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## Characterization and Dynamics of Air Pollutants in the Lower Rio Grande Valley

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### ABSTRACT

The Lower Rio Grande Valley (LRGV) has become a region of increasing interest because of its rapid economic development, increased international border crossing traffic, and extensive agricultural activities. Over the past few years, air pollution problems in the region have substantially increased. However, very few air quality studies have been performed in the area. This paper provides a characterization of air pollutant dynamics and a model in the LRGV, which include the comprehensive interactions of criteria pollutants, VOC's/SVOC's (volatile organic compounds/semi-volatile organic compounds) and fine particulate matter ( $PM_{\text{fine}}$ ). The analysis involved researchers on both sides of the U.S.-Mexican border. A highly mobile monitoring station equipped with a broad array of physical and chemical samplers and sensors was used in December 1995 and March 1998.  $PM_{10}$ /  $PM_{2.5}$  and oxides of nitrogen ( $NO_x$ ) (the latter only in the March 1998 study) concentrations were measured in Reynosa, Río Bravo, and Matamoros, Tamaulipas; Hidalgo,

Coahuila; Brownsville, Texas; and along the freeway between Brownsville and McAllen, Texas. The photochemical model predicted peak ozone concentrations that reached, and on some days exceeded, air quality standards. The concurrent  $PM_{10}/PM_{2.5}$  study involved both physical (size distributed counting) and time-resolved (two-hour) organic chemical (VOC/SVOC-type  $PM_{fine}$  adsorbates) characterization methods. Recently completed multivariate data analysis results from a December 1995 study at one of the sites (Hidalgo International Bridge) are presented to illustrate the capabilities of the time-resolved  $PM_{fine}$  characterization approach. The results of this work show that the LRGV region does not yet appear to have grave air pollution problems, with the possible exception of transient episodes of extremely high PM concentrations. However, with the increase in cross-border traffic over the next few years, air quality is likely to deteriorate.

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## Dinámica y Caracterización de Contaminantes del Aire en el Valle Bajo del Río Grande

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### RESUMEN

El Valle Bajo del Río Grande (VBRG) se ha convertido en una región de interés creciente debido a su rápido desarrollo económico, el incremento del cruce fronterizo internacional, y sus actividades agrícolas extensivas. En el transcurso de los últimos años, los problemas de contaminación del aire se han incrementado substancialmente en la región. Sin embargo, muy pocos estudios de calidad del aire han sido realizados en el área. Este capítulo proporciona una

caracterización de la dinámica de contaminantes del aire y un modelo en el VBRG, el cual incluye interacciones comprensibles de contaminantes criterio, COV/COSV (compuestos orgánicos volátiles/compuestos orgánicos semi-volátiles) y partículas finas de materia ( $PM_{\text{fina}}$ ). En el análisis participaron investigadores de ambos lados de la frontera E.U.-México. Una estación de monitoreo de alta movilidad equipada con una amplia gama de muestreadores físicos y químicos y sensores fue usada en diciembre de 1995 y marzo de 1998. Concentraciones de  $PM_{10}/PM_{2.5}$  y óxidos de nitrógeno ( $NO_x$ ) (el último solo para el estudio de 1998) fueron medidas en Reynosa, Río Bravo, y Matamoros, Tamaulipas; Hidalgo, Coahuila; Brownsville, Texas; y a lo largo de la autopista entre Brownsville y McAllen, Texas. El modelo fotoquímico predijo concentraciones máximas de ozono que alcanzaron, y en algunos días excedieron, estándares de calidad del aire. El estudio simultáneo de  $PM_{10}/PM_{2.5}$  involucró ambos tipos de caracterización, el físico (conteo por distribución de tamaño) y químico orgánico de solución por tiempo (dos-horas) ( $PM_{\text{fina}}$  absorbida de tipo COV/COSV). Los análisis multivariados de los datos completados recientemente de un estudio para diciembre de 1995 en uno de los sitios (Puente Internacional Hidalgo), son presentados para ilustrar las capacidades de la solución en tiempo para el enfoque  $PM_{\text{fina}}$ . Los resultados de este trabajo muestran que la región VBRG aún no parece tener problemas graves de contaminación del aire, con la excepción posible de episodios transitorios con concentraciones de PM sumamente altas. Sin embargo, con el aumento en el tránsito fronterizo durante los próximos años, la calidad del aire probablemente vaya a deteriorarse.

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## INTRODUCTION

Air quality throughout the Lower Rio Grande Valley (LRGV) is being threatened by rapid urbanization, extensive industrial and agricultural development, and significant increases in vehicular cross-border traffic (Gilbreath 1992). Yet, until recently, relatively few air quality studies of the LRGV area have been published, and emission inventory data for the LRGV area are far from complete. In 1997, results of the multi-media Lower Rio Grande Valley

Environmental Scoping Study (LRGVES) (Mukerjee 1997) began providing systematic data on air pollution sources, transboundary transport mechanisms, and exposure risks. Also, preliminary emission inventory data reported by Mejia and Rodriguez (1997) enabled the Instituto Tecnológico y de Estudios de Superiores de Monterrey (ITESM) team to perform a first assessment of photochemical pollution mechanisms (Mejia and Meuzelaar 1997).

In 1995, the University of Utah and ITESM started a collaborative effort, sponsored by the Southwest Center for Environmental Research and Policy (SCERP), aimed at physical, chemical, and biological characterization of fine particulate matter ( $PM_{\text{fine}}$  also known as  $PM_{2.5}$ ) in the LRGV (Mejia and Meuzelaar 1997). In December 1995, 48- to 72-hour-long scoping studies were carried out at four selected sites (Hidalgo International Bridge, Santa Ana Wildlife Refuge, Brownsville International Bridge, and Matamoros Industrial Park). Typically,  $PM_{\text{fine}}$  levels and size distributions were measured around-the-clock and microgram-sized samples were collected on quartz fiber filters at two-hour intervals for subsequent laboratory analysis by means of specialized GC/MS techniques. Simultaneously,  $PM_{\text{fine}}$  samples were taken for microbiological analysis, meteorological parameters were recorded, and a limited number of VOC samples were collected and analyzed on site using the University of Utah's mobile analytical laboratory with field-portable GC/MS equipment.

