles in the El Paso-Ciudad Juárez area. However, little has been known about the impacts on air quality from most area sources, including small industrial facilities. For this reason, TCEQ sponsored a study to improve emissions estimates for certain area source categories located in Ciudad Juárez, including dry cleaners, autobody repair shops, small foundries, brick kilns, and agricultural dust from tillage and harvest, among other sources. Although originally intended to focus on fine PM sources (PM_{10} and $PM_{2.5}$), the study was expanded to include sources of PM precursors and criteria pollutants. The study included a field survey to identify source locations and collect activity data from approximately 20% of the total population of facilities within the selected source categories. Using the inventory data, source-specific emissions for the surveyed sources were estimated (ERG 2003d). Additional global positioning system (GPS) data were collected to determine the location of more than 1,000 sources and extrapolation techniques and were used to estimate emissions for the entire population of sources within each area source category. The inventory results for 2002 were gridded for input into air quality dispersion models (PNEG and ERG 2003).

Results of the Ciudad Juárez area sources emissions inventory (in Mg/year) are summarized in Table 7 (PNEG and ERG 2003). Fuel combustion in the commercial, institutional, and residential sectors generates significant emissions of all pollutants, except ammonia. Although unpaved road dust is the largest area source of PM_{10} emissions, fuel combustion is the largest single source of $PM_{2.5}$ emissions in the area source inventory. Although these results do not include the larger point, mobile, and biogenic sources, they provide an accurate inventory for these select area source categories based on local activity data and “bottom-up” emissions inventory techniques. Also, these emissions provide a good foundation for an updated comprehensive criteria pollutant emissions inventory for the Ciudad Juárez area in the future.

Mexico National Emissions Inventory

Subsequent to the early efforts by GCVTC and WGA to build emissions inventory capacity in Mexico, a project to develop the first comprehensive NEI for Mexico began in 2000. The Mexico NEI project has financial support from WGA, INE, EPA, and CEC. Representatives from these partners, along with other stakeholders from government, academia, and private sector entities on both sides of the U.S.-Mexican border, participate in the Technical Advisory Committee (TAC) and provide technical guidance for this project.

Title VI of the Ley General del Equilibrio Ecológico y la Protección al Ambiente (General Law of Ecological Balance and Environmental Protection, in Spanish LGEEPA) establishes the regulatory framework for Mexico’s air quality program. INE, as the research entity within SEMARNAT, is the lead agency for the development of the Mexico NEI. Maintaining and updating the Mexico NEI is the responsibility of SEMARNAT’s Subsecretaría de Gestión para la Protección Ambiental (Under-Secretariat of Environmental Management).

Table 7. 2002 Ciudad Juárez Area Sources Emissions Inventory

Area Source Types	Emissions Estimates (Mg/day)						
	NO_x	SO_x	VOC	CO	PM_{10}	$PM_{2.5}$	NH_3
Small industries[a]	26.8	88.7	381.2	89.8	1,367	68.6	nd
Watewater treatment	0.4	nd	1,227.7	0.1	nd	nd	nd
Gas/Diesel/LPG marketing	nd	nd	3,308.9	nd	nd	nd	nd
Restaurants/Street vendors	25.3	nd	37.5	1,074.7	303.7	242.9	nd
Ammonia sources[b]	nd	nd	nd	nd	nd	nd	3,353.5
Brick kilns	25.9	nd	337.1	1,527.0	244.8	244.8	nd
Fires[c]	31.4	5.3	52.5	600.9	192.2	176.5	nd
Agricultural tilling	nd	nd	nd	nd	527.3	116.9	nd
Feedlots/Dairies	nd	nd	nd	nd	918.0	137.7	nd
Wind erosion	nd	nd	nd	nd	3,346.5	741.9	nd
Fuel combustion[d]	1,112.4	804.1	6,022.9	26,314.0	3,504.5	3,369.9	nd
Miscellaneous[e]	nd	nd	3.1	nd	75.7	17.6	nd
Consumer solvents	nd	nd	4,339.0	nd	nd	nd	nd
Paved roads	nd	nd	nd	nd	3,348.1	800.6	nd
Unpaved roads	nd	nd	nd	nd	13,594.6	1,986.9	nd
Border crossing	116.3	nd	739.2	8,474.7	nd	nd	nd
Total	1,338.5	898.1	16,449.1	38,081.1	27,423.2	7,904.4	3,353.5

Notes: [a]Small industries include asphalt and concrete batch plants, foundries, woodworking facilities, small quarries, autobody repair shops, dry cleaners, bakeries, grain mills, graphic arts facilities, and ice plants; [b]Ammonia sources include fertilizer use and livestock and domestic ammonia generation; [c]Fires include open burning of waste, agriculture residue burning, and structural fires; [d]Fuel combustion includes fuel burned in the commercial, institutional, and (mainly) residential sectors; [e]Miscellaneous sources include a landfill, construction dust, and pesticide use; nd = no data.

Sources: ERG 2003d, PNEG and ERG 2003

Process, Objectives, and Scope

The work to estimate the NEI is divided into three phases. Phase I focused on organizing TAC and developing the Inventory Preparation Plan (ERG 2003f). Phase II covered the development of the inventory for the six northern states (ERG 2003c). Phase III, scheduled for completion in late 2004, will result in a final, municipality-level emissions inventory for 1999 for the entire country, which includes 32 states and 2,444 municipalities.

The objectives of the Mexico NEI, as identified by TAC, are as follows:

- Provide a technical basis for improved air quality analyses within Mexico and along both sides of its borders
- Assist with regional haze requirements in the United States
- Support the development of a tri-national emissions inventory of criteria pollutants for Mexico, the United States, and Canada

Some specific end uses for the Mexico NEI are to provide the technical data needed for national-level analyses of air emission sources affecting air quality and public health in Mexico, and eventually provide the input data needed to conduct air quality modeling on both sides of the U.S.-Mexican border and for regions within Mexico. Also, some of the data used and methods developed for the Mexico NEI will be useful in updating the existing air quality planning inventories and their associated control programs.

The geographic domain of the Mexico NEI includes the entire country of Mexico. The base year of 1999 was chosen because it was believed that most governmental agencies would possess complete sets of the types of data needed to estimate emissions for that year. Also, 1999 corresponds with EPA's NEI triennial reporting cycle.

The pollutants for the Mexico NEI include the air pollutants and pollutant precursors for which Mexico has air quality standards (NO_x, SO_x, VOCs, carbon monoxide, and PM_{10}), plus $PM_{2.5}$ and ammonia, which are both important visibility pollutants.

The source types included in the Mexico NEI encompass all sources of air pollution, including point, area, motor vehicle, nonroad mobile, and natural. The preliminary emissions inventory does not include emissions from some area source categories and there are no non-road mobile sources because research is still underway to collect data, run models, and provide estimates for these sources.

Emission Estimation Methods

Point source emissions were estimated using information from SEMARNAT, the state environmental agencies (SEAs), the Secretaría de Energía (Secretariat of Energy, in Spanish SENER), and Petróleos Mexicanos (Pemex). These data included the point source emissions from the various air quality planning inventories (see Table 2), along with more current Cédulas de Operación (Annual Operating Reports, in Spanish COAs) provided by facilities directly to SEMARNAT. The data were quality-assured to check for duplication, emissions factors, and calculation errors, among other issues. Also, a threshold of 10 Mg/year was established to focus project resources on the most significant sources. Facilities emitting less than 10 Mg/year were not included within the point source inventory; their combustion emissions were incorporated into the area source inventory.

Emissions for most area source categories and the natural sources were estimated according to the Emissions Inventory Improvement Program (EIIP) Technical Reports (EPA 1997) and the Mexico Emissions Inventory Program Manuals (Radian 1997b; ERG 2002).

The activity data needed to use some of the empirical emission factors provided by this guidance are lacking for many source categories in Mexico. Therefore, Mexico-specific activity data were developed for several potentially-significant source categories. Satellite imagery and orthographic photography were used to determine the percentages of paved versus unpaved roadway surfaces. Then, this percentage, split between paved and unpaved roads, was applied to per capita VKT rates to estimate paved and unpaved road dust emissions (Wolf, Fields, and González-Ayala 2003). A national fuels balance was conducted using data obtained from SENER and Pemex (ERG 2003c). This fuels balance provides fuel usage quantities that are combined with emission factors to estimate emissions for the area source combustion categories (for example, industrial, commercial, and residential fuel combustion). Also, the fuels balance is used to quality-assure results of the point and mobile source emissions inventory.

The Mexico-specific version of EPA's MOBILE6a model (MOBILE6-Mexico) was developed and used to estimate mobile source emission factors for the Mexico NEI (ERG 2003b). The Global Biosphere Emissions and Interactions System Version 3 (GloBEIS3) was used with the Biogenic Emissions Landcover Database (BELD) to estimate biogenic NO_x and VOC emissions (Yarwood, et al. 2002; EPA 2001). BELD was used in conjunction with meteorological data from the National Climatic Data Center as submitted by the Mexican National Weather Service. Also, agricultural and forest species were "mapped" to land cover and vegetation types with emissions factors within GloBEIS; additional information on tree species within each forest type was obtained from the 1994 National Forest Inventory (FAO 2003).

Preliminary Mexico NEI Results

Table 8 summarizes the preliminary results (in Mg/year) for each of the six northern Mexican states. The results shown in Table 8 are based on the published preliminary Mexico NEI (ERG 2003c), with two modifications:

- The natural source emissions were completed after the draft report was issued, so these are included in Table 8
- The point source emissions have been adjusted based on some initial comments received on the preliminary inventory

Regardless of these changes, the results shown in Table 8 are considered preliminary because they are still undergoing extensive review by TAC and other stakeholders, and some area source categories and all non-road mobile sources were not estimated (as noted above). The next version of the Mexico NEI will be issued in a final format for the six northern states and will reflect changes made as a result of the review of the preliminary inventory. Subsequent versions of the Mexico NEI will include a draft-final format containing

Table 8. 1999 Preliminary Mexico National Emissions Inventory for the Six Northern States

State	Source Type	Emissions Estimates (Mg/year)						
		NO_x	SO_x	VOCs	CO	PM_{10}	$PM_{2.5}$	NH_3
Baja California	Point	5,695	26,605	16,567	758	6,079	4,679	0
	Area	6,546	21,295	58,757	70,101	74,377	19,520	9,045
	Mobile	18,760	6,984	18,397	239,048	718	658	244
	Natural	27,805	0	171,130	0	0	0	0
	Total	58,807	54,885	264,851	309,907	81,174	24,856	9,290
Coahuila	Point	113,760	157,762	917	18,888	106,903	96,347	0
	Area	10,248	17,980	57,520	53,390	73,223	18,772	24,166
	Mobile	8,983	4,844	8,674	113,675	498	456	169
	Natural	78,651	0	202,724	0	0	0	0
	Total	211,642	180,586	269,834	185,953	180,623	115,575	24,336
Chihuahua	Point	18,133	65,187	2,308	13,822	7,241	6,279	0
	Area	17,577	29,179	83,484	143,998	127,569	35,423	57,374
	Mobile	15,579	7,084	15,179	197,958	728	667	248
	Natural	66,669	0	961,260	0	0	0	0
	Total	117,959	101,450	1,062,231	355,777	135,539	42,369	57,622
Nuevo León	Point	20,502	81,996	20,671	22,753	13,881	10,172	0
	Area	13,324	28,471	77,274	89,387	225,207	47,574	31,291
	Mobile	32,746	16,099	29,285	305,309	1,655	1,516	563
	Natural	24,637	0	222,163	0	0	0	0
	Total	91,209	126,566	349,392	417,449	240,743	59,262	31,854
Sonora	Point	13,190	160,485	2,098	3,185	30,865	14,728	0
	Area	7,617	15,001	55,572	65,815	81,634	20,028	70,311
	Mobile	6,878	4,394	6,684	87,263	452	414	154
	Natural	61,057	0	1,194,634	0	0	0	0
	Total	88,742	179,881	1,258,988	156,263	112,951	35,169	70,464
Tamaulipas	Point	12,882	133,568	1,124	2,769	3,805	2,969	0
	Area	10,203	18,267	57,368	73,897	81,650	21,764	51,166
	Mobile	10,422	6,277	10,060	131,864	645	591	219
	Natural	159,064	0	368,717	0	0	0	0
	Total	192,570	158,112	437,269	208,530	86,100	25,324	51,385
All Six States	Total	760,929	801,480	3,642,565	1,633,878	837,130	302,554	244,951

Source: ERG 2003c

new estimates for the remaining states as well as municipality-level estimates for the entire country. The final format will reflect changes made as a result of the review of the draft final inventory.

Considering the limitations of this preliminary inventory for the northern states, certain observations can be made about these overall state-level results:

1. Natural sources (i.e., biogenic emissions from the soil and vegetation) are the most significant contributors to NO_x and VOC emissions in every state with two exceptions—in Coahuila, where point sources emit the majority of the NO_x emissions, and in Nuevo León, where mobile sources emit most (more than one-third) of the NO_x emissions. Improvements in BELD data for Mexico—such as inclusion of Mexico-specific vegetation species and use of more accurate meteorological data from more sites—will improve the accuracy of the biogenic emissions in the future.
2. In every state, point sources contribute the most SO_x emissions. Power plants in Coahuila and Sonora and a refinery in Tamaulipas are the largest emitters of SO_x in the overall inventory.
3. Area source emissions contribute the most PM_{10} and $PM_{2.5}$ emissions in every state (except Coahuila). These emissions stem mostly from paved and unpaved road reentrainment. Coahuila's chemical and transportation manufacturing sectors also contribute significantly to the PM_{10} and $PM_{2.5}$ inventories for the northern Mexican states.
4. Livestock and domestic ammonia sources comprise the total ammonia inventory.

Table 9 shows the preliminary Mexico NEI for anthropogenic sources—point, area, and mobile sources—only. This table helps establish priorities for additional analysis based on the largest sources that provide opportunities for emission reductions. Notwithstanding the fact that some area source categories and all non-road mobile sources are not included in this table, important observations can be made:

1. Point sources dominate the anthropogenic NO_x and SO_x inventory for the northern Mexican states, although these per-

centages (53.7% and 78.1% of the total) will decline when all of the area and non-road mobile sources are included in the next version of the inventory.

2. Area sources contribute the majority of the anthropogenic VOC emissions (i.e., residential wood combustion, liquefied petroleum gas [LPG] distribution, asphalt application, consumer solvent usage, industrial surface coatings, and gasoline distribution). However, ERG (2003c) notes that the point source VOC emissions are likely underestimated.

Table 9. 1999 Preliminary Mexico National Emissions Inventory for the Six Northern States (Anthropogenic Sources)

Anthropogenic Source Type	Anthropogenic Emissions (Mg/year)						
	NO_x	SO_x	VOCs	CO	PM_{10}	$PM_{2.5}$	NH_3
Point	184,163	625,604	43,684	62,175	168,775	135,172	nd
Area	65,516	130,194	389,975	496,587	663,659	163,080	243,354
Mobile	93,367	45,683	88,277	1,075,116	4,695	4,302	1,597
Total	343,045	801,480	521,936	1,633,878	837,130	302,554	244,951
Anthropogenic Source Type	Anthropogenic Emissions (Percent)						
	NO_x	SO_x	VOCs	CO	PM_{10}	$PM_{2.5}$	NH_3
Point	53.7	78.1	8.4	3.8	20.2	44.7	nd
Area	19.1	16.2	74.7	30.4	79.3	53.9	99.3
Mobile	27.2	5.7	16.9	65.8	0.5	1.4	0.7
Total	100	100	100	100	100	100	100

Note: nd = no data
Source: ERG 2003c

Future Updates of the Mexico NEI

The Mexico NEI belongs to Mexico. After the 1999 Mexico NEI is finalized under the WGA project, it becomes SEMARNAT's responsibility to maintain and update the inventory. The future of the Mexico NEI is dependent on SEMARNAT's ability to sustain adequate technical and financial resources to conduct the work. Insofar as SEMARNAT may delegate to or partner with state and municipal environmental agencies, the amount of resources dedicated to this effort by these other agencies will affect the future of the Mexico NEI.

Another important factor that will affect the quality and usefulness of the Mexico NEI in the future is the implementation of existing and pending laws that require mandatory submittal of emissions inventory data by industrial facilities and disclosure of these data to the public. On December 31, 2001, Article 109-bis of LGEEPA was modified to require industrial facilities to provide information to SEMARNAT (or states, municipalities, and the Federal District, depending on jurisdiction) for purposes of developing an inventory of emissions and transfers of pollutants to the air, water, soil and subsoil, materials, and waste. This inventory is called the Registro de Emissions y Transferencia de Contaminantes (Pollutant Releases and Transfers Register, in Spanish RETC). Article 109-bis, as modified, also requires that this information be made public and accessible. Since the regulations would not be retroactive, they would not affect the 1999 data used to develop the point source inventory for the Mexico NEI. However, future mandatory reporting and the level of information made available to the public will determine to a large extent the feasibility of future updates to the Mexico NEI.

Future Emissions Inventory Development in Northern Mexico

The future of inventory development in Mexico is dependent on four main factors:

- The ability of the Mexican agencies charged with inventory development and maintenance to secure the necessary capital to purchase sufficient electronic storage equipment and appropriate software
- The ability of those Mexican agencies to allocate sufficient human and capital resources to perform regular updates and system upgrades
- The need to coordinate among the various entities to ensure consistency in data entry formats, data accuracy, and timely updates

- The ability of federal, state, and local jurisdictions to embrace ownership of the inventory and sell its importance to business, industry, and elected officials

Over the last three years, emissions inventory development in Mexico has been given increased importance as an element of air quality planning. The decision by Mexico to partner with EPA, WGA, and CEC for the first-ever national emissions inventory creates an unprecedented potential for studying possible air quality improvement strategies.

Historical Barriers to Mexican Emissions Inventory Development

The combination of the historical barriers, such as political jurisdiction, data confidentiality, and resource limitations, will continue to affect completeness and accuracy. These barriers are discussed below.

Jurisdiction
Collection of emissions data for sources in Mexico is clearly divided along jurisdictional lines. Emissions data for the largest sources, the equivalent of major sources in the United States, are maintained by SEMARNAT. Data are generally collected locally but stored centrally in Mexico City. Emissions data for the second tier of sources, which are generally smaller in size and impact, are maintained at the state level. Finally, there may be a third tier of small individual sources, such as furniture refinishers, for which some emissions-related or activity data information is maintained at the local level. In developing the Mexico NEI, it was found that jurisdictional lines between agencies were distinct. At the very least this can lead to difficulty in assembling accurate point source information for specific geographical areas. It also can inhibit the potential of gaining economies of scale to identify and develop emissions inventories for these sources.

Data Confidentiality

Until very recently, Mexico has had strict confidentiality laws that made it difficult to report specific source information. Changes in legislation now allow current environmental impacts to be published, although historical levels are still covered by the previous confidentiality requirements. As with all changes, some sources will be slow to embrace the new requirements so full acceptance of the situation may take a few years.

Verification

While inventory management is in the purview of SEMARNAT, source enforcement in Mexico is handled by the Procuraduría Federal de Protección al Ambiente (Federal Attorney General for Environmental Protection, in Spanish PROFEPA). The agencies are cooperative with each other, but as with any similar situation, there is potential for delay in communicating between agencies and difficulty in matching information gathered separately.

It is also the case in Mexico that stack testing and continuous emissions monitors are not routinely required as part of operating conditions. This can make it difficult to objectively verify reports submitted by sources. It was not unusual to find sources reporting different data for the same parameters to different entities (for example, trade associations versus SEMARNAT).

Resources

Currently, SEMARNAT has only five people devoted to emissions inventory activities. This group is responsible for national inventories of both general source emissions data and toxic release data. By comparison, even small states in the United States typically have at least five emissions inventory staff collecting data and estimating and reporting emissions.

Mexico is also limited in its ability to fund large, sophisticated data management systems, and budgets have recently been shrinking in the government agencies. For the most part, data management is conducted with existing software that can run effectively on individual desktop computers.

Partnership

While Mexico has independently chosen to proceed with the completion of a comprehensive national inventory, the establishment of partnerships with the major Regional Planning Organizations in the United States—such as the Western Regional Air Partnership (WRAP) and the Central Regional Air Planning Association (CENRAP)—and CEC in Canada has created opportunities to share resources and expertise. It also creates the potential for the development of common database formats and storage platforms.

Future of Inventory Development in Mexico

The future of inventory development in Mexico is hopeful. Finalization of the northern states inventory in 2004 (under the Mexico NEI program) will immediately stimulate additional planning activities on the recently adopted Border 2012 plan and will allow for the initiation of modeling analyses for visibility plans in the United States. However, there is a great amount of continuing work necessary to improve the completeness and quality of the inventory.

One of the first elements of this continuing process is to secure the acceptance and support of the Mexican Congress, especially in view of tight resources. As the value of a comprehensive, accurate inventory becomes more accepted, it is likely that additional resources will be appropriated for inventory work.

Another opportunity for Mexico is to initiate integration of all levels of government into the inventory process. This will require a significant outreach and training effort as well as investment in computer equipment. However, if such an effort is successful, the network of trained experts will go a long way toward improving quality and completeness. To accomplish this, institutional barriers will have to be eliminated and a strong climate of information-sharing implemented.

In this era of unprecedented cooperation, Mexico can take advantage of efforts by the Regional Planning Organizations and CEC to become part of a North American system of inventory reporting. Establishing common platforms will not only create economies of scale, but will limit disagreements about input data for long-range transport analyses. Naturally, control of the data would remain with each respective country. Finally, as Mexico places more effort into its emissions inventory program, outreach efforts to business, industry, trade associations, and elected officials at all levels will ultimately result in greater compliance and cooperation.

References

Acosta-Ruiz, G., and B. Powers. 2003. "Preliminary Atmospheric Emissions Inventory of Mercury for Mexico." Paper presented at the 12th Annual U.S. EPA International Emissions Inventory Conference, 29 April–1 May, San Diego, California.

Burnette, A. D., S. Kishan, and M. E. Wolf. 2001. "MOBILE5-Mexico: An Emission Factor Model for On-Road Vehicles in Mexico." Paper presented at the 10th Annual U.S. EPA International Emissions Inventory Conference, 1–3 May, Denver, Colorado.

Eastern Research Group, Inc. 2000. *MOBILE5-Mexico Documentation and User's Guide.* Austin, Tex.: Prepared for Western Governors' Association and Binational Advisory Committee.

Eastern Research Group, Inc. 2001a. *Development of PART5-Juárez from PART5-TX1, Final.* Austin, Tex.: Prepared for TCEQ.

Eastern Research Group, Inc. 2001b. *Update of MOBILE-Juárez to MOBILE-Juárez2, Final.* Austin, Tex.: Prepared for TCEQ.

Eastern Research Group, Inc. 2002. *Mexico Emissions Inventory Program Manuals, Volume VII—Natural Source Inventory Development, Final.* Sacramento, Calif.: Technical report prepared for Western Governors' Association and Binational Advisory Committee.

Eastern Research Group, Inc. 2003a. *Mexico Emissions Inventory Program Manuals, Volume I—Emissions Inventory Program Planning, Final.* Sacramento, Calif.: Technical report prepared for Western Governors' Association and Binational Advisory Committee.

Eastern Research Group, Inc. 2003b. *MOBILE6-Mexico Documentation and User's Guide.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Eastern Research Group, Inc. 2003c. *Mexico National Emissions Inventory, 1999, Draft.* Sacramento, Calif.: Prepared for SEMARNAT, INE, EPA, Western Governors' Association, and CEC.

Eastern Research Group, Inc. 2003d. *Development of an Area Source Emissions Inventory for Ciudad Juárez, Chihuahua, Mexico. Final.* Sacramento, Calif.: Prepared for TCEQ.

Eastern Research Group, Inc. 2003e. *Tijuana Air Emissions Inventory: Summary and Comments.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Eastern Research Group, Inc. 2003f. *Emissions Inventory Preparation Plan for the Mexico National Emissions Inventory, Final.* Sacramento, Calif.: Prepared for SEMARNAT, INE, EPA, Western Governors' Association, and CEC.

Fields, P. G., L. J. Murphy, M. E. Wolf, B. J. Morrison, A. D. Burnette, M. A. Sabisch, S. Kishan, R. Ramos-Villegas, and E. Nava-Lopez. 1998. "Continuing Development in the National Emissions Inventory Program for Mexico." Paper presented at U.S. EPA/A&WMA Specialty Conference: The Emission Inventory: Living in a Global Environment, 9–10 December, New Orleans, Louisiana.

Food and Agriculture Organization of the United Nations. 2003. "1994 Forest National Inventory." Cited 21 May. http://www.fao.org/forestry/fo/country/nav_world.jsp.

Funk, T., D. Coe, and L. Chinkin. 2001. "Recommendations for Emission Estimates for the Northern Baja California Region of the SCOS97-NARSTO Domain." Technical memorandum prepared for Paul Allen, California Air Resources Board.

Government of the State of Baja California, the Municipal Government of Mexicali, Secretaría de Medio Ambiente y Recursos Naturales, and Secretaría de Salud. 1999. *Programa para Mejorar la Calidad del Aire de Mexicali 2000-2005.* Mexicali, Baja California.

Government of the State of Baja California, the Municipal Government of Tijuana, the Municipal Government of Playas de Rosarito, Secretaría de Medio Ambiente y Recursos Naturales, and Secretaría de Salud. 2000. *Programa para Mejorar la Calidad del Aire de Tijuana Rosarito 2000-2005.* Tijuana, Baja California.

Government of the State of Chihuahua, Municipal Government of Juárez, Secretaría de Medio Ambiente y Recursos Naturales, and Secretaría de Salud. 1998. *Programa de Gestión de la Calidad del Aire de Ciudad Juárez 1998-2002.* Ciudad Juárez, Chihuahua.

Government of the Federal District, Secretaría del Medio Ambiente, Secretaría de Ecología del Gobierno del Estado de México, and Secretaría de Medio Ambiente y Recursos Naturales, and Instituto Nacional de Ecología. 2002. *Inventario de Emisiones, Zona Metropolitana del Valle de México, 1998.* Mexico City, Mexico.

Government of the State of Nuevo León, Secretaría del Medio Ambiente, Secretaría de Medio Ambiente y Recursos Naturales, and Secretaría de Salud. 1997. *Programa de Administración de la Calidad del Aire del Area Metropolitana de Monterrey 1997-2000.* Monterrey, Nuevo León.

Grupo Trafalgar. 2000. *Population of Vehicles in Mexico City's Metropolitan Area and Their Emission Levels, Final.* Mexico City: Prepared for World Bank.

Halvey, R. 2002. "Border Congestion, Air Quality and Commerce." Pages 281–304 in *Both Sides of the Border: Transboundary Environmental Management Issues Facing Mexico and the United States,* Linda Fernandez and Richard T. Carson, eds. New York: Kluwer Academic Publishers.

Haste, T. L., N. Kumar, L. Chinkin, P. T. Roberts, M. Saeger, and S. Mulligan. 1998. *Compilation and Evaluation of A Gridded Emission Inventory for the Paso del Norte Area.* Petaluma, Calif.: Prepared for EPA Region 6.

Johnson, A. M., and R. Alvarez. 2003. *Pollution Without Borders: How Power Plants in the U.S.-Mexico Border States Threaten Human Health and the Environment.* New York: Environmental Defense.

Kuhns, H., M. Green, and V. Etyemezian. 2001. *Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Emissions Inventory.* Las Vegas: Prepared for the BRAVO Steering Committee.

Kuhns, H., and J. Vukovich. 2003. "The Emissions Inventories and SMOKE Modeling Efforts Used to Support the BRAVO Study." Paper presented at the 12th Annual U.S. EPA International Emissions Inventory Conference, 29 April–1 May, San Diego, California.

Mejía, G., F. Obregón, J. Sánchez, J. Daumerie, J. Horne, and A. Burnette. 2003. "Characteristics of the Monterrey Metropolitan Area Vehicle Fleet and its Estimated Emissions." Paper presented at the NARSTO Workshop on Innovative Methods for Emission Inventory Development and Evaluation, 14–17 October, Austin, Texas.

Meszler, D., M. Causley, D. Arons, G. Acosta, J. Diem, R. Jones, and S. Reynolds, 2002. *Emissions Inventories for Douglas, Arizona and Agua Prieta, Sonora, Mexico.* Prepared for ADEQ.

Parks, N. J., W.-W. Li, C. D. Turner, R. W. Gray, R. Currey, S. Dattner, J. Saenz, V. Valenzuela, and J. A. VanDerslice. 2003. "Air Quality in the Paso del Norte Airshed: Historical and Contemporary." Pages 81–96 in *The U.S.-Mexican Border Environment: Air Quality Issues along the U.S.-Mexican Border* SCERP Monograph Series No. 6, Alan Sweedler, ed. San Diego: SCERP.

Paso del Norte Environmental Group and Eastern Research Group, Inc. 2003. *Development of GIS-based Maps for the Ciudad Juárez Area Source Emissions Inventory Project. Final.* El Paso: Prepared for TCEQ.

Peach, J., and J. Williams. 2004. "Population Projections for the U.S. Mexican Border Region." Forthcoming SCERP Monograph. San Diego: SDSU Press.

Perrusquía-Máximo, R. 2003. "Mexico City Inspection and Maintenance (I/M) Data." (March). Mexico City: Provided under authority of the Secretaría de Medio Ambiente del Distrito Federal. Unpublished.

Radian. 1996a. *Mexico Emissions Inventory Program Manuals, Volume III—Basic Emission Estimating Techniques, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian. 1996b. *Mexico Emissions Inventory Program Manuals, Volume IV—Point Source Inventory Development, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian. 1996c. *Development of Mobile Emissions Factor Model for Ciudad Juárez, Chihuahua.* Austin, Tex.: Prepared for TNRCC, Air Quality Planning Division.

Radian. 1997a. *Mexico Emissions Inventory Program Manuals, Volume I—Emissions Inventory Fundamentals, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian. 1997b. *Mexico Emissions Inventory Program Manuals, Volume V—Area Source Inventory Development, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian. 1997c. *Mexico Emissions Inventory Program Manuals, Volume VI—Motor Vehicle Inventory Development, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian. 1997d. *Development of the Hazardous Air Pollutant Emissions Inventory for Ambos Nogales.* Sacramento, Calif.: Prepared for ADEQ.

Radian. 2000a. *Mexico Emissions Inventory Program Manuals, Volume VII—Modeling Inventory Development, Final.* Sacramento, Calif.: Prepared for Western Governors' Association and Binational Advisory Committee.

Radian 2000b. *Air Emissions Inventory for Mexicali, Baja California. Final.* Sacramento, Calif.: Prepared for the Mexicali Inventory Technical Group and Binational Advisory Committee.

Roberts, P. T., H. H. Main, and M. A. Yocke 1996. *Operating Plan for Ozone Modeling Data Collection in El Paso-Ciudad Juárez-Sunland Park.* Petaluma, Calif.: Sonoma Technologies, Inc. Prepared for EPA Region 6.

Systems Applications International, Inc. 1997. *Preparation of a Draft 1990 Gridded Emission Inventory for Southern California.* SYSAPP-97/08. San Rafael, Calif.: Prepared for the California Air Resources Board.

Schifter, I., L. Díaz, J. Durán, E. Guzmán, O. Chávez, and E. López-Salinas. 2003. "Remote Sensing Study of Emissions from Motor Vehicles in the Metropolitan Area of Mexico City." *Environmental Science and Technology* 37(2): 395–401.

Shah, M., C. Taylor, D. Shimp, R. Romero, A. De Salvio, C. Selnick, A. Ballard, Z. Pirveysian, G. McGaugh, and W. O'Connell. 1998. "The 1997 Southern California Ozone Study-NARSTO: Preparation of the 1997 Gridded Emission Inventory." Paper presented at the 91st Annual Meeting of the Air & Waste Management Association, 14–19 June, San Diego, California.

Snow, C., S. Kishan, L. Borhen, C. Rincón, H. González, and K. Knapp. 1997. "Development of a Mobile Emissions Factor Model for Ciudad Juárez, Chihuahua." Paper presented at the 90th Annual Meeting of the Air & Waste Management Association, 8–13 June, Toronto, Ontario, Canada.

Snow, C., G. Velasquez, and K. Hardison. 2002. *Ciudad Juárez Heavy-Duty Vehicle Survey, Volume 1: Field Data Gathering. Final Report.* Austin, Tex.: Prepared for TCEQ.

Turner, C. D., Parks, N. J., S. L. Dattner, J. Saenz, V. Valenzuela, J. A. VanDerslice, O. E. Chavez, E. Tarin, N. Castro, R. Orquiz, and R. W. Gray. 1998. "Trans-Border Visibility Analysis of Dynamic, Multi-Site Video Images of the Paso del Norte Airshed." Southwest Center for Environmental Research and Policy Project No. AQ96-1. San Diego: SCERP. http://www.scerp.org.

U.S. Environmental Protection Agency. 1997. "Emissions Inventory Improvement Program Technical Reports." U.S. EPA Technology Transfer Network, Clearinghouse for Inventories and Emission Factors. Cited 10 December 2003. http://www.epa.gov/ttn/chief/eiip/techreport/index.html.

U.S. Environmental Protection Agency. 2001. "Biogenics Emissions Landcover Database, Version 3.1." Cited 5 May 2003. http://ftp.epa.gov/amd/asmd/beld3.

U.S. Environmental Protection Agency. 2002. *User's Guide to MOBILE6.1 and MOBILE6.2: Mobile Source Emission Factor Model.* EPA420-R-02-028. Ann Arbor, Mich.: EPA Office of Air and Radiation.

Wolf, M. E., P. G. Fields, and S. González-Ayala. 2003. "Estimation of Paved and Unpaved Road Dust Emissions In Mexico." Paper presented at the NARSTO Emissions Inventory Workshop, 14–17 October, Austin, Texas.

Yarwood, G., G. Wilson, S. Shepard, and A. Guenther. 2002. *User's Guide to the Global Biosphere Emissions and Interactions System (GloBEIS3), Version 3.0.* Novato, Calif.: ENVIRON International. Prepared for TCEQ.

Yocke, M. A. 1997. *A Protocol for Application and Evaluation of Ozone Models for the Paso del Norte Region.* Novato, Calif.: ENV-IRON International. Prepared for EPA Region 6.

Yocke, M. A., C. Emery, M. Jimenez, C. Tran, R. Evans, M. Capuano, and K. Atchison. 2001. *Evaluation of Ambient Ozone and Carbon Monoxide Concentrations Resulting from Automotive Fuel Changes in the Paso del Norte Air Shed, Volume I, Final Report.* Novato, Calif.: ENVIRON International. Prepared for EPA Region 6.

III

Experimental Design, Methods, and Results of Ambient Particulate Matter Characterization in the Paso del Norte Region

W.-W. Li, R. Orquiz, R. M. Currey, V. H. Valenzuela, A. F. Sarofim, H. L. C. Meuzelaar, S. A. Sheya, K. E. Kelly, J. R. Anderson, J. C. Chow, and J. G. Watson

Abstract

The increase of PM_{10} concentration in recent years and the temporal and spatial characteristics of PM pollution in the Paso del Norte airbasin are not well understood. In light of this and the new and sometimes controversial findings on the health effects of $PM_{2.5}$, the uniqueness of the PM pollution in the region, and the new National Ambient Air Quality Standard for $PM_{2.5}$, it is important to characterize both fine and coarse fractions of the atmospheric aerosols to identify the sources of PM for the Paso del Norte region. To improve understanding, an air quality study to characterize the ambient PM pollution in the region was developed by the University of Texas at El Paso in collaboration with four Southwest Consortium for Environmental Research and Policy (SCERP) universities

(University of Utah, New Mexico State University, Arizona State University, and Universidad Autónoma de Ciudad Juárez) and several U.S. and Mexican agencies.

Diseño Experimental, Métodos, y Resultados de la Caracterización de Materia Particulada Ambiental en el la Región Paso del Norte

W.-W. Li, R. Orquiz, R. M. Currey, V. H. Valenzuela, A. F. Sarofim, H. L. C. Meuzelaar, S. A. Sheya, K. E. Kelly, J. R. Anderson, J. C. Chow, y J. G. Watson

Resumen

El incremento de concentración de PM_{10} en años recientes y las características temporales y espaciales de contaminación del medio ambiente por PM en la cuenca atmosférica del Paso del Norte no son bien conocidos. En virtud de ello, y los nuevos y algunas veces controversiales descubrimientos sobre los efectos de $PM_{2.5}$ en la salud, la particularidad de la contaminación por PM en la región, y el nuevo Estándar Nacional de $PM_{2.5}$ para Calidad de Aire Ambiental, es importante el caracterizar ambos fragmentos de los aerosoles atmosféricos finos y gruesos para identificar las fuentes de PM para la región Paso del Norte. Para mejorar el conocimiento, fue desarrollado un estudio de calidad de aire para caracterizar la contaminación de PM del medio ambiente en la región por la Universidad de Texas en El Paso en cooperación con cuatro universidades del Consorcio de Investigacion y Política Ambiental del Suroeste

(CIPAS), (las Universidades del Estado de Utah, Nuevo México, Estado de Arizona, y Universidad Autónoma de Ciudad Juárez) y varias agencias mexicanas y de los E.U.

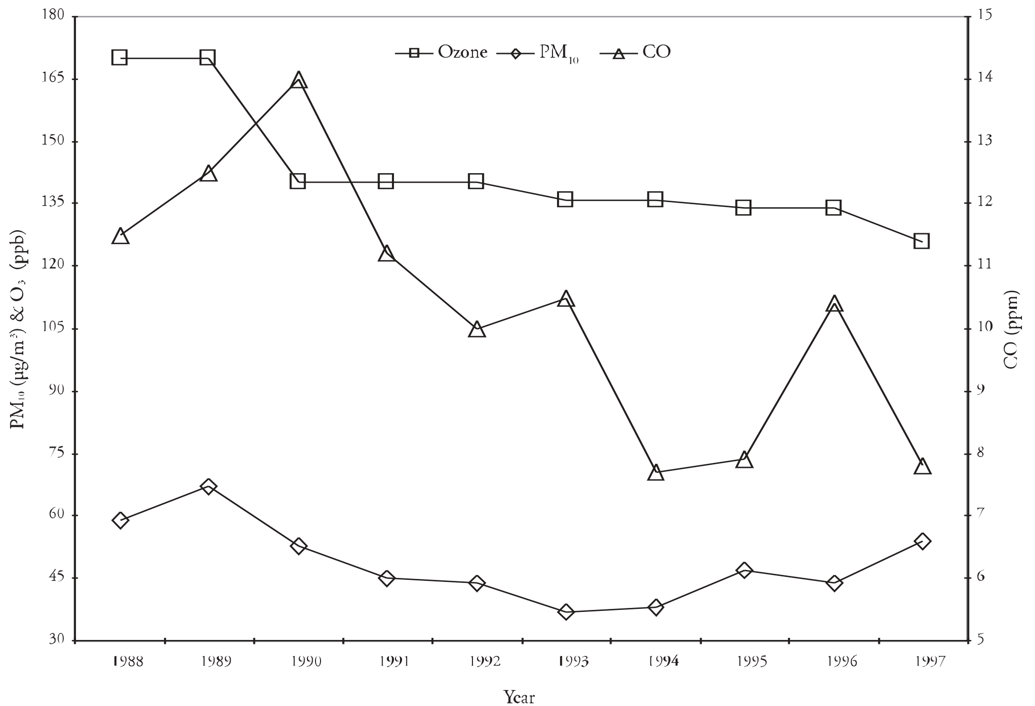
Previous Studies

Air quality in El Paso, Tex., has improved gradually since 1990, as shown in Figure 1. Although El Paso is still classified as non-attainment for ozone (O_3), carbon monoxide (CO), and particulate matter measuring 10 micrometers (μm) or less (PM_{10}), reductions in all three criteria pollutants have been reported by the Texas Commission on Environmental Quality (TCEQ; formerly Texas Natural Resource Conservation Commission [TNRCC]) (TNRCC 1999a, 1999b, 1999c). Ozone and carbon monoxide concentrations have decreased to levels close to or below their respective National Ambient Air Quality Standard (NAAQS). The annual average ambient PM_{10} level decreased from the peak of 67 micrograms per cubic meter (μg/m^3) in 1989 to 37 μg/m^3 in 1993, but increased to 55 μg/m^3 from 1993 to 1997.

A brief modeling feasibility study in December 1990 collected 12-hour (day and night) dichotomous samples at five sites in El Paso for gravimetric, elemental, and carbon analyses (Dattner 1994). During that study, PM_{10} exceeded the 150 μg/m^3 24-hour standard 15 times over the five sites during the 18 sample days. Substantial spatial variation of PM_{10} during air pollution episodes was observed and nighttime concentrations were reported to be greater than daytime concentrations. Geologic material accounted for most of the mass in $PM_{2.5\text{-}10}$. Concentrations of trace elements (chromium [Cr], copper [Cu], arsenic [As], lead [Pb], and cadmium [Cd]) were higher in particulate matter with an aerodynamic diameter of 2.5 μm or less ($PM_{2.5}$) than in $PM_{2.5\text{-}10}$. Surprisingly, the amount of chlorine present in El Paso air during 1990 was also higher than what was found in Texas coastal cities.

Additional PM monitoring in El Paso has been performed by the state of Texas and the U.S. Environmental Protection Agency (EPA) since 1997 for the review of the proposed $PM_{2.5}$ NAAQS. A 1997 TNRCC study (Price, et al. 1998) in central El Paso showed that

Figure 1. Annual Average PM_{10} and Maximum
One-Hour Ozone and Carbon Monoxide Concentrations for El Paso



Source: TNRCC 1999a

geologic material ([AlO+AlO_2] $_{average}$ + SiO_2 + [FeO+FeO_2] $_{average}$) accounted for 22% of the mass in $PM_{2.5}$, while other elements (Sum of XRF species – Al + Si + Ca + Fe + S + Cl) accounted for 2% of the total mass in $PM_{2.5}$. In addition, unexplained chlorine concentrations continued to be higher in El Paso than in any city in Texas during the study period. EPA began its first nationwide network of PM monitoring in 1999 and the results (Fitz-Simons, et al. 2000) showed that El Paso had the lowest $PM_{2.5}$ mass among major U.S. metropolitan areas. The annual mean of daily $PM_{2.5}$:PM_{10} ratio for El Paso varied from 0.15 to 0.32 with a seven-site average of 0.27. This ratio is considered a qualitative reference because the $PM_{2.5}$ and PM_{10} monitors do not use identical monitoring protocols.

Project Design

The study was implemented in two phases: first exploratory, then full-scale. The exploratory study was designed to determine optimum spatial deployment of the PM sampling equipment and to identify major sources of PM emissions. Based on the results of the exploratory study, a full-scale study was performed to characterize the PM concentrations in the airbasin. Experimental design and results of the exploratory study have been presented and discussed elsewhere (Sheya, et al. 2000; Jeon, et al. 2001). Thus, the focus here is on the description of the full-scale study.

Site Description

The PM monitoring program began August 1, 1999, and ended March 7, 2000. It started with collection of 24-hour dichotomous samples on alternate days at two El Paso sites—Chamizal National Park (Chamizal) and Sun Metro Bus Terminal (Sun Metro), as shown in Appendix Figure 1 (page 305). Three additional sites in Ciudad Juárez (Club 20-30, Advanced Transformer, and Misión) were added to the sampling program during the winter months (January 3, 2000–March 7, 2000). Appendix Figure 1 (page 305) shows the locations of the five monitoring sites and the major geologic features in the Paso del Norte airbasin. These locations represent different activities in the airbasin and supplement the study measurements with Federal Reference Method (FRM) $PM_{2.5}$, hourly PM, and meteorological data. Continuous hourly monitoring of PM_{10} by Beta Attenuation Monitor (BAM) was replaced by a tapered element oscillating microbalance (TEOM) for $PM_{2.5}$ on January 1, 2001, due to a change in PM monitoring strategy in Texas. Both BAM and TEOM were in operation at Sun Metro during the University of Texas at El Paso (UTEP) study period.

Sample Collection, Handling, and Processing

Two dichotomous air samplers (EPA 1998; Lodge 1989) were placed at each of the two U.S. sites where one sampler was operated every other day to collect 24-hour air samples and the other was operated selectively for collocated samples. Only one dichotomous sampler was operated at each of the three Mexican sites. Samples were collected every 24 hours from 0001 to 2359 MST on 37 millimeter (mm) diameter ringed Teflon filters (Gelman Science Inc., ID No. R2PJ037) at an actual (not adjusted to standard temperature and pressure [STP]) flow rate of 1.0 cubic meter per hour (m^3/hr). The filter has high particle collection efficiency, 99%, which is measured using the DOP test with a 0.3-µm particle at the sampler's operating face velocity (Lodge 1989). Quality control was managed by following EPA guidelines and procedures for PM monitoring (EPA 1994) and gravimetric weighing (EPA 1998). A mini-Buck bubble calibrator (Model M-30), a primary standard calibration device traceable to the National Institutes of Standards and Technology (NIST), was used to calibrate the rotameters on the dichotomous samplers (A. P. Buck 1987). Collocated samples were collected at the El Paso sites for every 10 samples. All samplers (except at the Misión site) were positioned at least eight feet away from TCEQ's eight-foot tall instrument shacks with the inlet head standing five feet above the ground. The sampler at the Misión site was positioned on the roof of a one-story cinder block storage structure and the inlet head was five feet above the roof.

Analysis of Mass

Filters were conditioned at 25°C ± 5°C and 30% ± 5% RH for 24 hours, pre-weighed, and stored in petri dishes for less than 30 days prior to sampling. Loaded filters were removed from the field and transported to the laboratory at UTEP for gravimetric analysis with a CAHN model C-33 microbalance (± 1 µg sensitivity) after conditioning (Orion 1997). Mass concentrations were reported as micrograms of PM per cubic meter of air at EPA's STP conditions of 298°K and 760 millimeters (mm) mercury (Hg). The adjustment for EPA standard conditions is required for determining compliance with the federal PM_{10} standard, but not for compliance with the federal $PM_{2.5}$ standard.

X-Ray Fluorescence Elemental Analysis

$PM_{2.5}$ and $PM_{2.5\text{-}10}$ Teflon filters were analyzed by x-ray fluorescence (XRF) analysis for 38 elements[1]. Calibration standards, sensitivity factors for each excitation condition, quality control standards and procedures, and detailed laboratory methods and operation procedures are kept the same as those used at the Desert Research Institute (DRI) (Watson, et al. 1999; Chow 1995).

Results and Discussion

Mass Concentrations: Collocated Samples

Superior collocated precision of ±1% for both $PM_{2.5}$ and $PM_{2.5\text{-}10}$ was observed in the current study. Regression statistics for samples collected at the Chamizal and Sun Metro sites show high correlations (R^2 = 0.99), near-unity slope (1.03), and low intercepts (<3 µg/m^3).

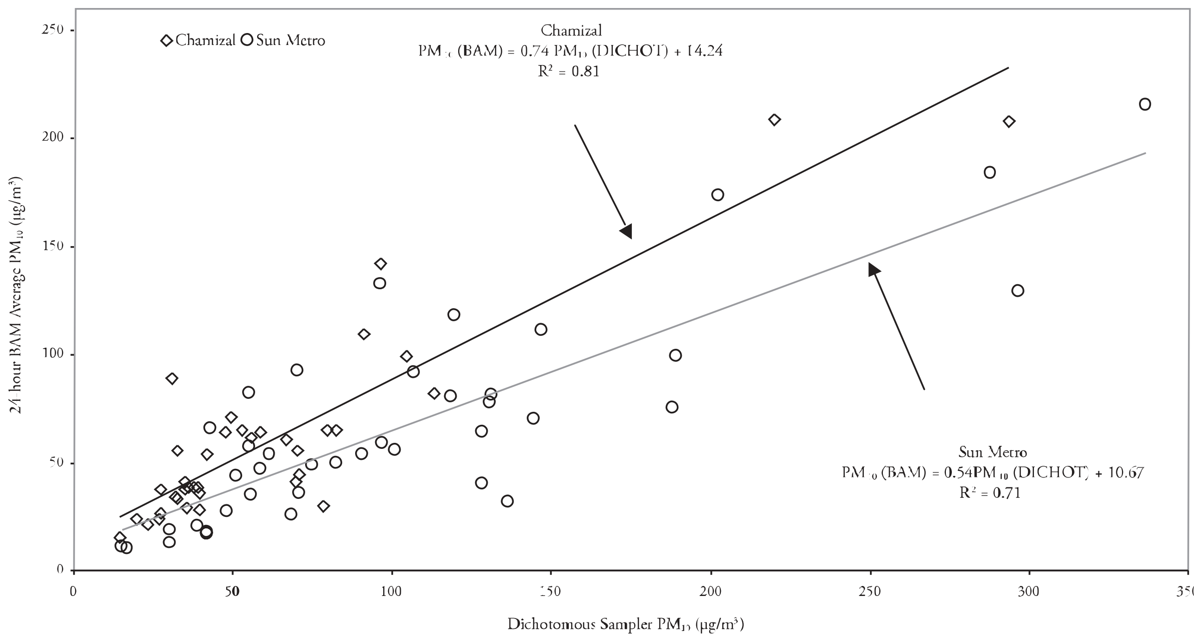
Comparison to TCEQ's BAM

Figure 2 shows substantially poorer comparisons between the dichotomous sampler PM_{10} and what was derived from BAM. On average, BAM reported lower PM_{10} than the dichotomous samplers by 20% to 40%. The difference became more pronounced at high concentrations. Previous studies on the compatibility between BAM and integrated samplers showed that BAM tends to observe lower PM concentrations (0.57 ~ 1.10 of that observed by sequential filter samplers and 0.85 ~ 1.0 of that observed by dichotomous samplers) and scattered distributions (less than 70% of all paired BAM and dichotomous data fall within ∀ 3 Φ interval) than other filter-based monitors (Watson, et al. 1998). Discrepancies between BAM and the dichotomous sampler at high PM_{10} concentrations could be caused by the amount of particles with sizes greater than 10 µm (Hinds 1999) on the filter or the difference in humidity, calibration standards, and the beta attenuation coefficient for soot and geologic aerosols (Macias and Husar 1976; Jaklevic, et al. 1981; Wedding and Weigand 1993).

Temporal Variation of PM Concentrations

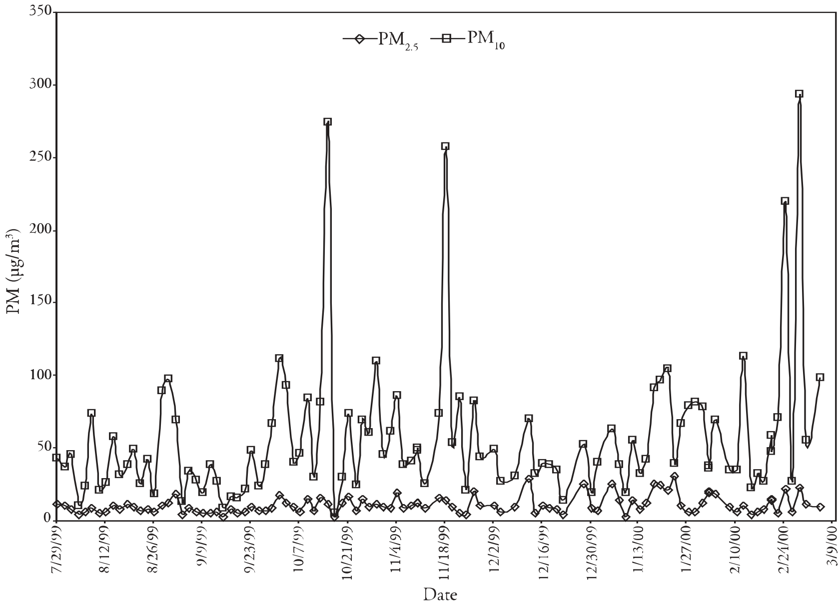
Figure 3 presents the time series plot of PM_{10} and $PM_{2.5}$ concentration for samples acquired on an every-other-day schedule at Chamizal. Regardless of the PM_{10} concentrations, $PM_{2.5}$ consists of only a small but steady fraction of PM_{10}, indicating that anthropogenic emissions (in the form of $PM_{2.5}$) in this area, are rather independent of the temporal variation of 24-hour average PM_{10} concentrations. The temporal variation of PM concentrations at Sun Metro is shown in Figure 4. The average $PM_{2.5}$ and PM_{10} concentrations of 22.5 µg/m³ and 109 µg/m³ at Sun Metro are considerably higher than Chamizal's 11.0 µg/m³ of $PM_{2.5}$ and 56.9 µg/m³ of PM_{10}. Table 1 summarizes the monthly average PM concentrations and temperatures obtained for the two El Paso sites. Both $PM_{2.5}$ and PM_{10} increase during winter months as temperature inversions increase in frequency and duration and wood burning intensifies. Because of the nearby highway and unpaved residential area in Ciudad Juárez, the PM concentrations at Sun Metro were expected to be higher than at Chamizal. Although it appears in Figure 4 that $PM_{2.5}$ follows the pattern of PM_{10} at Sun Metro, Table 2 shows that the 24-hour average PM_{10} concentrations at both U.S. sites were strongly correlated to $PM_{2.5-10}$ (with $R^2 = 0.97$ for both sites) and weakly associated with $PM_{2.5}$ (with $R^2 = 0.21$ and 0.28, respec-

Figure 2. Comparison of PM_{10} Concentrations Acquired by the Dichotomous and Beta Attenuation Monitors at Chamizal and Sun Metro for the Period of December 2, 1999, through March 7, 2000



Note: All concentrations were reported under STP conditions.
Source: Authors

Figure 3. Temporal PM_{10} and $PM_{2.5}$ Variation at Chamizal



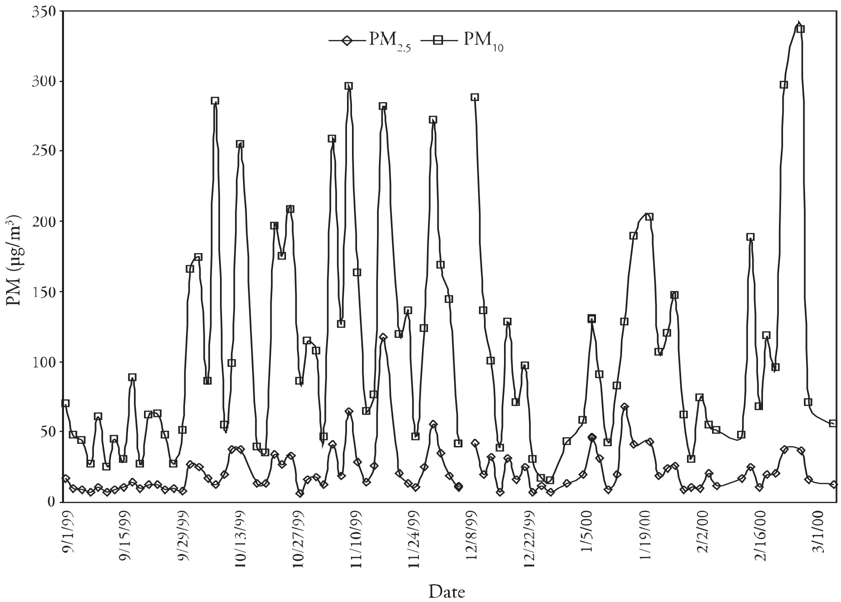
Note: Line break refers to missing data.
Source: Authors

tively). As mentioned previously, the slightly higher correlation between $PM_{2.5}$ and PM_{10} at Sun Metro could be caused by its proximity to a highway.

The average wintertime $PM_{2.5}$:PM_{10} ratio at Chamizal, 0.22, agrees well with the EPA's annual mean of 0.23 at the same site. The ratios for both sites fall within the range (0.15 to 0.32) reported by EPA (Fitz-Simons, et al. 2000). These ratios are significantly lower than 0.5, a value reported for a typical arid city at Spokane, Wash., (Haller, et al. 1999) where the ratio varies from 0.20 to 0.37 during dust storms and 0.33 to 0.75 during non-dust storm days (Claibon, et al. 2000).

