

US EPA ARCHIVE DOCUMENT

Section 5 Results And Discussion

5.1 Data Presentation

Air monitoring results for the TAPP are summarized for each air pollutant by site. Overall summaries of the 24-h data for each site are shown in Table 5.1 for $PM_{2.5}$ mass and associated elements, Table 5.2 for $PM_{2.5-10}$ mass and associated elements, Table 5.3 for VOCs (in units of ppbV [Table 5.3a] and $\mu\text{g}/\text{m}^3$ [Table 5.3b]), Table 5.4 for PAHs, and Table 5.5 for pesticides. Although samples for carbon analysis were collected by the dichotomous sampler and not the DFPSS, carbon concentrations were measured in the fine particle ($PM_{2.5}$) mode and are, therefore, summarized with the other fine particulate matter data in Table 5.1. Presentation of the TAPP data includes formats presented in the community report for air pollution data from the LRGVSS. It should be noted that only data above detection limits are summarized in these tables. This results in the minimum, mean, and median values in Tables 5.1 - 5.5 to be higher than if the data below detection were included, as shown in Table 2.1. Summarizations are as follows.

- (1) The number of times the pollutant is detected during analysis is the sample number of detectable values (n).
- (2) The number of times the pollutant is not detected during analysis is the sample number of non-detectable values (ND).
- (3) The minimum value (Min) is the lowest detected concentration for that pollutant.
- (4) The mean (or average) of n detectable concentrations for that pollutant is the sum of detectable values divided by n.
- (5) The median of n detectable concentrations is the value of detectable data that falls in the middle when detectable values are arranged in order of magnitude. In other words, about one-half of the detectable concentrations are less than the median and about one-half of these concentrations are greater than the median. The median is especially useful as a measure of central tendency to avoid the bias introduced by extreme values of the arithmetic mean when n is small or if the data are skewed.
- (6) The maximum value (Max) is the highest detected concentration for that pollutant.

The minimum and maximum values for a given pollutant provide the range of the data. The sum of detectable and non-detectable values are the total number of samples that are analyzed for that pollutant.

The continuous, hourly averaged PM_{2.5} data acquired by the TEOM are summarized in Table 5.6a for each site. The associated meteorological data are also summarized with the TEOM data. The hourly data are also averaged on a 24-h basis and are summarized in Table 5.6b together with 24-h averaged meteorology.

As in the LRGV ESS, the air pollutant data shown in Tables 5.1 to 5.5 for this study were first compared with corresponding health/welfare-based screening levels set by the TNRCC; these health/welfare-based screening levels are known as Effects Screening Levels (ESLs). Mean and median values were compared with an annual ESL; maximum values (based on the highest 24-h measurement) were compared with 24-h ESLs. ESLs are based on data concerning health effects or welfare effects such as odor nuisance potential, vegetation effects, or corrosion effects. Specifically, ESLs are based on current scientific literature, including occupational exposure data, experimental data, and on-line data bases and are set at one-hundredth to one-thousandth of the levels at which adverse effects have been observed. These safety factors are used in ESLs to protect the public, including children and sensitive individuals and to account for long-term exposures. ESLs are to be used for screening purposes and are not ambient air standards; since the Federal Government has established standards for only six air pollutants, the TNRCC has developed ESLs to review airborne chemicals for which there are no standards. If measured airborne levels of a certain constituent do not exceed its respective ESL, adverse health or welfare effects are not expected. If the measured level exceeds the ESL, it does not necessarily mean there is a health or welfare problem, but is an indication that further review is warranted (TNRCC, 1997c). Further review may include additional comparisons or sampling of ambient levels in the environment. It was for this reason that the TAPP data in this report are compared with U.S. EPA and other peer-reviewed air monitoring data bases, not just ESLs, alone. As with all toxicity indicators, ESLs undergo periodic, critical review (see McConnell *et al.*, 1997 as an example) and revision to insure that they are based on current scientific literature. ESLs related to health effects were used in this study. Finally, VOC ESLs are expressed in units of ppbV, only; since presentation of data and ESLs in units of $\mu\text{g}/\text{m}^3$ is a mere conversion from ppbV, this does not change any of the findings.

The TAPP data were also compared with contaminant concentrations from other monitoring studies. For some pollutants, an extensive database exists, whereas for other pollutants, comparative data is not available. The ability to offer interpretation of the levels of air contamination reported in the TAPP, with respect to levels found elsewhere, varies by pollutant. Table 5.7 for fine particulate matter and associated carbon and elements, Table 5.8 for VOCs, Table 5.9 for PAHs, and Table 5.10 for pesticides show such comparative data taken from the literature. Air pollutants shown in these tables were also selected based on availability of comparative data and potential associations with emissions that may be occurring in the Lower Rio Grande Valley.

Finally, concentrations of pollutants in precipitation are shown in Table 5.11 for metals and Table 5.12 for PAHs and pesticides. Due to a drought in the Valley during the TAPP monitoring period, precipitation data were sparse. Thus, all the precipitation results are presented in these tables along with comparison data from the literature.

Tables 5.1 to 5.10 provide a general overview of how air pollutant concentrations in this study compare with ESLs and/or pollutant concentrations reported elsewhere. To provide an indication of the direction from which air pollutant concentrations were coming, meteorological data along with air pollution data collected at each site were used in the development of both bar charts and wind sector plots for selected air pollutants. Bar chart and wind sector plots for air pollutants were developed based on their association with certain emission sources (as indicated in the Emissions column in Tables 5.7 to 5.10). These are shown as Figures 5.7 to 5.23 for elemental concentration data in fine particulate matter, Figures 5.24 to 5.40 for elemental concentration data in coarse particulate matter, and Figures 5.41 to 5.65 for VOCs; each chemical specie is listed in alphabetical order. The bar chart and wind sector plot for a given pollutant collected at a site are shown side-by-side. All three sites' data are shown together on one page for ease of inspection and interpretation. Data in bar charts and wind sector plots are presented from eight wind sectors: North (N, 337.6E to 22.5E), Northeast (NE, 22.6E to 67.5E), East (E, 67.6E to 112.5E), Southeast (SE, 112.6E to 157.5E), South (S, 157.6E to 202.5E), Southwest (SW, 202.6E to 247.5E), West (W, 247.6E to 292.5E), and Northwest (NW, 292.6E to 337.5E). In the bar chart figures, the air pollutant concentration data are averaged according to the sector from which the air pollutant is measured as coming. The number of observations used in developing the average is shown on the top of the respective bar. The overall average is shown as a horizontal line.

For wind sector plots, air pollution data are displayed in a format similar to wind rose plots with the direction from where the pollutant was coming from being plotted based on a 360E circle with 0E (or 360E) indicating North, 90E indicating East, 180E indicating South, and 270E indicating West. The magnitude of each pollutant concentration is proportional to its distance from the origin of the plot. The overall average values of the plotted data, shown as lines in the bar charts, are represented by circles. The dotted lines are the boundaries for the eight wind sectors divided in the same way as explained for the bar charts.

5.2 Overall Results

For the air pollutants detected at the three sites, the vast majority of air pollutants did not indicate high levels of a persistent nature. This suggested that air quality in the Brownsville area of the Valley was good. For all but seven of the over 250 air pollutants measured, the reported levels were below the ESLs (see Tables 5.1 to 5.5). The seven pollutants that exceeded their respective ESLs were: silver (Ag) in $PM_{2.5}$ and the VOCs 2-nitropropane, acrolein, benzene, methanol, methylene chloride, and vinyl acetate. Many of these pollutants (such as methanol, methylene chloride, and vinyl acetate) were also above levels reported in other surveys (Brodzinsky and Singh, 1983; Singh *et al.*, 1985; Shah and Heyerdahl, 1988; Kelly *et al.*, 1993; Kelly *et al.*, 1994). As is true for all air monitoring investigations, sampling and analysis difficulties exist for acrolein and methanol; therefore, caution should be exercised in interpreting these pollutants. Other pollutants, such as chlorine (Cl), iron (Fe), potassium (K), silicon (Si), 2,3-dimethylpentane, 3-methylhexane, 3-methylpentane, cyclohexane, methylcyclohexane, methylcyclopentane, and pentane were also above comparison data (see Tables 5.7, 5.8a, and 5.8b). Most of these elevated pollutants represented maximum values at Site 2.

Four of these seven pollutants had a one-time exceedance over their respective ESL; these were 2-nitropropane, benzene, methylene chloride, and vinyl acetate. According to TNRCC, the concentrations for these pollutants were below levels which would result in acute health effects. In addition, these one-time exceedances indicated that uncertainties due to intrinsic variability in the data may have been a factor in these values. Two pollutants that showed a mean and/or median value above their annual ESL were Ag (detected less than 1% of the time) and acrolein (detected in 50% of the samples). While acrolein was detected in canister samples, the standard monitoring/analysis method for it (U.S. EPA Compendium Method TO-11; Winberry *et al.*, 1988; 1990) was not employed in this study. Sampling and analysis of aldehydes and ketones such as acrolein were not part of this study; thus, monitoring for acrolein using standard methods would need to be explored to confirm exceedances of acrolein. Methanol exceeded the ESL five times though this was not apparent in the mean or median values. Sampling of methanol in air has proven to be extremely difficult due to its chemical reactivity so caution should be exercised in interpreting these values.

Although a mean and/or median value above the annual ESL may be perceived as a high persistent value, the concentrations presented need to be placed in the context of the number of detectable values used to generate the summary data. For example, the mean concentration for Ag at Site 1 was above the annual ESL based on only three detectable concentrations - this out of 256 samples analyzed for Ag. In comparison of a full year's worth of measurements to health-based levels, it is common practice to include measured data at or below detection as half the detection limit. This was how the data above the ESL were shown in Table 2.1 of the Conclusions section. If all samples, including those at or below detection are averaged together, the mean value for Ag at Site 1 (and for other pollutants identified in this study) is below the annual ESL.

Acrolein was the only air pollutant that was usually above its respective ESL at Site 2; again, standard methods for measuring acrolein would be required before confirming these exceedances. Site 1 recorded two of the seven pollutants that exceeded ESLs (Ag and benzene). Site 2 recorded five of the seven exceedances (2-nitropropane, acrolein, methanol, methylene chloride, and vinyl acetate). No air pollutants exceeded ESLs at Site 3. From a pollutant species perspective, elements and VOCs were above the ESL.