Although detailed multivariate analysis of the extensive data sets obtained continued into 1998, preliminary evaluation of the voluminous data revealed modest overall  $PM_{\text{fine}}$ - and VOC-type air pollutant levels when compared with earlier field tests in Nogales, Arizona (Dworzanski et al. 1993), with the exception of one severe nocturnal  $PM_{\text{fine}}$  episode at the Hidalgo site and unexpectedly high levels of airborne fecal bacteria at the Brownsville site. The application of a diagnostic meteorological model for the LRGV at the Hidalgo site provided plausible explanations for the observed severe  $PM_{\text{fine}}$  episode, which apparently followed the passage of a cold front accompanied by low inversion layer and urban dust trapped above Reynosa slow drifting into the Hidalgo International Bridge area. The specific origin of the high levels of airborne fecal bacteria at the Brownsville International Bridge is still unknown, but they

probably originate from the Rio Grande.

Based on the preliminary VOC and  $PM_{\text{fine}}$  findings of the scoping studies, a follow-up field study was performed that focused on detailed physical (including size distribution) and organic chemical characterization of  $PM_{\text{fine}}$  at selected receptor sites on both sides of the border. In addition, an attempt was made to model simultaneously and monitor criteria pollutants such as  $NO_x$ , ozone ( $O_3$ ), and sulfur dioxide ( $SO_2$ ) in order to understand the origin and dynamics of both primary and secondary  $PM_{\text{fine}}$  in the LRGV section of the U.S.-Mexican border. Consequently, in March 1998, a second five-day field study was undertaken on both sides of the U.S.-Mexican border between the twin cities of Brownsville-Matamoros and McAllen-Reynosa. During this study,  $PM_{10}$ ,  $PM_{2.5}$ , and  $NO_x$  concentrations were measured in Reynosa, Rio Bravo, and Matamoros, Tamaulipas; Hidalgo, Coahuila; Brownsville, Texas; and along the freeway between Brownsville and McAllen, Texas. A diagnostic meteorological model was applied to the region to simulate wind patterns during the sampling period.

This work consisted of two parts: (1) development of a comprehensive criteria pollutant model for selected LRGV areas involving the integrated use of emission, dispersion, and photochemical sub-models that attempted validation by field monitoring data obtained in March 1998, and (2) development of a novel time-resolved  $PM_{10}/PM_{2.5}$  characterization approach. This approach combined fast, sensitive physical and chemical receptor monitoring techniques. The work used principal component analysis techniques to detect and identify the dominant emission sources for the selected sites and time windows. It focused on the Hidalgo International Bridge data obtained in December 1995.

## METHODOLOGY

### *Data Collection*

On-site monitoring and sample collection were performed with the University of Utah's mobile laboratory, which is equipped with a Medium Vol (50 l/s)  $PM_{10}$  sampling tower with a QFF (quartz fiber filter) sample collector, a 400 Ah battery bank with 2000 W battery

charger/inverter, a four kW propane-driven generator, a Peltier-cooled refrigerator for sample storage, and a broad range of air pollutant measurement and sampling devices as described below.

Physical measurements included particle size distribution determinations obtained from a six-channel CLIMET aerosol counter, and meteorological measurements (temperature, pressure, humidity, wind speed, and direction) using a Davis model III weather station. Planned on-site chemical analyses involved  $\text{NO}_x$  and  $\text{O}_3$  measurements, as well as VOC/SVOC speciation using a novel GC/MS technique with miniaturized, fast GC and Curie-point desorption modules. Off-site chemical analyses of QFFs obtained at two-hour intervals were performed at the University of Utah Center for Micro Analysis with a standard HP GC/MSD equipped with a special Curie-point desorption/pyrolysis inlet. Detailed descriptions of these techniques have been given elsewhere (Mejia and Meuzelaar 1997; Dworzanski et al. 1993). Multivariate analysis of physical and chemical measurement data involved the use of principal component analysis (PCA) techniques in combination with graphical rotation methods (Dworzanski et al. 1993).

Several problems were encountered during the 72-hour measurement period (March 11–14, 1998), namely: (1) frequent rain showers that reduced pollutant levels and necessitated longer collection periods while turning monitoring sites into mud pools; (2) electrical failure of the ozone analyzer; and (3) intermittent leaks in the VOC/SVOC desorption inlet. As a result, the number of monitoring sites, originally anticipated to be as high as 20, had to be reduced to six.

### *Modeling of Photochemical Pollutants*

Modeling techniques used by the ITESM group included the application of a diagnostic meteorological model, the use of GIS to generate an emission database, and the application of a photochemical model. The meteorological model was used to reconstruct wind fields in the LRGV during the periods studied. Data from United States and Mexican monitoring stations and airports in the region were used as input to the model. The GIS was used to create a database of meteorological, emission, and predicted concentration. The database made it easier to create input data files for the photochem-

ical model and to display wind, emission, and concentration data in a map of the LRGV for better understanding of the results.

The CIT Photochemical Model (McRae, et al. 1982) was applied to study the dynamics of pollutants in the region. Input data files included emissions, wind fields, incoming solar and UV radiation, and land use. Outputs of the model are maps of pollutant concentrations in the region and time series for different pollutants. In this paper, the predicted SO<sub>2</sub> and O<sub>3</sub> concentrations when a cold front passed through the region on December 6, 1995, are discussed. Predicted NO<sub>x</sub> concentrations are compared with data collected during the monitoring study in March 1998.

Emissions in Mexico were estimated using the Mobile5 Juárez model developed for Ciudad Juárez by the United States Environmental Protection Agency (U.S. EPA) (Tejeda and Mejia 1998; Kishan et al. 1996). Other emissions in the area were estimated in a previous study based on fuel consumption and emission factors (Mejia and Rodriguez 1997). Stationary source emissions in Texas were obtained from the Texas Commission on Environmental Quality (TCEQ). Mobile source emissions were not available but were estimated using a regression analysis of population and emissions of other counties in Texas made in a previous study of the border area (Mendoza 1996). Wind fields were reconstructed with a diagnostic meteorology model developed to interact with the CIT model. Data obtained with the monitoring station and from the airports were used for this purpose. Land use data of the LRGV were obtained from Instituto Nacional de Estadística, Geográfica, e Informática (INEGI) and from the United States Geological Survey in digitized form. Solar radiation measurements were not available and, therefore, data were estimated from the geographical coordinates and calculated incoming solar radiation (Seinfeld 1986).