Based on the observed $PM_{2.5}$:PM_{10} ratios and PM_{10} concentrations, many of the high PM_{10} days would have been attributed to fugitive dust generated by high winds. However, concurrent wind measurements at the sites do not support such an argument. For

Figure 4. Temporal PM Variations at Sun Metro



Note: Line break refers to missing data.
Source: Authors

example, two of the highest 24-hour PM_{10} concentrations measured at Chamizal were 275 µg/m^3 on October 15 and 258 µg/m^3 on November 18. The respective $PM_{2.5}$ concentrations for these two days at Chamizal were 11.2 µg/m^3 and 14.7 µg/m^3, which resulted in $PM_{2.5}$:PM_{10} ratios of 0.04 and 0.06. The average wind speeds for these two days, however, were not considered high—4.3 meters per second (m/s) (with occasional gusts up to 8.9 m/s) and 2.8 m/s, respectively. Wind gusts reaching 8.9 m/s may have made a significant impact on the elevated PM_{10} concentration on October 15. Additionally, on January 19 at Sun Metro, the average wind speed for the day was 3.2 m/s (with maximum wind gusts of up to 4.6 m/s) and the PM_{10} and $PM_{2.5}$ concentrations were 203 µg/m^3 and 43.1 µg/m^3, respectively. On February 12, the PM_{10} and $PM_{2.5}$ concentrations were 188 µg/m^3 and 24.8 µg/m^3, with average wind speed of 5.1 m/s and occasional wind gusts up to 10.3 m/s. When wind gusts reach levels of 13.1 m/s, as on February 24, the PM_{10} and $PM_{2.5}$

Table 1. Summary of 24-Hour-Average PM Concentrations (μg/m³) and Temperatures (°F) at the Two El Paso Sites

Month	Chamizal			Sun Metro		
	$PM_{2.5} \pm STD$	$PM_{10} \pm STD$	Temp.	$PM_{2.5} \pm STD$	$PM_{10} \pm STD$	Temp.
August 1999	8.6 ± 2.4	43.5 ± 24.6	84.5	No sample collected		
September 1999	7.2 ± 3.6	31.5 ± 18.4	78.5	10.5 ± 2.7	47.8 ± 18.8	77.1
October 1999	11.2 ± 4.3	73.8 ± 61.8	68.0	22.6 ± 9.9	138.9 ± 76.9	66.6
November 1999	11.5 ± 4.6	69.2 ± 58.2	60.9	34.6 ± 28.8	155.8 ± 88.5	59.3
December 1999	11.6 ± 8.0	37.3 ± 15.8	47.3	18.2 ± 11.0	85.2 ± 73.3	45.9
January 2000	12.7 ± 7.5	58.2 ± 26.0	53.4	28.4 ± 17.5	106.4 ± 50.5	51.6
February 2000	12.5 ± 6.7	75.1 ± 78.5	57.5	21.5 ± 9.4	133.0 ± 106.0	55.8
Average	10.95	56.9		22.5	109.0	

Source: Authors

Table 2. Summary of 24-Hour-Average Winter Month PM Concentrations (μg/m³) at All Sites

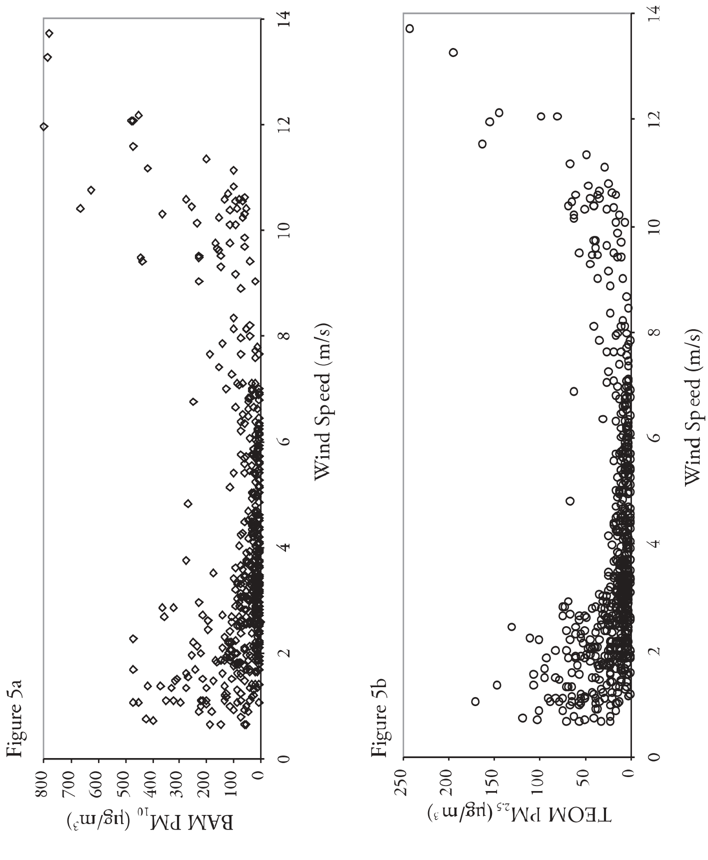
UTEP Study Average Values (January 3 through March 7, 2000)						
Site Name	$PM_{2.5}$ (μg/m³)	$PM_{2.5-10}$ (μg/m³)	PM_{10} (μg/m³)	$PM_{2.5}$:PM_{10} Ratio (unitless)	R^2 for $PM_{2.5}$ to PM_{10}	R^2 for $PM_{2.5-10}$ to PM_{10}
	Avg ± S.D.	Avg ± S.D.	Avg ± S.D.	Avg ± S.D.		
Chamizal[a]	12.6 ± 6.50	57.7 ± 54.7	70.3 ± 57.9	0.22 ± 0.12	0.21	0.97
Sun Metro[a]	23.1 ± 14.2	90.0 ± 71.0	113.0 ± 79.2	0.23 ± 0.10	0.28	0.97
Club 20-30[b]	20.0 ± 11.5	36.0 ± 17.0	56.3 ± 26.0	0.36 ± 0.10	0.73	0.87
Advance Transformer[b]	50.9 ± 59.3	146.0 ± 68.5	197.0 ± 107.0	0.23 ± 0.11	0.56	0.67
Misión[b]	26.8 ± 11.6	142.0 ± 50.7	169.0 ± 58.2	0.16 ± 0.60	0.49	0.97

Notes: [a]El Paso; [b]Ciudad Juarez
Source: Authors

concentrations reached 337 μg/m^3 and 37.2 μg/m^3, respectively. The $PM_{2.5}$:PM_{10} ratio was 0.21 for January 19, 0.13 for February 12, and dropped to 0.11 on February 24, which is consistent with the changes in wind speed and maximum wind gusts.

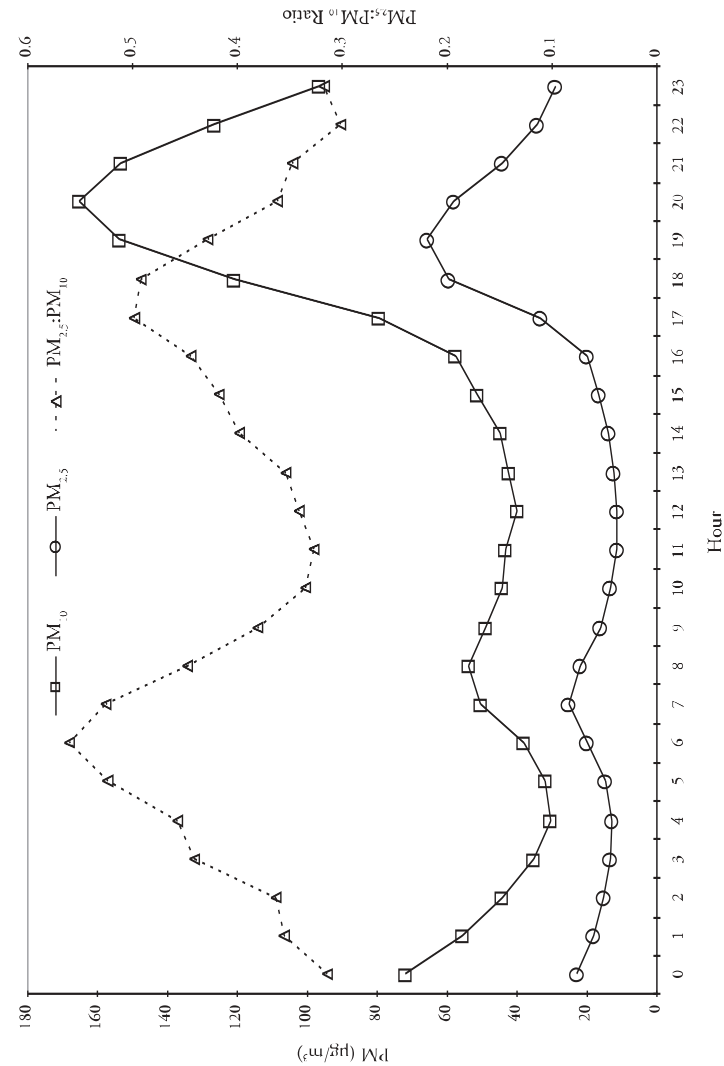
The low-wind-high-PM and high-wind-high-PM phenomena have been observed at several locations and throughout the year in the airbasin (Becerril, et al. 1999). Figure 5, based on the hourly BAM PM_{10} and TEOM $PM_{2.5}$ data (TNRCC 1999d; 1999e), shows that hours with low or extremely high wind speeds (exceeding the wind erosion threshold wind speed of approximately 7 m/s) tend to yield higher PM concentrations than hours with light-to-moderate wind speeds. Furthermore, the hourly PM data show a strong diurnal pattern. Both $PM_{2.5}$ and PM_{10} peak at two distinct time intervals in Figure 6. The first PM peak was during the morning hours when ground-based inversions occurred and morning traffic began. The second PM peak occurred in the evening when radiation inversions started to form and wood burning and home cooking prevailed in the airbasin. Similar diurnal variations in PM_{10} were observed in southern California. Pronounced morning and evening peaks in PM_{10} were observed at urban and rural sites (Doloslager and Motallebi 1999). However, the most pronounced peak was observed at a suburban location where shifts in meteorology (winds and atmospheric pressure) were considered the major causes of the peak (Doloslager and Motallebi 1999). Figure 6 also shows the average hourly $PM_{2.5}$:PM_{10} ratio. It peaks at the same time intervals as $PM_{2.5}$ and PM_{10} but arrives one hour ahead of the $PM_{2.5}$ and two hours before the PM_{10}. The hourly $PM_{2.5}$:PM_{10} ratios (0.3 ~ 0.6) observed by the continuous monitors appear to be much higher than the 24-hour averages (0.15 to 0.32) obtained by the authors' dichotomous samplers. The phenomenon is expected when the mass of $PM_{2.5}$ generated from anthropogenic/mobile sources remains steady while coarse PM mass, mostly associated with wind-blown dust, remains low during some low-wind hours. In addition, errors caused by measurement imprecision, systematic bias caused by different monitoring devices, characteristics of wind-direction related emissions, and dominance of $PM_{2.5-10}$ in PM_{10} during higher PM hours all could contribute to the discrepancies. Time-resolved PM monitoring and associated chemical specification during the peak

Figure 5. Relationship of Hourly PM_{10} and $PM_{2.5}$ with Wind Speed at Sun Metro from December 1, 1999, through February 28, 2000



Source: Authors

Figure 6. PM_{10}, $PM_{2.5}$, and $PM_{2.5}$:PM_{10} Diurnal Variation at Sun Metro from December 1, 1999, to February 28, 2000



Source: Authors

hours would provide further information for understanding the causes of the low daily $PM_{2.5\text{-}10}$:PM_{10} ratios and controlling the PM pollution in the airbasin.

Spatial Variation of PM Concentrations

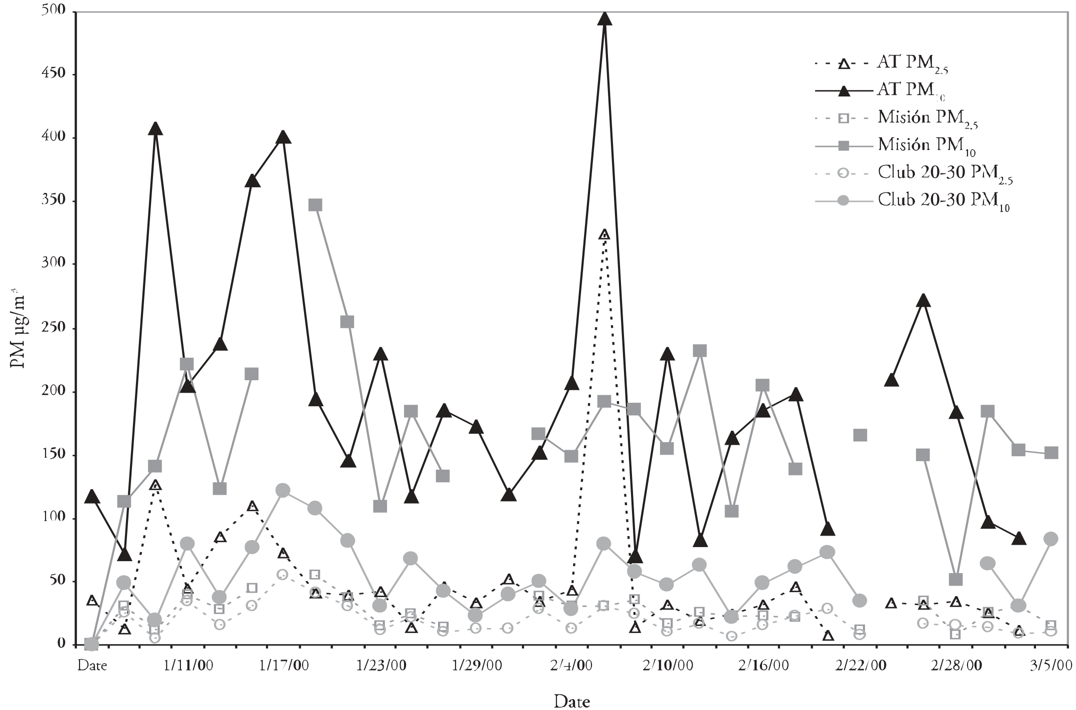
Figure 7 contains the temporal variation of 24-hour PM_{10} and $PM_{2.5}$ at the three Ciudad Juárez sites. The $PM_{2.5}$ concentrations visibly followed the PM_{10} trend. At the Ciudad Juárez downtown site (Club 20-30), the PM_{10} concentration is consistently lower than what was observed at other Ciudad Juárez sites. However, the average $PM_{2.5}$:PM_{10} ratio, 0.36 with a Φ value of 0.11, appears to be the highest among all U.S. and Mexican sites, obviously affected by the increased anthropogenic (most likely the mobile) emissions in downtown Ciudad Juárez.

At the Misión site, it is expected that the PM_{10} concentration will be high and mostly made up of $PM_{2.5\text{-}10}$. Indeed, Table 2 shows that the average $PM_{2.5\text{-}10}$ concentration at this site was 142 µg/m^3, a value much higher than that monitored in El Paso or downtown Ciudad Juárez. The high PM concentrations could be attributed to a cement factory located in the vicinity of the site and the large number of wood stoves, unpaved roads, and kerosene heaters in the area. Also as expected, the $PM_{2.5}$:PM_{10} ratio, 0.16 (with a Φ value of 0.06), is significantly lower than at other sites and is a good indication of the dominance of PM pollution by geologic sources. Table 2 shows that $PM_{2.5\text{-}10}$ dominates the PM_{10} at the Misión site and the two El Paso sites (with R^2 = 0.97 at all three sites).

At Advanced Transformer, the average $PM_{2.5}$ concentration of 50.9 µg/m^3 and PM_{10} concentration of 197 µg/m^3 are the highest of all sites (Table 2), reflecting the unique mixed emission sources (brick kilns, automobiles, unpaved roads, and industrial sources) in the immediate vicinity of the site. For the Ciudad Juárez sites, $PM_{2.5}$ correlated moderately to PM_{10} (with R^2 varing from 0.49 to 0.73), as seen in Table 2, indicating that anthropogenic emissions are more pronounced in Ciudad Juárez than in El Paso.

PM pollution in the area appears to be dominated by $PM_{2.5\text{-}10}$ and increases from El Paso toward the outskirts of Ciudad Juárez. $PM_{2.5\text{-}10}$ is likely to be fugitive dust generated by wind erosion

Figure 7. Temporal Variation of PM_{10} and $PM_{2.5}$ at the Ciudad Juárez Sites



Note: Line break refers to missing data.
Source: Authors

(when wind speeds exceeded 7 m/s) from bare soil or by vehicular movement/mechanical disturbance on paved or unpaved surfaces. Contributions to PM pollution by mobile emissions (primarily as $PM_{2.5}$) may be quite localized both temporally and spatially and do not significantly affect the overall 24-hour averaged PM_{10} concentrations in the airbasin. Perhaps $PM_{2.5}$ in the area is dominated by resuspension of urban dust due to vehicular movement and the frequently occurring temperature inversions that are likely to trap PM in the airbasin.

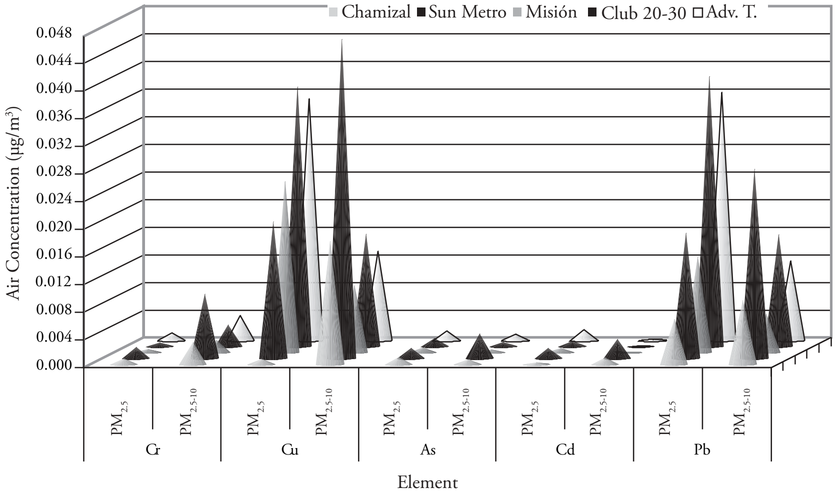
Elemental Analysis

A total of 149 filters collected at the five sites were analyzed using XRF for rapid evaluation of the elemental composition of PM. XRF analysis was performed for samples collected at Chamizal and Sun Metro for the month of September 1999 and from December 2, 1999, to March 5, 2000. At the Ciudad Juárez sites, filters were analyzed for samples collected from January 3, 2000, to March 7, 2000.

Element Concentrations

Figure 8 shows the average ambient toxic trace element concentrations (copper, chromium, arsenic, cadmium, and lead) at all sites. These elements were selected for their associations with the operations of local industrial sources. Concentrations for the five indicator elements were higher in $PM_{2.5\text{-}10}$ than in $PM_{2.5}$ for the El Paso sites, but lower (except chromium) in $PM_{2.5}$ than in $PM_{2.5\text{-}10}$ for the Ciudad Juárez sites. This observation is the opposite of what was discovered in 1990. It implies that the toxic trace elements in El Paso are more likely caused by wind erosion of natural surfaces or mechanical disturbance of road dust, but less likely to be caused by anthropogenic emissions of smelters or foundries. Localized emission sources in Ciudad Juárez could be the reason for higher trace element concentrations in $PM_{2.5}$. Nevertheless, toxic trace elements in the air of Paso del Norte are relatively low compared to the concentration ranges of these elements associated with PM in the atmosphere reported for rural or urban areas in the United States, Canada, or Europe (Schroeder, et al. 1987).

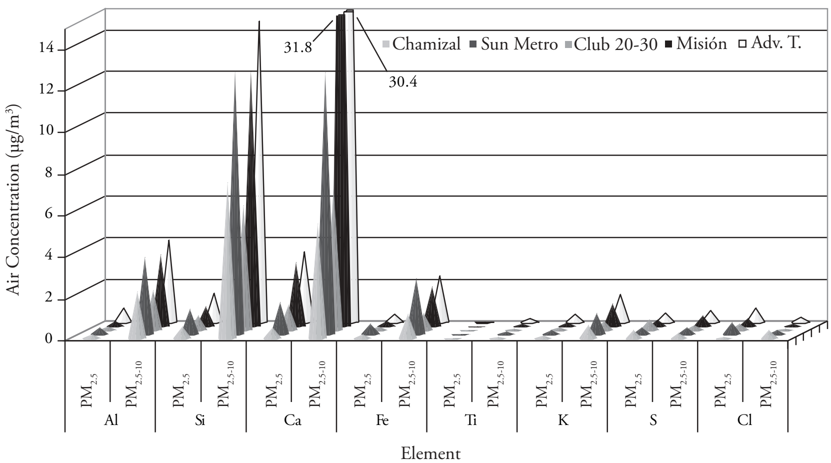
Figure 8. Average Toxic Trace Element Concentrations at All Sites



Source: Authors

Geologic elements (aluminum [Al], silicon [Si], calcium [Ca], iron [Fe], titanium [Ti], and potassium [K]) appear to dominate the coarse fraction of PM_{10} (Figure 9). These elements are expected to be of higher concentrations because low $PM_{2.5}$:PM_{10} ratios and high correlations between $PM_{2.5\text{-}10}$ and PM_{10} were observed at all sites. Based on the results of the XRF analysis, geologic elements account for 35% of $PM_{2.5\text{-}10}$ and 12% of $PM_{2.5}$ concentrations. PM concentrations at all Ciudad Juárez sites, particularly the rural Misión site, are heavily weighted by the geologic elements, signifying the impacts of unpaved roads and the surrounding desert on local air quality. The central Ciudad Juárez site, which is located far from unpaved roads and the bare soil of the desert, showed low concentrations for all geologic elements.

Figure 9. Average Element Concentrations of Geologic Origin, Chlorine (Cl), and Sulfur (S) at All Sites



Source: Authors

Figure 9 also shows that sulfur concentrations are low but similar in the fine and coarse fractions of PM. Potential emission sources in the region for sulfur are fuel combustion and re-entrainment of fall-out from past smelting of sulfide-containing ores. Occasional high chlorine concentrations (not seen in the average concentration) were detected in $PM_{2.5}$, indicating the existence of possible anthropogenic sources of chlorine-containing substances. Chlorine levels at Sun Metro and Advance Transformer appeared to be higher than at other areas in the airbasin. Nevertheless, the level has decreased significantly from what was observed in 1990, but remained at approximately the same level as reported in TNRCC's 1997 statewide $PM_{2.5}$ study.

PM Trends

Tables 3 and 4 compare elemental composition of the $PM_{2.5}$ and $PM_{2.5\text{-}10}$ observed in this study to those observed by TNRCC in 1990 and 1997. The 1990 TNRCC study was conducted using the same dichotomous samplers and sampling media as used in the current study. The 1997 TNRCC study used FRM $PM_{2.5}$ samplers. All samples were analyzed by DRI using the XRF method. The laboratory procedures, calibration standards, instrument precisions, and detection limits for the three studies were identical or similar and are documented by DRI (Watson, et al. 1999) or available in the literature (Schroeder, et al. 1987). Although the comparison may still include uncertainties, it provides the best available information of historical PM data for the airbasin.

In general, arsenic, chromium, and lead in either $PM_{2.5}$ or $PM_{2.5\text{-}10}$ were lower in 1997 and 2000 than a decade ago at the two El Paso sites. Arsenic and chromium levels were consistently low in the airbasin throughout the study period, which may reflect the closure of a local copper smelting operation. Levels of lead and copper, although reduced, are still high in the airbasin. The mean concentration of almost every elemental composition decreased from 1990 to 2000 at both El Paso sites (Table 3). $PM_{2.5}$ lead concentrations are significantly lower today than in the previous studies. Reasons for the lower lead concentration lie in the elimination of lead from gasoline (eliminated recently in Ciudad Juárez) and the shutdown of a major smelting operation in the city. Arsenic and other smelter emissions have experienced the same decrease in concentration as lead. $PM_{2.5}$, chlorine, and sulfur concentrations have also experienced decreases in concentration.

Table 3. Comparison of the UTEP Winter Study $PM_{2.5}$ Elemental Composition to Those of the 1990 and 1997 TNRCC Studies

Element	Chamizal		Sun Metro		Advance Transformer	Club 20-30	Misión	Central El Paso
	UTEP Study	1990 TNRCC Study	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	1997 TNRCC Study*
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Sodium	64.0	<IDL	54.0	<IDL	83.0	54.0	66.0	18.0
Magnesium	41.0	<IDL	69.0	<IDL	75.0	43.0	73.0	53.0
Aluminum	190.0	440.0	357.0	497.0	761.0	218.0	285.0	243.0
Silicon	593.0	440.0	1264.0	1071.0	1436.0	726.0	1010.0	928.0
Phosphorus	2.0	<IDL	2.0	<IDL	1.0	2.0	2.0	1.0
Sulfur	409.0	1169.0	341.0	1349.0	492.0	514.0	374.0	0.1
Chlorine	89.0	565.0	625.0	1741.0	742.0	349.0	405.0	594.0
Potassium	128.0	186.0	217.0	365.0	381.0	183.0	242.0	362.0
Calcium	542.0	559.0	1540.0	1989	3411.0	1257.0	3063.0	191.0
Titanium	8.0	10.0	19.0	20.0	28.0	11.0	18.0	1407.0
Vanadium	1.0	7.0	1.0	9.0	1.0	1.0	1.0	20.0
Chromium	0.4	4.0	1.0	5.0	1.0	0.0	1.0	3.0
Manganese	4.0	13.0	9.0	12.0	15.0	6.0	11.0	1.0
Iron	231.0	179.0	508.0	411.0	397.0	243.0	291.0	9.0
Cobalt	0.1	<IDL	0.1	<IDL	0.3	0.0	0.1	324.0
Nickel	0.2	<IDL	0.1	<IDL	1.0	0.3	0.4	1.0
Cooper	15.0	49.0	22.0	119.0	35.0	25.0	38.0	1.0
Zinc	24.0	90.0	38.0	242.0	159.0	98.0	73.0	61.0
Gallium	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	64.0
Arsenic	1.0	51.0	1.0	94.0	1.0	1.0	1.0	0.0
Selenium	0.0	6.0	0.0	21.0	0.0	0.0	0.1	19.0
Bromine	7.0	33.0	1.0	38.0	52.0	14.0	16.0	8.0
Rubidium	0.3	<IDL	1.0	<IDL	1.0	0.5	1.0	9.0
Strontium	3.0	3.0	6.0	8.0	10.0	5.0	7.0	1.0

Table 3. continued

Element	Chamizal		Sun Metro		Advance Transformer	Club 20-30	Misión	Central El Paso
	UTEP Study	1990 TNRCC Study	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	1997 TNRCC Study*
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Yttrium	0.2	<IDL	0.4	<IDL	0.3	0.3	0.2	5.0
Zirconium	1.0	<IDL	1.0	<IDL	1.0	1.0	1.0	0.0
Molybdenum	0.1	<IDL	0.3	<IDL	0.2	0.1	0.2	1.0
Palladium	0.3	<IDL	0.5	<IDL	1.0	1.0	1.0	1.0
Silver	0.1	<IDL	0.3	<IDL	0.2	1.0	0.0	1.0
Cadmium	0.3	5.0	1.0	8.0	2.0	1.0	1.0	1.0
Indium	0.1	<IDL	1.0	<IDL	1.0	1.0	0.0	2.0
Tin	1.0	3.0	3.0	7.0	3.0	3.0	3.0	1.0
Antimony	2.0	8.0	14.0	18.0	23.0	11.0	15.0	3.0
Barium	17.0	7.0	22.0	12.0	21.0	22.0	18.0	8.0
Lanthanum	10.0	<IDL	12.0	<IDL	9.0	15.0	12.0	9.0
Gold	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	0.0
Mercury	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	0.0
Thallium	0.0	<IDL	0.1	<IDL	0.1	0.0	0.1	0.0
Lead	7.0	188.0	22.0	301.0	36.0	14.0	39.0	37.0
Uranium	0.0	<IDL	0.0	<IDL	0.1	0.1	0.1	0.0

Notes: Samples from the 1990 TNRCC study and the UTEP study were collected with dichotomous samplers, while the 1997 TNRCC samples were collected with the $FRM_{2.5}$ sampler. All samples were analyzed by the XRF method.
*Only 17 samples were analyzed.
<IDL = Less than instrument detection limits
ng/m^3 = nanograms per cubic meter
Source: Authors

Table 4. Comparison of Elemental $PM_{2.5\text{-}10}$ Between Those of the 1990 TNRCC Study and the UTEP Winter Study

Element	Chamizal		Sun Metro	Advance Transformer	Club 20-30	Misión
	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	UTEP Study
	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Sodium	126.0	<IDL	92.0	162.0	73.0	153.0
Magnesium	179.0	<IDL	254.0	324.0	149.0	355.0
Aluminum	2233.0	934.0	3729.0	3990.0	1919.0	3496.0
Silicon	7491.0	4242.0	12652.0	14525.0	606.0	12316.0
Phosphorus	14.0249.0	<IDL	38.0	64.0	28.0	64.0
Sulfur	249.0	283.0	335.0	622.0	265.0	569.0
Chlorine	396.0	138.0	215.0	284.0	110.0	183.0
Potassium	665.0	614.0	1071.0	1397.0	487.0	1080.0
Calcium	5500.0	6672.0	12627.0	30365.0	6918.0	31819.0
Titanium	90.0	100.0	150.0	200.0	71.0	159.0
Vanadium	1.0	6.0	1.0	3.0	1.0	4.0
Chromium	3.0	12.0	10.0	4.0	2.0	3.0
Manganese	24.0	36.0	49.0	50.0	17.0	39.0
Iron	1187.0	1253.0	2714.0	2282.0	852.0	1932.0
Cobalt	1.0	<IDL	1.0	3.0	0.2	1.0
Nickel	1.0	<IDL	2.0	3.0	1.0	3.0
Cooper	18.0	57.0	36.0	13.0	10.0	16.0
Zinc	30.0	49.0	51.0	70.0	68.0	49.0
Gallium	0.0	<IDL	0.0	0.0	0.0	0.0
Arsenic	1.0	7.0	3.0	1.0	0.0	1.0
Selenium	0.0	1.0	0.0	0.1	0.0	0.0
Bromine	1.0	6.0	5.0	4.0	2.0	3.0
Rubidium	3.0	33.0	5.0	7.0	2.0	5.0
Strontium	20.0	27.0	38.0	78.0	21.0	74.0

Table 4. continued

Element	Chamizal		Sun Metro	Advance Transformer	Club 20-30	Misión
	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	UTEP Study
	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³
Yttrium	1.0	<IDL	2.0	2.0	1.0	2.0
Zirconium	5.0	4.0	8.0	11.0	3.0	8.0
Molybdenum	1.0	<IDL	2.0	2.0	0.0	2.0
Palladium	1.0	<IDL	0.0	2.0	0.0	7.0
Silver	1.0	<IDL	2.0	0.0	0.0	0.0
Cadmium	1.0	3.0	3.0	0.0	0.0	0.0
Indium	0.4	<IDL	0.0	3.0	0.3	2.0
Tin	2.0	6.0	2.0	0.0	1.0	2.0
Antimony	2.0	1.0	1.0	3.0	2.0	4.0
Barium	46.0	40.0	64.0	87.0	32.0	57.0
Lanthanum	7.0	<IDL	13.0	3.0	12.0	3.0
Gold	0.0	<IDL	0.0	0.0	0.0	0.0
Mercury	0.0	<IDL	0.2	0.2	0.0	0.0
Thallium	0.1	<IDL	1.0	1.0	0.0	1.0
Lead	9.0	55.0	23.0	12.0	6.0	16.0
Uranium	0.1	<IDL	0.4	0.3	0.1	1.0

Notes: Samples from the 1990 TNRCC study and the UTEP study were collected with dichotomous samplers. All samples were analyzed by the XRF method.
*TNRCC did not report element concentrations for $PM_{2.5\text{-}10}$ samples in 1990.
<IDL = Less than instrument detection limits
ng/m³ = nanograms per cubic meter
Source: Authors

The student-t test was performed to evaluate the trend of element concentrations in the air. For $PM_{2.5}$, although the mean concentrations of geologic elements seem to decrease over the past decade, the trend cannot be established because of significant data scattering (1.5 > F/Mean > 0.5). For example, aluminum concentrations in El Paso decreased from an average of 0.47 $\mu g/m^3$ in 1990 to 0.27 $\mu g/m^3$ in 2000 and calcium decreased from 1.27 $\mu g/m^3$ in 1990 to 1.04 $\mu g/m^3$ in 2000, yet the trend cannot be established based on the data. Based on the paired student-t tests of three data sets for the six geologic elements, it appears that the geologic elements associated with $PM_{2.5}$ in the Paso del Norte air remain at the same levels as in the past decade. Chlorine, however, shows a decreasing trend between 1990 and 2000.

Levels of toxic trace elements in $PM_{2.5}$ decreased significantly from 1990 to 2000. The trends are statistically significant based on the paired statistical analyses for the five indicator trace elements. The decreases are quite dramatic. For example, arsenic concentration in $PM_{2.5}$ decreased by 57-fold (from 0.073 $\mu g/m^3$ to 0.0013 $\mu g/m^3$) and lead by 18-fold (from 0.24 $\mu g/m^3$ to 0.014 $\mu g/m^3$) in El Paso.

The decrease in the $PM_{2.5}$ mass concentration is also obvious. $PM_{2.5}$ decreased from 32.8 $\mu g/m^3$ and 55.6 $\mu g/m^3$ in 1990 at Chamizal and Sun Metro to 11.0 $\mu g/m^3$ and 22.5 $\mu g/m^3$ in 2000, respectively. Consequently, the fraction of geologic elements in $PM_{2.5}$ (based on the sum of aluminum, silicon, calcium, iron, titanium, and potassium) increased from 6% to 12%, which implies that the contribution of anthropogenic emissions to $PM_{2.5}$ decreased and the overall $PM_{2.5}$ concentration in the air improved in the past decade. The ratio of trace elements to $PM_{2.5}$ concentration also increased. The ratio of copper to $PM_{2.5}$ increased from 0.19% in 1990 to 0.27% in 1997, but decreased to 0.12% in 2000. Table 5 shows that ratios for the dominant trace elements (except for chromium and copper) in the region decreased less impressively from 1990 to 1997, but rather significantly (except that for chromium) until 2000 after a major smelter halted its operations in early 2000. This is indicative of improvement in both geologic and industrial emissions in the past decade and further reduction of toxic trace elements from industrial emissions in the past year.

Table 5. Fraction of Trace Metals in $PM_{2.5}$

Element	1990	1997	UTEP Study				
	TNRCC Sutdy	TNRCC Study	El Paso, Texas		Ciudad Juárez, Mexico		
	Chamizal/ Sun Metro	Central El Paso	Chamizal	Sun Metro	Advanced Transformer	Misión	Club 20-30
Chromium	0.001	0.004	0.005	0.011	0.001	0.001	0.002
Cooper	0.190	0.270	0.110	0.098	0.068	0.124	0.104
Arsenic	0.164	0.086	0.009	0.009	0.003	0.004	0.002
Cadmium	0.015	0.008	0.003	0.006	0.003	0.003	0.003
Lead	0.552	0.163	0.046	0.078	0.070	0.122	0.055

Source: Authors

Table 4 compares the composition of $PM_{2.5\text{-}10}$ obtained in the present study to those measured in 1990. Concentrations of the geologic elements associated with $PM_{2.5\text{-}10}$ are indistinguishable between 1990 and 2000, while the trace elements decreased significantly from 1990 to 2000. As expected, elements associated with geologic sources are high in $PM_{2.5\text{-}10}$. Based on the sum of the mass of the six indicator geologic elements and the mass of the $PM_{2.5\text{-}10}$ derived from Table 1, individual geologic elements account for about 35% of the mass for the coarse fraction of PM_{10}. Because the majority of metals in this study are related to geologic/crustal material, they are predominantly present as oxides (such as Al_2O_3, SiO_2, CaO, FeO/Fe_2O_3, and TiO_2). To account for the dominant forms of these elements, the mineral mass can be estimated by the following equation (Seinfeld 1986):

$$\text{Mineral mass} = (2.2 \times \text{Al}) + (2.49 \times \text{Si}) + (1.63 \times \text{Ca}) + (2.42 \times \text{Fe}) + (1.94 \times \text{Ti})$$

Alternatively, the mineral mass may be estimated from an indicator element (Taylor and McLennan 1995) by multiplying, for example, the aluminium concentration by 12.4 (while not including data for silicon, calcium, etc.). Using these algorithms and the values presented in Tables 2 and 4, the mineral materials could account for up to 70% of the mass for the coarse fraction of PM_{10}.

Chlorine concentrations at all sites (except Chamizal) were high in $PM_{2.5}$ but low in $PM_{2.5\text{-}10}$. The Chamizal site is less influenced by the emission sources of Ciudad Juárez because of its location and the prevailing southeast-northwest winds. The fact that chlorine concentrations are high in $PM_{2.5}$ indicates the existence of local chlorine sources in the southwest region of the airbasin. Further investigation of the seasonal and spatial variations of chlorine concentrations as well as the locations of these sources may provide answers to the unexplained high ozone concentrations in the region.

Summary and Conclusions

The seven-month study of PM concentrations in El Paso shows that the average $PM_{2.5}$ and PM_{10} concentrations are 11 $\mu g/m^3$ and 57 $\mu g/m^3$ for Chamizal and 22 $\mu g/m^3$ and 109 $\mu g/m^3$ for Sun Metro, respectively. The PM_{10} concentration increases toward the suburban area of Ciudad Juárez while $PM_{2.5}$ peaks in areas surrounded by brick kiln emissions and unpaved roads. $PM_{2.5\text{-}10}$ dominates the PM_{10} mass concentration, and geologic sources are the major contributors to $PM_{2.5\text{-}10}$. The 24-hour average $PM_{2.5}$ concentration is maintained as a steady portion of PM_{10} and is less sensitive to the spatial and diurnal variations of PM pollution.

The diurnal variation of PM concentrations at Sun Metro shows that $PM_{2.5}$, PM_{10}, and the $PM_{2.5}$:PM_{10} ratio all peak in the morning and at night. Characterization of time-resolved PM concentrations will be extremely helpful in determining the sources responsible for the high morning and nighttime pollution.

Trace elements in the air are lower today than historical values. Elements of geologic origin dominate the coarse fraction of PM_{10} and are persistent due to the abundance of unpaved roads and complex terrain. Further investigation using source fingerprints and chemical, both organic and elemental (in progress), compositions of air samples could provide mitigation alternatives for controlling PM pollution in the El Paso-Ciudad Juárez border region.

Acknowledgements

Assistance received from the Center for Environmental Resource Management (CERM) at UTEP, University of Utah, DRI, TNRCC, and the Environmental Department of Ciudad Juárez is appreciated.

Endnote

[1] aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), arsenic (As), selenium (Se), bromine (Br), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), molybdenum (Mo), palladium (Pd), silver (Ag), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), barium (Ba), lanthanum (La), gold (Au), mercury (Hg), thallium (Tl), lead (Pb), and uranium (U).

References

A. P. Buck, Inc. 1987. *Mini-Buck Calibrator Instruction Manual.* Orlando, Fla.: A. P. Buck, Inc.

Becerril, I, W.-W. Li, and K. G. Gallardo. 1999. "Implication of Potential PM Sources Based on Hourly Meteorological and PM Concentrations in El Paso." Poster Presentation at The U.S.-Mexico Border: An Exchange of Ideas, SCERP Technical Conference, 18 November, Las Cruces, New Mexico.

Chow, J. C. 1995. "Critical Review: Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles." *Journal of the Air & Waste Management Association* 45(5): 320–382.

Claiborn, C. S., D. Finn, T. V. Larson, and J. Q. Koenig. 2000. "Windblown Dust Contributes to High $PM_{2.5}$ Concentrations." *Journal of the Air & Waste Management Association* 50(8): 1440–1445.

Dattner, S. L. 1994. "El Paso/Juárez 1990 PM_{10} Receptor Modeling Feasibility Study." Texas Natural Resource Conservation Commission Report AS-43.

Dolislager, L. J., and N. Motallebi. 1999. "Characterization of Particulate Matter in California." *Journal of the Air & Waste Management Association* 49: PM 45–56.

El Paso City-County Health and Environmental District. 1999. "Quarterly Air Quality Data." Presented at the 10th meeting of the Joint Advisory Committee for the Improvement of Air Quality in the Ciudad Juárez/El Paso/Doña Ana County Airbasin, 25 February.

El Paso Metropolitan Planning Organization. 1998. *El Paso Metropolitan Transportation Plan* 2020. El Paso: El Paso Metropolitan Planning Organization.

Evans, J. S., and P. B. Ryan. 1983. "Statistical Uncertainties in Aerosol Mass Concentrations Measured by Virtual Impactors." *Aerosol Science and Technology* 2: 531–536.

Fitz-Simons, T., S. Mathias, and M. Rizzo. 2000. Analyses of 1999 *PM Data for the PM NAAQS Review.* Research Triangle Park, N.C.: EPA Office of Air Quality Planning and Standards. http://www.epa.gov/oar/oaqps/pm25/analyses.html.

Haller, L., C. S. Claiborn, T. V. Larson, J. Koenig, G. Norris, and R. Edgar. "Airborne Particulate Matter Size Distributions in an Arid Urban Area." *Journal of the Air & Waste Management Association* 49(2): 161–168.

Hinds, W. C. 1999. *Aerosol Technology.* New York: John Wiley & Sons, Inc.

Jaklevic, J. M., R. C. Gatti, F. S. Goulding, and B. W. Loo. 1981. "A Beta-gauge Method Applied to Aerosol Samples." *Environmental Science and Technology* 15: 680–686.

Jeon, S. J., H. L. C. Meuzelaar, S. A. N. Sheya, J. S. Lighty, W. M. Jarman, C. Kasteler, A. F. Sarofim, and B. R. T. Simoneit. 2001. "Exploratory Studies of PM_{10} Receptor and Source Profiling by GC/MS and Principal Component Analysis of Temporally and Spatially Resolved Ambient Samples." *Journal of the Air & Waste Management Association* 51(5): 766–784.

Macias, E. S., and R. B. Husar. 1976. "Atmospheric Particulate Mass Measurement with Beta Attenuation Mass Monitor." *Environmental Science and Technology* 10: 904–907.

Lodge, J. P. 1989. *Methods of Air Sampling and Analysis 3rd ed.* Chelsea, Mich.: Lewis Publishers, Inc.

Orion Research. 1997. *Cahn Model C-33 Microbalance Instruction Manual.* Beverly, Mass.: Orion Research Inc.

Price, J. H., S. L. Dattner, B. Lambeth, J. Kamrath, M. Aguirre Jr., G. McMullen, K. Loos, W. Crow, R. J. Tropp, and J. C. Chow. 1998. "Preliminary Results of Early $PM_{2.5}$ Monitoring in Texas: Separating the Impacts of Transport and Local Contributions." Pages 191–202 in *Proceedings, $PM_{2.5}$: A Fine Particle Standard*, J. C. Chow, P. Koutrakis, eds. Pittsburgh, Penn.: Air & Waste Management Association.

Schroeder, W. H., M. Dobson, D. M. Kane, and N. D. Johnson. 1987. "Toxic Trace Elements Associated with Airborne Particulate Matter: A Review." *Journal of the Air Pollution Control Association* November: 1267–1285.

Secretaría de Medio Ambiente y Recursos Naturales y Pescas. 1998. *Ciudad Juárez Air Quality Management Plan.* Mexico City: SEMARNAT.

Seinfeld, J. H. 1986. *Atmospheric Chemistry and Physics of Air Pollution.* New York: John Wiley and Sons.

Sheya, S. A. N., H. L. C. Meuzelaar, S. J. Jeon, J. P. Dworzanski, W. Jarman, C. Kastelar, J. Lighty, A. Sarofim, W.-W. Li, V. Valenzuela, J. Anderson, S. Banerji, G. Mejia, M. Zavala, and B. Simoneit. 2000. "Novel Analytical Dimensions in Exploratory Field Studies of Air Particulate Matter." Paper #00-669 in *Proceedings of the 93rd AW&MA Annual Meeting and Exhibition,* 18–22 June, Salt Lake City, Utah.

Taylor, S. R., and S. M. McLennan. 1995. "The Geochemical Evolution of the Continental Crust." *Reviews of Geophysics* 33: 241–265.

Texas Natural Resources Conservation Commission. 1996. *Revision to the Texas State Implementation Plan for PM_{10} for El Paso, TX.* Austin, Tex.: TNRCC.

Texas Natural Resource Conservation Commission. 1999a. "El Paso Eight-Hour Ozone Design Value 1988-1997." http://www.tnrcc.state.tx.us/air/monops/eloz.html.

Texas Natural Resource Conservation Commission. 1999b. "El Paso Annual Average Respirable Particulate Matter of 10 Microns or Less 1988-1997." http://www.tnrcc.state.tx.us/air/monops/elppm10.html.

Texas Natural Resource Conservation Commission. 1999c. "El Paso Second Highest Eight-Hour Maximum Carbon Monoxide Concentrations 1988-1997." http://www.tnrcc.state.tx.us/air/monops/elpco.html.

Texas Natural Resource Conservation Commission. 1999d. "CAMS 41 Data by Month by Monitoring Site by Parameter." http://www.tnrcc.state.tx.us/cgi-bin/monops/monthly_summary?41.

Texas Natural Resource Conservation Commission. 1999e. "CAMS 40 Data by Month by Monitoring Site by Parameter." http://www.tnrcc.state.tx.us/cgi-bin/monops/monthly_summary?40.

Timmons, W. H. 1990. *El Paso—A Borderlands History.* El Paso: Texas Western Press.

Tropp, R. J., S. D. Kohl, J. C. Chow, and C. A. Frazier. 1998. *Final Report for the Texas $PM_{2.5}$ Sampling and Analysis Study.* Document No. 6570-685-7770.1F. Reno, Nevada: Desert Research Institute.

U.S. Environmental Protection Agency. 1990. *Clean Air Act Amendments.* Section 179b; 42.U.S.C. 7509a. Washington, D.C.: EPA.

U.S. Environmental Protection Agency. 1994. "Section 2.10—Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere (Dichotomous Sampler Method)." *In Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods.* EPA/600/R-94/038b. Washington, D.C.: EPA Office of Research and Development.

U.S. Environmental Protection Agency. 1998. *Quality Assurance Document, Method Compendium: Field Standard Operating Procedure for the $PM_{2.5}$ Performance Evaluation Program.* http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/pepfield.pdf.

Watson, J. G., J. C. Chow, and C. A. Frazier. 1999. "X-ray Fluorescence Analysis of Ambient Air Samples." Pages 67–96 in *Elemental Analysis of Airborne Particles, Vol. 1,* S. Landsberger and M. Creatchman, eds. Amsterdam: Gordon and Breach Science.

Watson, J. G., J. C. Chow, H. Moosmüller, M. C. Green, N. H. Frank, and M. L. Pitchford. 1998. "Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks." EPA-454/R-98-012. Prepared for EPA Office of Air Quality Planning and Standards by Desert Research Institute. http://www.epa.gov/ttn/amtic/pmpolgud.html.

Wedding, J. B., and M. A. Weigand. 1993. "An Automatic Particle Sampler with Beta Gauging." *Journal of the Air & Waste Management Association* 43(4): 475–479.

IV

Characterization of Airborne Particulate Matter in the Paso del Norte Air Quality Basin: Morphology and Chemistry

W-W. Li, J. J. Bang, R. R. Chianelli, M. J. Yacaman, and R. Ortiz

Abstract

Five sites in the twin cities of El Paso, Tex.-Ciudad Juárez, Chih., with different topographical, industrial, and traffic conditions were selected for a detailed analysis of particulate matter (PM) from 24-hour, Sierra Anderson dichotomous samplers. Filter samples were analyzed by scanning electron microscopy for their morphology and X-ray fluorescence for elemental composition. The studies illustrate how individual particle morphology and chemical analysis can be used to identify sources and complements the source attribution studies in Chapter VI.

Five observations have been made from this study:

- Road conditions (paved or unpaved) and traffic volume influence the levels of both fine and coarse PM levels
- Industrial activities also dictate the composition of PM
- Coarse fraction of PM_{10} is strongly associated with high wind speed and mostly originates from soil

- Carbonaceous material with various forms is ubiquitous, as anticipated, although pinpointing potential sources is a difficult task
- Particles in aggregated forms of smaller components are one major component

---

Caracterización de Materia Particulada Atmosférica en la Cuenca del Paso del Norte: Morfología y Química

W-W. Li, J. J. Bang, R. R. Chianelli, M. J. Yacaman, y R. Ortiz

Resumen

Cinco sitios en las ciudades de El Paso-Ciudad Juárez con diferentes condiciones topográficas, industriales, y de tráfico fueron seleccionadas para un análisis detallado de materia particulada (PM) durante 24 horas con muestreadores dicotómicos Sierra Anderson. Las muestras de los filtros fueron analizadas por microscopía electrónica de barrido para su morfología y mediante fluorescencia de rayos X para su composición elemental. Los estudios ilustran cómo la morfología individual de las partículas y el análisis químico pueden usarse para identificar fuentes y complementa los estudios de fuentes atribuidas del capítulo VI.

Se han hecho cinco observaciones en este estudio:

- Las condiciones de la carretera (pavimentada o terracería) y el volumen de tráfico influyen en el nivel de ambos niveles finos y gruesos de PM
- Las actividades industriales también determinan la composición de PM

- El fragmento grueso de PM_{10} es fuertemente asociado con velocidades altas de viento y en su mayor parte se origina del suelo
- El material carbonado en diversas formas es ubicuo, como era esperado, aunque el indicar fuentes potenciales de manera precisa es una tarea difícil
- Las partículas en formas agregadas de componentes más pequeños son un componente mayor

---

Introduction

As noted already in this volume, particulate matter (PM) is a complex issue that would be better understood by knowing the sources, physical characteristics, and chemical compositions of the components. PM characterization is also believed to be a critical step for reassuring the validity of currently imposed regulations and for finding efficient abatement programs.

To understand Paso del Norte's PM issues better, five strategic sites in the twin cities of El Paso, Tex.-Ciudad Juárez, Chih., were selected for collection purposes and a series of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ filters were collected. Sets of $PM_{2.5}$ and $PM_{2.5\text{-}10}$ filters were submitted for characterization of physical properties such as morphology and size via scanning electron microscopy (SEM). The SEM study was followed by analyses of elemental constituents with X-ray fluorescence (XRF) mounted on the microscope. The studies were conducted at five sites: Chamizal, Sun Metro, Club 20-30, Advanced Transformer, and Misión (the location and description of the sites are provided in Appendix Figure 1 [page 305]). Two dichotomous air samplers (Anderson Instruments) were placed at each of the two U.S. sites. One sampler was operated every other day to collect 24-hour air samples and the other was operated selectively for collocated (duplicate) samples. Only one dichotomous sampler was operated at each of the three Mexican sites. All samplers (except at the Misión site) were positioned at least eight feet away from the Texas Commission on Environmental Quality's (TCEQ) eight-foot tall instrument shacks with the inlet head standing five feet above the ground. The sampler at the Misión site was positioned on the roof of a one-story cinder block storage structure and the inlet head was five feet above the roof. The dichotomous air samplers had PM size cutoffs of $PM_{2.5}$ and PM_{10} (particulate matter that measures less than 2.5 micrometers [μm] or 10 μm or less, respectively, in diameter). However, these size cutoffs are based on a particle's aerodynamic size; a particle's morphology will affect whether a particle can pass into the dichotomous sampler. For example, some of the results in this section show particles greater than 2.5 micrometers (μm) in size being deposited on a $PM_{2.5}$ filter; this is consistent with the aerodynamic sizing cutoff of the dichotomous samplers.

Ten filters collected on January 15, 2000, at the five locations throughout the Paso del Norte airbasin were subjected to SEM and XRF. The study was performed with a Phillips Scanning Electron Microscope model XL30 equipped with an Energy Dispersive X-Ray Spectrometer (EDX) for elemental chemical analysis by XRF. Due to interference experienced using the filter supports, the filters were placed in a double roll of carbon and inside an aluminum pan for the analysis. Different representative areas were selected for each filter to perform the elemental chemical analysis. The observations were performed at 25 kilovolts (kV) of energy for electron acceleration with a 65 microampere (μA) emission current at high vacuum with varying amplifications. The chemical XRF analysis was performed at 25kV energy with 65 μA of current, obtaining the XRF spectra for different particles.

Results

Teflon filters were used for the 24-hour collection period. There is a visible and inherent difference in color—$PM_{2.5}$ is black and $PM_{2.5\text{-}10}$ is light brown to gray. One can make the assumption that each filter is loaded with different chemical constituents. Each constituent has a different density and therefore a different mass. $PM_{2.5}$ tends to contain more organic constituents while $PM_{2.5\text{-}10}$ is considered to be more geologic.

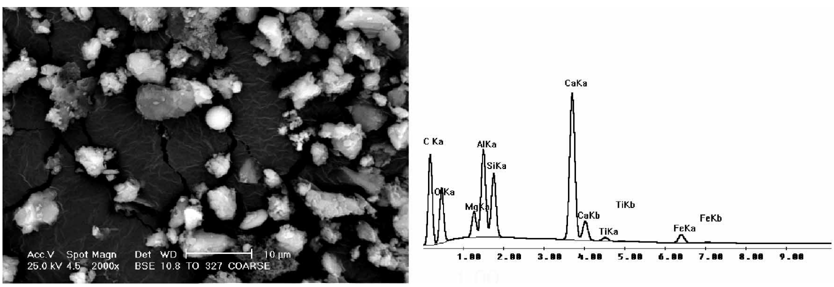
To determine the morphology of PM, a set of samples were subjected to SEM analyses. The selected specimens were collected at the five sites on January 15, 2000. Certain representative particles of different shapes from each filter were subjected to XRF analyses for elemental determination. The Materials Science Division of the Instituto Nacional de Investigaciones Nucleare, located in Mexico City, conducted the analysis.

The SEM images showed that the shapes of the $PM_{2.5}$ particles were quite diverse, although the majority were irregularly shaped. Most of the PM ranged in size from 1 µm to 2.5 µm. Some of the particles were spherical, and some had a laminar shape, approximately 5 µm in size, with smaller particles adhered to the surfaces of the dominant particles. It is also notable that many particles were present in aggregated or cumulus forms. The cumulus particles formed long chains of up to 5 µm in longitudinal length. Representative electron micrographs are shown in Figures 1 and 2. Particle classes useful for identification include the following:

1. Soot particles. These are emitted by a wide range of combustors, including poorly operated furnaces, diesel engines, and forest fires. The soot particles typically consist of chains of primary particles with a characteristic dimension of 20 nanometers (nm) to 60 nm, such as those seen in Figure 3. The soot particles also occur as clusters (Figure 4). The XRF analysis of the cluster shows the dominance of carbon. It also shows that trace amounts of calcium (Ca) and sulfur (S) are a trait of diesel-generated soot. The inorganic content of the soot particle provides an indication of its source.
2. Spherical particles. Spherical particles such as those seen toward the middle of Figure 1 are typically associated with particles that have been formed in a high-temperature furnace, such as a coal-fired boiler. These are typically alumino-silicates, often with significant concentrations of iron that come from pyrites and other iron-containing minerals in coal. Smelting operations will also generate spherical particles, including elements specific to the ores being processed.
3. Cubical particles. Sodium chloride produced by the evaporation of saline solutions form cubical particles such as those seen in Figure 5, as confirmed by the elemental composition obtained using XRF.

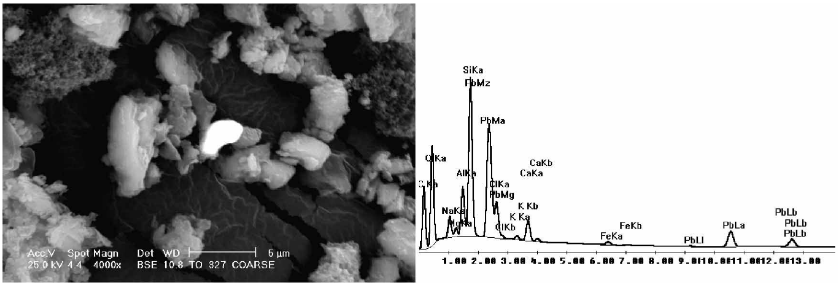
4. Irregularly shaped minerals. Crustal material suspended by the wind and particles generated during the processing of limestone and other minerals have irregular shapes indicative of the minerals being processed.
5. Cumulus Inorganic Particles. Agglomerates of smaller mineral particles of primary size of one micron to several microns were often observed. Cumulus particles were comprised of carbon, oxygen, silicon, calcium, aluminum, sodium, sulfur, chlorine, potassium, and iron (Figure 6). The origin of these is uncertain.

Figure 1. SEM Image with XRF of Spherical Particles from the Chamizal Site



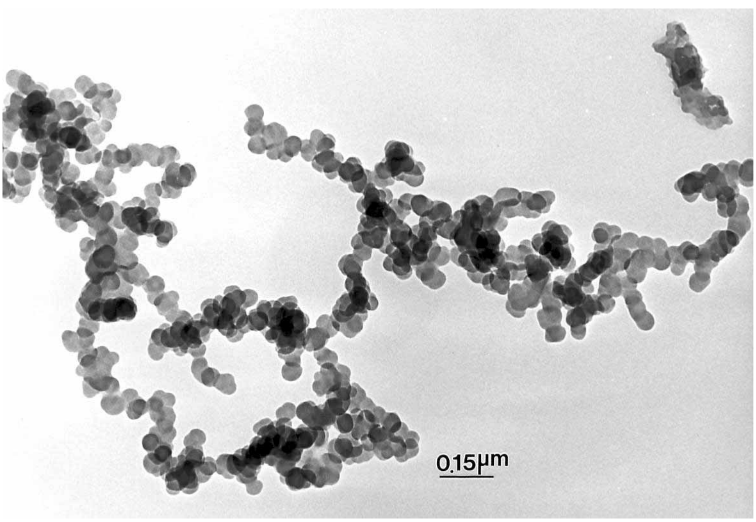
Source: Authors

Figure 2. SEM Image with XRF of Irregular Shiny Particles from the Chamizal Site



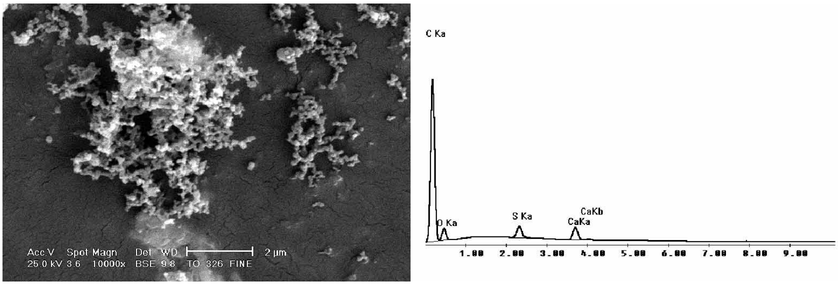
Source: Authors

Figure 3. Transmission Electron Microscopy (TEM) Image of Particles from a Diesel Engine



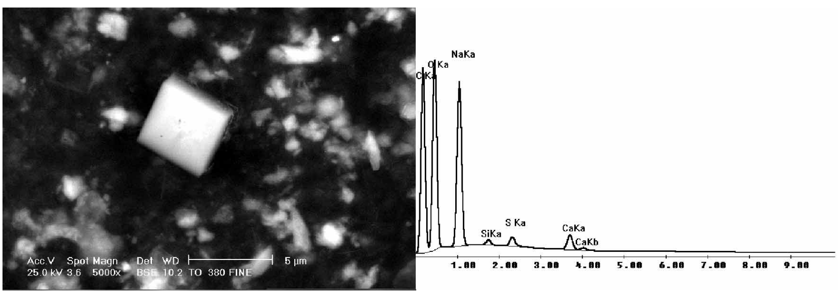
Source: Authors

Figure 4. SEM Image with XRF of Shiny Particles from the Chamizal Site



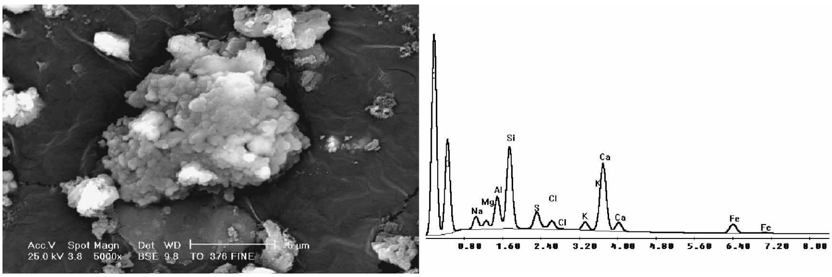
Source: Authors

Figure 5. SEM Image with XRF of Cubical Shaped Particles from the Misión Site



Source: Authors

Figure 6. SEM Image with XRF of Conglomerated Particles from the Club 20-30 Site



Source: Authors

The above classes of compounds were found at the five sites in amounts reflecting the local emissions sources. A summary of the observations at the different sites is presented below.