5.2.1 Particulate Mass Results

5.2.1.1 Overall Particulate Results

Although daily PM_{2.5} data from the TAPP are not available for direct comparison with the revised National Ambient Air Quality Standard (NAAQS) for PM_{2.5}, the annual average of the daily PM_{2.5} data is an indication of this comparison. Briefly, the revised U.S. EPA NAAQS for PM_{2.5} mass is the three-year average of annual average PM_{2.5}, spatially averaged across an area (not yet defined by the standard). Furthermore, the level of the three-year spatially averaged value should not exceed 15 µg/m³ (U.S. EPA, 1997b; Schaefer *et al.*, 1997; Watson, 1997). Tables 5.6a and 5.6b show that the average of the 24-h TEOM values over the duration of the TAPP was at most 9.30 µg/m³ for the three sites. Likewise, Table 5.7 shows that the average of the DFPSS did not exceed 10.37 µg/m³ at any of the three sites. Thus, the

annual means calculated for the TAPP are not likely in themselves to lead to violations of the proposed U.S. EPA NAAQS for PM_{2.5}.

Similarly for PM₁₀, the revised NAAQS for PM₁₀ is a three-year average of annual average daily PM₁₀ concentration at each monitor. The three-year average of annual average PM₁₀ is not to exceed 50 µg/m³ at each monitor (U.S. EPA, 1997b; Schaefer *et al.*, 1997; Watson, 1997). PM₁₀ values were calculated for the TAPP data by adding the average of PM_{2.5} from the DFPSS (Table 5.7) and the average of PM_{2.5-10} from the dichotomous sampler (Table 5.2). The calculated PM₁₀ values did not exceed 28.88 µg/m³ for any of the three sites (note that direct summation of the daily values leads to an average of 29.96 µg/m³). Thus, the annual means calculated for the TAPP are not likely in themselves to lead to violations of the proposed U.S. EPA NAAQS for PM₁₀.

Air monitoring by TNRCC at Site 1 and San Benito in 1996 did not indicate any exceedance of the previous NAAQS annual or 24-h standards for PM₁₀ (TNRCC, 1998); this was also the case for previous air monitoring data in Cameron County done by TNRCC (TNRCC, 1996a; TNRCC, 1996b; TNRCC, 1997b). A recent review of the revised PM_{2.5} and PM₁₀ standards (EM, 1997) did not indicate Cameron County, TX, to be out of compliance with the revised NAAQS using 1993-1995 ambient air data; this conclusion was independently verified using 1994-1996 and 1995-1997 data. In addition, a report by the U.S.-Mexico Border XXI Program did not indicate Brownsville, Texas or Matamoros, Mexico as exceeding or potentially exceeding ambient air quality standards of the respective country using ambient data before 1996 (U.S. EPA, 1998).

As previously stated, monitoring systems to determine whether an area is out of compliance for PM_{2.5} must follow the Federal Reference Method (FRM) to collect PM_{2.5} (U.S. EPA, 1997c). FRM guidelines for measuring PM_{2.5} were developed after completion of the TAPP. Accordingly, PM_{2.5} collected in this study cannot be used for compliance purposes. However, the PM_{2.5} data collected is comparable to FRM PM_{2.5} data.

PM_{2.5} was comparable to or lower than in previous air monitoring surveys done in the central region of the U.S., where Brownsville is located (U.S. EPA, 1996a). PM_{2.5} was also lower when compared with other air monitoring surveys (see Table 5.7). This was a possible indication that, overall, anthropogenic sources were minor contributors to PM_{2.5}.

The highest levels of one-hour PM_{2.5} from the TEOMs at the three site network came from the South or Southeast. Figure 5.1 shows the bar charts and wind sector plots for PM_{2.5} at the three sites. Development of these bar charts and wind sector plots are the same as discussed for Figures 5.7 to 5.64. These higher PM_{2.5} levels from the South or Southeast may have been due to emission influences from Mexico (see the starred values in Figure 5.1 wind sector plots). Another probable reason was the fact that there was a greater chance for elevated particulate matter levels to come from these directions. Winds from the East, Southeast, and South represented approximately 50 percent of the one-hour winds during the monitoring period. Examination of PM_{2.5} on a 24-h basis measured by the DFPSS revealed highest levels to be coming from the Southeast since approximately 50 percent of 24-h averaged winds came from

that direction (Figure 5.2). Previous meteorological assessments of circulation patterns in the U.S.-Mexican border region show winds to be primarily coming from the South-Southeast and East in the Lower Rio Grande Valley (Comrie, 1996). In addition, these wind patterns tend to follow the local orientation of the Valley, which parallels the general southeast flow of the Rio Grande River towards the Gulf (Mejía-Velázquez *et al.* and Meuzelaar *et al.*, 1997). Winds from the West and Southwest, the direction where upwind sources near the sites may be located, occurred less than ten percent of the time.

5.2.1.2 Hourly and Daily Averaged Real-Time PM_{2.5} Data to Assess Episodic Events

As stated in Section 4.4.1, hourly-averaged PM_{2.5} data from the TEOM was used to assess episodic particulate pollution events. The top half of Figures 5.3a to 5.3k (Site 1), 5.4a to 5.4l (Site 2), and 5.5a to 5.5o (Site 3) shows time series plots of hourly PM_{2.5} concentration from the TEOM on a monthly basis; starred values indicate PM_{2.5} data above 100 µg/m³. The bottom half of these figures shows wind direction (shown as a dashed line) and relative humidity (shown as a solid line). Meteorological data were recorded at Site 1 by the TNRCC and only wind direction data were used. Relative humidity is also shown since it can affect hourly TEOM results. Observations recorded by site operators are presented in the following discussion and should be used with the hourly TEOM data to interpret potential episodic events.

Overall, all three sites showed similar PM_{2.5} fluctuations and patterns from an hourly perspective, indicating that regional influences dominated the Valley. Most of the regional influences affecting particulate mass loadings were due to naturally occurring events such as strong sea breeze winds (see around April 20, 1996 [4/20/96] at Sites 1 and 2), rain events (see August 8, 1996 [8/8/96] at all sites), and cold temperatures (see from December 18, 1996 to January 15, 1996 [12/18/96 - 1/15/96] at all sites).

A strong regional influence that affected the sites occurred around August 2, 1996 (8/2/96) with the highest hourly and daily PM_{2.5} levels from the TEOM at Sites 1 and 2 occurring on and around this day. At Site 1, PM_{2.5} concentrations reached hourly maximum levels of 43.79 µg/m³ and 24-h average levels of 26.07 µg/m³ on 8/2/96. For 24-h averaging times, the U.S. EPA NAAQS for PM_{2.5} is set at 65 µg/m³ based on a three-year average of the 98th percentile of 24-h PM_{2.5} concentrations. Although daily PM_{2.5} from the TAPP cannot be directly compared with the 24-h PM_{2.5} NAAQS, examination of the PM_{2.5} daily values from the TAPP (based on one year of monitoring) suggests that successive years would have to be far higher than 65 µg/m³ for potential violation of the NAAQS to occur.

Hourly PM₁₀ concentrations measured by TNRCC using a beta gauge monitor at Site 1 reached 168 µg/m³ from 1:00 P.M. to 4:00 P.M. Central Standard Time (CST) on 8/2/96. The 24-h average PM₁₀ concentration at Site 1 on this date was 103 µg/m³. For 24-h averaging times, the U.S. EPA NAAQS for PM₁₀ is set at 150 µg/m³ based on a three-year average of the 99th percentile of 24-h PM₁₀ concentrations. Although not directly comparable, successive years would have to experience significant levels above 150 µg/m³ for potential violations of daily PM₁₀ to occur.

At Site 2, hourly PM_{2.5} concentrations on 8/2/96 were 52.30 µg/m³ with the daily average being 27.18 µg/m³. Although not the highest value for Site 3, daily average PM_{2.5} levels on 8/2/96 were elevated

at $20.55 \mu\text{g}/\text{m}^3$. Time lapse images from satellite data acquired by TNRCC showed visible long range Saharan dust plume transport from North Africa to regions of North America, including the Valley, during this period. TNRCC reported elevated levels for particulate matter at other air monitoring stations in South Texas during this time. It has been well documented that Saharan dust plumes that are emitted westward are transported and deposited in the tropical North Atlantic Ocean. Nearly 20% of this transport and deposition in the tropical North Atlantic occur in the Caribbean Sea region (Schütz, 1980; Warneck, 1988). Deposition of Saharan dust plumes in the Caribbean Sea occur most often during summer (Schütz, 1980) which was when the presumed Saharan dust influence occurred in this study. Average mass concentrations of Saharan dust in air have been recorded as high as $80 \mu\text{g}/\text{m}^3$ in the Caribbean Sea region during the summer (Savoie and Prospero, 1977), this being in the range of ambient particulate mass concentrations observed on 8/2/96 in Brownsville. Trajectory analysis revealed Northwest transport of winds from the Caribbean Sea to the Gulf of Mexico and the Brownsville/Matamoros vicinity during this period.

While it is conceivable that the elevated $\text{PM}_{2.5}$ levels previously discussed may be attributable to Saharan dust transport, further analysis would be needed to provide definitive proof that such an occurrence existed. Recent studies of $\text{PM}_{2.5}$ have shown a calculated soil dust concentration (using crustal elements, see Malm *et al.*, 1994) with a value $\$ 3 \mu\text{g}/\text{m}^3$ and a characteristic Al/Ca ratio $\$ 3.8$ to suggest Saharan dust transport to the eastern U.S. (Perry *et al.*, 1997). Using these indicators, a Saharan dust influence was not detected on 8/2/96. It is worth noting, however, that satellite data revealed a Saharan plume influence in Brownsville from 6/28/96 to 7/1/96 that was also confirmed in the calculated soil and Al/Ca ratios for that period.