## RESULTS

### *Wind Patterns in the LRGV*

Transport of air pollutants in the LRGV is dominated by air flowing in from the Gulf of Mexico (from east to west), although at night, quiet periods are common and sometimes the wind blows from the

land to the sea (“land breeze”). In winter, cold fronts coming from the north transport pollutants from west to east at ground level, while the warm air from the Gulf of Mexico flows in the opposite direction in the upper part of the atmosphere. This effect may cause periods with high concentrations of particles and other air pollutants in some areas of the LRGV, especially when occurring in combination with low mixing heights.

Meteorology data from the Matamoros and Reynosa airports and United States monitoring stations in the LRGV were used in the meteorology model to estimate wind field vectors in the region for December 1995 and March 1998. The data analyzed showed dominant winds coming from the Gulf of Mexico, the east, and the southeast for the two periods. In particular, on December 6, 1995, a cold front coming from the northwest collided with the warm air coming from the southeast. The leading edge of the cold front slid below the warm front but over the lowest elevations, trapping urban dust (mostly from unpaved roads) under a low inversion ceiling and also causing precipitation of air pollutants emitted upwind in the warm air. This explained the high levels of  $PM_{10}$  measured in Hidalgo at the same time and day during the 1998 monitoring trip, as discussed in the following sections.

### *PM<sub>10</sub> Physical Size Distribution*

Table 1 shows the average particle size distribution for the different sites and monitoring periods covered during the field trip in March 1998. The data from five of the six channels of the CLIMET are shown in the first column, and covered the range from 0.3 microns to 10 microns. Three of these ranges covered  $PM_{2.5}$ . The sixth channel covered the number of particles larger than 10 microns, but it is not shown in this table. The average number of particles per every  $2ft^3$  sampled are shown in the second column,  $N(dp)$ . The flow rate of the CLIMET was  $1ft^3/min$ . The volume of particles in each range ( $V_i$ ) was calculated assuming that particles were spherical (Seinfeld 1986). The total volume ( $V_t$ ) is the sum of the  $V_i$ , hence,  $V_i/V_t$  represents the volume fraction of each range of particles.

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Table 1. Average Particle Size Distribution at the Monitoring Sites in the Lower Rio Grande Valley

Hidalgo, Texas, March 11, 1998. Sampling period: 10:30 to 18:30 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	801026	26.84	0.0482	0.0482
0.5-1.0	124480	27.5	0.0494	0.1550
1.0-2.5	20935	58.75	0.1056	0.2033
2.5-5.0	7061	194.95	0.3504	0.5536
5.0-10.0	1124	248.35	0.4464	1.0000
Total	954626	556.39	1.0000	
Matamoros, Tamps. March 12, 1998. Sampling period: 0:00 to 4:30 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	889181	29.8	0.0374	0.0374
0.5-1.0	130958	28.93	0.0363	0.0738
1.0-2.5	28517	80.02	0.1005	0.1743
2.5-5.0	13737	379.31	0.4766	0.6509
5.0-10.0	1258	277.88	0.3491	1.0000
Total	1063652	795.94	1.0000	
Reynosa, Tamps. March 13, 1998. Sampling period: 0:00 to 2:00 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	1377389	46.16	0.0233	0.0233
0.5-1.0	469544	103.72	0.0523	0.0756
1.0-2.5	62086	174.22	0.0879	0.1635
2.5-5.0	36804	1016.22	0.5126	0.6761
5.0-10.0	2908	642.25	0.3239	1.0000
Total	1948730	1982.57	1.0000	
Reynosa, Tamps. March 13, 1998. Sampling period: 6:00 to 12:00 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	653962	21.91	0.3075	0.3075
0.5-1.0	47599	10.51	0.1475	0.4550
1.0-2.5	2420	6.79	0.0953	0.5503
2.5-5.0	520	14.35	0.2013	0.7516
5.0-10.0	80	17.7	0.2484	1.0000
Total	704580	71.27	1.0000	
Rio Bravo, Tamps. March 13, 1998. Sampling period: 16:00 to 18:30 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	1538943	51.57	0.0722	0.0722
0.5-1.0	629158	138.98	0.1946	0.2668
1.0-2.5	37294	104.65	0.1465	0.4133
2.5-5.0	5736	158.38	0.2217	0.635
5.0-10.0	1180	260.71	0.365	1.0000
Total	2212311	714.29	1.0000	
Brownsville, Texas, March 14, 1998. Sampling period: 9:00 to 13:00 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	1026347	34.39	0.0175	0.0175
0.5-1.0	225479	49.81	0.0253	0.0428
1.0-2.5	81753	229.41	0.1165	0.1593
2.5-5.0	30711	847.97	0.4306	0.5899
5.0-10.0	3655	807.47	0.4101	1.0000
Total	1367945	1969.05	1.0000	
Hidalgo, Texas, March 14, 1998. Sampling period: 15:00 to 17:00 hrs.				
dp (microns)	N (dp)	Vi (thousand of microns <sup>3</sup> )	Vi/Vt	ΣVi/Vt
0.3-0.5	1236071	41.42	0.0229	0.0229
0.5-1.0	229274	50.65	0.0281	0.0510
1.0-2.5	72259	202.77	0.1123	0.1634
2.5-5.0	32180	888.55	0.4923	0.6557
5.0-10.0	2813	621.47	0.3443	1.0000
Total	1572598	1804.87	1.0000	

In general, Table 1 shows that although small particles are large in number, big particles are more important in volume and, consequently, in mass. On the other hand,  $PM_{2.5}$  represents the fraction of  $PM_{10}$  most hazardous to health. During the monitoring trip,  $PM_{2.5}$  were found to represent approximately 16% to 20% of  $PM_{10}$  in Hidalgo and Brownsville. Similar values were found in Matamoros. In the case of Reynosa and Río Bravo,  $PM_{2.5}$  was found to account for 55% and 41.3% of  $PM_{10}$ , respectively. These values were found during monitoring periods that corresponded to high traffic at the sites—0600–1200 in Reynosa and 1600–1830 hours in Río Bravo. These two cities are located downwind, have many unpaved streets, and receive most of the pollutants emitted from the highway between Matamoros and Reynosa. In Reynosa, during a monitoring period from 0000 to 0200 it was found that  $PM_{2.5}$  accounted for 16.3% of  $PM_{10}$ . This value was obtained at night after a rainy period and at a monitoring site with very low traffic. From these results,  $PM_{2.5}$  was observed to be an important fraction of  $PM_{10}$  in locations downwind of the LRGV. However, to obtain more reliable results and conclusions, more data collected during different seasons of the year are necessary, as are measurements of mass concentration of  $PM_{10}$  to obtain concentrations of  $PM_{2.5}$ , which can then be used to evaluate the population's health exposure to particles.