Samples Collected at Chamizal

The PM_{10} concentration at the Chamizal National Park site was 41.9 micrograms per cubic meter (µg/m^3). The $PM_{2.5}$ concentration was 12.2 µg/m^3, and the $PM_{2.5\text{-}10}$ concentration was 29.7 µg/m^3. The average wind speed recorded for the day was 1.6 meters per second (m/s). The average wind gust for the day was 4.2 m/s and the maximum wind gust was 7.3 m/s.

The XRF elemental analysis determined that some spherical particles had a high iron content and others had high copper, titanium, or aluminum content. XRF analysis performed on laminar adhered particles indicates a high lead content. The lead and copper are indicative of metallurgical processing. Substantial amounts of carbon and calcium were found in the particles forming long chains, as would be expected in diesel soot. Sulfur was detected in the majority of analyzed particles.

From the SEM images of the $PM_{2.5\text{-}10}$ filter it was observed that particles were of various shapes, some spherical and some irregular. The size ranged from 0.5 µm to 11.0 µm. XRF performed on the particles of spherical shape found high contents of calcium, silicon, and aluminum with low iron content, which is indicative of a high-temperature origin. Irregularly shaped particles, on the other hand, had high heavy metal content of elements such as lead and iron.

Samples Collected at Sun Metro

At the Sun Metro Bus Station Site, the PM_{10} concentration was 189 μg/m^3, the $PM_{2.5}$ concentration was 41.5 μg/m^3, and the $PM_{2.5\text{-}10}$ concentration was 148 μg/m^3. The average wind speed recorded for the day was 2.02 m/s. The average wind gusts for the day were 3.7 m/s with maximum hourly gusts of up to 4.9 m/s.

$PM_{2.5}$ particles observed from the SEM images ranged from 0.6 μm to 16 μm with various irregular shapes, including spherical. The larger particles appeared to be made up of clusters of smaller particles. In a recent study (Bang and Murr 2003), more than 70% of the particles collected from ambient air in the El Paso-Ciudad Juárez region were clusters of smaller particles. Chemical analysis determined high iron, silicon, and calcium contents, with small quantities of magnesium and sulfur in some of the particles. Irregularly shaped particles contained high levels of iron and low levels of sulfur.

SEM images of the $PM_{2.5\text{-}10}$ filters revealed that the size varied from 1 μm to 7.7 μm; the majority were of irregular shape and some had spherically shaped particles. It was observed that small particles were adhered to larger particles, and in fact, some large particles are made up of an accumulation of smaller particles. XRF analysis demonstrates that in general, particles are comprised mainly of carbon, oxygen, silicon, and low quantities of aluminum and calcium. Spherical particles contain high concentrations of iron, oxygen, and carbon. Cumulus particles had carbon and calcium with small quantities of sulfur and potassium, again indicative of diesel soot.

Samples Collected at Club 20-30 in Ciudad Juárez

At the Club 20-30 site, the PM_{10} concentration was 76.9 µg/m³ for the day, the $PM_{2.5}$ concentration was 31.1 µg/m³, and the $PM_{2.5\text{-}10}$ concentration was 45.5 µg/m³. The average wind speed recorded for the day was 0.84 m/s.

From the SEM images of the $PM_{2.5}$ filter it was observed that particles were of various shapes with sizes ranging from 0.8 µm to 20 µm. Most of the particles are of irregular shape, some were large spherical particles. Accumulation of particles of approximately 0.6 µm combined to form cumulus larger than 10 µm. Elemental analysis determined that the larger particles (those greater than 15 µm) exhibit carbon, oxygen, silicon, sodium, and calcium in substantial quantities. Cumulus inorganic particles were also observed (Figure 6).

The SEM images showed that the $PM_{2.5\text{-}10}$ particles were of diverse sizes and shapes. Spherical particles ranged from 2 µm to 3.9 µm, and rectangular particles ranged from 2.8 µm to 9 µm long. Others with semi-spherical shapes ranged up to 13.5 µm. Elemental analysis indicates that a large portion of the spherical particles contain elevated concentrations of carbon, oxygen, and silicon and lesser quantities of magnesium, sodium, aluminum, sulfur, calcium, and silicon. Rectangular particles, including cube-shaped particles, had high concentrations of sodium and chlorine, including carbon, oxygen, and a substantial concentration of iron.

Samples Collected at Advanced Transformer in Ciudad Juárez

The PM_{10} concentration at the Advanced Transformer site was 238 µg/m³. The $PM_{2.5}$ concentration was 85.8 µg/m³, and the $PM_{2.5\text{-}10}$ concentration was 152 µg/m³. The average wind speed recorded for the day was 0.9 m/s.

The SEM images of the $PM_{2.5}$ filter showed that the morphology of the particles was irregular. Also, there were particles that formed layers. The $PM_{2.5}$ particles ranged from 0.78 µm to 4 µm, with the larger particles formed by aggregation or agglomerations of smaller particles. Elemental analyses on some irregularly shaped particles represented high concentrations of carbon and calcium. There were elevated portions of titanium accompanied by lower portions of iron in a spherical particle.

The SEM images of the $PM_{2.5\text{-}10}$ filter showed that the particles were of irregular shape and some particles had a cubical shape. The sizes ranged from 0.6 µm to 8 µm while the cubical particles, indicative of sodium chloride (NaCl), ranged from 0.6 µm to 1.9 µm. Small particles arranged together and simulating chains were comprised of high concentrations of calcium with lesser quantities of aluminum and silicon. Some irregularly shaped particles contained substantial portions of metals. Again, cube-shaped particles had substantial quantities of sodium, chlorine, and calcium.

Samples Collected at Misión in Ciudad Juárez

The PM_{10} concentration at the Misión Site was 214 µg/m^3. The $PM_{2.5}$ concentration was 44.3 µg/m^3, and the $PM_{2.5\text{-}10}$ concentration was 170 µg/m^3. Meteorological data were not available at this site.

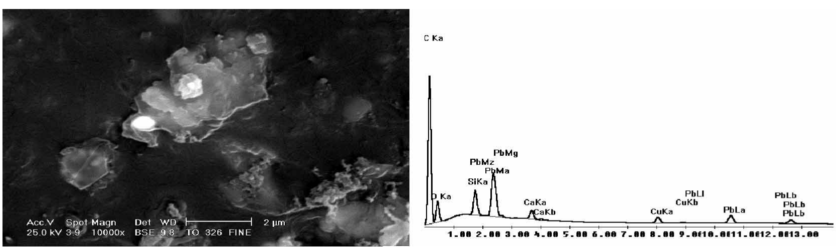
The SEM images of the $PM_{2.5}$ filter showed particles of various shapes, including irregular and spherical shapes. The sizes ranged from 0.6 µm to 1.2 µm. Other cubical shaped particles had a size range from 2 µm to 4.5 µm. Elemental analysis determined that, in general, particulates have high carbon, oxygen, silicon, and calcium contents. On the other hand, spherically shaped particles contained substantial quantities of iron. Cubical particles represent high sodium, oxygen, and carbon content and small sulfur content.

The SEM images of the $PM_{2.5\text{-}10}$ filter showed that the particles were of irregular shape, with sizes varying from 0.7 µm up to 11 µm. There were also distinct spherical particles with diameters from 1.6 µm to 5.6 µm. Cubical particles were also found on the coarse filter. Elemental analysis determined that those irregularly shaped particles, including those that were spherical, contained substantial quantities of calcium, silicon, oxygen, carbon, and sulfur. In addition, spherical particles represented high concentrations of lead, zinc, or iron, while the cubical particles presented sodium, aluminum, and calcium.

Discussion and Conclusions

Some samples collected at the Chamizal area showed layered structures with metallic particles of different sizes attached to their surfaces. Particles with layered structures of carbonaceous material are often present in ambient air (Bang and Murr 2002). Bang and Murr speculated that brake pads and linings or other graphitic materials used in various industries were a likely source of the particles with layered structures. Particles with a laminar-adhesion form contained several elements, predominantly lead, that attached on the surface of a parent particle (Figure 7). It is believed that lead elements are attached to the surface of the carbon particles in the air after they are generated from separate sources. Particles in aggregated forms with high carbon and silicon indicate an influence of various combustion activities, including automobiles. Unlike the previous case (Figure 7), the shiny particles with high carbon and sulfur are more likely to be generated from the same source without a significant time lapse.

Figure 7. SEM Image with XRF of Shiny Particles from the Chamizal Site



Source: Authors

Spherical coarse particles from the Chamizal area (Figure 1) resemble particles from natural sources, such as soil or disturbed roadsides, but are more homogeneous and regular. In Figure 2, the XRF of the coarse particles presents the mixture of elements from both natural and anthropogenic sources. The shiny particles are probably lead with other elements mingled together. At the upper left corner of the picture, particles similar to the cumulus soot shown in Figure 4 are present.

A striking characteristic among the samples collected from the Sun Metro site when compared with those from Chamizal, regardless of their sizes and elemental compositions, is that a majority of the particles are aggregates or clusters of smaller-size components. As stated before, a similar observation was made in a more recent study (Bang and Murr 2003). In fact, the majority of the collected ultrafine PM observed under transmission electron microscopy was aggregates of much smaller particles.

Both fine and coarse particles collected from Club 20-30 show a higher percentage of elemental carbon than at other sites. The elemental composition of the particles in both categories from this site is unremarkable except that the majority seems to be suspended soil. Because the Club 20-30 site had the lowest wind speed among the five collection sites during the collection period, the elements shown in XRF studies are believed to best represent the particles generated locally. Similar forms of the conglomerated particles in Figure 6 also have been observed from the tailpipe of an old gasoline engine during a preliminary study (Bang 2003). One speculation was that, as shown in XRF data in Figure 6, carbonaceous particles intermingle with soil elements made available in the chamber during the internal combustion process.

As anticipated, the levels of both fine and coarse PM collected from Advanced Transformer, where industrial activities are more common than other sections of El Paso-Ciudad Juárez, were among the highest. The amount of carbonaceous material represented in a form of carbon in XRF is notable in these samples. The wide variation in composition and morphology (aggregates, layered structures, chains, etc.) of particles at this site are indicative of the diversity of industrial sources. The elemental composition of the layered structures shows that they are a mixture of carbonaceous material and soil components. The majority of soil components might have been added on the surfaces of carbonaceous particles produced by some industrial activities or automobiles.

The presence of some cubical particles shown in SEM pictures (sodium, calcium, and chlorine) at the Advanced Transformer site, the Club 20-30 site, and the Misión site indicate the possibility of a local source rather than long-range transfer of sodium chloride or calcium chloride, although long-range transfer from the Gulf of Mexico is a possibility. Identification of the source of chlorine or precursors of chlorine would not be an easy task, mainly due to the lack of monitoring procedures in Ciudad Juárez. However, the routine use of chlorine for disinfecting heavily concentrated healthcare buildings, including local hospitals, pharmacies, clinics, and public buildings in the Club 20-30 area, could be one major source for the high chlorine levels. Although, these are unlikely to react in the atmosphere to yield cubical sodium chloride crystals. At the time of this study, official data about chlorine use in industrial sectors were not available for Ciudad Juárez. The source identification of chlorine would be an interesting follow-up task for the future.

The presence of cement manufacturing factories in addition to unpaved roads in the heavily populated Misión site leads one to expect high levels of PM in both fine and coarse categories. The PM from this site is mostly from unpaved roads and cement factories and mixed with carbonaceous components from combustion sources located in nearby residential areas. The source of substantial quantities of iron in the PM collected at the Misión site is unclear.

Trace metal concentrations are lower today than historical values. They are mostly contained in spherically shaped particles in the $PM_{2.5}$ fraction and in irregularly shaped particles, presumably as coatings, in the $PM_{2.5\text{-}10}$ fraction. Misión had the highest lead and copper concentration in the $PM_{2.5}$ fraction, Sun Metro had the second highest levels of lead, and Sun Metro also ranked third for copper, which is expected because Sun Metro is situated nearby an old refinery. There is evidence that trace elements in $PM_{2.5}$ might be attributed to wind or mechanical erosion at some locations such as Sun Metro, but spherical shapes determined by SEM analysis suggest that trace metals in $PM_{2.5}$ are from smelting or combustion sources. On the other hand, Sun Metro had the highest lead and copper concentrations in $PM_{2.5\text{-}10}$, which were frequently associated with particles of an irregular shape. Given the site's location close to an old refinery, Sun Metro's $PM_{2.5\text{-}10}$ is likely influenced by wind or mechanical erosion.

Elements of geologic origin dominate the coarse fraction of PM_{10} and are persistent due to the abundance of unpaved roads, dry terrain, and high wind episodes, as can be seen in the high aluminum, silica, and calcium concentrations at all five sites. Misión, located in the foothills of the Sierra de Juárez Mountains; Advanced Transformer, located next to the brick kiln district with unpaved roads; and Sun Metro, located close to high geologic emission sources, had the highest silicon and calcium concentrations, as expected. In the fine fraction of PM_{10}, geologic particles were of irregular shape, which is opposite of what was observed with the trace metals, and highest at the sites close to unpaved roads, as at the Advanced Transformer and Misión sites.

The data from the five sites indicate that road conditions, industrial activities, and the volume of traffic in a region dictate the levels of both fine and coarse PM when weather-related factors are ruled out. The composition of fine and coarse PM seems to be influenced by the unique characteristics of each site.

Lead levels in both fine and coarse PM were high in the samples from the Chamizal site, which indicates that there may be a source of new lead generation, in addition to some pre-existing lead in the local environment. Automobiles crossing the international bridges, various small factories in the region, and metal recycling sites in the vicinity are all believed to be contributing sources of the high lead levels. The presence of fine lead at this site can be contrasted to the conditions at the Advanced Transformer and Misión sites, where most of the lead is in coarse form. The significance of this contrast is not well documented. However, it is thought that these differences are related to the various levels of industrial activities. Such observations can help guide future investigations of sources of lead in the atmosphere.

References

Bang, J. J. 2003. "Characterization of Representative Ambient Air Ultra-fine and Nanoparticles in El Paso-Juárez Metroplex: Morphology, Chemical Composition, and Speciation." Ph.D. diss., Department of Environmental Science and Engineering, University of Texas at El Paso, El Paso, Texas.

Bang, J., and L. Murr. 2002. "Collecting and Characterizing Atmospheric Nanoparticles." *Journal of the Minerals, Metals and Materials Society* 54(12): 28–30.

Bang, J., and L. Murr. 2003. "Utilization of Selected Area Electron Diffraction (SAED) Patterns for Characterization of Air Submicron Particulate Matter Collected by a Thermophorecitc Precipitator." *Journal of the Air & Waste Management Association* 53: 1-10

Tropp, R. J., J. C. Chow, S. D. Kohl, B. Lambeth, and J. H. Price. 1998. "Use of Data Quality Objectives as a Tool: Quality Management and Project Planning." Paper presented at the Air & Waste Management Association 87th Annual Meeting and Exhibition, 19–24 June, Cincinnati, Ohio.

V

Toxic Metals in the Air and Soil of the Paso del Norte Region

N. E. Pingitore Jr., T. T. Espino, B. E. Barnes, J. L. Gardea-Torresdey, J. W. Clague, W. P. Mackay, M. A. Amaya, J. J. Reynoso, W.-W. Li, R. M. Currey, R. D. Moss, M. Delgado, P. Juárez, J. Bader, J. C. Zevallos, and I. Herrera

Abstract

In the first of the individual studies that comprise this chapter, air concentrations are presented for four toxic metals—copper (Cu), lead (Pb), arsenic (As), and chromium (Cr)—based on particulate matter (PM) trapped on filters from eight sampling stations in the Paso del Norte airshed in 1994, 1995, and 1996. One representative low-wind day in each season (spring, summer, fall, and winter) was chosen for analysis by inductively coupled plasma mass spectrometry (ICP-MS). The resultant data set thus can be interrogated to reveal both geographic and seasonal variation trends in airborne toxic metals.

Concentrations of copper, lead, chromium, and arsenic were found to increase during fall and winter, relative to spring and summer. Ground-level atmospheric inversions during the colder seasons in this desert region are believed to trap anthropogenic particulates by preventing vertical mixing. Elevated metal levels characterized

sampling stations in the urban core, with lower values at more distal samplers. This suggests the importance of local sources of the metals.

The chapter also details a study in which levels of lead, copper, and arsenic in PM in the El Paso, Tex.-Ciudad Juárez, Chih., airshed were found to exhibit significant decreases over the past quarter-century. These overall trends are evident even in a limited data set of samples from 1977, 1980, 1987, 1994, and 2001. Decreases in lead are dramatic and a significant contribution to the public health of the El Paso-Ciudad Juárez binational community.

The chapter further details the collection of soil samples from areas surrounding various facilities in El Paso that are potential point sources (historical as well as current) for metals contamination. Areas of interest include the American Smelting and Refining Company (Asarco) smelter on the west side of El Paso, Memorial Park in central El Paso (where the Federal smelter was formerly located), and the Phelps Dodge copper refinery on the east side of El Paso. Soil samples were also collected from outlying areas north and east of El Paso in an effort to observe the effects of distance from urban sources.

The soil samples were prepared and analyzed for arsenic, barium, calcium, cadmium, copper, chromium, lead, nickel, selenium, and zinc. Values for arsenic, lead, copper, and chromium are presented on maps of the El Paso area and correlations between concentrations of the various metals were determined.

Concentrations of arsenic, lead, copper, and chromium were highest in the area around the Asarco smelter. Higher concentrations were observed in the surface (2.5 centimeter [cm]) samples than in the samples taken at greater depths. The Memorial Park area exhibited slightly elevated levels of these metals relative to the El Paso urban background values. The samples from the Phelps Dodge refinery region were generally indistinguishable from the background samples.

Finally, the geographic distribution of lead in El Paso soils is presented in maps based on more than 300 composite soil samples collected in the region. The use of such composites highlights the distribution of lead at the neighborhood level, and de-emphasizes any anomalous elevated level associated with an individual house or structure.

Lead levels are highest in the downtown commercial district; in the adjacent area to the east, which comprises an old central business, transport, and light industry complex; and to the west in the area of the Asarco smelter. The continuity of this zone and the age of its structures make it difficult to differentiate lead sources. Lead values decrease systematically away from this urban core zone, with the lowest levels generally encountered in the peripheral, lightly populated developments and communities.

This geographic distribution of lead in soil is consistent with lead measurements reported on PM taken from four air monitoring stations during the 1990s. Soil data thus can complement air studies by providing an essentially infinite geographic network of sampling sites that, with varying accuracy, record and integrate air conditions over years and decades.

Metales Tóxicos en el Aire y Suelo de la Región Paso del Norte

N. E. Pingitore Jr., T. T. Espino, B. E. Barnes, J. L. Gardea-Torresdey, J. W. Clague, W. P. Mackay, M. A. Amaya, J. J. Reynoso, W.-W. Li, R. M. Currey, R. D. Moss, M. Delgado, P. Juárez, J. Bader, J. C. Zevallos, y I. Herrera

Resumen

En el primero de los estudios individuales que comprende este capítulo, las concentraciones del aire son presentadas para cuatro metales tóxicos—cobre (Cu), plomo (Pb), arsénico (As), y cromo (Cr)—basados en la materia particulada (PM) atrapada en filtros de ocho estaciones de muestreo en la cuenca atmosférica Paso del Norte en 1994, 1995, y 1996. Se eligió un día representativo de bajos vientos en cada estación (primavera, verano, otoño, e invierno) para el análisis por espectrometría de masas (ICP-MS) acoplado con plasma. El conjunto de datos resultante revela ambas tendencias geográficas y estacionales de variación en metales tóxicos aerotransportados.

Se encontró que las concentraciones de cobre, plomo, cromo, y arsénico aumentan durante el otoño e invierno, con relación a la primavera y el verano. Se cree que inversiones atmosféricas en niveles del suelo durante las estaciones más frías en esta región desértica atrapan partículas antropogénicas al prevenir la mezcla vertical. Niveles elevados de metal caracterizaron a las estaciones de prueba en el núcleo urbano, con valores inferiores en muestras distantes. Esto sugiere la importancia de las fuentes locales de los metales.

El capítulo también detalla un estudio en el cual se encontró que los niveles de plomo, cobre, y arsénico en PM en la cuenca atmosférica de El Paso-Ciudad Juárez exhiben disminuciones significativas en el pasado cuarto de siglo. Estas tendencias generales son evi-

dentes aun en un conjunto de datos limitado de pruebas de 1977, 1980, 1987, 1994, y 2001. Las disminuciones de plomo son dramáticas y una contribución significativa para la salud pública de la comunidad binacional El Paso- Ciudad Juárez.

El capítulo detalla sobre la colección de muestras del suelo de áreas que rodean diversas instalaciones en El Paso que son fuentes puntuales potenciales (Históricas y actuales) de contaminación por metales. Las áreas de interés incluyen a la American Smelting and Refining Company (Asarco) en el lado del oeste de El Paso, el Parque Memorial en el centro de El Paso (donde anteriormente estaba ubicada la fundición Federal), y la refinería de cobre Phelps Dodge en el lado Este de El Paso. Muestras de suelo fueron también obtenidas de áreas en las afueras al Norte y Este de El Paso en un esfuerzo por observar los efectos de la distancia con fuentes urbanas.

Las pruebas de suelo fueron preparadas y analizadas para arsénico, bario, calcio, cadmio, cobre, cromo, plomo, níquel, selenio, y zinc. Los valores para el arsénico, plomo, cobre, y cromo son presentados en mapas del área de El Paso y se obtuvieron las correlaciones entre las concentraciones de los diversos metales.

Las concentraciones de arsénico, plomo, cobre, y cromo fueron las más altas en el área alrededor de la fundición Asarco. Concentraciones superiores fueron observadas en las muestras superficiales (2.5 centímetros [cm]) que en las de profundidades mayores. El área del Parque Memorial exhibió niveles ligeramente elevados de estos metales en relación con valores anteriores urbanos de El Paso. Las pruebas de la región de la refinería Phelps Dodge fueron generalmente indistinguibles de los valores anteriores de referencia.

Finalmente, la distribución geográfica de plomo en suelos en El Paso se presenta en mapas basados en más de 300 muestras del suelo obtenidas en la región. El uso de los mapas permite resaltar la distribución de plomo en el nivel vecindad, y resta importancia a cualquier nivel anómalo elevado asociado a una estructura o casa individual.

Los niveles de la plomo son más altos en el distrito comercial del centro de la ciudad; en el área adyacente hacia el Este, que comprende una vieja central de negocios, de transporte, y un complejo de industria ligera; y hacia el oeste en el área de la fundición Asarco. La continuidad de esta zona y la edad de sus estructuras dificultan el diferenciar fuentes de plomo. Los valores de plomo disminuyen sistemáticamente fuera de esta zona urbana núcleo, con los niveles más bajos generalmente encontrados en las comunidades y desarrollos periféricos poco poblados.

Esta distribución geográfica de plomo en el suelo es consistente con medidas de plomo reportadas en PM tomada de cuatro estaciones de monitoreo de aire durante los 1990s. Los datos del terreno pueden así complementar estudios de aire al proveer una red geográfica esencialmente infinita de sitios de muestreo que, con exactitud variable, registran e integran condiciones del aire a través de años y décadas.

Seasonal and Spatial Variation of Metals in Airborne Particulate Matter in the El Paso-Ciudad Juárez Airshed[1]

Previous Studies

Einfeld and Church (1995) reported on a short-term (December 3–21, 1990) investigation of particulate matter (PM) in the El Paso-Ciudad Juárez airshed. Their study identified the importance of biomass combustion and crustal sources of PM, and the relatively small contribution (< 20%) from vehicles. Levels of PM were higher in Ciudad Juárez than in El Paso, and much of this was found to be aerosol carbon. Winter stagnation events exacerbated the particulate load by preventing dilution. Einfeld and Church (1995) also provided a comprehensive summary (to 1995) of the findings of earlier research on all aspects of air quality in the region.

Dattner (1994) furnished additional details of x-ray fluorescence (XRF) analysis of 72 (22 coarse, 50 fine) 12-hour filters also collected during the December 1990 study. He indicated that elevated metal values were consistent with a smelter source, and that high lead values in Ciudad Juárez were related to leaded gasoline. Note that by the mid-1990s leaded gasoline was severely restricted in Mexico.

Materials and Methods

Meteorology and Sample Selection

Meteorological records were investigated from two sources—a local newspaper, *The El Paso Times,* and the U.S. National Weather Service. The goal was to find one low wind velocity day in each of the four seasons of 1994, 1995, and 1996. Samples taken on days with low wind velocity would emphasize local production of particulates, which might assist in source determination.

Pearson and Fitzgerald (2001) applied the MM5 wind model for the El Paso-Ciudad Juárez airshed; their model was concerned with high ozone concentration days. They found that high ozone episodes occur primarily during periods of low wind speeds for the Paso del Norte region.

Samples for this study were selected to meet three criteria: low wind speed, wind direction consistent with seasonal trend (Chapter I, Figure 2), and lack of such confounding conditions as rain or snow. Among the available filters, the authors were able to select days with average wind speeds between 5.8 kilometers per hour (km/hr) and 14.0 km/hr (3.6 miles per hour [mph] to 8.8 mph) (Table 1).

Filter Samples

Qualifying filters were selected from the archives at the laboratory of the El Paso City-County Health and Environmental District (EPCCHED). A total of 141 PM_{10} (particulate matter with an aerodynamic diameter of 10 micrometers [μm] or less) quartz filters were sub-sampled for analyses by removing 1-inch-by-3-inch strips with a ceramic knife (zirconia) to prevent contamination with metals of interest. These 24-hour samples had been taken from four sites in El Paso and four in Ciudad Juárez. The sampling period was midnight to midnight, scheduled every sixth day. The sampler systems—two-stage Sierra Andersen PM_{10}—were impaction type with size-selective inlet and a design flow rate of 1.13 cubic meters per minute (m^3/min) (EPA 1992).

The four El Paso sites were Tillman, Riverside, Northeast, and Ivanhoe, and the four Ciudad Juárez sites were Pestalozzi, Tecnológico, Advance Transformer, and Zenco. Data from a ninth

Table 1. Weather Data Used for Selection of Appropriate PM_{10} Filters

	Wind Average Speed (mph)	Peak Wind (mph)
1996		
October 30	3.6	10
July 26	4.8	15
April 15	8.2	22
January 10	7.8	24
1995		
October 18	5.3	16
July 8	5.3	16
April 27	7.3	23
January 3	5.4	16
1994		
October 11	4.6	14
July 31	7.2	23
April 20	8.8	22
January 8	4.8	9

Source: Authors

station, Club 20-30 in Ciudad Juárez, are not reported here because of the limited number of samples available. Appendix Figure 1 (page 305) presents these locations and a regional map. Duplicate samplers are sited at Tillman (Tillman A and B) and Tecnológico (Tecnológico 1 and 2); these collocated samplers replicated analytic results. The sites had been selected previously using criteria under the 1987 PM_{10} regulation (EPA 1987).

The four outermost sites (Northeast, Ivanhoe, Zenco, and Tillman) enclose or define a roughly rhomboidal area of approximately 250 km^2. Appendix Figure 1 (page 305) indicates that the two western sides of the rhomboid abut, respectively, the Franklin Mountains in Texas and the Sierra de Juárez in Chihuahua.

Instrumental Analysis Procedures

For microwave extraction, the authors followed the protocols of U.S. Environmental Protection Agency (EPA) Method 3051, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils* (EPA 1994). Extractions were performed in a CEM MDS-2000 microwave unit with sealed Teflon reaction vessels. For quality control, in each carousel of 12 reaction vessels the authors included a laboratory-fortified blank and a laboratory-fortified sample (matrix blank) with U.S. National Institute of Standards and Technology (NIST)-traceable spikes.

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis was performed on the filter extracts. The ICP method of analysis offers the advantage of high sensitivity and multi-element (up to 65 cations) quantification; however, it consumes the filter sample. For ICP-MS analyses, a Hewlett Packard HP 4500 instrument was used, following appropriate protocols in two EPA methods: *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry* and *Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS).* The first of these is Method 200.8 and the second is a preliminary draft method, EPA/625/R-96/010a (EPA 1991, 1997). Interferences from polyatomic ions from gas, air, reagents, and sample matrices were corrected using appropriate protocols (EPA 1991, 1997). Samples were analyzed for 65 elements, of which some 30 elements typically were present at quantifiable levels. All results presented herein fell within the relevant EPA guidelines. Additional analytic details are found in Espino (2000).

Results and Discussion

The authors focused their attention on four elements of particular interest in the Paso del Norte airshed: copper, lead, arsenic, and chromium. There are no significant natural sources of these elements beyond the typical crustal (rock) background in the region; thus they represent chiefly anthropogenic input. The selection of four elements from 30 is based on concerns about their toxicity and on simplicity of presentation.

Geographic Patterns
Examination of Tables 2, 3, 4, and 5 indicates that the concentrations of the elements correlate across stations on each sampled day. There are days with high values across the map and other days with low values. This reflects a degree of interconnectedness of the airshed in terms of meteorological conditions and production of pollutants.

Table 2. Seasonal (Spring, Summer, Fall, Winter) Concentrations (in Nanograms per Cubic Meter [ng/m^3]) of Copper for 1994, 1995, and 1996 at Sampling Stations in the El Paso-Ciudad Juárez Area

Copper (ng/m^3)	1994				1995				1996			
	S	S	F	W	S	S	F	W	S	S	F	W
Tillman A	24	30	51	230	28	25	150	62	36	58	420	320
Tillman B	20	38	55	220	28	27	184	64	31	91	460	360
Riverside	12	16	50	199	12	20	46	20	20	42	108	140
Ivanhoe	19	37	29	nd	10	30	85	19	17	31	141	121
Northeast	21	34	71	116	30	44	60	59	31	47	49	114
Tecnológico 1	40	65	99	780	45	31	143	nd	69	nd	125	156
Tecnológico 2	28	103	118	420	120	31	133	47	67	nd	66	180
Pestalozzi	11	84	79	156	39	35	89	35	nd	96	174	163
Zenco	nd	30	nd	nd	nd	13	98	22	65	88	nd	128
Advance Transformer	50	38	89	210	66	29	55	41	41	116	210	96

Note: nd = no data
Source: Authors

Table 3. Seasonal (Spring, Summer, Fall, Winter) Concentrations (ng/m^3) of Lead for 1994, 1995, and 1996 at Sampling Stations in the El Paso-Ciudad Juárez Area

Lead (ng/m^3)	1994				1995				1996			
	S	S	F	W	S	S	F	W	S	S	F	W
Tillman A	8	17	29	85	10	5	50	29	6	6	75	98
Tillman B	12	9	26	78	7	4	47	27	6	6	122	103
Riverside	7	4	32	72	4	2	22	11	7	5	16	38
Ivanhoe	3	4	7	21	4	2	16	7	3	4	5	23
Northeast	4	7	8	28	4	3	13	10	4	3	5	17
Tecnológico 1	4	3	24	76	5	1	65	nd	27	nd	33	59
Tecnológico 2	4	6	26	76	6	1	73	8	23	nd	16	60
Pestalozzi	6	24	34	105	nd	4	71	22	nd	13	90	62
Zenco	nd	7	nd	nd	9	4	56	9	13	30	nd	71
Advance Transformer	26	3	125	185	51	7	115	34	22	7	133	71

Note: nd = no data
Source: Authors

Table 4. Seasonal (Spring, Summer, Fall, Winter) Concentrations (ng/m³) of Arsenic for 1994, 1995, and 1996 at Sampling Stations in the El Paso-Ciudad Juárez Area

Arsenic (ng/m³)	1994				1995				1996			
	S	S	F	W	S	S	F	W	S	S	F	W
Tillman A	2	1	2	46	2	1	18	10	2	3	39	66
Tillman B	2	1	1	42	3	1	18	9	1	3	39	69
Riverside	1	0	1	19	2	0	8	2	8	7	6	23
Ivanhoe	0	0	0	10	2	0	4	2	3	7	9	39
Northeast	1	0	1	15	3	0	4	6	2	6	13	20
Tecnológico 1	1	0	1	18	3	0	7	nd	2	nd	7	23
Tecnológico 2	1	1	1	19	2	0	7	2	2	nd	3	21
Pestalozzi	1	4	2	13	nd	0	14	3	nd	7	53	25
Zenco	nd	1	nd	nd	2	0	14	3	4	5	nd	16
Advance Transformer	3	1	3	42	5	0	7	3	4	3	40	11

Note: nd = no data
Source: Authors

Table 5. Seasonal (Spring, Summer, Fall, Winter) Concentrations (ng/m^3) of Chromium for 1994, 1995, and 1996 at Sampling Stations in the El Paso-Ciudad Juárez Area

Chromium (ng/m^3)	1994				1995				1996			
	S	S	F	W	S	S	F	W	S	S	F	W
Tillman A	2	4	6	5	3	3	5	11	4	2	13	11
Tillman B	2	3	3	5	4	4	6	7	3	2	10	13
Riverside	2	4	3	6	3	3	4	6	5	2	6	4
Ivanhoe	3	5	3	0	4	3	3	6	3	1	3	2
Northeast	6	5	2	2	4	3	2	8	4	2	2	2
Tecnológico 1	3	2	11	4	4	1	6	nd	3	nd	5	8
Tecnológico 2	4	2	11	4	5	1	6	11	2	nd	2	5
Pestalozzi	7	4	15	5	nd	1	10	3	nd	4	13	6
Zenco	nd	3	nd	nd	5	1	7	7	3	6	nd	6
Advance Transformer	6	3	19	6	5	1	5	8	5	3	8	6

Note: nd = no data
Source: Authors

Interconnectedness notwithstanding, outlying stations—those most distant from the industrial districts and other known or expected pollutant sources in both El Paso and Ciudad Juárez—consistently show the lowest concentrations. This obviously reflects both the greater production of pollutants in the core urban areas and the limited degree of mixing in the airshed on these generally calm-wind days. For example, the Northeast station in El Paso records higher quality air (for these four elements in PM), resulting from low-density residential land-use, its distance from major pollutant sources, and the open land that surrounds this neighborhood on three sides.

In contrast, the stations in the urban core—Tillman in El Paso and Advanced Transformer, Tecnológico, and Pestalozzi in Ciudad Juárez—typically show the highest values. The northern part of Ciudad Juárez is the site of many maquiladoras and other local industries. Although environmental regulations are similar, enforcement is often difficult in Mexico when compared to the United States. The large American Smelting and Refining Company (Asarco) copper-ore smelter is located less than five kilometers northwest of the Tillman station in downtown El Paso. This operation apparently was a significant, but not dominant, point source of metal and semi-metal particulates in the past. The Asarco smelter was shut down in February 1999 after more than a century of operation; no plans or date for reopening had been announced as of March 2004.

Seasonal Patterns

Tables 2, 3, 4, and 5 also demonstrate the seasonal variation in particulate pollution. Fall and winter levels of copper, lead, arsenic, and chromium are considerably higher than spring and summer values—often by more than an order of magnitude at individual stations. This effect is seen most dramatically in fall and winter of 1995 and 1996 for all four elements.

With one exception, there is no evidence of significant seasonal changes in pollutant releases in the region. The burning of nonstandard materials in fireplaces and stoves for residential heating does occur in Ciudad Juárez during the colder months of the year. This practice is unusual in El Paso. Burning such materials as tires and trash may release metals to the air and contribute to pollutant levels, mainly in or contiguous to Ciudad Juárez.

Discussion

Retarded vertical circulation in the Paso del Norte airshed is believed to be the major cause of the increased levels of anthropogenic pollutants—i.e., the copper, lead, arsenic, and chromium—in fall and winter. Atmospheric inversions are common at that time of year, with rapid radiative cooling at ground level at night due to elevation and the typical lack of cloud cover. Occasionally these inversions last several days, with consequent trapping of pollutants near ground level and significant deterioration of air quality.

It has long been realized that the Paso del Norte airshed has a high loading of natural mineral material in its ambient PM (Dattner 1994; Einfeld and Church 1995). The extremely dry climate, often windy weather, sparsity of vegetation, and prevalence of unpaved streets and roads, particularly in Ciudad Juárez, combine to release natural PM into the local atmosphere. These processes are augmented by production and escape of mineral PM from quarry operations within the municipal limits of both cities. These geologic dusts are not significant contributors of the four metals documented herein.

There are no current metal-ore mining operations in the region and no extensive mining spoil piles to act as a source of the copper, lead, arsenic, and chromium observed. The local geologic section consists chiefly of Paleozoic and Mesozoic sediments, many of which are carbonates, and unconsolidated Tertiary and Quaternary sediments (Hawley 1978). The relatively minor exposures of igneous and metamorphic rocks also are not significant sources of those metals.

Obvious industrial sources of metals in the airshed include a copper-ore smelter and light industry in El Paso. Ciudad Juárez hosts a large number (several hundred) of maquiladoras, various industries, and small, essentially unregulated operations such as brick kilns (these often burn tires, pallets, and sawdust as fuel).

Conclusions

Metals concentrations (copper, lead, arsenic, and chromium) are highest in the fall and winter seasons, apparently due to retarded vertical circulation associated with inversions. Fall and winter levels may be an order of magnitude higher than spring and summer levels. Geographically, metal concentrations in the urban core of El Paso-Ciudad Juárez often exceed those recorded at distal stations by an order of magnitude or more. Smelter operations in El Paso appear to have made a significant, but not dominant, contribution to metals in PM in the airshed. Industrialization and population growth combined with poverty are contributing to emissions in Ciudad Juárez. Continuing international cooperation is required to monitor, assess, and regulate anthropogenic sources of metals in the air shared by El Paso and Ciudad Juárez.

Reduction in Levels of Toxic Elements in Particulate Matter in the El Paso-Ciudad Juárez Airshed Over the Past Quarter-Century[2]

Introduction

Archived PM air filters provide contemporary and future researchers an opportunity to document secular changes in air quality throughout the collection period represented in a given filter library. In El Paso, the EPCCHED and its predecessor organizations have maintained an exceptional archive with an extensive collection of filters dating back to the late 1970s. Of particular interest to air quality in this period are the implementation of restrictions on leaded gasoline in both the United States and Mexico, significant alterations at the Asarco plant in El Paso, and a changing regulatory and enforcement climate.

The earliest year for which filters representing broad areal and temporal coverage are available in the EPCCHED collection is 1977. This section presents analyses of filters for selected elements (chromium, copper, arsenic, and lead) for samples from 1977, 1980, 1987, 1994, and 2001. Although the data set is sparse, the overall trend toward cleaner air is unmistakable.

In cooperation with EPCCHED, a group at the University of Texas at El Paso (UTEP) is currently engaged in a large-scale project to document changes in toxic elements in PM at five-year intervals, starting in 1977. That research involves hundreds of samples from multiple stations and sampling periods throughout each year, and should provide a definitive record of change through time.

Materials and Methods

Samples and Analysis

Filters from the EPCCHED archives representing days with low wind velocities were selected for examination. Samples were from different available sites in El Paso and Ciudad Juárez; these had been collected on a single day in each of the summers of 1977, 1980, and

1994, the spring of 1987, and the winter of 1994. The 1994 samples are also reported in the section titled "Seasonal and Spatial Variation of Metals in Airborne Particulate Matter in the El Paso-Ciudad Juárez Airshed."

The 2001 samples were collected by UTEP researchers using dichot samplers at various sites on the UTEP campus. After analysis, the compositions of the separated $PM_{2.5}$ fine and PM_{10} coarse components were totaled. Stations at five sites were operated continuously from February 19, 2001, through March 23, 2001. Sampling times ranged from three days to seven days, yielding six filters at each site. There was no evidence that loading beyond the usual 24 hours adversely affected air flow rates to a degree that compromised the validity of the elemental data for the purposes of this study.

All samples underwent microwave-assisted acid digestion, followed by multi-element analysis by ICP-MS. These procedures are described in the section titled "Seasonal and Spatial Variation of Metals in Airborne Particulate Matter in the El Paso-Ciudad Juárez Airshed."

Results and Discussion

Air Sample Analyses

Concentrations of chromium, copper, arsenic, and lead in air filters from respective years are presented in Table 6. Data for winter 1994 are included for comparison inasmuch as this season typically yields higher values for pollutants (see the section titled "Seasonal and Spatial Variation of Metals in Airborne Particulate Matter in the El Paso-Ciudad Juárez Airshed"). Additional data for 1977 from Herbert, Candelaria, and Applegate are presented to validate the present results with those generated at a time closer to the collection of the samples. The Herbert, Candelaria, and Applegate study was presented at a symposium held in November 1979. These data are based on quarterly averages of typically 15 samples at each site; the three-site quarterly averages were averaged in turn. The UTEP data for 2001 are part of an unpublished study of air quality on campus and are included to represent more recent conditions.

Table 6. Average Particulate Composition in Nanograms per Cubic Meter of Air

Sampling Season	Number of Sites	Location of Sites	Chromium	Cooper	Arsenic	Lead
Summer 1977	5	El Paso, Ciudad Juárez	19	680	15	850
Summer 1977*	3	El Paso	nd	nd	10	500
Winter 1977*	3	El Paso	nd	nd	45	1250
Summer 1980	15	El Paso, Ciudad Juárez	4	170	15	270
Spring 1987	3	El Paso, Ciudad Juárez	16	176	24	211
Summer 1994	9	El Paso, Ciudad Juárez	4	49	1	9
Winter 1994	8	El Paso, Ciudad Juárez	4	300	23	81
Spring 2001	6	UTEP	14	52	5	23

Note: nd = no data
Source: *Data derived from Herbert, Candelaria, and Applegate (No Date); authors

Limitations of the Data

The data in Table 6 are not comprehensive nor definitive conditions during a given season or year in the El Paso-Ciudad Juárez airshed. In some cases, the number of sites averaged is small; in others, data for a single day can have only limited significance. There are also differences in the types of samplers used for collection of the particulates. Nonetheless, the overall large and consistent differences between the 1977 through 1987 data and the 1994 through 2001 results show an unmistakable trend toward better air quality.

Lead Reduction

Table 6 reveals significant changes in the levels of toxic elements in the El Paso-Ciudad Juárez airshed over the last quarter century. The data for lead are the most dramatic, with a decrease between one and two orders of magnitude. Much of this decrease is likely attributable to two transitions during that period—the phase-out of leaded gasoline and changes at the Asarco smelter.

In 1970, amendments to the 1963 Clean Air Act addressed the issue of leaded gasoline, the gradual phase-out of which was initiated in 1973. Although lead at other-than-trace levels was not eliminated officially in motor-vehicle fuel until the end of 1995, the use of leaded gasoline in the U.S. vehicle fleet was largely over at that time. By 1980, lead used in gasoline had dropped to half the 1976 levels, and in 1982 the U.S. Environmental Protection Agency (EPA) stepped up its campaign to decrease lead in gasoline. The decrease in ambient lead that accompanied this change throughout the United States has been documented in numerous studies (Lin-Fu 1992; Warren 2000). The official end of leaded gasoline in Mexico came in 1998.

During the study period, a number of changes in the Asarco smelting operation occurred. These included installation of an ore unloading and handling facility in 1978, installation of a sinter plant in 1979, shut down of the zinc plant in 1982, suspension of the lead plant operations in 1985, installation of continuous top-feed oxygen process technology in 1993, and placing the plant on care and maintenance status in 1999 (Asarco 2004).

Most of the dramatic decreases in airborne lead during this period undoubtedly can be attributed to these changes in leaded fuel consumption and in the smelter's fugitive dust and stack emissions. Currently, there do not appear to be any data that can apportion the reduction between these two sources. Additional contributing factors in reducing the El Paso-Ciudad Juárez burden of airborne lead may include mandated phase-outs of lead in such products as paint and solder.

Changes in Copper, Arsenic, and Chromium

Among these elements, copper and arsenic decrease, whereas a trend for chromium is unresolved. The drop in copper probably can be attributed to both the changes at Asarco and its closing. The levels of arsenic in the recent spring and summer data are lower than those of the corresponding seasons in the early years in Table 6; the same is true of the more limited winter data. Arsenic is common in sulfide ores and its release is often associated with smelting operations of the El Paso Asarco type. Other sources of airborne arsenic include open burning of arsenic-treated lumber, various industrial operations, and, in the past, fugitive dusts laden with arsenic from agricultural chemicals.

The origin and significance of the minor amounts of chromium in local air are uncertain. Although chromium may be present in some of the ores that Asarco processed, high chromium concentrations typically are associated with minerals in unrelated rare ore deposits in ultramafic rocks. Chromium is a common industrial metal and a significant component of stainless steels and certain pigments. Its presence in the air is likely due to a variety of urban and industrial sources. The values encountered in the UTEP study may reflect the location of the campus, which is bordered by an interstate highway (I-10) and an active railroad line to the west, and a busy commercial state highway to the east (Mesa Street). UTEP also hosts thousands of vehicles on its parking lots daily. Thus, the values for chromium listed in 1994, which are based on a broad areal network of sampling stations, may better summarize current levels of chromium in the El Paso-Ciudad Juárez airshed.

Significance

An overall decrease in the concentrations of three (lead, arsenic, and copper) of four toxic elements in the air is indicated by this limited historical study. The data suggest that none of the current levels in the airshed represents a regulatory violation or a significant known threat to public health. Such was not the case a quarter-century ago.

Toxic Metals in El Paso Soils: Introduction[3]

The two following sections on concentrations of toxic metals and semi-metals in El Paso soils are included because of the often close association between the elemental contaminants encountered in soil and air particulates. Airborne deposition links soil composition to that of the PM; soil entrainment by wind drives the reverse transfer. Such exchanges may comprise natural and/or anthropogenic particles, and these in turn may be innocuous or toxic. Soil data can complement air studies by serving as a proxy network of sampling sites that record and integrate, albeit imperfectly, air conditions over years and decades.

In the El Paso region, strong winds, a desert climate, and sparse vegetative cover ensure the presence of a significant geologic component in the local air particulates (as discussed in Chapter I and Chapter III). Likewise, dusts and particles produced by local commerce and industry may be subject to cycles of injection or entrainment, deposition, and re-entrainment because of the Chihuahuan desert climate.

Significant local anthropogenic sources, discussed in Chapter I, include ore smelters, brick kilns, open burning, unpaved streets, and unwatered quarry and earth-moving operations. Smelter emissions have received particular attention because of the known toxicity of such elements as arsenic, lead, and cadmium and their compounds. These can be released as stack emissions or as dusts and particulates in ground operations involving crushing, processing, transport, and loading of raw ore and smelter byproducts.

The section titled "Levels of Toxic Metals in El Paso Soils Proximal to Three Potential Industrial Point Sources," presents the results of a study completed in 1993 that was designed to document levels of toxic metals in soil proximal to then-current or former smelting and refining operations. As such, the sampling strategy was non-random geographically, emphasizing areas adjacent to those industrial sites. This section also provides a concise history of smelting and refining in El Paso.

The section titled "Lead in El Paso Soil," presents a uniquely detailed map of lead in El Paso soil. This contemporary study employed a randomized sampling strategy, based on population density, to choose 500 city blocks for soil testing. The research team is producing a similar map for Ciudad Juárez.

Recently, El Paso soils have been in the news because of an ongoing EPA investigation of arsenic and lead levels in soils proximal to the Asarco smelter. Topsoil removal from selected residential yards in nearby neighborhoods was underway in 2003 and 2004.

Levels of Toxic Metals in El Paso Soils Proximal to Three Potential Industrial Point Sources[4]

Introduction

At least three metal smelters and one metal refinery have been located within what is now the City of El Paso. All three smelters were established and operating around the start of the 20th century, long before any environmental controls on atmospheric emissions were implemented or even considered necessary. The purpose of this study was to collect and analyze soil samples from areas near these sites to quantify levels of metals contamination. Sites of special interest in this study are the Asarco smelter, the Memorial Park area where the Federal smelter was located, and the Phelps Dodge refinery area.

The El Paso Smelter, owned by Asarco, was constructed at its current location in 1887. Lead, copper, and zinc were extracted from ores at the smelter (Lee 1950). Two additional smelters were located in El Paso in the past. The International smelter was located at the present site of Guillen School (formerly Bowie High School) at Sixth Street and Cotton Avenue in central El Paso (Lee 1950) and was operated sporadically from 1888 until 1894. It was not a part of this study. The Federal smelter was located off Gold Street near what is now Memorial Park. The Federal smelter began smelting copper in 1901 and after four years of financial difficulties was closed due to bankruptcy in 1904. The property changed hands several times, but the smelter was never re-opened and was dismantled in 1907 (Rand 1977). The City of El Paso acquired the property and in 1921 planted several thousand trees and shrubs on what was to become Memorial Park (Stockwell 1926). The Nichols Copper Company constructed and began operating its El Paso Refinery in the late 1920s (Corwin and Harloff 1930). The refinery, currently owned by the Phelps Dodge Corporation, receives anodes of copper and electrolytically removes the impurities; the refined metals are then cast into bars (Bailey 1983).

Previous Studies

Studies of the effects of industrial pollution on the El Paso area have been performed since the early 1950s (Schatzman 1977). The studies have included air monitoring by local, state, and federal air pollution control agencies, blood lead level testing of residents, and soil and dust testing for metals concentrations.

The El Paso City County Health Unit performed a comprehensive study in the early 1970s that included sampling of ambient air, soil, household dust, food and water, pottery, and human blood (Rosenblum, Shoults, and Candelaria 1975). In conjunction with that study, the Centers for Disease Control collected paint samples for lead analysis (Landrigan, et al. 1975). Abnormally high lead levels were found in the blood of children 1 to 19 years of age who lived within one mile (1.6 km) of the Asarco smelter. The geographic distribution of high blood lead levels was similar to the ambient lead levels found in household dust. Although lead levels in soils near the smelter were found to be high (ranging from 1,000 parts per million [ppm] to 3,600 ppm), it was determined that lead in the soils contributed to adverse health effects to a lesser extent than lead in household dust. The study concluded that neither paint ingestion, the culinary use of glazed pottery with high lead content, nor vehicular lead could adequately account for the high blood lead levels encountered.

At this time, the Secretaría de Salud (Secretariat of Health) in Mexico performed a similar study in Ciudad Juárez in 1974 (Ordonez No date). Blood samples and glazed pottery were analyzed for lead while soils from gardens and courtyards and household dust were analyzed for lead, copper, zinc, and cadmium. Concentrations of these metals in dust and soils were found to be higher near the Asarco smelter and decreased with distance from the smelter. A positive correlation was found between blood lead levels and lead concentrations of soils and dust.

New Mexico followed suit with an investigation of lead in soils of various communities in southern New Mexico (Summers 1972). Soil samples collected from Anthony, Anapra, and Meadow Vista exhibited lead concentrations from below instrument detection limits to 220 ppm (or milligrams per kilogram [mg/kg]).

Miller (1972) documented lead levels of soils of the Rio Grande Flood Plain in the "Upper Valley" and "Lower Valley" of El Paso. The study found lead contents of the soils ranging from 0.4 ppm to 35.0 ppm. No correlation was found between lead content and either vehicular traffic or soil type. Relationships were noted between lead content and distances from five potential point sources of lead contamination, which included Smeltertown, the junction of Alameda Avenue and Paisano Drive (Highways 20-85 and 180-62), the Standard Oil and Texaco refineries, Fort Bliss, and the El Paso International Airport.

Schatzman (1977) detailed stationary air pollution in El Paso from 1951 to 1975 and observed that political decisions made about air pollution in El Paso appeared more often to favor economics than potential impacts on human health and the environment.

In 1989, the Texas Air Control Board performed a heavy metals analysis of soils from various sites in Texas. Concentrations ranging from below instrument detection limits to 1,100 ppm were found in soil samples from El Paso. The concentrations were highest near the Asarco smelter and declined rapidly away from the smelter. The levels encountered were judged to pose no threat to human health because the areas with highest concentrations were not considered to be places "frequented by the general public" (Dydek 1990).

EPA in 2001 initiated an investigation of arsenic and lead levels in soils proximal to the Asarco smelter. The project is still underway and topsoil is being removed from selected residential yards in nearby neighborhoods. Although EPA has released copies of several reports from their subcontractors, a full report authored by EPA is not yet available.

Materials and Methods

Field Sampling Procedures

Sample collection locations include the area around the Asarco smelter on the west side of El Paso, Memorial Park in central El Paso (where the Federal smelter was located), and the Phelps Dodge Copper Refinery on the east side of El Paso. Additional sample collection points were located in outlying areas north, northeast, and east of El Paso. Full descriptions of the sampling locations and procedures are available in Barnes (1993).

Soil samples were collected from apparently undisturbed locations, where possible, using protocols established by EPA. Samples from the surface (0.0 centimeters [cm] to 2.5 cm) and from various depths ranging from 10 cm to 60 cm below the surface were collected from selected sample locations in an effort to document downward migration of metals.

After collection, the samples were refrigerated for approximately three weeks until they were carried through the sample preparation processes, in accordance with EPA protocols (EPA 1986).

Sample Preparation

EPA Method 3050, *Acid Digestion of Sediments, Sludges and Soils,* was followed for the initial digestion of the soil samples (EPA 1986). A set of selected soil samples that exhibited high total metals concentrations was prepared for analysis using the Toxicity Characteristic Leaching Procedure (TCLP) (Code of Federal Regulations 1991). At the time of this study, the TCLP procedure was used to determine whether a substance could be classified as a "hazardous waste." EPA considers the total metals analysis a preliminary test. If a sample exhibits high total metals concentrations, EPA then requires TCLP for determination of the leachability of a contaminant. TCLP was designed by EPA to approximate the rainfall conditions to which a substance would be exposed in the natural environment. Details of the total digestion and TCLP procedures are provided in Barnes (1993).

Instrumental Analysis

A Beckman SpectraSpan VI Direct Current Plasma (DCP) Atomic Emission Spectrometer was used for analysis of the digestates prepared from the samples, following EPA Method 6010, *Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP).* Method 6010 was chosen because EPA has not provided a method specifically for use with DCP, but the two spectroscopic instruments (DCP and ICP) are equivalent, except for the source of the plasma. Metals examined were arsenic, barium, cadmium, calcium, chromium, copper, lead, nickel, selenium, and zinc. Wavelengths and instrument detection limits for each of the elements studied are provided in Table 7. The analytical and quality assurance/quality control (QA/QC) procedures followed in the study are presented in full in Barnes (1993).

Results and Discussion

Soil Sample Analyses

Concentrations of lead, copper, arsenic, and cadmium in surface samples from the Asarco area are presented in Figure 1. Table 8 and Figure 2 give the ranges of each metal in nine geographic subdivisions of El Paso. Additional maps and complete data sets (for Memorial Park and Phelps Dodge area maps, subsurface samples, and TCLP values) are found in Barnes (1993).

General Findings

The highest levels of lead, copper, arsenic, and cadmium are centered in the downtown region and on the west side of the Franklin Mountains (Figure 1, Table 8, and Figure 2). The north-south trending Franklin Mountains bisect the city and the commercial downtown district is at the southern tip of the Franklins, where the U.S.-Mexican border bulges southward. Low concentrations characterize the less-populated peripheral regions to the north, east, and southeast of the central business district.

The map of the contiguous portions of the west side and downtown areas, Figure 1, reveals the highest metals concentrations encountered in this study. These elevated values appear to be associated with the location of the Asarco smelter.

Some elevated metals values are encountered at Memorial Park, the site of the Federal smelter a century ago. Memorial Park lies along the railroad tracks between downtown and Fort Bliss. Note that the upper metal levels here are approximately one-tenth of those encountered near the Asarco smelter (Table 8).

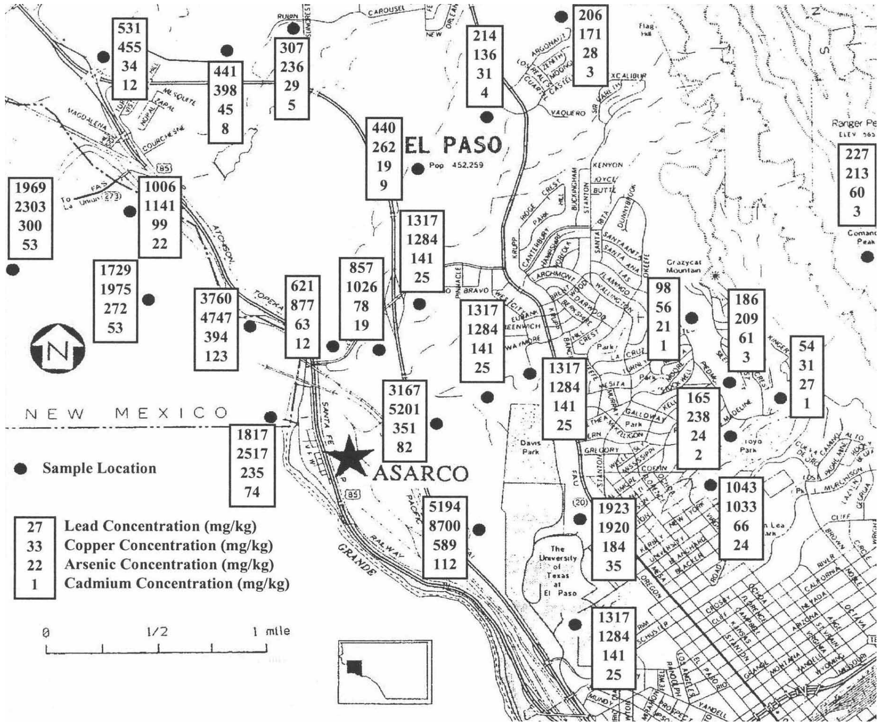
Low metal values characterize samples taken near the Phelps Dodge refinery (Table 8). These metal concentrations correspond to those encountered in the peripheral areas of El Paso.

