

US EPA ARCHIVE DOCUMENT

EPA/600/R-99/047
April 1999

Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP)

by

Shaibal Mukerjee
Human Exposure and Atmospheric Sciences Division
National Exposure Research Laboratory
Research Triangle Park, North Carolina 27711

Douglas S. Shadwick
ManTech Environmental Technology, Inc.
Research Triangle Park, North Carolina 27709-2313

Kirk E. Dean
Texas Natural Resource Conservation Commission
Austin, Texas 78711-3087

Linda Y. Carmichael, Jon J. Bowser, and Larry J. Purdue
QST Environmental, Durham, North Carolina 27713

Contracts 68-D2-0134 and 68-D5-0049

Project Officer (68-D2-0134)
V. Presnell
Office of Air Quality Planning and Standards

Project Officer (68-D5-0049)
P. Britt
National Exposure Research Laboratory
Human Exposure and Atmospheric Sciences Division

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Notice

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract 68-D2-0134 to QST Environmental, Inc and Contract 68-D5-0049 to ManTech Environmental, Inc. It has been subjected to agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Preface

This Project Report provides detailed analyses performed during the 1996-1997 Lower Rio Grande Valley Transboundary Air Pollution Project. The study was funded by the U.S. Environmental Protection Agency under the Environmental Health Workgroup of the U.S. Mexico Border XXI Program^a. A brief summary of this study has been presented in implementation plan documents of this Program^{b,c}.

A Project Summary^d has also been developed to announce key findings of the Project Report. Copies of the Project Report and the Project Summary are available from the U.S. EPA Co-Chair of the Border XXI Environmental Health Workgroup, Dr. Harold Zenick, Associate Director for Health, National Health & Environmental Effects Research Laboratory, U.S. Environmental Protection Agency Research Triangle Park, NC 27711.

^aU.S. Environmental Protection Agency (U.S. EPA). US-Mexico Border XXI Program. Executive Summary. EPA-160-S-96-001. Washington, DC: U.S. EPA; October 1996.

^bU.S. Environmental Protection Agency (U.S. EPA). US-Mexico Border XXI Program. Framework Document. EPA-160-R-96-003. Washington, DC: U.S. EPA; October 1996.

^cU.S. Environmental Protection Agency (U.S. EPA). US-Mexico Border XXI Program. 1997-1998 Implementation Plans and 1996 Accomplishments Report. EPA-160-R-98-001. Washington, DC: U.S. EPA; 1998.

^dMukerjee, S.; Shadwick, D.S.; Dean, K.E.; Carmichael, L.Y.; Bowser, J.J.; Purdue, L.J. Project Summary. Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP). Research Triangle Park, NC: U.S. Environmental Protection Agency; 1999.

Abstract

The purpose of the Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP) was to obtain air quality data for a full year at three border monitoring sites to assess anthropogenic and biogenic emission impacts and transboundary air pollution transport in the Lower Rio Grande Valley of Texas. Performed by the U.S. Environmental Protection Agency (U.S. EPA), in cooperation with the Texas Natural Resource Conservation Commission (TNRCC) as part of the U.S.-Mexico Border XXI Program, the TAPP collected air quality, precipitation, and meteorological data at three sites in and near Brownsville, Texas and close to the U.S.-Mexican border. Monitoring was performed on a near real-time basis for fine particulate matter ($PM_{2.5}$); time-integrated continuous monitoring was performed for $PM_{2.5}$ with associated elements, coarse particulate matter ($PM_{2.5-10}$) with associated elements, particulate carbon, volatile organic compounds, polycyclic aromatic hydrocarbons, and pesticides.

Using these data, comparisons with Effects Screening Level (ESL) data were initially done. ESLs are health/welfare-based screening levels established by the TNRCC and are not ambient air standards. Comparisons with data from U.S. EPA and other environmental exposure monitoring studies were also done. Chemical tracer analyses, wind sector analyses, and rudimentary source apportionment analyses were also conducted.

The vast majority of the approximately 2650 air pollutant samples acquired in this study were low or comparable to ESLs or environmental monitoring data from the literature. Overall, air quality in the Brownsville area of the Valley was good. The few observations of pollutants exceeding these levels appeared to be caused by uncertainties due to intrinsic variability of the data or occasional local events (such as automotive traffic, local scrap fires, etc.), not by regional phenomena or persistent transboundary plumes. With the exception of silver, methanol, and acrolein, the rest of the seven air pollutants were above their ESLs only once. Of these three persistent pollutants, sampling difficulties associated with acrolein and methanol means that these values should be interpreted with caution.

Transboundary transport of air pollution plumes did not appear to cause noticeable deterioration of air quality on the U.S. side of the Lower Rio Grande Valley border. The dominance of winds from the Gulf of Mexico was largely responsible for the clean air conditions in the Brownsville air shed.