### *Multivariate Data Analysis and Integration*

Preliminary findings from the 1998 field tests showed:

- $PM_{10}/PM_{2.5}$  and VOC levels well below the maximum levels allowed by all applicable United States and Mexican air quality standards at all monitoring sites
- Repeated  $NO_x$  levels in excess of 100ppb at the Hidalgo International Bridge and along the freeway near the city of Harlingen, Texas

Organic  $PM_{fine}$  characterization data are still being integrated and processed. However, multivariate analysis of the 1995 scoping study data for the Brownsville and Hidalgo International Bridge sites has been completed and some results for the latter site, also

included in our 1998 field study, are discussed.

Table 2 shows the variables included in the final principal component analysis of the Hidalgo  $PM_{\text{fine}}$  scoping study involving 24 samples obtained at two-hour intervals. Note that this includes organic chemical compounds and meteorological parameters, as well as  $PM_{10}$  and  $PM_{2.5}$  density estimates. After varimax rotation, only five principal components were needed to explain nearly 80% of the total variance in the data set. The loadings for these five (varimax-rotated) factors are listed in Table 2 and reveal a relatively well-behaved clustering of the variables along the different principal component axes. Fortunately, a reasonable chemical and physical interpretation of the first four factors appears to be relatively straightforward and is in agreement with the dominant trends observed by Mukerjee et al. in their varimax-rotated principal component analysis of inorganic  $PM_{\text{Fine}}$  characterization data for the LRGV region (1999).

Figure 1 shows the power of the time-resolved  $PM_{\text{fine}}$  analysis approach in that it provides the opportunity to help tie observed receptor sample patterns to possible emission sources on the basis of known circadian human activity cycles and events (e.g. traffic peaks, waste burning) or observed meteorological patterns and events. (Note characteristic morning and afternoon rush hour peaks “in automotive emissions” component and major “urban dust” event in the late evening of the second day.)

Air Quality Issues Along the U.S.-Mexican Border

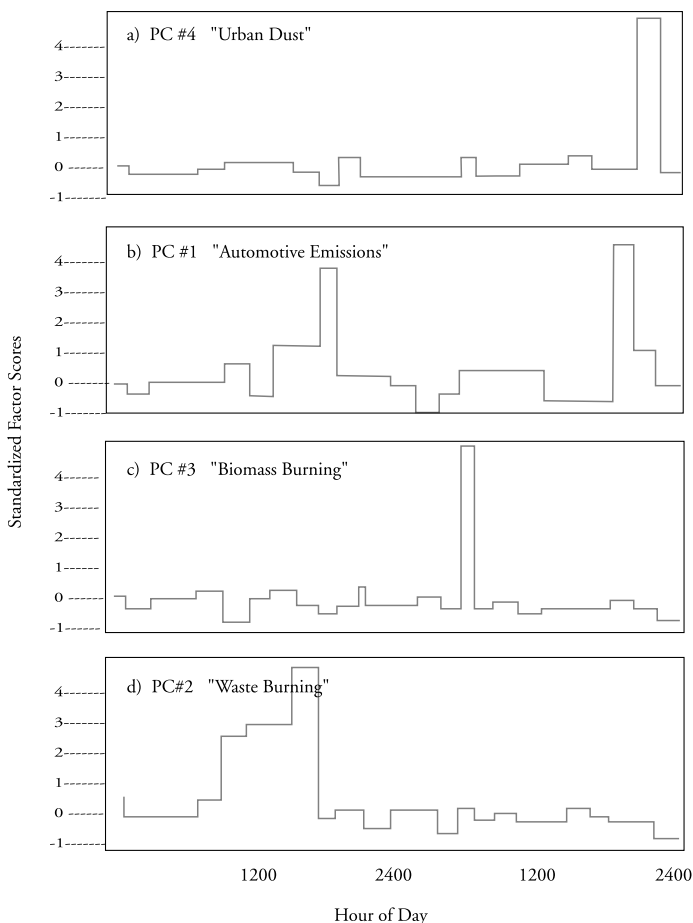
Table 2. Factor Loadings After Varimax Rotation in Hidalgo, 1995 Study

