Section 4
Methods And Quality Assurance

4.1 Study Design

The primary objective of the Lower Rio Grande Valley Transboundary Air Pollution Project (TAPP) was to obtain air quality and meteorological data for a full year to assess the extent of transboundary air transport of pollutants in a region of the Lower Rio Grande Valley in and near Brownsville, Texas. To accomplish this objective, a network of three air quality monitoring stations was established to operate from March 1996 to March 1997 in Cameron County, Texas, where Brownsville is located. All three sites were approximately one kilometer (km) from the Rio Grande River, which forms the boundary between Texas, U.S.A. and Tamaulipas, Mexico.

Figure 4.1 shows the location of the TAPP air monitoring sites. Although the sites were primarily influenced by nearby sources, as is true with all air monitoring sites, their proximity to the border allowed the assessment of potential transport of air pollutants from the Mexican side of the border. The air monitoring station locations were selected by U.S. Environmental Protection Agency (U.S. EPA) personnel, with input from the Texas Natural Resource Conservation Commission (TNRCC) and local community leaders. The three site locations were chosen according to the following criteria:

> Site 1: The site is at 344 Porter Drive on the grounds of the National Guard Armory, just south of the University of Texas-Pan American campus in the east-central part of Brownsville. This site is next to a TNRCC Community Air Toxics Network site that is part of a national VOC monitoring network. Some of the ambient data acquired by TNRCC at this site were used in this study. The site is also adjacent to downtown Brownsville and is just southeast of the Gateway International Bridge between Brownsville and Matamoros, Mexico. It is located near automotive, diesel truck, and industrial emissions. It is also near the central site where air monitoring was done during the 1993 Lower Rio Grande Valley Environmental Scoping Study (LRGVESS) and is on the grounds of the same facility that housed the border site in that study (see Mukerjee *et al.* [1997a] for further details of this site). Geographical coordinates of this site are: latitude 25E53'32"North (N); longitude 97E29'35"West (W).
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> Site 2: This site is next to the Galaxia Residential Subdivision of Brownsville on Military Highway 281, approximately 5 km (3 miles) northwest of Site 1. This site is ideally suited to measure impacts of emissions from Brownsville to the east and southeast, emissions from Matamoros to the south and southeast, and agricultural activities to the north. Man-made

(anthropogenic) transboundary emissions can be assessed at this site due to its location, which is usually downwind from those sources where predominant wind flows came from (southeast). Geographical coordinates of this site are: latitude 25E56'27"N, longitude 97E32'17"W.

<u>Site 3:</u> This site is next to the Military Highway Water Supply Company on Military Highway 281 near Los Indios, Texas, approximately 35 km (22 miles) northwest of Site 2. Site 3 is in a rural community, near agricultural fields and is relatively free from local industrial emissions. The Free Trade Bridge at Los Indios is approximately 2-3 km (1-2 miles) southeast. This site was selected primarily to provide information about the air pollution impact from agricultural activities. Geographical coordinates of this site are: latitude 26E03'04"N, longitude 97E45'23"W.

As for other site-selection criteria, accessibility under all weather conditions, availability of adequate electricity, and security of the monitoring devices were considered. Based on this information, the sites were selected and air monitoring stations were established at each location following the siting requirements outlined in the U.S. EPA Ambient Air Quality Surveillance regulations (40 U.S. CFR, Part 58, Appendix E, 1988). Information acquired from siting the central monitoring station during the LRGVESS (U.S. EPA, 1994; Ellenson *et al.*, 1997; Mukerjee *et al.*, 1997a) were also incorporated into the TAPP site selection. As shown in Table 4.1, the air monitoring program at all three sites included most of the monitoring devices to be discussed in Section 4.4. While sampling inlets for all devices were located outside (at recommended heights), all monitoring equipment was housed in temperature-controlled shelters specifically constructed for such devices when applicable.

4.2 Selection of Ambient Air Pollutants

As in the LRGVESS, a principal objective of the TAPP was to examine potential transboundary transport of air pollutants from industrial, agricultural, and other anthropogenic activities and to assess their impact on the Brownsville border and vicinity. Particulate and gaseous air pollutants are generated by both anthropogenic and natural (biogenic) sources and have been regulated and researched extensively due to their impact on human health and welfare; particles represent both solid and liquid phases (Godish, 1997). Most industrial emissions into air are the result of combustion processes. Other anthropogenic emissions can be the result of: 1) combustion processes such as automobile exhausts or home heating, 2) evaporative emissions as with volatiles from paints, glues, and other chemical processes, and 3) pollutant entrainment such as aerial spraying of pesticides. Specific emissions of pollutants for all operations in the Valley are not fully characterized although general anthropogenic activities in the Valley are known. Potential, unreported or accidental releases are very difficult to verify. Consequently, the measurement of a broad range of particulate and gaseous air pollutant species associated with combustion-related activities was addressed. It is important to note that many of these pollutants are ubiquitous and could also be found in natural sources such as vegetation, dusts, or large bodies of water. Almost all of the air pollutants monitored in the TAPP were also measured during the LRGVESS except pollutants measured in precipitation (from rain or wet deposition).

Fine inhalable particles, defined as less than or equal to 2.5 micrometers (µm) in aerodynamic mass median diameter ($PM_{2.5}$) were sampled and analyzed for mass and associated inorganic elements. Elements included heavy metals such as lead. Particles in this size range are commonly derived from combustion processes or gas-to-particle conversion and remain suspended in the atmosphere for longer periods than do coarser particles. High temperature combustion sources such as fossil fuel burning, incineration, smelting or hot processing of metals, other industrial operations, and mobile sources are known to emit fine particles (U.S. EPA, 1996a). As opposed to $PM_{2.5-10}$, $PM_{2.5}$ has been found to be more evenly distributed across a community. As a result, $PM_{2.5}$ at community monitoring sites has been found to most likely represent average, daily fine particle concentration over an entire community (Wilson and Suh, 1997). $PM_{2.5}$ is also called “respirable” particulate matter since it can be transported and deposited further into the human respiratory tract than larger-sized particles (U.S. EPA 1996b; Godish, 1997).

As with other pollutant species monitored, $PM_{2.5}$ samples were collected for 24-hour (h) periods (from midnight to midnight). Time-integrated continuous sampling for a 24-h period is a routine monitoring approach in air monitoring studies. Automated $PM_{2.5}$ analyzers operated in near real-time and integrated in hourly intervals were used at the three-site network to assess the potential for intermittent air emissions that might occur within a given day. Results were reported as integrated, hourly averages.

Particles in the aerodynamic diameter size range of 2.5-10 µm are indicators of coarse particulate matter; they are given the abbreviation: $PM_{2.5-10}$. $PM_{2.5-10}$ was collected and analyzed for mass and associated elements. Sources of coarse particulate matter include mixing of fertilizers and pesticides, agricultural burning and open burning, road construction, and sea salt/sea spray production. Dust emissions from soils or other material formed by the crushing, grinding, or abrasion of surfaces can be suspended as coarse particulate matter by wind forces or anthropogenic activities (such as road traffic on paved and unpaved roads or tilling). A large contribution of surface air particulate matter from wind blown dusts can be encountered in the Western U.S. where conditions are arid to semiarid (U.S. EPA, 1996a). In the LRGVESS it was noted that the $PM_{2.5-10}$ fraction was dominated by a soil (crustal)/sea salt component. The TAPP focused on collecting $PM_{2.5}$ samples on a daily basis since it is more associated with anthropogenic emissions. Coarse particle samples were collected on a once-every-third-day schedule.