Contents

	Page
Preface	iii
Abstract	iv
Tables	vii
Figures	x
Acknowledgments	xvi
1 Introduction	1
2 Conclusions	3
3 Recommendations and Future Activities	8
4 Methods and Quality Assurance	10
4.1 Study Design	10
4.2 Selection of Ambient Air Pollutants	11
4.3 Air Quality Monitoring Strategy	14
4.4 Air Sampling and Analysis	15
4.4.1 Automatic/Continuous PM _{2.5} Mass Measurements	15
4.4.2 Manual/Integrative Measurements	16
4.4.2.1 Dual Fine Particle Sequential Sampler (DFPSS)	16
4.4.2.2 Mass (Gravimetric) Determinations	17
4.4.2.3 X-ray Fluorescence (XRF) Analysis	18
4.4.2.4 Pesticide and Polycyclic Aromatic Hydrocarbon (PAH) Analyses	19
4.4.2.5 Dichotomous Sampler	20
4.4.2.6 Carbon Analysis	20
4.4.2.7 Scanning Electron Microscopy (SEM)	21
4.4.2.8 Volatile Organic Compound (VOC) Sampling	21
4.4.2.9 VOC Analysis	22
4.4.2.10 Precipitation Samplers	23
4.4.2.11 Precipitation Analysis	24
4.4.2.12 Meteorological Measurements	24
4.5 Quality Assurance/Quality Control (QA/QC) Program	25
4.5.1 Automated/Continuous Monitors	26
4.5.2 Manual/Integrated Samplers	26

4.5.3	Systems and Performance Audits	27
5	Results and Discussion	37
5.1	Data Presentation	37
5.2	Overall Results	39
5.2.1	Particulate Mass Results	40
5.2.1.1	Overall Particulate Results	40
5.2.1.2	Hourly and Daily Averaged Real-Time PM _{2.5} Data to Assess Episodic Events	42
5.2.1.3	Carbon Results	44
5.2.1.4	X-ray Fluorescence (XRF) Elemental Analysis Results	45
5.2.1.5	Particle Chemistry and Morphology by Scanning Electron Microscopy (SEM)	48
5.2.2	VOC Results	48
5.2.3	PAH Results	51
5.2.4	Pesticide Results	52
5.2.5	Precipitation Results	53
5.3	Comparison of Transboundary Study Data with the 1993 Lower Rio Grande Valley Environmental Scoping Study (LRGVES)	53
5.4	Principal Component Analysis (PCA)	54
5.4.1	PCA Results for PM _{2.5}	54
5.4.2	PCA Results for VOCs	55
6	References	210

Tables

Number		Page
2.1	Measurements for air pollutants above the ESL. Data below detection designated as ½ detection limit	6
4.1	Measurements performed at the three Transboundary Air Pollution Project sites	29
4.2	Sampling methods for air and precipitation monitoring	30
4.3	Analytical methods for time-integrated monitoring	31
5.1	PM _{2.5} (fine fraction) and constituent element concentrations (in ng/m ³) from Dual Fine Particle Sequential Sampler (DFPSS). Fine fraction elemental and volatilizable carbon data measured from Dichotomous Sampler. Air pollutants summarized for detected values (for elements at 3 times measurement uncertainty)	57
5.2	PM _{2.5-10} (coarse fraction) and constituent element concentrations (in ng/m ³) from Dichotomous Sampler. Air pollutants summarized for detected values (for elements at 3 times measurement uncertainty)	59
5.3a	Volatile Organic Compounds (VOCs, concentrations in ppbV) from canister samplers at Site 1 (by Texas Natural Resource Conservation Commission, TNRCC) and Site 2 (by U.S. EPA). Air pollutants summarized for detected values, only	61
5.3b	Volatile Organic Compounds (VOCs, same data as in Table 5.3a in µg/m ³) from canister samplers at Site 1 (by Texas Natural Resource Conservation Commission, TNRCC) and Site 2 (by U.S. EPA). Air pollutants summarized for detected values, only	65
5.4	Polycyclic Aromatic Hydrocarbon (PAH) concentrations (in ng/m ³) from Dual Fine Particle Sequential Sampler (DFPSS). Air pollutants summarized for detected values, only	68
5.5	Pesticide concentrations (in ng/m ³) from Dual Fine Particle Sequential	

Sampler (DFPSS). Air pollutants summarized for detected values, only 69

5.6a Hourly PM_{2.5} (fine fraction) mass concentrations (in µg/m³) from Tapered Element Oscillating Microbalance (TEOM) sampler. Hourly meteorological measurement summaries included. Site 1 meteorological measurements performed by Texas Natural Resource Conservation Commission (TNRCC); Sites 2 and 3 meteorological measurements performed by U.S. EPA 70

5.6b Daily PM_{2.5} (fine fraction) mass concentrations (in µg/m³) from Tapered Element Oscillating Microbalance (TEOM) sampler. Daily meteorological measurement summaries included. Site 1 meteorological measurements performed by TNRCC; Sites 2 and 3 meteorological measurements performed by U.S. EPA 70