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
4-hour daytime intercal	-0.376	-0.055	0.217	-0.320	0.216
Ambient temperature	-0.099	<b>-0.942</b>	0.045	0.100	-0.136
Ambient pressure	0.209	0.205	-0.071	0.218	-0.121
Wind speed	0.371	0.030	-0.131	0.107	<b>-0.710</b>
N/S wind vector	-0.362	-0.177	-0.083	-0.066	0.050
E/W wind vector	-0.081	-0.193	-0.081	0.168	<b>-0.910</b>
PM10 concentration	-0.299	0.102	0.125	<b>-0.949</b>	0.087
PM2.5 concentration	-0.210	0.121	0.118	<b>-0.955</b>	0.061
D PM (PM10-PM2.5)	-0.397	-0.130	0.178	-0.672	0.361
m/z 83-85 alkanes/alkenes (f)	-0.500	-0.011	-0.017	<b>-0.846</b>	-0.009
m/z 99 tributylphosphate (f)	-0.196	<b>-0.910</b>	0.088	-0.039	0.084
m/z 129 quinoline	-0.165	0.073	-0.348	0.065	<b>0.731</b>
m/z 149 DEP (f)	0.163	0.092	<b>-0.945</b>	0.092	0.121
m/z 149 DBP (f)	0.027	<b>-0.920</b>	-0.071	0.161	-0.194
m/z 149 DPP (f)	-0.075	<b>-0.964</b>	0.124	0.108	0.007
m/z 149 DOP (f)	0.013	-0.145	0.058	0.069	-0.087
m/z 151 4-acetyl-2-methoxyphenol (f)	-0.099	<b>-0.930</b>	0.124	0.088	0.009
m/z 153 4-acetyl-2,5-dimethoxyphenol (f)	0.338	0.205	-0.542	0.332	-0.179
m/z 165 4-vinyl-2,6-dimethoxyphenol (f)	0.145	0.088	<b>-0.922</b>	0.188	-0.204
m/z 191 17a(H),21b(H)-hopanes (f)	<b>-0.917</b>	-0.136	0.085	-0.243	-0.009
m/z 191a hopane [C29H50] (f)	<b>-0.916</b>	-0.037	0.073	-0.335	-0.005
m/z 191b hopane [C30H52] (f)	<b>-0.892</b>	-0.216	0.092	-0.159	-0.013
m/z 202 PNAHs [C16H10]	<b>-0.930</b>	-0.053	0.150	-0.210	0.114
m/z 202a fluoranthene	<b>0.830</b>	-0.018	0.046	-0.456	0.145
m/z 202b pyrene	<b>-0.931</b>	-0.076	0.218	0.001	0.080
m/z 219 retene (f)	0.131	0.060	<b>-0.957</b>	0.083	0.079
m/z 239 methyl dehydroabietate (f)	-0.092	0.139	0.112	<b>-0.972</b>	0.036
m/z 306 tetraphenylene	-0.128	0.136	0.088	<b>-0.975</b>	-0.012

(f) fragment ion, DEP = diethyl phthalate, DBP = dibutyl phthalate, DPP = dipentyl phthalate, DOP = dioethyl phthalate. Bolded figures are those above 0.6, underlined figures are above 0.8.

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Figure 1. Standardized Principal Component Scores (varimax-rotated) Corresponding to the Loadings of Ambient Temperature, Pressure, Wind Speed and Direction over Two Days



The factor scores in the abscissa of Figure 1 are standardized, thereby permitting a rough estimate of the statistical significance of the various events. Assuming multivariate normal distributions, both the (inferred) “urban dust” event in Figure 1a, which followed the arrival of the cold front on day two, and the “biomass burning” (primarily hardwood-markers dominated) event in Figure 1c can be

classified as being well in the four-sigma range. The high amplitude of both events may create the mistaken impression that the corresponding chemical markers were only detected during these events. In fact, even when leaving out these extreme episodes, the nature of the underlying parameter associations does not change much at all. In addition, the first principal component (“automotive emissions,” Figure 1b) shows regular, traffic-peak-related fluctuations dominated by the afternoon rush hours when most of the traffic was passing on the same (downwind) side of the bridge on which the mobile lab was stationed. The proposed “urban dust” factor is speculative at this point since the peaks at  $m/z$  239 (abietic acid, a prominent filler in car tires) and at  $m/z$  306 (tetraphenylene, perhaps an oily-road tire stabilizer) have not yet been positively identified in local source profiles and the “waste burning” events are inferred from the prominent contributions of alkylphthalate-type plasticizers. However, the “automotive emissions” and “biomass burning” events are firmly rooted in the pioneering GC/MS studies of well defined source samples described by Rogge et al. (1991). Also, the inferred, broad “waste burning” event in Figure 1d was primarily characterized by the presence of several different types of plasticizers, plus a fire retardant. Finally, the very similar “urban dust,” “automotive emissions,” “biomass burning,” and “waste burning” factor loading and score behavior was observed in the Brownsville International Bridge site data obtained during the same 1995 scoping study, as well as in two earlier December time window studies at the U.S.-Mexican border (Nogales, Arizona in 1991 and Mexicali, California in 1993). This suggests a marked degree of similarity in major  $PM_{\text{Fine}}$  sources along the border and further supporting the chemical and physical significance of the numerically extracted principal component patterns.

### *Sulfur Dioxide and Ozone Dynamics*

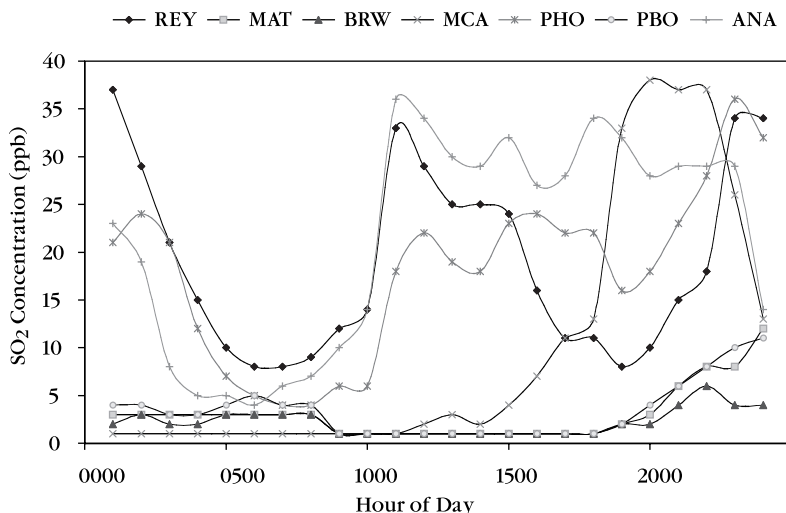
Emission sources in the LRGV include mobile sources in Mexico and the United States, small stationary sources in Cameron and Hidalgo counties in the United States, a Pemex refinery in Reynosa, and a power plant in Río Bravo. Several uncertainties exist in the estimated emissions used to create the data files for the CIT photo-

chemical model. These uncertainties include aspects such as a lack of data to estimate mobile source emissions from both the United States and Mexico. Furthermore, an official emission inventory of stationary sources in Mexico is not yet available; biogenic emissions from vegetation are not known and were estimated from land use; distribution of mobile emissions in highways is not well known; emissions from diesel trucks were estimated; and diurnal variations in emissions of mobile sources were not considered. These uncertainties represent research areas from which results are needed to improve the data necessary to obtain more reliable results. Nevertheless, the results represent general trends of transport of air pollutants and potential areas affected by high levels of pollution.