Carbonaceous material is a component of particulate matter which is emitted by sources that burn organic fuels (Muhlbaier and Williams, 1982; Hamilton and Mansfield, 1991). Elemental carbon (C_E) and volatilizable carbon (C_V) were carbonaceous material measured in samples collected on filter media. C_E, (present as soot) was measured to address contributions of emissions from residential wood burning and diesel particulate matter known to contain this form of carbon. Sources related to wood burning include field burning or trash burning activities. Diesel is a less-refined fuel than conventional gasoline and, as such, emits more carbonaceous particulate matter when combusted; diesel emissions are considered a major source of C_E (Hamilton and Mansfield, 1991). C_V was also measured since it can be emitted from the combustion sources mentioned above and from chemical, fossil fuel, and biogenic sources (U.S. EPA, 1996a). C_V also has potential carcinogenic effects (Hamilton and Mansfield, 1991).

A limited number of samples collected from air and precipitation were analyzed for polycyclic aromatic hydrocarbons (PAHs). PAHs are ubiquitous in nature and are formed by chemical reactions during incomplete combustion of fuels such as wood, coal, oil, diesel, and gasoline. Such sources include open burning, industrial processes, residential heating, and mobile sources (National Research Council, 1983; U.S. EPA, 1996a). PAHs have also been found in sources such as oil refining, metal working, and chemical production. Many PAHs have toxic or carcinogenic properties (ATSDR, 1995).

A limited number of samples were collected and analyzed for volatile organic compounds (VOCs) since they are emitted by many anthropogenic and biogenic sources. While industrial combustion processes are major contributors, another dominant source of VOCs, particularly those that form ozone, is evaporative emissions and exhausts from incomplete fuel combustion from transportation (mobile) sources (Warneck, 1988; Purdue *et al.*, 1992; Godish, 1997). Industrial sources principally include emissions from petroleum and petrochemical industries. Other industrial processes can include iron and steel manufacturing, nonferrous metal manufacturing, and pulp and paper manufacturing. Another major emission source of VOCs related to non-combusted industrial emissions include organic solvent evaporation. This would include metal surface coating, degreasing, and printing and fabric coating operations. VOCs monitored in this study included hazardous chemicals that were likely to be present in the ambient atmosphere such benzene, methylene chloride, chloroform, carbon tetrachloride, trichloroethylene, and toluene (Brodzinsky and Singh, 1983) to name a few. The VOC, methylene chloride (or dichloromethane), is a solvent and a probable carcinogen. Methylene chloride was known to have been used and emitted by an electronic-manufacturing maquiladora in Matamoros (Feldstein and Singer, 1997). Agricultural operations, from open burning to use of fertilizers, can also emit VOCs (Ciccioli, 1993). Finally, trees and plants emit certain VOCs, such as isoprene, and alpha ("-) and beta (ß-) pinene (Graedel, 1978; Warneck, 1988).

Use of pesticides is well-characterized in the Valley area since agriculture is a major economic activity in the region (Texas Department of Agriculture, 1988; Norman and Sparks, 1995). To address agricultural influences, a limited number of these pesticides were measured in air and precipitation samples. Pesticides monitored included herbicides, insecticides, and fungicides measured in the LRGVESS except dicamba, metalachlor, carbaryl, and pentachlorophenol. The pesticides measured in this study included those used in the U.S. and Mexico (Texas Department of Agriculture, 1988; GAO, 1992).

As in most air monitoring studies, on-site meteorological measurement data (wind speed, direction, temperature, and relative humidity) were acquired. Meteorological measurements are considered a fundamental aspect of ambient air monitoring; it has even been suggested that a corresponding meteorological network be established with an air monitoring network if existing sources of meteorological data are insufficient (Bryan, 1968). This was important in the TAPP since knowing whether air pollutants were coming from a northerly or southerly direction in relation to the border was necessary. Although local meteorological data can be collected from airport measurements to assess macro-scale conditions or for long-term trend analysis, site-specific meteorological data was deemed necessary for this study to relate ambient air quality measurements with wind trajectories. Since episodic emission events are a consideration in the TAPP, standard procedure dictates that a meteorological station should be in the vicinity of the air quality sensor (U.S. EPA, 1995). In addition, micro-scale measurements are important since meteorology can be different in urban versus rural locations. Coastal areas, such as certain areas of the Valley, may be affected by land-sea breeze influences and would require micro-scale measurements (U.S. EPA, 1987). In spite of these potential micro-scale differences, visual examination of the wind direction data at all three sites found them to be well correlated with each other indicating regional wind patterns were dominant. Previous assessments of wind direction at the LRGVESS central site (close to Site 1) and the Brownsville/South Padre Island International Airport also revealed good correlations (Crescenti, 1997). Most of the transboundary assessments in TAPP were developed using air pollution meteorology.

4.3 Air Quality Monitoring Strategy

The monitoring strategy for this study called for collection and analysis of daily samples at all three monitoring sites during the study's one-year period. Continuous, automated monitoring devices were used to the extent feasible to capture the impact of intermittent emissions or accidental releases into the air and to determine diurnal variation in pollutant concentrations where applicable. Continuous meteorological measurements were collected to support the interpretation of air quality monitoring data (e.g., to determine which direction emissions were coming from). The monitoring strategy also relied on information gathered from evaluation studies conducted in the LRGVESS. Table 4.1 shows the types of sampling made at the three sites.

Automated monitoring instruments were used by the U.S. EPA for the continuous collection of hourly-averaged $PM_{2.5}$ mass and meteorological measurements. A manual integrative sequential sampler (discussed in detail in Section 4.4.2.1) was used to collect daily samples of $PM_{2.5}$ over 24-h periods for subsequent $PM_{2.5}$ mass and trace element analysis; pesticide and PAH samples were also obtained with this sampler. This sequential sampler permitted samples to be collected on a daily basis with minimal attendance by a site operator to change filters and other collection media. The sequential sampler used in the TAPP is being evaluated by U.S. EPA as part of the recent PM Research Program Strategy to address issues arising from recent epidemiological observations indicating an association between fine particulate matter air pollution and mortality (Dockery *et al.*, 1993). All daily fine particle samples were analyzed for mass and trace elements. Pesticides and PAHs were determined from 60 of these collected samples. Selection of samples for pesticide and PAH analysis was based on wind direction and season of the year to have a representative sample. For example, samples were chosen from northerly and southerly directions to determine pesticide/PAH concentration differences between samples and which position that could be potentially indicative of transboundary transport.

A dichotomous sampler was used to collect $PM_{2.5}$ and $PM_{2.5\text{-}10}$ samples on an every third-day schedule (see Section 4.4.2.5). $PM_{2.5}$ was collected on a quartz-fiber filter for C_E and C_V. $PM_{2.5\text{-}10}$ sampled with the dichotomous sampler was collected on polycarbonate filters and analyzed for mass and trace element concentrations. Selected $PM_{2.5\text{-}10}$ filter samples were also analyzed for elemental concentrations and particle morphology using scanning electron microscopy (SEM).

As previously stated, Site 2 was the principal site for transboundary assessments due to its location downwind from anthropogenic influences that may be crossing the U.S.-Mexican border. In addition to the instrumentation discussed, 24-h integrated direct (whole air) samples were collected in evacuated electropolished stainless-steel canisters on an every sixth-day schedule by TNRCC at Site 1 and by U.S. EPA at Site 2 for VOCs. Finally, two precipitation samplers were operated at Site 2 to collect rain events for trace element, pesticides and PAH determinations. A Belfort Weighing Rain Gauge was also installed and used for determining amounts of precipitation.