5.7 Transboundary fine particulate air monitoring and comparison with literature data. Units for PM_{2.5}, C_E, and C_V in µg/m³; elements in ng/m³ 71

5.8a Transboundary VOC air monitoring and comparison with literature data. Units in µg/m³. Dominant emission sources are indicated in **bold** 76

5.8b Transboundary VOC air monitoring and comparison data from the U.S. EPA National Ambient VOC Data Base. Units in ppbV 86

5.9 Transboundary PAH air monitoring and comparison with literature data. Units in ng/m³ 90

5.10 Transboundary pesticide air monitoring and comparison with literature data. Units in ng/m³ 93

5.11 Transboundary metal concentrations in precipitation measurements and comparison with literature data (measured at Site 2 only). TAPP results present detected results for all five measurements; all data presented in µg/L 94

5.12	Transboundary pesticide and PAH concentrations in precipitation measurements and comparison with literature data (measured at Site 2 only). TAPP results present detected results for all two measurements; all data presented in ng/L	96
5.13	Comparison of fine particle data from this study at Site 1 and 1993 LRGVSS at central site. Same time frame used for comparison. TAPP data from DFPSS and LRGVSS data from Versatile Air Pollution Sampler. All data in ng/m ³	97
5.14	Comparison of VOC data from this study at Site 1 and 1993 LRGVSS at central site. Same time frame used for comparison. Both TAPP and LRGVSS data from active canister samplers. All data in µg/m ³	98
5.15	Comparison of PAH data from this study at Site 1 and 1993 LRGVSS at central site. Same time frame used for comparison. TAPP data from DFPSS and LRGVSS data. Spring monitoring in LRGVSS by Versatile Air Pollution Sampler and summer monitoring for LRGVSS by Low Volume Sampler. All data in ng/m ³	100
5.16a	Varimax-rotated factor pattern for fine particulate element data at Site 1	101
5.16b	Varimax-rotated factor pattern for fine particulate element data at Site 2	102
5.16c	Varimax-rotated factor pattern for fine particulate element data at Site 3	103
5.17a	Varimax-rotated factor pattern for VOC data at Site 1	104
5.17b	Varimax-rotated factor pattern for VOC data at Site 2	106

Figures

Number		Page
2.1	Air monitoring Sites 1, 2, and 3 used in this study other sites established by TNRCC in the Lower Rio Grande Valley	4
4.1	Locations of the three air monitoring stations for the Transboundary Air Pollution Project	32
4.2	Layout of tapered element oscillating microbalance (TEOM) used in this study	33
4.3	Layout of the dual fine particle sequential sampler (DFPSS) used in this study. Quartz-polyurethane foam traps follow filter pack (not shown)	34
4.4	Layout of the dichotomous sampler	35
4.5	Diagram of the automated volatile organic carbon (VOC) sampler used in this study. Six-liter canister not shown	36
5.1	Bar charts and wind sector plots of hourly PM _{2.5} concentrations (µg/m ³) at the three sites. See page 39 for a detailed explanation of figures	107
5.2	Bar charts and wind sector plots of hourly PM _{2.5} concentrations (µg/m ³) at the three sites. See page 39 for a detailed explanation of figures	108
5.3	Time series plots of hourly PM _{2.5} concentrations with wind direction and relative humidity at Site 1 from June 1996 to April 1997	109
5.4	Time series plots of hourly PM _{2.5} concentrations with wind direction and relative humidity at Site 2 from March 1996 to March 1997	120
5.5	Time series plots of hourly PM _{2.5} concentrations with wind direction and relative humidity at Site 3 from March 1996 to April 1997	133
5.6	Diurnal average for PM _{2.5} based on hourly TEOM data	147
5.7	Bar charts and wind sector plots of fine fraction Silver (Ag) concentrations	

(ng/m³) at the three sites. See page 39 for a detailed explanation of figures 148

5.8 Bar charts and wind sector plots of fine fraction Aluminum (Al) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 149

5.9 Bar charts and wind sector plots of fine fraction Arsenic (As) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 150

5.10 Bar charts and wind sector plots of fine fraction Bromine (Br) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 151

5.11 Bar charts and wind sector plots of fine fraction Calcium (Ca) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 152

5.12 Bar charts and wind sector plots of fine fraction Chlorine (Cl) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 153

5.13 Bar charts and wind sector plots of fine fraction Iron (Fe) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 154

5.14 Bar charts and wind sector plots of fine fraction Potassium (K) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 155

5.15 Bar charts and wind sector plots of fine fraction Manganese (Mn) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 156

5.16 Bar charts and wind sector plots of fine fraction Nickel (Ni) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 157

5.17 Bar charts and wind sector plots of fine fraction Lead (Pb) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 158

5.18 Bar charts and wind sector plots of fine fraction Sulfur (S) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 159