The region of study, the domain, and computational mesh covered with the photochemical model covered a surface of 180km X 180km, with cells of 5km X 5km (i.e., 1,296 cells). Five layers were defined in the vertical dimension, which makes a total of 6,480 cells. A GIS database was loaded with the necessary emission and land use data files to create the input files to run the CIT Photochemical Model. The files were created using a procedure developed within the GIS for automatic transfer data to each cell. This procedure was generated with a computer, minimizing processing time and numerical errors when data were assigned to each cell.

The results of the model give average hourly concentration data for the different pollutants in each cell in the three spatial dimensions. Understanding results given as lists of numbers is very difficult and usually visualization techniques are used to facilitate this procedure. In this paper, the predicted SO<sub>2</sub> and O<sub>3</sub> concentrations in the different monitoring sites during December 6, 1995, are analyzed. Figure 2 shows plots of SO<sub>2</sub> concentrations for seven sites in the domain: Reynosa (REY), McAllen (MCA), Hidalgo Bridge (PHO), Santa Ana Park (ANA), Matamoros (MAT), Brownsville (BRW), and Brownsville Bridge (PBO).

Figure 2. SO<sub>2</sub> Concentrations Predicted by the Photochemical Model on December 6, 1995, for Seven Sites in the Domain



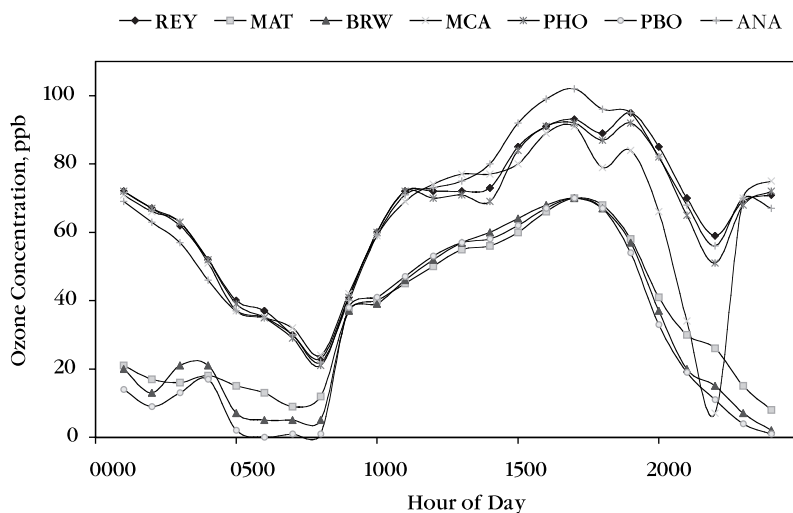
The data displayed in this figure show higher concentrations of SO<sub>2</sub> in the area of Reynosa-McAllen. This is expected since air is blowing from the sea and SO<sub>2</sub> emissions of the Emilio Portes-Gil power plant and the Pemex refinery in Reynosa are transported west of the source. The figure also shows the effect of dispersion predicting different concentrations in REY, MCA, PHO, and ANA, which are located downwind. It is important to note that the higher concentrations predicted by the model are close to 40ppb, which is well below the Mexican air quality standard for SO<sub>2</sub> of 130ppb. The effect of the cold front passing that day is reflected in Figure 2. The model also predicts low concentrations of SO<sub>2</sub> in the area of Matamoros-Brownsville. This, too, is expected since air is blowing from east to west and emission sources are located west of these cities. When the cold front arrived in the region, the wind changed direction and the air blew from west to east, bring SO<sub>2</sub> emissions to the area of Matamoros-Brownsville and thus decreasing SO<sub>2</sub> concentrations in the area of Reynosa-McAllen. As mentioned above, if sulfur content in fuel is lower than the values assumed, lower SO<sub>2</sub> con-

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centrations are expected in the area. Fluctuations in  $\text{SO}_2$  concentrations are most often caused by changes in atmospheric stability during the day and the night. During the day, dispersion increases in the atmosphere and  $\text{SO}_2$  concentration increases at ground level in McAllen, Reynosa, and Río Bravo. At night the atmosphere becomes stable and, in the same locations, the ground level concentrations decrease.

Emissions of mobile and industry sources have a significant direct impact on carbon monoxide (CO), hydrocarbon (HC), and  $\text{NO}_x$  concentrations, which indirectly react to produce  $\text{O}_3$ . Concentrations of this pollutant for the same seven sites are shown in Figure 3.

Figure 3. Ozone Concentrations Predicted by the Photochemical Model on December 6, 1995, for Seven Sites in the Domain

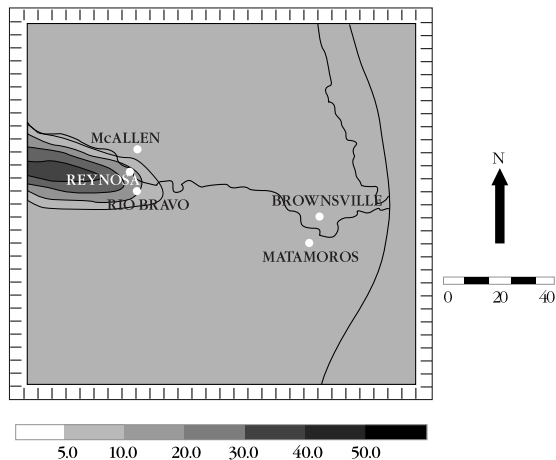


This figure shows the same levels of predicted ozone concentrations in nearby sites. This is due to mobile source pollutants emitted mainly in the cities and highways along the domain. Higher concentrations of  $\text{O}_3$  in sites located downwind in McAllen-Reynosa, as is the case for  $\text{SO}_2$  concentrations, were found. As expected, the figure shows the cycle in ozone formation during the day. Ozone is

formed by photolysis of nitrogen dioxide ( $\text{NO}_2$ ) and, consequently, its concentration increases during the morning, peaks early in the afternoon, and decreases at night. High levels of ozone may be encountered at night if it is not dispersed in the atmosphere or if it is not consumed by nitric oxide ( $\text{NO}$ ) when the concentration or emission of this pollutant are low at night. The model predicts peak ozone concentration of approximately 90ppb to 100ppb, which is close to the Mexican and United States air quality standards for ozone of 110ppb and 120ppb respectively.