While discussion of the sampling, analysis and quality assurance procedures follows, readers interested in a brief summary of sampling and analysis methods should examine Tables 4.2 and 4.3, respectively. Table 4.2 presents the sampling methods; Table 4.3 presents a summary of analysis methods.

4.4 Air Sampling and Analysis

4.4.1 Automatic/Continuous $PM_{2.5}$ Mass Measurements

Ambient $PM_{2.5}$ mass samples were collected continuously at all three sites using a tapered element oscillating microbalance (TEOM® Series 1400a) (Rupprecht & Patashnick Co., Inc., Albany, NY). The TEOM is a U.S. EPA equivalent method for direct mass measurement of PM_{10} (U.S. EPA equivalent method designation number EQPM-1090-079 [U.S. EPA, 1990c]). A schematic of the TEOMs used is shown in Figure 4.2. The TEOMs were fitted with 2.5 µm cyclone inlets (Model URG-2000-30EH, URG Corp., Chapel Hill, NC) to collect $PM_{2.5}$.

To comply with the revised U.S. EPA National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$, measurements must be collected according to Federal Reference Method (FRM) specifications (U.S. EPA, 1997c). FRM specifications for fine mass were established after completion of this study so the $PM_{2.5}$ data in this study can only be used for research purposes. However, the cyclonic separation techniques used in this study are valid and the data are comparable to FRM $PM_{2.5}$ data.

TEOMs were configured to provide continuous, integrated 1-minute (min) and 1-h measurements of $PM_{2.5}$ that penetrated the inlets of the monitors (defined by the 50% of the inlet effectiveness curve). The TEOM is sensitive to rapid temperature and line voltage fluctuations, and vibrations; this holds true for all microbalance instrumentation. These changes average out over longer periods of time but can be highly influential for shorter intervals (Allen and Burton, 1991) such as time frames less than one hour. In the TAPP, both 1-h and 24-h averaged TEOM data were used.

TEOMs continuously monitor $PM_{2.5}$ by capturing particles on a sample filter mounted on the free end of a clamped, vibrating, inertial, hollow-tapered tube. This tube functions as a mass transducer. An analogy of this vibrating tube as a mass transducer is that of a tuning fork with the frequency of oscillation decreasing with increasing particle mass loading on an imaginary filter mounted at the free end. Using the rate of mass accumulation on the filter and the flow rate through the sample flow controller, the TEOMs microprocessor determines the mass concentration. Further details of the TEOM can be found in Patashnick and Rupprecht (1991).

The flow-rate through the sample filter was set at a nominal rate of 3.0 liters per minute (L/min). A bypass flow was used to provide an additional 13.7 L/min for a total flow-rate of 16.7 L/min, this being the proper flow rate for the PM$_{2.5}$ size selective inlets (Figure 4.2). Inlet assemblies of the TEOMs were at least 6 meters (m) above the ground and 1 m above the station shelter according to U.S. EPA Ambient Air Quality Surveillance regulations (40 U.S. CFR, Part 58, 1988). The micro-balance assemblies were located inside the shelter and maintained at 40 degrees Celsius (EC). Microbalance filters were replaced at approximately two week intervals followed by calibration checks. Data were reported as hourly mass concentrations of PM$_{2.5}$ in Fg/m^3 at standard conditions [25EC and 1 atmosphere (atm) pressure]. One-minute average values were computed and stored for diagnostic purposes.

TEOMs sample particulate matter at a predetermined temperature level. The manufacturer recommends the TEOM be operated at a controlled temperature of 50EC to minimize adsorption/desorption effects of atmospheric moisture on the microbalance filter. While this relatively high temperature does reduce moisture effects (especially on 1-h averages), it can result in a loss of semi-volatile species such as ammonium nitrate and semi-volatile organic compounds, thereby resulting in the loss of some mass (Allen et al., 1997). To decrease the potential for semivolatile compound and mass losses while minimizing moisture effects, the TEOMs were operated at 40EC. This was only 5EC above maximum ambient temperatures encountered during the study. Although losses of semivolatile species and mass can occur with this instrument, **all** particulate matter monitoring devices (including time-integrated samplers like the dichotomous sampler [see Keeler *et al.* (1988) as an example]) also have potential losses of mass (Patashnick, 1998). Applications of real time particulate devices, in light of heightened interest in PM$_{2.5}$, are undergoing continual evaluation by U.S. EPA.

4.4.2 Manual/Integrative Measurements

4.4.2.1 Dual Fine Particle Sequential Sampler (DFPSS)

Integrated 24-h samples were collected every day at all three sites for PM$_{2.5}$ and associated elements using dual fine particle sequential samplers (DFPSS Model URG-2000-01K) (URG Corp., Chapel Hill, NC). A diagram of the DFPSS used in this study is shown in Figure 4.3. The DFPSS is a research sampling device that is currently being used and evaluated by the U.S. EPA as part of the recent Particulate Matter Research Program Strategy. As with TEOMs, inlet assemblies of the DFPSSs were located in accordance with the U.S. EPA Ambient Air Quality Surveillance regulations (40 U.S. CFR, Part 58, 1988, Appendix E). The DFPSS was operated with two separate channels, each with separate, identical inlets (rain-caps) and 2.5 Fm cyclonic separators (Model URG-2000-30EH) through which samples are collected simultaneously at a flow rate of 16.7 L/min. The 2.5 Fm cyclonic separators were identical to the inlets used with the TEOM monitors to capture PM$_{2.5}$. The DFPSS was ideal for use in remote areas (such as Site 3), required low maintenance (since cost was a factor), and could simultaneously collect a number of different pollutant species. The DFPSS also cost-effectively facilitated everyday sampling since the site operator only needed to visit each site once every three days.

Rain cap inlets for the DFPSS were outside the monitoring shelter at the same height as TEOM inlets. The 2.5 Fm cyclone separators, filter packs, and distribution manifolds were inside the shelter and maintained at room temperature. The 2.5 Fm cyclone separators were configured inside the housing of the DFPSS to reduce possible loss of semi-volatile compounds and surface reactions resulting from the high, outdoor, summertime temperatures.

One channel of the DFPSS was configured with four sets of filter packs (Model URG-2000-22ABB-37-1), each filter pack holding a 37-millimeter (mm) diameter Teflon® filter with 0.2 µm pore size (Gelman Sciences Inc., Ann Arbor, MI). Each filter collected $PM_{2.5}$ and was later analyzed for chemical element composition including metals. The Teflon filters were pre- and post-weighed under controlled temperature and humidity conditions to determine the 24-h average mass concentration of fine particles in $\mu g/m^3$ (see Section 4.4.2.2). These filters were also analyzed for trace elements by X-ray fluorescence (XRF) (see Section 4.4.2.3). The other channel of the DFPSS was configured with four additional sets of collection assemblies (Model URG-2000-30PUF), each assembly holding a 37 mm quartz-fiber filter along with a polyurethane foam (PUF) sorbent trap (URG, Chapel Hill, NC). PUF is frequently used in the sampling of semi-volatile organic compounds in air, such as pesticides and PAHs (Lewis and Gordon, 1996). Quartz-PUF assemblies enabled sampling of pesticides and PAHs in particle and vapor phases; the quartz filter collected semi-volatile compounds absorbed in fine particulate matter while the PUF collected the vapor phase of the same species. Two samples, one on the Teflon filter and one on the quartz-PUF assembly, were collected every day for a 24-h monitoring period, starting at midnight and ending at midnight the following day. Sixty of the nearly 400 quartz-PUF cartridges collected at the three-site network were extracted for subsequent analysis for pesticides and PAHs (see Section 4.4.2.4).