5.19	Bar charts and wind sector plots of fine fraction Selenium (Se) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	160
5.20	Bar charts and wind sector plots of fine fraction Silicon (Si) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	161
5.21	Bar charts and wind sector plots of fine fraction Titanium (Ti) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	162
5.22	Bar charts and wind sector plots of fine fraction Vanadium (V) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	163
5.23	Bar charts and wind sector plots of fine fraction Zinc (Zn) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	164
5.24	Bar charts and wind sector plots of coarse fraction Silver (Ag) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	165
5.25	Bar charts and wind sector plots of coarse fraction Aluminum (Al) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	166
5.26	Bar charts and wind sector plots of coarse fraction Arsenic (As) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	167
5.27	Bar charts and wind sector plots of coarse fraction Bromine (Br) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	168
5.28	Bar charts and wind sector plots of coarse fraction Calcium (Ca) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	169
5.29	Bar charts and wind sector plots of coarse fraction Chlorine (Cl) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	170
5.30	Bar charts and wind sector plots of coarse fraction Iron (Fe) concentrations (ng/m ³) at the three sites. See page 39 for a detailed explanation of figures	171

5.31 Bar charts and wind sector plots of coarse fraction Potassium (K) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 172

5.32 Bar charts and wind sector plots of coarse fraction Manganese (Mn) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 173

5.33 Bar charts and wind sector plots of coarse fraction Nickel (Ni) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 174

5.34 Bar charts and wind sector plots of coarse fraction Lead (Pb) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 175

5.35 Bar charts and wind sector plots of coarse fraction Sulfur (S) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 176

5.36 Bar charts and wind sector plots of coarse fraction Selenium (Se) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 177

5.37 Bar charts and wind sector plots of coarse fraction Silicon (Si) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 178

5.38 Bar charts and wind sector plots of coarse fraction Titanium (Ti) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 179

5.39 Bar charts and wind sector plots of coarse fraction Vanadium (V) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 180

5.40 Bar charts and wind sector plots of coarse fraction Zinc (Zn) concentrations (ng/m³) at the three sites. See page 39 for a detailed explanation of figures 181

5.41 Bar charts and wind sector plots of 1,2,4-Trimethylbenzene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures 182

5.42 Bar charts and wind sector plots of 2-Methylpentane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures 183

5.43 Bar charts and wind sector plots of 2-Nitropropane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures 184

5.44	Bar charts and wind sector plots of 3-Methylhexane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	185
5.45	Bar charts and wind sector plots of 3-Methylpentane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	186
5.46	Bar charts and wind sector plots of Acrolein (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	187
5.47	Bar charts and wind sector plots of alpha-Pinene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	188
5.48	Bar charts and wind sector plots of beta-Pinene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	189
5.49	Bar charts and wind sector plots of Benzene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	190
5.50	Bar charts and wind sector plots of Cyclohexane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	191
5.51	Bar charts and wind sector plots of Isooctane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	192
5.52	Bar charts and wind sector plots of Isopentane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	193
5.53	Bar charts and wind sector plots of Isoprene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	194
5.54	Bar charts and wind sector plots of Methanol (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	195
5.55	Bar charts and wind sector plots of Methylcyclopentane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	196
5.56	Bar charts and wind sector plots of Methylene chloride (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	197
5.57	Bar charts and wind sector plots of m,p-Xylene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	198
5.58	Bar charts and wind sector plots of n-Butane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	199

5.59	Bar charts and wind sector plots of n-Heptane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	200
5.60	Bar charts and wind sector plots of n-Hexane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	201
5.61	Bar charts and wind sector plots of o-Xylene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	202
5.62	Bar charts and wind sector plots of Pentane (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	203
5.63	Bar charts and wind sector plots of Propylene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	204
5.64	Bar charts and wind sector plots of Toluene (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	205
5.65	Bar charts and wind sector plots of Vinyl acetate (in ppbV) at the two sites. See page 39 for a detailed explanation of figures	206
5.66	Photomicrographs of air samples showing alumino-silicate particles (crustal origin)	207
5.67	Photomicrographs of air samples showing alumino-silicate particles with Ca or S (crustal/marine origin)	208
5.68	Photomicrographs of air samples showing NaCl particles (sea salt origin)	209

Acknowledgments

The authors thank Gerald G. Akland and Robert K. Stevens (both formerly with the U.S. EPA) for initiating this study. We also thank Stephen C. Hern, Joseph V. Behar, Gary L. Robertson, and Dr. Roy B. Zweidinger of the U.S. EPA, and the Transboundary Community Review Team for their thoughtful reviews of all reports developed throughout development and completion of this study. Thanks is also given to Dr. Andrew R. McFarland of Texas A&M University, Terry A. Lockamy of the Texas Agricultural Extension Service, and Dr. Maria T. Morandi at the University of Texas-Houston School of Public Health for their review of this report and the study's proposal. Additional review by Dr. Lowell E. Sever of the Battelle Centers for Public Health Research and Evaluation, and Dr. David W. Sullivan, Stuart L. Dattner, and Steve Niemeyer of the Texas Natural Resource Conservation Commission (TNRCC) is also appreciated. We also thank Janet Pichette of TNRCC for providing the Effects Screening Level data used in this report and Monica Havelka (TNRCC) for developing the maps. Monitoring support conducted by Michael and Karen Stowe and Ronald Moser of Brownsville is gratefully acknowledged. A personal thanks goes to Mr. Cyrus Reed of the Texas Center for Policy Studies for providing the many valuable comments from the Transboundary Community Review Team. This document is dedicated to the memory of the Late Dr. Jackie Shields who initiated environmental interest in the Texas-Mexican border region and served on the scientific panel who reviewed the study's proposal.