Local emission impacts were minimal at the three sites, most of them being burning activities that occurred in the immediate vicinity of the sites. One notable burning activity was at Site 3 on August 14, 1996 (8/14/96). A trash and scrap tire fire occurred approximately 50 meters southeast of Site 3 during this time. $\text{PM}_{2.5}$ concentrations from the TEOM on this day (a daily concentration of $42.4 \mu\text{g}/\text{m}^3$ and maximum hourly concentration of $894.69 \mu\text{g}/\text{m}^3$ between 4:00 P.M. and 5:00 P.M. CST) were higher than any other day of monitoring at this site. As will be discussed later, PAH levels for this day indicated a scrap tire fire influence. Another fire event, occurring near the Rio Grande River area on 8/1/96, may have affected $\text{PM}_{2.5}$ concentrations at Site 2. The $\text{PM}_{2.5}$ concentration at Site 2 (daily average of $16.91 \mu\text{g}/\text{m}^3$) was slightly higher than Site 1 (daily average of $14.89 \mu\text{g}/\text{m}^3$) and Site 3 (daily average of $11.49 \mu\text{g}/\text{m}^3$). Other noted local events, such as a fire works display in Brownsville on June 29, 1996 (6/29/96) and field burning activities in San Benito on March 22, 1996 (3/22/96) did not result in noticeable, site-specific changes in hourly $\text{PM}_{2.5}$ data.

While hourly-averaged $\text{PM}_{2.5}$ concentrations revealed unique episode events, examination of TEOM data from a diurnal average perspective revealed a more dominant influence. Figure 5.6 is the diurnal-averaged fine particulate data from the TEOM at each site for the full year of monitoring. A diurnal pattern was revealed at all three sites with maximum $\text{PM}_{2.5}$ levels occurring during morning periods (7:00 A.M. to 8:00 A.M., CST) and evening periods (8:00 P.M. to 10:00 P.M., CST) of the day and slight dips occurring in early morning and mid-afternoon. Mejía-Velázquez *et al.* and Meuzelaar *et al.* (1997) found

this diurnal pattern for $PM_{2.5}$ at the Brownsville/Matamoros Gateway International Bridge. Examination of carbon monoxide (CO) data, measured by TNRCC at Site 1, revealed similar coincidence of peaks. In North America, CO emissions are dominated by mobile sources (Godish, 1997). The diurnal patterns encountered were probably attributable to three factors: 1) rush hour and/or bridge traffic emitting particulate matter from exhausts and stirring-up road dusts, 2) wind speeds increasing during the morning and late afternoon/early evening periods, and 3) a decrease in height of the inversion layer of the atmosphere in the evening-to-morning periods. This pattern was most dramatic at Site 2, which was downwind of central Brownsville/Matamoros and the Gateway International Bridge where most of the urban traffic was expected. Despite being considered a rural site, Site 3 also revealed this pattern; this was likely due to factors 2 and 3 mentioned above and, possibly, bridge traffic on the Free Trade Bridge at Los Indios.

5.2.1.3 Carbon Results

Elemental and volatilizable carbon (C_E and C_V , respectively; see Table 5.7) amounted, on average, to no more than 8% of fine particulate mass. This suggests that combustion sources were minor contributors to $PM_{2.5}$ mass; this observation is consistent with other assessments of particulate matter results discussed below. Previous studies have shown total carbon contributions to be approximately 4% of fine particulate mass in rural areas (Tuncel *et al.*, 1985; Vossler *et al.*, 1989) and approximately 14%-70% of fine particulate mass in urban locations (Dzubay *et al.*, 1988; Lewis *et al.*, 1986; Purdue *et al.*, 1997; Shreffler and Suggs, 1997). The Houston fine particulate data shown in Table 5.7 indicated carbon contributions as high as 19%.

The minimum value, mean value, and maximum value concentrations of C_V suggest regional background levels influenced by marine aerosol since organic carbon (contained in C_V) associated with marine aerosols in the Caribbean/tropical North Atlantic region ranges from 150 to 930 ng/m^3 (Warneck, 1988). On average, C_V comprised 74% of total carbon, consistent with previous assumptions and assessments of carbonaceous content in aerosols (Shah *et al.*, 1984; Hamilton and Mansfield, 1991). It had been assumed that total carbon would have been a larger fraction of fine particulate mass since transportation sources such as diesel vehicles and paved road dust can be significant sources of C_E and C_V , respectively (Hildemann *et al.*, 1991), particularly in the Western U.S. including Texas (Dickson *et al.*, 1997). In addition, it was thought that carbon would possibly be an indicator of home heating since many U.S.-Mexican border community residents heat their homes at night with wood- or refuse-burning stoves that emit carbonaceous material, particulate matter, and other toxic air pollutants (U.S. EPA, 1992a).

5.2.1.4 X-ray Fluorescence (XRF) Elemental Analysis Results

At Site 1, a single Ag air measurement in $PM_{2.5}$ exceeded the 24-h ESL (see Table 5.1). Silver was the only contaminant in fine particulate matter that exceeded the ESL. Silver was detected in less than 1% of all samples at Site 1; this suggests that this exceedance was incidental in nature.

The nearby Gulf of Mexico had a pronounced effect, both on meteorology and particle-bound air pollutants measured at all three sites. Climatological assessments of meteorological data recorded over several years have shown the Cameron County area of the Lower Rio Grande Valley to be more influenced by ocean effects than most other coastal areas of the U.S.; this region of the Valley also has the highest ocean climatological influences in the Texas Gulf coast (Jehn, 1977). Average total chlorine (Cl) and total sodium (Na) concentrations in particulate matter were generally higher in comparison to other regions of Texas or the other areas of the U.S. (Davis *et al.*, 1984; U.S. EPA, 1996a) which is indicative of the marine influence from Gulf of Mexico sea breeze winds. This observation was confirmed in earlier findings in the Valley (Ellenson *et al.*, 1997). Maximum Cl concentrations in particulate matter samples occurred when winds were from the East and Southeast (see Figures 5.12 and 5.29), these being directions of Gulf winds.

Wind speeds at the three sites averaged 3.9 meters per second (m/s) with maximum values reaching nearly 10 m/s, which are considered to be strong gusts. Strong coastal winds and semiarid conditions in the Valley (Crescenti, 1997) as well as surface emissions were found to occur during the study. Surface emissions common to Texas are agricultural field burning and tillage operations, vehicular traffic on paved and unpaved roads, and construction activities (Evans and Cooper, 1980; Warneck, 1988). Together, these conditions facilitated the breakup and resuspension of soil-derived aggregates and released plant (vegetation) material into windblown dusts. As previously encountered in Brownsville (Ellenson *et al.*, 1997), this study revealed $PM_{2.5-10}$ and $PM_{2.5}$ to be enriched in minerals of soil-derived (crustal) origin such as aluminum (Al), calcium (Ca), iron (Fe), potassium (K), silicon (Si), and titanium (Ti) (see Tables 5.1 and 5.2). Calcium is a predominant element in suspended particulate matter for this region of Texas (Rhodes *et al.*, 1972). These crustal pollutant species were also higher in concentration compared with other studies (see Table 5.7). This may explain the fact that $PM_{2.5-10}$ concentrations were generally higher than previously observed in the Western U.S. (Cahill *et al.*, 1981). $PM_{2.5}$ concentrations were, on average, similar to levels reported by Cahill *et al.* (1981). The dominance of a sea salt and mineral component in ambient air particles was expected since such emissions dominate global production rates of total particulate matter and $PM_{2.5}$ (Warneck, 1988). In addition, agricultural activities, strong winds blowing over arid soils, and vehicular traffic over unpaved roads have been found to contribute to high particulate concentrations in the U.S.-Mexican border region (U.S. EPA, 1992a).

While sea breeze winds were found to occur in the Valley, such influences decayed with distance from the Gulf shore line. This is evident in Al, Ca, Cl, Fe, K, Si, and Ti content of $PM_{2.5}$ (see Figures 5.8, 5.11, 5.12, 5.13, 5.14, 5.20, and 5.21) and these same elements in $PM_{2.5-10}$ (see Figures 5.25, 5.28, 5.29, 5.30, 5.31, 5.37, and 5.38). Examination of these wind sector plots revealed that the sea salt and aeolian dust components decreased from Site 1 (closest to the Gulf) to Site 3 (farthest from the Gulf). While sea breeze winds seemed to decrease further inland, overall wind direction patterns were still largely dominated by east and southeast winds from the Gulf. It should also be noted that the location of Site 3, in a mainly rural setting and farthest West of Sites 1 and 2 may have also resulted in particulate pollutant levels to decrease significantly at this site in comparison to Sites 1 and 2.

As encountered in other studies (U.S. EPA, 1996a), sulfur (S) was the dominant element in $PM_{2.5}$ (see Table 5.1). Average S concentrations in $PM_{2.5}$ were comparable to levels found elsewhere in Texas (Davis *et al.*, 1984; Table 5.7). Average S concentrations in $PM_{2.5-10}$ were higher than other Texas locations yet comparable to other areas of the U.S. (U.S. EPA, 1996a). Since S can come from man-made (anthropogenic) or natural (biogenic) sources, an assessment to determine S source(s) near the sites was done.

Particulate S in ambient air primarily exists as sulfate. Gaseous sulfur oxides such as sulfur dioxide (SO_2), emitted from sources like fossil fuel combustion and some natural sources, can oxidize in the atmosphere to form particulate sulfate. Sulfur can be emitted from automobiles (Watson *et al.*, 1994) since it is contained in gasoline. Other processes that burn fossil fuels, such as coal and petroleum, are dominant anthropogenic sources of SO_2 (Cullis and Hirschler, 1980). A large carbo-electric facility in Northeastern Mexico near the border of Eagle Pass, Texas was determined to be one of the largest emitters of SO_2 in the Western U.S./Northern Mexico region based on emissions data as of 1990 (Dickson *et al.*, 1997).