4.4.2.2 Mass (Gravimetric) Determinations

Ambient particle samples collected on Teflon filters using the DFPSS were equilibrated and weighed before and after sampling (gravimetric analysis under controlled temperature and humidity conditions) using an ATI Cahn Model 35 (Analytical Technology, Inc., Boston, MA) microbalance with an accuracy of 0.1 µg. Gravimetric analyses were performed under controlled temperature and humidity conditions. Weight measurements were conducted in a temperature-controlled (24-30EC) and humidity-controlled (20-45% relative humidity) room with the filters being placed in the room approximately 24-h in advance of gravimetry to equilibrate. Electrostatic charge was removed from each filter before actual weighing. Before and after deployment in the field, all filters were inspected for holes or other imperfections and kept in labeled Petri dishes.

The pre-sample (tare) filter mass was determined to the nearest microgram (µg). Final filter masses were determined as the difference between the pre-sample and final weights. The balance's zero reading was checked regularly and the balance was re-calibrated if zero or precision tests failed. Every seventh filter placed on the balance (after a set of six other filters had been weighed) was a re-weigh of the last filter before a routine check of the balance was done using a 200 mg NIST traceable weight (a Class "M" weight). If the NIST traceable mass exceeded a 2 µg limit, the balance was re-calibrated and the previous set of six filters was re-weighed. The micro-balance was calibrated at the beginning of each weighing session with the NIST traceable mass.

4.4.2.3 X-ray Fluorescence (XRF) Analysis

After mass determination, all Teflon filters from the DFPSS and coarse channel of the dichotomous sampler (discussed in Section 4.4.2.5) were submitted for elemental analysis using energy-dispersive x-ray fluorescence (XRF) spectrometry. A Lawrence Berkeley Laboratory (LBL) XRF spectrometer, custom built for air filter analysis, was the principal XRF instrument used in this study. Since the LBL could not analyze Sodium (Na) and Magnesium (Mg), 21 samples from Site 1 and approximately 90 samples, each, from Sites 2 and 3 were re-analyzed for these two elements by XRF using a Kevex EDX-771 (Kevex, Valencia, CA). The basic principle of XRF is that an X-ray beam irradiates the filter sample that causes each element in the sample to emit characteristic X-rays. These X-ray emissions are then detected by a solid state detector, this being the spectrometer. The concentration for each element was calculated from the area under the analytical peaks for each element (Dzubay and Stevens, 1991). XRF only measures total element concentrations; it cannot distinguish elements in specific chemical compounds or ionic species.

XRF data consist of elemental concentrations in fine particles in nanograms per cubic meter (ng/m^3; a nanogram is one-millionth of a milligram) for up to 45 elements ranging in atomic number from 11 (Na) to 82 (Pb); this range includes most metals of environmental concern. Associated with each concentration is an uncertainty value at the 68% (1F) confidence level. This value is determined by propagating the errors (uncertainties) in the parameters used in calculating the concentrations. These parameters are volume, x-ray attenuation by the layer of fine particles, calibration standard concentrations, counting statistics, interference corrections, and system stability. Data reported here follow general recommendations that a concentration must be greater than 3 times its uncertainty for an element to be considered as detected.

U.S. EPA-approved Standard Operating Procedures (SOPs) for the LBL and Kevex XRF analytical instrumentation were followed for all measurements (Kellogg, 1993; Kellogg, 1994). Calibration of the XRFs were based on instrument response to single-element, thin-film standards. Additional calibration of the Kevex was based on instrument response to two elements in the form of organo-metallic compounds dissolved in a polymer. Accuracy (± 10%) was validated by comparison to National Institute of Standards and Technology (NIST) standards. Precision (approximately ± 7%) was determined by repeated analyses of quality control (QC) standards. A maximum of 72 samples per session for the LBL using a set of 6 QC standards and up to 60 samples per session for the Kevex using a set of 3 QC standards were used. The set of QC samples was measured at the start and end of each analysis session. QC charts were maintained automatically for each element.

4.4.2.4 Pesticide and Polycyclic Aromatic Hydrocarbon (PAH) Analyses

All daily quartz-fiber filters and PUF plugs from the PUF cartridges collected with the DFPSS were extracted after sample collection; sixty of these samples were analyzed for pesticides and PAHs. Selection of the samples for analysis was based on meteorological conditions (e.g., wind direction) and season of the year. Quartz-fiber filters and PUF plugs were obtained from commercial suppliers (QST Environmental, Gainesville, FL), pre-cleaned, and acceptance-tested for blank concentrations.

Each filter and PUF plug chosen for analysis of pesticides and PAHs in air were continuously solvent-extracted in a Soxhlet apparatus for 18 h using 500 milliliters (mL) of 10% volume-by-volume diethyl ether in hexane (pesticide residue grade). Solvent reflux rates were approximately 4 cycles per hour. Before extraction, surrogate, deuterated (i.e., heavy hydrogen isotope) semi-volatile compounds were added (i.e., spiked) to each Soxhlet apparatus containing the filter and PUF material. This was done to monitor extraction efficiency and assess overall method performance. After extraction, the 500 mL extract was transferred from the Soxhlet apparatus through a sodium sulfate drying column into a Kuderna-Danish apparatus and was concentrated down to about 5 mL on a hot water bath. The extract was further concentrated in a 5-mL graduated receiver and placed under a gentle stream of nitrogen to be reduced to a final volume of 1 mL. The solvent extract was then transferred with a disposable glass pipette to a glass auto-sampler vial, sealed with a Teflon-lined crimp top, and refrigerated at 4EC until analysis.

Analyses of pesticide and PAH samples from air and precipitation (discussed later) were performed using gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM). Two SIM analyses of each extract were performed. The analytical procedure was based on U.S. EPA Ambient Air Toxic Protocol (a.k.a., U.S. EPA Compendium Method) TO-4 (Modified) for pesticides and U.S. EPA Compendium Method TO-13 for PAHs (Winberry *et al.*, 1988; 1990). The instrument used for analysis was a Hewlett-Packard (HP) 5890 Series II GC (Hewlett-Packard, Palo Alto, CA) with a mass selective detector (Model HP 5972A MSD with an HP Chemstation data system to collect chromatographic data). The GC was equipped with an electronic pressure control split/splitless injection port and an HP 7673 auto-sampler. The GC column was a DB-5 MS (J&W Scientific, Folsom, CA) fused silica capillary column (0.25 mm internal diameter (ID) x 30 meters (m) length, 0.25 µm film thickness). Helium was used as the carrier gas and the GC injection port temperature was 280EC. The GC was temperature-programmed with analysis performed by initially maintaining the GC oven start temperature at 50EC for 2 min, increased at a rate 20EC per minute up to 120EC, and then increased again at a rate of 10EC per minute from 120EC to 320EC. Quantification was performed using a five-point calibration curve.