Section 1 Introduction

The Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP) was a cross-border air pollution study conducted during 1996 - 1997 by the U.S. Environmental Protection Agency (U.S. EPA), in cooperation with the Texas Natural Resource Conservation Commission (TNRCC), as part of the U.S.-Mexico Border XXI Program. The study assessed transboundary pollution conditions on the U.S. side of the border region in Texas known as the Lower Rio Grande Valley, hereinafter called "the Valley." The area of monitoring in the Valley was focused in and near the border city of Brownsville, Texas, which shares a common air shed with its Mexican sister city, Matamoros, Tamaulipas. The TAPP was developed as a follow up investigation to air pollution findings from a previous monitoring effort in the Valley in 1993 known as the Lower Rio Grande Valley Environmental Scoping Study (LRGVESS). The study was also known to the Valley community as the Lower Rio Grande Valley Environmental Monitoring Study. The LRGVESS involved multimedia sampling and analysis of a broad range of environmental contaminants in an attempt to identify sources that might contribute to environmental exposures experienced by border residents in the Valley. A community report (U.S. EPA, 1994) and a series of papers published in a peer-reviewed journal (*Environ. Int.*, 1997) presented the multimedia monitoring findings and lessons learned from the LRGVESS.

Besides knowledge gained from exposure measurements conducted in the other media, a major lesson learned in that study was the need for more information concerning overall contact with air pollutants from cross-border transport and pesticide applications. In the LRGVESS, ambient air samples were collected at a fixed (central) location in the city of Brownsville, near the U.S.-Mexican border, and at a variety of residential locations. Although these locations were selected to address transboundary transport and environmental exposure issues, there were several limitations to the assessment of these issues. Assessments of transboundary air pollution impacts were limited due to location of the central site relative to the major pollution sources in the Valley and meteorological conditions that prevailed during the sampling periods (Ellenson *et al.*, 1997). Lack of real-time measurements in the LRGVESS also limited assessment of air pollution episodes. Finally, assessment of pesticide use in the Valley was restricted because samples were not collected over different seasons and the location of the central site in Brownsville was not in a rural area.

In the TAPP, a three-site air monitoring network in and near Brownsville and very close to the border, selected in consultation with community residents, was established to capture the direct impact of local sources and transboundary transport. Ambient air quality and meteorological data similar to those collected in the LRGVESS were acquired at each site for a year (March 1996 - March 1997). Semi-continuous, fine ($\leq 2.5 \mu\text{m}$) particulate mass measurements were also conducted

at the three-site network to capture potential pollutant plume events that may have occurred over short (1 to 12 hour) periods. Sites were located in urban and agricultural locations that provided for assessment of the differences in pesticide levels at these sites. Supplementary air quality and meteorological data measured in Brownsville were provided by the TNRCC. The data were summarized and compared to Effects Screening Levels and other environmental monitoring data to assess general air pollution impacts on nearby border communities. Time series plots, wind sector analyses, chemical tracer analyses, principal component analyses, and other analyses were performed to assess the extent of transboundary transport of air pollutants during the sampling period and to identify possible transboundary air pollution sources. Ancillary goals of this study were to provide TNRCC with background air pollution data against which future changes in air pollutant levels in the Brownsville area could be assessed and to evaluate and demonstrate a cost-effective monitoring approach for use by the TNRCC and other agencies for addressing transboundary air pollution transport issues in other border communities.

Section 2 Conclusions

The Transboundary Air Pollution Project (TAPP) was an air monitoring study conducted by the U.S. Environmental Protection Agency in cooperation with the Texas Natural Resource Conservation Commission (TNRCC). Its purpose was to assess transboundary transport and other air pollution events by monitoring ambient air quality for a year on a section of the U.S. side of the Lower Rio Grande Valley in and near Brownsville, Texas. A three-site air monitoring network was established near the Rio Grande River, which forms the boundary between Texas in the United States and Mexico (Figure 2.1). Sites 1 and 2 were located in central and northwest Brownsville, respectively, to capture possible industrial and other emissions due to human activity (i.e., anthropogenic) coming from Mexico. TNRCC also conducted monitoring activities at Site 1; some of those data were used in this report. Site 3 was located in a rural area of westernmost Cameron County (where Brownsville is located) to assess agricultural influences. Near real-time sampling, on a 1-h average basis, for particulate matter equal to or less than 2.5 μm aerodynamic diameter ($\text{PM}_{2.5}$) was also performed to identify episodic events. Air monitoring devices were used to collect $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ (with particle-associated elements and carbon), and volatile organic compounds (VOCs) on a 24-hour (h) average basis. Selected pesticides and polycyclic aromatic hydrocarbons (PAHs) were also collected on a 24-h basis. Precipitation samples were collected on an event basis and analyzed for metals and pesticides. Meteorological measurements were collected at each site to complement ambient air measurements in order to assess transboundary pollutant plume transport. An extensive quality assurance/quality control plan was developed and applied to the collection of all air monitoring data.