Table 7. Wavelengths and Instrument Detection Limits (IDL) for Each Metal Quantified

Metal	Wavelength (nm)	EPA-Suggested Wavelength	Linear Range (ppm)	Total Metals IDL (mg/L)	Total Metals IDL (mg/kg)	TCLP Metals IDL (mg/L)	TCLP Metals IDL (mg/kg)
Arsenic	193.696	yes	0.8–100	0.3	20	0.2	4
Barium	455.403	yes	0.2–1,000	0.06	4	0.06	1.2
Cadmium	288.802	no	0.05–10	0.02	1.3	0.06	1.2
Calcium	318.128	no	100–5,000	22	1500	NA	NA
Chromium	267.716	yes	0.1–1,000	0.1	7	0.03	0.6
Copper	213.598	no	0.3–1,000	0.2	13	NA	NA
Lead	220.353	yes	2–1,000	0.8	50	0.9	18
Nickel	243.789	no	0.9–1,000	1.3	90	NA	NA
Selenium	196.026	yes	1–1,000	0.4	27	0.2	4
Zinc	202.548	no	0.06–600	0.003	0.2	NA	NA

Note: NA = Not analyzed
Source:

Figure 1. Sample Concentrations—Asarco Area



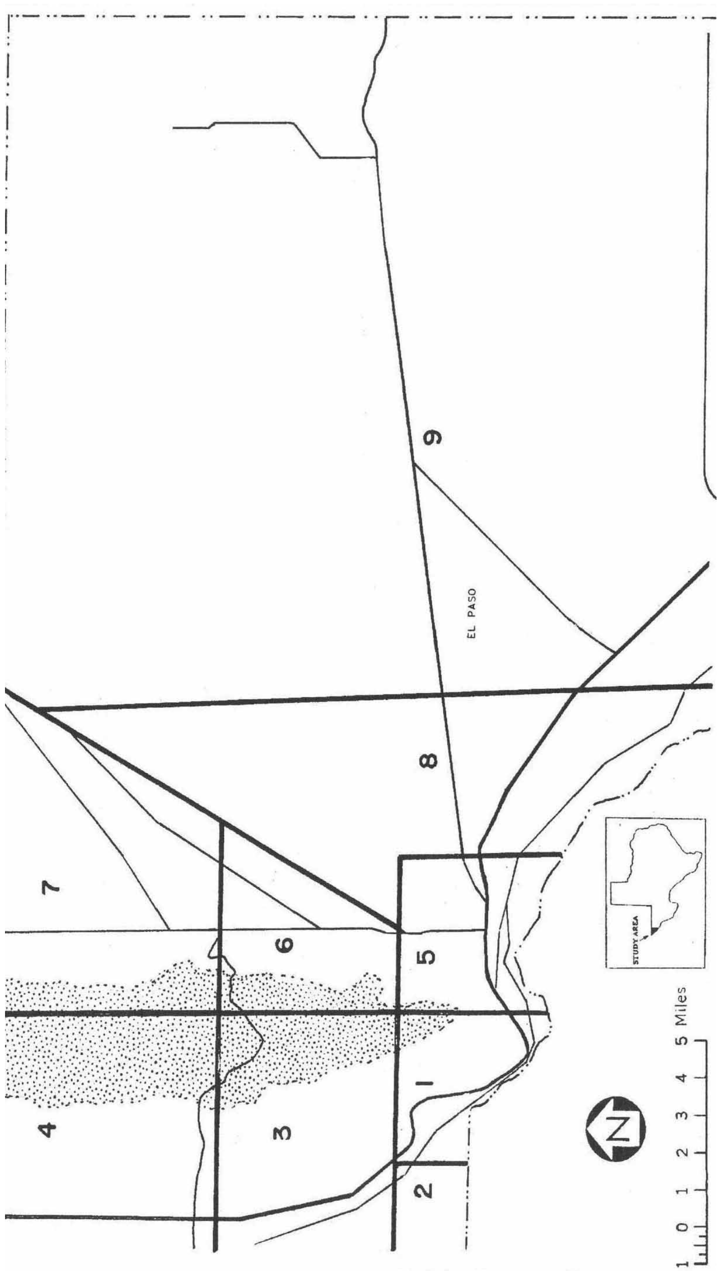
Source: Authors

Table 8. Ranges of Total Metal Concentrations in Surface Samples

Area of El Paso	# of Samples	Arsenic	Barium	Cadmium	Chromium	Copper	Lead	Nickel	Selenium	Zinc
Asarco Area (1)	32	<IDL – 589	34 – 319	<IDL – 123	<IDL – 22	30 – 8,700	50 – 5,190	<IDL – 140	<IDL – 58	46 – 3,398
Far West (2)	5	<IDL – 23	<IDL – 187	<IDL – 14	<IDL – 15	<IDL – 100	<IDL – 110	ALL <IDL	<IDL – 34	38 – 87
West Side (3)	11	<IDL – 43	<IDL – 278	<IDL – 19	<IDL – 18	<IDL – 180	60 – 290	<IDL – 130	<IDL – 41	44 – 169
Far Northwest (4)	10	<IDL – 48	<IDL – 127	<IDL – 2.9	<IDL – 18	<IDL – 90	<IDL – 270	<IDL – 110	<IDL – 36	30 – 154
Memorial Park (5)	11	<IDL – 40	<IDL – 281	<IDL – 16	<IDL – 12	30 – 340	<IDL – 390	<IDL – 120	<IDL – 39	39 – 210
Northeast (6)	3	26 – 35	106 – 151	<IDL – 1.3	11 – 18	30 – 50	<IDL – 100	<IDL – 100	<IDL – 16	49 – 77
Far Northeast (7)	10	<IDL – 40	<IDL – 81	<IDL – 5.8	<IDL – 16	<IDL – 50	<IDL – 90	<IDL – 120	<IDL – 34	21 – 115
Phelps Dodge (8)	2	ALL <IDL	ALL <IDL	ALL <IDL	ALL <IDL	20 – 100	<IDL – 80	ALL <IDL	ALL <IDL	20 – 153
East Side (9)	10	<IDL – 66	<IDL – 23	<IDL – 9	ALL <IDL	<IDL – 120	<IDL – 70	<IDL – 110	<IDL – 36	13 – 53

Notes: All values in mg metal/kg soil; numbers in parentheses correspond to the areas on Figure 2; <IDL = less than Instrument Detection Limit.
Source: Authors

Figure 2. Geographic Areas Used in Statistical Analysis



Source: Authors

Overall, the ranges observed for specific metals are similar to those documented in previous studies of the area using comparable sample preparation and analytical techniques (Dydek 1990; Ordonez No date; Shoults 1972; Summers 1972).

Significance

Concentrations of the metals associated with the smelting process—arsenic, cadmium, copper, lead, and zinc (not shown)—were highest in the area surrounding the Asarco smelter and generally decreased with distance from it (Figure 1). Concentrations of arsenic, lead, and copper were higher, typically by several fold, in the surface samples than in the subsurface samples (Barnes 1993). This suggests an above-ground source rather than derivation from the underlying bedrock. The levels of toxic metals and their geographic distribution suggest origination in smelter operations.

The lower levels, by a factor of 10, of these same metals in Memorial Park are consistent with the short-term operation of the Federal smelter on that site a century ago. The low levels of metals proximal to the Phelps Dodge refinery presumably reflect the very different nature of this operation, relative to ore smelting.

Using all of the total metals data, statistically significant (99% confidence level) inter-element correlations were found between arsenic, cadmium, copper, lead, and zinc (Barnes 1993). Generally, correlation coefficients between the metals increased when the data from the sub-surface samples were removed from the analysis, and when the data were limited to the West Side (areas 1, 2, and 3 on Figure 2) or the Asarco area (area 1). These correlations among metals commonly associated with lead and copper smelting operations again underscore the probable source of these metals in the areas proximal to Asarco.

Lead in El Paso Soil[5]

Introduction

In 2001, the National Institute of Environmental Health Sciences funded a five-year study by researchers at the University of Texas at El Paso and the Texas Tech University Health Sciences Center of lead exposure risks in El Paso, Ciudad Juárez, and the surrounding communities. As part of this project, the researchers are conducting a comprehensive survey of lead levels in soil throughout this area. The aim is to produce a uniquely detailed map of lead for the region.

Scope and Strategy of the Research Project

A total of 1,000 municipal blocks, apportioned equally to both sides of the border, are being studied. Superficial soil in the public area in front of each house or structure around the circumference of the block is being sampled. This typically involves collecting 10 samples per block. Many structures did not have soil present, but instead were surrounded by desert landscaping (crushed rock) or concrete. To ease the burden of analyzing the resultant thousands of samples for lead, two samples are taken from each site. The first is archived and the second is combined with a sample of identical volume from every other parcel on the block. The second procedure produces a composite sample, the analysis of which represents the overall or average conditions of the entire block. In this approach, analysis of the 1,000 composite samples provides a map of lead values that can be considered "smoothed" at the block level. Construction of a map with values for thousands of individual houses would pose graphical challenges, and, in fact, would be too detailed for meaningful regional analysis. The maps of lead in soil in the El Paso area presented herein comprise the data from the 339 blocks that have been sampled and analyzed to date.

The archived samples are being used for both quality control and investigational purposes. For every 50th block, the individual samples are analyzed, their values averaged, and this average then compared to the value obtained from the composite sample. The expectation, of course, is that these values should be similar, and this has been the case thus far. In addition, for selected blocks with high levels of lead, the individual samples are being analyzed. This will suggest whether the elevated levels represent a regional trend or whether the high composite value results from a single anomalous sample, such as one house with peeling lead-based paint.

For an examination of lead in El Paso soil focused on airborne contamination from three potential point sources, see the section "Levels of Toxic Metals in El Paso Soils Proximal to Three Potential Industrial Point Sources."

Materials and Methods

Sampling

El Paso County, excluding Fort Bliss, was divided into 50 area strata by combining adjacent census tracts (from the 126 tracts in the 2000 U.S. Census) such that each stratum contained 13,000 +/- 2,000 residents. Ten blocks, each with at least six households, were then selected at random from each stratum for sampling. This sampling strategy was designed to ensure that the distribution of sampled blocks was random with respect to population, rather than random with respect to geography, such as land area. As a result, the sampled blocks are often smaller and situated closer together in the more densely settled parts of the region. A geographic information system containing geographic, infrastructure, and census data was used to develop the sampling plan and, subsequently, to display the results of the lead analyses.

Field Sampling Procedures

One 50-milliliter (ml) plastic centrifuge tube was used as a scoop to remove loose soil, and then was capped. A second sample was taken with a 10-ml cup that was then emptied into a sealable plastic bag for the composite sample. Before the start of sampling, all containers, samplers, and other materials that could come in contact with the soil samples were analyzed for lead with an XRF instrument, and none contained more than nominal levels. Field assistants used a new pair of laboratory gloves for taking each sample to prevent cross-contamination.

Sample Preparation and Instrumental Analysis

The general procedures of EPA Method 6200 (EPA 1998) for field-portable XRF were followed for preparation of the samples for XRF analysis. These included homogenization of the sample, grinding, sieving, and sealing in a standard XRF sample holder.

Soil samples were analyzed with a Spectrace 9000 field-portable XRF unit equipped with three isotope excitation sources (55Fe, 109Cd, and 241Am), operated in the laboratory. Lead L-series XRF was excited with the 109Cd source. Analysis and quality assurance/quality control were performed in general accordance with the procedures of EPA Method 6200 (EPA 1998) for field-portable XRF. The typical detection limit for lead in a typical soil matrix with the instrument is 20 ppm. NIST Standard Reference Materials 2586 and 2587, Trace Elements in Soil Containing Lead from Paint, nominally 500 mg/kg and 3,000 mg/kg lead respectively, and an analytical-grade Teflon disc (nominally lead-free) were used as primary instrument calibration standards.

Because most soil analyses fell below 500 ppm, the researchers created three additional standards by gravimetric dilution of NIST 2586 (actual NIST certification of 432 ppm lead) with silica sand to 216 ppm, 108 ppm, and 54 ppm. The mean and reproducibility (one relative standard deviation) of 10 repeated measurements were 50 ppm (+/- 30%), 107 ppm (+/- 10%), 233 ppm (+/- 7%), and 414 ppm (+/- 5%) for the 54 ppm, 108 ppm, 216 ppm, and 432 ppm lead standards, respectively.

Results and Discussion

Soil Lead Concentrations

The location, shape, and dimensions (at scale) of the blocks sampled in El Paso are presented in Appendix Figure 3 (page 307). Concentrations of lead in the composite samples from these blocks are color-coded into four categories: blocks with less than 50 ppm lead are green, those with 50 ppm to 99 ppm lead are gray, those with 100 ppm to 150 ppm lead are orange, and blocks in excess of 150 ppm lead are red. The highest composite value encountered was 421 ppm, for a block near western downtown.

Findings and Interpretation

The lowest values of lead are encountered in the peripheral areas away from the urban core (Appendix Figure 3 [page 307], green blocks). Thus, the northeast, far east, southeast, and west (with a single anomalous block) sections of the city and surrounding areas have low soil lead levels, despite nearly explosive growth and development over the past two decades. In the newer neighborhoods, any soil brought in to replace the humus-poor desert soil has not been exposed to local conditions for very long. Low lead levels would be expected, assuming the imported soil itself was produced in a low-lead, rural environment. Nonetheless, some very old neighborhoods and blocks were sampled in these peripheral areas, and these also were below 50 ppm lead.

The observed low values of lead—less than 50 ppm—are consistent with the generally low population and commercial density of the neighborhoods in Appendix Figure 3 (page 307). These include rural and agricultural settings (parts of the so-called upper and lower valley of the Rio Grande), subdivisions (west and east sides), and separate communities (Horizon City) not contiguous with urban El Paso. For comparison, the average abundance of lead in the earth's crust is estimated to be approximately 15 ppm (Adriano 1986; Li 2000), and 10 ppm to 50 ppm lead is typical of soils in so-called "uncontaminated" settings (Davidson and Rabinowitz 1992).

Blocks with 50 ppm to 99 ppm lead, seen in gray in Appendix Figure 3 (page 307), plot in a general zone strikingly more proximal to the downtown and core central area of the city than the blocks with less than 50 ppm lead. Only a few blocks in that central area are represented on the 50 ppm to 99 ppm map.

Analytical confidence in samples in the 50 ppm range is limited because these are close to the instrumental detection limit (20 ppm lead) and relative standard deviations are high. Nonetheless, the geographic distribution of samples in Appendix Figure 3 (page 307) and its consistency with population density indicates that instrumental precision was sufficient to provide valid discrimination of sample groups even at levels below 100 ppm.

Elevated levels (100 ppm to 150 ppm, seen in orange in Appendix Figure 3 [page 307]) of lead concentrate in a broad swath from the west side of the Franklin Mountains (leftmost part of map), through the downtown business district, and eastward through central El Paso. The highest values, those in excess of 150 ppm and depicted in red, are concentrated in the downtown and central core district, with a noticeable outlier (apparently related to an automobile radiator repair shop) in the far northwest of the city.

The geographic pattern of elevated lead values obviously is not random. The elevated values in the area near the Asarco smelter have been attributed to operations at the plant for more than a century (see, for example, Landrigan, et al. 1975; Barnes 1993; current EPA press releases; García, et al. 2004). The high values in the downtown business and commercial district are consistent with general urban congestion; concentrated vehicular traffic, including Interstate Highway 10, during the leaded-gasoline era; traverse by a major railway system; and vintage construction, with the associated lead hazards, including paint. Elevated values headed east of downtown may reflect the confluence of the interstate, Montana Avenue (a state highway and major commercial district and conduit), extensive railroad yards, a concentration of marginal light industries and shops (such as auto repair), and older residences.

The proximity of the downtown and central districts to Asarco, and their downwind lie, confound the ability to distinguish the relative contributions of lead from the smelter point source and from the local areal sources. The present data do not resolve this issue.

Significance

The geographic distribution of lead in this extensive set of soil analysis is similar to the pattern of lead in PM in air filters from around the city collected in the mid-1990s (see the first two sections of this chapter). In the first section, the Tillman (downtown) station (see Appendix Figure 1 [page 305] for locations) was consistently the highest for lead, sometimes by an order of magnitude. The Northeast and Ivanhoe stations yielded the lowest values. The Riverside station (southeast), closer to downtown, showed values between those of downtown and northeast and east.

The similar spatial variation in lead levels in soil and air samples reflects the inevitable interplay between air deposition, local sources, and re-entrainment. Levels of metals in soil represent an important record of air quality, which complements that obtained from conventional air samplers. Soil analysis provides a proxy signal that integrates exposure at street level over years or decades. The method requires no deployment of filter collectors and can provide spatial resolution down to the level of the individual home.

Acknowledgements

This research was supported by the U.S. Environmental Protection Agency (EPA) through the Southwest Consortium for Environmental Research and Policy (SCERP). For the section titled "Levels of Toxic Metals in El Paso Soils Proximal to Three Potential Industrial Point Sources," the authors acknowledge the invaluable assistance provided by the Center for Environmental Resource Management of the University of Texas at El Paso, and in particular C. Wesley Leonard and Robert M. Currey. They also thank Jesus Reynoso and Rene Hernandez from the Air Quality Program of the El Paso City-County Health and Environmental District, which provided the air filters used in this research.

Support for the work presented in the section titled "Lead in El Paso Soil" was provided by a grant from the National Institute of Environmental Health Sciences, National Institutes of Health, grant number 1RO1 ES11367. The authors thank their community consortium, the Federacion Mexicana de Asociaciones Privadas (FEMAP) Foundation, and Adults and Youth United Development Association (AYUDA). Special thanks to the community health workers who performed the field sampling, to the city of El Paso, and to Dan Green for assistance setting up the GIS system.

Endnotes

[1] This section authored by T. T. Espino, N. E. Pingitore Jr., J. L. Gardea-Torresdey, and J. J. Reynoso.

[2] This section authored by N. E. Pingitore Jr., J. L. Gardea-Torresdey, T. T. Espino, J. J. Reynoso, W.-W. Li, R. M. Currey, and R. D. Moss.

[3] This section authored by N. E. Pingitore Jr.

[4] This section authored by B. E. Barnes, N. E. Pingitore Jr., and W. P. Mackay.

[5] This section authored by N. E. Pingitore Jr., J. W. Clague, M. A. Amaya, M. Delgado, J. L. Gardea-Torresdey, P. Juárez, J. Bader, J. C. Zevallos, and I. Herrera.

References

Adriano, D. C. 1986. *Trace Elements in the Terrestrial Environment.* New York: Springer.

American Smelting and Refining Company. 2004. "El Paso Plant." Cited 13 October 2004. http://www.asarco.com/elpasoj.html.

Bailey, G. L. 1983. "A History of Refining at the Phelps Dodge Plant in El Paso." Pages 449–454 in *Geology and Mineral Resources of North-Central Chihuahua, Guidebook for the 1983 Field Conference,* K. F. Clark and P. C. Goodell, eds. El Paso: El Paso Geological Society.

Barnes, B. E. 1993. "An Evaluation of Metals Concentrations in Surficial Soils, El Paso County, Texas." Master's thesis, Department of Geological Sciences, University of Texas at El Paso, El Paso, Texas.

Code of Federal Regulations. 1991. *Title 40, Protection of Environment.* Office of the Federal Register, National Archives and Records Administration. Washington, D.C.: U.S. Government Printing Office.

Corwin, F. R., and C. S. Harloff. 1930. "El Paso Refinery of the Nichols Copper Company." *Mining and Metallurgy* October.

Dattner, S. 1994. "El Paso/Juárez 1990 PM_{10} Receptor Modeling Feasibility Study." Austin, Tex: TNRCC.

Davidson, C. I., and M. Rabinowitz. 1992. "Lead in the Environment: From Sources to Human Receptors." Pages 65–86 in *Human Lead Exposure,* H. L. Needleman, ed. Boca Raton, Fla.: CRC Press.

Dydek, T. 1990. "Heavy Metals in Soils Project: Final Report." Memorandum to Doyle Pendleton, Director, Monitoring Program, Texas Air Control Board. Unpublished.

Einfeld, W., and H. W. Church. 1995. "Winter Season Air Pollution in El Paso-Ciudad Juárez." Report SAND95-0273 UC-603. Albuquerque, N.M.: Sandia National Laboratories.

Espino, T. 2000. "Use of Microwave Digestion and ICP-MS to Determine Elemental Composition of Air Particulates in El Paso/Juárez Airshed." Master's thesis, Department of Chemistry, University of Texas at El Paso, El Paso, Texas.

García, J. H., W.-W. Li, R. Arimoto, R. Okrasinski, J. Greenlee, J. Walton, C. Schloesslin, and S. Sage. 2004. "Characterization and Implications of Potential Fugitive Dust Sources in the Paso del Norte Region." *Science of the Total Environment* 325: 95–112.

Hawley, J. W. 1978. *Guidebook to the Rio Grande Rift in New Mexico and Colorado.* Circular 163. Socorro, N.M.: New Mexico Bureau of Mines and Mineral Resources.

Herbert, J. S., R. M. Candelaria, and H. Applegate. No date. "A Survey of Total Suspended Particulates and Heavy Metal Levels in the Ambient Air of El Paso, Texas, From 1972–1979." Pages 4–7 in *Air Quality Issues in the El Paso/Cd. Juárez Border Region* Occasional Papers #5, W. P. Gingerich, ed. El Paso: Center for Inter-American Studies.

Landrigan, P. J., S. H. Gehlbach, B. F. Rosenblum, J. M. Shoults, R. M. Candelaria, W. F. Barthel, J. A. Liddle, A. L. Smrek, N. W. Staehling, and J. F. Sanders. 1975. "Epidemic Lead Absorption Near an Ore Smelter." *The New England Journal of Medicine* 292(3): 123–129.

Lee, M. A. 1950. "A Historical Survey of the American Smelting and Refining Company in El Paso, 1887–1950." Master's Thesis, The University of Texas at El Paso, El Paso, Texas.

Li, Y.-H. 2000. *A Compendium of Geochemistry.* Princeton, N.J.: Princeton University Press.

Lin-Fu, J. S. 1992. "Modern History of Lead Poisoning: A Century of Discovery and Rediscovery." Pages 23–43 in *Human Lead Exposure,* H. L. Needleman, ed., Boca Raton, Fla.: CRC Press.

Miller, C. B. 1972. "Environmental Lead Analysis of Soils, Rio Grande Flood Plain, El Paso County, Texas." Master's thesis, University of Texas at El Paso, El Paso, Texas.

Ordonez, B. R. No date. "Community Smelter Study in Ciudad Juárez, Mexico." Unpublished.

Pearson, R., and R. Fitzgerald. 2001. "Application of a Wind Model for the El Paso-Juárez Airshed." *Journal of the Air & Waste Management Association* 51: 669–680.

Rand, P. 1977. "The Federal Smelter." *The El Paso Historical Society Password* XV (56): 109–115.

Rosenblum, B. F., J. M. Shoults, and R. Candelaria. 1975. "A Lead Health Hazard." Paper presented at the Annual Session of the Texas Medical Association, San Antonio, Texas.

Schatzman, C. G. 1977. "The Regulation of Stationary Air Pollution in El Paso, Texas, 1951–1975." Master's thesis, University of Texas at El Paso, El Paso, Texas.

Shoults, J. M. 1972. "Soil Samples for Lead." Unpublished memorandum to John Morrison, El Paso City-County Health Department.

Stockwell, W. E. 1926. "City Plan Committee Aids Development of Memorial Par." *The American City Magazine* January: 27–28.

Summers, B. 1972. "Lead Results in Soils from Doña Ana County." Memorandum to Caroline Wienke, New Mexico Environmental Improvement Agency. Unpublished.

U.S. Environmental Protection Agency. 1986. *Test Methods for Evaluating Solid Waste, Volume 1A: Laboratory Manual Physical/Chemical Methods (Third Edition).* Washington, D.C.: Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency. 1987. "PM_{10} SIP Development Guideline." Report No. EPS-450/2-86-001. http://www.epa.gov.

U.S. Environmental Protection Agency. 1991. *Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry.* http://www.epa.gov.

U.S. Environmental Protection Agency. 1992. *Determination of the Strong Acidity of Atmospheric Fine-Particles (<2.5 µm) Using Annular Denuder Technology.* Report no. EPA/600/R-93/037. http://www.epa.gov

U.S. Environmental Protection Agency. 1994. *Method 3051, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oil.* http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3051.pdf.

U.S. Environmental Protection Agency. 1997. *Preliminary Draft Method EPA/625/R-96/010a, Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry.* http://www.epa.gov.

U.S. Environmental Protection Agency. 1998. *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.* http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6200.pdf.

Warren, C. 2000. *Brush with Death: A Social History of Lead Poisoning.* Baltimore: John Hopkins Press.

VI

Receptor Modeling of Organic Particulate Matter Components: Preliminary Attribution and Apportionment of Local Source Contributions

H. L. C. Meuzelaar, J. S. Lighty, I. C. Jaramillo, S. A. Sheya, H. Zhang, S. Jeon, N. S. Arnold, and G. M. Mejía Velázquez

Abstract

Because strong correlations exist between urban particulate matter (PM) levels and mortality and morbidity rates, the potential health affects and economic costs of these PM emissions are substantial. Thus, a sustained, systematic effort toward the establishment of comprehensive PM source emission inventories and the development of reliable receptor-based PM source attribution and apportionment models for the Paso del Norte airshed are warranted. Advanced methods for continuous monitoring, collection, and characterization, as well as high-resolution wind direction and velocity measurements are needed to produce adequate data for comprehensive, basin-wide model development and validation. Lack of advanced capabilities and resources, particularly on the Mexican side of the

border, makes it difficult to investigate important PM emission, dispersion, and exposure phenomena. The lack of data also prevents calculation of PM exposure risks, which is especially important for susceptible pediatric and geriatric groups. Key information can be obtained through "scoping studies" of limited range and duration that have been designed to reveal some of the major underlying PM components, trends, and gradients through the use of new, advanced methodologies.

Four primary analytical techniques were used sequentially to volatilize, separate, identify, and deconvolute organic chemical components in ambient PM, namely thermal desorption (TD), gas chromatography (GC), mass spectrometry (MS), and multivariate data analysis (MDA), respectively. Essentially, all four techniques were combined into a single TD-GC/MS/MDA method.

Varimax-rotated principal component analysis (PCA) results for TD-GC/MS profiles of spatially and temporally resolved receptor samples collected in 1998 reveal major source attributions from automotive emissions plus urban dust, biomass combustion related to cooking and brick kilns, burning of agricultural and/or native vegetation, and biomass combustion related to trash and firewood. Quantitative PM source apportionment using chemical mass balance (CMB) and principal component regression (PCR) techniques on TD-GC/MS profiles from a set of 24 receptor samples obtained at two-hour intervals at the Texas Commission on Environmental Quality (TCEQ) Sodar site was able to account for 70% to 80% of the measured PM mass. By contrast, the attempted use of CMB and PCR techniques on a set of TD-GC/MS profiles from 12 different high-volume sampling sites produced relatively low model variances (in the 50% range), apparently due to a loss of volatile PM components during storage of the large quartz filters used.

Because of the substantial losses from these 1998 filter samples, it was decided to use a new set of receptor sample data collected in January 2001. Varimax-rotated PCA results for TD-GC/MS profiles of spatially resolved receptor samples collected in 2001 show strongly correlated behavior of polynuclear aromatic hydrocarbons (PNAHs) (factor 1), normal alkanes (factors 2 and 3), and fossil terpenoids (factor 4). Mexican receptor site samples tend to be dominated by small and large PNAHs (brick kiln), large alkanes (waste burning), alcohols, and ketones (firewood, biomass burning). By contrast, U.S. samples show automotive emissions (diesel trucks and autos with catalytic converters), trash (waste burning), and firewood combustion. Contributions of some medium-sized alkanes and polycyclic aromatic hydrocarbons (PAHs) (including retene), as well as heteroaromatic compounds (including phenalenone, anthracenedione, butoxyethoxyethanol, quinoline, and methylpyrrolidine) plus amyrin on factor 6, may provide valuable clues about the nature and composition of missing sources.

PM source apportionment of this suite of TD-GC/MS profiles of spatially resolved receptor samples by using CMB and PCR models in combination with a referenced source pattern library achieved model variances in the 70% to 80% range. This revealed that the dominant PM sources were related to automotive emissions plus brick kilns, cooking, trash, and biomass combustion processes, as well as aerosolized road dust.

Finally, PCA analysis of PCR residuals reveals a significant difference between U.S. and Mexican receptor sites. The results also reveal a split between PNAHs and larger PNAHs, suggestive of some type of overlooked combustion process. Moreover, a combination of fossil hopanoids (associated with engine lubricants or related petroleum products), dehydroabietic acid (often found to correlate with overall PM_{10} [particulate matter with an aerodynamic diameter of 10 micrometers or less] levels), and some common aliphatic compounds may well represent reaerosolized urban dust, whereas the high loadings of both aromatic nitrogen compounds and benzoic acid could point to some type industrial or agricultural combustion process.

Modelado Receptor de Componentes de Materia Orgánica Particulada: Atribución Preliminar e Identificación de Aportes en la Contribución de Fuentes Locales

H. L. C. Meuzelaar, J. S. Lighty, I. C. Jaramillo, S. A. Sheya, H. Zhang, S. Jeon, N. S. Arnold, y G. M. Mejía Velázquez

Resumen

A causa de que existen fuertes correlaciones entre niveles urbanos de materia particulada (PM), mortalidad y las tasas de morbilidad, los efectos potenciales de salud y costos económicos de estas emisiones son sustanciales. Por lo tanto, un esfuerzo sistemático sostenido, hacia el establecimiento de inventarios de fuentes de emisiones comprensibles de PM y el desarrollo de modelos confiables de identificación de fuentes de PM basados en receptores fidedignos y modelos de prorrateo para la cuenca de el Paso del Norte son garantizados. Métodos avanzados para el monitoreo continuo, el muestreo, y la caracterización, así como medidas de alta resolución de dirección y velocidad de viento son necesarios para producir datos adecuados para el desarrollo y validación de un modelo comprensivo que abarque toda la cuenca. La falta de capacidades avanzadas y recursos, particularmente en el lado mexicano de la frontera, dificulta el investigar fenómenos importantes de emisión, dispersión, y exposición de PM. La falta de datos también impide el cálculo de riesgos de exposición de PM, lo cual es especialmente importante para grupos susceptibles pediátricos y geriátricos. Información clave puede ser obtenida a través de "estudios de sondeo" de rango y duración

limitada que han sido diseñados para revelar algunos de los mayores componentes, tendencias, y gradientes de PM a través del uso de nuevas metodologías avanzadas.

Cuatro técnicas analíticas primarias fueron usadas secuencialmente para volatilizar, separar, identificar, y desagregar componentes químicos orgánicos ambientales de PM, a saber desorción termal (TD), cromatografía de gases (GC), espectrometría de masas (MS) y análisis de datos multivariado (MDA), respectivamente. Esencialmente, las cuatro técnicas fueron combinadas en un solo método TD-GC/MS/MDA.

El análisis de componentes principales Varimax-rotados (PCA) para los perfiles TD-GC/MS de muestras receptoras espacial y temporalmente resueltas colectadas en 1998, revelan fuentes mayores atribuidas a emisiones de automotores y polvo urbano, combustión de biomasa relacionada con el cocimiento y los hornos del ladrillo, la quema de vegetación agrícola y/o nativa, y combustión de biomasa relacionada con la basura y leña.

El prorrateo cuantitativo de fuentes de PM usando técnicas de balance químico de masas (CMB) y regresión de componentes principales (PCR) en perfiles TD-GC/MS de una serie de 24 pruebas de muestras obtenidas en intervalos de dos horas en la Comisión en Calidad Ambiental de Texas (TCEQ) Sodar contribuyó con un 70% al 80% de la PM medida. En contraste, el intento de uso de técnicas CMB y PCR en un set de perfiles TD-GC/MS de 12 diferentes sitios de muestreo de volumen alto produjeron variancias relativamente bajas (dentro el rango de 50%), aparentemente debido a una pérdida de componentes volátiles de PM durante el almacenamiento de los grandes filtros de cuarzo usados.

Debido a las pérdidas sustanciales de estas pruebas de filtro de 1998, se decidió usar un nuevo set de datos de la prueba del receptor colectado en enero del 2001. Los resultados PCA Varimax-rotados para perfiles TD-GC/MS receptor de muestras espacialmente resueltas colectadas en 2001 muestran un comportamiento fuertemente correlacionado de hidrocarburos aromáticos polinucleares (PNAHs) (factor 1), alcanos normales (factores 2 y 3), y terpenoides fósiles (factor 4). Muestras de sitios receptores en México tienden a ser dominadas por PNAHs pequeños y grandes (de hornos de ladrillo), alcanos grandes (quema de desechos), alcoholes, y cetonas (quema de biomasa y leña). En cambio, las pruebas de los E.U. muestran emisiones de automotores (camiones de diesel y automóviles con convertidores catalíticos), basura (quema de desechos), y combustión de leña. Las contribuciones de algunos alcanos medianos e hidrocarburos aromáticos policíclicos (PAHs) (incluyendo al retano), así como componentes heteroaromáticos (incluyendo la fenalenona, antracenediona, butoxietoxietanol, quinolina, y metilpirrolidina) y amirina en el factor 6, pueden proveer valiosas pistas acerca de la naturaleza y la composición de fuentes faltantes.

El prorrateo de fuentes de PM de este set de perfiles TD-GC/MS receptores espacialmente resueltos utilizando modelos CMB y PCR en combinación con una biblioteca de fuentes de patrones arrojó valores de fuentes de variancia para el modelo en el rango del 70% al 80%. Esto reveló que las fuentes dominantes de PM estaban relacionadas a las emisiones de automotores, los hornos de cocimiento de ladrillo, cocina casera, desechos y procesos de combustión de biomasa, así como también el polvo aerosol de la carretera.

Finalmente, el análisis de residuos PCR revela una diferencia significativa entre los sitios receptores de México y los E.U. Los resultados también revelan una separación entre PNAHs y PNAHs mayores, proveniente de algún tipo de proceso de combustión. Además, una combinación de hopanoides fósiles (asociado a lubricantes de motor o productos relacionados de petróleo), ácido dehidroabietico (a menudo encontrándose correlacionado con niveles generales de PM_{10}), y algunos compuestos comunes alifáticos podrían representar polvo urbano reaerosolizado, mientras que las cargas altas de ambos compuestos nitrogenados aromáticos y el ácido benzoico podrían apuntar hacia algún tipo de proceso de combustión industrial o agrícola.

Background and Rationale

Role and Importance of Small Scale Studies

As discussed in Chapters I and II, particulate matter (PM) emissions from numerous point, area, and mobile sources in Paso del Norte contribute to the severe air quality problems of this highly complex airshed. Because strong correlations exist between urban PM levels and mortality and morbidity rates (Pope 2002), the potential health affects and economic costs of these PM emissions are substantial. Thus, a sustained, systematic effort toward the establishment of comprehensive PM source emission inventories, as well as the development of reliable receptor-based PM source attribution and apportionment models, for the Paso del Norte airshed are warranted.

In view of the chemical and physical complexity of ambient PM in the Paso del Norte airbasin and the intricacy of the spatial and temporal signatures, advanced methods are need for continuous monitoring, collection, and characterization. As well, high-resolution wind direction and velocity measurements are needed to produce adequate data for comprehensive, basin-wide model development and validation. Lack of advanced capabilities and resources, particularly on the Mexican side of the border, makes it difficult to investigate important PM emission, dispersion, and exposure phenomena and prevents calculation of PM exposure risks, which is especially important for susceptible pediatric and geriatric groups.

As will be demonstrated in this chapter, key information can be obtained through "scoping studies" of limited range and duration that have been designed to reveal some of the major underlying PM components, trends, and gradients through the use of new, advanced methodologies. Some of the most informative results from small-scale studies by the authors have been:

- PM source attribution in spatially or temporally resolved organic gas chromatography/mass spectrometry (GC/MS) profiles of PM receptor samples by means of non-supervised multivariate data analysis (MDA) techniques

- Partial PM source apportionment agreement using two different receptor-modeling techniques, in spite of incomplete source pattern libraries
- Determination of potential “missing source” library patterns by means of multivariate comparisons between available receptor and source patterns

Nonetheless, because of the unpredictable nature of some of the underlying meteorological and human activity factors, small-scale studies of short duration cannot substitute for basin-wide, long-term studies. Therefore, in addition to providing preliminary data for the design of future studies, an important secondary function of small-scale studies is to facilitate the development, testing, and validation of some of the new methodologies needed to eventually make full-scale investigations practical at acceptable cost-benefit ratios.

SCERP-Sponsored PM Characterization Studies in the Paso del Norte Airshed

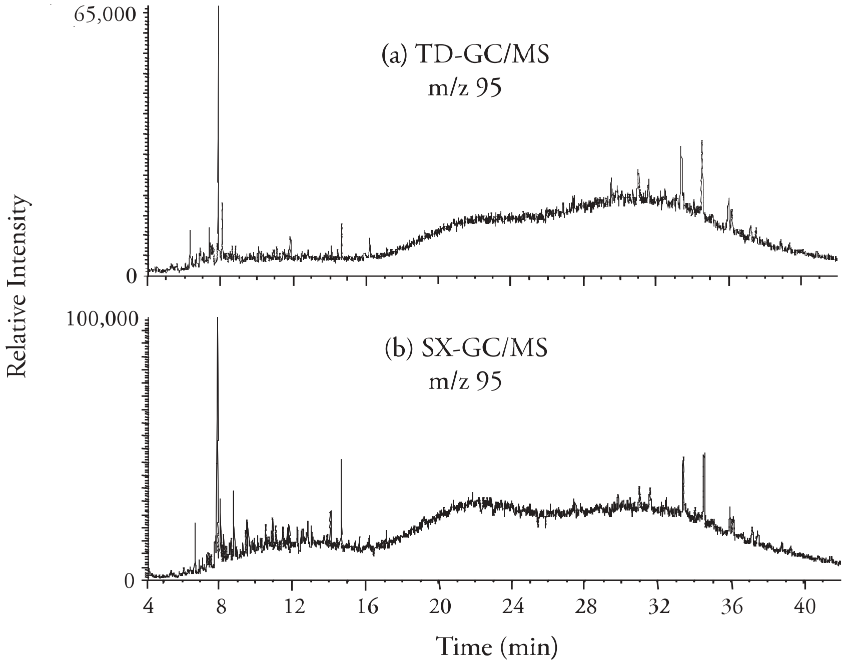
To put the new data presented in this chapter in a proper perspective, it is necessary to review some previously reported results from Southwest Consortium for Environmental Research and Policy (SCERP)-sponsored scoping studies carried out in the Paso del Norte airbasin. The studies were completed between 1998 and 2002 by University of Utah researchers in collaboration with research groups at other SCERP member institutions within the United States and Mexico.

Thermal desorption (TD) GC/MS results from spatially and temporally resolved PM_{10} (particulate matter with an aerodynamic diameter of 10 micrometers [µm] or less) receptor sample series collected in the Paso del Norte airbasin were reported by Jeon, et al. (2001). Varimax-rotated principal component analysis (PCA) of the combined Paso del Norte PM_{10} receptor data set produced four major factors, tentatively attributed to automotive emissions plus urban dust, biomass combustion related to cooking and brick kilns, burning of agricultural and/or native vegetation, and biomass combustion related to trash and firewood. Time-resolved PM receptor characterization at two-hour intervals over a 48-hour period at two consecutive U.S. border sites revealed the occurrence of a strong PM peak in the evening. This PM event appeared to be similar to previously observed events near other large border population centers, namely Mexicali and Reynosa. Finally, as expected, the automotive emissions factor exhibited peaks during the morning and late afternoon traffic spikes.

In addition to TD-based analyses of small quartz fiber (QF) filter strips, conventional solvent extraction (SX) GC/MS analyses of the bulk of the 12 spatially resolved high-volume filters were performed in the Jarman laboratory. This enabled validation of direct TD-GC/MS against the time-consuming and laborious SX-GC/MS methods described in more detail by Sheya (2002) and Jeon, et al. (2001).

Figure 1 compares GC/MS profiles produced by TD- versus SX-based techniques, demonstrating a high-enough degree of similarity to clear the way for source apportionment efforts using PM receptor profiles obtained by TD-GC/MS and PM source patterns obtained by SX-GC/MS. Nearly all GC/MS-type PM source patterns published in the literature, however, were obtained in the United States, particularly in California (Rogge 1993a, 1993b, 1993c, 1993d, 1994, 1997). Because existing PM sources—emissions from older vehicles, unpaved roads, food preparation activities, and a multitude of open combustion sources—are different on the Mexican side of the border, the team in the Paso del Norte airbasin carried out additional PM_{10} source sampling on several occasions.

Figure 1. Comparison of GC/MS Profiles Produced by TD- and SX-based Techniques



Note: Identical intensities of low volatile compounds (i.e., at longer retention times) combined with a loss of higher volatile compounds in the GC/MS profile are due to long-term storage of filter aliquots.
Source: Authors

Nonetheless, PM source apportionment attempts by means of receptor modeling techniques such as chemical mass balance (CMB) and principal component regression (PCR), in combination with the growing collection of GC/MS-type source profiles listed in Tables 1 and 2, gave less than satisfactory results. For the majority of spatially resolved receptor sample profiles, the variance explained by the various linear combinations of source patterns produced by the CMB and PCR models remained relatively low.

Table 1. Literature Source Profiles Used in the Receptor Models

Literature Source Information	Source Pattern	Description
Charbroilers and Meat Cooking Operations (Rogge, 1)	Fat and lean of hamburger meat cooked using two methods, charbroiling over a natural gas and frying	Fine Organic Aerosol
		A local commercial-scale kitchen was used to conduct the meat cooking experiments (Los Angeles, Calif.)
Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks (Rogge, 2)	Non-catalyst and catalyst automobiles, and heavy-duty diesel trucks	Fine Organic Aerosol
		The tailpipe of the vehicle was introduced directly into the dilution source sampler (Los Angeles, Calif.)
Road Dust, Tire Debris, and Organometallic Brake Lining Dust: Roads as Sources and Sinks (Rogge, 3)	Paved road dust	Paved road dust samples from several streets within a residential area in Pasadena, Calif.
	Tire wear	Tire wear particles were produced by mechanic tire-testing for several days
Particulate Abrasion Products from Leaf Surfaces of Urban Plants (Rogge, 4)	Dead leaves	Dead leaves from 62 plant species characteristic of the Los Angeles area
		Leaf surface abrasion by the wind was simulated before analysis
Aerosol.5: Natural Gas Home Appliances (Rogge, 5)	Natural gas	Fine particle emissions from the combined exhaust of a vented natural gas-fired residential space heater and a water heater were fired in a furnace similar to those used in a neighborhood of older homes close to Pasadena, Calif.
Cigarette Smoke in Urban Atmosphere (Rogge, 6)	Cigarette smoke	Four different cigarette types (no filter, filter, light, and menthol); a dilution tunnel was used to collect the smoke generated by human smokers
Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces (Rogge, 9)	Fireplaces (pine and oak)	Wood combustion experiments were conducted in a undampered brick fireplace in southern California

Source: Rogge, et al. 1991, 1993a, 1993b, 1993c, 1993d, 1994

Table 2. Local Source Profiles Used in the Receptor Models

Location	Source Pattern	Description
Brick kiln neighborhood (N 31°41.229', W 106°27.408'). Time: 2/12/01. Two hour run time 1:30 p.m.–3:30 p.m.	Brick kiln	Sunny breezy day with wind predominantly from the southwest. Monitoring stations located about 100 feet away from the kilns, which were fueled with sawdust. Unpaved roads were surrounding the kilns.
Pedro Mora's house (N 31°42.743', W 106°25.143'). Time: 2/12/01. Two hour run time 8:12 p.m.–10:12 p.m.	Cookout	Carne asada (marinated beef), pork, potatoes, onions, chilies, and tortillas were cooked on a new charcoal grill, which was started with lighter fluid. Samplers located approximately 10 feet from the grill.
Neighborhood downwind and slightly uphill from the power plant (N 31°42.096', W 106°23.615'). Time: 2/13/01. Approximate two hour run time, 7:22 p.m–9:50 p.m.	Diesel power plant	Sampling station located about 300 yards away. Rain cleared just before sampling began. Power plant stopped operating at approximately 9:50 p.m.
Tania Espino's house (N 31°41.337', W 106°22.945'). Time: 90 minute run time 9:01 p.m.–10:31 p.m.	Trash burning	Trash collected in a nice neighborhood (not necessarily a representative sample of Ciudad Juárez trash). It included plastic bags, paper, cardboard, drink bottles, aluminum cans, and kitchen waste. It was burned in a 55-gallon metal drum. The wind was strong and gusty.

Source: Authors

To attempt to explain the underlying causes of the observed poor model fits, an exploratory analysis of the multivariate data spaces occupied by the receptor profiles and the selected source sample patterns was carried out by means of PCA-type rotation and projection methods. These new data processing results will be discussed later.

Methods and Procedures

Overall Analytical Approach

Four primary analytical techniques were used sequentially to volatilize, separate, identify, and deconvolute organic chemical components in ambient PM, namely TD, GC, MS, and MDA, respectively. Essentially, all four techniques were combined into a single TD-GC/MS/MDA method. Such integrated multidimensional methods are often referred to as "hyphenated" analytical techniques, although the individual terms may either be separated by a hyphen or a slash, depending on international recommendations (such as from the International Union of Pure and Applied Chemists). Although a four-stage hyphenated approach may seem cumbersome, it should be remembered that the organic chemical composition of ambient PM tends to be quite complex and that even with four steps, a comprehensive measurement and identification of all organic chemical structures within a given PM sample remains well beyond current capabilities.

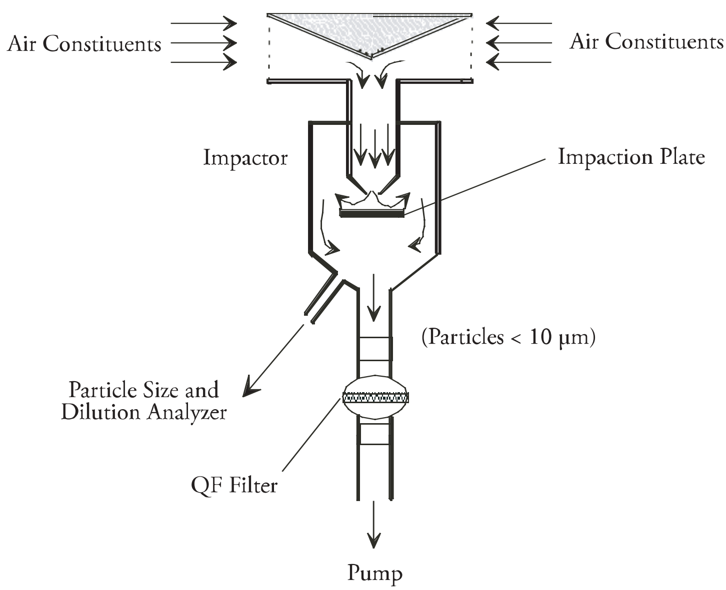
Because the use of MDA methods involves extensive data manipulations with which many may be unfamiliar, the need for MDA requires further explanation. It should be pointed out that every PM receptor sample tends to consist of highly complex mixtures of organic and inorganic compounds representing the various PM sources contributing to that receptor location. The chemical composition of such source material mixtures is further modified and modulated by physicochemical and chemical reactions and processes occurring during the residence time of the particles in the ambient environment. In fact, some particles may be formed entirely by atmospheric processes and are therefore referred to as secondary PM.

Sample Collection, Preparation, and Analysis

To collect the PM aerosols, standard high volume samplers (one square meter per minute [m^2/min]) with 500 centimeter square (cm^2) QF filters were used. Eleven two-hour samples were collected in December 1998 at 11 scattered sites, five on the Mexican side and six on the U.S. side. Similarly, 12 samples were collected on January 17 and 18, 2001, at 12 sites, six on the Mexican side for the Delphi site (replicates) and six on the U.S. side. Maps of the sampling sites are shown in Appendix Figure 1 (page 305).

A dichot sampling inlet was used to collect the time-resolved PM_{10} air particulates. In the dichot sampler, the aerosol is drawn through an isokinetic sampling inlet with a subsequent impactor stage that deposits particles greater than 10 µm on a plate immediately in front of the impactor nozzle, as shown in Figure 2. A flow rate of 20 milliliters per minute (ml/min) was used and the air flowed through the sampler for two hours. The flows were verified using a laboratory calibrated mass flow controller (model 5850 E, Emerson Electric Co., Hatfield, Penn.). The sampling port was placed into a stand at a height of approximately seven feet above ground level.

Figure 2. Schematic Diagram of the Sample Collection System with Modified Dichot Inlet Used for Collection of PM_{10} at Two-Hourly Intervals Sampling on QF Filters



Source: Authors

The PM_{10} receptor samples were analyzed using SX-GC/MS and solvent-free TD-GC/MS. For TD-GC/MS, a 2 millimeter (mm) x 19 mm strip was cut from PM-loaded filters using a strip cutter consisting of parallel razor blades and a pair of forceps cleaned by ultrasonication in methanol and dichloromethane. The strip was positioned inside a special borosilicate glass desorption tube, which was lined with a ferromagnetic foil. The filters were introduced and placed into a Curie-point desorption reactor for flash desorption of volatile and semi-volatile organic compounds. Subsequent to sample desorption, the compounds were introduced into a fused silica capillary column that was then temperature programmed from 40°C to 200°C at a rate of 15°C per minute (°C/min), and from 200°C to 320°C at 5°C/min. This temperature profile increased the resolution of the later-eluting semi-volatile compounds. A continuous flow of helium transferred the vaporized compounds from the reaction zone into a fused silica capillary column of the gas chromatograph, coupled to a mass spectrometer. The spectrometer was operated at a standard energy of 70 electron volts (ev), which enabled the unique mass spectrum obtained from the organic constituents to be compared to the standard mass spectral National Institute for Standards and Technology (NIST) 98.1 library. Chromatographic peaks were initially selected for integration based on chromatographic and practical considerations. The sample collection, preparation, and analysis procedure has been described in detail elsewhere (Jeon, et al. 2001).

Multivariate Data Analysis and Receptor Modeling Techniques

In this study, TD-GC/MS profiles consisting of a total of 57 organic compounds were identified, interpreted, and evaluated by means of multivariate techniques (Windig, Chakravarty, and Meuzelaar 1986). These 57 chemicals were organized into 16 groups (Table 3).

Table 3. Classification of the Organic Compounds Used for Modeling

Group Number	Groups	Compound Number	Component
1	Alkanes (C19-22)	1	n-nonadecane
		2	n-eicosane
		3	n-heneicosane
		4	n-docosane
2	Alkanes (C23-26)	5	n-tricosane
		6	n-tetracosane
		7	n-pentacosane
		8	n-hexacosane
3	Alkanes (C27-33)	9	n-heptacosane
		10	n-octacosane
		11	n-nonacosane
		12	n-triacontane
		13	n-hentriacontane
		14	n-dotriacontane
		15	n-tritriacontane
4	Alkanoic acids (10, 12, 13, 18)	17	n-decanoic acid
		18	n-dodecanoic acid
		19	n-tridecanoic acid
		23	n-octadecanoic acid
5	Alkanoic acids (14, 16, 17)	20	n-tetradecanoic acid
		21	n-pentadecanoic acid
		22	n-hexadecanoic acid
6	Alkanoic acids (9, 28, 30)	16	n-nonanoic acid
		24	n-octacosanoic acid
		25	n-triacontanoic acid
7	Alkahols and ketones	26	hexadecanol
		27	docosanol
		28	nonanal
		29	tridecanal
8	Dehydrobietic acid	30	dehydroabietic acid

Table 3. continued

Group Number	Groups	Compound Number	Component
9	Benzaldehyde and amyrin	32	3-methoxy-4-hydroxybenzaldehyde
		33	trimethylbenzaldehyde
		34	4-hydroxy-3,5-dimethoxy-benzaldehyde (syringaldehyde)
		35	β-amyrin (3β-olean-12-en-3-ol)
10	Small and medium (PAH)	36	phenanthrene
		37	1-methyl-7-isopropylphenanthrene (retene)
		38	fluoranthene
		39	pyrene
		40	benz[a]anthracene
		41	chrysene/triphenylene
		42	benzo[j]fluoranthene
		43	benzo[e]pyrene
		44	benzo[a]pyrene
11	Large PAH	45	perylene
		46	indeno[1,2,3-cd]pyrene
		47	indeno[1,2,3-cd]fluoranthene
		48	benzo[ghi]perylene
12	Arones	49	1H-phenalen-1-one
		50	9,10-anthracenedione (anthraquinone)
13	Terpenoids	51	(20S and R)-5α(H),14(α or β)(H), 17(α or β)(H)-cholestanes
		52	22,29,30-trisnorneohopane
		53	17α(H), 21β(H)-29-norhopane
		54	17α(H), 21β(H)-hopane
14	N-containing and O-containing	55	quinoline
15	M-pyrol and ethanol	56	1-methyl-2-pyrrolidinone (m-pyrol)
		57	2-(2-butoxyethoxy)ethanol
16	Benzoic acid	31	benzoic acid

Source: Authors

MDA is primarily based on an exploratory analysis approach with subsequent orthogonal rotation of the PCA data analysis, thereby reducing the large number of interrelated variables while retaining as much of the information (variance) as possible. PCA calculates a non-correlated set of variables (factors) ordered so that the first few retain most of the variance present in the original variables. The first step in PCA is usually to create an autoscaled data matrix by subtracting the variable mean and dividing by the standard deviation.

A receptor modeling approach to source apportionment is based on detailed analysis of receptor sample compositions with subsequent apportionment of the pollutant concentrations using a source pattern library (Hopke 1991). CMB and PCR were selected as the primary receptor modeling techniques for this study. PCR is a technique for analyzing multiple regression data that suffer from multicollinearity. When multicollinearity occurs, least squares estimates are unbiased but their variances are large, so they may be far from the true value. By adding a degree of bias to the regression estimates, principal components regression reduces the standard errors. It is hoped that the net effect will be to give more reliable estimates (NCSS 2000). A commercially available NCSS Statistical Software package was used to perform PCA and PCR. CMB consists of a set of linear equations that express the ambient concentrations of chemical species as the sum of products of source compositions and source contributions; the equations are a result of the mass conservation law (Watson, et al. 1998).

The results presented in this section and Appendices A and B include plots of factor loadings and factor scores. The factor scores explain how the sources and receptors are related. For example, if a location like Advanced Transformer is near the brick kiln source on a factor score plot, it is likely affected by brick kilns. The loadings explain the relationship between the chemicals. Factor score plots and factor loading plots can be superimposed (if properly scaled) because they reflect the projections of objects (receptor profiles) and variables (chemical compounds) coexisting in multidimensional data space onto the same two-dimensional subspace. For example, looking at Figure A1a and A2a in Appendix A will explain the relationship between the chemicals and sources/receptors.

PCA-Based PM Source Attribution

The PCA results (factor scores and factor loading plots are presented in Appendix A) for the 1998 receptor data set revealed a major problem in that the receptor sample profiles are clustered relatively tightly outside the source sample pattern envelope. Clearly, the main source of variance in the data set is caused by differences between the source and receptor sample profiles rather than by the common sources of variance needed for successful modeling attempts. In addition, much of the volatile compound fractions from the small QF filter strips were lost while waiting for the time-consuming solvent extraction procedures to be completed on the samples taken in 1998. Consequently, the researchers decided to use the 1998 receptor sample data in a stand-alone fashion rather than in combination with source data sets. This allows a closer look at some of the source attribution information first examined by Jeon, et al. (2001). A more detailed description of the PCA results can be found in Appendix A.

Varimax-rotated PCA results of the receptor samples collected in 1998 reveal major source attributions from automotive emissions, plus urban dust; biomass combustion related to cooking and brick kilns; burning of agricultural and/or native vegetation; and biomass combustion related to trash and firewood. In addition, the results in Appendix A (Figure A1a, 30 degree counter-clockwise rotation) reveal a complete separation between the U.S. and Mexican receptor sites along a single axis. In view of well-known differences in anthropogenic PM emission sources—automotive exhaust, cooking, brick kilns, and trash burns, among others—this finding is not unexpected.

New Receptor Data Set (January 2001)

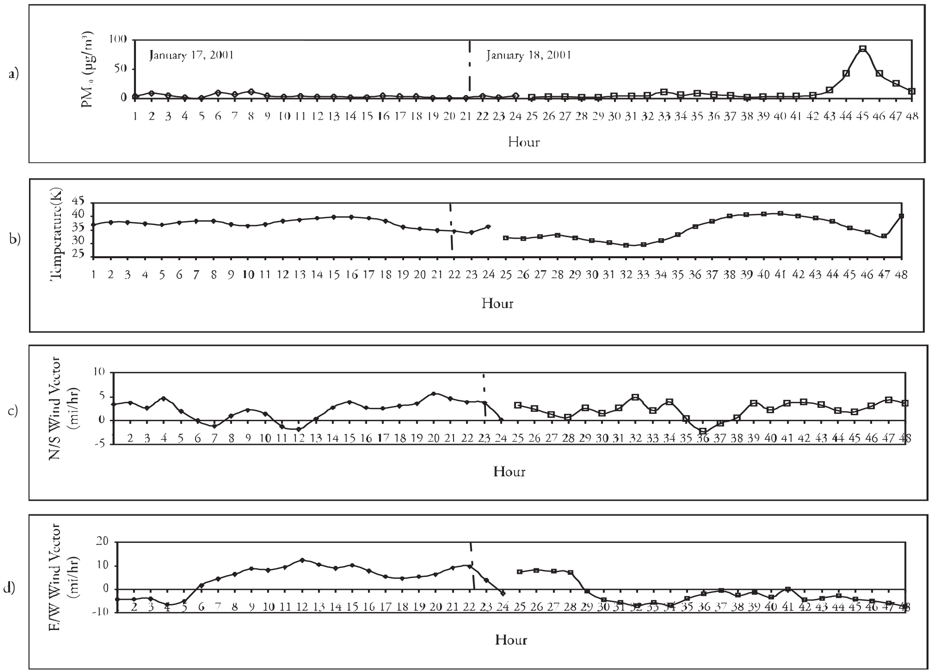
In light of the disappointing source apportionment attempts with the first receptor sample set, a new set of receptor samples was collected in the Paso del Norte airshed on January 17 and 18, 2001. Meteorological conditions and PM concentrations recorded at the Sun Metro Continuous Air Monitoring Station (CAMS) 40 during the same period are illustrated in Figure 3. Note that the 12 locations (see map in Appendix Figure 1 [page 305]) are fairly evenly divided between the United States and Mexico. Co-located high-volume samplers at the Delphi site served as a control for the total amount of variance contributed by sampling, transport, storage, aliquotting, and analytical procedures.