One of the pollutants of higher concern in the LRGV is  $\text{SO}_2$ . With the application of the photochemical model, it is possible to study the daily variations and impacted areas of the different pollutants. Maps of predicted concentrations of  $\text{SO}_2$  are shown in Figures 4 through 7 for the study of December 6, 1995. These figures show the daily variations in concentrations and expected areas impacted by emissions of this pollutant. Figure 4 shows a map of  $\text{SO}_2$  concentrations at 0300.

Figure 4. Map of  $\text{SO}_2$  Concentrations in the LRGV at 0300, December 6, 1995

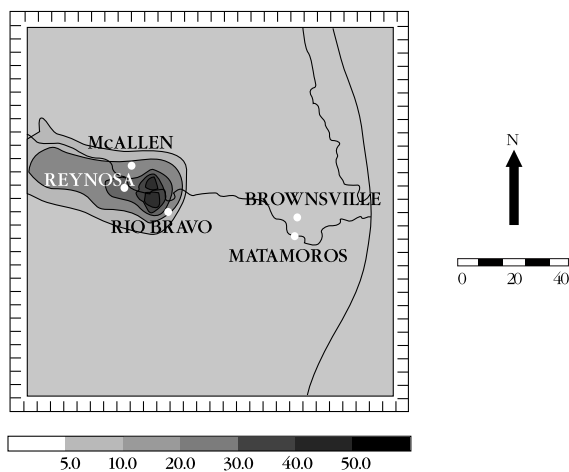


Although several sources of this pollutant exist in the area (Mejia and Rodriguez 1997) and were considered in the application of the model, this figure shows that the impact on air quality results most-

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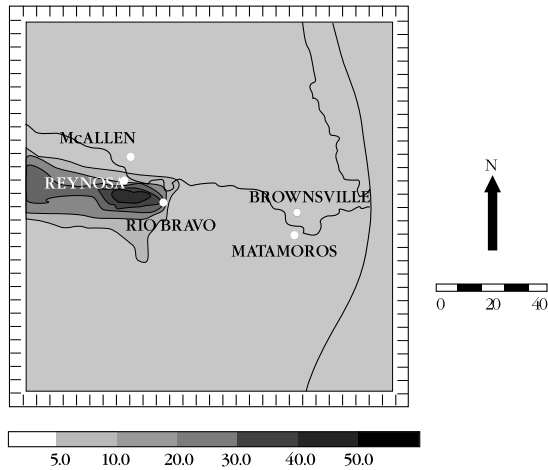
ly from the power plant located in Río Bravo. This plant's emissions were calculated assuming that fuel oil with 3.5% of sulfur and natural gas with 0.5% of sulfur were consumed. Today, this plant has been using fuel oil and natural gas with lower sulfur content. Therefore,  $\text{SO}_2$  emissions are expected to be lower than those used in the model. Nevertheless, even with high  $\text{SO}_2$  emissions, values of concentrations of this pollutant are below 40ppb west of the urban areas of Reynosa and McAllen, and this value is well below the Mexican air quality standard of 130ppb for 24-hour average. At 0900 hours, the conditions of the atmosphere become unstable, and the mixing is favored by buoyancy forces. At this hour, Figure 5 shows that concentrations close to Reynosa increase to values between 50ppb and 60ppb, which are still below the air quality standard.

Figure 5. Map of  $\text{SO}_2$  Concentrations in the LRGV at 0900, Hours, December 6, 1995



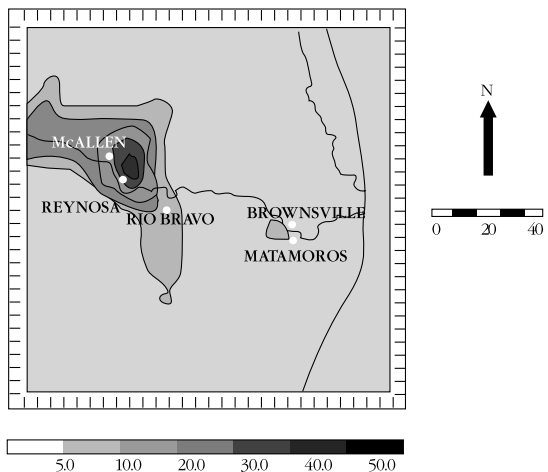
With higher temperatures, the land reaches its peak temperature during the day, and, for example, at 1500 hours the atmosphere becomes unstable and the higher values of  $\text{SO}_2$  concentration are located between Río Bravo and Reynosa. However, the values are only in the range of 40ppb to 60ppb as shown in Figure 6.

Figure 6. Map of SO<sub>2</sub> Concentrations in the LRGV at 1500 Hours, December 6, 1995



In the evening, the atmosphere becomes stable and the dispersion of pollutants decreases. In this case, Figure 7 shows the higher concentrations of SO<sub>2</sub> at 2100 hours are now found downwind in the urban areas of Reynosa and McAllen.

Figure 7. Map of SO<sub>2</sub> Concentrations in the LRGV at 2100, December 6, 1995

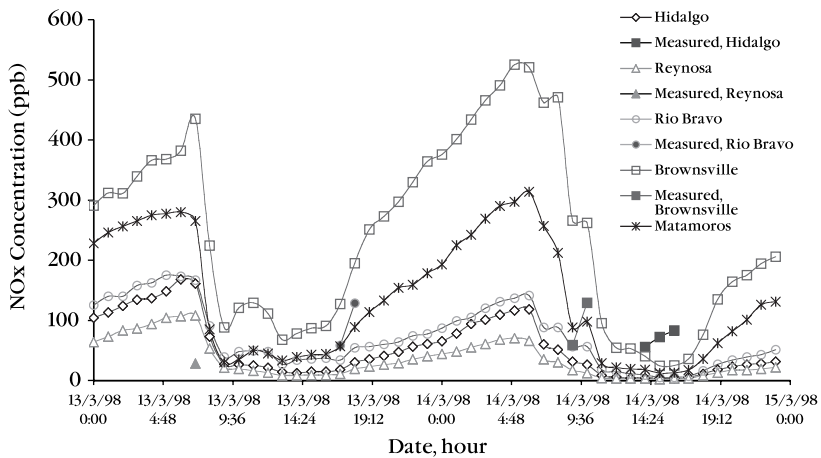


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As before, the predicted higher values are around 50ppb and occur in McAllen. Figures 4 to 7 also show that, because of transport and dispersion of gases and particles in the atmosphere, higher concentrations of pollutants may be found in rural areas rather than in urban areas. An important limitation is that these results obtained with the model were not validated since actual air pollutant concentration data did not exist for the December 1995 study.