Overall conclusions of this study indicated typical air quality conditions similar to those in other parts of the U.S. Pollution levels were generally low (close to background) compared with other urban and agricultural rural areas in Texas and elsewhere. In addition, transboundary transport of air pollution plumes originating in Mexico did not appear to cause noticeable deterioration of air quality on the U.S. side of the Lower Rio Grande Valley border. The dominance of winds from the Gulf of Mexico are largely responsible for the clean air conditions in the Brownsville air shed. Finally, the few observations of pollutant concentrations exceeding their ESLs and/or other comparative data appeared to be primarily caused by local events, immediate local sources, or randomness in the data, not by regional phenomena or persistent transboundary plumes.

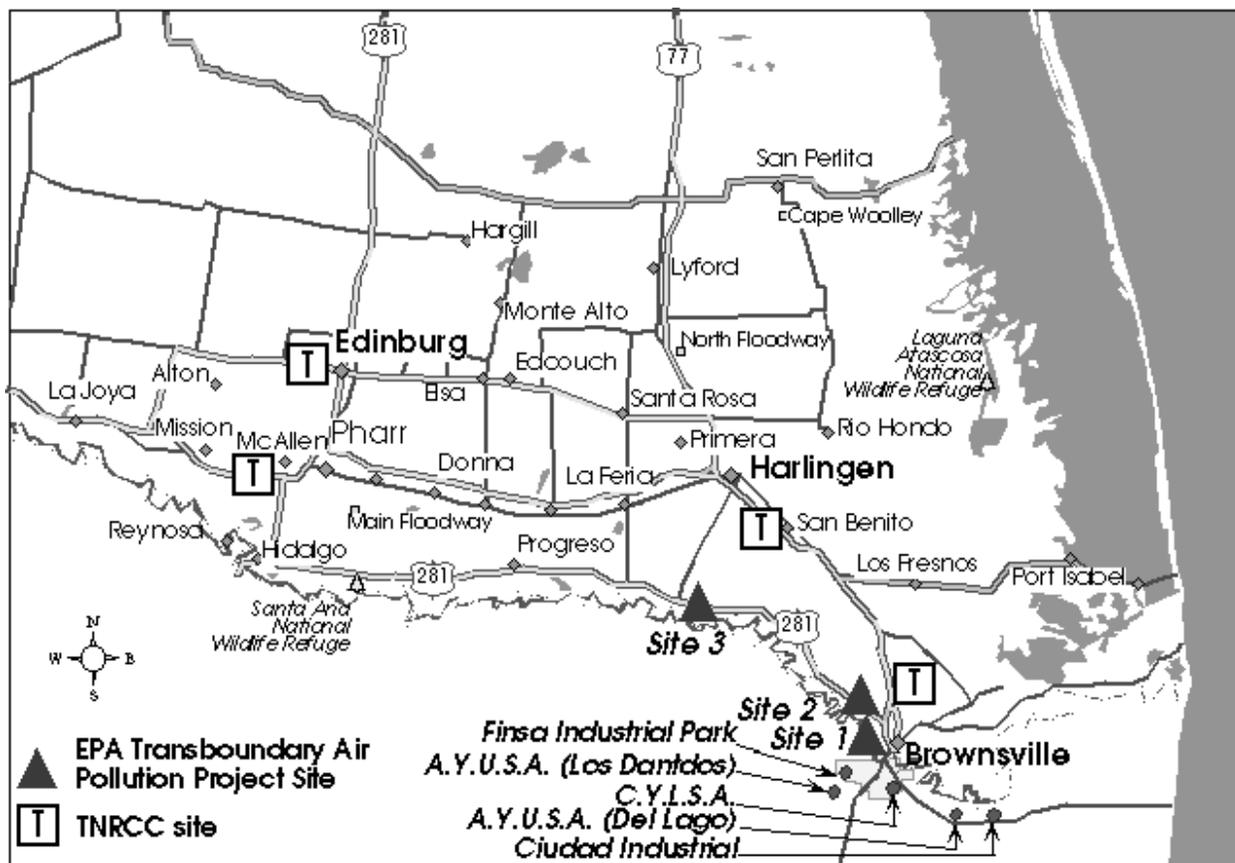


Figure 2.1. Air monitoring Sites 1, 2, and 3 used in this study and other sites established by TNRCC in the Lower Rio Grande Valley. Maquiladora industrial parks listed and identified by arrows to show location relative to monitoring sites.