TD-GC/MS analyses of small aliquots from the QF filters were carried out within a week of collection. Initial PCA results (not shown) demonstrated that only the fifth-largest (10.6% variance) of the first six Varimax-rotated principal components (together explaining 75% of the total variance) showed appreciable differences in factor scores between the two Delphi samples. This suggests that variance introduced by methodological errors is comparatively small when compared to the variance attributable to location-dependent variations in the composition of organic components desorbed from the receptor samples.

To explore a combined data space in which the 12 new receptor profiles would be framed by relevant source patterns, a set of eight source patterns was selected. Of the eight source patterns, five were derived from the literature (several of which were through averaging multiple related literature profiles) and three represent sources specially sampled by the researchers because they are known to be characteristic of the U.S.-Mexican border region, including emissions from brick kilns, trash burning, and idling bridge traffic. The bridge traffic source profile is unusually rich in aliphatic alcohols, aldehydes, and ketones, presumably representing incompletely combusted fuel components produced by extended idling of car engines on the bridge. Both the trash burning and brick kiln emissions profiles can only be expected to be representative of more or less arbitrarily selected fuel components burned under specific sets of conditions.

It should be pointed out that the brick kiln and bridge traffic samples represent clusters of multiple individual sources. In view of the extreme complexity of the Paso del Norte airshed, source cluster sampling may well often be the only practical technique to obtain usable source patterns. It is of interest to note that cluster sampling will change the spatial and temporal characteristics of the source types involved by the de facto transformation of mobile sources into line sources (e.g. representing roads and bridges), of brick kiln point sources into area sources, and so on.

Figure 3. Hourly Data from the CAMS 40 Monitor at the Sun Metro Site for the January 17–18, 2001 Period



Notes: (a) PM_{10} levels; (b) temperature (°F); (c) north/south wind direction; (d) east/west wind direction.
Source: Authors

Varimax-rotated PCA results for TD-GC/MS profiles of spatially resolved receptor samples collected in 2001 are detailed in Appendix B. Summarized results have been included in the next section.

Conclusions and Recommendations

Varimax-rotated PCA results for TD-GC/MS profiles of spatially and temporally resolved receptor samples collected in 1998 reveal major source attributions from automotive emissions plus urban dust, biomass combustion related to cooking and brick kilns, burning of agricultural and/or native vegetation, and biomass combustion related to trash and firewood.

Varimax-rotated PCA results for TD-GC/MS profiles from a new set of spatially resolved high volume receptor samples collected in January 2001 show strongly correlated behavior of polynuclear aromatic hydrocarbons (PNAHs) (factor 1), normal alkanes (factors 2 and 3), and fossil terpenoids (factor 4). Mexican receptor site samples tend to be dominated by small and large PNAHs (brick kiln), large alkanes (waste burning), alcohols, and ketones (firewood, biomass burning). By contrast, U.S. samples show automotive emissions (diesel trucks and autos with catalytic converters), trash (waste burning), and firewood combustion.

Contributions of some medium-sized alkanes and polycyclic aromatic hydrocarbons (PAHs) (including retene), as well as heteroaromatic compounds (including phenalenone, anthracenedione, butoxyethoxyethanol, quinoline, and methylpyrrolidine) plus amyrin on factor 6 appear to provide valuable clues about the nature and composition of missing sources (also see the section on Exploratory Residual Profile Analysis in this chapter).

PM Source Apportionment

Introduction

To make the information obtained from PM receptor sample characterization studies available and useful for purposes of environmental regulation, compliance monitoring, urban planning, and health risk evaluation, it is generally necessary to quantitatively apportion the various source contributions. Therefore, source apportionment remains the final challenge for all PM characterization studies in complex airsheds such as Paso del Norte. Of particular interest to the Paso del Norte airbasin would be the ability to perform PM exposure risk modeling based on reliable source apportionment. Moreover, it is becoming abundantly clear that not all PM components are equally hazardous to human health (Pope 2002). This limits the usefulness of total PM concentration as a predictor for health impacts and points the way toward the use of source apportionment results for deconvoluting the overlapping health effects of different PM constituents.

Among the diverse source apportionment approaches suitable for use with chemical PM data, so-called receptor modeling techniques—such as CMB, PCR, partial least squares (PLS), positive matrix factorization (PMF), and UNMIX (named for its function, which is to "unmix" the concentrations of chemical species measured in the ambient air to arrive at the magnitudes of the underlying sources, according to the U.S. Environmental Protection Agency's National Exposure Research Laboratory)—appear to have proved most successful in the hands of environmental chemists and physicists thus far. For the PM apportionment studies reported here, both CMB and PCR were selected. CMB—based on multilinear regression of individual variables in combination with a variance weighting approach—currently appears to be the most widely used source apportionment method for air quality applications and, as a result, has reached a higher level of user-friendliness in terms of documentation, customization, and validation than most competing techniques. PCR—based on multilinear regression of orthogonal, linear combinations of variables—has the advantage of removing collinearities from highly redundant PM characterization data while remaining transparent enough to allow easy visualization of the (fully reversible) transformation processes connecting input and output data. Moreover, the close relationship between PCR and PCA (the method used for exploratory data analysis and source attribution in the previous section of this chapter) often makes it possible to predict and/or verify quantitative PCR outcomes from a careful evaluation of the PCA results.

Nonetheless, the researchers are actively interested in the aforementioned alternative receptor-modeling techniques. At this point, the statistical requirements of the UNMIX method appear to prevent its use for small-scale scoping studies. However, comparisons between both the PLS and PMF methods versus the CMB and PCR techniques are planned or underway. Moreover, as will be discussed in Chapter VII, full integration of PM receptor modeling and source modeling approaches remains the "holy grail" of air quality research and therefore deserves continuing attention and effort.

With the exception of UNMIX, the primary requirement of all aforementioned receptor modeling techniques is the availability of a comprehensive set of representative source patterns. For example, the CMB program (version 8) warns the user that contributions from unknown source patterns should not exceed 10% to 15% in order to produce reliable quantitative apportionment results. Based on the outcome of the source attribution efforts discussed in the previous section, the researchers are presently unable to fulfill that requirement. Nonetheless, as will be demonstrated in the following paragraphs, an iterative approach to PM source apportionment in an exceptionally complex airbasin can produce informative and useful results, particularly when using two complementary methods such as CMB and PCR.

Again, it should be pointed out that all source and receptor patterns used in the source apportionment studies of spatially resolved PM receptor site samples reported here were normalized to 100%. As discussed before, the main advantage is that source pattern normalization tends to produce well-ordered hypertetrahedron configurations in which the effects of orthogonal rotations such as Varimax can be readily followed. The research team is still actively pursuing an iterative approach to source apportionment. The scoping study results presented here do not yet meet important quality assurance criteria (such as with regard to maximum percent contribution from unknown sources) and thus should not be considered ready for end-use purposes requiring quantitative data.

However, since calibration is fairly straightforward (though quite laborious), a section will be included on source apportionment of a unique time-resolved PM receptor sample series for which the necessary quantitative apportionment steps were completed. This will demonstrate the feasibility of quantitative source apportionment using PM characterization data obtained by direct TD-GC/MS analysis of small QF filter samples.

Qualitative Apportionment of Spatially Resolved Receptor Profiles

The 12 PM receptor and 12 source profiles used for these apportionment studies were identical to those analyzed above (see Tables 1 and 2). Application of the CMB model, as previously described, resulted in R^2 values between 70% and 80% for all 12 receptor samples (see Table 4) and intuitively reasonable source coefficients. Considering the previously estimated noise levels (5% to 10%) in the data set, as well as the estimated percentage of unknown source contributions (10% to 15%) one would not expect to obtain R^2 values much higher than that.

In light of the observed systematic separation of U.S. and Mexican receptor sample patterns in principal component space, the research team further calculated average receptor patterns for each side of the border and applied the CMB model to these synthetic patterns. According to the CMB model (see Table 4), the average PM_{10} receptor pattern on the U.S. side of the border has dominant contributions from automotive emissions (35%), followed by an unknown fraction (25%), then brick kiln plus trash emissions (15%), and near-equal contributions of biomass burning (9%), cooking (7%), and road dust (9%), all rounded off to the nearest integer value. By contrast, the average PM_{10} receptor pattern on the Mexican side of the border, on average just a few miles away from the U.S. sites, has a dominant unknown fraction (27%), followed by automotive emissions (21%), brick kiln plus trash (23%), biomass burning (10%), road dust (9%), and cooking (9%).

Notwithstanding the encouraging preliminary CMB results obtained with this comparatively well-behaved receptor data set, the relatively large contribution of unknown variance sources would appear to be a little high to guarantee reliable, stable apportionment results. So, in order to validate the CMB results while trying to shed more light on the nature of the missing PM sources, the researchers performed PCR-based source apportionment as well.

Initial PCR analysis results produced too many negative regression coefficients to be meaningful. After normalizing each of the receptor and source patterns to 100%, far fewer negative coefficients were observed. Average R^2 values started hovering around 60% to 70% when eight of the 11 principal components, together explaining 90% of the total variance, were included in the model. Surprisingly, the R^2 values for Riverside (53%), Pestalozzi (50%), and especially Socorro (29%) remain much lower than those produced by the CMB model. Although it is possible to improve these values by adding more components, the danger of including too much noise in the model to make the results statistically meaningful (have any predictive value) is a constant threat. Without having duplicate receptor samples from these sites it would be hard to decide whether the CMB model is overestimating the R^2 by letting too much collinearity between variables slip through, or the PCR model is underestimating the common variance by being too parsimonious.

The decision to select eight components for the PCR model was based on a marked increase in observed variance inflation factors (VIFs) when including more (nine or 10) components, as well as a strong increase in correlated variance among the residuals from the PCR procedure when including fewer factors than eight. Nonetheless, for optimum results it may be necessary to use individual cut-off points for the various receptor samples. For example, the optimum component number for the Advanced Transformer site sample was found to be approximately 10 in order not to lose valuable chemical information. As discussed in the previous paragraphs, some other PCR site models also may need to include additional components.

The pie charts in Figure 4 show a comparison of the relative apportionment results produced by CMB versus PCR for both the average U.S. and Mexican receptor profiles. An encouraging result is that source apportionment coefficients for average Mexican and U.S. receptor patterns do agree well, as long as the somewhat arbitrary values for "unknown sources" produced by both techniques are excluded. After all, whereas one can say with some confidence the origin of the common variance portion of the receptor profiles shared with the source patterns (as measured by the R^2 value), the

Table 4. Source Contribution Estimates from CMB (in micrograms per cubic meter [μg/m³])

Mexican Sites							
	Advance Transformer	Club 20-30	Delphi 1	Delphi 2	Pestalozzi	Zenco	Mexican Total
Car gasoline	10.71	25.24	27.57	42.83	17.54	24.53	148.42
Diesel	3.07	0.00	0.00	0.00	17.56	0.00	20.63
Road dust	5.01	18.10	14.30	5.03	12.43	18.10	72.97
Kiln and trash	77.47	18.88	24.59	28.15	9.72	26.44	185.25
Biomass burns	2.80	6.72	10.52	13.49	27.03	14.59	75.15
Cooking	0.00	30.95	15.16	9.73	5.45	10.34	71.64
Oil gas	0.95	0.10	7.85	0.77	10.27	6.01	25.95
Unknown	20.48	28.21	33.33	42.86	42.86	42.86	210.59
R^2	0.83	0.78	0.75	0.70	0.70	0.70	0.74
U.S. Sites							
	Ivanhoe	Lindberg	Northeast	Riverside	Socorro	Tillman	U.S. Total
Car gasoline	9.81	22.21	9.04	22.68	33.58	3.13	100.45
Diesel	17.76	39.72	44.56	5.03	15.21	54.03	176.33
Road dust	8.43	2.65	8.65	9.26	32.62	12.37	73.99
Kiln and trash	39.64	13.81	31.62	16.82	0.00	12.68	114.56
Biomass burns	10.98	9.15	5.69	23.81	12.28	8.46	70.37
Cooking	13.38	12.07	0.00	20.59	0.00	8.35	54.39
Oil gas	0.00	0.39	0.43	1.81	6.30	0.97	9.91
Unknown	38.89	29.87	38.89	38.89	35.14	20.48	202.15
R^2	0.72	0.77	0.72	0.72	0.74	0.83	0.75

Source: Authors

remaining variance tends to be much more heterogeneous in origin. In addition to contributions from unknown sources and noise, many potential physical and/or chemical processes in the atmosphere, on the collection filters, and in the rest of the analytical procedure are capable of creating signal bias that could masquerade as pseudo-components. Currently, there is no method for partitioning the non-model variance into its various components other than to perform non-supervised, exploratory MDA while relying on intuition and experience. Provisional results of such an exploratory approach to variance attribution of receptor profile components outside the multidimensional data domain shared with the source patterns will be presented later.

Figure 4. CMB and PCR Results

a) USA (CMB)

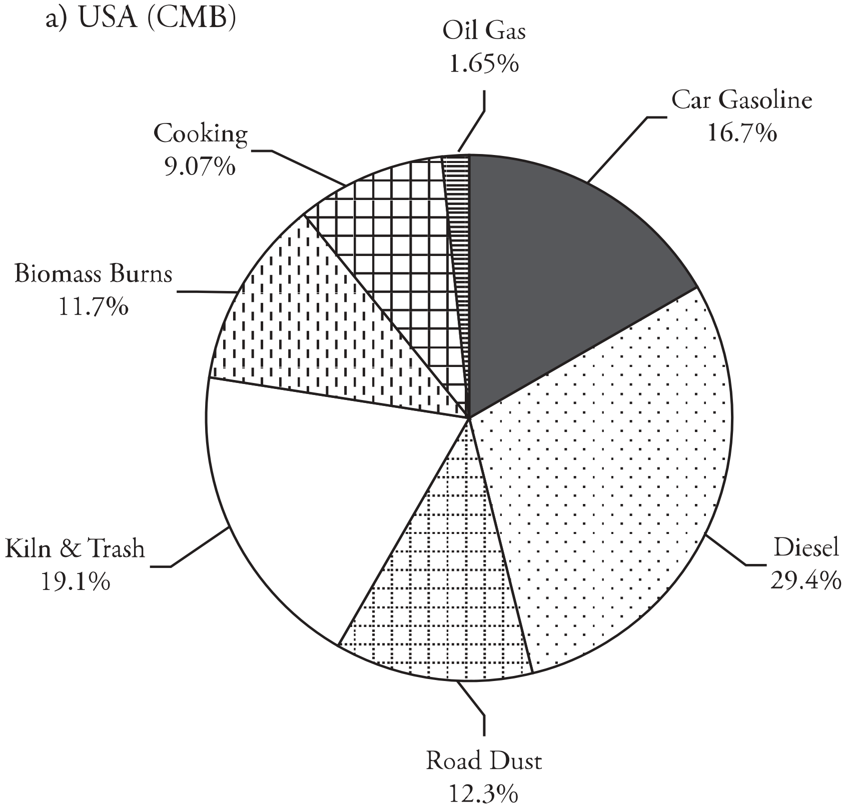


Figure 4. continued

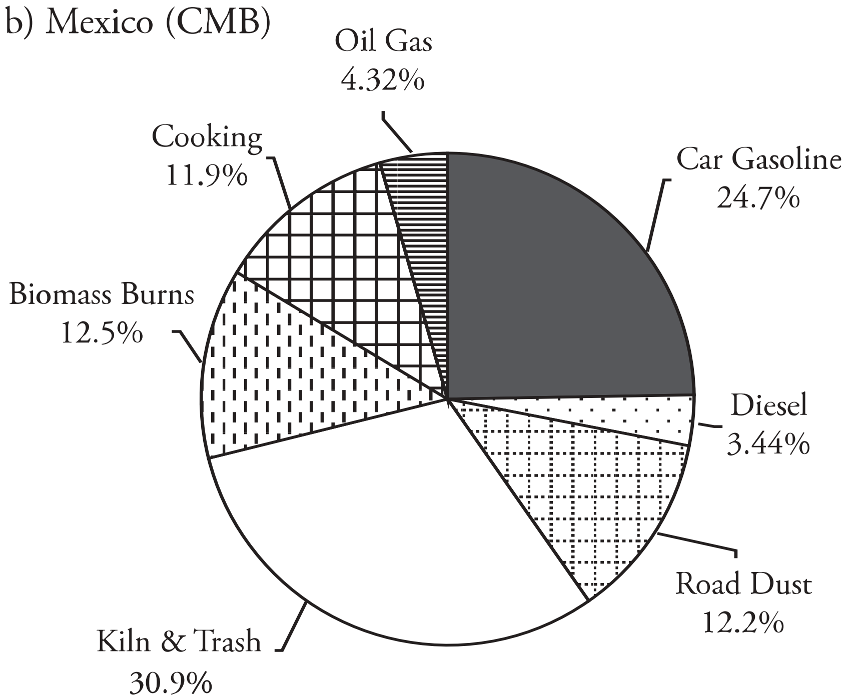


Figure 4. continued

c) U.S. (PCR)

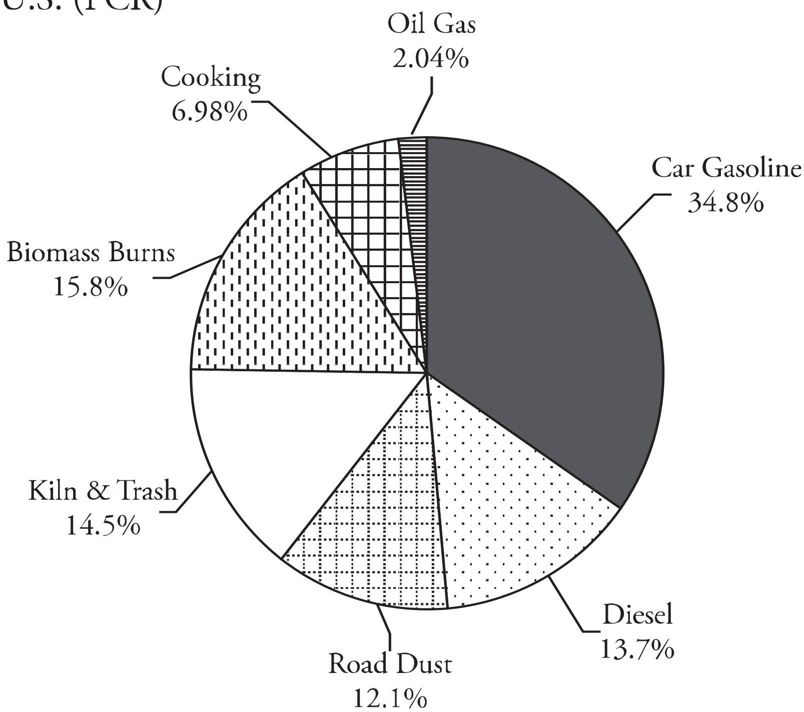
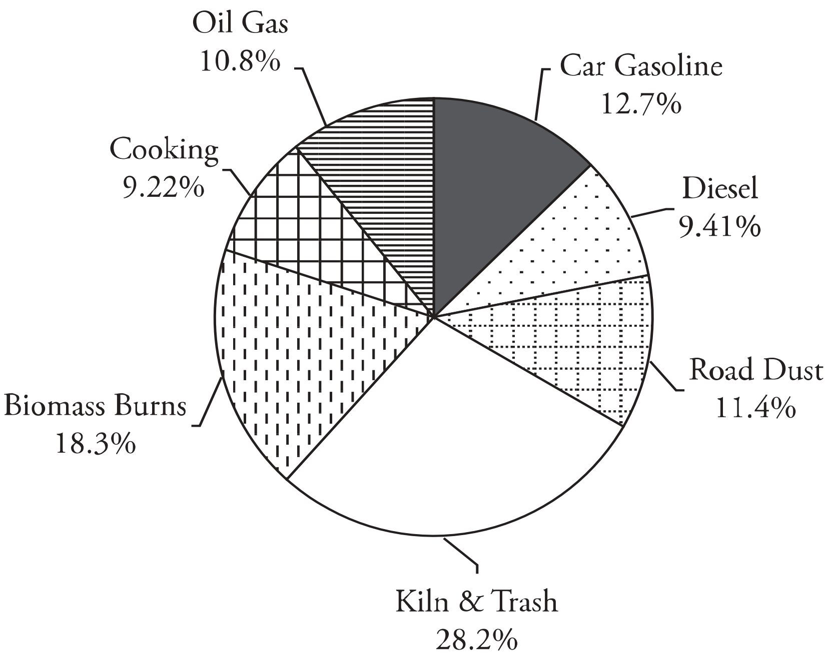


Figure 4. continued

d) Mexico (PCR)

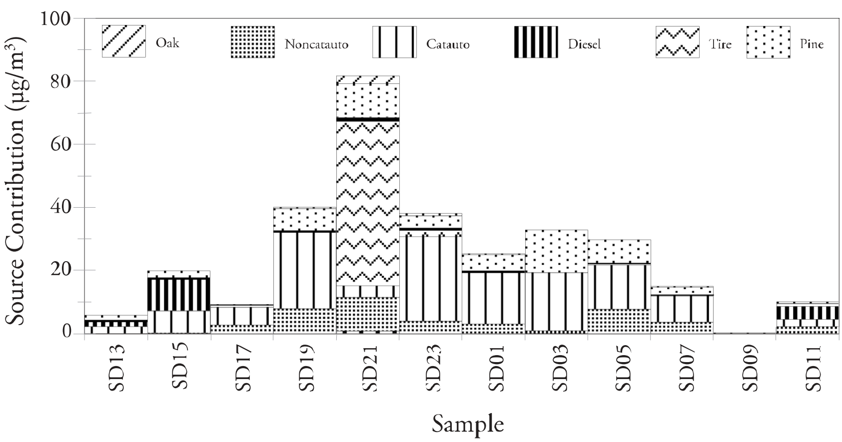


Source: Authors

Quantitative Apportionment of Temporally Resolved Receptor Profiles

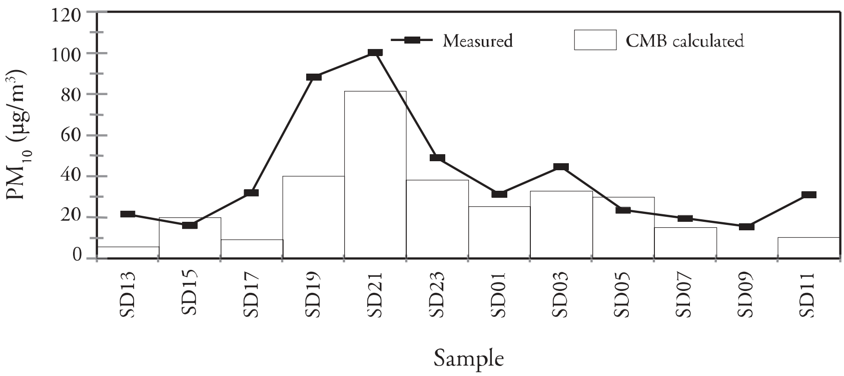
TD-GC/MS profiles from a series of 24 time-resolved PM receptor samples collected during two consecutive 24-hour periods at the Sun Metro and Sodar sites (Figures 5a and 5b) were used in combination with a subset of PM source patterns from Tables 1 and 2 to obtain quantitative source apportionment results using the CMB model (version 8). PCA results for this receptor profile series, as well as general source category attributions, have been discussed by Jeon, et al. (2001).

Figure 5a. CMB Model Source Apportionment Results for Time Resolved Receptor Sample Series from the Sodar Side



Source: Authors

Figure 5b. Comparison of Model Predictions with Measured PM_{10} Ambient Concentrations



Source: Authors

To obtain the quantitative, mass-balanced source apportionment results shown in Figure 5, several steps had to be taken to transform relative apportionment coefficients into mass-balanced parameters:

- Source pattern intensities needed to be presented in concentration units (e.g., microgram amounts of each individual chemical component per gram of total PM from that source)
- TD-GC/MS profiles from PM receptor samples needed to be recalculated in units of mass concentration (e.g., microgram amounts of a given compound per microgram of desorbed PM)
- The amount of PM on each filter aliquot needed to be related to the ambient PM_{10} density

Only PM source patterns with published chemical marker concentrations (see Table 3) were used in this experiment, so the first transformation step was relatively easy. Recalculating receptor sample profiles into concentration units was more time-consuming because it requires knowing the GC/MS response factors of all 57 compounds analyzed. The majority of these factors, shown in Tables 1 and 2, were obtained from the literature. Others were calculated based on physicochemical properties and a few were estimated by comparison with analogous and/or homologous compounds. The amount of PM injected was calculated from the known filter fragment size, ambient airflow, and PM density (see Materials and Methods).

Figure 5b shows the fraction of measured PM mass accounted for by the set of source patterns used for the CMB model, whereas Figure 5a identifies the calculated individual source contributions. The average percentage of total PM mass explained by the quantitative use of the CMB source model in these time-resolved receptor samples obtained at the Sodar site, viz. 70% to 80%, appears roughly comparable to the fraction of total variance explained by the CMB model in the relative source apportionment results. This may simply reflect the fact that average response factors for the various compounds tend to vary by less than one order of magnitude. Yet, contributions from sources producing particularly low organic signal intensities, such as road dust, may be expected to show more dramatic differences between variance- and mass-based apportionment approaches, as illustrated by the very high calculated dust percentage at the height of the pronounced evening PM peak occurring between 2000 hours and 2300 hours. As reported by Sheya (2002), PM_{10} levels during this evening episode reached well over 600 $\mu g/m^3$. The frequency, origin, and possible health impacts of these high evening PM episodes, previously reported by some of the authors at several other peri-metropolitan sites at the U.S.-Mexican border, will be discussed in more detail in Chapter VII.

The feasibility of using TD-GC/MS receptor profiles in general, and time-resolved profiles in particular, for quantitative source apportionment studies while achieving credible results offers considerable promise for larger scale studies aimed at providing a more complete overview of PM source emission activities and potential exposure risks in the Paso del Norte airshed. Yet, the results also confirm that more work remains to be done in identifying missing sources (and/or possible physicochemical processes) contributing to PM receptor samples obtained in this airbasin. An attempt to obtain some indications of and directions on the types of missing sources that may need to be considered in future studies by re-analyzing the residual variance produced during PCR will be described in the following paragraphs.

Conclusions and Recommendations

Quantitative PM source apportionment using CMB and PCR techniques on TD-GC/MS profiles of 24 receptor samples obtained at two-hour intervals at the Texas Commission on Environmental Quality Sodar site was able to account for 70% to 80% of the measured PM mass. By contrast, the attempted use of CMB as well as PCR techniques on a set of TD-GC/MS profiles from 12 different high-volume sampling sites produced relatively low model variances (in to 50% range), apparently do to a loss of volatile PM components during storage of the large quartz filters used.

Because of the substantial volatile compound peak intensity loss in the 1998 TD-GC/MS profiles, it was decided to use a new set of receptor sample data collected in January 2001. PM source apportionment of TD-GC/MS profiles of these spatially resolved receptor samples by using CMB and PCR models in combination with a referenced source pattern library achieved model variances in the 70% to 80% range. This revealed that the dominant PM sources were related to automotive emissions plus brick kilns, cooking, trash, and biomass combustion processes, as well as aerosolized road dust.

Exploratory Residual Profile Analysis

Introduction

One of the primary objectives of any "scoping study" is to find out where the main gaps are and what needs to be accomplished before full-scale efforts can be mounted. The small-scale Paso del Norte studies have established a clear need for improved PM source pattern libraries, both with regard to completeness and to how representative each source pattern is for the Paso del Norte airbasin. Thus, it is important to scrutinize the Paso del Norte receptor data for any clues about the nature and origin of all PM components that cannot be explained by direct comparison with the current PM source pattern library. In view of the known complexity of PM receptor profiles in the Paso del Norte airbasin, it seems logical to first attempt to subtract known source components to highlight unknown residual patterns.

Although intuitively simple, direct subtraction approaches tend to be stymied by practical difficulties, particularly if residues are relatively small and subtraction of large patterns threatens to propagate substantial noise and error contributions. During the PCR procedures discussed in the previous paragraphs, residual variance percentages were fairly large, whereas overall noise levels remained low throughout. This encouraged the research team to inspect the residual receptor profile variance unexplained by the PCR model for clues to the nature and identity of any "missing" PM sources.

In attempting to do so, it is important to point out that PCR-type receptor model residues should be expected to exhibit considerable heterogeneity with regard to the sources of the residual variance. Besides receptor profile components unexplained by known source patterns, one may expect to encounter random noise as well as the effects of a broad range of potential atmospheric, sampling, storage, or sample preparation processes capable of biasing the original source patterns. Considering the open-ended nature of the quest, the researchers decided to use a non-supervised MDA approach, such as PCA, as the primary tool to explore the nature and origin of residual PM receptor profiles.

Principal Component Analysis of PCR Residuals

The list of PCA eigenvalues in Table 5 shows six components rising above the maximum 10% of noise variance possibly hiding in the tail of the variance distribution. The loadings of these six components, together explaining 84.4% of the total variance, reveals the presence of strongly correlated chemical compound suites among the four largest principal components (68.3% total variance) that appear worthy of further investigation.

Table 5. PCA Variance Table for PCR Residuals (First Nine Factors) for Residual Profile Analysis

No.	Eigenvalue	Individual Percent	Cumulative Percent
1	13.30	23.3	23.3
2	11.35	19.9	43.3
3	8.42	14.8	58.0
4	5.87	10.3	68.3
5	5.12	8.99	77.3
6	4.04	7.09	84.4
7	3.07	5.39	89.8
8	2.51	4.4	94.2
9	2.06	3.61	97.8

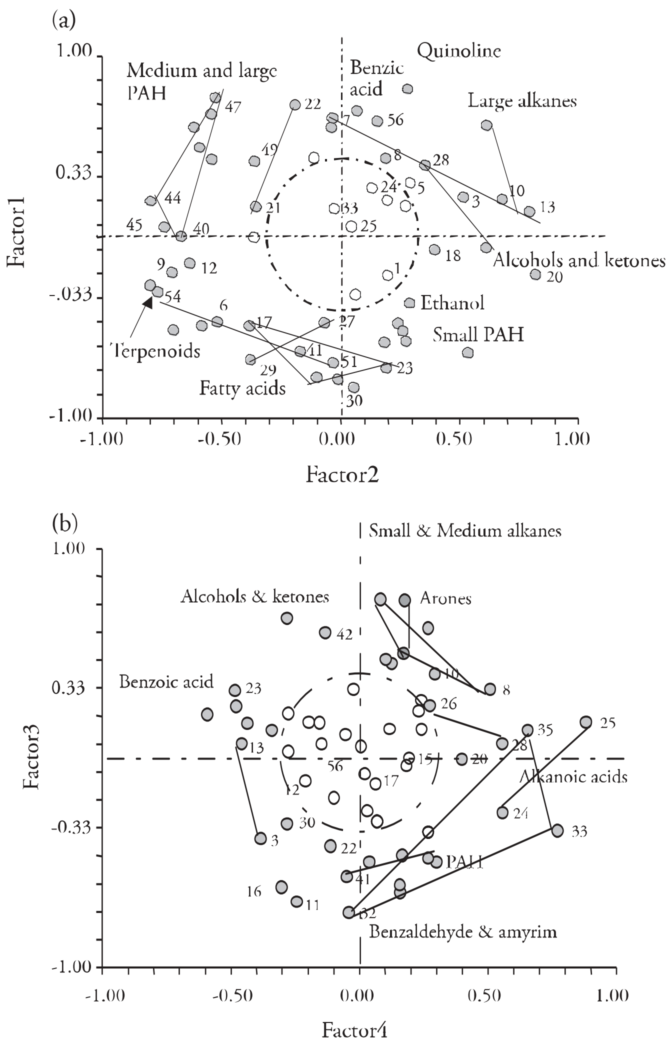
Source: Authors

As is evident from the F1/F2 loadings plot in Figure 6a, the largest of these suites reveals a split between smaller PNAHs on F1-/F2+ and larger PNAHs on F1+/F2-, which is strongly suggestive of some type of overlooked combustion process. Moreover, a combination of fossil hopanoids (associated with fossil engine lubricants or related petroleum products), dehydroabietic acid (often found to correlate with overall PM_{10} levels), and some common aliphatic compounds on F1-/F2- may well represent reaerosolized urban dust, whereas the high loadings of both aromatic nitrogen compounds and benzoic acid on F1+ could point to some type of industrial or agricultural combustion process. Projecting the factor loadings onto F3/F4 (see Figure 6b) reveals marked contributions from various biomarker signals that appear to be split into three different directions:

- The two large fatty acids and the amyrin thought to represent plant material contributions on F4+
- The highly characteristic syringaldehyde marker plus benzoic acid and docosanol on F3-/F4-, pointing to some type of hardwood burning (such as fireplaces)

- The guaiacaldehyde marker plus small PNAHs (including retene) on F3, pointing to biomass, or possibly low-rank coal, combustion

Figure 6. Bivariate Plot of Factor Scores for Residual PCR Profile Data



Notes: (a) F1 vs. F2; (b) F3 vs. F4; gray circles denote sites, white circles denote sources.
Source: Authors

Additional information about the possible nature of these components can be inferred by considering the spatial distributions of the various PM receptor sites, shown by the factor score plots in Figures 7a and 7b. As pointed out before, the factor score plots can be directly overlaid with the corresponding loading plots in order to correlate the known spatial relationships between receptor and source sites with the observed chemical components and trends. A first inspection of the F1/F2 score plot shows a distinct separation between the residual receptor profiles from both sides of the U.S.-Mexican border that is reminiscent of the even more pronounced separation in the original receptor profile data set. This implies that the unexplained portions of the receptor profiles on both sides of the border are clearly different—the missing sources and/or processes on each side of the border expressed in the F1/F2 space show relatively little overlap.

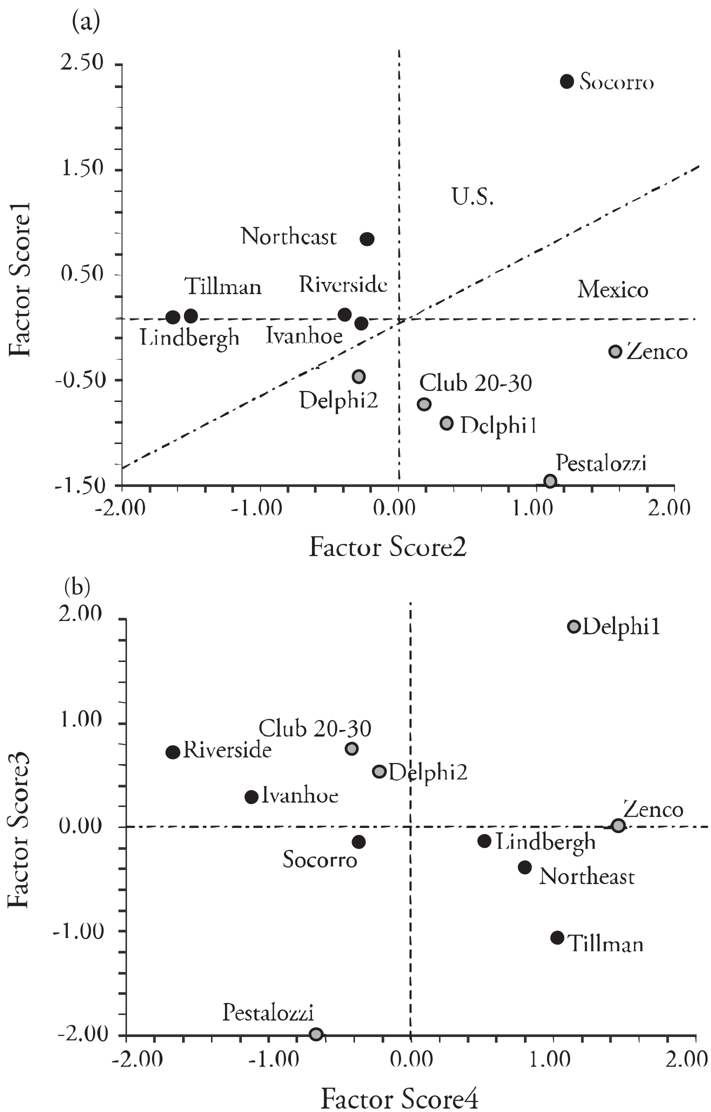
At the same time, however, it is important to note that the residual profiles of the two co-located PM_{10} receptor samples at the Delphi site are no longer as similar as the original profiles. To some extent, this may be explained by the inevitable introduction of a certain amount of error variance during the subtraction procedure used to calculate the residual profiles. However, it is quite possible that some of the missing sources produced relatively large particles that were less evenly distributed over the big high-volume quartz-filters. Note that the direction of separation between the two Delphi samples is roughly aligned with the major difference in larger versus smaller soot-like PNAH compounds.

Finally, attention should be paid to some of the residual receptor profiles that appear to dominate the F1/F2 score space in Figure 7a. In this regard, it is interesting to note that the F1+/F2- position of the large PNAH compound cluster in the loading plot (Figure 6a) does not directly correlate with any receptor sites in the corresponding score plot (Figure 7a). In fact, that quadrant of the score plot is void of high-scoring sites. Since loading plot directions only indicate chemical gradients, negative correlations with low concentrations of a given suite of compounds or positive correlations with high concentrations of the same compound suite can produce exactly the same result. In other words, the most logical explanation of the present observation is to assume that the Pestalozzi site, and to a lesser extent the Zenco, Delphi 1, and Club 20-30 sites, are characterized by relatively high concentrations of smaller PNAH compounds combined with low concentrations of larger PNAHs.

A potential clue to the possible origin of these smaller PNAHs at the Pestalozzi site is the presence of retene, a well-known biomarker for certain types of creosotes formed during wood combustion. It appears to be generally overlooked, however, that considerable amounts of retene can also be formed during combustion of low-rank coals. The combination of relatively high contributions of smaller PNAHs and retene is suggestive of a furnace- or stove-type combustion process in which either wood or low-rank coals are being burned. In this context, the known presence of a college complex at the Pestalozzi site might offer an explanation. Alternatively, some of the brick kilns in this part of the city (see map in Appendix Figure 1 [page 305]) could also produce a possible source. However, the known brick kiln soot contributions at the Advanced Transformer site (not included in the residual study) were seen to be dominated by relatively large PNAH compounds, consistent with the inefficient, open nature of most brick kilns. These were not included because the brick-kiln contributions were represented strongly enough in the original receptor data set to be directly subtracted out by PCR. Nonetheless, it is quite possible that molecular size distributions in PNAH emissions from brick kilns may vary during the various phases of a typical burn characterized by a relatively cool, inefficient start followed by a much hotter bulk combustion phase.

A strongly outlying position in the F1+/F2+ quadrant is occupied by a residual pattern from the Socorro site. Considering the low R^2 value of the Socorro sample in the PCR model, this is not surprising. Yet, the chemical nature of the Socorro residue profile in the F1/F2 space is dominated by benzoic acid, a common combustion product, plus two aromatic nitrogen compounds—quinoline and methylpyrrolidinone—that are often found along the U.S.-Mexican border but have not yet been clearly identified with a particular PM source. Unless further clues emerge about special local sources in Socorro, a speculative assignment would be “industrial combustion source(s), including agricultural burns.”

Figure 7. Bivariate Plot of Factor Loadings for Residual Profile



Notes: (a) F1 vs. F2; (b) F3 vs. F4; gray circles denote Mexican sites, black circles denote U.S. sites.
Source: Authors

Another receptor site's residue can be seen occupying an outlying position on F2+. This Zenco site is characterized by a rather heterogeneous group of straight chain aliphatic compounds, including several fairly large hydrocarbons, one alcohol, and one or two fatty acids. Because of the varying degrees of oxidation, this type of pattern again suggests some type of relatively inefficient combustion process, possibly trash burning (in view of the site location).

Turning attention to the F3/F4 score plot, the earlier-observed split of biomass-related compounds into three subgroups appears to be caused by strong contributions of the hardwood (such as fireplace) compounds to two U.S. sites, namely Riverside and, to a lesser extent, Ivanhoe. This agrees with earlier observations of hardwood combustion products at U.S. receptor sites (Jeon, et al. 2001). Similarly, the Pestalozzi site residue associates again with small PNAHs in combination with a well-known wood combustion marker, guaiacylaldehyde, thereby reinforcing the earlier conclusion about the possible contributions of furnace or stove emissions, whether stoked with wood, low rank coal, or a combination of both.

Finally, the Delphi 1 and Zenco site residues show unmistakable markers for inefficient combustion of plant materials, releasing both large fatty acids and amyrin. This could be due either to agricultural burns or to burning of trash (containing plant constituents) near the sites. Because of the previously noted correlation between open biomass burning and relatively bigger particles, the unusually large distance between the two co-located Delphi site residues in the F3/F4 space could well be due to heterogeneous QF filter deposition. For example, a single 10 μm biomass particle would be expected to produce slightly higher product concentrations during the analytical procedure than 100 2-μm particles of similar origin and composition. Considering the low incidence of particles in the larger size ranges, sampling statistics tends to play a much larger role here.

Conclusions and Recommendations

PCA and PCR of residuals reveal a significant difference between U.S. and Mexican receptor sites. The results also reveal a split between PNAHs and larger PNAHs, suggestive of some type of overlooked combustion process.

Moreover, a combination of fossil hopanoids (associated with engine lubricants or related petroleum products), dehydroabietic acid (often found to correlate with overall PM_{10} levels), and some common aliphatic compounds may well represent reaerosolized urban dust, whereas the high loadings of both aromatic nitrogen compounds and benzoic acid could point to some type of industrial or agricultural combustion process.

Acknowledgments

The authors acknowledge the invaluable help and advice of Wen-Whai Li, Adel Sarofim, Victor Valenzuela, Gerardo Tarín, Bob Curry, Jacek Dworzanski, Wally Jarman, Miguel Zavala, Paul Cole, Christian Kasteler, Tania Espino, Pedro Mora, Kerry Kelly, Dave Wagner, and Jorge Ramses.

References

Adgate, J. L., R. D. Willis, T. J. Buckley, J. C. Chow, J. G. Watson, G. G. Rhoads, and P. J. Lioy. 1998. "Chemical Mass Balance Source Apportionment of Lead in House Dust." *Environmental Science & Technology* 32(1): 108–114.

Anngarn, H. J., G. M. Braga Marcazza, E. Cereda, M. Marchinoni, and A. Zucchiatti. 1992. "Source Profiles by Unique Ratios (SPUR) Analysis: Determination of Source Profiles from Receptor-site Streaker Samples." *Environmental Science & Technology* 26(2): 333–346.

Chakravarty, T. 1993. "Use Canonical Correlation Analysis Instead of Regression." *Chemical Engineering Progress* 89(10): 76–83.

Chow, J. C., J. G. Watson, D. H. Lowenthal, P. A. Solomon, K. L. Magliano, S. D. Ziman, and L. W. Richards. 1992. "PM_{10} Source Apportionment in California's San Joaquin Valley." *Atmospheric Environment* 26(18): 3335–3354.

Chow, J. C., J. G. Watson, D. H. Lowenthal, P. A. Solomon, K. L. Magliano, S. D. Ziman, and L. W. Richards. 1993. "PM_{10} and $PM_{2.5}$ Compositions in California's San Joaquin Valley." *Atmospheric Environment* 18(2): 105–128.

Chow, J. C., D. Fairley, J. G. Watson, R. DeMandel, E. M. Fujita, D. H. Lowenthal, Z. Lu, C. A. Frazier, G. Long, and J. Cordova. 1995. "Source Apportionment of Wintertime PM_{10} at San Jose, Calif." *Journal of Environmental Engineering* 121(5): 378–387.

Chow, J. C., J. G. Watson, D. H. Lowenthal, B. Bates, W. Oslund, and G. Torres. 2000. "Cross-Border Transportation and Spatial Variability of Suspended Particles in Mexicali and California's Imperial Valley." *Atmospheric Environment* 34(11): 1833–1843.

Chow, J. C., and J. G. Watson. 2002. "Review of $PM_{2.5}$ and PM_{10} Apportionment for Fossil Fuel Combustion and Other Sources by Chemical Mass Balance Receptor Model." *Energy and Fuels* 16(2): 222–260.

Chow, J. C., J. G. Watson, S. A. Edgerton, and E. Vega. 2002. "Chemical Composition of $PM_{2.5}$ and PM_{10} in Mexico City during Winter 1997." *Science of the Total Environment* 287(3): 177–201.

Chow, J. C., J. G. Watson, K. F. Ho, and S. C. Lee. 2003. "Characterization of PM_{10} and $PM_{2.5}$ Source Profiles for Fugitive Dust in Hong Kong." *Atmospheric Environment* 37(8): 1023–1032.

Dworzanski, J. P., S. N. Thornton, D. J. Wager, W. H. McClennen, and H. L. C. Meuzelaar. 1997. "Environmental Monitoring of Organic Aerosols and Vapors by GC/MS through Preconcentration, Thermal Flash Deportion and Pyrolysis Techniques." Presented at the 1996 Specialist Workshop on Field-Portable Chromatography & Spectrometry, 3–5 June, Snowbird, Utah.

Fujita, E. M., Z. Lu, N. F. Robinson, and J. G. Watson. 1996. "Application of the Chemical Mass Balance Model to Coast Oxidant Assessment for Southeast Texas Volatile Organic Compound Data." *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition* 96-FA149.03. Pittsburgh: A&WMA.

Fujita, E. M., J. G. Watson, J. C. Chow, and Z. Lu. 1994. "Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Southern California Air Quality Study." *Environmental Science & Technology* 28(9): 1633–1649.

Fujita, E. M., J. D. McDonald, T. L. Hayes, B. Zielinska, J. C. Sagebiel, J. C. Chow, and J. G. Watson. 1998. "Northern Front Range Air Quality Study: Apportionment of Carbonaceous Particles." *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition* 98-TP 43.04. Pittsburgh: A&WMA.

Fraser, Z. W., and B. B. Yue. 2003. "Source Apportionment of Fine Particulate Matter in Houston, TX, Using Organic Molecular Markers." *Atmospheric Environment* 37(15): 2117–2123.

Fraser, M. P., and K. Lakshmanan. 2000. "Using Levoglucosan as a Molecular Marker for the Long-Range Transport of Biomass Combustion Aerosols." *Environmental Science & Technology* 34(21): 4560–4564.

Hintze, J. L. 1997. *NCSS User's Guide.* Kaysville, Utah: NCSS

Hopke, P. K., ed. 1991. *Receptor Modeling for Air Quality Management.* Amsterdam: Elsevier.

Javitz, H. S., J. W. Watson, J. P. Guertin, and P. K. Mueller. 1988. "Results of a Receptor Modeling Feasibility Study." *Journal of the Air Pollution Control Association* 38(5): 661–667

Jeon, S. J., H. L. C. Meuzelaar, S. A. N. Sheya, J. S. Lighty, W. M. Jarman, C. Kasteler, and A. F. Sarofim. 2001. "Exploratory Studies of PM_{10} Receptor and Source Profiling by GC/MS and Principal Component Analysis of Temporally and Spatially Resolved Ambient Samples." *Journal of the Air & Waste Management Association* 51: 174–185.

Jeon, S. J., H. L. C. Meuzelaar, S. A. N. Sheya, J. S. Lighty, W. M. Jarman, C. Kasteler, and A. F. Sarofim. 2001. "PM_{10} Receptor and Source Profiling by GC/MS and Principal Component Analysis of Temporally and Spatially Resolved Ambient Samples." *Journal of the Air & Waste Management Association* 51: 766–784.

Johnson, R. B. 1997. *Applied Multivariate Statistical Analysis.* Upper Saddle River, N.J.: Prentice Hall.

McDonald, J., B. Zielinska, E. Fujita, J. Chow, J. Watson, J. Sagebiel, L. Sheetz, and S. Batie. "Chemical Speciation of $PM_{2.5}$ Emissions from Residential Wood Combustion and Meat Cooking." *Proceedings of the Air & Waste Management Association's Annual Meeting & Exhibition* 98-RP 92B.02. Pittsburgh: A&WMA.

NCSS. 2000. *Statistical software package.* Kaysville, Utah: NCSS.

Polissar, A. V., P. K. Hopke, and R. L. Poirot. 2001. "Atmospheric Aerosol Over Vermont: Chemical Composition and Sources." *Environmental Science & Technology* 35(23): 4604–4621.

Pope, C. A. 2002. "Lung Cancer, Cardiopulmonary Mortality, and Long-Term Exposure to Fine Particulate Air Pollution." *Journal of the American Medical Association* 287: 1123–1141.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1991. "Source of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations." *Environmental Science & Technology* 25(6): 1112–1125.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1993a. "Source of Fine Organic Aerosol. 2. Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks." *Environmental Science & Technology* 27(4): 636–651.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1993b. "Source of Fine Organic Aerosol. 3. Road Dust, Tire Debris, and Organometallic Brake Lining Dust: Road as Sources and Sinks." *Environmental Science & Technology* 27(9): 1892–1904.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1993c. "Source of Fine Organic Aerosol. 4. Particulate Abrasion Products from Leaf Surfaces of Plants." *Environmental Science & Technology* 27(13): 2700–2711.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1993d. "Source of Fine Organic Aerosol. 5. Natural Gas Home Appliances." *Environmental Science & Technology* 27(13): 2736–2744.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1994. "Source of Fine Organic Aerosol. 6. Cigarette Smoke in Urban Atmosphere." *Environmental Science & Technology* 28(7): 1375–1388.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1997. "Source of Fine Organic Aerosol. 7. Hot Asphalt Roofing Tar Pot Fumes." *Environmental Science & Technology* 31(10): 2726–2730.

Rogge, W. F., L. M. Hildemann, M. A. Mazurek, and G. R. Cass. 1998. "Source of Fine Organic Aerosol. 9. Pine, Oak, and Synthetic Log Combustion in Residential Fireplaces." *Environmental Science & Technology* 32(1): 13–22.

Schauer, J. J., W. F. Rogge, G. R. Cass, L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. 1996. "Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers." *Environmental Science & Technology* 30(22): 3837–3855.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit. 2001. "Measurement of Emissions from Air Pollution Sources. 5. C1-C32 Organic Compounds from Fireplace Combustion of Wood." *Environmental Science & Technology* 35(9): 1716–1728.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit. 2002. "Measurement of Emissions from Air Pollution Sources. 5. C_1-C_{32} Organic Compounds from Gasoline-Powered Motor Vehicles." *Environmental Science & Technology* 36(6): 1169–1180.

Schauer, J. J., and G. R. Cass. 2000. "Source Apportionment of Wintertime Gas-Phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers." *Environmental Science & Technology* 34(9): 1821–1832.

Seigneur, C., P. K. Hopke, P. Paatero, and E. S. Edgerson. 1999. "Modeling Atmospheric Particulate Matter." *Environmental Science & Technology* 33(3): 80–85.

Sheya, S. A. 2002. "Development of Thermal Desorption Gas Chromatography/Mass Spectrometry as a Rapid Method for Ambient Particulate Characterization." Ph.D. diss., Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah.

Simoneit., B. R. T., J. J. Schauer, C. G. Nolte, D. R. Oros, V. O. Elias, M. P. Frase, W. F. Rogge, and G. R. Cass. 1999. "Levoglucosan, a Tracer for Cellulose in Biomass Burning and Atmospheric Particles." *Atmospheric Environment* 33(2): 173–182.

Watson, J. G., N. F. Robinson, E. M. Fujita, J. C. Chow, T. G. Pace, C. Lewis, and T. Coulter. 1998 "CMB Applications and Validation Protocol for $PM_{2.5}$ and VOCS." Desert Research Institute Document No. 1808.2D1. http://www.dri.edu.

Westad, F., and M. Kermint. 2003. "Cross Validation and Uncertainty Estimates in Independent Component Analysis." *Analytica Chimica Acta* 490(1): 341–354.

Windig, W., T. Chakravarty, J. M. Richards, and H. L. C. Meuzelaar. 1986. "Multivariate Analysis of Time-Resolved Mass Spectral Data." *Analytica Chimica Acta* 191: 205–218.

Windig, W., and H. L. C. Meuzelaar. 1987. "Numerical Extraction of Components from Mixture Spectra by Multivariate Data Analysis." Pages 67–102 in *Computer-Enhanced Analytical Spectroscopy,* H. L. C. Meuzelaar and T. L. Meuzelaar, eds. New York: Plenum Publishing Co.

Xin, H. S., and P. K. Hopke. 1996. "Solving the Chemical Mass Balance Problem Using and Artificial Neural Network." *Environmental Science & Technology* 30(2): 531–535.

Xhoffer, C., P. Bernard, and R. Van Grieken. 1991. "Chemical Characterization and Source Apportionment of Individual Aerosol Particles over the North Sea and the English Channel Using Multivariate Techniques." *Environmental Science & Technology* 25(8): 1470–1478.

Appendix A

Principal Component Analysis Results of 1998 Receptor Data

The scatter plot of the scores in the F1/F2 space (Figure A1a), together explaining 70% of the total variance in the combined (receptor + source) data set, reveals a major problem in that the receptor sample profiles are clustered relatively tightly outside the source sample pattern envelope. Clearly, the main source of variance in the data set is caused by differences between the source and receptor sample profiles rather than by the common sources of variance needed for successful modeling attempts. Moreover, even if the receptor profiles would be less tightly clustered and exhibit some common variance with the source group in the F1/F2 space, the then-lack of major overlap between both domains would still force the models to extrapolate, rather than interpolate, thereby greatly reducing the predictive value of the results.

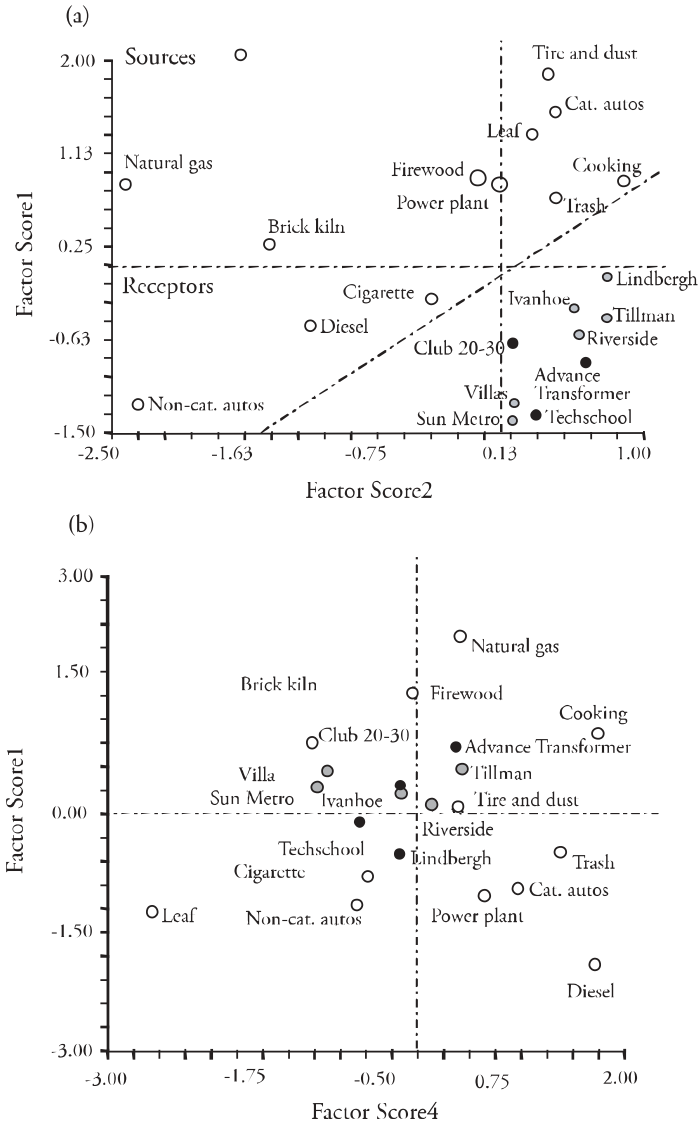
Careful inspection of the corresponding factor loadings in the F1/F2 space (Figure A2a) reveals that the major chemical trends separating the two domains represent increased relative concentrations of most of the larger aliphatic and aromatic hydrocarbon compounds, as well as a few of the smaller alkanes. This finding confirms the loss of substantial volatile compound fractions from the small QF filter strips used for TD-GC/MS analysis while waiting for the time-consuming solvent extraction procedures to be completed on the remainder of the filters, as already reported by Jeon, et al. (2001). Although MDA techniques such as the canonical correlation methods reported by Chakravarty (1993) could be used to correct for systematic bias of the type encountered here, the large fraction of variance requiring some type of "surgical" correction is likely to bias the data too much to prevent identification of important smaller features and trends. Consequently, the research team decided to use the 1998 receptor sample in a stand-alone fashion rather than in combination with source data sets. This allowed a closer look at some of the source attribution information first examined by Jeon (2001).

A scatter plot of the F1/F2 scores in Figure A1a, representing 34.5% of the total variance, reveals that a simple 30-degree counterclockwise rotation of the F1/F2 space would produce a complete separation between the U.S. and Mexican receptor sites along a single axis. In view of well-known differences in anthropogenic PM emission sources—automotive exhaust, cooking, brick kilns, and trash burns, among others—this finding is not unexpected. Yet, it suggests a strong effect of local PM emission sources on PM receptor composition, even for closely neighboring sampling sites, thus fulfilling one of the main requirements for PCA-based source attribution, namely that there needs to be sufficient source-related variance in the data to enable successful decomposition of complex mixture spectra into their underlying component patterns.

A closer look at Figure A1a fails to reveal any direct correspondence with the actual geographic locations of the various sites. While the "F1/F2 space border" between the United States and Mexico is more clear cut than its rather contorted geographic counterpart, a lack of separation between some geographically well-separated sites, and vice versa, is noted. In light of the geographically heterogeneous distribution of known PM sources, which prevents the establishment of simple linear gradients likely to produce prominent PCA components, this lack of correspondence is not surprising.