To assess coal burning influences at the sites, a ratio of sulfur to selenium (S:Se) in particulate matter was used to determine the distance of these possible sources. In rural areas of the Midwestern U.S. not immediately influenced by coal burning sources, it has been observed that fine particulate S:Se ratios range from 2000 to 3500; however, at sites in the Midwestern and Eastern U.S. that are close to such sources, this ratio drops to about 1000 or less (Tuncel *et al.*, 1985; Vossler *et al.*, 1989). Fine particulate S:Se ratios at Site 1 (1162 ± 172), Site 2 (1065 ± 192), and Site 3 (977 ± 105) could be initially interpreted as suggesting a possible coal burning influence, particularly at Site 3. In an examination of wind sector plots, Se concentrations in $PM_{2.5}$ were almost constant among the three sites (Figure 5.19); with no known local sources in the area that emit Se this could have also indicated coal burning influences. While this influence may be present, it should also be realized that Se was detected in less than 10% of the samples used to develop S:Se ratios whereas S was almost always detected. With prevailing winds from the Southeast, the ability to assess emissions from the carbo-electric facility near Eagle Pass were limited since winds would have had to come from the Northwest. Therefore, definitive identification of coal burning influences was not possible.

As a further assessment of coal burning influences, elemental calcium (Ca) to magnesium (Mg) ratios have been used to assess coal fly ash influences from the coal burning sources. Calcium-magnesium ratios of 14 ± 8 have been indicative of coals mined in the Western U.S. (Parekh and Husain, 1987). The Ca:Mg ratios for $PM_{2.5}$ at Site 1 (4.1 ± 0.4), Site 2 (2.2 ± 1), and Site 3 (2.7 ± 0.2) were lower, indicating dominance of crust-like sources. Another elemental ratio indicative of potential coal burning sources in the Valley using Midwestern U.S. coal is a Fe:Mg ratio of 53 ± 40 (Parekh and Husain, 1987). Iron-magnesium ratios for $PM_{2.5}$ at Site 1 (1.4 ± 0.1), Site 2 (2.2 ± 0.1), and Site 3 (2.4 ± 0.1) also suggested mainly crustal influences as opposed to coal burning influences. It is conceivable that some Mg measured came from other sources, thereby affecting Ca:Mg and Fe:Mg ratios. Water-soluble Mg has been found over Caribbean waters to come from sea salt aerosols (Savioe and Prospero, 1980).

Finally, it was thought that perhaps S (and Ca) may have also been associated with calcium sulfate dust emissions from a large byproduct pile near the Rio Grande River in Matamoros. Site 2 was across the River from this byproduct pile in a North-Northeast direction; the calcium sulfate byproduct pile was produced by a major hydrofluoric acid processing plant in Matamoros (Dwyer, 1994). Calcium sulfate is also commonly called gypsum. Elemental analysis of a sample of the calcium sulfate byproduct acquired from another field investigation (Lorenz, 1998) confirmed the dominance of S and Ca; no traces of fluorine were evident. Examination of the wind sector plots for coarse calcium (Figure 5.28) and coarse sulfur (Figure 5.35) at Site 2 did not indicate elevated patterns of these two elements coming from the South-Southwest. Winds kicking up any of the byproduct pile material would produce particulate matter in the $PM_{2.5-10}$ fraction rather than $PM_{2.5}$; nevertheless, examination of fine Ca (Figure 5.11) and fine S (Figure 5.18) also did not provide definitive evidence of the pile's influence at Site 2.

A possible source for the S observed was biogenic. Phytoplanktonic algae in ocean bodies such as the Gulf of Mexico emit dimethylsulfide (DMS) gas as a metabolic by-product. DMS undergoes oxidation in the atmosphere to form non-sea-salt sulfate aerosols that coalesce into cloud-condensation nuclei. Precipitation from clouds removes this sulfate and can result in the deposition of particulate sulfate (Charlson *et al.*, 1987). Parungo *et al.* (1990) reported that a significant source of atmospheric S from the Gulf of Mexico is DMS flux from the sea into the atmosphere. DMS emissions into the atmosphere are converted to SO_2 and major organic sulfide products are methanesulfonic acid (MSA) and formaldehyde (Warneck, 1988). MSA has been found in the Gulf of Mexico (Saltzman *et al.*, 1983); it along with DMS are sources for non-sea salt sulfate from marine environments (Saltzman *et al.*, 1983; Charlson *et al.*, 1987). Scanning electron microscopy (SEM) analyses of aerosol samples indicate that S emissions from oceans can be found as submicron-sized ammonium sulfate (Mészáros and Vissy, 1974). Ammonium sulfate is a common form of fine particulate sulfur. Soils, shallow coastal waters (such as the Laguna Madre), and coastal wetlands east of Brownsville contain microbes that degrade organic material; this degradation process emits hydrogen sulfide gas (H_2S) and can also contribute a small amount to the total sulfur budget (Charlson *et al.*, 1987). Elevated sulfur concentrations in $PM_{2.5-10}$ were found to occur from the Northeast (Figure 5.35), this being the upwind location of the Cameron County coastal wet lands. While anthropogenic releases of S did not appear to be a dominant factor, a combination of biogenic and anthropogenic sources were probably contributing to the particulate sulfates measured in Brownsville.

It was assumed that lead (Pb) and bromine (Br) would suggest use of leaded gasoline fuel from Mexico. Lead and Br are well-known emission tracers for automobiles that use leaded fuel (Hopke, 1985). Although leaded gasoline is sold in limited quantities in Brownsville's sister city of Matamoros, Mexico, it is not sold in many other parts of Northern Mexico and is expected to disappear from the Mexican market within the next two years (Mejia-Velazquez and Rodriguez-Gallegos, 1997). Mexico has also been reducing the lead content in leaded fuel in recent years (Driscoll *et al.*, 1992). Nevertheless, Pb and Br measurements were used to provide an indication of transboundary transport of mobile source pollutants.

Lead and Br concentrations in this study were lower than in other field studies (see Table 5.7 and U.S. EPA (1996a)); this may have suggested reduced leaded fuel consumption in Matamoros. In fact, Pb

concentrations in cities in the 1970's and early 1980's (when leaded fuel cars were still prevalent in the U.S.) were typically 1,000 ng/m³ (Ondov *et al.*, 1982). Average Pb values in this study for PM_{2.5} and PM_{2.5-10} were less than 5 ng/m³; the maximum particle-bound Pb value was in PM_{2.5} at Site 1 (16.1 µg/m³). These concentrations were typical of ambient Pb levels in urban areas of the U.S. during this decade (U.S. EPA, 1996a). Previous research has indicated that fresh, leaded, automotive exhaust emits a persistent Br:Pb mass ratio of approximately 0.386 which is known as the ethyl ratio (Sturges and Harrison, 1986a). In this study, Br:Pb ratios in PM_{2.5} at Site 1 (0.953 ± 0.064), Site 2 (0.982 ± 0.059), and Site 3 (1.116 ± 0.07) were higher than the ethyl ratio. These higher ratios were probably indicative of secondary sea salt influences from the Gulf of Mexico sea breezes since Br is also naturally emitted from the sea (Sturges and Harrison, 1986b), and also the reduced use of leaded fuels.

5.2.1.5 Particle Chemistry and Morphology by SEM

SEM analyses of fine and coarse particles in selected samples confirmed the dominance of crustal and marine influences. Samples were chosen at each of the three sites based on wind direction and/or pollution episodes. Figure 5.66 shows representative photomicrographs and X-ray element spectra of particles dominated by alumino-silicate minerals indicating a crustal influence. Alumino-silicates represented at least 50 percent of all particles examined by SEM. Other particles also contained Na, magnesium (Mg), K, Ca, and/or Fe (Figure 5.67) while others showed particles containing Na, Mg, Cl, K, and S (Figure 5.68); these elements can be found in oceans, sea salts and/or soils. This provided further evidence of a dominance of crustal influences and secondary marine influences in Valley air.

Particles were also examined to determine if they displayed a smooth, rounded morphology and non-crustal chemistry characteristic of combustion sources such as industrial emissions. Of the particles analyzed by SEM, no clear evidence of an industrial influence was found.

5.2.2 VOC Results

Except for particle-bound Ag, the other pollutant species that exceeded ESLs or other comparison data were VOCs. As shown in Table 5.3, VOCs that exceeded ESLs were: 2-nitropropane, acrolein, benzene, methanol, methylene chloride, and vinyl acetate. Some of these pollutants such as methanol, methylene chloride, and vinyl acetate were also above levels reported in other surveys (see Tables 5.8a and 5.8b). As stated previously, acrolein and methanol values should be interpreted with caution due to sampling and analysis difficulties.

Benzene, in particular, was above the 24-h ESL value at Site 1 on one day (15.46 ppbV or 49.39 µg/m³; see Table 5.3). This value exceeded the 24-hour ESL (4 ppb) by 3.75 times. According to TNRCC, this measured benzene concentration was well below levels which have been reported to cause acute effects such as irritation. As shown in Table 5.8a, benzene is a ubiquitous VOC that is predominant in automotive, solvent, petroleum, and waste water emissions; it is also a well-known carcinogen that causes leukemia (ATSDR, 1997). Previous assessments of Brownsville air quality revealed 24-h benzene levels as high as 49 µg/m³ (Aponte-Pons and Miller, 1994), which was also the highest value at Site 1 (and for this study); higher levels of benzene in ambient air have been reported elsewhere (see Table 5.8a and IARC, 1982). Since Site 1 was in the central Brownsville/Matamoros area, where anthropogenic

emissions are predominant, this exceedance for benzene was not unexpected. The highest benzene concentration at Site 1 that resulted in the exceedance of the ESL came from the North (see Figure 5.49). Thus, it is possible that this emission came from the Armory, University of Texas/Brownsville campus, urban traffic, or another anthropogenic source in central Brownsville. It is interesting that the highest benzene concentration at Site 2, although below the ESL, also came from the North and may have been from automotive traffic on Military Highway 281. The fact that both sites had their highest benzene levels coming from the North suggests that emissions for benzene were from the immediate Brownsville vicinity. It is also conceivable that transboundary transport of benzene from the U.S. to Mexico may have occurred. Further examination of the benzene levels at Site 1 indicated that some benzene concentrations above the overall average came from the South, Southeast, and Northwest (see Figure 5.49). This may have been due to emissions associated with anthropogenic activities in Mexico and/or Brownsville. Urban traffic in Matamoros, South and Southeast of Site 1, and cross-border traffic on the Gateway International Bridge are probable sources; long lines of idling automobiles at the border crossing areas in the U.S.-Mexican border region are known to cause air pollution problems (U.S. EPA, 1992a). However, as with particulate matter, the predominant sea breeze winds from the Southeast enabled a greater chance that elevated VOC levels would come from that direction. Further monitoring, including the acquisition of emissions inventories and tailpipe emissions data from both sides of the border, is needed to determine whether these exceedances are of a sustained nature and, if so, what are the possible sources of those pollutants.