Usually, air pollutant levels were below the Effects Screening Levels (ESLs) established by the TNRCC and were comparable to air pollution data measured in other air monitoring studies. These results indicated that air quality in the Brownsville area of the Valley was good. Of the vast list of pollutants analyzed in air (44 elements each in $PM_{2.5}$ and $PM_{2.5-10}$, elemental and volatilizable carbon, 122 VOCs, 16 PAHs, and 25 pesticides) only one element (silver [Ag] in $PM_{2.5}$) and six VOCs (2-nitropropane, acrolein, benzene, methanol, methylene chloride, and vinyl acetate) exceeded their respective ESLs (see Table 2.1); other comparative data besides ESLs are shown. The data summarized in Table 2.1 include data below detection at one-half the detection limit. Although data in subsequent tables are for detected values; the pollutants listed above the ESLs are the same. Air pollutants above the ESL were, in general, observed from a single sampling period or a small number of samples and were most likely associated with uncertainties due to inherent variability of the data or the presence of a local, short-term source or activity.

Elevated pollutant levels were almost always associated with prevailing southeasterly wind and the downwind geographic orientation of the Valley. Although the methanol values should be interpreted with caution, exceedances of the ESL for this pollutant occurred from both the South and North. A one-time exceedance for benzene occurred at Site 1 with wind direction from the North. The highest exceedance for 2-nitropropane occurred at Site 2 also from the same wind direction. A one-time exceedance for methylene chloride came from the South-Southeast at Site 2 and may have been associated with transboundary emissions. Site 2 was probably affected by more immediate VOC emission sources, such as a propane/butane liquified petroleum filling station. Further investigation in the vicinity of Site 2 would be necessary to provide more definitive evidence of transboundary influences.

Analysis of hourly $PM_{2.5}$ mass levels at all three sites revealed a minimal number of episodic events for fine particles. Hourly $PM_{2.5}$ levels on August 2, 1996, were elevated, particularly at Site 1 ($65 \mu\text{g}/\text{m}^3$ during a single, 1-h period). Based on assessments of time-lapse satellite imagery data, these elevated levels may have resulted from long-range aerial transport of Saharan dust from North Africa to the Valley area. The only local episodic event identified was a scrap tire fire on August 14, 1996, at Site 3 in which elevated hourly and 24-h $PM_{2.5}$ and 24-h PAH levels were found.

As in the 1993 Lower Rio Grande Valley Environmental Scoping Study (LRGVES), air monitoring results from the TAPP indicate that the Valley air shed is dominated by regional background influences such as aolian-generated soil dusts and sea salts from strong, prevailing sea breezes from the Gulf of Mexico. Trace metal analysis results of precipitation samples were consistent with these findings. Transportation emissions (such as automotive and diesel truck exhaust) were estimated from $PM_{2.5}$ and carbon monoxide diurnal patterns as well as from VOC levels and selected VOC ratios; transportation emissions may have been associated with local as well as international bridge traffic. Most of the airborne particle mass, VOC and PAH concentrations were lower than or comparable to results from previous air monitoring surveys.

Table 2.1. Measurements for air pollutants above the ESL. Other comparative data shown.

ESL ^b (annual)	Site 1				Site 2				Site 3				ESL ^a (24 h)	
	Min (Max)	Mean	Max	n	Min	Mean	Max	n	Min	Mean	Max	n		
Other														
Comparative														
Data														
(Mean)	n	Min	Mean	Max	n	Min	Mean	Max	n	Min	Mean	Max	n	ESL ^a (24 h)
PM _{2.5} (concentrations in nanograms per cubic meter, ng/m ³) ^c														
Silver	256	1.8	3.4	45.8	287	1.8	4.9	16.4	295	1.8	4.8	30.1	40	
10														
VOCs (concentrations in parts per billion by volume, ppbV) ^c														
2-Nitropropane	NM	NM	NM	NM	59	0.25	0.45	8.10	NM	NM	NM	NM	NM	5.60
1.40														
Acrolein	NM	NM	NM	NM	59	0.25	0.60	2.99	NM	NM	NM	NM	NM	0.40
0.10														
Benzene	58	0.003	0.90	15.46	59	0.16	0.47	2.86	NM	NM	NM	NM	NM	4
1														
Methanol	2,800 ^d	3,343 ^d			59	1.50	169.23	2330.00	NM	NM	NM	NM	NM	800
200														
Methylene chloride	58	0.003	0.05	0.39	59	0.02	1.11	50.30	NM	NM	NM	NM	NM	30
7.5														
Vinyl acetate	1,809 ^d				59	0.25	0.73	17.30	NM	NM	NM	NM	NM	16
4														

n = number of samples measured

Min = minimum or lowest value

Mean = average

Max = maximum or highest value

NM = not measured

^aESL (24 h) = Effects Screening Levels (based on 24-hour time frame). Developed by the Texas Natural Resource

The number of detected pesticide concentrations was sparse. With predominant Gulf breezes flushing out Valley air, overall concentrations of anthropogenic species remained low.