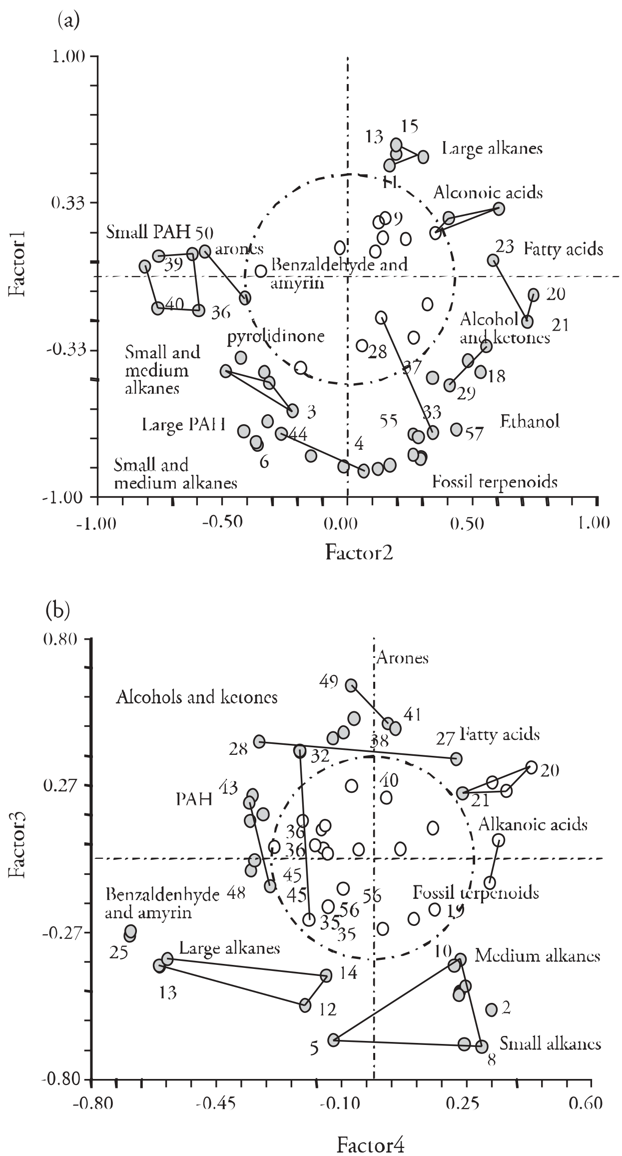
The F1/F2 loading plot in Figure A2a reveals the main chemical trends underlying the observed relationships between the 12 receptor profiles in Figure A1a. Note that the circle occupying the center of Figure A2a envelopes all compounds with loadings <0.4, which are presumed to be indistinguishable from the chemical background noise in the F1/F2 space and therefore not labeled individually. Although it has long been customary to talk about factor "loading space" versus "score space," it is important to understand that Figures A1a and A2a can actually be superimposed (if properly scaled), as they reflect the projections of objects (receptor profiles) and variables (chemical compounds) coexisting in multidimensional data space onto the same two-dimensional F1/F2 subspace.

Figure A1. Bivariate Plot of Factor Scores for Original Receptor Data Set (December 1998)



Notes: (a) F1 vs. F2; (b) F3 vs. F4; gray circles denote Mexican sites, black circles denote U.S. sites, white circles denote sources.
Source: Authors

Figure A2. Bivariate Plot of Factor Loadings for Original Receptor Data Set (December 1998)



Notes: (a) F1 vs. F2; (b) F3 vs. F4; gray circles denote chemical compounds with higher variance, white circles denote compounds with lower variance.
Source: Authors

To highlight the chemical components in Figure A2a underlying the observed separation between U.S. and Mexican receptor samples, look in a direction orthogonal to the imaginary factor space "border" seen in Figure A1a. This shows that the Mexican samples are especially rich in medium-sized aromatic and aliphatic hydrocarbons, whereas U.S. samples contain more hopanes, small aromatic, and aliphatic hydrocarbons, as well as arones. These chemical differences appear to be combustion-related and are consistent with the prominent use of soot-generating open burning (brick-kilns, trash, biomass) on the Mexican side of the border.

By contrast, receptor patterns on the U.S. side are dominated by mobile sources emitting smaller products of incomplete combustion (PICs) as well as fossil engine-oil markers (hopanes) and possible products of incomplete catalytic conversion (such as arones). Nearly orthogonal to these prominent chemical trends there appears to be a set of medium-sized fatty acids generally associated with cooking and, on the opposite side, a suite of aliphatic alcohols and ketones often associated with biomass burning. The fact that both components more or less straddle the imaginary "border" may indicate that the underlying sources are active on both sides while still allowing for relatively subtle variations in the corresponding source patterns on each side.

It is important to point out that only relative, rather than absolute, differences in chemical composition are shown in the F1/F2 space. Since there are currently no reliable procedures available to determine the precise weight of PM deposits on the specially cleaned high-volume QF filters used for these experiments, the summed peak intensities for each receptor profile were normalized to 100%. Therefore, it is certainly possible—and even likely—that the contributions from soot-producing open burn sources on the Mexican side are high enough to make the relative concentrations of hopanes and other mobile source products appear lower than on the U.S. side.

Figures A1b and A2b show the respective factor score and loading scatter plots in the F3/F4 space, explaining 24.5% of the total variance, thus bringing the fraction of total variance explained by the largest four principal components to approximately 65%. This space is dominated by chemical gradients thought to be associated with reaerosolized dust, waste burning, and fugitive fuel vapor emissions.

Appendix B

Principal Component Analysis Results of 2001 Receptor Data

As shown by Figures B1 and B2, the structure of the combined data space spanned by the six most prominent factors confirms the working hypothesis underlying all source attribution studies, namely that—at first approximation—PM receptor samples can be regarded as linear combinations of the selected source profiles. The occurrence of large triangles in all three two-dimensional score plots (Figures B1a, B1b, and B1c), together helping visualize the six largest orthogonal dimensions in the data space, is no coincidence—it highlights a fundamental property of data spaces composed by normalized measurement variables. Whereas three variables normalized to 100% will produce a ternary diagram and four variables will form a tetrahydron, a normalized data space formed by more than four variables will take the shape of a so-called hypertetrahydron.

As demonstrated by Windig and Meuzelaar (1987), the largest principal components (i.e., directions of maximum correlated variance) tend to orient themselves toward the apices and vertices of such data spaces, frequently producing near-perfect ternary diagram projections in selected two-dimensional score plots. Often, this tendency is further enhanced by the use of the Varimax rotation method to find directions in which maximum contrast is seen between variables with high and low loadings—directions in which major underlying chemical components, trends, or gradients tend to present themselves.

Overall evaluation of the combined factor space suggests that 10% to 15% of the correlated receptor profile variance are not explained by the eight source patterns and therefore may be derived from “missing sources.” Moreover, an additional 5% to 10% of the total variance in the combined (receptor + source) data set has a random character and appears to represent noise.

Armed with this background information, the researchers examined the F1/F4 and F2/F5 score and loading plots, together representing nearly 50% of the total variance in the data set. Both plots exhibit triangular domains with source patterns at the apices while the receptor profiles, as well as the remaining source patterns, are distributed within the ternary diagram formation or are straddling the vertices. Finding the brick kiln source pattern at the lower apex of the first triangle in Figure B1a, it comes as no surprise that the closest receptor profile is the Advanced Transformer site located directly adjacent to a major brick kiln cluster in Ciudad Juárez, from which the source sample was obtained. The corresponding F1/F4 loading plot (Figure B1a) shows the dominant PAH compound contributions characteristic of the soot emissions for which brick kilns at the U.S.-Mexican border are notorious.

The Club 20-30 site also exhibits some variance in the direction of the brick kiln emission pattern. However, the Club 20-30 receptor profile effectively straddles the vertex connecting the brick kiln and cooking apices, thereby suggesting contributions from both sources and little, if any, from the autos with catalytic converter sources at the third apex. Interestingly, four U.S. receptor sites—Ivanhoe, Socorro, Tillman, and Riverside—all appear to have contributions from cooking source emissions, identified in the corresponding loading plot as rich in fatty acids as well as aliphatic alcohols and ketones. The trash source emission pattern being found relatively close to the cooking pattern in this projection is understandable in view of the fact that the "trash" burned contained substantial amounts of kitchen disposal waste.

With the exception of the bridge and diesel truck source patterns, few, if any, patterns appear to exhibit higher-than-average autos with catalytic converter emission contributions. These emissions contain relatively high amounts of hydrocarbon oxidation products ranging from small fatty acids to benzoic acid and trimethylbenzaldehyde, in addition to the fossil terpenoids (e.g., hopanes) known to be ubiquitous for mobile sources using fossil lubricants.

The F2/F5 score plot in Figure B1b can be similarly analyzed, with its apices occupied by diesel truck, wood burning, and trash source patterns, respectively. The position of the bridge source sample outside the triangle is probably due to a combination of shared

Figure B1. Bivariate Plot of Factor Scores for New Receptor Data Set (January 2001)

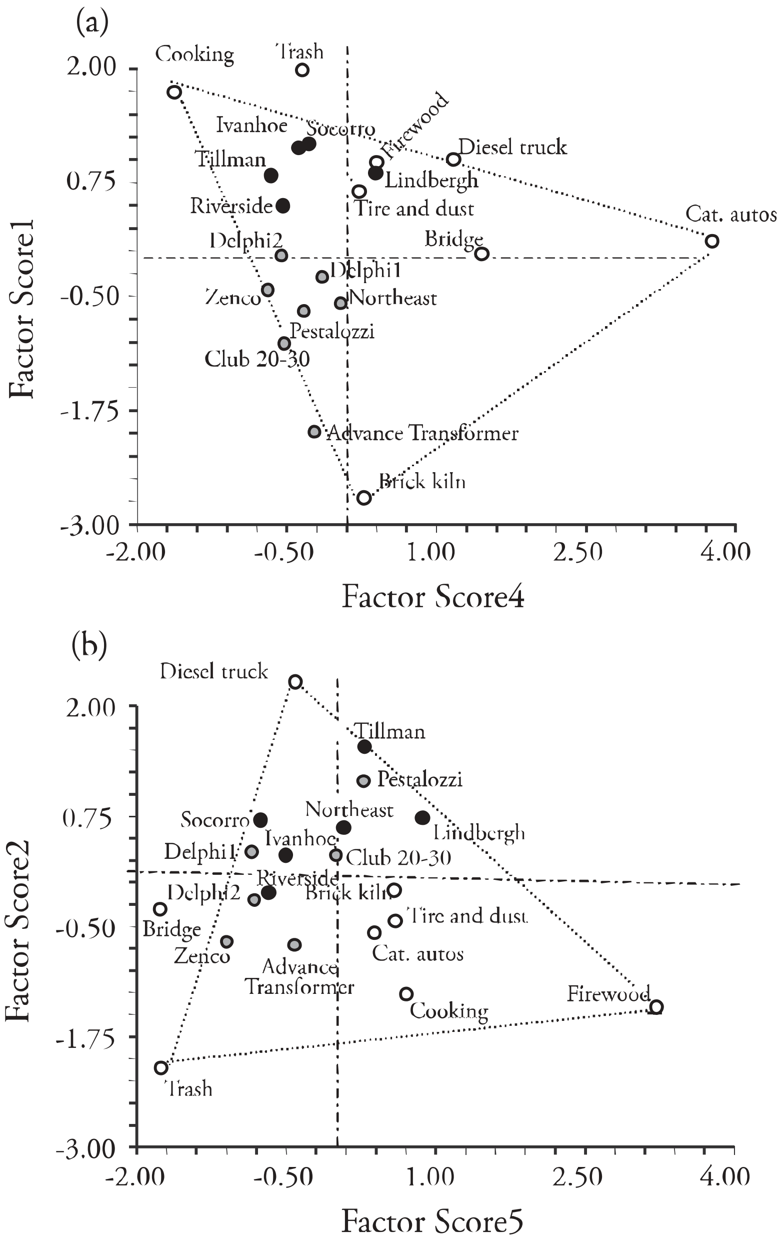
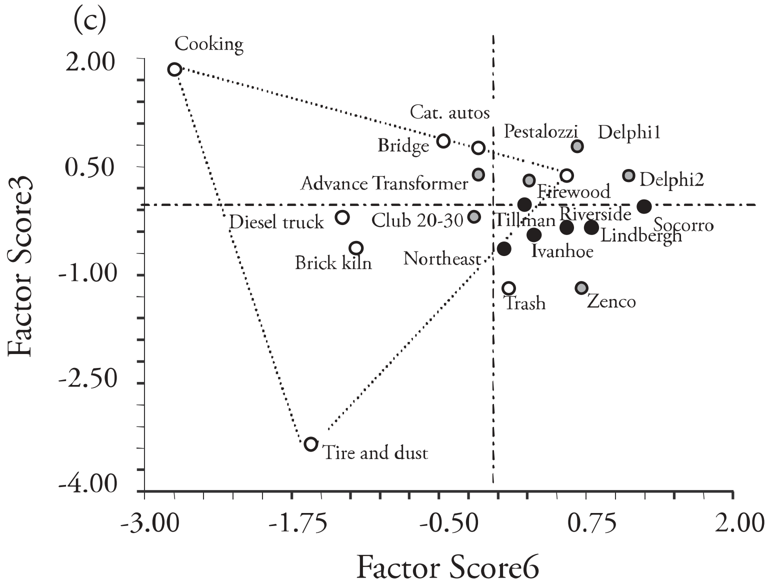


Figure B1. continued



Notes: (a) F1 vs. F4; (b) F2 vs. F5; (c) F3 vs. F6; gray circles denote Mexican sites, black circles denote U.S. sites, white circles denote souces.
Source: Authors

Figure B2. Bivariate Plot of Factor Loadings for New Receptor Data Set (January 2001)

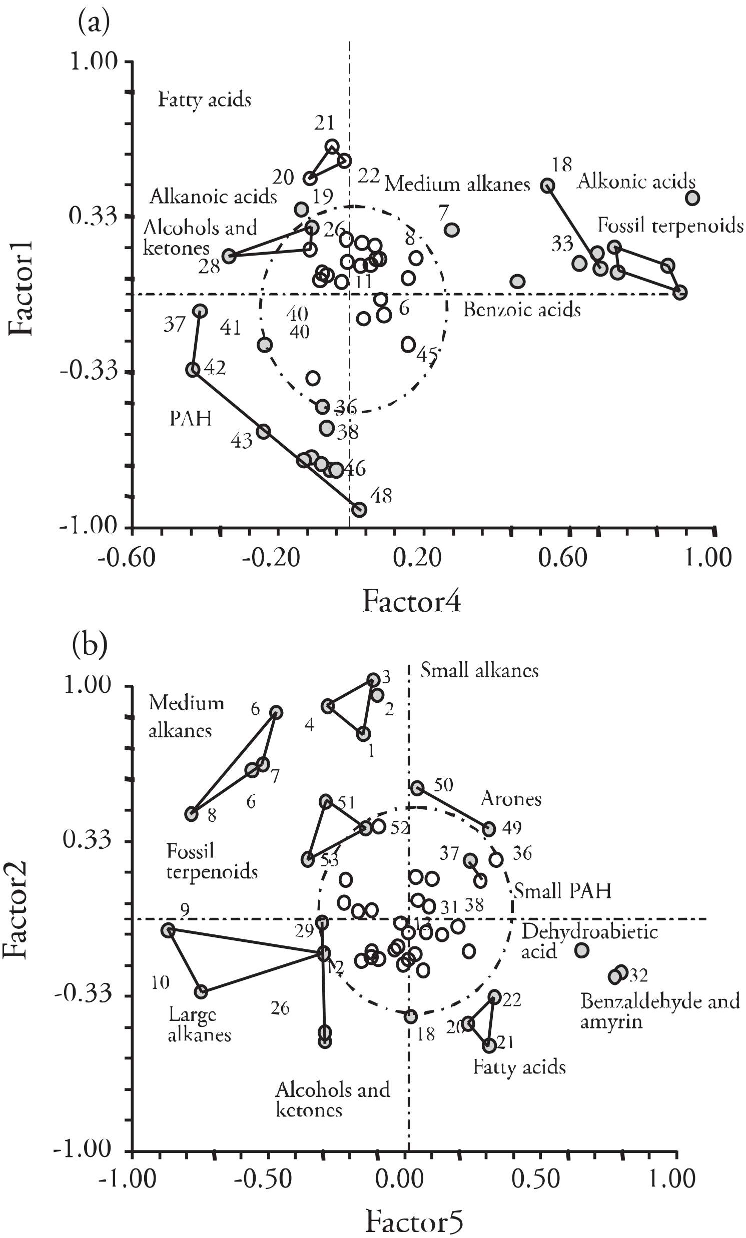
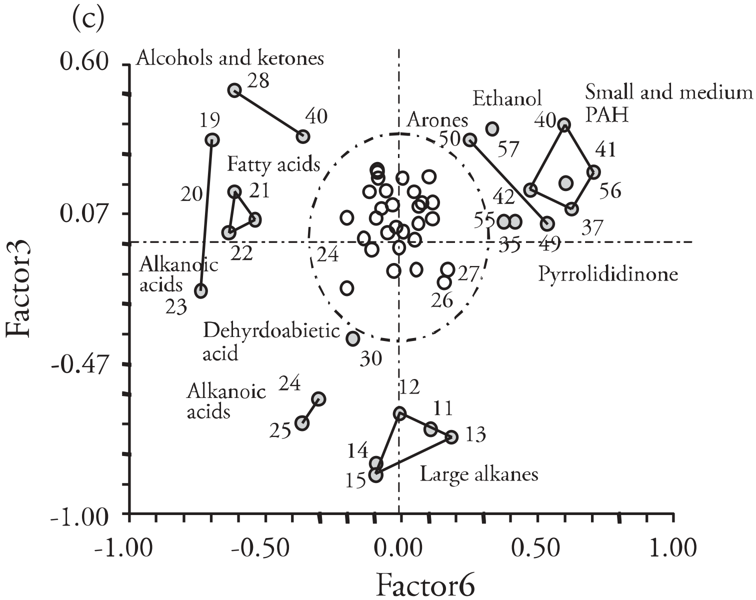


Figure B2. continued



Notes: (a) F1 vs. F4; (b) F3 vs. F5; (c) F3 vs. F6; gray circles denote chemical compounds with higher variance, white circles denote compounds with lower variance.
Source: Authors

variance with both apex sources and shows that orthogonal Varimax rotations do not necessarily produce perfect ternary diagram configuration. Furthermore, receptor profiles such as Advanced Transformer and Zenco show modest variance levels in the direction of the trash emissions (in this projection they were found to correspond with high levels of larger alkanes and some alcohols and ketones) whereas receptor profiles from the Tillman, Pestalozzi, and Lindbergh sites suggest a combined contribution from wood-burning smoke (characterized by substituted phenols plus fatty acids) and diesel truck emissions (corresponding to high alkane and fossil terpenoid concentrations in the loading plot).

The F3/F6 score plot in Figure B1c deserves special attention because it demonstrates how the F3 factor score extremes are still dominated by source patterns, with cooking topping the F3+/F6- variance direction. This demonstrates that not all of its variance is explained by F1+, as confirmed by the corresponding loading plot in Figure B2a, where tire and dust source emissions score strongly on F3- while exhibiting the large alkane and fatty acid signals characteristic of plant residues. In addition, the dehydroabietic acid signal often exhibits strong correlations with measured ambient PM concentrations (Sheya 2002) due to its presence in both plant residues and car tires. Neither of these two source components appears to have a strong "following" among the 12 receptor samples.

A real nugget of information about this high-dimensional data space is found in Factor 6, explaining 12.7% of the total variance in the data set. The positive component of this factor clearly represents chemical trends in the receptor profiles of several U.S. (Socorro, Lindbergh, Ivanhoe) and Mexican (Delphi) sites that do not exist among the eight source profiles. Consequently, the researchers observed a group of receptor sample profiles "breaking out" of the confines of the multidimensional source pattern domain. Clearly, one or more relevant source patterns appear to be missing here.

The loading plot (Figure B2c) shows contributions of some small to medium alkanes and PAHs (including retene), as well as heteroatomic compounds (such as phenalenone, anthracenedione, butoxyethoxyethanol, quinoline, and methylpyrrolidine) plus a plant terpenoid (amyrin), all of which may provide valuable clues about the nature and composition of any missing sources. Although some compounds are rather suggestive of biomass combustion emissions, the aromatic nitrogen compounds and butoxyethoxyethanol could also point to industrial sources.

VII

Estimating Particulate Matter Exposure Risks and Evaluating Health Effects of Evening Particulate Matter Peaks Using GIS-Referenced Data Fusion Methods: A Pilot Study

H. L. C. Meuzelaar, N. S. Arnold, B. Nookala, G. M. Mejía Velázquez, P. O. Medina, J. Ramses-Sánchez, W.-W. Li, J. J. Bang, H. J. S. Fernando, and S.-M. Lee

Abstract

Although far from comprehensive with regard to temporal and spatial coverage, the first geographic information system (GIS)-referenced database on Paso del Norte air quality parameters and impacts is already facilitating development of a variety of advanced models, including diagnostic meteorological models and particulate matter (PM) source and receptor models. When used in conjunction with each other, these models shed light on some of the complex atmospheric transport, reaction, and deposition processes that have confounded past attempts at understanding and predicting Paso del Norte air quality problems in general and fluctuations in ambient PM composition and concentrations in particular.

A typical example is provided by the now-widely recognized evening PM events in the Paso del Norte airshed discussed herein. In combination with the novel, GIS-referenced health risk exposure modeling techniques demonstrated by Mejía and co-workers in this chapter, the advanced diagnostic meteorological models developed by Fernandez and co-workers, also detailed in this chapter, promise to provide key information about atmospheric transport mechanisms linking source-rich PM emission areas with vulnerable receptor sites.

In the course of this research, it was found that all peri-metropolitan particulate matter (or $\{PM\}^2$) episodes recorded thus far reveal a common pattern of near-windless, nocturnal conditions with falling ambient temperatures and low to zero mixing layer heights. In the summer months, the enormous quantities of PM produced by a bustling Mexican border metropolis during the evening traffic peak generally have a chance to disperse before pronounced atmospheric cooling and decreasing mixing layer heights produce stagnant conditions. During the winter months, however, reduced solar heating and early sunsets tend to produce stagnant conditions well before the evening traffic peak is over. This causes the trapping of a thin, high-density PM blanket close to the ground.

During the evening, the dense, low PM cloud tends to move slowly across adjacent suburban and rural areas, driven by nocturnal drainage flows and other low velocity winds, thereby creating the observed $\{PM\}^2$ events. Additionally, there are likely to be episodes in which the PM cloud remains entirely stagnant, thus not leading to marked PM increases outside the perimeter. Moreover, due to their transient nature, many nocturnal $\{PM\}^2$ events and their urban parent episodes will tend to remain hidden in conventional 24-hour PM_{10} and $PM_{2.5}$ (PM with an aerodynamic diameter of 10 micrometers [µm] and 2.5 µm, respectively) statistics.

Researchers also found that zones of higher individual risk for all population groups are located south and southwest of the Paso del Norte region where hazard coefficient (HC) values exceed 1.0 for chronic PM_{10} exposure. Because of the high population density in Ciudad Juárez, the highest social risk areas are also located south and southwest of the Paso del Norte region. In addition, integrated source-receptor models can help identify and apportion potentially harmful PM sources, thereby providing a more reliable basis for future actions to reduce pollution in the region. Finally, GIS-referenced data collection and modeling approaches have proven excellent tools for air quality data management and visualization, thereby facilitating effective communication of health risks to non-experts.

Preliminary cardiopulmonary monitoring of subjectively healthy people is testing the now more widely supported hypothesis that severe transient PM episodes not only can have disproportionally large effects on very young or old patients with compromised cardiopulmonary systems, but may perhaps have measurable (patho)physiological effects on relatively healthy subjects. The use of multiple time-series of complete, Fourier-transformed electrocardiogram (ECG) profiles and moment-transformed spirometry profiles, obtained on test subjects exposed to ambient PM levels in the field at 30-minute intervals, produced a wealth of data about rapid physiological response and control phenomena at time scales fast enough to resolve not only variations in the repetition rate between different profiles but also size and shape variations within a single ECG or spirometry profile.

Of five subjectively healthy test subjects in their 20s exposed to ambient PM levels at the Sodar site, one 25-year-old overweight male in relatively poor physical condition showed strong spontaneous associations between PM levels and ECG and spirometry time-series results in a combined Karhunen Loeve principal component plot. Subsequent principal component regression, using tapered element oscillating microbalance (TEOM)-recorded ambient $PM_{2.5}$ concentrations as the dependent variable, produced R^2 values of 90.9% (99.9% confidence level; F-ratio 10.0) for ECG profiles and 83.4% (99.7% confidence level; F-ratio 7.2) for the corresponding spirometry profiles of this test subject, as recorded during the occurrence of a typical, strong evening PM peak matched with a low-PM control evening.

Most potential causes of spurious and/or trivial correlations appear to be ruled out by meta-analysis of the test results, including comparison of principal component regression results with low PM control evening data and physiological interpretation of the correlating ECG and spirometry features. The fact that incremental, 30-

minute time offsets in both directions weaken the observed correlations indicates the presence of a relatively fast physiological response mechanism.

Estimando Riesgos de Exposición a la Materia Particulada y Evaluando Efectos en la Salud de Picos de Materia Particulada al Atardecer Utilizando Métodos de Fusión de Datos: Un Estudio Piloto

H. L. C. Meuzelaar, N. S. Arnold, B. Nookala, G. M. Mejía Velázquez, P. O. Medina, J. Ramses-Sánchez, W.- W. Li, J. J. Bang, H. J. S. Fernando, y S.-M. Lee

Resumen

Aunque lejos de ser comprensivo en lo que respecta a cobertura temporal y espacial, el primer Sistema De Información Geográfico (GIS) de base de datos de referencia e impactos de parámetros de calidad de aire en el Paso del Norte ya facilita el desarrollo de una variedad de modelos avanzados, incluyendo modelos de diagnósticos meteorológicos así como de fuentes y receptores de materia particulada PM. Al ser utilizados en conjunción uno con el otro, estos modelos nos dan información sobre algunos de los procesos complejos de transporte atmosférico, de reacción, y depositación que han confundido intentos previos por entender y predecir problemas de calidad de aire y fluctuaciones en la composición del PM ambiental y sus concentraciones en particular en el Paso del Norte.

Un ejemplo típico lo proporcionan los acontecimientos ahora ampliamente reconocidos de PM al atardecer en la cuenca del Paso del Norte (discutido en este artículo). En combinación con las nuevas técnicas de modelado de referencia GIS para riesgo de salud por exposición demostradas por Mejía y coautores de este capítulo, los modelos avanzados de diagnóstico meteorológico desarrollados por Fernandez y coautores, también incluidos en este capítulo, prometen proveer información crucial acerca de mecanismos de transporte atmosférico que relacionan áreas de abundante emisión de PM con sitios receptores vulnerables.

En el transcurso de esta investigación, se encontró que todos los episodios de materia particulada peri-metropolitana ($\{PM\}^2$) registrados hasta ahora revelan un patrón común en condiciones nocturnas de vientos bajos y temperaturas ambientales descendentes y alturas de zona de mezcla bajos a cero. En los meses de verano, las enormes cantidades de PM producidas por una metrópoli mexicana fronteriza acarreada durante horas pico de tráfico en la noche generalmente tienen posibilidad de dispersarse antes de que el enfriamiento atmosférico pronunciado y el decrecimiento del estrato de mezcla produzcan condiciones estancadas. Sin embargo, durante los meses de invierno las puestas de sol tempranas y el reducido calor solar tienden a producir condiciones de estancamiento mucho antes de que las horas pico de tráfico vespertino terminen. Esto causa el atrapamiento de una capa delgada de PM de alta densidad cerca del suelo.

Durante la tarde, la densa nube baja de PM tiende a avanzar lentamente a través de las áreas suburbanas y rurales adyacentes, conducidas por flujos de drenaje nocturnos y vientos de velocidad baja, y por consiguiente creando los eventos de $\{PM\}^2$ observados. Adicionalmente, es probable que haya episodios en los cuales la nube de PM permanezca completamente estancada, y por lo tanto no llevando a incrementos de PM fuera del perímetro. Además, debido a su naturaleza transitoria, muchos acontecimientos de $\{PM\}^2$ nocturnos y sus episodios urbanos relacionados tenderán a permanecer escondidos en estadísticas convencionales de 24 horas de PM_{10} y $PM_{2.5}$ (PM con diámetro aerodinámico de 10 micras [µm] de diámetro y 2.5 µm, respectivamente).

Los investigadores también encontraron que las zonas de mayor riesgo individual para todos los grupos de población se encuentran ubicados al sur y suroeste de la región Paso del Norte donde los valores de coeficiente de riesgo (HC) excedían el 1.0 para exposición crónica de PM_{10}. A causa de la alta densidad de población en Ciudad Juárez, las áreas de más alto riesgo social también se encuentran localizadas al sur y sudoeste de la región Paso del Norte. Además, modelos de receptores de fuentes pueden ayudar a identificar y ponderar fuentes potencialmente dañinas, proporcionando con esto una base más confiable para acciones futuras de reducción de contaminación del medio ambiente en la región. Por último, los enfoques de obtención de datos con referencia en Sistemas de Información Geográfica y modelado han probado ser herramientas excelentes para la administración de datos de calidad del aire y visualización, facilitando por consiguiente la comunicación efectiva de riesgos para la salud a no-expertos.

El monitoreo preliminar cardiopulmonar de personas subjetivamente saludables está probando la, ahora más ampliamente soportada hipótesis, de que los episodios transitorios severos de PM no sólo pueden tener efectos grandes desproporcionados en pacientes muy jóvenes o viejos con sistemas cardiovasculares delicados, sino quizá puede tener efectos fisiológicos medibles en sujetos relativamente saludables. El uso de múltiples series transformadas de Fourier de perfiles de electrocardiogramas (ECG) y perfiles de espirometría de momento-transformado, obtenidas en sujetos experimentales expuestos a niveles ambientales de PM en el campo en intervalos de 30 minutos, produjo una riqueza de datos acerca de fenómenos de respuesta fisiológica rápida y control en períodos de tiempo lo suficientemente rápidos como para resolver no sólo variaciones en la frecuencia de repetición entre perfiles diferentes sino también variaciones en tamaño y forma dentro de un solo perfil de ECG o de espirometría.

De cinco sujetos experimentales en sus 20s y subjetivamente saludables expuestos a niveles ambientales de PM en la estación Sodar, un varón de 25 años pasado de peso y en condiciones físicas relativamente pobres mostró fuertes asociaciones espontáneas entre niveles de PM y los resultados de series temporales de espirometría y ECG en un esquema de componentes principales combinado de

Loeve Karhunen. La subsiguiente regresión de componentes principales, utilizando microbalances de elementos oscilando (TEOM) registraron a $PM_{2.5}$ ambiental como la variable dependiente, y valores R^2 del 90.9% (99.9% nivel de confianza; valor F 10.0) para perfiles ECG y 83.4% (99.7% nivel de confianza; valor F 7.2) para los perfiles de espirometría correspondientes a este sujeto de prueba, registrados durante la ocurrencia de un pico de PM nocturno típico, en conjunto con un atardecer de bajo PM.

La mayoría de las causas potenciales de correlaciones triviales y/o esporádicas parecen descartarse por el meta análisis de los resultados de las pruebas, incluyendo la comparación de los resultados de regresión de componentes principales con datos de atardeceres de bajo PM y la interpretación fisiológica de la correlación entre características de ECG y espirometría. El hecho de que las fluctuaciones incrementales en tiempos, de 30 minutos en ambas direcciones debilitan las correlaciones observadas, indica la presencia de un mecanismo de respuesta fisiológica relativamente rápido.

GIS-Referenced Data Fusion

Until recently, researchers studying health effects of ambient particulate matter (PM) at the U.S.-Mexican border had to rely on data and modeling tools only capable of revealing broad associations between PM levels and relatively non-specific health endpoints such as regional mortality and morbidity trends. Neither the comprehensive databases nor the processing and modeling tools were available to investigate the underlying PM dispersion and deposition mechanisms, the possible role of specific PM sources, the exposure risks for susceptible population groups, or the potential impacts of severe PM episodes on the “normal,” relatively healthy human body.

Today, however, multiple studies sponsored by the Southwest Consortium for Environmental Research and Policy (SCERP) and other border-oriented research initiatives are helping produce the first geographic information system (GIS)-referenced database on Paso del Norte air quality parameters and impacts. The core of this database is formed by continuous suites of hourly criteria pollutant measurements, including PM_{10} and $PM_{2.5}$ (PM with an aerodynamic diameter of 10 micrometers [μm] and 2.5 μm or less, respectively) levels, as well as meteorological variables reported by the Texas Commission on Environmental Quality (TCEQ). This core can be readily underbuilt with layers of GIS-referenced socioeconomic and geographic data, plus selected regional mortality and morbidity parameters. Moreover, depending on the specific application, the database core can be overlaid with spatially and temporally resolved emission inventories as well as PM source and receptor sample composition data such as what has been produced by the SCERP-Paso del Norte Air Research Program (PdNARP) (Jeon, et al. 2001).

Although far from comprehensive with regard to temporal and spatial coverage, this GIS-referenced Paso del Norte database is already facilitating development of a variety of advanced models, including diagnostic meteorological models and PM source and receptor models. When used in conjunction with each other, these models shed light on some of the complex atmospheric transport, reaction, and deposition processes that have confounded past attempts at understanding and predicting Paso del Norte air quality problems in general and fluctuations in ambient PM composition and concentrations in particular.

A typical example is provided by the now-widely recognized evening PM events in the Paso del Norte airshed discussed later in this chapter. In combination with the novel, GIS-referenced health risk exposure modeling techniques demonstrated by Mejía and co-workers later in this chapter, the advanced diagnostic meteorological models developed by Fernandez and co-workers, also detailed in this chapter, promise to provide key information about atmospheric transport mechanisms linking source-rich PM emission areas with vulnerable receptor sites. A long-term promise of the various modeling approaches described here is the eventual ability to distinguish between the effects of specific PM sources and dispersion processes, rather than total PM burdens, on measurable morbidity and mortality endpoints. The PM risk assessment model described by Mejía and co-workers, in which exposure risks for selected neighborhoods and population subgroups are linked to specific PM sources such as brick kilns (provided reliable local emission inventories are available) is laying the groundwork for future correlations between specific PM sources and measurable health endpoints among these groups and neighborhoods.

Furthermore, as will be discussed in this chapter, preliminary cardiopulmonary monitoring of subjectively healthy people is testing the now-more widely supported hypothesis that severe transient PM episodes not only can have disproportionally large effects on very young or old patients with compromised cardiopulmonary systems, but may perhaps have measurable (patho)physiological effects on relatively healthy subjects. If this hypothesis can be confirmed by further experimental work, transient severe PM exposures might, in fact, prove to have an epidemiology all their own.

The rationale behind the combination of these seemingly diverse topics into a single chapter is that they are closely connected by a common technical and scientific thread, namely attempted integration of multiple GIS-referenced data sets with all their attendant problems inherent to fusion, correlation, and evaluation of high-dimensional data matrices. This requires the use of special multivariate data fusion and modeling tools, as will be described in the following paragraphs.

Effective fusion of complex data sets obtained by a battery of test methods and collection procedures requires minimally two steps, namely, choosing a compatible format followed by determining the degree of correspondence and overlap between the data. For integration into the overall GIS-referenced Paso del Norte air quality and health effects database, the only formal requirement is that the spatial and temporal relationships of the data points relative to each other as well as to other database components are known and formatted in a compatible manner, such as latitudes and longitudes plus some type of standard time code. In order to achieve *meaningful* integration, however, it is essential that the degrees of correlation, and thus redundancy, between the various data sets in a database are determined in a transparent, user-friendly manner.

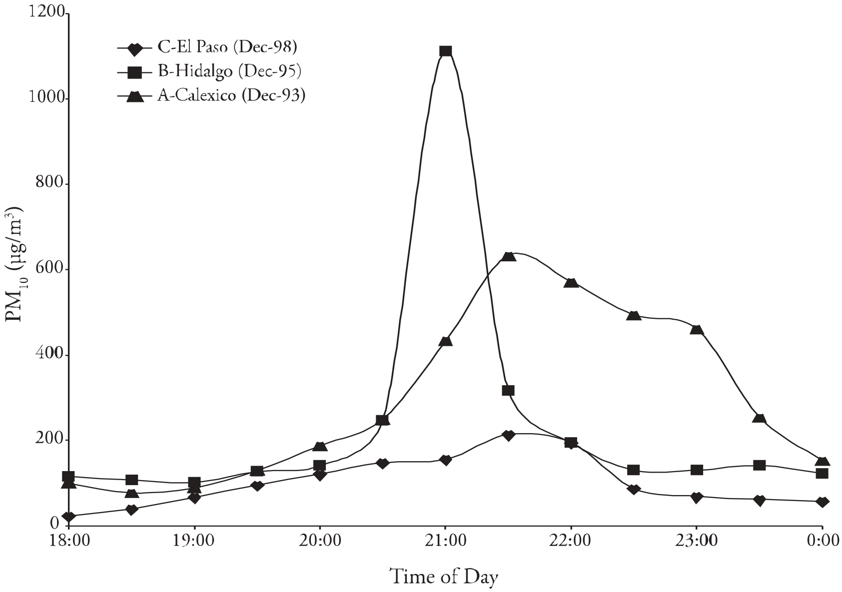
At the current state of the art in integrating and evaluating high-dimensional datasets, principal component analysis (PCA)-based orthogonal rotation methods such as Varimax, principal component regression (PCR), and canonical correlation analysis (CCA) are among the most highly transparent methods available, as discussed by Windig and Meuzelaar (1987). Unlike non-orthogonal rotation procedures, these methods do preserve the total variance in the system. Although the final evaluation step may often require consideration of non-orthogonality—after all, relationships in the physical world are rarely fully orthogonal—such oblique rotations can be performed under direct visual control by the operator using so-called graphical rotation methods (Windig and Meuzelaar 1984).

Frequency and Origin of Evening PM Episodes in the Paso del Norte Airshed

Background

Within the suburban and/or rural zones directly surrounding a typical, sprawling metropolis at the U.S.-Mexican border, the research team has repeatedly encountered severe, two- to four-hour long nocturnal PM episodes, with PM_{10} concentrations ranging from 250 micrograms per cubic meter ($\mu g/m^3$) to more than 1,000 $\mu g/m^3$ (Figure 1). These events are also noted in Chapters III and VI. Over cumulative 24-hour monitoring periods totaling approximately eight days in the direct vicinity of Mexicali (December 1993), Reynosa (December 1995), and Ciudad Juárez (December 1998), three such episodes were observed. Thus, severe evening PM episodes appear to be neither infrequent nor confined to a single border location. Because of the close proximity of large Mexican border cities to all three sites and the strong contributions of "re-aerosolized urban dust" in the filter samples obtained during these events, the phrase "peri-metropolitan particulate matter," or $\{PM\}^2$ events, has been coined (Meuzelaar 1998).

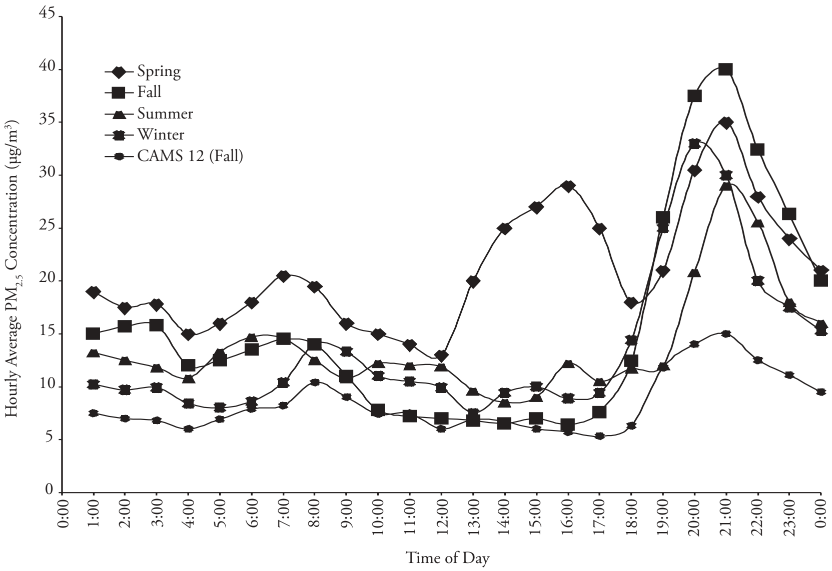
Figure 1. Typical Evening PM_{10} Peak Events Observed Under Low Wind Conditions by University of Utah Teams at Three Different Peri-Metropolitan U.S.-Mexican Border Locations Between 1993 and 1998



Source: Authors

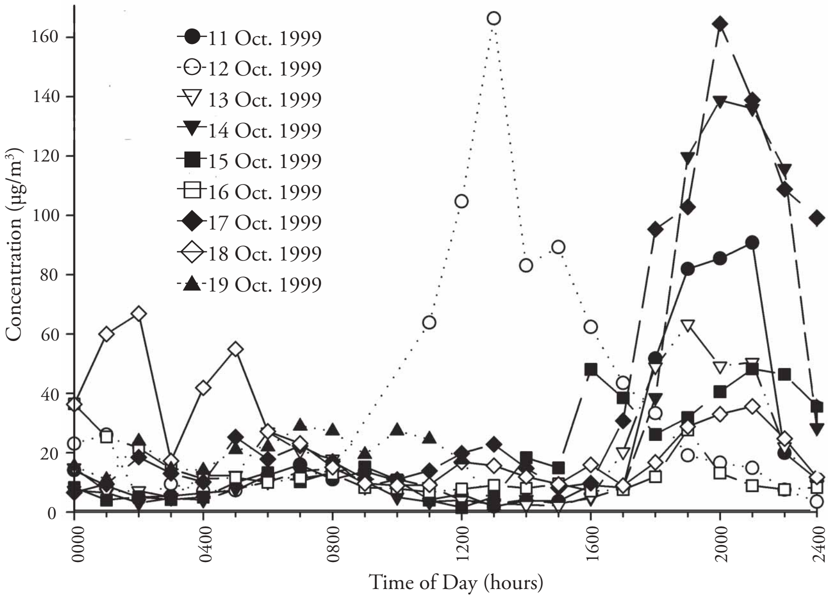
Circadian plots of hourly $PM_{2.5}$ profiles, averaged over each of the four seasons as reported in 2001 by TCEQ for the Continuous Air Monitoring Station (CAMS) 40 (Sun Metro) site in El Paso, are shown in Figure 2. Appendix Figure 1 (page 305) shows the locations of the sampling sites. Furthermore, a representative sequence of 10 individual $PM_{2.5}$ profiles from the same site is depicted in Figure 3. The most prominent features in Figures 2 and 3 are the large, transient evening PM events (centered around 2100 hours to 2200 hours) that appear to occur at two- to four-day intervals. As Figure 2 shows, the height of the average evening $PM_{2.5}$ peak is two to three times the average $PM_{2.5}$ level during the earlier parts of the day; typical evening PM events at the CAMS 40 site do reach $PM_{2.5}$ levels approximately five to 10 times typical daytime $PM_{2.5}$ levels for the overall Paso del Norte basin.

Figure 2. Hourly $PM_{2.5}$ Concentrations Recorded by TCEQ at the CAMS 40 Border Site in El Paso, Averaged Over the Four Seasons in 2000



Notes: The figure shows the dominant evening PM peak events as a regular phenomenon, although they only occur every three evenings on average. Note the much lower evening PM peak at the nearby CAMS 12 site, located a few hundred feet higher above the Rio Grande drainage. The strong afternoon PM event peaks recorded during the unusually windy Spring 2000 season were not seen as clearly in several other years.
Source: Authors

Figure 3. Hourly $PM_{2.5}$ Concentrations Recorded by TCEQ at the CAMS 40 Border Site in El Paso During Nine Arbitrarily Selected Consecutive Days in Fall 1999



Note: The figure shows both the recurring strong evening PM events and one or two typical afternoon wind PM events.
Source: Authors

Even when calculating 24-hour averages for the observed $PM_{2.5}$ levels, as required by current U.S. Environmental Protection Agency (EPA) standards, the evening peak alone contributes nearly 50% of the 24-hour value in late fall and early winter, and diminishes to approximately 30% in late spring and early summer. Average circadian PM_{10} levels (not shown here) are five to six times the corresponding $PM_{2.5}$ levels while generally matching the latter in overall shape, except on windy days when PM_{10}:$PM_{2.5}$ ratios may easily double due to re-aerosolization of relatively coarse crustal material. Thus, TCEQ PM_{10} profiles tend to show more pronounced incidental afternoon peaks caused by transient strong afternoon breezes.

Not only are the two- to three-hour evening peak episodes often high enough to have a substantial effect on 24-hour $PM_{2.5}$ averages, thus meriting further study from a regulatory point of view alone, there is mounting evidence for a direct association between transient high PM events and physiological and pathological effects (Michaels and Kleinman 2000). Moreover, at the January 2002 SCERP meeting at the University of Texas at El Paso (UTEP), a possible statistical link between PM evening peak intensities and mortality statistics in the El Paso region was reported by Parks, et al. (1999).

Nature and Origin of Severe Evening PM Episodes

When interviewed by SCERP team members, local bridge toll booth operators and other border workers or residents generally tend to blame the frequent episodes of poor ambient air quality during the evenings on either automotive emissions or open burning of waste and biomass on the Mexican side of the border. While observing and analyzing the extreme evening PM event at the Hidalgo International Bridge shown in Figure 1, it became clear that automotive traffic could not be blamed directly because evening rush hour was over and PM levels had already gone down markedly when a two- to three-hour transient PM event appeared suddenly, peaked out at well over 1,000 μg/m^3, and vanished again. Curiously, there was little or no measurable wind blowing that evening that could explain the transient character of this intense PM cloud or provide ready clues about the direction from which this cloud came.

As reported by Sheya (2002), careful thermal desorption organic gas chromatography/mass spectrometry (TD-GC/MS) analysis of two-hour PM_{10} samples confirmed that the dominant chemical composition of the organic PM adsorbates during that evening peak was different from typical automotive emissions and also did not point conclusively toward any waste or biomass burning emissions. Rather, the highly complex mixture of a great many different compounds, including dihydroabietic acid, which is commonly found in urban road dust, suggested that the bulk of this evening PM consisted of re-aerosolized urban dust. Since the only urban area near Hidalgo was the Mexican metropolis of Reynosa, just across the border, it became clear that the researchers would have to find a plausible mechanism to explain frequent nocturnal transport of re-aerosolized urban dust from across the river.

Fortuitously, a typical nocturnal $\{PM\}^2$ episode was recorded near Ciudad Juárez during a 48-hour pilot study of the Paso del Norte airshed in December 1998 (Figure 1). The two-hour PM_{10} samples collected on quartz fiber filters were analyzed not only for organic constituents by means of TD-GC/MS, but also for inorganic constituents by means of particle induced X-ray emission (PIXE) and computer-controlled scanning electron microscopy analyses performed by the Anderson laboratory at the University of Arizona. In addition to the detailed organic and inorganic PM characterization data, as well as size-distributed particle data already being obtained as part of the PdNARP scoping study, one of the two receptor sites used was equipped with a Sodar system operated by TCEQ. The high resolution wind, air temperature, and mixing height ("inversion layer") data produced by this system were provided by Victor Valenzuela and colleagues at TCEQ. This extensive data set, further supported by diagnostic meteorological models of the Paso del Norte airshed prepared at the Instituto Tecnológico y de Estudios Superiores de Monterrey (ITESM), allowed the research team to start tackling the fundamental question of the nature and origin of typical $\{PM\}^2$ events.

This time, several SCERP team members witnessed the slow drift of a dense, low PM cloud from the Ciudad Juárez side of the border across the river drainage toward the Sodar receptor-monitoring site. After passing over the site, the cloud slowly continued on across some of the residential areas on the U.S. side of the international boundary. About one or two hours later, the cloud seemingly reappeared from the residential side and swept across the Sodar site for a second time, although traveling in the opposite direction. As discussed by Jeon, et al. (2001) time-resolved TD-GC/MS analysis results again showed large contributions from re-aerosolized road dust mixed with smaller contributions from many different sources. The time resolved receptor profiles shown by Jeon, et al. (2001) further illustrate that the chemical composition of the $\{PM\}^2$ cloud was far from homogeneous. Apparently, it had undergone relatively little mixing and seemed to reflect the complex spatial and temporal mix of combustion, fugitive emission, and resuspended dust sources characteristic of its metropolitan origin.

Altogether, there is now detailed chemical analysis data on all three {PM}² episodes recorded by the teams and illustrated in Figure 1. All episodes show that the leading edge of the PM_{10} cloud is rich in automotive emissions components and, in fact, coincides with the expected evening traffic peak in these emissions, followed by a heterogeneous mix of resuspended road dust, wood smoke, and waste combustion products. Because all observations point to low velocity, gravity-driven flows moving the dense, re-aerosolized dust clouds accumulating over metropolitan border areas during near-windless conditions into the natural drainage formed by the border river, a more detailed study was undertaken. This study investigated the effect of wind strength and direction on severe evening PM episodes in the hope of being able to better understand, model, and predict the occurrence of such episodes along the border.

Effects of Wind Strength and Direction on Evening PM Episodes

Fusion of hourly PM_{10} data recorded by Li and co-workers at the Sodar site in April 2002 by means of tapered element oscillating microbalance (TEOM) instrumentation, with the corresponding wind strength and direction data recorded by TCEQ at the same site, enabled the research team to compare the average wind direction under three different scenarios:

- High evening PM levels at high wind speeds (peaking at well over 10 miles per hour [mph])
- Low evening PM levels at moderate wind speeds (typically between 5 mph and 10 mph)
- High evening PM levels at low wind speeds (less than 5 mph)

By plotting these hourly wind speed and direction observations as two-dimensional vector diagrams with the corresponding PM values indicated for each data point (see Figures 4a–4c), it becomes possible to distinguish the overall patterns. As shown clearly by the vector plot in Figure 4d, where the observations within each category have been averaged, the average wind direction on high-PM/low-wind evenings was south to south by west. In other words, these high PM flows tend to come across the border from the Ciudad Juárez metropolitan area. By contrast, the average wind direction on low-PM/moderate-wind evenings was from the north to north by east, thus representing flows coming into the air basin through the pass in the north. Interestingly, average wind directions on high-PM/high-wind evenings were primarily from eastern or diametrically opposite western angles.

Figure 4. Hourly Wind Vector Sequences Constructed from Wind Direction and Speed Data Recorded by TCEQ at the Sodar Border Site in El Paso Between 5 p.m. and 2 a.m. during April 2002

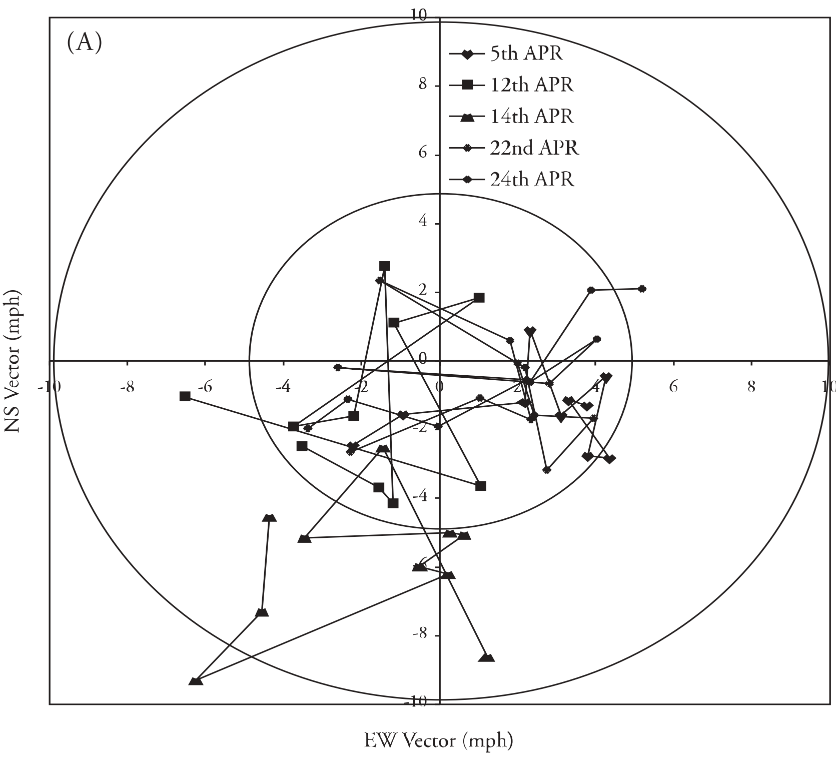


Figure 4. continued

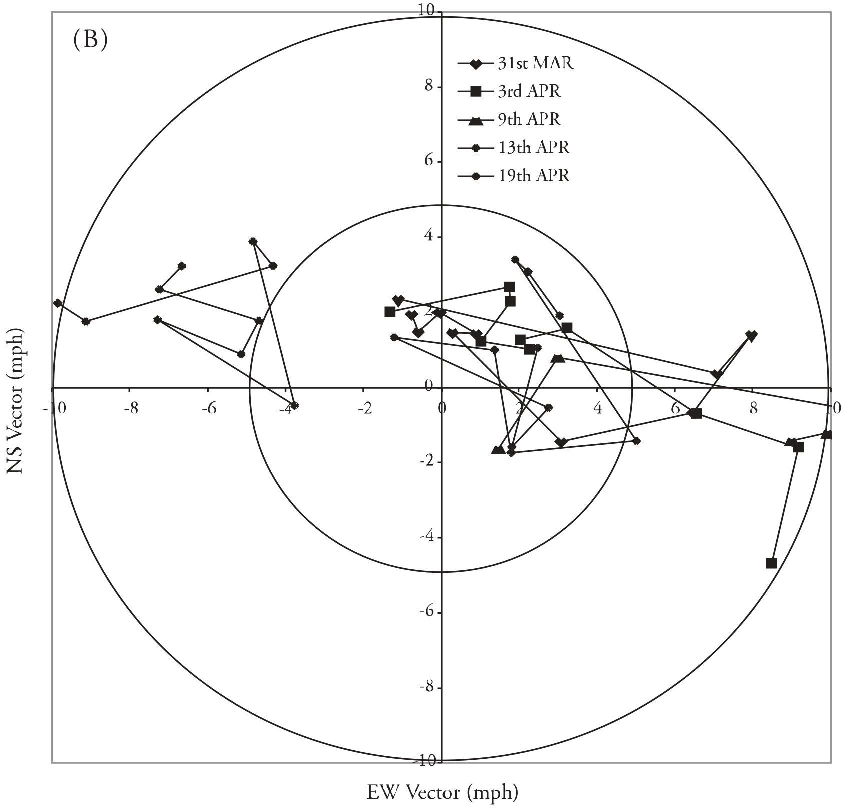


Figure 4. continued

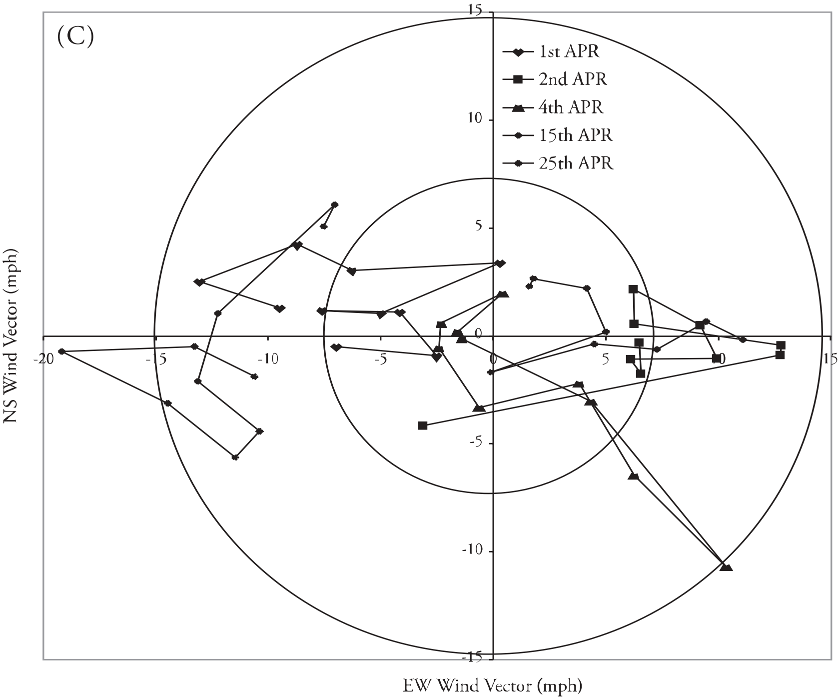
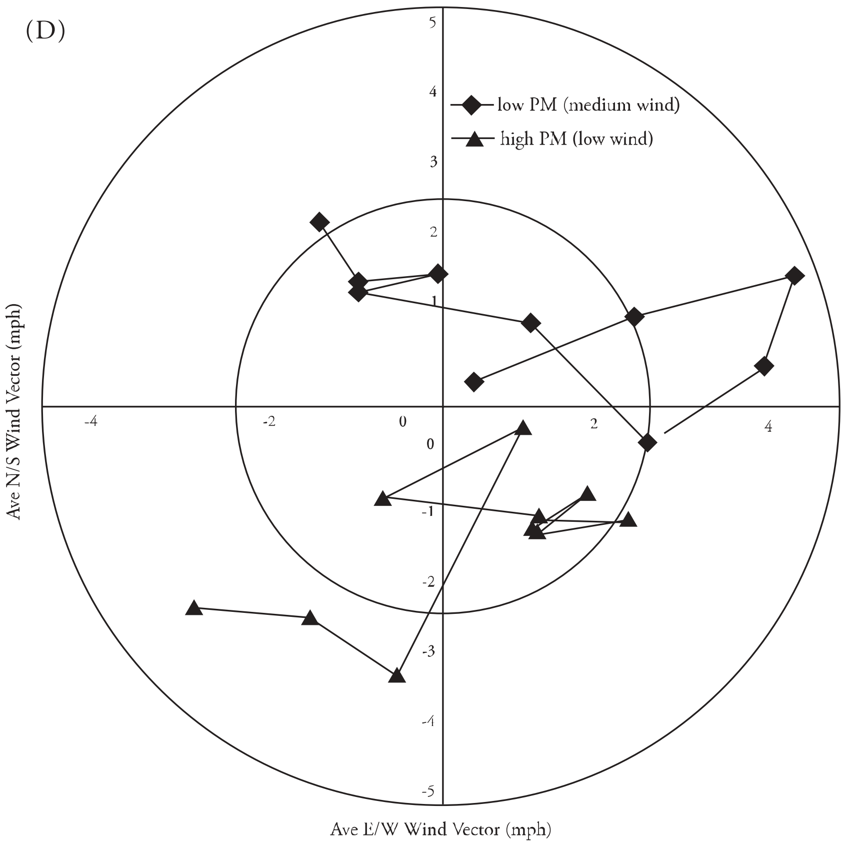


Figure 4. continued



Notes: Graphs (a), (b), and (c) each depict five selected days characterized by (a) high evening PM, (b) low evening PM, and (c) high evening PM plus high afternoon PM conditions. Graph (d) shows average vector sequences for conditions (a) and (b). See text for interpretation.
Source: Authors

To better understand these low-velocity south or southeast evening winds that slowly carry concentrated urban dust clouds across the border, or at least into the river drainage, meteorological wind fields of the Paso del Norte airshed were simulated at the Fernando laboratory at Arizona State University for the December 4–6, 1998, period using the non-hydrostatic mesoscale model MM5.