Other VOC emissions above ESLs were encountered at Site 2; this was also almost always the case in comparison of VOCs with other data in Tables 5.8a and 5.8b. One VOC, methanol, is a ubiquitous VOC found in automotive, petroleum storage, solvent, plastics combustion, refuse combustion, printing, and forest fire emissions to name a few. Methanol has even been found in biogenic emissions such as animal waste, microbes, and insects (Graedel, 1978). Methanol levels above the ESL were found to come from the South and North (Figure 5.54); however, sampling of this VOC using canisters (in this study) or automated GC systems can result in losses or false positives due to its reactivity. Isoprene is the most abundant volatile hydrocarbon emitted by vegetation; its occurrence in an agricultural region like the Lower Rio Grande Valley is not surprising. Previous research summarized by Warneck (1988) has indicated that the Southern U.S. has the highest emission rates for isoprene. Acrolein is also a ubiquitous VOC that can be found in automotive and diesel emissions, forest fires, lithographic coating, plastics combustion, spray painting, pesticide application and synthetic rubber manufacturing (Graedel, 1978; IARC, 1985a). 2-nitropropane and methylene chloride can be used as solvents (Graedel, 1978; IARC, 1982); however, methylene chloride is also associated with chemical manufacturing, landfill, and foaming agent emissions (Graedel, 1978). The 2-nitropropane level above the ESL was found to come from the North at Site 2 (Figure 5.43). Vinyl acetate is a VOC found in paint, textiles, and other industrial products and also occurs in forest fire emissions (Graedel, 1978; IARC, 1985b). Like most VOCs from industrial process emissions, vinyl acetate is produced in the U.S. and Mexico; although the location is unknown, one particular industrial plant in Mexico is a major worldwide source for vinyl acetate (IARC, 1985b). Industrial, solvent, and chemical-related manufacturing emissions may have been encountered since a small-to-medium maquiladora industrial park in Matamoros was about 5 miles South of Site 2. Elevated methanol and methylene chloride levels came from the South and Southeast, respectively, at Site 2. Methylene chloride is reported to have been used by a maquiladora in Matamoros (Feldstein and Singer,

1997) in the manufacturing of capacitors (Dwyer, 1994). As shown in Table 5.8, methanol can be associated with a myriad of biogenic, transportation, and industrial emissions. Sampling and analysis difficulties of methanol should be taken into account when interpreting this data. It should be noted that a recent assessment of air emissions in Brownsville and Matamoros revealed no measurable levels of VOCs associated with industrial solvents from maquiladora industrial parks. In fact, most of the VOCs measured near these industrial parks were suggestive of automotive traffic going in and out of these industrial parks (Mejía-Velázquez *et al.* and Meuzelaar *et al.*, 1997).

A likely source for many of these VOCs was from an immediate location. A wholesale propane/butane liquified petroleum filling station with two, above-ground, gas storage tanks was approximately 500 feet, East to Southeast of Site 2. This would be the most probable source for methanol, acrolein, and other petroleum- and transportation-related VOCs like benzene and toluene. For both Sites 1 and 2, actual source profiles and additional monitoring would be needed from both sides of the border to ascertain sources for VOCs fully.

Another immediate VOC source was found to influence Site 2. Elevated levels of 1,2,4-trimethylbenzene (Figure 5.41), 2-methylpentane (Figure 5.42), 3-methylhexane (Figure 5.44), 3-methylpentane (Figure 5.45), cyclohexane (Figure 5.50), methanol (Figure 5.54), m,p-xylene (Figure 5.57), n-heptane (Figure 5.59), n-hexane (Figure 5.60), o-xylene (Figure 5.61), and toluene (Figure 5.64) came from the North-Northeast on the same day at Site 2. This may have been associated with evaporation of a gasoline spill near this site combined with contributions from the filling station and other sources. Although the concentrations were below the ESLs, other monitoring data in Tables 5.8a and 5.8b also indicated that concentrations on this day (presented as the maximum value in these tables) were comparatively high. Such a gasoline spill or other event, if major and persistent, could have transboundary air quality implications for air pollution from the U.S. to Mexico.

Despite the lack of source profile data, concentration ratios for certain VOCs were used to assess the potential influence of VOC sources at Sites 1 and 2. The ratio of m,p-xylene to ethylbenzene has been used to assess the extent of chemical reaction of VOC emissions from anthropogenic sources. This ratio has been observed to be a constant 3.5 ± 0.4 in VOC sources, such as automobile exhausts, gasoline and gas vapors, solvents, and industrial process emissions. Decreases in the m,p-xylene:ethylbenzene ratio occur after VOC emissions undergo chemical reaction and deposition (Nelson *et al.*, 1983). In this study, m,p-xylene:ethylbenzene ratios at Site 1 (3.4 ± 0.2) and Site 2 (3.4 ± 0.1) indicated that anthropogenic VOC sources were present in the immediate vicinity. The proximity to Site 1 of nearby bridge traffic and other transportation-related emissions in central Brownsville/Matamoros and the proximity to Site 2 of local traffic, industrial emissions, and the filling station may explain these findings.

Toluene:benzene concentration ratios have also been used to assess the transport distance of automotive-related emissions. As traffic distances increase, this ratio has been found to decrease and approach a value of one (Gelencsér *et al.*, 1997). In this study, the benzene:toluene ratios were 1.62 ± 0.15 at Site 1 and 2.4 ± 0.08 at Site 2 suggesting the proximity of the sites to mobile sources. Local traffic

emissions near Site 1 and traffic emissions confounded by the filling station emissions at Site 2 were possible influences.

The upwind vicinities of the filling station, maquiladoras, and overall urban traffic in Brownsville-Matamoros in relation to Site 2 were probable reasons for the greater occurrence of elevated VOCs at this site versus Site 1 (see Table 5.3). When compared with previous measurements made at Site 1 from 1993 to 1995 (TNRCC, 1997a), many of these VOCs at Site 2 had higher mean and/or maximum values. Some VOCs at Site 2 with higher mean and maximum values included: 2- and 3-methylheptane, 2-methylpentane, 3-methylhexane, cyclohexane, cyclopentane, heptane, hexane, isopentane, methylcyclohexane, nonane, octane, and pentane. Additional monitoring in the vicinity of Site 2 would have to be performed to confirm these higher VOC findings.

Comparison of other VOC database summaries for urban locations such as Houston (in a location away from major sources) and other locations in the U.S. (including Texas) were performed using the U.S. EPA National Ambient VOC Data Base summaries (Brodzinsky and Singh, 1983; Edgerton *et al.*, 1989; Shah and Singh, 1988; Shah and Joseph, 1993; Singh *et al.*, 1985). Other measurements from Columbus, Ohio (Spicer *et al.*, 1996) were also compared. These comparative data are shown in Tables 5.8a and 5.8b with the detected TAPP data. Average pollutant levels for these species were comparable. Certain VOCs such as acetone, cyclohexane, and isobutane were higher at Site 2 than some of this data probably due to the proximity of the filling station and gas tanks. Because most of these VOC database summaries included measurements of less than a 24-h duration, only average values were compared. This is because a maximum VOC value for a 24-h span may be higher than a maximum value for the same species monitored in a shorter time span.

5.2.3 PAH Results

PAHs, overall, were low in comparison to other data sets and all PAHs at the three sites (including maximum values) were below ESLs (see Tables 5.4 and 5.9). Most of the PAHs were only slightly above background levels for rural areas that range from 0.02 to 1.2 ng/m³ (ATSDR, 1995). Phenanthrene had the highest mean and maximum concentration of any semi-volatile compound at Sites 1 and 2 and was the only PAH detected in all samples. Phenanthrene is a PAH commonly found in diesel and non-catalyst automobile exhaust (Rogge *et al.*, 1993; Lowenthal *et al.*, 1994; Khalili *et al.*, 1995); it has even been found in marine emissions. Marine emissions of phenanthrene are from non-combusted petroleum residues and combustion-formed substances that contaminate oceans and are ultimately emitted by them (Marty *et al.*, 1984). In addition to phenanthrene, other PAHs associated with diesel emissions and emissions from automobiles not equipped with catalytic converters include anthracene, fluoranthene, fluorene, naphthalene, and pyrene (Rogge *et al.*, 1993; Lowenthal *et al.*, 1994; Westerholm and Li, 1994). The occurrence of these PAHs at the three sites may have been the result of emissions from these transportation sources. It was expected that the bridge traffic near Site 1 and the downwind location of Site 2 compared with central Brownsville-Matamoros traffic would have resulted in higher PAH levels at these sites but this did not occur.

The only significantly-elevated concentration for PAHs occurred for one sample at Site 3. This sample was chosen due to the occurrence of a scrap tire fire noted in the immediate vicinity (U.S. side) of this site on 8/14/96. Refuse fires are known to occur in the Valley and, as such, this sample was chosen for that purpose. All of the maximum PAH values in Table 5.4 for Site 3 occurred during this incident. These elevated PAHs are known to be emitted from scrap tire fires (Lemieux and Ryan, 1993). As with VOCs, immediate emission sources seemed to influence maximum PAH levels.

5.2.4 Pesticide Results

As shown in Table 5.5, pesticides were sparsely detected in this study and all concentrations were below their respective ESLs. This was also the case for the rural site (Site 3). This was not entirely surprising since the transport and concentration of pesticides can be highly influenced by atmospheric temperature (Burgoyne and Hites, 1993). While pesticide drift can occur due to aerial spraying (Ghassemi *et al.*, 1982), as encountered in the Valley, pesticide concentrations are known to decrease significantly with distance (Graedel, 1978). Aerial spraying applications involve mixing pesticides with water and other inerts to improve performance and reduce drift or atmospheric transport (Plimmer, 1990).