4.4.2.5 Dichotomous Sampler

Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particle samples were collected at all three sites for 24-h periods on an every third-day schedule using a manual dichotomous sampler (Sierra Model 242, Graseby-Andersen, Smyrna, GA). The dichotomous sampler is a U.S. EPA-approved equivalent method for measuring PM_{10} (U.S. EPA, 1990b); it is capable of separating and collecting particles less than 10 Fm aerodynamic diameter into fine and coarse fractions. Figure 4.4 is a diagram of the dichotomous sampler. $PM_{2.5}$ collected with the dichotomous sampler was analyzed for C_E and C_V; $PM_{2.5-10}$ was analyzed for mass by gravimetry, elemental concentrations by XRF, and inorganic particle chemical composition/morphology by SEM.

The dichotomous sampler consists of an inlet that collects particles of less than 10 µm in aerodynamic diameter and separates them into $PM_{2.5}$ and $PM_{2.5-10}$ fractions. The inlet for this sampler is engineered to prevent passive loading of particulate matter due to wind-blown dust. Dichotomous samplers were located in accordance with 40 U.S. CFR, Part 58 (1988). Once past the inlet, the 10 µm particles are fractionated by means of a virtual impaction method so that $PM_{2.5}$ is collected on one filter and $PM_{2.5-10}$ is collected on the other filter. The flow rate for the dichotomous inlet/separator system is 16.7 L/min with

10% of the flow passing through the coarse particle channel and 90% passing through the fine particle channel. $PM_{2.5}$ was collected on 37 mm quartz-fiber filter media for carbon analysis. The coarse particle fraction was collected on 37 mm polycarbonate filters with 0.4 Fm pore size for mass and constituent element determinations. In the dichotomous sampler, the coarse particle fraction filter normally contains about 10% of the fine particle fraction collected. Thus, these filters were archived and the fine particles on them were analyzed by SEM as well.

4.4.2.6 Carbon Analysis

Air samples collected on quartz-fiber filters using the dichotomous sampler were analyzed for C_E and C_V concentrations (Sunset Laboratory, Forest Grove, OR). An approximate 1.5 cm^2 plug was cut from each quartz-fiber filter for analysis. The carbon analyzer consists of a thermal and an optical system known as Thermal Optical Transmission (TOT). The basic principle of TOT is to heat the filter, progressively, to liberate the carbon species; during combustion, the liberated species are continuously analyzed by a helium-neon laser beam that passes through the filter to monitor filter transmittance.

The sample is placed in the combustion oven of the instrument and heated to 350^{o}C in a 2% oxygen (O_2) - 98% helium (He) atmosphere to remove as much apparent C_V as possible on the filter. As organic compounds are vaporized, they are immediately oxidized to carbon dioxide (CO_2) in a manganese-oxygen bed in the oven. The CO_2 then goes to a methanator oven where it is converted to methane and analyzed by a flame ionization detector (FID); this methane is measured to estimate apparent C_V. The combustion oven is then purged with He to remove O_2.

Transition to higher temperature steps (from 500EC to 700EC) quickly decomposes inorganic carbon; during this phase some organic compounds, sometimes as high as 30%, are pyrolytically converted to C_E. This carbon is called carbon-char; if not corrected, some charred C_V would be incorrectly characterized as C_E. To account for charring, the combustion oven is cooled to 525EC and the 2% O_2/98 % He atmosphere is switched into the combustion oven; this is followed by temperature increments up to 850EC for complete combustion of C_E. In distinguishing C_V from C_E, the point in time on the thermogram readout at which initial filter transmittance occurs is termed as the "split" between C_V and C_E. Carbon before this "split" in time is termed C_V and carbon after the "split" is termed C_E. Based on the FID response and laser transmission data, the amounts of C_V and C_E are calculated and reported in Fg/m^3. C_V concentrations were multiplied by 1.4 to account for unmeasured contributions to aerosol mass of oxygen, hydrogen, and nitrogen of the organic aerosol compounds (U.S. EPA, 1996a). Further details of carbon analysis by TOT are discussed in Birch and Cary (1996) and Birch (1998).

4.4.2.7 Scanning Electron Microscopy (SEM)

$PM_{2.5-10}$ samples collected on polycarbonate filters obtained using the dichotomous sampler were weighed for coarse particulate mass by gravimetry, followed by individual particle chemistry and morphology by Scanning Electron Microscopy (SEM). Computer controlled SEM coupled with energy dispersive x-ray analysis (EDX) was done on selected samples using an R.J. Lee Personal SEM Model PSM-75 (R.J. Lee Group, Monroeville, PA). Both fine and coarse particles were analyzed on the polycarbonate filters since approximately 10% of fine fraction particulate matter collected with the dichotomous sampler deposits on the coarse fraction filter. Hopke and Casuccio (1991) provide further details on SEM as a tool for characterizing aerosol for source apportionment.

For each sample, a predetermined number of particles were characterized in both the coarse and fine size fraction by SEM/EDX. Size, morphology and chemistry data were tabulated for each particle, and then assigned to one of several classes based on these properties. A total of 20 samples were analyzed in this manner.

4.4.2.8 Volatile Organic Compound (VOC) Sampling

Integrated 24-h whole air samples were collected by the U.S. EPA on an every sixth day schedule at Site 2 for VOC analysis using an ambient VOC collection system with time/event control (Graseby, Smyrna, GA). The TNRCC conducted VOC sampling at Site 1 using similar instrumentation (TNRCC, 1986). Unlike inorganic particles, VOCs are present in the atmosphere in the gas phase due to their high vapor pressures; this is the reason that they are collected in whole air samples and not on filter media. VOCs sampled included benzene, a well-known carcinogen. VOC sampling was based on U.S. EPA Compendium Methods TO-14A and TO-15 (Winberry *et al.*, 1988; 1990; McClenny *et al.*, 1991; U.S. EPA, 1997a). Sampling instrumentation and canister samplers were certified to be clean according to these methods. Canisters were cleaned by heating them in an isothermal oven to 100EC to remove the less volatile VOCs from the walls of the canisters. The certified clean collection system consists of a stainless-steel inlet, a stainless-steel air pump to pressurize the sampled air, a mass flow controller that regulates the pressurized air flow, an open/close solenoid valve, and a glass and stainless steel manifold that directs sampled air into a certified clean, 6-liter (L), SUMMA®-polished stainless-steel canister (BRC/Rasmussen, Hillsboro, OR). SUMMA (electro-)polishing is performed on the interior surface of all VOC canisters to prevent VOCs from reacting with the canister interior. Particles are removed by a stainless-steel filter upstream of the flow control devices. Sample flow rate into the canister was controlled at a constant rate by the mass flow controller. The mass flow controller was set so that only a fixed flow rate was possible; flow rate was set at about 8 cubic centimeters/min (cc/min) to fill the 6-L canister to about 200 kPa (2 atmospheres) pressure in 24 hours. Ambient air was collected by a side stream sampling technique from a larger manifold flow to avoid contamination or sample loss from the low flow through the manifold system. All flows were activated/deactivated with an electronic timer system. Actual sampling duration for canister samplers was recorded on an elapsed time meter. In the LRGVESS, this sampling system was called an active canister sampler (Mukerjee*et al.*, 1997a). Figure 4.5 is a diagram of the VOC sampler system used in TAPP.

As previously stated, 6-L canisters were certified clean according to the U.S. EPA Compendium Methods TO-14A and TO-15 cleaning procedure before sampling. An Entech Model 3000 Canister Conditioning System (Entech Instruments, Simi Valley, CA) was used to clean and leak check the canisters. Clean canisters were pressurized with humidified ultra-pure air and analyzed by a gas chromatograph/mass spectrometer system (GC/MS, discussed in Section 4.4.2.9) to certify that target analytes were not above the reporting limits (<0.2 parts per billion by volume, ppbV). The 6-L canisters were then evacuated to about -29.72 in of mercury (vacuum). The sample inlet manifold was conditioned by purging with ambient air at a rate of 150 mL/min for at least 12 h before the onset of canister sampling.