In the study of March 1998,  $\text{NO}_x$  concentrations were measured at the different sites. The results of the predicted values with the photochemical model and the actual concentrations measured are shown in Figure 8.

Figure 8.  $\text{NO}_x$  Concentrations Predicted with the Photochemical Model and Actual Measurements in the LRGV in March 1998



In this figure, the model predicts concentrations of  $\text{NO}_x$  in Brownsville and Matamoros that exceed the one-hour air quality standard of 210ppb, while measured concentrations of  $\text{NO}_x$  and values predicted for other cities are below this standard. Reasonable correspondence was observed between predicted and measured  $\text{NO}_x$  concentration profiles or trends at some sites. The discrepancies between measured and modeled  $\text{NO}_x$  values at other sites are

thought to be due to the highly unusual weather conditions, the lack of sufficient data points to fully calibrate the models, and the lack of complete emission inventories (particularly the fact that United States emission data are summed per county and not specified by highway).

## CONCLUSIONS

The results of this study show that the LRGV has, in general, relatively low levels of  $PM_{10}$ . Depending on meteorological conditions, these levels may increase to high concentrations during some periods of the day. Size distribution results show that  $PM_{2.5}$  seems to be an important component of  $PM_{10}$ . It is important to obtain data for longer periods and different seasons in the year to achieve more reliable results for the size composition of  $PM_{10}$ . To obtain better calculated values of ozone,  $SO_2$ , and other pollutants it is necessary to have better emission estimates of stationary and mobile sources as well as their diurnal and spatial variation.

The predicted concentrations of  $SO_2$  do not exceed the air quality standard in the LRGV, including the impact of the power plant located in Río Bravo. Moreover, this plant's emissions were estimated consuming fuel oil and natural gas with high sulfur content and, since today it is using combined cycles with natural gas that has a lower sulfur content, it is expected that its impact will be below the predicted values of  $SO_2$  concentrations.

It is necessary to obtain actual concentrations of air pollutants to validate their predicted concentrations with the photochemical model. Usually air quality data are collected in urban areas. However, transport of pollutants to rural areas may cause higher concentrations there. Technical and logistic achievements were trouble-free crossing (twice) of the U.S.-Mexican border with a fully equipped mobile laboratory and successful (nearly around-the-clock) operation of a mobile laboratory on both sides of the U.S.-Mexican border with a binational team of investigators while covering six sites over a 200-mile distance within a 72-hour period.

## ACKNOWLEDGMENTS

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## REFERENCES

- Dworzanski, J. P.; H. L. C. Meuzelaar, W. Maswadeh, X. Nie, P. A. Cole, and N. S. Arnold. 1993. "Development of Field Portable Mass Spectrometric Techniques for Particulate Organic Matter in PM-10." Proceedings of the 1993 International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, Nevada.
- Gilbreath, J. 1992. *Planning for the Border's Future: The U.S.-Mexican Integrated Border Environmental Plan*. U.S.-Mexican Occasional Paper No. 1. Austin, Texas: U.S.-Mexican Policy Studies Program, Lyndon B. Johnson School of Public Affairs, The University of Texas at Austin.
- Kishan, S.; R. Meredith, and C. Weyn. 1998. *Development of Mobile Emissions Factor Model for Ciudad Juárez, Chihuahua*. Austin, Texas: Air Quality Planning Division Texas Commission on Environmental Quality.
- McRae, G. J.; W. R. Goodin, and J. H. Seinfeld. 1982. "Development of a Second-Generation Mathematical Model for Urban Air Pollution – I. Model Formulation." *Atmospheric Environment* 16 (4): 679–696.
- Mendoza, A. 1996. "Aplicación Preliminar del Modelo Fotoquímico de Calidad del Aire CIT a la Zona de la Frontera Mexico-Estados Unidos." Masters Thesis, Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Nuevo León, Mexico.
- Mejia, G. M. and H. L. Meuzelaar. 1997. "Characterization and Dynamics of Air Pollutants in the Southeastern Mexico-U.S.

- Border Area.” Final Report, Southwest Center for Environmental Research and Policy (SCERP) Project No. AQ95-10. San Diego: SCERP.
- Mejia, G. M. and M. Rodriguez. 1997. “Characteristics and Estimated Air Pollutant Emissions of the Industry and Vehicles in the Matamoros-Reynosa Border Region.” *Environment International* 23 (5): 733-744.
- Mukerjee, S; W. Ellenson, R. Lewis, K. Stevens, M. Somerville, D. Shadwick, and R. Willis. 1997. “An Environmental Scoping Study in the Lower Rio Grande Valley of Texas (parts I, II, and III).” *Environment International* 23: 611-628 and 643-674.
- Mukerjee, S.; D. S. Shadwick, K. E. Dean, and L. Y. Carmichael. 1999. “Assessing Transboundary Issues in the Lower Rio Grande Valley.” 92nd Annual Air & Waste Management Association Meeting, St. Louis, Missouri.
- Rogge, W. F.; L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. 1998. “Sources of Fine Organic Aerosol, 1-9.” *Environmental Science & Technology* 24: 1112-1125.
- Seinfeld, J. 1986. *Atmospheric Chemistry and Physics of Air Pollution*. New York: John Wiley and Sons.
- Tejeda, D. and G. Mejia. 1998. “Impact of NAFTA on Mobile Source Emissions Along the Dallas-Salttillo Corridor.” Proceedings of the International Symposium on Environmental Engineering and Earth Sciences, 26-30 October, Cholula, Puebla, Mexico.