The highest pesticide concentration encountered was that of chlorpyrifos which was higher than comparison values from other studies (see Table 5.10). Although chlorpyrifos is a pesticide occasionally used in the Valley on cotton, sorghum, and corn, its use in agriculture has waned in favor of synthetic pyrethroid insecticides (Norman and Sparks, 1997; Lockamy, 1998). Chlorpyrifos is used largely in home in the Valley, both inside and in outside yards and gardens (Lockamy, 1998).

Malathion, methyl parathion, pendimethalin, and trifluralin are known to be used on cotton. Some of these pesticides are also used on sorghum and sugar cane crops in the Valley (Texas Department of Agriculture, 1988). At the time of this study, these crops were known to be predominantly grown in the Valley.

5.2.5 Precipitation Results

Due to severe drought conditions that occurred in the Valley during the TAPP monitoring period, only a handful of precipitation samples adequate for trace metal and pesticide/PAH analyses could be collected. As a result, caution should be exercised in deriving definitive conclusions from these few data.

For trace metals, a total of five samples was analyzed; these results are presented in their entirety and compared with data from other rainfall surveys in Table 5.11. Elevated trace metal concentrations of Fe revealed the occurrence of wind blown dusts. Elevated levels of Mg and manganese (Mn), with vanadium (V), may have indicated the occurrence of marine rain deposition of sea salt components. These trace metals have been measured and/or calculated as present in marine rain over the Western Atlantic Ocean (Church *et al.*, 1984). Trace metals in precipitation associated with anthropogenic emissions, such as cadmium (Cd), Pb, nickel (Ni), and Zn (Helmers and Schrems, 1995), were at levels similar to other precipitation surveys. In summary, the preliminary results for trace metals in precipitation confirmed earlier findings in particulate matter that indicated a dominance of crustal and marine influences in the Valley atmosphere.

Table 5.12 presents the findings for PAHs and pesticides in precipitation. As found in air, PAH and pesticide data in precipitation was sparse. Phenanthrene levels in precipitation were comparable to other surveys while naphthalene levels were higher; caution should be exercised in coming to definitive conclusions based on two observations in this study. Of the pesticides measured, only carbofuran was found. Carbofuran is an insecticide used in the Valley on sorghum and corn (Texas Department of Agriculture, 1988). It can also be used on sugarcane (Farm Chemicals Handbook, 1996).

5.3 Comparison of Transboundary Study Data with the 1993 Lower Rio Grande Valley Environmental Scoping Study (LRGVES)

Air pollution data collected during the 1993 LRGVES (Ellenson *et al.*, 1997) was compared with the TAPP data; this was done since both studies measured the same pollutant species. Though a short time frame is available for comparison, these data can be compared to assess possible temporal changes that may have occurred in Brownsville from 1993 and 1996. Since Site 1 was in the immediate vicinity where ambient air monitoring was done in the LRGVES (at the University of Texas at Brownsville campus), only these data were used for this comparison. The monitoring period in the LRGVES was short (March 18 - April 9, 1993 in the spring and July 21 - August 3, 1993 in the summer). Accordingly, this period (plus an additional one-week window for beginning and end periods) was used in summarizing air pollution data from the TAPP for comparison.

PM_{2.5} mass and elements (Table 5.13) showed remarkable similarity between the two studies, since the air monitoring devices used to collect particulate matter were different. Again, a strong marine influence from the Gulf of Mexico and soil dust contributions were dominant sources for PM_{2.5} during the LRGVES and the TAPP. This was indicated by the fact that Al, Ca, Cl, Fe, K, and S had higher concentrations than other elements in PM_{2.5}. It is interesting that fine particulate S had similar levels between the two studies. Since predominant winds in both studies were from the Gulf of Mexico, the S monitored was probably the

result of persistent non-sea-salt-sulfate deposition from DMS emissions by phytoplanktonic algae in the Gulf.

For organic pollutants, VOCs also showed similar or lower concentrations in the TAPP as opposed to the LRGVSS (Table 5.14). A major exception was toluene that had a maximum value of $17.4 \mu\text{g}/\text{m}^3$ at Site 1 in the TAPP as opposed to $2.2 \mu\text{g}/\text{m}^3$ in the LRGVSS. Table 5.15 shows the TAPP-LRGVSS results for PAHs. Phenanthrene had the highest PAH concentration in both studies. As stated previously, the elevated phenanthrene levels may have been due to emissions from the Gulf of Mexico and/or diesel emissions.

Differences between the TAPP and the LRGVSS PAH data may be because the LRGVSS PAH data was analyzed for all days due to the short time frames of monitoring whereas only a select number of samples were analyzed for PAHs in the TAPP data. Pesticide results are not presented since no pesticides were detected at Site 1 during the LRGVSS time frame. Since pesticide concentrations at the central site during the LRGVSS were low (Ellenson *et al.*, 1997) and as Site 1 was in an urban setting, this is not surprising.

5.4 Principal Component Analysis (PCA)

The final analysis in this study was to attempt to identify possible local and regional influences that affect air quality in the Valley. This was done using a multivariate statistical technique known as Factor Analysis. Factor Analysis has been used as a screening tool to identify emission source categories and to select independent emission tracers. In Factor Analysis, the purpose is to group air pollutant tracers according to their common variations; each group of common variation is considered a factor or source. The factors are uncorrelated with each other and are ordered in terms of the amount of variability they explain. The first factor represents the maximum amount of variance in the data set with the maximum amount of remaining variance being incorporated into the second factor, and so on. A large proportion of the total variance can be explained by the first few principal factors. As is commonly performed in ambient air studies, a transformation technique known as orthogonal varimax rotation is used to aid in interpretation of the factors. As done in most air pollution studies using Factor Analysis, factors were extracted using principal components; therefore the term Principal Component Analysis (PCA). Factor loadings represent the association of each pollutant to a principal component and are used to help identify that component. High factor loadings on a component (usually greater than 0.5) are used to identify the component (Hopke, 1985). Since a large data set is needed in Factor Analysis approaches like PCA, and since the interest was principally on determining anthropogenic influences, the analysis was performed on the $\text{PM}_{2.5}$ and VOC data sets.

5.4.1 PCA Results for $\text{PM}_{2.5}$

Since PCA requires a large data set, element data were used in the PCA regardless of analytical uncertainty. Even though the numerical value of the concentration data may have been uncertain for extremely low concentrations, the variability in the concentration data was retained. Elements used were tracers for different sources in order to prevent biasing the PCA results in favor of a given source (Lioy *et*

al., 1985) Factors with eigenvalues greater than one were retained for varimax rotation; this resulted in the first five factors being retained.

Table 5.16a presents the varimax-rotated factor loadings of the fine fraction element species at Site 1. The first principal factor accounted for 38% of the variance in the data set (proportion of variation for each factor [prior to varimax rotation] x 100); Factor 1 was dominated by species that were primarily of crustal origin (Al, Ca, Fe, K, Mn, Si, and Ti with high factor loadings >0.5) and sea salt origin (Cl with a high factor loading > 0.5). Principal component analyses of PM_{2.5} near the northern coastal city of Boston have also revealed sources associated with soil dusts and sea salts (Thurston and Spengler, 1985). Previous analyses of fine particles from resuspended road dusts and yard soils in the LRGVSS confirmed that these elements (in Factor 1) were abundant in crustal/salt sources (Mukerjee *et al.*, 1997b). Factor 2, accounting for 15% of data variance, was dominated by species of possible marine influences (Br, and S) and/or crustal origin (intermediate K loading). Factor 3 (accounting for only 9% of variance) had high loadings for Pb and Zn; this may be associated with incineration emissions (Olmez *et al.*, 1988). Factor 4 (accounting for 8% of variance) had high loadings for Ni and V which was associated with oil burning from boilers or power plants (Hopke, 1985; Thurston and Spengler, 1985). Factor 5 was an unknown source of variation (high loading for arsenic [As]; this may have merely been an artifact of the PCA technique.

Tables 5.16b and 5.16c present varimax-rotated factor patterns at Sites 2 and 3, respectively. A similar factor solution as seen at Site 1 was also revealed at Sites 2 and 3. At Site 2, the five factors were interpreted as representing crustal (Factor 1), incineration (Factor 2), marine/crustal influence (Factor 3), boiler or electric utility oil combustion (Factor 4), and possible coal combustion for As and Se (Factor 5). At Site 3, the five factors were interpreted as representing a crustal influence (Factor 1), marine/crustal influence (Factor 2), boiler or electric utility oil burning (Factor 3), incineration (Factor 4), and possible coal combustion for As and Se (Factor 5).

In summary, PCA analysis of PM_{2.5} revealed the dominance of crustal/marine influences in the Valley; this is evident in the first two factors at Sites 1 and 3 explaining most of the variation in the data. Other influences included possible incineration (particularly at Site 2), boiler/electric utility oil combustion, and coal combustion. Actual source profile data from major and other air emission sources in the Valley is needed before definitive assessments can be made.

5.4.2 PCA Results for VOCs

Volatile organic compounds used in the PCA were for those species known to be probable markers for certain emission sources. In order to use a large VOC data set in the PCA, marker species that were below detection were given a value of half the detection limit. As seen in Table 5.17a for Site 1 and Table 5.17b for Site 2, the dominant source for VOCs was a transportation-related source; this would include sources as vehicle exhaust, gasoline, and gasoline evaporation. The dominance of a transportation source category in the Brownsville air shed for VOCs was expected since this was similar to findings in other VOC investigations in urban areas. Both Sites 1 and 2 were near areas where traffic influences occurred. Biogenic emissions in Brownsville were a distant second in overall contribution; this

was also expected since agriculture is an important economic factor in the Valley. As shown in Table 5.17b, some of the principal factors may have been the result of the nearby filling station and possible industrial sources. As with the PM_{2.5} results, actual VOC source profiles would be required before definitive conclusions can be made.

Table 5.1. PM_{2.5} (fine fraction) and constituent element concentrations¹ (in ng/m³) 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).