Evacuated canisters were installed for up to several days before the sample collection period. As required under 40 U.S. CFR 136 (1979), canisters were shipped to the analysis laboratory within 7 days after sample collection to avoid sample degradation.

4.4.2.9 VOC Analysis

VOCs analyzed by the U.S. EPA were done using a method based on U.S. EPA Compendium Method TO-14A (Winberry *et al.*, 1988; 1990; McClenny *et al.*, 1991; U.S. EPA, 1997a). A Finnigan INCOS 50XL Gas Chromatograph/Mass Spectrometer (GC/MS) (Finnigan MAT, San Jose, CA) system was used. According to Godish (1997), the basic principal of gas chromatography is that "...molecules are adsorbed on a column of granular packing material. The collected gases are desorbed from the chromatographic column by heating. Because of differences in the strength of adsorption, each gas [is] released at distinct intervals. Gases segregated by their differential desorption rates pass through a detector where the relative concentration of each is determined."

The GC/MS system was operated in the full SCAN mode to scan all ions repeatedly during the GC run; this provided positive compound identification. The GC/MS system was interfaced to an Entech Model 2000 Preconcentrator. The three-stage preconcentrator removed moisture and carbon dioxide to enable measurement of non-polar and polar VOCs at concentration levels as low as 0.05 ppbV. The Entech Model 2000 Preconcentrator was an automated cryogenic (liquid nitrogen cooled) trap equipped with a 16-position auto-sampler manifold. Canisters were connected to the manifold for analysis; leak checks of the connection were done.

Daily, routine tuning and calibration of the GC/MS were done; this was based on U.S. EPA Compendium Method TO-15 (U.S. EPA, 1997a). The QC procedure consisted of: 1) instrument tuning using a 4-bromofluorobenzene instrument performance standard before any samples were analyzed, 2) initial calibration at six concentration levels (0.05, 0.1, 0.5, 1, 5, and 10 ppbV) to determine linearity of GC/MS response for the target compounds, 3) continuing calibration using a laboratory 1 ppbV calibration standard of target compounds at the start of each 12-h period of analysis, 4) a laboratory method blank (cleaned canister pressurized with humidified ultra-pure grade nitrogen) after continuing calibration and before samples were analyzed, 5) a NIST reference standard analyzed in duplicate within a 24-h period to measure analytical precision, and 6) analysis of a laboratory standard/surrogate deuterated standard consisting of five compounds at certified concentrations done with each standard, blank, QC, and field sample to monitor repeatability and stability of the analytical system. If VOCs in a sample were greater than the initial calibration range, an aliquot of the original sample was diluted to get the largest analyte peak within the calibration range and re-analyzed.

The canister sampler was vented to a tee connection from which an aliquot of the air sample (500 mL in volume) was drawn using a mass flow controller and a pump. The air sample was introduced to the first stage of the preconcentrator where sample components were collected in a multi-bed glass bead cryogenic trap (1/8-in nickel tube) and cooled (via controlled-release) during sampling to -150°C with liquid nitrogen. This volume of sample was used so as not to exceed the GC column capacity. After the 500 mL sample volume was cryogenically trapped, the first stage of the preconcentrator was heated rapidly to room temperature and purged at 10 mL/min for 4 min with helium to transfer the trapped VOCs to a second-stage cryogenic trap (1/8-in nickel tube) containing Tenax® TA sorbent (Alltech Associates, Inc., Deerfield, IL) cooled to -10EC with liquid nitrogen. Nearly all of the sample water remaining in the first trap was purged with helium and baked off. The reduced-temperature Tenax trap re-trapped the VOCs but allowed the co-collected carbon dioxide to pass through. The second stage trap was then heated to 180EC and back-flushed with helium to a third stage, fused silica Megabore® (0.53-mm ID) cryofocusing trap (J&W Scientific, Folsom, CA) which was cooled (via controlled-release) to -160EC with liquid nitrogen. After completion of heating and back-flushing the second trap, the Megabore trap was heated very rapidly to above 100EC to facilitate efficient transfer of VOCs onto the GC column. The GC column used to separate volatile components was a DB-1 (J&W Scientific, Folsom, CA) fused silica capillary column (0.32 mm ID x 60 m, 1 µm film thickness).

The GC oven was started at 35EC and held for 5 min, ramped at 6EC/min to 180EC, and then programmed at 7.5EC/min to 225EC. The helium carrier gas flow was set at 1 mL/min. The MS SCAN rate was 0.8 seconds per scan, 29-31 atomic mass units (amu), then 33 to 270 amu.

4.4.2.10 Precipitation Samplers

Pesticide and PAH samples from precipitation were collected on an event basis at Site 2 only, using an MIC Series "C" automated rain sampler manufactured by M.I.C. Company (Richmond Hill, Ontario, Canada). The MIC system is equipped with a rain sensor connected to a lid control assembly. When precipitation is detected, the lid assembly opens and precipitation collection begins. Collection stops when precipitation is not detected. The precipitation is collected by a Teflon-coated, square funnel and drained through an XAD-2 resin cartridge into a polypropylene collection bottle. Further details of the MIC are discussed in Strachan and Huneault (1984) and Franz *et al.* (1991). The SOP called for the XAD-2 cartridges to be replaced after each rain event; if the rain event did not produce an adequate sample (which was always the case) the cartridges would be retained in the sampler and replaced weekly. Cartridges were extracted for pesticide/PAH analysis by GC/MS in the same manner as the quartz/PUF sampling train described in Section 4.4.2.4.

Measurements of metal and inorganic deposition from precipitation were done on an event basis using an automated Aerochem precipitation sampler (Model 301, Aerochem Metrics, Inc., Bushnell, FL). This device is commonly used in acid rain monitoring. While this sampler can collect wet and dry deposition, only wet deposition was measured. A recent review of precipitation research has advocated the need for wet-only precipitation collection in urban areas (Gatz, 1991). Wet-only collection with the Aerochem sampler has been conducted in other studies (Nations and Hallberg, 1992; Vermette *et al.*, 1995). The Aerochem sampler consists of two Teflon-coated containers and a common lid mounted on an aluminum table. Like the MIC system, the Aerochem Metrics sampler has a rain sensor that automates the lid to open only during precipitation events. The lid seals the wet deposition container when there is no precipitation to prevent significant evaporation and dry deposition contamination. When precipitation occurs, the lid moves to the dry deposition container and precipitation collection begins. Precipitation from the wet deposition container was poured into a 2-L collection bottle and subsequently analyzed for trace metals by inductively coupled plasma mass spectrometry (ICP/MS, see Section 4.4.2.11). Additional discussion of the Aerochem Metrics sampler can be found in U.S. EPA (1986) and Vermette *et al.* (1995).

4.4.2.11 Precipitation Analysis

Trace metals in precipitation were analyzed with a Perkin-Elmer Elan 5000 ICP/MS. ICP/MS was used since it can detect total metals in precipitation samples at very low concentrations. This method measures ions produced by the ICP. The ICP introduces the atomic ions entrained in plasma gas into a quadrapole MS via a water-cooled interface. The MS can provide a resolution of at least 1 amu peak width at 10% of the peak height. The elemental and molecular ions produced in the plasma and those ions formed during the introduction of the ion beam into the MS are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier.