Transboundary emissions of an anthropogenic nature from Mexico to the U.S. and vice versa may have occurred, as indicated by certain VOC measurements. Principal component analysis revealed the possibility of waste incineration and residual oil combustion emissions occurring throughout the Valley. However, emissions from more immediate sources (such as benzene emissions from the National Guard Armory area or local automobile traffic at Site 1, VOC emissions from a propane filling station near Site 2, and PAH emissions from a scrap tire fire near Site 3) seemed to affect air quality at the three sites to a much greater extent than transboundary influences.

Section 3

Recommendations and Future Activities

The purpose of the Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP) was to assess cross-border air pollution for a full year that could impact a specific region of the Valley. The data also provide a baseline for assessing future air quality conditions of a transboundary nature in the Valley. Obviously, a multi-year monitoring effort in other regions of the Valley would be required to assess air quality trends and the impact that continued growth of border-dependent industries (known as maquiladoras) have on potential transboundary air pollution. Reports in May 1998 of crop and forest fires in Southeast Mexico, Guatemala, and Honduras severely affecting air quality in Brownsville and most of Texas are an important reminder of the need for a continued air monitoring presence in the Valley. A report by the U.S.-Mexico Border XXI Program indicating air pollution as an environmental challenge facing border cities (U.S. EPA, 1998) is yet a further reason for continued air quality surveillance in this region.

In that regard, the Texas Natural Resource Conservation Commission (TNRCC) is conducting air monitoring studies throughout the Valley to assess these and other influences and their possible impacts on human health. In addition to the five-year monitoring effort in Brownsville (Site 1 in this study), the TNRCC has established within the last two years other air monitoring sites in Valley cities such as San Benito, Edinburg, and Mission. Figure 2.1 shows these sites in relation to the TAPP monitoring sites in the Valley. Air pollutants measured at these sites include similar pollutants collected in the TAPP as well other species such as ozone, carbon monoxide, and continuous PM₁₀. Although presentation of all these data is beyond the scope of this report, future data from these sites will provide additional information on temporal and spatial air quality conditions throughout the Valley. In addition, these sites further west of the TAPP sites might be able to assess potential deposition of emissions from Brownsville/Matamoros that are being dispersed or diluted by Gulf winds; a good example of this possibility would be with regards to ozone deposition.

While ambient air monitoring sites on the U.S. side of the Valley are becoming well-established, monitoring on the Mexican side is still almost non-existent. Air monitoring on the Mexican side of the border is essential to determine if emissions from maquiladoras and other industries as well as from other emission sources (such as automobiles, waste burning activities, etc.) are transported across the border or are emitted at such low levels that transboundary transport is not significant. It is also possible that pollutants emitted from industrial sources are not being transported across political boundaries due to their being deposited within the industrial plant's fence line; monitoring at sites at the fence line and on the border would provide more definitive assessments of transboundary transport from such sources. The collection of accurate source emissions data (addressing those pollutants identified from ambient measurements) from both sides of the border is

also necessary to ascertain which emission sources may be impacting border sites. Emissions inventories have been performed on Matamoros and some Brownsville industrial facilities for "total toxic chemicals" and used in air dispersion modeling (Tarr, 1994). While this is a first step at assessing emissions in the Valley, actual stack, vent, and tailpipe monitoring of the same air pollutants measured at air monitoring sites is needed to actually apportion which potential source processes (be they industrial, open burning, transportation, etc.) have transboundary implications.

There are other monitoring efforts being undertaken in Mexico. The TNRCC is working with Mexican authorities to conduct air monitoring in the Matamoros area. In addition, as part of the U.S.-Mexico Border XXI Program, limited air monitoring efforts have been conducted by the South West Center for Environmental Research and Policy (SCERP) to assess emissions from maquiladoras and other sources on the Mexican side of the Valley (see Mejía-Velázquez *et al.* and Meuzelaar *et al.*, 1997). Cooperative efforts, such as the use of the TAPP data set with SCERP results, should be continued to provide further information on transboundary air pollution transport and its impact on either side of the border.

Finally, the TAPP was designed to be an air quality monitoring study. While these ambient measurements can be used to estimate general environmental exposure conditions, they cannot be used to assess individual exposures. As done in the 1993 Lower Rio Grande Valley Environmental Scoping Study, measurement of pollutants in other media (such as soil, water, food, etc.) collected in residential sites along the border area is necessary to evaluate personal exposures to air pollutants in the context of total exposure. With the possible exception of farm workers, most people spend the majority of their day indoors. Thus, an indoor air monitoring component would be required to compare exposures from indoor air pollution sources versus transboundary emissions affecting outdoor air. In addition, other sampling methods (such as for acrolein) and inherent sampling difficulties for oxygenated organic species such as methanol need to be factored in so that comparison of similar exposure monitoring data or screening levels like ESLs are as close to equivalent as possible.