Species Max (24h)	ESL ² n	ESL ³ n	Site 1					Site 2					Site 3				
			ND	Min	Mean	Median	Max	ND	Min	Mean	Median	Max	n	ND	Min	Mean	Median
PM _{2.5} 21810	262	118	2310	10370	9280	34250	295	85	620	7550	6980	21580	299	81	760	6720	6370
Ag (Silver) 30.1 40	3	377	35.3	39.60	37.70	45.8	0	380	1	379	30.1	30.10	30.10
Al (Aluminum) 355.1 20000	93	287	20.1	283.56	141.30	1264.2	64	316	18.0	124.98	77.80	614.4	77	303	18.3	94.11	64.30
As (Arsenic) 2.7 40	2	378	1.5	1.70	1.70	1.9	6	374	1.0	1.50	1.60	1.8	11	369	0.9	1.45	1.40
Au (Gold) NA	2	378	2.1	2.10	2.10	2.1	0	380	0	380	.	.
Ba (Barium) 76.8 2000	23	357	15.3	23.30	19.90	71.3	17	363	15.2	27.79	19.40	68.0	13	367	15.4	32.49	18.30
Br (Bromine) 8.5 NA	211	169	0.9	3.45	2.90	12.3	249	131	0.7	3.01	2.70	9.5	227	153	0.7	3.08	2.80
Ca (Calcium) 448.0 NA	249	131	15.1	172.71	115.70	1413.3	283	97	8.4	35.53	29.60	186.7	290	90	4.7	36.42	26.70
Cd (Cadmium) 40	0	380	0	380	0	380	.	.	.
Cl (Chlorine) 374.9 NA	215	165	5.1	221.49	131.30	822.9	152	228	5.0	37.30	24.75	166.3	155	225	4.9	33.99	18.00
Co (Cobalt) 0.9 80	0	380	0	380	1	379	0.9	0.90	0.90
Cr (Chromium) 1.8 400	5	375	1.3	1.88	1.60	3.1	2	378	3.2	3.75	3.75	4.3	4	376	0.9	1.15	0.95
Cs (Cesium) 62.1 NA	2	378	9.7	11.95	11.95	14.2	4	376	11.4	12.48	12.20	14.1	6	374	10.9	28.27	13.15
Cu (Copper) 5.2 4000	67	313	0.7	3.04	2.30	12.4	106	274	0.7	2.16	1.65	13.3	82	298	0.7	1.49	1.10
Fe (Iron) 187.8 20000	251	129	6.3	85.23	38.70	751.6	281	99	3.7	31.11	16.70	351.4	290	90	0.9	23.73	13.60
Ga (Gallium) 0	0	380	0	380	1	379	1.6	1.60	1.60

Table 5.2. PM_{2.5-10} (coarse fraction) and constituent element concentrations¹ (in ng/m³) from Dichotomous Sampler. Air pollutants summarized for detected values (for elements at 3 times measurement uncertainty).

Species Median	Max	Site 1			Site 2			Site 3										
		ESL ² n	ESL ³ ND	(24h) (annual)	Mean	Median	Max	n	ND	Mean	Median	Max	n	ND	Mean	Median	Max	n
PM _{2.5-10}	10800	41100	0	102	500	18450	17580	53810	106	0	880	17020	16510	47170	100	1	1010	10410
Ag (Silver)	0	100	0	100	0	100	1	96	5.7	5.70
Al (Aluminum)	55	45	137.5	818.14	579.50	3097.4	51	49	98.5	806.80	568.90	3391.1	51	46	79.1	454.76		
As (Arsenic)	1	99	1.7	1.70	1.70	1.7	0	100	1	96	2.0	2.00		
Au (Gold)	0	100	NA	NA	.	.	.	0	100	0	97	.	.	
Ba (Barium)	51	49	15.0	46.95	30.90	123.5	36	64	15.0	41.93	28.70	103.2	31	66	15.3	50.33		
Br (Bromine)	93	7	1.5	4.04	3.40	9.8	90	10	1.4	4.01	3.85	11.5	78	19	1.5	2.84		
Ca (Calcium)	97	3	43.8	1777.86	1347.80	12615.0	98	2	11.4	1325.17	1183.15	4931.8	95	2	19.8	606.09		
Cd (Cadmium)	0	100	40	10	.	.	.	0	100	0	97	.	.	
Cl (Chlorine)	95	5	9.4	2275.44	2206.80	5546.6	94	6	9.8	2266.56	2036.40	8170.9	90	7	14.3	1019.84		
Co (Cobalt)	0	100	80	20	.	.	.	0	100	0	97	.	.	
Cr (Chromium)	39	61	1.5	2.49	2.40	4.5	40	60	1.5	2.65	2.70	4.2	33	64	1.3	2.46		
Cs (Cesium)	12	88	9.9	48.39	56.90	89.1	11	89	14.3	58.29	56.10	83.7	20	77	11.1	67.15		
Cu (Copper)	24	76	0.7	2.14	1.60	6.7	21	79	0.7	1.42	1.10	3.2	35	62	0.7	1.83		
Fe (Iron)	93.65	549.3	20000	5000	3.1	293.93	212.90	1533.1	99	1	2.5	277.24	216.60	1345.5	94	3	4.1	136.27
Ga (Gallium)	0	100	1.30	1.3	.	.	2	98	1.3	1.30	1.30	1.3	2	95	1.3	1.30		

Site 1 Site 2 Site 3
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Species	Median	Max	ESL ² n (24h)	ESL ³ ND (annual)	Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max	n	ND	Min	Mean
Te (Tellurium)	2	98	8.4	23.10	23.10	37.8	1	99	33.0	33.00	33.00	33.0	33.00	33.0	1	96	42.6	42.60
42.60	42.6	400	100															
Ti (Titanium)	70	30	7.5	38.08	28.45	164.4	77	23	8.9	34.94	25.50	182.8	41	56	9.2	28.83		
24.70	72.5	20000	5000															
V (Vanadium)	5	95	2.8	4.88	4.60	8.2	10	90	3.4	5.16	4.65	7.7	4	93	4.0	4.95		
4.65	6.5	NA	NA															
W (Tungsten)	1	99	4.1	4.10	4.10	4.1	4	96	3.2	3.50	3.55	3.7	5	92	3.0	3.40		
3.40	4.0	20000	5000															
Y (Yttrium)	0	100	0	100	0	97	.	.		
.	.	4000	1000															
Zn (Zinc)	87	13	1.4	4.79	4.10	14.4	93	7	2.1	5.31	4.50	17.2	48	49	1.5	3.95		
2.90	39.2	20000	5000															
Zr (Zirconium)	9	91	2.0	3.21	2.90	5.4	11	89	1.8	3.21	2.70	6.2	1	96	2.0	2.00		
2.00	2.0	20000	5000															

n = number of detects during analysis
 ND = number of non-detects
 Min = minimum or lowest detected value
 Mean = average of n detects
 Median = value of detected data that fall in middle when detected values are arranged in order of magnitude
 Max = maximum or highest detected value
 . = data below detection
 NA = no available ESL data for comparison
¹Measured element concentrations greater than 3 times their analytical uncertainty were used to calculate summary statistics.
²ESL (24h) = Effects Screening Levels (24 h time frame). Developed by the Texas Natural Resource Conservation Commission (TNRCC). The TNRCC ESLs are screening levels and are not ambient air standards. If measured airborne levels of a certain chemical do not exceed the screening level, it is interpreted to mean that adverse health or welfare effects are not expected. If the measured level exceeds the screening level, it does not necessarily mean there is a health or welfare problem, but rather is an indication that further review is warranted (TNRCC, 1997c). Minimum and maximum values can only be compared with 24 h ESLs since they are both based on the same time.
³ESL (annual) = Effects Screening Levels (annual time frame). Developed by the Texas Natural Resource Conservation Commission (TNRCC). The TNRCC ESLs are screening levels and are not ambient air standards. If measured airborne levels of a certain chemical do not exceed the screening level, it is interpreted to mean that adverse health or welfare effects are not expected. If the measured level exceeds the screening level, it does not necessarily mean there is a health or welfare problem, but rather is an indication that further review is warranted (TNRCC, 1997c). Mean and median values can only be compared with annual ESLs since they are both derived from annual data.

Table 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.

VOC (annual)	Site 1							Site 2							ESL ¹ (24 h)
	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean	Med	Max			
1, 1, 1-Tri chl oroethane	56	2	0.05	0.145	0.110	0.49	59	0	0.07	0.112	0.110	0.19	800.00		
200.00															
1, 1, 2, 2-Tetrachl oroethane	NM	NM	NM	NM	NM	NM	0	59	4.00		
1.00															
1, 1, 2-Tri chl oroethane	0	58	0	59	40.00		
10.00															
1, 1-Di chl oroethane	0	58	0	59	400.00		
100.00															
1, 1-Di chl oroethyl ene	1	57	0.01	0.010	0.010	0.01	0	59	4.00		
1.00															
1, 2, 4-Tri chl orobenzene	NM	NM	NM	NM	NM	NM	4	55	0.23	0.498	0.495	0.77	20.00		
5.00															
1, 2, 4-Tri methyl benzene	34	24	0.03	0.214	0.145	0.73	59	0	0.07	0.423	0.280	6.08	100.00		
25.00															
1, 2-Dibromoethane	2	56	0.03	0.100	0.100	0.17	2	57	0.06	0.065	0.065	0.07	0.20		
0.05															
1, 2-Di chl orobenzene	1	0	0.01	0.010	0.010	0.01	1	58	0.08	0.080	0.080	0.08	100.00		
25.00															
1, 2-Di chl oroethane	7	51	0.01	0.066	0.070	0.18	1	58	0.05	0.050	0.050	0.05	4.00		
1.00															
1, 2-Di chl oropropane	0	58	0	59	300.00		
75.00															
1, 3, 5-Tri methyl benzene	28	30	0.01	0.106	0.060	0.65	41	18	0.05	0.181	0.100	2.38	250.00		
25.00															
1, 3-Butadi ene	12	46	0.01	0.113	0.040	0.63	50	9	0.05	0.131	0.110	0.44	20.00		
5.00															
1, 3-Di chl orobenzene	3	0	0.02	0.107	0.050	0.25	2	57	0.05	0.065	0.065	0.08	166.00		
41.50															
1, 4-Di chl orobenzene	7	0	0.01	0.110	0.030	0.64	19	40	0.06	0.127	0.100	0.42	40.00		
10.00															
1, 4-Di oxane	NM	NM	NM	NM	NM	NM	0	59	100.00		
25.00															
1-Butanol	NM	NM	NM	NM	NM	NM	14	45	0.55	1.506	1.415	2.96	100.00		