XAD-2 cartridges collected with the MIC sampler were analyzed for the same pesticide and PAH species as the quartz filters and PUF cartridges from the DFPSS.

4.4.2.12 Meteorological Measurements

Standard meteorological parameters were measured continuously at each site by a Model 05305 AQ wind monitoring system (R.M. Young Co., Traverse City, MI) which was attached at the top of a 10-m tower. Meteorological parameters measured were scalar-averaged wind speed in meters per second (m/sec), vector-averaged wind speed (m/sec), vector-averaged wind direction (degrees) and its standard deviation (degrees), temperature (EC), and relative humidity (percent). Meteorological measurements were conducted according to standard methods (U.S. EPA, 1995). The meteorological measurements for Site 1 were provided by the TNRCC. Complete meteorological systems were installed and operated at Sites 2 and 3.

The meteorological system consisted of a wind vane to measure wind direction and a propeller to measure wind speed. A magnetic compass adjusted for the published local direction of the magnetic field was used to align the wind vane. Temperature at the mast was monitored with a Rotronics MP-100 1000-S temperature sensor. The sensor was mounted in a gill-aspirated radiation shield (R.M. Young Model 43408) that was ventilated by a continuous electric fan. Data outputs were collected every second and stored in an on-site computer that were then averaged over 1-minute periods; these 1-minute results were eventually converted to averages compatible with the averaging times for the air pollutant monitoring devices.

Daily averaged values were calculated using the period of midnight to midnight the following day to be compatible with the daily integrated sampling of the other devices. Average wind directions were calculated only for those hours and days where meteorological sensor results having a minimum wind speed of 0.5 m/sec were available for at least 75% of the hours. If this condition was not met, the result was considered calm; this is a standard meteorological measurement practice (U.S. EPA, 1987). The occurrence of calm winds during the monitoring study were rare. It should be noted that **all** air pollution data collected were summarized in tabular form, even if a wind direction could not be adequately calculated.

4.5 Quality Assurance/Quality Control (QA/QC) Program

The primary objective of the quality assurance/quality control (QA/QC) program for this study was to ensure that valid data were collected and to provide the best standards in maintenance and operation of the monitoring stations. To accomplish this objective, a Quality Systems Implementation Plan (QSIP) was developed using U.S. EPA QA guidelines (U.S. EPA, 1980). The QSIP ensured that work plans and operations procedures were developed for all measurement, monitoring, and data reduction activities prior to the initiation of data gathering activities. Aspects of the QSIP are detailed throughout Sections 4.4 and this section. Overall quality of operation was evaluated by routine systems audits, performance audits, and data management system audits. Instrument error was minimized by periodic calibration, proper maintenance, and a consistent sampling methodology. TNRCC also met data quality objectives for their measurements in accordance with these procedures (TNRCC, 1986).

Upon implementation of site operations, routine visits by site operators to the stations occurred on an every third day basis, beginning at approximately 0800 hours, Central Standard Time. Such visits included inspection, maintenance, and cleaning of monitoring equipment, performance of routine operations (e.g., monitor checks, and filter changes), evaluation of equipment status and performance, and shipment of samples, data printouts, data disks, and associated documentation. Non-routine site visits were done in response to equipment malfunctions, data anomalies, or other problems identified by project staff. All site operator duties were prescribed in appropriate Standard Operation Procedures (SOPs).

4.5.1 Automated/Continuous Monitors

TEOM monitors and meteorological equipment were inspected to verify overall system integrity and performance. Current values for flow rates, concentrations, and other critical parameters were recorded and revised for reasonableness. As stated previously, microbalance filters were changed biweekly. Sample inlets were inspected for damage; cables and power cords were inspected for damage, signs of wear and tear, and proper connection.

Acceptance criteria for hourly average concentrations from the TEOM were as follows: 1) microbalance mass verification checks were to be within 2.5% of the manufacturer's program-value specifications, 2) biweekly checks of main (3 L/min) and bypass flows (13.7 L/min) were to be within 5% of preset flow, 3) microbalance filter mass loading checks were to be no greater than 80% of the loading limit set by the manufacturer, 4) microbalance assembly temperature was to be within 1% of setting (40EC), and 5) daily (24-h) averaging from 1-h intervals had to have at least 18 h available data.

Data quality objectives for meteorological measurements were based on the following factors: 1) wind direction was to be accurate to within ± 5E, 2) wind speed to be accurate at ± 0.25 m/sec for wind speeds < 5 m/sec, and ± 5% for wind speeds > 5 m/sec, 3) ambient temperature accuracy was to be within ± 0.5EC, and 4) relative humidity was to be accurate to within ± 5% over the range of 10 to 95%.

Operations of all continuous instruments were reviewed by a data acquisition system (DAS) established at each site. The DAS is a computer-based system that allows site operators and off-site project personnel (in Research Triangle Park [RTP], NC) to view data from all continuous instruments and for off-site queries of data. Each DAS was queried every day automatically for flow and recorded. Site operators checked the date and time of the DAS and reviewed data to ensure correct operation. Stored data were transferred (downloaded) electronically every day. Study coordinators reviewed the status checks and hourly minimum and maximum values from the DAS. If a problem was detected, the field operations supervisor contacted the site operator to pursue corrective action or arrange a non-routine site visit.

Telephone communications between site operator and project personnel in RTP took place regularly. Following every site change-out, site operators reported results, QC sheets, personal observations, and other information contained on the check sheets. If the field operations supervisor detected a problem from inspection of the sheets, corrective action (orders, instructions, etc.) would be issued to the site operator.

4.5.2 Manual/Integrated Samplers

Site operators inspected aerosol sampling systems every third day to verify overall system integrity and performance. During each filter exchange, the operator determined that the mass flow controllers were set at desired flow rates based on the last calibration data. Adjustments to flow controller settings were made before operation to ensure that design flow rates were achieved for each sample event. Flow systems were leak-tested biweekly. Dates, times, elapsed times, initial and final flow rates, and leak and flow checks were recorded on the system's multi-copy sample log sheet. Aerosol filter packs (quartz-fiber and Teflon filters) were changed after every third day of exposure; quartz filter/PUF samples were stored in an on-site refrigerator. Field blank samples (samples taken to the field and returned without use) were sent to the site, returned to the analytical laboratory, and analyzed with each filter shipment. Sample probes were inspected for damage and contamination and repaired and cleaned, if necessary.

Sample filters were packaged in petri dishes and shipped in cushioned shipping containers along with documentation. Filters were retained on-site until the last sample of a biweekly period was removed from each sampler unit. When shipping samples, a chain-of-custody form was completed, that included all of the samples in the shipment, date of shipment, shipping method, sender's name, and any special notes or events relating to those samples. A copy of the chain-of-custody form was kept on-site. Quartz-fiber filter/PUF samples were shipped cold in insulated Thermos containers to appropriate laboratories for analysis. Chain-of-custody forms were copied for site records, and the original returned with the samples.

QA/QC procedures for the dichotomous sampler were followed according to U.S. EPA (1992b) and were verified in the field audit discussed in Section 4.5.3. Collection and analysis of canister samples were according to U.S. EPA Compendium Method TO-14. Finally, quality assurance objectives for the analysis of ambient air pesticides and PAHs were according to U.S. EPA Compendium Method TO-13.

4.5.3 Systems and Performance Audits

Beyond internal and independent audits of field sampling and laboratory analysis procedures previously discussed, all air monitoring sites were audited by the U.S. EPA. In general, the system audit revealed that Contractor personnel were following procedures written in the QSIP. The evaluation audit of mass flow controllers for the TEOM, dichotomous samplers, and DFPSSs were within the required ± 10%.