The efficacy of three different planetary boundary layer parameterization schemes (i.e. Gayno-Seaman, Blackadder, and Hong-Pan) was compared and found to produce nearly equal correlation coefficients between observed and predicted temperatures (viz. R^2 values up to 0.9), as well as u- and v-components (R^2 values up to 0.8 and 0.7, respectively) of winds at 250 meters (m) above ground level. The main difference between the schemes appeared to be in computational demand—the Hong-Pan non-local K-scheme required nearly 30% less computational processing time than the other two schemes. For a full description of the synoptic data, mesoscale models, and computational methods used, see previous reports by Fernando, et al. (2001).

The results of the local wind simulations are illustrated by the sequence of selected GIS-referenced images (taken from an animated .gif series) shown in Figures 5a through 5d. The complete model output animation can be viewed on the SCERP website at http://www.scerp.org. The model output confirms the presence of low-velocity south and southeast flows, which slowly crossed the border during the early evening of December 5, 1998. This would explain the observed slow movement of the dense metropolitan dust cloud above Ciudad Juárez across the border river valley to the Sodar site. Moreover, the direction of these drainage flows indeed tends to reverse later in the evening due to increasing downslope flows from the U.S. side of the border, thus explaining the dual PM peaks observed on several occasions (Jeon, et al. 2001). For a more detailed description of these low velocity surface winds, see Fernando, et al. (2001).

Figure 5. Surface Level Wind Vector Maps for the Paso del Norte Airbasin Calculated from Synoptic Weather Data for December 4, 1998

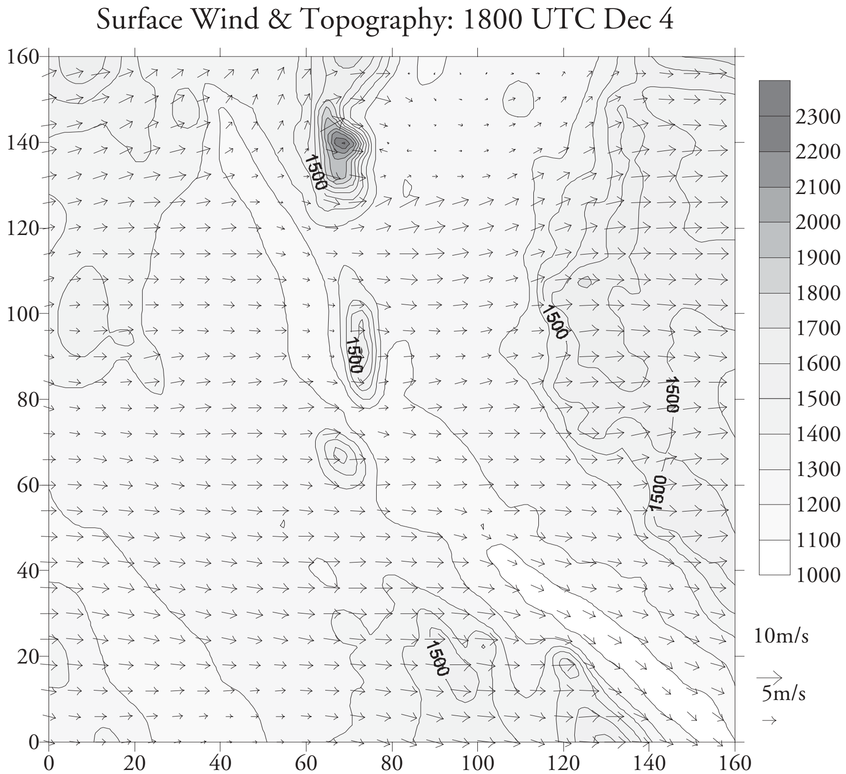


Figure 5. continued

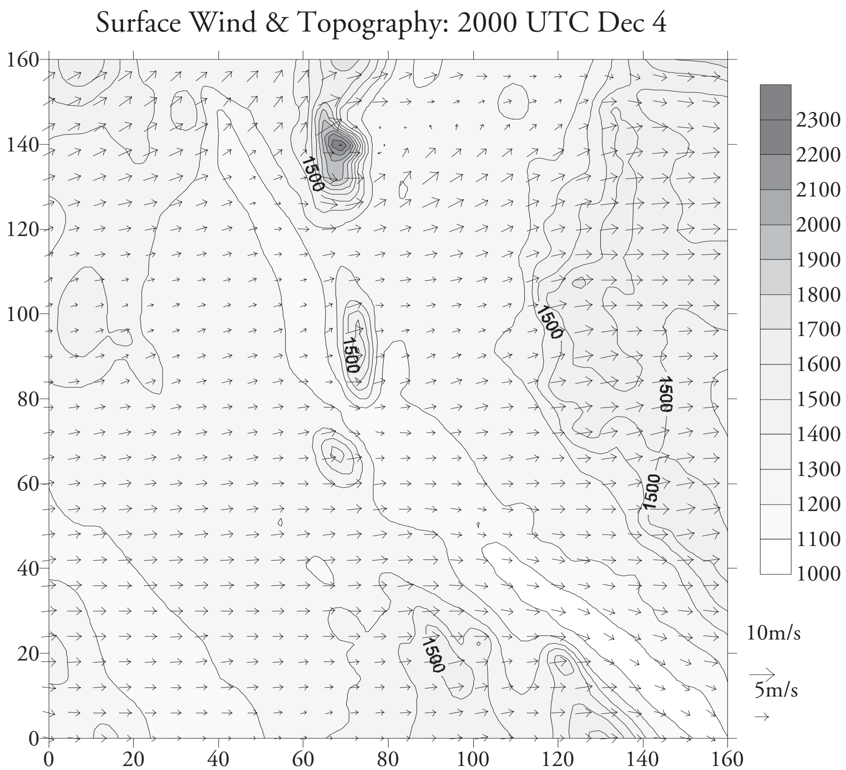


Figure 5. continued

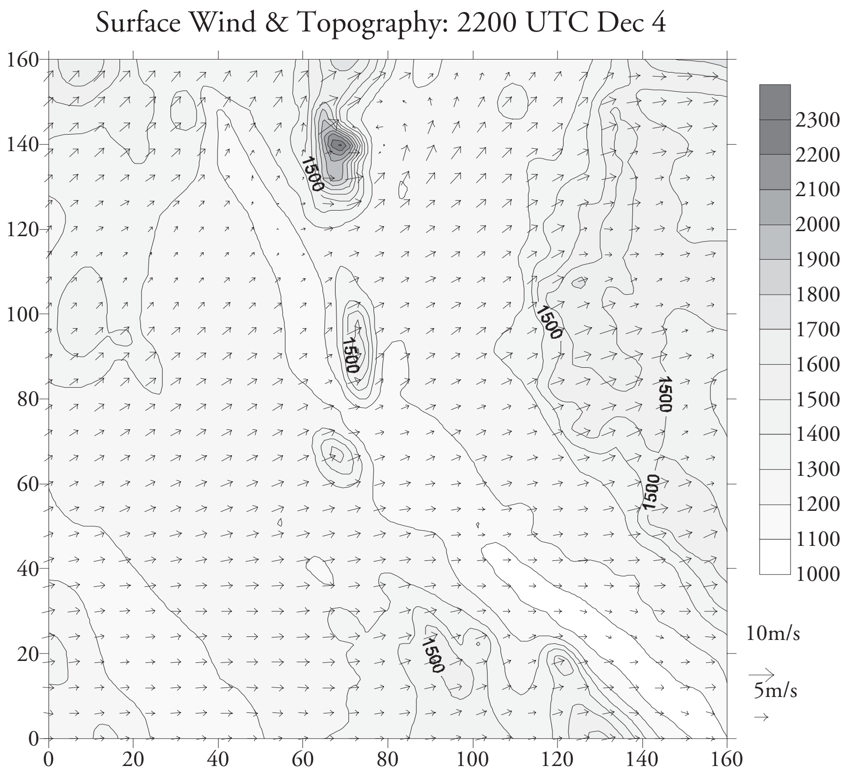
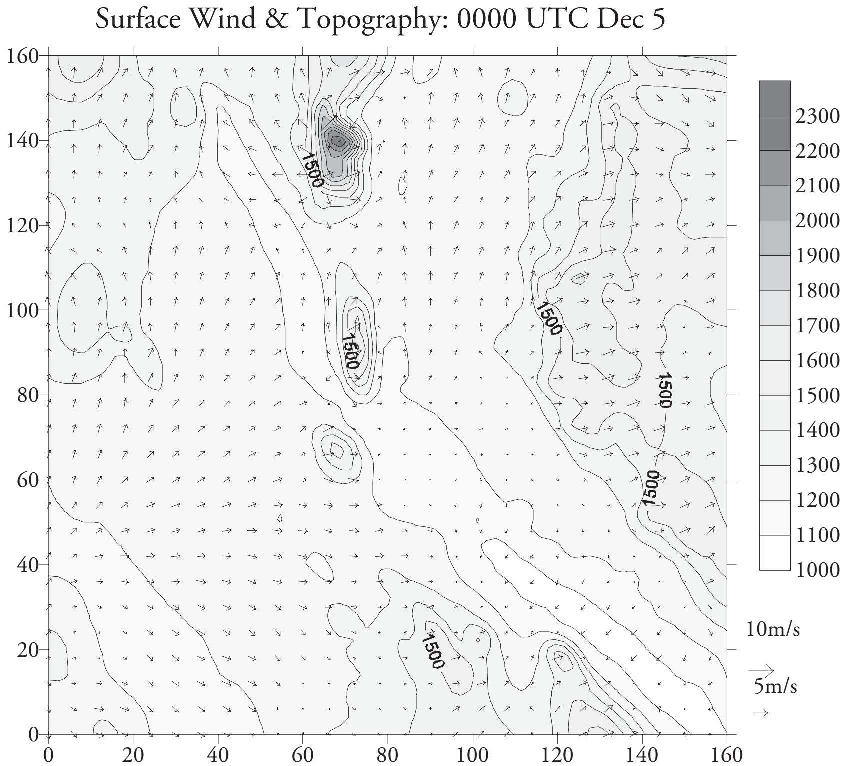


Figure 5. continued



Notes: Observe the near windless conditions at 1800 hours with the initiation of low velocity flows down the Rio Grande drainage. They increase at 2000 hours, decrease at 2200 hours, and end in near-windless conditions again at 2400 hours. Compare with the corresponding, time-resolved PM profiles in Chapter VI, Figure 5.
Source: Authors

In short, it appears that typical, gravity-driven drainage flows may occasionally overshoot the river drainage banks somewhat, but by and large tend to remain concentrated within the river drainage. This helps explain the earlier noted difference between the evening PM levels recorded at the CAMS 40 (Sun Metro) site located close to the border river and the CAMS 12 site located on the UTEP campus less than two miles away and a few hundred feet above the CAMS 40 site (see Figure 2 and Appendix Figure 1 [page 305]).

Conclusions

All {PM}^{2} episodes recorded thus far reveal a common pattern of near windless, nocturnal conditions with falling ambient temperatures and low to zero mixing layer heights. In the summer months, the enormous quantities of PM produced by a bustling Mexican border metropolis during the evening traffic peak generally have a chance to disperse before pronounced atmospheric cooling and decreasing mixing layer heights produce stagnant conditions. During the winter months, however, reduced solar heating and early sunsets tend to produce stagnant conditions well before the evening traffic peak is over. This causes the trapping of a thin, high-density PM blanket close to the ground.

In the course of the evening, the dense, low PM cloud tends to move slowly across adjacent suburban and rural areas, driven by nocturnal drainage flows and other low velocity winds, thereby creating the observed {PM}^{2} events. Additionally, there are likely to be episodes in which the PM cloud remains entirely stagnant, thus not leading to marked PM increases outside the perimeter. Moreover, due to their transient nature, many nocturnal {PM}^{2} events and their urban parent episodes will tend to remain hidden in conventional 24-hour PM_{10} and $PM_{2.5}$ statistics.

Recommendations

Although the intuitive reaction to air pollution events dominated by a combination of meteorological phenomena and longstanding developmental issues (unpaved roads, older cars, traffic jams at border crossings) may perhaps tend toward resignation, there are relatively simple and effective ways in which those working within affected areas can reduce their PM exposure. These include staying indoors, especially in a well-filtered home or vehicle, and avoiding strenuous exercise and dust-generating activities. At the metropolitan level, long-term measures that reduce road dust (paving and sweeping roads) and the idling of thousands of cars and trucks near the border crossings are likely to have the greatest long-term impacts.

Integrated Approach to PM Source Exposure Risk Calculation

Background

Among the various source apportionment approaches suitable for use with chemical PM composition data, so-called receptor modeling techniques have thus far proved most successful in the hands of chemists and physicists. By contrast, source modeling techniques have been most successful in the hands of researchers and planners using GIS-referenced emission inventories and meteorological data. Although it is widely recognized that both approaches are highly complementary and preferably should be used together, few if any studies manage to achieve that goal. Not only is it difficult to produce PM characterization data with adequate spatial resolution to be GIS-referenced in a meaningful way, the lack of adequate PM emission inventory data and reliable PM dispersion modeling techniques has thus far prevented successful use of source modeling approaches in most urban PM source apportionment studies.

At ITESM, a methodology was developed based on GIS that combines the successive application of source dispersion models to evaluate the source apportionment to PM_{10} in the Monterrey metropolitan area (Mejía and Cardona 2000). Also, a GIS-based procedure was developed to generate maps of individual and social risks of population exposed to airborne pollutants (Mejía and Zavala 2003). This methodology seems to be a promising technique to evaluate air pollution strategy benefits based on health risk reduction rather than on air pollutant concentration reductions. Moreover, the risk maps are an excellent communication tool to use with the community, which is interested in risk rather than data on air pollutant concentrations. The methodology to develop maps of individual and social health risks and its application to the Paso del Norte region are described in the following sections.

GIS-Referenced Database Development for Exposure Risk Modeling

Usually, the personal health risk is presented as a value for the population of a certain city or region. However, areas of high and low risk may compensate and give values that may not represent adequately the actual exposure of people to pollutants in the environment. Health risk maps can be generated for different population groups—children, women, elderly, adults, workers, etc.—by combining maps of air pollutant concentrations and maps of population. Data can then be obtained for personal health risk indexes and placed in a master modeling grid using the same approach to evaluate values of health risk index. Then, the values can be interpolated and maps of individual risk can be obtained. Considering the number of people in the different population groups under study, maps of social risk may be obtained by multiplying the number of people in each grid cell by its value of health risk in each cell. Then, maps of social health risks that consider the personal risk and number of people exposed may be easily generated. This methodology is based on data management through GIS software (Mejía and Zavala 2003).

The equation used to evaluate risk is based on the calculation of a hazard coefficient:

$$HC = \frac{CID}{R_fD} = \frac{\dfrac{(c)(IR)(HED)(EF)(EP)}{(BW)(AEP)}}{R_fD}$$

where,
HC = hazard coefficient
CID = chronic intake/day
R_fD = reference dose
c = average pollutant concentration
IR = inhalation rate
HED = hours of exposure per day
EF = exposure frequency
EP = exposure period
BW = body weight
AEP = average exposure period

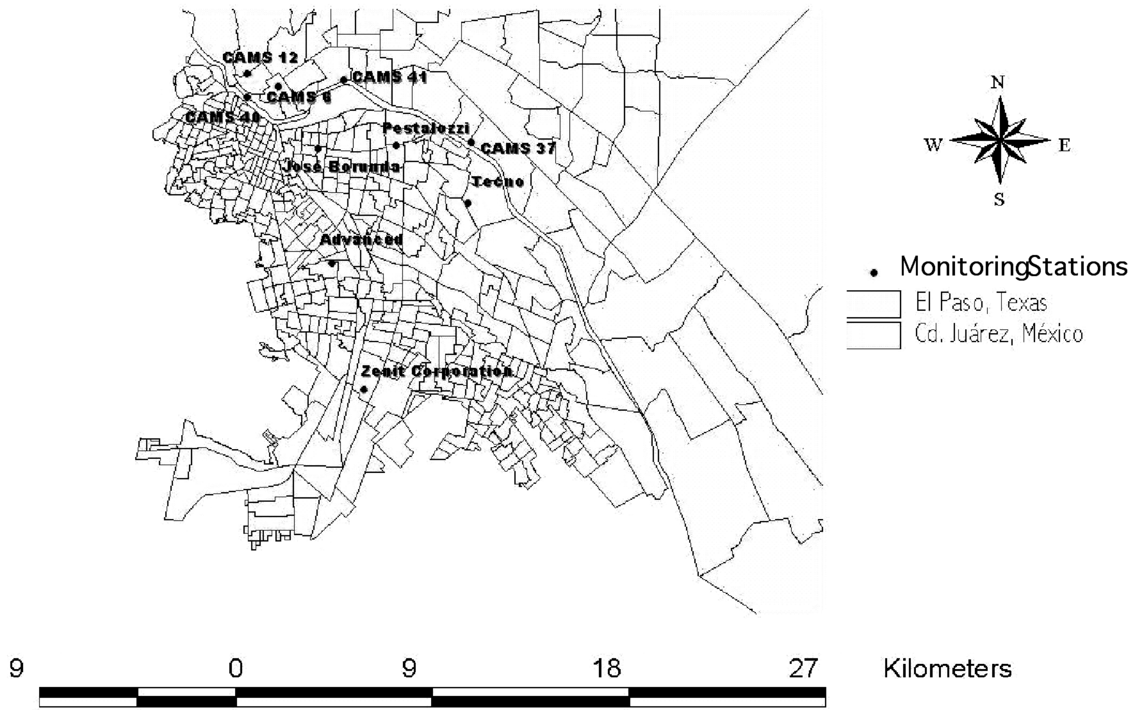
Reference dose values are calculated assuming that the safe maximum concentration exposure is the air quality standard for the period of evaluation. In this case, chronic exposure to air pollution in the health risk assessment for Paso del Norte is considered. The values of the variables in the equation depend on the group of the population studied. In this case, values reported by EPA for children and adults were used.

Exposure Risk of Paso del Norte Population Groups

The Paso del Norte region includes the cities of Ciudad Juárez and El Paso. These cities and the PM_{10} monitoring stations used in this study are shown in Figure 6. Air pollution levels are of great concern to the population, particularly the possible effects of emissions from brick kilns located in Ciudad Juárez. The location of these kilns is shown in Figure 7. Most of these kilns emit PM_{10}. In El Paso this pollutant is measured every hour while in Ciudad Juárez 24-hour averages are measured every six days.

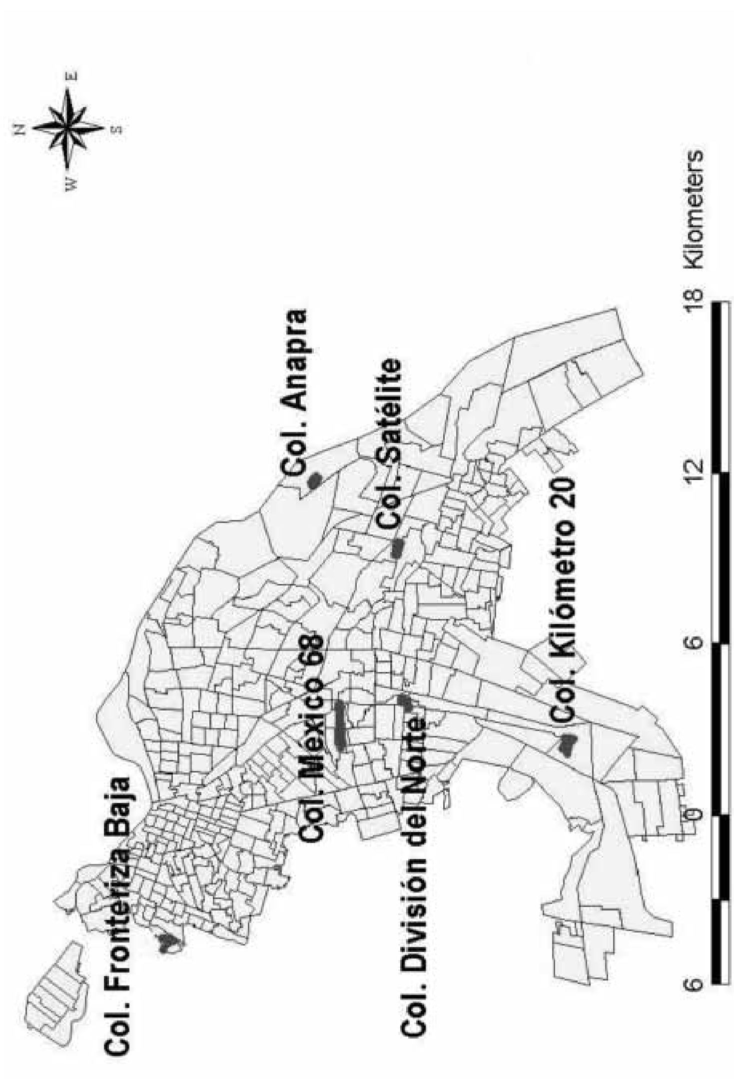
The purpose of this study was to assess the chronic personal health risk of the population exposed to PM_{10} in the region, and then evaluate the social health risk. Medina (2002) reported the results of the study. PM_{10} concentration data for the period 1997 through 2001 were collected and a map of yearly average concentrations for the region was prepared using a mass-balance interpolation model for the 1x1 kilometer (km) grid. The map of yearly average PM_{10} concentrations is shown in Appendix Figure 4 (page 308). This figure shows that high concentrations predominate during the year in the south and southwest of Paso del Norte, exceeding the annual average air quality standard of 50 $\mu g/m^3$ for PM_{10} and reaching values of more than 90 $\mu g/m^3$ in areas south of Ciudad Juárez.

Figure 6. Paso del Norte Airbasin Monitoring Sites Used in the PM Exposure Risk Study



Source: Authors

Figure 7. Brick Kilns in Ciudad Juárez

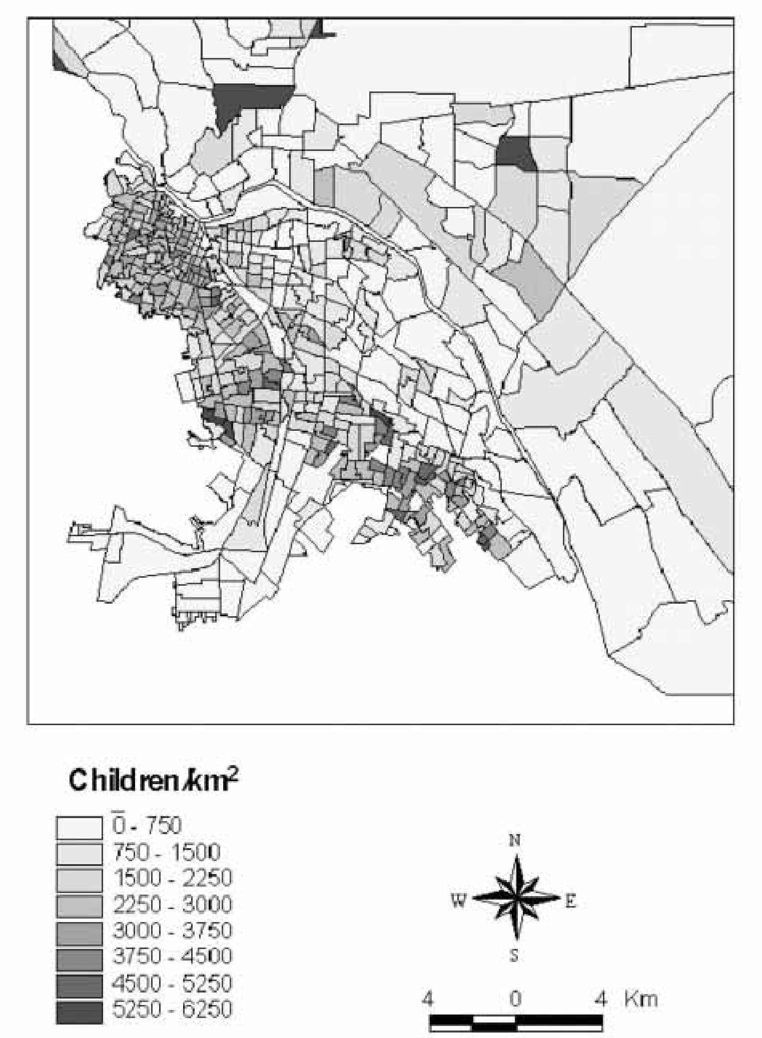


Source: Authors

Maps of air pollutant concentrations can be used to explain the possible effects of pollutants on health. Such a map for the Paso del Norte basin is shown in Appendix Figure 4 (page 308). This task may be confusing because different air quality standards exist for hourly, daily, or yearly averages. The average person living in a community usually does not relate concentrations with time of exposure. Therefore, it may be confusing to explain that different health effects may occur from acute or chronic exposure. However, when the concentration maps are used to prepare chronic health risk maps, as was done in this case, understanding the problem becomes simpler and communication is facilitated.

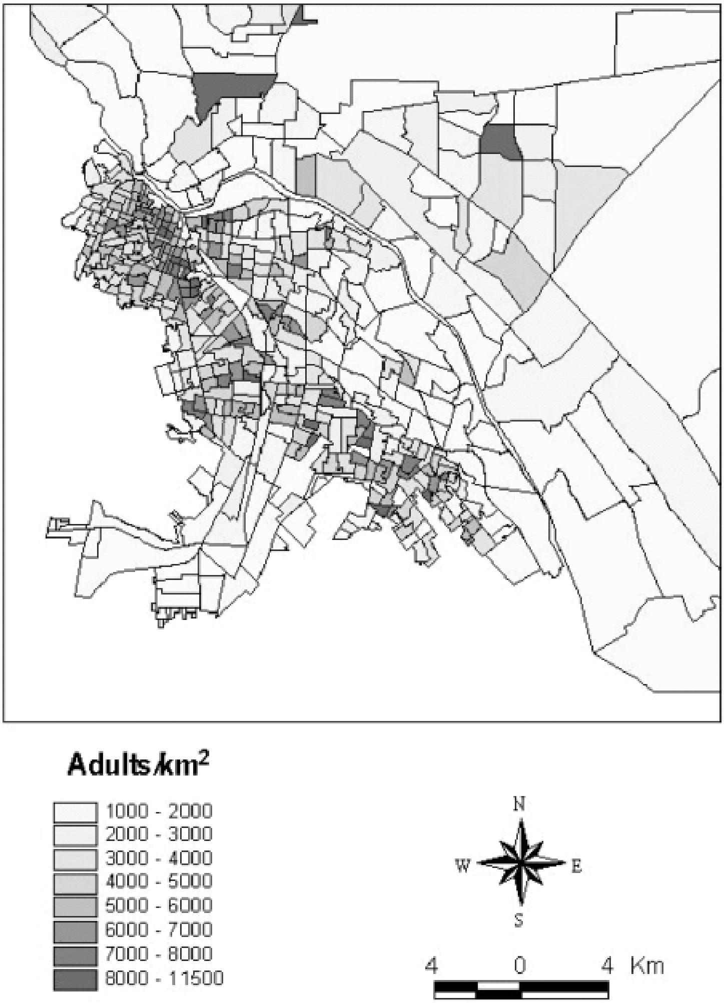
An important aspect of decision-making is to evaluate the benefits of air pollution concentration reductions. One of the main benefits is based on the reductions in health costs. In this case, it is important to consider the number of people affected in each population. The social risk is obtained by multiplying the values of individual risk by the number of people. Here, the estimated values of individual risk in each grid cell were multiplied by the number of people living in that cell. With this procedure, values of social risk in each cell of the domain and maps of social risk for Paso del Norte could be generated. Maps of population density for children and adults are shown in Figures 8a and 8b. The maps show the high population density in Ciudad Juárez and the relatively sparse population in El Paso. Using these maps, social risk maps for children and adults for chronic exposure to PM_{10} were prepared and are shown in Appendix Figures 5a and 5b (pages 309 and 310). The maps clearly show that the highest social risk is related to exposure and number of people exposed to PM_{10}. The region of Ciudad Juárez shows high risk values compared with El Paso. Strategies to improve air quality in the region may be based on personal and social risk reduction rather than on air pollutant concentration. People seem to react and participate more actively when they understand the possible risks to health exposure. Air quality modeling and GIS tools are excellent for combining air quality data with risk assessment for these purposes.

Figure 8a. Child Population per Square Kilometer in El Paso-Ciudad Juárez in Each Mexican AGEB (census block)/U.S. Census Trac



Source: Authors

Figure 8b. Adult Population per Square Kilometer in El Paso-Ciudad Juárez in Each Mexican AGEB/U.S. Census Trac



Source: Authors

Conclusions

Zones of higher individual risk for all population groups are located south and southwest of the Paso del Norte region where hazard coefficient (HC) values exceed 1.0 for chronic PM_{10} exposure. Because of the high population density in Ciudad Juárez, the highest social risk areas are also located south and southwest of the Paso del Norte region. In addition, integrated source-receptor models can help identify and apportion potentially harmful PM sources, thereby providing a more reliable basis for future actions to reduce pollution in the region. Finally, GIS-referenced data collection and modeling approaches have proven excellent tools for air quality data management and visualization, thereby facilitating effective communication of health risks to non-experts.

Recommendations

PM concentrations in Ciudad Juárez should be monitored on an hourly basis and the results of this study should be re-evaluated. Moreover, since elevated $PM_{2.5}$ levels in urban environments have been shown to be an important health risk, particularly with regard to potential life expectancy losses, measurement of $PM_{2.5}$ concentration levels in Ciudad Juárez on a regular basis is highly recommended.

Cardiopulmonary Effects of Evening PM Peaks in Young Adults

Background

Current knowledge of the relationship between PM episodes and human health or fitness is primarily statistical in nature. There are disturbingly strong statistical correlations between episodes of high PM levels and high mortality levels in urban environments (Pope 1999a). Moreover, there are similar statistical correlations between high PM episodes and the number of patient visits to doctor's offices and clinics (Calderon-Garciduenas, et al. 2000). However, the precise mechanisms involved, as well as the possible relationships between particle composition and health effects, remain largely unknown. Until recently, the only emerging consensus was that individuals with already-compromised cardiopulmonary systems were most readily affected. In 1998, however, Pope and coworkers found in six elderly Utahns measurable changes in heart rate variability (HRV) that correlated with ambient PM levels (Pope 1999b). This important observation, subsequently confirmed by several other research groups (Pope 1999b), opens up the area of statistically observable PM health effects to systematic experimental verification.

As reviewed by Michaels and Kleinman (2000), literature reports on the effects of ultrafine particles on the human body, as well as on test animals, indicate that short-term exposure to high PM levels may be associated with a host of physiological and pathological responses ranging from minor changes in cardiovascular or pulmonary performance to life-threatening asthma attacks or allergic reactions. Michaels and KIeinman conclude that these findings should eventually lead to new one-hour PM exposure standards, rather than the current 24-hour standards. Recent literature reports are shedding more light on possible cardiovascular (Brook, et al. 2002) and pulmonary (McNee and Donaldson 1999) response mechanisms underlying the experimentally observed effects of short-lasting exposures to high $PM_{2.5}$ levels.

The severe evening PM episodes observed in suburban and rural areas surrounding large metropolitan areas, also referred to as peri-metropolitan particulate matter $\{PM\}^2$ events, at the U.S.-Mexican border are thought to represent only the tip of the iceberg since each of these events is likely to correspond to a parent episode of equal or greater intensity and duration inside the metropolis. Confirmation of this hypothesis awaits the availability of suitable, time-resolved PM monitoring records for large Mexican border cities. In the absence of such data, the researchers decided to focus on possibly measurable cardiopulmonary effects in subjectively healthy young adults being exposed to transient evening PM peaks in the peri-metropolitan border zone where these $\{PM\}^2$ events are frequently observed.

In the study by Pope, et al. (1999a), correlations were observed between daily HRV measurements in six elderly people and ambient PM levels recorded by regional monitoring stations. By contrast, the research approach used here capitalizes on the transient, high-intensity character of $\{PM\}^2$ events to look for a broader spectrum of time-resolved cardiac (electrocardiography) and pulmonary (spirometry) responses in five relatively healthy young adults in their 20s while simultaneously monitoring local PM and weather conditions. Further, these physiological measurements were performed outdoors using a screen-walled, gazebo-style enclosure to enhance the connection between individual exposure and the on-site, outdoor PM measurements.

The Sodar site, where this study was conducted, is situated within the Rio Grande drainage, down-slope from some of the most heavily populated and industrialized neighborhoods of Ciudad Juárez but without known major local PM sources other than nearby roads and highways on the U.S. side of the border. As discussed earlier, as well as in Chapter VI, a severe evening PM episode was previously recorded at this site and, de facto, allowed the research team to perform preliminary source apportionments (see Chapter VI, Figure 7).

The meaning and significance of a physiological study involving only a handful of subjects need consideration here. In time-series experiments involving transient phenomena, each subject serves as his or her own control. Statistically significant patterns may be detectable in a single subject, provided there are sufficient numbers of measurement points. For this study, the target number of original measurement points in each time profile was set at 10. If all 10 measurements provide usable data, the correlation coefficients providing the foundation for subsequent multivariate statistical analysis will have coefficients of variation equal to 0.30. Therefore, correlation coefficients greater than 0.60 will be significant at the 95% level (assuming multivariate normal distributions). In practice, however, one or two measurements often have to be discarded, thereby enhancing the probability of obtaining occasional high correlation values by chance alone and increasing the contribution of noise to principal component loadings and scores. Therefore, minimally two time series were merged before performing PCA. The presence of at least 17 measurement points makes correlation coefficients greater than 0.50 significant at the 95% level.

The larger question is, To what extent can five subjects represent any given target population? For example, a reaction pattern present in only 30% of the study target population stands at least a $(0.70)^5 = 16.8\%$ chance of not being represented in a five-member sample group (assuming randomized selection procedures and normal distributions). However, inability to reliably detect reaction patterns present only in smaller subpopulations is the unavoidable Achilles heel of any small-scale study of this type.

Collection of Electrocardiogram and Spirometry Data from Subjectively Healthy Individuals

Between March 28, 2002, and April 23, 2002, electrocardiogram (ECG) and spirometry measurements were taken at half-hour intervals on three pairs of subjectively healthy adults, each consisting of one male and one female, during a total of eight evenings between 6 p.m. and 12 p.m. In addition to the ECG and spirometry measurements taken at the Sodar site, PM_{10} and $PM_{2.5}$ levels at the Sodar site were recorded at 10-minute intervals by means of TEOM instruments by Li and co-workers, and hourly wind direction and speed were recorded by the on-site meteorological station operated by TCEQ.

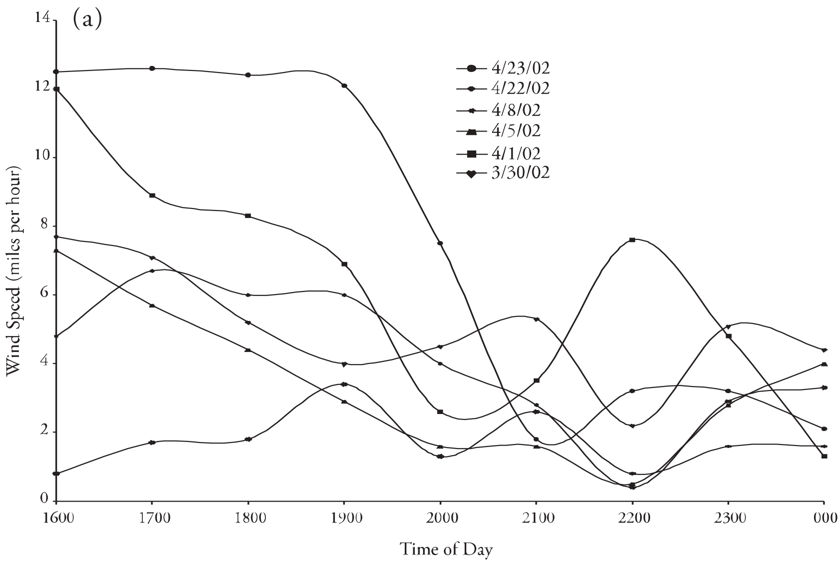
Between half-hour ECG and spirometry measurements, test subjects remained seated or standing inside an unheated, fully screened gazebo-type enclosure that provided ready access to PM-laden airflows. This particular experimental arrangement was designed to approximate typical receptor exposure conditions for border area workers such as parking lot attendants or bridge toll operators, while excluding direct exposures to local sources such as car exhaust. Three of the five subjects already lived and worked in the Paso del Norte border region and were assumed to have been exposed to similar ambient PM conditions on a regular basis. In order to maintain double-blind test conditions, neither the test subjects nor the medical technician assisting with the ECG and spirometry measurements were kept informed of ambient PM levels and trends throughout the evening. Moreover, in order to prevent both the test subjects and the medical technician from directly observing external visibility conditions indicative of PM levels the transparency of the gazebo's screen walls was reduced by directed interior lighting.

Although it would have been preferable to record cardiopulmonary test data only on evenings with high PM peak events or on evenings with low-enough PM levels to be usable as controls, it soon became clear that the chosen test period was characterized by frequent gusty winds and relatively few evening PM episodes. In fact, the screened gazebo set up for the volunteer subjects suffered damage from strong wind gusts and multiple measurement episodes involving test subjects had to be postponed due to high wind forecasts. In addition to the risks to volunteers and equipment, gusty winds tend to disperse urban PM clouds, disrupt drainage flows, and re-aerosolize enough crustal matter to prevent useful background measurements for control purposes.

Hourly wind speed averages for six of the eight evenings during which ECG and spirometry measurements were performed are shown in Figure 9a. Although several windy episodes are readily recognizable, even seemingly calm evenings were sometimes disrupted by wind gusts capable of re-aerosolizing significant amounts of crustal matter but too brief in duration to have much effect on the corresponding hourly wind speed values. Altogether, three of the eight sets of evening measurements were found to represent moderate to high evening PM events with minimal to moderate wind disturbance, while three sets of low PM evening measurements appeared to qualify as potential control data sets.

Of the two TEOM instruments monitoring $PM_{2.5}$ and PM_{10} levels, the $PM_{2.5}$ instrument repeatedly malfunctioned, providing complete $PM_{2.5}$ sequences for only five of eight evenings. As shown in Figure 9b, during three of these evenings $PM_{2.5}$ and PM_{10} measurements were highly correlated. Two evenings, however, showed occasional readings with excessively high PM_{10}:$PM_{2.5}$ ratios, presumably as a result of re-aerosolization of crustal PM by transient wind gusts. This illustrates the need for recording wind patterns at much higher time-resolution when correlations need to be made between physio-

Figure 9. Wind Speed (a), $PM_{2.5}$ Levels (b), and PM_{10} Levels (c) on Six Selected Evenings in March and April 2002 when ECG and Spirometry Readings were Recorded on Subjects A through E



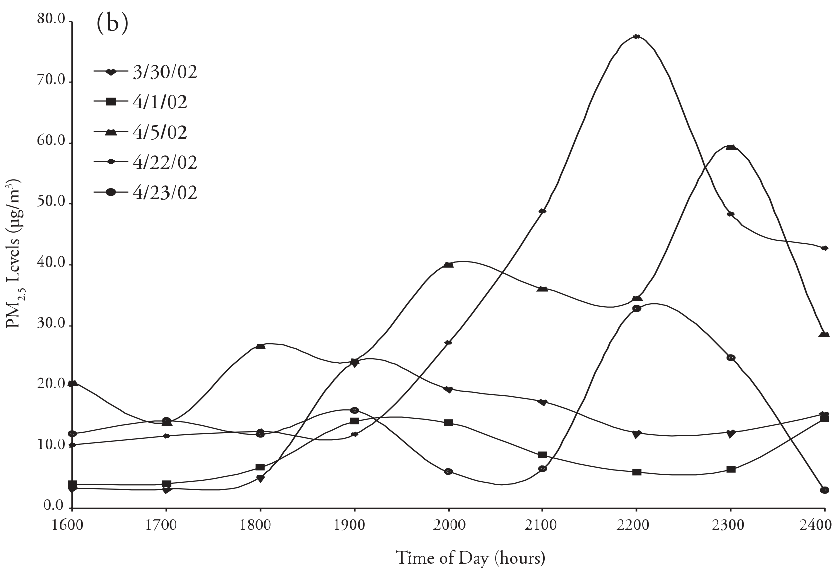
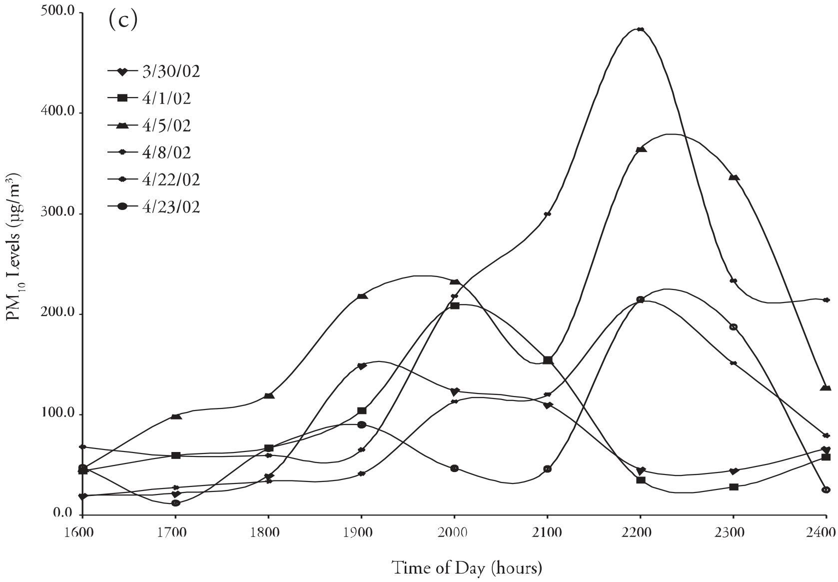


Figure 9. continued



Notes: The missing $PM_{2.5}$ profile for April 8 was due to equipment malfunction. Notice the low PM levels on "control evenings" March 30 and April 1, as well as a strong evening PM event on April 22.
Source: Authors

logical time-series measurements and local wind conditions. Details about the processing and evaluation of ECG and spirometry data have been summarized in Appendix A.

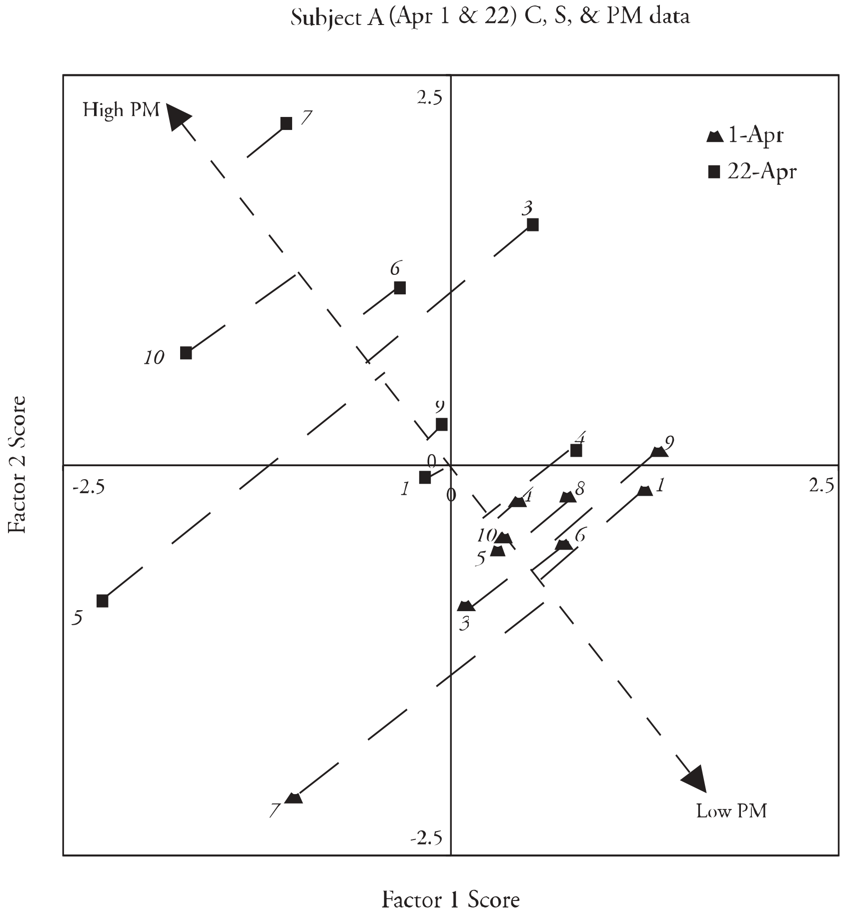
Correlation of ECG and Spirometry Data with PM_{10} and $PM_{2.5}$ Levels

In order to enable an exploratory look at the correlations between subject A's ECG and spirometry profiles, as well as ambient $PM_{2.5}$ and PM_{10} levels, a combined data set was prepared. It incorporated subject A's ECG and spirometry profiles, plus the corresponding $PM_{2.5}$ and PM_{10} levels, for two evenings thought to represent typical high PM and low PM "control" conditions. The corresponding PCA loading and score plots are shown in Appedix Figure 6 (page 311) and Figure 10. Although direct combination of data sets produced by different methods is sometimes frowned upon, it should be noted here that the ECG and spirometry data sets were found to possess substantial shared variance during the CCA pre-testing step.

Because all variables were autoscaled to unit variance, removal of the two PM variables among the 75 ECG and 13 spirometry variables does not cause appreciable quantitative or qualitative changes in the first few principal components of interest here. For all practical purposes, the position of the $PM_{2.5}$ and PM_{10} variables in the F1/F2 loading plot in Appendix Figure 6 (page 311), representing 51% of the total variance in the combined data set, can be regarded as equivalent to a direct projection of two external parameters into the combined ECG/spirometry data space. The presence of compact, irregularly shaped clusters of variables, most of which occupy the peripheral regions of the plot, indicate that this is a data space in which strong correlations exist between groups of variables. Moreover, the absence of a clear tendency of ECG, spirometry, or PM variables to separate from each other along simple dividing lines strongly encourages and justifies a more detailed exploration.

Clearly, both PM variables are strongly represented in this joint factor space, with no less than 85% of the $PM_{2.5}$ variance projecting into the F1-/F2+ quadrant. The positive, "high" side of both PM vectors appears to be strongly associated with the very same set of low-frequency ECG variables (C1 through C13) noted before as

Figure 10. Score Plot of a Combined ECG/Spirometry Data Set for Subject A



Notes: The figure contains two series of measurements recorded on April 1 (no evening PM peak) and April 22 (high evening PM peak). The loading plot (a) also depicts the relative positions of the corresponding $PM_{2.5}$, PM_{10}, and heart rate variables in the F1/F2 space. This demonstrates positive correlations between both PM levels and lower ECG frequency components, plus exhalation duration. It also demonstrates negative correlations with ECG-Fast Fourier Transform (FFT) peak and shoulder intensities and various spirometry parameters representing flow and volume. Note the low correlations with heart rate. The F1/F2 score plot (b) shows the expected differentiation between the two test dates when individual data points are projected onto the known PM vector in (a). For a more detailed interpretation, see text.
Source: Authors

characteristic for some of subject A's high PM ECG profiles (see the F1/F4 loading plot of the combined ECG data space for all test subjects in Figure A2d in Appendix A). Keeping in mind that the fundamental beat frequency in channel 8 has effectively been removed by re-scaling all series of eight ECG beats to a unit time base and normalizing all channel intensities to C8, the neighboring channels (C4 through C7 and C9 through C13) should express most of the remaining variability in fundamental beat frequency (see Figure 9b), whereas the lowest ECG frequency channels (C1 through C3) should correspond directly to the "LF" and "HF" frequency bands used in HRV analysis by means of beat frequency monitors (Task Force of the European Society of Cardiology and the North American Society of Pacing and Electrophysiology 1996).

In other words, the same shift in HRV toward lower frequencies reported to occur during human or animal exposure experiments (Holquin, et al. 2003) is evident, except that this shift has been transposed to the much higher frequency domain of the ECG profiles and now primarily manifests itself as a shift in spectral power from higher beat frequency overtones in the C14 to C28 range to the fundamental frequency bands. However, as discussed before, some of the lowest frequencies could also represent ECG profile contributions from respiratory muscle action potential. Better understanding of these potentially overlapping factors awaits further experiments with model ECG profiles as well as expansion of the ECG sequences to 16 or more profiles in order to obtain greater overlap with the heart rate monitor literature on HRV effects of PM exposure.

Both the spirometry "volume" and "flow" variables can be seen to surround the negative component of the PM vector in the F1+/F2- quadrant, thus indicating increased maximum exhaled respiratory volume and flow velocity during exposure to low PM levels. The maximum volume parameter is joined by the even-moment variables, suggesting that all volume-related curve measurements have increased. To a lesser extent, the same association can be seen between the maximum flow parameter and the higher odd moments (S3, S5, S7, and S9) with S1 being found in the vicinity. At the same time, the exhalation time parameter displays a moderately strong association with high PM levels.

Also, it is interesting to note the behavior of the various FFT modulo-8 "top," "shoulder," "slope," and "valley" channel variables, as defined in Appendix A. The top channels representing the prominent modulo eight-beat frequency peaks load heavily on the positive side of factor 1. The C24, C32, and C40 top channels, together with the corresponding C31/33 and C39/41 shoulder channels, thought to represent primarily T-wave-dominated frequency bands, associate strongly with low PM, suggesting that fairly broad but regularly shaped T-waves tend to be observed then. By contrast, the corresponding down-slope channels (C27, C35, and C43) of the T-wave-dominated frequency band associate fairly strongly with high PM levels, suggesting possible broadening or other changes in T-wave peak shape.

Notwithstanding the spontaneous, strong associations among ECG, spirometry, and PM variables, the F1/F2 space depicted in Appendix Figure 6 (page 311) and Figure 10 is unlikely to represent the optimum orthogonal rotation of factor space for model-building purposes. In spite of the fact that 85% of the $PM_{2.5}$ variance is represented here, orthogonal rotations and/or extensions to higher factor spaces calculated by means of "supervised" multivariate calibration methods are likely to reveal the presence of even stronger correlations. In fact, the corresponding F1/F2 score plot, although exhibiting strong agreement between known PM concentrations and individual score positions, as illustrated by the results of a simple orthogonal projection shown in Appendix Figure 7 (page 312), also reveals apparent discrepancies.

PCR is one of the most direct PCA-based multivariate calibration methods available to determine the maximum degree of correlation between the multidimensional physiological data sets and the corresponding $PM_{2.5}$ and PM_{10} values. Although computationally more complex than simple multilinear regression (MLR), PCR (essentially MLR performed on principal component scores rather than on the original variables) is the preferable regression method when dealing with highly redundant dependent variables such as those that constitute the ECG and spirometry data sets. This raises the questions of what the dependent and independent variables in these regressions should be and whether it is it wise to attempt to predict the environmental parameters from the physiological measurements, or vice versa. One way to bypass those questions entirely in the exploratory data analysis stage is to use CCA rather than MLR or PCR, as is recommended by Chakravarty (1993).

In this particular case, however, the intrinsic dimensionality of the available physiological data is far higher than that of the corresponding environmental data. Since one is more likely to succeed in predicting low-dimensional data configurations from high-dimensional data spaces than vice versa, the choice of the physiology variables as the independent parameters is more or less predetermined. Furthermore, although it might intuitively make more sense to attempt to predict health effects from environmental parameters than the other way around because of the known causal relationships between PM levels and cardiopulmonary end points, it should be remembered that statistical correlation methods are by definition blind to causality. Therefore, the following paragraphs will describe the use of PCR with ECG and/or spirometry data as the independent variables, and PM levels or other environmental data as the predicted variables.

Table 1 lists the PCR results for all five subjects and a total of 122 ECG profiles when regressed against PM_{10} and $PM_{2.5}$ as the dependent variables, using a minimum of two time-series (18 profiles) and a maximum of nine PC components (a 2:1 profile-to-variable ratio) to reduce the probability of chance correlations. Because for subjects C and D reliable $PM_{2.5}$ measurements were only available for one evening, their two time series were combined for the $PM_{2.5}$ regression. As seen in Table 1, subject A's ECG profiles show strong associations with PM_{10} (R^2 81.0%, $p < 2.2\%$) and very strong associations with $PM_{2.5}$ (R^2 90.9%, $p < 0.1\%$), whereas all of the R^2 and p-values for subjects B, C, and D fall within the 19% to 31% and 73% to 96% ranges. Only subject E (a younger sister of subject A but in better overall condition) reaches R^2 values of 42.3% and 55.1% for PM_{10} and $PM_{2.5}$, respectively, with corresponding p-values remaining at the 78% and 54% levels.

Table 1. PCR Results for ECG versus PM Profile Regressions

Test Subjects and Dates				Y = $PM_{2.5}$			Y = PM_{10}		
ID	Sex	Age	2002	R^2(%)	F-Ratio	p<	R^2(%)	F-Ratio	p<
A	M	25	March 30, April 1, April 22, April 23	90.9	10.0	0.00	81.0	4.2	0.021
B	F	22	March 30, April 1	22.4	0.29	0.96	26.5	0.36	0.93
C	M	24	April 5, April 8	(19.3)	(0.37)	(0.93)	30.8	0.67	0.73
D	F	23	April 5, April 8	--	--	--	19.4	0.30	0.93
E	F	22	April 22, April 23	55.1	0.95	0.54	42.3	0.58	0.78

Note: The two time series for subjects C and D were combined for the $PM_{2.5}$ regression because reliable $PM_{2.5}$ measurements were available for only one evening.
Source: Authors

As more is being learned about the properties of the ECG and spirometry data spaces, especially with regard to preferred frequency cut-off levels, and additional raw spirometry data sets are being converted, the search for underlying associations between cardiovascular and/or pulmonary physiological data and ambient PM levels will continue, particularly for subjects B through E. Until now, most attention has been focused on performing additional tests on subject A's time series data to verify the validity and nature of the observed strong associations. This includes a series of PCR analyses on different spirometry and ECG time-series, as shown in Table 2 and Figures A2b and A2c in Appendix A. The spirometry data for subject A are found to model $PM_{2.5}$ and PM_{10} levels during the same high-PM and low-PM evenings included in Table 1 at the 83.4% and 60.7% R^2 values level, respectively, with the corresponding p-values reaching 0.3% and 12.4%. Whereas the spirometry results for $PM_{2.5}$ are quite good, as was to be expected from the spontaneous strong associations observed in the F1/F2 subspace of the combined cardiology/spirometry data shown in Appendix Figure 6 (page 311) and Figure 10, it should be noted that the relative strengths of the associations with $PM_{2.5}$ and with PM_{10} appear to be even more different than for the ECG data.

Table 2. PCR Results for ECG and Spirometry versus PM Profile Regressions (Subject A)

Test Dates	Data Type	Y = $PM_{2.5}$			Y = PM_{10}		
		R^2(%)	F-Ratio	p<	R^2(%)	F-Ratio	p<
April 1, April 22	ECG	90.9	10.0	0.001	81.0	4.2	0.021
April 1, April 22	Spirometry	83.4	7.2	0.003	60.7	2.2	0.124
March 30, April 1, April 22	ECG	77.5	4.6	0.003	63.0	3.5	0.009
March 30, April 1, April 22	Spirometry	62.0	4.2	0.006	44.3	2.0	0.105

Source: Authors

In order to check for the presence of possible time-lags in the physiological response of Subject A, as well as for potential bias in the recorded measurement times, perhaps due to the use of improper time calibration procedures, 30-minute artificial time-offsets (in both directions) were introduced into the data sets. These offsets were found to invariably weaken the observed correlations, thus indicating a relatively fast physiological response. Finally, application of the same PCR procedures to 10 sets of randomized PM data was found to produce an average R^2 value of approximately 20 +/- 9%, thus making it highly unlikely that the PCR results for subject A's actual PM data in Tables 1 and 2 could have been due to accidental modeling of random noise components in the data sets.

Thus far, the large number of data sets available has precluded completion of all multivariate analyses and tests that should be performed to present a full account of the nature and strength of the correlation structures in all data sets. Although none of the other four test subjects produces similarly strong correlations between ECG and/or spirometry profiles and evening PM levels as obtained for subject A, the presence of weaker, but perhaps statistically significant, relationships cannot yet be systematically excluded.

Therefore, work on these data sets is continuing and will be more fully reported in Bhaskar Nookala's graduate thesis at the University of Utah.

Although some of the findings in subject A are likely to have been influenced to a smaller or larger degree by the notable difference in overall constitution and physical fitness compared to the other test subjects, the results reported here would seem to justify a follow-up with other subjectively healthy but poorly conditioned test subjects, not to mention patients with known conditions compromising their cardiopulmonary health, as is the case for a sizeable fraction of elderly people in the United States and Mexico.

Conclusions

The use of multiple time-series of complete, Fourier-transformed ECG profiles and moment-transformed spirometry profiles, obtained on test subjects exposed to ambient PM levels in the field at 30-minute intervals, produced a wealth of data about rapid physiological response and control phenomena at time scales fast enough to resolve not only variations in the repetition rate between different profiles but also size and shape variations within a single ECG or spirometry profile.