Temperature and relative humidity sensors were within reasonable values (temperature sensor within 0.5EC and relative humidity probe within ± 10%) of the results obtained from NIST audit instruments. Wind direction, 1 min averages were within a reasonable value of sighting along the wind vane with a pocket transit (approximately 5E at Sites 2 and 3 although buffeting by the wind was substantial). TEOM mass verifications were within ± 2.5% of the manufacturer's program value required by the QSIP and recommended by the manufacturer. SOPs required by the QSIP were not complete and were not final documents. The auditor did not observe any of the SOPs required by the QSIP available at the sites.

The meteorological tower at Site 2 was aligned to magnetic North instead of true North as required by the QSIP. The TNRCC meteorological tower at Site 1 was also aligned to magnetic North.

The Contractor responded to this audit by providing appropriate SOPs at each station and realigning the meteorological tower at Site 2 to true North. The wind direction data was corrected in all files collected prior to realignment based on the EPA audit findings; all other quality assurance objectives for meteorology as stated in U.S. EPA (1995) were followed. Meteorological data for Site 1 was collected by TNRCC and provided to U.S. EPA under an agreement initiated at the beginning of the study. According to TNRCC, wind direction data at Site 1 were corrected to true North before transmission for data analysis. Meteorological data from Site 2 was adjusted to compensate for the 6.5E easterly magnetic declination of Brownsville; only after adjustment to true North was the wind direction data at Sites 1 and 2 used.

An extended drought condition in the Lower Rio Grande Valley, which existed since the beginning of the study, occurred during the U.S. EPA audit. As a result, none of the precipitation samplers were audited by the U.S. EPA.

Table 4.1. Measurements performed at the three Transboundary Air Pollution Project sites.

		Site S))))))))))))))))))))))))))))))))))))Q		
Monitoring Component		1	2	3
Automated (near real-time) Fine Particulate Mass (PM$_{2.5}$) from TEOM[a]	Duration **Frequency**	1-h avg **hourly**	1-h avg **hourly**	1-h avg **hourly**
PM$_{2.5}$ from DFPSS[b] Trace Elements	Samples Analyzed **Frequency**	~365 **daily**	~365 **daily**	~365 **daily**
Pesticides/PAHs[c]	Samples Analyzed	<S))))Q60 for all three sitesS))))Q>		
Dichotomous Sampler Particulate Carbon[d] (PM$_{2.5}$)	Samples Analyzed **Frequency**	~120 **3rd day**	~120 **3rd day**	~120 **3rd day**
Coarse Particulate Mass (PM$_{2.5\text{-}10}$)	Samples Analyzed **Frequency**	~120 **3rd day**	~120 **3rd day**	~120 **3rd day**
Particle Shape & Chemistry Coarse Particulate Mass (PM$_{2.5\text{-}10}$)	Samples Analyzed	<S))))Q20 for all three sitesS))))Q>		
VOCs[e] from 6-L Canister Sampler	Duration **Frequency**	24 h **6th day**[f]	24 h **6th day**	N/M[g]
Precipitation (rain) sampler Metals	Duration	N/M	event	N/M
Pesticides/PAHs	Duration	N/M	event	N/M
Meteorology (Wind Speed, Dir.[h], Temp.[i], Rel. Humidity[j])	Duration **Frequency**	1-h avg[f] **hourly**[k]	1-h avg **hourly**	1-h avg **hourly**

[a] TEOM = Tapered Element Oscillating Microbalance (near real-time monitor)

[b] DFPSS = Dual Fine Particle Sequential Sampler

[c] PAHs = Polycyclic Aromatic Hydrocarbons

[d] Carbon = Elemental Carbon (C_E) and Volatilizable Carbon (C_V, from combustion activities)

[e] VOCs = Volatile Organic Compounds

[f] Measured by Texas Natural Resource Conservation Commission

[g] N/M = No Samples Measured

[h] Dir. = Wind Direction

[i] Temp. = Temperature

[j] Rel. Humidity = Relative Humidity

[k] Only wind direction data provided by TNRCC on hourly basis; Wind speed, Dir., and Temp. provided on 24-h avg along with a 24-h avg Dir.

Table 4.2. Sampling methods for air and precipitation monitoring.

Sampler Type	Operating Flow Rate (L/min)	Collection Media	Parameters Measured	Reference
TEOM®[a]	3[b]	Teflon-coated glass fiber filter	Mass (<2.5 µm, continuous)	Patashnick and Rupprecht, 1991
DFPSS[a]	16.7	Teflon®[c] filter	Mass, trace elements (<2.5 µm)[c]	
		quartz filter, polyurethane foam (PUF)[d]	Semi-volatiles (Pesticides, polycyclic aromatic hydrocarbons [PAHs])[d]	
Dichotomous Sampler	16.7	quartz filter	Elemental & semi-volatile carbon (<2.5 µm)	U.S. EPA, 1990b
		Polycarbonate filter	Mass, trace elements (2.5-10 µm)	
Active canister sampler	0.016	6-L evacuated canister	Volatile organic compounds (VOCs)	U.S.EPA Compendium Methods TO-14[e] and TO-15[f]
MIC Sampler	N/A[e]	XAD-2	Pesticides, PAHs (Precipitation)	Strachan and Huneault, 1984
Aerochem Metrics® sampler	N/A	Teflon® bucket	Metals (Precipitation)	Vermette et al., 1995
Meteorology	N/A	N/A	Wind speed, wind direction, air temp. humidity	U.S. EPA, 1995

[a] Tapered element oscillating microbalance
[b] Flow rate on filter; bypass flow of 13.67 l/min
[c] First channel
[d] Second channel
[e] N/A = not applicable

Table 4.3. Analytical methods for time-integrated monitoring.

Species	Method	Preparation	Reference
$PM_{2.5}$	Gravimetry	24-h conditioning, 24-30°C, 20-45% relative humidity	Chow, 1995; ESE, 1996
Carbon (C_V and C_E)	Thermal-optical Transmittance	Cold storage	Birch and Cary, 1996 Birch, 1998
Trace elements (fine and coarse)	X-ray fluorescence		Dzubay and Stevens 1975; Kellogg 1993; Chow, 1995
Trace metals (precipitation)	ICP-MS[a]		Vermette et al., 1995
Fine particles	Scanning electron microscopy	4x4-mm section of polycarbonate (coarse fraction) filters on 13-mm-diameter carbon planchets	Hopke, 1985; Hopke and Casuccio, 1991; Chow, 1995
Volatile organic compounds (VOCs)	GC/MS/SCAN[b]		U.S. EPA Compendium Methods TO-14A[c,d], TO-15[d]
Pesticides and Polycyclic aromatic hydrocarbons (PAHs) (air)	GC/MS/SIM[e]	Soxhlet-extraction in 10% diethyl ether in hexane for 16-18 h; concentrated to 0.5 mL by Kuderna-Danish apparatus and low nitrogen-assisted evaporation	U.S. EPA Compendium Method TO-13[c]
Pesticides and PAHs (precipitation)	GC/MS/SIM		

[a] Inductively coupled plasma mass spectrometry
[b] GC/MS/SCAN = gas chromatography/mass spectrometry in the SCAN mode
[c] Winberry et al. 1988; 1990
[d] U.S. EPA, 1997a
[e] GC/MS/SIM = gas chromatography/mass spectrometry with selected ion monitoring