Out of five subjectively healthy test subjects in their 20s exposed to ambient PM levels at the Sodar site, one 25-year-old overweight male in relatively poor physical condition showed strong spontaneous associations between PM levels and ECG and spirometry time-series results in a combined Karhunen Loeve principal component plot. Subsequent principal component regression, using TEOM-recorded ambient $PM_{2.5}$ concentrations as the dependent variable, produced R^2 values of 90.9% (99.9% confidence level; F-ratio 10.0) for ECG profiles and 83.4% (99.7% confidence level; F-ratio 7.2) for the corresponding spirometry profiles of this test subject, as recorded during the occurrence of a typical, strong evening PM peak and matched with a low-PM control evening.

Most potential causes of spurious and/or trivial correlations appear to be ruled out by meta-analysis of the test results, including comparison of principal component regression results with low PM control evening data and physiological interpretation of the correlating ECG and spirometry features. The fact that incremental, 30-minute time offsets in both directions weaken the observed correlations indicates the presence of a relatively fast physiological response mechanism.

The other four subjects, one of which was subjected to the same strong evening PM peak whereas the other three were only exposed to evening peaks of lesser magnitude, showed much weaker associations that remain to be fully analyzed.

To the best knowledge, these observations represent the first direct experimental evidence reported thus far of near-instantaneous physiological effects of transient high PM levels on the ECG and spirometry patterns of a subjectively healthy young adult under ambient test conditions.

Recommendations

Because the experimental design of this small-scale physiological effect study, i.e. time-series measurements on a very limited number of test subjects, prevents generalization of these findings to the population at large, larger groups of test subjects should be studied to ascertain whether Subject A's ECG and spirometry responses represent an unusual occurrence or may be relatively common among young adults. Future ECG and spirometry monitoring studies should also include Paso del Norte area residents with compromised cardiopulmonary systems who happen to be living in close proximity to the Rio Grande drainage.

Full-scale time-resolved $PM_{2.5}$ monitoring efforts are urgently needed to tackle the "submerged part of the iceberg,"—the potential health effects of the parent PM episodes within the metropolitan areas themselves. The sheer complexity of these environments with regard to the number of potentially interacting sources of variance likely to affect environmental and health endpoints make it virtually impossible to design small-scale studies with sufficiently interpretable outcomes.

Acknowledgments

The authors acknowledge the invaluable scientific support and advice of Adel Sarofim, Joann Lighty, Dale Stephenson, and Victor Valenzuela, as well as the professional technical support of Gerardo Tarín, Kerry Kelly, Kiran Yelisetty, and Lori Walk.

References

Brook, R. D., J. R. Brook, B. Urch, R. Vincent, S. Rajagopalan, and F. Silverman. 2002. "Inhalation of Fine Particulate Air Pollution and Ozone Causes Acute Arterial Vasoconstriction in Healthy Adults." *Circulation* 105: 1534.

Calderon-Garciduenas, L., A. Mora-Tiscareno, C. J. Chung, G. Valencia, L. A. Fordham, R. Garcia, N. Osnaya, L. Romero, H. Acuna, A. Villarreal-Calderon, R. B. Devlin, and H. S. Koren. 2000. "Exposure to Air Pollution is Associated with Lung Hyperinflation in Healthy Children and Adolescents in Southwest Mexico: A Pilot Study." *Inhalation Toxicology* 12(6).

Chakravarty, T. 1993. "Use Canonical Correlation Analysis Instead of Regression." *Chemical Engineering Progress* 89(10): 76–83.

Fernando, H. J. S., S.-M. Lee, J. Anderson, M. Princevac, E. Pardyjak, and S. Grossman-Clarke. 2001. "Urban Fluid Mechanics: Air Circulation and Contaminant Dispersion in Cities." *Environmental Fluid Mechanics* 1: 107–164.

Holquin, F., M. M. Tellez-Rojo, M. Cortes, J. Chow, D. Mannino, I. Romieu, and M. Hernandez. 2003. "Exposure to Fine Particulate Matter $PM_{2.5}$ and Heart Autonomic Regulation in a Sample of Elderly Residents of Mexico City." Presented at the Sixth Workshop on Mexico City Air Quality, 19–23 January, Mexico City, Mexico.

Jeon, S. J., H. L. C. Meuzelaar, S. N. Sheya, J. S. Lighty, W. M. Jarman, C. Kasteler, A. F. Sarofim, and B. R. T. Simoneit. 2001. "Exploratory Studies of PM_{10} Receptor and Source Profiling by GC/MS and Principal Component Analysis of Temporally and Spatially Resolved Ambient Samples." *Journal of the Air & Waste Management Association* 51: 766–784.

McNee, W., and K. Donaldson. 1999. "Particulate Air Pollution: Injurious and Protective Mechanisms in the Lungs." Pages 653–672 in *Air Pollution and Health,* S. T. Holgate, J. M. Samet, R. L. Maynard, H. S. Koren, eds. London: Academic Press.

Meuzelaar, H. L. C. 1998. "Frequency and Origin of Extreme PM_{10} Air Pollution Episodes at the Hidalgo/Reynosa Border Crossing." Southwest Center for Environmental Research and Policy Proposal for the FY98 Competitive Research Program. http://www.scerp.org.

Mejía, G., and M. Zavala. 2003. "A GIS Based Methodology for Chronic Risk Assessment to Air Pollutants Exposure and Its Application to the Monterrey Metropolitan Area." Presented at the 96th Air & Waste Management Association Annual Conference, 22–26 June, San Diego, California.

Mejía, G., and J. Cardona. 2000. "A Methodology to Determine the Impact of Particle Sources in the Monterrey Metropolitan Area." Presented at the Air & Waste Management Association 93rd Annual Meeting & Exhibition, 18–22 June, Salt Lake City, Utah.

Medina, F. P. 2002. "Aplicación de una Metodología Basada en SIG para Evaluar los Posibles Riesgos en Salud por Exposición a PM_{10} en la Región del PdN." Master's Thesis, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, N.L.

Michaels, R. A., and M. L. Kleinman. 2000. "Clinical, Epidemiological and Bioassay Evidence that Brief Exposure to Aerosols at High Concentrations Documented in Excursions Can Cause Morbidity and Mortality." Paper presented at the Air & Waste Management Association Special Conference on PM2000: Particulate Matter and Health, January, Charleston, South Carolina.

Parks, N. J., J. G. Staniswalis, J. Bader, and Y. Munoz. 1999. "Association of Particulate Matter and Other Priority Air Pollution Levels with Daily Mortality after Windstorms, Still-Air Inversions and Closely-Timed Combinations." Report to the Center for Border Health Research.

Pope, C. A., and D. Dockery. 1999a. "Epidemiology of Particle Effects." In *Air Pollution and Health,* S. Holgate, H. Koren, R. Maynard, and J. Samet, eds. London: Academic Press.

Pope, C. A., R. L. Verrier, E. G. Lovett, A. C. Larson, M. E. Raizenne, R. E. Kanner, J. Schwartz, G. M. Villegas, D. R. Gold, and D. W. Dockery. 1999b. "Heart Rate Variability Associated with Particulate Air Pollution." *American Heart Journal* 138: 890–899.

Sheya, S. N. 2002. "Development of Thermal Desorption-Gas Chromatography/Mass Spectrometry as a Rapid Method for Ambient Particulate Characterization." Ph.D. diss., Material Science Engineering, University of Utah, Salt Lake City, Utah.

Task Force of the European Society of Cardiology and the North American Society of Pacing and Electrophysiology. 2003. "Heart Rate Variability: Standards of Measurement, Physiological Interpretation and Clinical Use, Technical Report." Elk Grove Village, Ill.: BioTechplex Corporation.

Windig, W., and H. L. C. Meuzelaar. 1987. "Numerical Extraction of Components from Mixture Spectra by Multivariate Data Analysis." Pages 67–102 in *Computer-Enhanced Analytical Spectroscopy,* H. L. C. Meuzelaar and T. L. Isenhour, eds. New York: Plenum Publishing.

Windig, W., and H. L. C. Meuzelaar. 1984. "Nonsupervised Numerical Component Extraction from Pyrolysis Mass Spectra of Complex Mixtures." *Analytical Chemistry* 56: 2297–2303.

Appendix A

Processing and Evaluation of ECG Measurement Profiles

Collection of physiological measurement data on human subjects under field conditions is likely to introduce multiple sources of unwanted variance, such as electrical background noise and/or involuntary muscle activity of less than completely resting test subjects. In order to minimize the latter effects as far as possible, test subjects were asked to relax for five minutes in the reclined passenger seat of a car parked next to the gazebo prior to starting the ECG measurements. Doors and windows of the car were kept open to allow the evening breeze to blow through and keep the subjects breathing the same air as during the previous 20 minutes to 25 minutes since the last ECG measurement.

Output from the King of Hearts home cardiac monitors (Instromedix, San Diego, CA) is normally encoded as sound (for transmission over regular phone lines to a medical professional at a remote site). This output includes both digital and analog information. The analog information is the specific ECG profile of the test subject as a frequency modulated signal imposed on a ~1.9 kHz carrier signal. Extraction of these ECG traces was compounded by difficulties in recording the signal. A standard numerical approach to decoding this signal involves the use of an FFT algorithm to convert the signal into the frequency space where it is demodulated. During this procedure it was noted that the recorded ECG signals had been accidentally "clipped" due to recording with excessive gain and only eight bits of digital resolution. This clipping resulted in significant distortion of the analog signal when decoded. Therefore, a numerical analog to Phase-Locked Loop (PLL) decoding was employed to recover the original signal with relatively high fidelity. The output of the PLL algorithm is a plot of frequency shift versus time, which is equivalent—within a scale factor—to the original ECG trace.

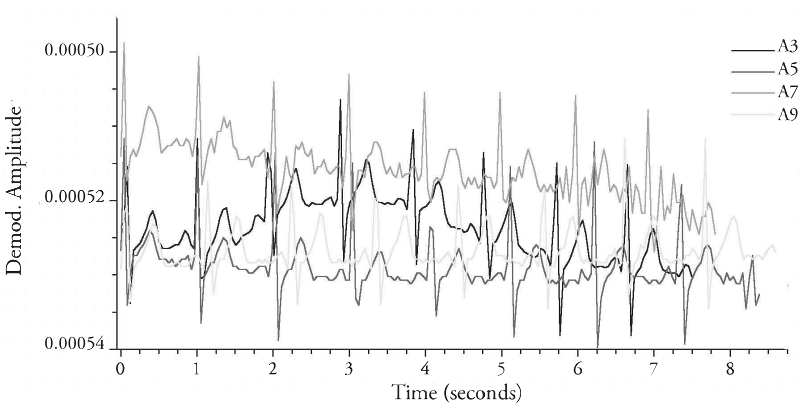
Having successfully repaired the damaged ECG traces using the PLL approach, a new set of problems presented themselves: time-based ECG traces are not suitable for PCA-based multivariate statistical analysis. Variations in pulse rate make it difficult to simply overlay cardiac cycles. Further, HRV, or rather lack thereof, is associated with known sensitivity to ambient PM levels in people with compromised cardiopulmonary systems (Chandra 2003). Reformatting the ECG traces via FFT into a frequency spectrum indicating patterns of repetition in the profiles, however, offers the opportunity to compare structural features associated with the harmonics of the cardiac cycle between subjects. The key to this strategy is to renormalize the time scales of all of the cardiac profiles to yield a common pulse frequency.

The transformation to this common pulse frequency was performed as part of the process of generating the FFT spectrum. For each ECG trace, the first eight complete cardiac cycles of the time series were selected. All the traces were digitally recorded at a common sampling rate, and thus, the number of data points in the eight-cycle sequence is inversely proportional to the pulse rate. In order to perform the FFT procedure—which requires 2^N data points where N is an integer (Chakravarty 1993)—these profiles were interpolated onto 512 (2^9) data points prior to the transformation into frequency space. The result of this procedure was that the amplitude of the principle frequency in the spectrum, which matches the pulse frequency, always occurs in the eighth "channel" of the FFT spectrum, and all the harmonics of the pulse occur at modulo eight channels, e.g. at integer multiples of eight. Thus, each channel of the FFT spectrum was made suitable for use as an individual variable in the multivariate data analysis.

Figures A1a, A1b, and A1c illustrate two of the key steps as individual eight-cycle cardiac profiles are interpolated onto the same number of sample points and then Fourier-transformed into frequency space. The frequency information in Figure 9c is displayed in a simplified form known as a power spectrum. The power spectrum of the signal (the magnitude of the complex frequency amplitudes produced by FFT) along with the original pulse rate, were then used for subsequent data processing. For computational reasons, only power spectra limited to the first 75 data points (plus the original pulse rate) were used in the multivariate data analysis. These 75 points included frequencies up through the eighth overtone of the pulse frequency (i.e., the harmonic). Finally, the spectra were normalized to a common amplitude for the principal frequency component in the eighth channel of the FFT profile.

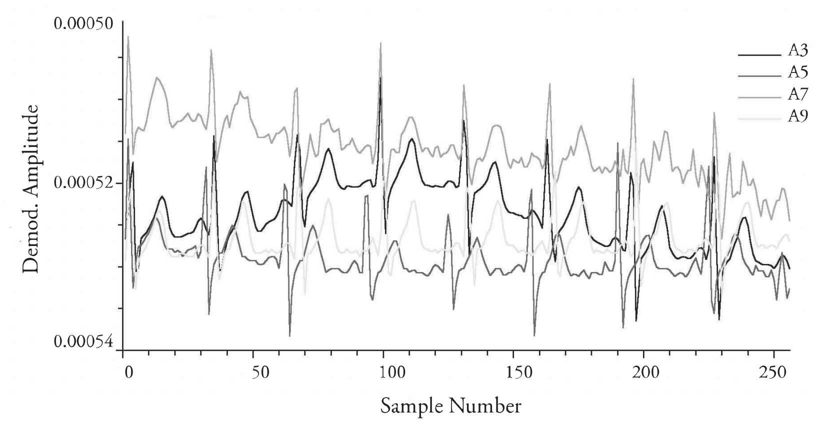
The FFT approach has additional advantages. Because the baselines of many of the ECG profiles exhibit variable offsets, strong drift, and not infrequently other strong low frequency disturbances (see Figure A1a), the variation in the trace associated with these signals masked all of the (higher frequency) structural features of the cardiac trace. As seen in Figure A1c, the Fourier transform separated and concentrated this information in a small set of frequencies below and around the fundamental (pulse) frequency. Notice the comparative closeness of the frequency spectra at frequencies above the harmonic. The clear advantage of the FFT procedure is that repetitive signal characteristics, such as those related to average heart rate and its degree of variability, tend to be preserved and even highlighted.

Figure A1a. Heart Data Preprocessing Steps: Raw Sequences of Eight Consecutive ECG Complexes Obtained from Subject A on April 22



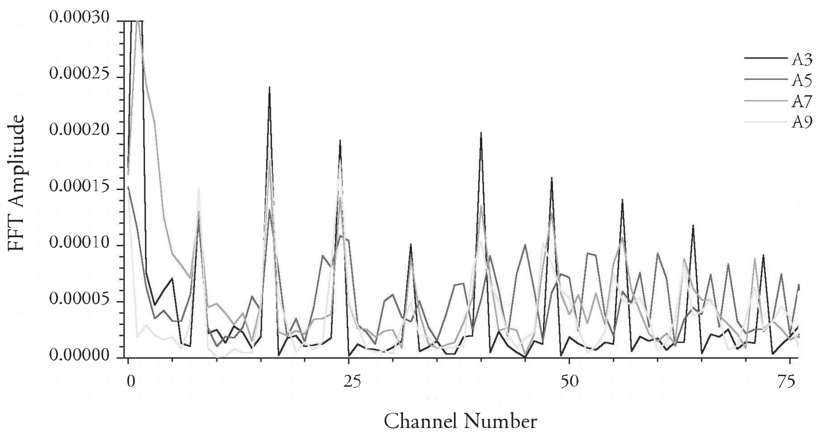
Source: Authors

Figure A1b. Heart Data Preprocessing Steps: Same ECG Sequences After Time-Base Standardization to a Single Eight-Beat Interval



Source: Authors

Figure A1c. Heart Data Preprocessing Steps: Corresponding Fourier-Transformed Profiles



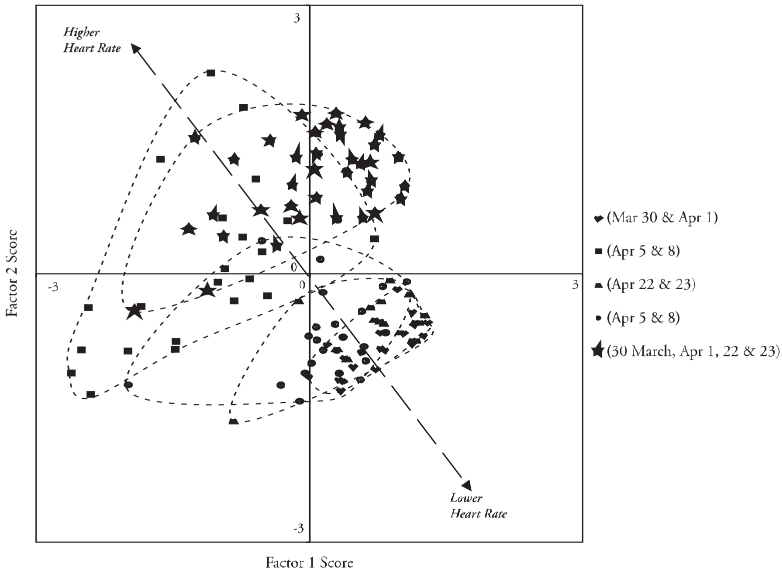
Notes: Hourly interval sequences shown only to avoid excessive clutter. In the figure legend, A indicates the subject identifier and the number indicates the sample number.
Source: Authors

Various ECG data sets and subsets were compiled for subsequent exploratory multivariate analysis by means of PCA, with or without Varimax rotation, to help bring out informative associations and trends by projecting component scores and loadings into lower-dimensional subspaces. More detailed examples of this PCA-based approach to exploratory multivariate analysis are shown in Chapter VI. For a primer on the possibilities and limitations of PCA-based multivariate data analysis in complex high-dimensional data sets, see Windig, et al. (1986) as well as textbooks by Massart, et al. (1988) and Sharaff, Illman, and Kowalski (1986). For the purposes of this chapter, it should be noted that the terms "factor" and "factor analysis" (FA) will be used synonymously with "principal component" and "principal component analysis" or PCA, respectively.

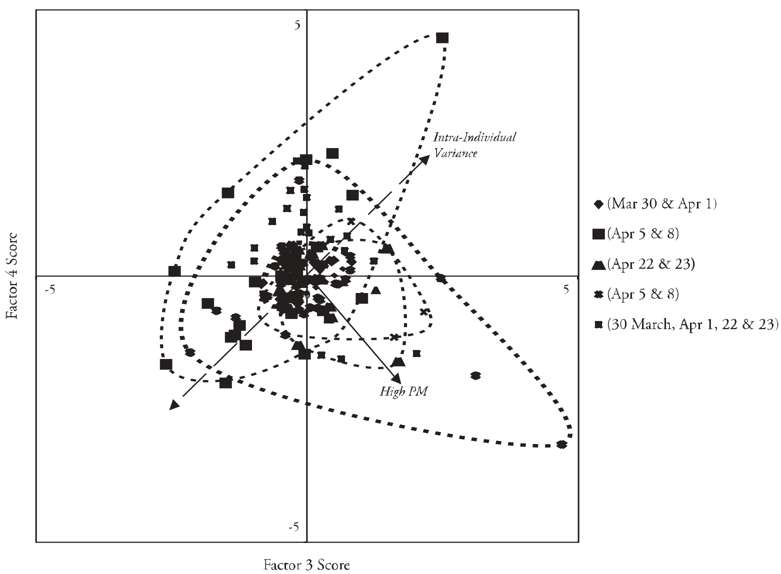
Examples of PCA scores and loadings for one such data set involving 12 different evening sequences with between nine and 10 ECG profiles each, obtained from two male and three female subjects (see Table 1), are shown in Figures A2a, A2b, A2c, and A2d. The primary usefulness of such composite data spaces is to detect outliers among the profiles (viz. scores) that can be traced back to experimental error and/or excessive noise and that should be repaired or removed to prevent error propagation among the other profiles and variables during subsequent normalization procedures. The data set shown in Figures A2a, A2b, A2c, and A2d has already been pruned of three or four outlier profiles with standardized scores well above the "five sigma" level. Consequently, there are no extreme outliers.

Figures A2a, A2b, A2c, and A2d. Factor Score and Loading Plots for the Complete ECG Data Set with All Five Subjects and 12 Evening Sequences (Nine to 10 Profiles Each) Recorded at the Sodar Site

(a)

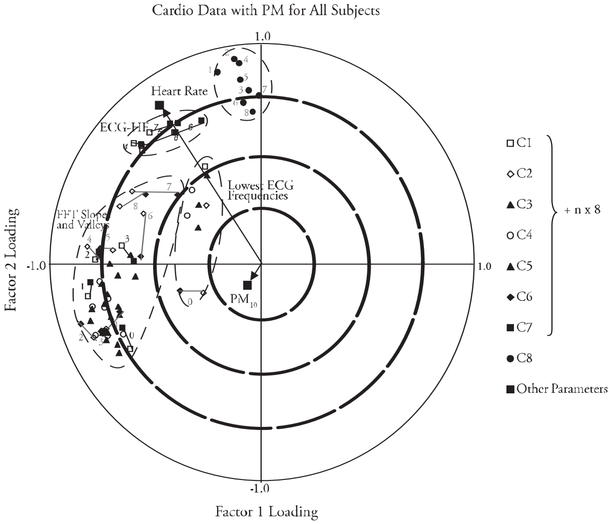


(b)

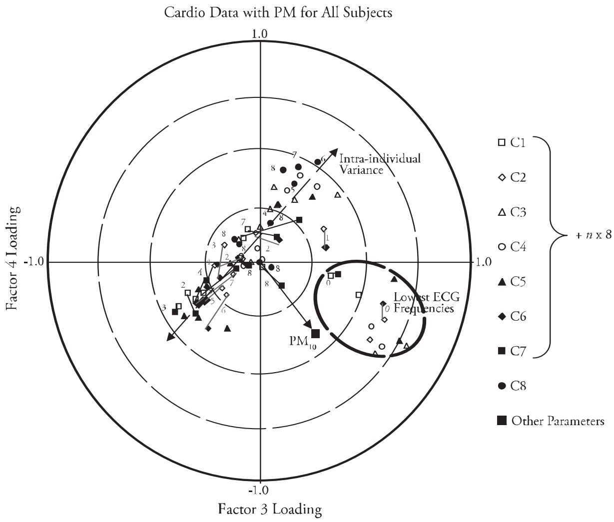


Figures A2a, A2b, A2c, and A2d.

(c)



(d)



Notes: Whereas pronounced inter- and intra-individual variations, such as correlating strongly with heart rate, dominate the F1/F2 score plot (a), the F3/F4 plot (b) shows a modest but clear PM correlation for subject A. Examination of the corresponding loading plots, (c) and (d), suggests that high heart rates correspond with more pronounced peak top and shoulder channel intensities in the FFT-transformed ECG profiles, whereas higher PM values may correlate with relatively low FFT frequencies.
Source: Authors

A second question that can be addressed with the help of this data space is the overall degree of correspondence between sequences of ECG profiles obtained from a single subject on the same evening, as well as on different evenings. Clearly, time series obtained from each individual tend to produce more or less tightly clustered groups in the four-dimensional data subspace spanned by F1 through F4, together explaining 65.3% of the total variance in the data set. Nonetheless, in the F1/F2 score plot shown in Figure A2a, subject A (a 25-year old male represented by four time series) and subject C (a 24-year old female with two time series) clearly show a higher degree of intra-individual profile variation than the other three subjects, including their respective test partners (see Table 1). In the F3/F4 score space (Figure A2b), subjects A and C still exhibit the highest degree of intra-individual variation but are now more or less co-centered with the other subjects. However, a loosely clustered streak of approximately seven profiles, dominated by Subject A, is seen to radiate out into the F3+/F4- quadrant, thereby indicating the possible presence of a special component.

Before examining the corresponding loading plots in Figures A2c and A2d, it should be pointed out that the "correct" way of depicting standardized PCA loadings is by means of vector plots in which the cosine of the angle between individual variables, as well as between variables and component axes, equals the cosine of the correlation coefficient (R), whereas the length of the vector shows the variance represented within that space (Windig, et al. 1986). Drawing 75 vector arrows in this plot would tend to obscure valuable detail. Therefore, most of the individual vector positions have been labeled only with their variable name or number.

Inspection of the F1/F2 loading plot (Figure A2c) reveals the main source of variance in this large subspace to be due to a broad band of high-loading variables stretching all the way across the F1-/F2+ quadrant into the F1-/F2- quadrant. The overall direction of this band aligns itself with the major direction of intra-individual variance in score plot 15a. Along this broad band, the center channels (C8) of the strong modulo eight peaks in the frequency domain—the "overtones of the fundamental frequency"—can be seen to clearly separate themselves from two clusters of "shoulder channels" (modulo C1 and C7) on each side. From several clusters of adjoining "slope channels" (modulo C2 and C6), with the three "valley channels" (modulo C3, C4, and C5), they close the procession while overlapping with some of the previous signal groups. It is clear that various types of heart rate and ECG peak shape variabilities are displayed in great detail. The lowest frequency peaks represent changes in beat frequencies (i.e., HRV), the intermediate frequencies depict changes in the broad ventricular repolarization peak (know as "T-wave"), and the highest frequencies represent the sharp ventricular depolarization peaks (known as "QRS complex").

In a nearly orthogonal direction to the HRV band, the single heart rate variable (HR) is found loading strongly on the F1+/F2- quarter, thus displaying a strong association with the main direction of inter-individual variation in the corresponding score plot (Figure A2a). Since HR was scored as the inverse of heart rate, subjects A and C distinguish themselves from the other three subjects by their relatively high heart rates. Finally, it should be noted that the PM_{10} variable, projected into this space as a quick-and-dirty check for possible associations, has practically zero loading in the F1/F2 space and thus appears not to be associated with the main intra-individual and inter-individual trends in the ECG profiles exhibited here, together explaining 52.7% of the total variance in the data set.

Although all five subjects were "subjectively healthy" (they regarded themselves as not being sick), as required by the original study design, subject A was clearly overweight and in such a poor overall physical shape that fulfilling the relatively simple task of blowing hard and deep into the spirometer mouthpiece already tended to upset his normal breathing pattern and heart rate for several minutes. Therefore, it is quite possible that the five-minute resting period in a reclined car seat before his ECG was recorded may not have been sufficient.

Subject C, however, was neither obese nor in poor physical condition. Interestingly, the literature on pattern recognition of ECG profiles provides several references about relatively high intra-individual variability in healthy young females, generally attributed to a relatively strong parasympathetic neural component (Evans, et al. 2001). Subject C might have been a bit more excited or nervous since she was personally involved in some of the technical aspects of this study and had effectively filled in for a volunteer test subject who failed to arrive. Thus, her ECG and spirometry data might perhaps need to be rejected for some types of statistical processing and testing, such as for failing some of the original study design criteria or the double-blind requirement.

The F3/F4 loading plots in Figure A2d demonstrate that the special behavior of subject A's profiles is due to the increased relative intensities of a series of low frequency signals representing channels 1 through 13 of the FFT power spectrum. It should be pointed out that the ECG FFT channel 1 roughly corresponds to the low frequency (LF) region (0.04 Hz–0.15 Hz) of the literature on frequency domain HRV studies by means of conventional heart beat monitors, whereas channels 2 and 3 roughly correspond with the so-called high frequency (HF) region (0.15 Hz–0.40 Hz). In these crucially important pioneering studies, PM effects are usually found to lower the HF/LF spectral power ratio, presumably as a result of shifts in the heart's autonomic control where vagal nerve-mediated mechanisms dominating the HF region are being replaced by slower sympathetic and parasympathetic control mechanisms. HRV-shifts due to PM exposure effects appear particularly well-documented in test subjects with compromised cardiopulmonary systems (Gold, et al. 1998).

By contrast, the ECG-based study design reported here opens up a much higher region of the frequency domain (0.10 Hz–10.0 Hz range, with possible extensions to well over 100 Hz). This enables examinations of variations in the shape, amplitude, and regularity of specific features within each ECG cycle, such as in the T-wave or QRS complex. At the same time, it is still possible to reconstruct the same frequency domain studied by heart rate monitoring, provided enough consecutive beats have been registered to effectively access the LF domain. Preferably, the current eight-beat sequence should be replaced with minimally 16 beats to provide a more detailed view of the LF region and enable a more direct comparison with the data presented in the classical HRV literature.

The interpretation and meaning of the lower frequency signals in the F3/F4 loading plot (Figure A2d), thought to explain the loosely clustered streak of profiles radiating into the F3+/F4- quadrant of the score plot in Figure A2b, will be discussed in more detail in the following paragraphs. Here attention should be drawn to the PM_{10}

vector projection into this space, which shows a moderately strong loading into the same direction as the loose streak dominated by subject A's ECG profiles. In addition to the previously discussed potential causes of shifts to lower channels in the frequency domain, the possibility of interference from respiratory muscle action potentials on the ECG recording deserves consideration as well. As discussed, it is quite possible that the five-minute resting period in a reclined car seat before his ECG was recorded may not have been sufficient for subject A, perhaps leaving him slightly out of breath.

Although it is tempting to inquire whether the observed inter-individual differences in the data might perhaps allow detection of systematic trends with regard to gender, age, race, and physical condition, among other characteristics, it should again be pointed out that the special experimental design of this study (i.e. analysis of time-series profiles obtained on a very small group of test subjects) only allows questions to be asked regarding intra-individual variations and their degree of correlation with concurrent variations in selected environmental parameters. Although this does not take away the possibility of trying to explain some of the observed inter-individual patterns and trends on the basis of prior knowledge, such as through literature reports, it categorically prevents generalizations about observed differences between individuals or potential subgroups.

Processing and Evaluation of Spirometry Data

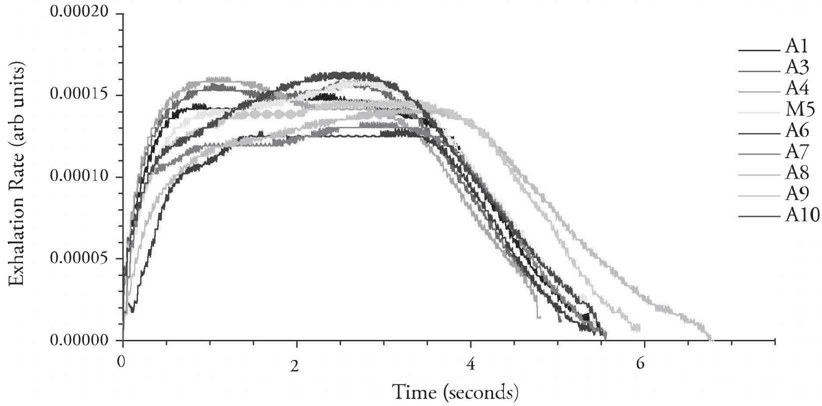
The LifeSigns SP Spirometer (Instromedix, San Diego, CA) used the same type of frequency-modulated signal encoding as the cardiac monitor. Both the volume displaced as a function of time during exhalation and the flow rate as a function of time during the exhalation are available as analog output signals—the second of these being the primary measurement. The special requirements of the spirometry tests, typically performed about five minutes after the ECG measurement, made it necessary to have the subjects stand up in order to achieve maximum chest cavity and lung volume expansion and reduction with minimum resistance.

On-site digital conversion and storage of the standard spirometer audio output created the same signal corruption issues as with the cardiac monitor, and they were resolved the same way—using PLL-based decoding (see above). Attempts to compare these signals via PCA-based methods presented many of the same challenges in terms of variations in exhalation time as the cardiac signals. Though the ECG and spirometry signals posed common problems, the interpolation and FFT method used for the cardiac data proved unsuitable for the spirometry data due to the lack of pronounced repetitive modulations in a single spirometry profile. The FFT-based normalization method was replaced by measures of the size and shape of the exhalation curve using a series of common calculated parameters and statistical moments.

Thus, the following 13 spirometry parameters were computed: S1–S10 = first 10 moments of the exhalation flow profiles; S11 = maximum exhalation flow rate; S12 = total exhalation time; and S13 = mean exhaled flow. Of particular importance among the 10 moments are the first four, namely: S1 = half-volume time fraction; S2 = variance; S3 = skewness; and S4 = kurtosis. The rest of the moments, not surprisingly, follow the pattern of the first four with even moments S6, S8, and S10 conforming closely to variance and kurtosis as expressions of profile "fullness," a measure of expelled volume. Odd moments S5, S7, and S9 followed skewness as a measure of profile symmetry, for example, changes in flow rate.

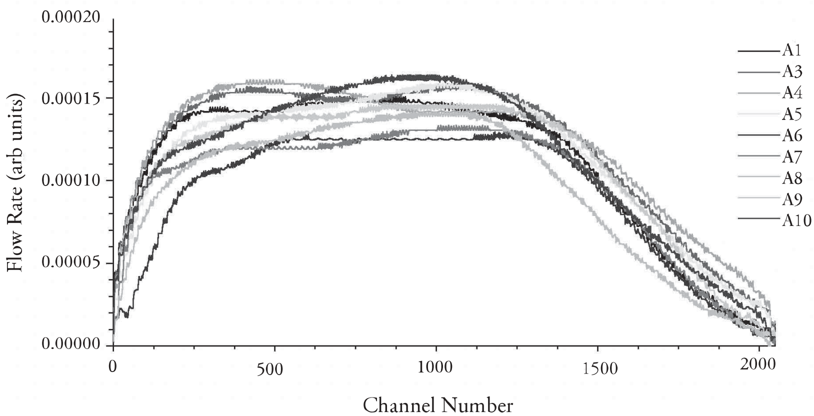
A few selected half-hourly spirometry profiles, obtained from Subject A on the same evening that the strongly varying ECG profiles illustrated in Figure 9a were recorded, are shown in Figure A3a and exhibit marked variations over the course of the evening as well. Figure A3b shows the transformation to a standardized "unit" time base, whereas selected moment-transformed profiles for the entire time series of spirometry profiles are illustrated in Figure A3c.

Figure A3a. Spirometry Data Preprocessing Steps: Raw, Consecutive Exhalation Profiles Obtained from Subject A on April 22



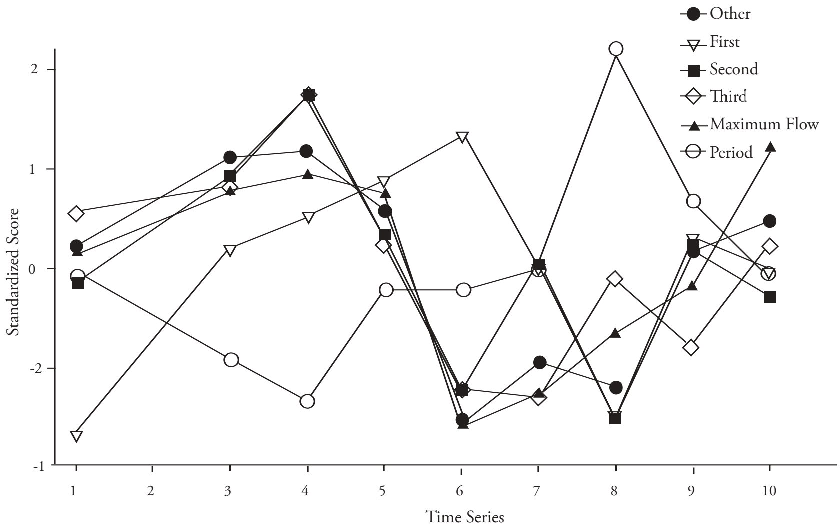
Source: Authors

Figure A3b. Spirometry Data Preprocessing Steps: Same Profiles After Time-Base Standardization to a Single Exhalation Interval



Source: Authors

Figure A3c. Spirometry Data Preprocessing Steps: Corresponding Moment-Transformed Profiles



Note: Only six moment profiles are shown to avoid excessive clutter.
Source: Authors

PCA of moment-transformed spirometry profiles (not shown here because of space limitations) revealed similarly distinct behavior for the profiles of Subject A as observed for the corresponding ECG profiles. This observation prompted an examination of the possible degree of correlation between the ECG and spirometry profiles by means of CCA. This revealed that the factor spaces spanned by the first 10 ECG factors (approximately 95% total variance) and the first seven spirometry factors (approximately 70% total variance) shared well over 50% of their respective variances in a common 1–2 dimensional subspace. This finding raises the question of the physical nature of this correlation. As discussed previously, muscular activity potentials associated with strong breathing can obviously affect ECG profiles (Saul 1998), thereby providing a direct—though somewhat trivial—potential link between the ECG and spirometry data sets. On the other hand, if a strong correlation were known to exist with PM levels for both the ECG and spirometry profiles, some degree of correlation between the latter data sets would be expected to occur as well. As discussed in the section on "Cardiopulmonary Effects of Evening PM Peaks in Young Adults" the latter hypothesis appears to be born out by a more systematic and comprehensive evaluation of the available data.

References

Chakravarty, T. 1993. "Use Canonical Correlation Analysis Instead of Regression." *Chemical Engineering Progress* 89(10): 76–83.

Chandra, T., D. B. Yeats, and L. B. Wong. 2003. "Heart Rate Variability Analysis—Current and Future Trends." Cited 17 November 2004. http://www.bbriefings.com/pdf/28/gh031_t_Biotex~1.pdf.

Evans, J. M., M. G. Ziegler, A. R. Patwardhan, J. B. Ott, C. S. Kim, F. M. Leonelli, and C. F. Knapp. 2001. "Gender Differences in Autonomic Cardiovascular Regulation: Spectral, Hormonal, and Hemodynamic Indexes." *Journal of Applied Physiology* 91(6): 2611–2618.

Gold, D. R., A. Litonjua, J. Schwartz, M. Verrier, R. Milstein, A. Larson, E. Lovett, and R. Verrier. 1988. "Cardiovascular Vulnerability to Particulate Pollution." *American Journal of Respiratory Critical Care Medical* 157(3): A261.

Massart, D. L., B. G. M. Vandeginste, S. N. Deming, Y. Michotte, and L. Kaufman. 1988. *Chemometrics: A Textbook.* Amsterdam: Elsevier.

Saul, J. P. 1998. "Respiration and Blood Pressure Variability: Mechanical and Autonomic Influences." *Fundamental Clinical Pharmacology* 12(Suppl. 1): 17s–22s.

Sharaff, M. A., D. L. Illman, and B. R. Kowalski. 1986. *Chemometrics.* New York: Wiley-Interscience.

Task Force of the European Society of Cardiology and the North American Society of Pacing and Electrophysiology. 2003. "Heart Rate Variability: Standards of Measurement, Physiological Interpretation and Clinical Use, Technical Report." Elk Grove Village, Ill.: BioTechplex Corporation.

Windig, W., W. H. McClennen, H. Stolk, and H. L. C. Meuzelaar. 1986. "Unsupervised Chemical Pattern Recognition in Complex Mass Spectra." *Optical Engineering* 25(1): 117–122.

Index

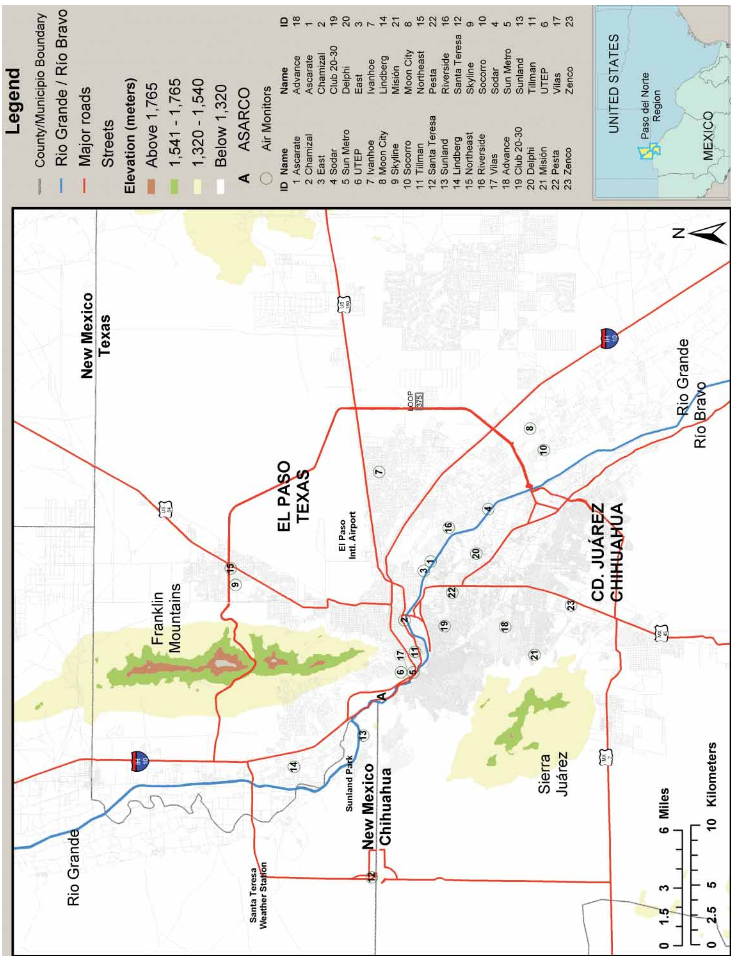
Q

R

S

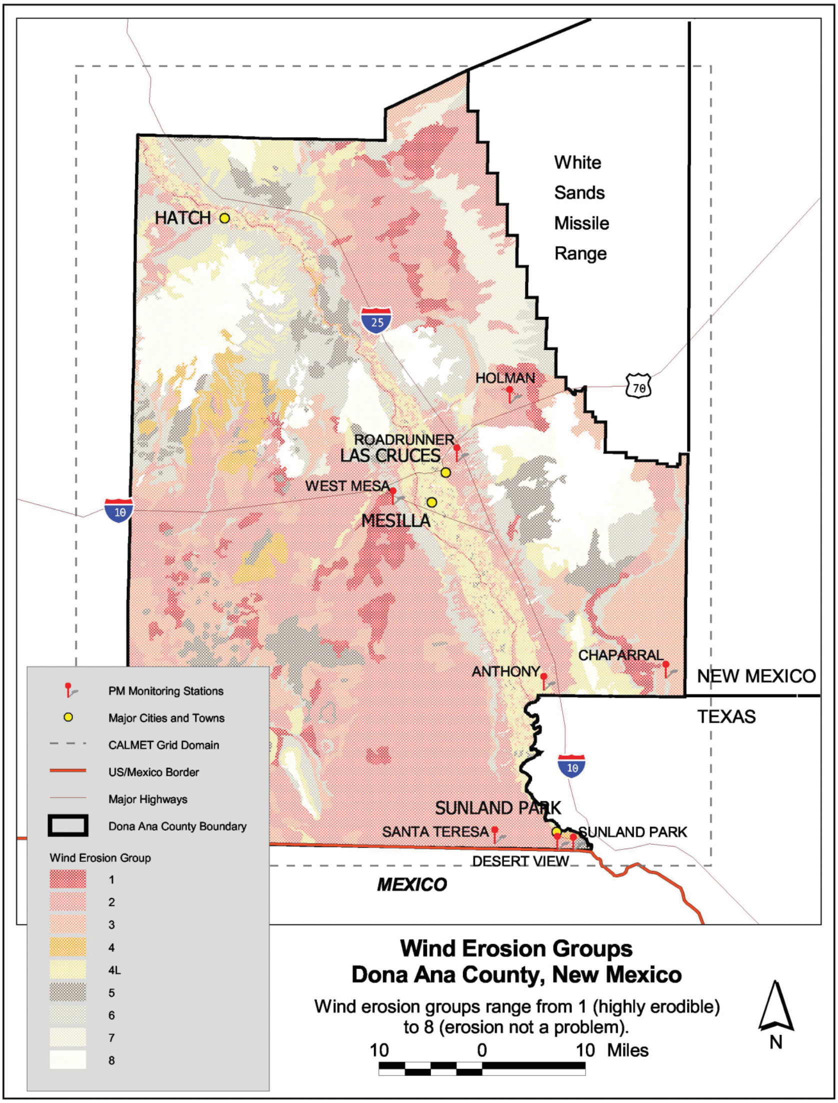
Appendix
Color Figures

Figure 1. Map of the Paso del Norte Region



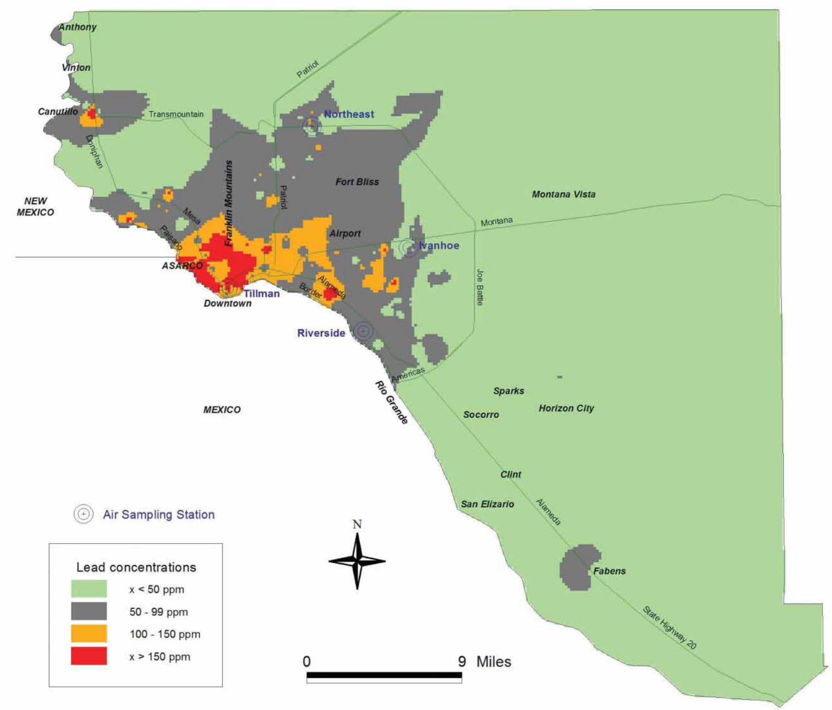
Source: Authors

Figure 2. Wind Erodibility in Doña Ana County



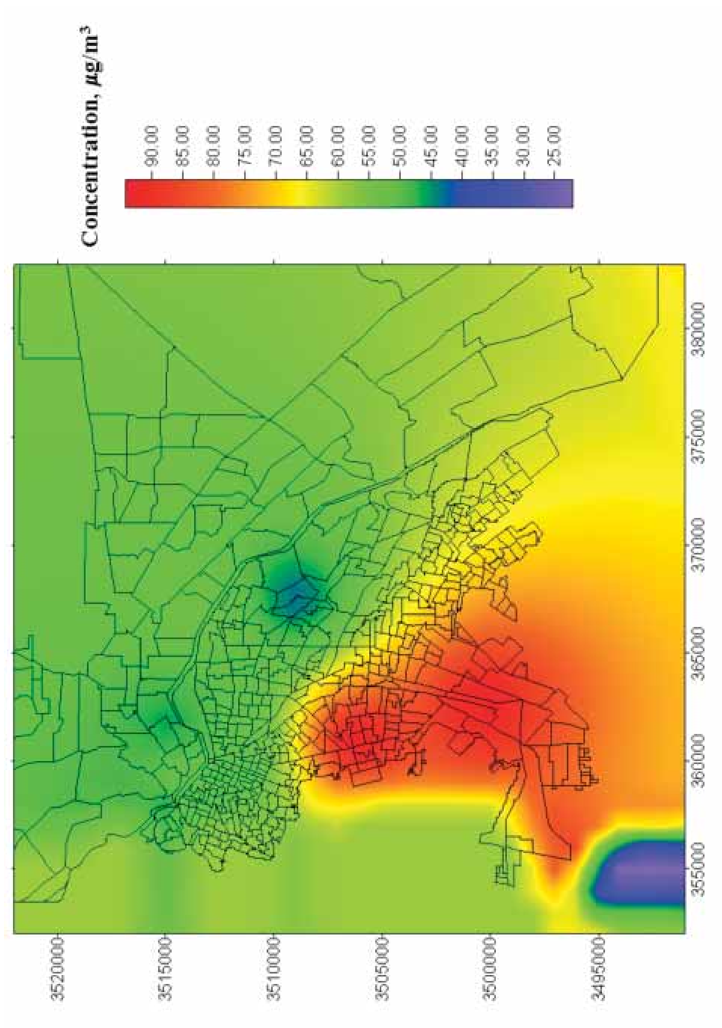
Note: Wind erodibility groups (WEG) range from 1 to 8; group 1 has the greatest wind erosion potential and group 8 has the smallest.
Source: Okrasinski and Greenlee 2000

Figure 3. Lead Levels in Composite Samples from Blocks in El Paso



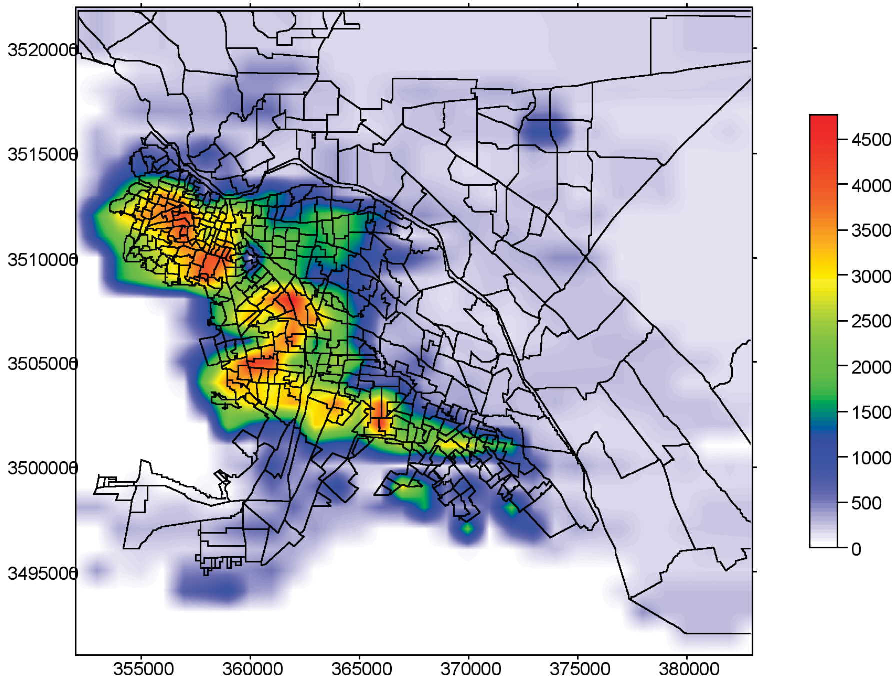
Source: Author

Figure 4. Yearly Average PM_{10} Concentration in El Paso-Ciudad Juárez



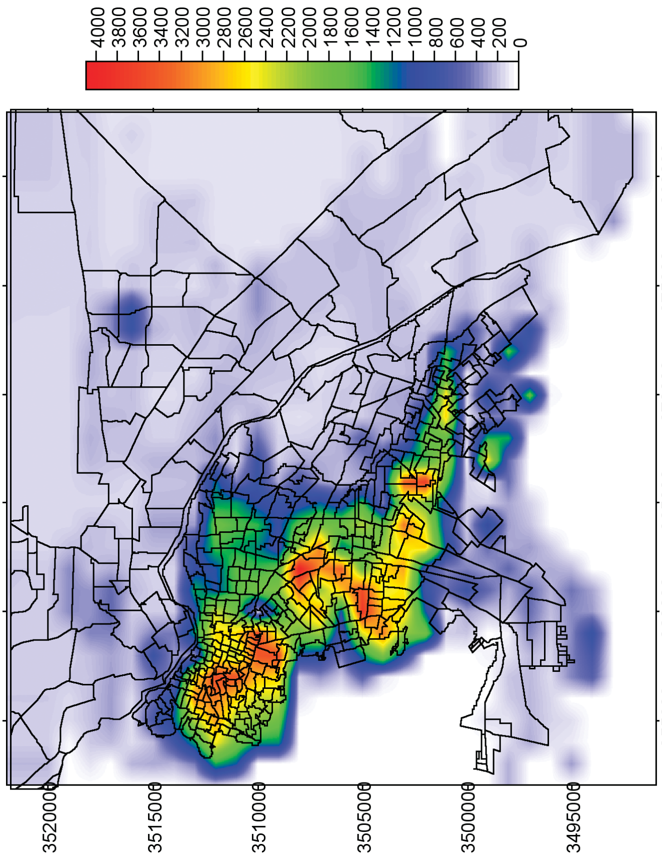
Source: Authors

Figure 5a. Social Risk for Children for Chronic Exposure to PM_{10}



Notes: Social risk is calculated by multiplying the hazard coefficient (unitless) by the population of interest in each cell; the units on the scale are population.
Source: Authors

Figure 5b. Social Risk for Adults for Chronic Exposure to PM_{10}



Notes: Social risk is calculated by multiplying the hazard coefficient (unitless) by the population of interest in each cell; the units on the scale are population.
Source: Authors

Figure 6. F1/F2 Loading Plots of a Combined ECG/Spirometry Data Set for Subject A

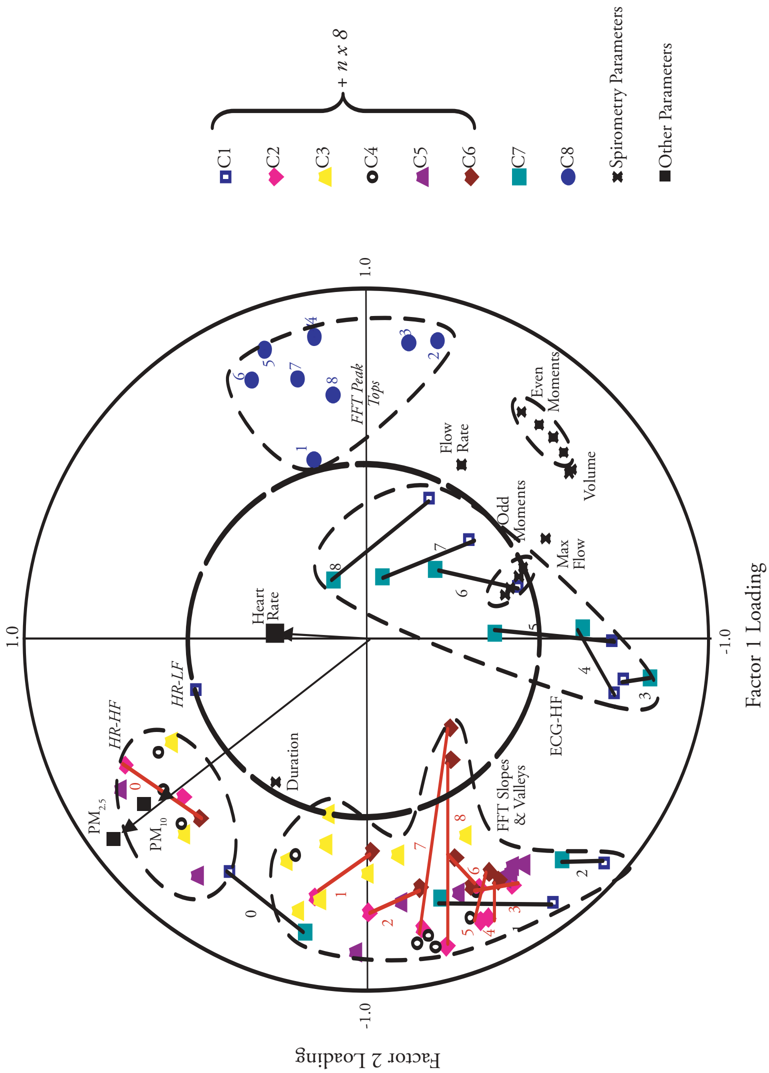
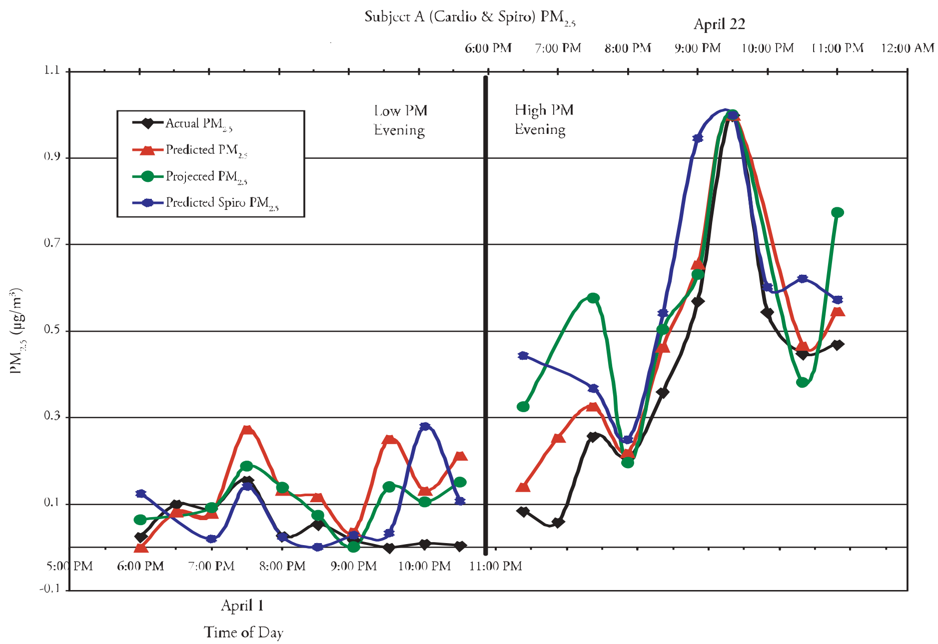


Figure 7. Comparison of Measured and Calculated ("Predicted") $PM_{2.5}$ Levels on April 1 and April 22



Notes: The figure uses the projected F1/F2 scores in Chapter VII, Figure 10 and the results of PCR of the ECG and spirometry data sets, respectively. See Table 2. For a more detailed interpretation, see text.
Source: Authors