Site 1 Site 2

ESL ² Compound (annual)	Site 1					Site 2					ESL ¹ (24 h)		
	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean		Med	Max
3-Methyl pentane 100.00	50	8	0.04	0.262	0.160	1.97	47	12	0.10	0.877	0.340	20.80	400.00
4-Methyl-1-Pentane 800.00	3	55	0.01	0.010	0.010	0.01	1	58	0.06	0.060	0.060	0.06	3200.00
Acetone 250.00	NM	NM	NM	NM	NM	NM	58	1	1.48	8.811	3.560	75.30	1000.00
Acetonitrile 20.00	NM	NM	NM	NM	NM	NM	0	59	80.00
Acetophenone 10.00	NM	NM	NM	NM	NM	NM	7	52	0.50	0.690	0.650	1.00	40.00
Acetylene 2500.00	11	0	0.51	1.47	1.38	2.73	NM	NM	NM	NM	NM	NM	10000.00
Acrolein 0.10	NM	NM	NM	NM	NM	NM	19	40	0.51	1.314	1.200	2.99	0.40
Acrylonitrile 2.00	NM	NM	NM	NM	NM	NM	0	59	8.00
alpha-methyl-Styrene 50.00	NM	NM	NM	NM	NM	NM	1	58	0.09	0.090	0.090	0.09	250.00
alpha-pinene NA	3	55	0.01	0.040	0.050	0.06	6	53	0.05	0.065	0.065	0.09	NA
Benzene 1.00	57	1	0.05	0.92	0.26	15.46	59	0	0.16	0.473	0.350	2.86	4.00
Benzonitrile 12.00	NM	NM	NM	NM	NM	NM	0	59	48.00
Benzyl chloride 1.00	NM	NM	NM	NM	NM	NM	0	59	4.00
beta-Pinene NA	3	55	0.01	0.113	0.030	0.30	24	35	0.05	1.169	0.870	4.62	NA
Bromodi chloromethane NA	NM	NM	NM	NM	NM	NM	0	59	NA
Bromoform 0.50	7	0	0.07	0.224	0.180	0.60	0	59	2.00
Bromomethane 1.00	5	53	0.01	0.02	0.01	0.08	3	56	0.05	0.100	0.050	0.20	4.00
Carbon disulfide 1.00	NM	NM	NM	NM	NM	NM	11	48	0.58	0.715	0.710	0.89	4.00
Carbon tetrachloride	55	3	0.01	0.118	0.090	1.27	59	0	0.07	0.095	0.090	0.16	8.00

Site 1 Site 2

ESL ²	Compound (annual)	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean	Med	Max	ESL ¹ (24 h)
		57	1	0.06	1.053	0.450	15.51	54	5	0.75	2.281	1.905	6.00	3200.00
	Isobutane 800.00													
	Isopentane 100.00	57	1	0.42	2.059	1.480	18.22	55	4	0.53	19.352	1.550	165.00	400.00
	Isoprene 14.00	28	30	0.02	0.071	0.050	0.22	23	36	0.05	0.269	0.080	4.05	140.00
	Isopropyl alcohol 400.00	NM	NM	NM	NM	NM	NM	11	48	0.63	1.372	1.030	4.73	1600.00
	Isopropylbenzene 50.00	10	48	0.01	0.028	0.020	0.08	15	44	0.09	0.333	0.300	1.06	200.00
	m,p-Xylene 100.00	52	6	0.01	0.25	0.15	1.48	59	0	0.19	1.125	0.510	20.80	400.00
	Methacrylonitrile 1.00	NM	NM	NM	NM	NM	NM	0	59	4.00
	Methanol 200.00	NM	NM	NM	NM	NM	NM	59	0	1.50	169.228	4.150	2330.00	800.00
	Methyl ethyl ketone 200.00	NM	NM	NM	NM	NM	NM	19	40	0.59	7.038	6.430	26.70	800.00
	Methyl Isobut' ketone 50.00	NM	NM	NM	NM	NM	NM	0	59	200.00
	Methyl methacrylate 50.00	NM	NM	NM	NM	NM	NM	0	59	200.00
	Methyl tert-butyl ether 40.00	NM	NM	NM	NM	NM	NM	0	59	160.00
	Methylcyclohexane 400.00	14	44	0.02	0.304	0.060	3.07	35	24	0.05	1.381	0.080	44.30	1600.00
	Methylcyclopentane 75.00	26	32	0.02	0.222	0.130	1.97	55	4	0.05	0.710	0.140	29.60	300.00
	Methylene chloride 7.50	42	22	0.01	0.082	0.060	0.39	58	1	0.06	1.125	0.140	50.30	30.00
	N-Butane 800.00	NM	NM	NM	NM	NM	NM	59	0	0.45	2.307	1.690	8.32	3200.00
	N-Decane 173.00	19	39	0.01	0.091	0.080	0.31	NM	NM	NM	NM	NM	NM	690.00
	N-Heptane 85.00	15	43	0.01	0.221	0.080	1.72	59	0	0.06	1.118	0.130	56.00	340.00
	N-Hexane	47	11	0.04	0.284	0.180	2.98	59	0	0.10	1.246	0.300	49.30	200.00

n = number of detects during analysis
 ND = number of non-detects
 Min = minimum or lowest detected value
 Mean = average of n detects
 Median = value of detected data that fall in middle when detected values are arranged in order of magnitude
 Max = maximum or highest detected value
 . = data below detection
 NA = no available ESL data for comparison
 NM = not measured

¹ESL (24 h) = Effects Screening Levels (24 h time frame). Developed by the Texas Natural Resource Conservation Commission (TNRCC). The TNRCC ESLs are screening levels and are not ambient air standards. If measured airborne levels of a certain chemical do not exceed the screening level, it is interpreted to mean that adverse health or welfare effects are not expected. If the measured level exceeds the screening level, it does not necessarily mean there is a health or welfare problem, but rather is an indication that further review is warranted (TNRCC, 1997c). Minimum and maximum values can be compared with 24 h ESLs since they are both based on the same time.

²ESL (annual) = Effects Screening Levels (annual time frame). Developed by the Texas Natural Resource Conservation Commission (TNRCC). The TNRCC ESLs are screening levels and are not ambient air standards. If measured airborne levels of a certain chemical do not exceed the screening level, it is interpreted to mean that adverse health or welfare effects are not expected. If the measured level exceeds the screening level, it does not necessarily mean there is a health or welfare problem, but rather is an indication that further review is warranted (TNRCC, 1997c). Mean and median values can be compared with annual ESLs since they are both derived from annual data.

Table 5.3b. Volatile Organic Compounds (VOCs, same data as in Table 5.3a in $\mu\text{g}/\text{m}^3$) 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.

Compound	Site 1						Site 2					
	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean	Med	Max
1, 1, 1-Tri chloroethane	56	2	0.27	0.76	0.60	2.67	59	0	0.38	0.61	0.60	1.04
1, 1, 2, 2-Tetrachl oroethane	NM	NM	NM	NM	NM	NM	0	59
1, 1, 2-Tri chl oroethane	0	58	0	59
1, 1-Di chl oroethane	0	58	0	59
1, 1-Di chl oroethyl ene	1	57	0.04	0.04	0.04	0.04	0	59
1, 2, 4-Tri chl orobenzene	NM	NM	NM	NM	NM	NM	4	55	1.71	3.69	3.67	5.71
1, 2, 4-Tri methyl benzene	34	24	0.15	1.05	0.71	3.59	59	0	0.34	2.08	1.38	29.89
1, 2-Di bromoethane	2	56	0.23	0.77	0.77	1.31	2	57	0.46	0.50	0.50	0.54
1, 2-Di chl orobenzene	1	0	0.06	0.06	0.06	0.06	1	58	0.48	0.48	0.48	0.48
1, 2-Di chl oroethane	7	51	0.04	0.27	0.28	0.73	1	58	0.20	0.20	0.20	0.20
1, 2-Di chl oropropane	0	58	0	59
1, 3, 5-Tri methyl benzene	28	30	0.05	0.52	0.29	3.20	41	18	0.25	0.89	0.49	11.70
1, 3-Butadi ene	12	46	0.02	0.24	0.08	1.39	50	9	0.11	0.29	0.24	0.97
1, 3-Di chl orobenzene	3	0	0.12	0.64	0.30	1.50	2	57	0.30	0.39	0.39	0.48
1, 4-Di chl orobenzene	7	0	0.06	0.66	0.18	3.85	19	40	0.36	0.76	0.60	2.53
1, 4-Di oxane	NM	NM	NM	NM	NM	NM	0	59
1-Butanol	NM	NM	NM	NM	NM	NM	14	45	1.67	4.57	4.29	8.97
1-Butene	57	1	0.21	0.81	0.64	5.30	59	0	0.28	0.83	0.71	2.71
1-Pentene	18	40	0.03	0.40	0.30	1.75	38	21	0.14	0.39	0.27	1.29
2, 2, 4-Tri methyl pentane	40	18	0.05	0.55	0.28	4.34	48	11	0.28	0.95	0.79	2.85
2, 2-Di methyl butane	23	35	0.07	0.41	0.21	1.73	47	12	0.21	1.17	0.74	17.59
2, 3, 4-Tri methyl pentane	18	40	0.05	0.26	0.19	1.12	22	37	0.23	0.54	0.35	3.69
2, 3-Di methyl butane	42	16	0.07	0.52	0.42	2.04	54	5	0.18	1.49	0.35	55.34
2, 3-Di methyl pentane	8	50	0.08	0.41	0.20	1.15	23	36	0.20	1.62	0.33	29.22
2, 4-Di methyl pentane	13	45	0.05	0.30	0.19	1.09	NM	NM	NM	NM	NM	NM
2-chl oro-1, 3-Butadi ene	NM	NM	NM	NM	NM	NM	0	59
2-Chl oropentane	1	57	0.04	0.04	0.04	0.04	NM	NM	NM	NM	NM	NM
2-Hexanone	NM	NM	NM	NM	NM	NM	0	59
2-methyl -1- Pentene	4	54	0.10	0.17	0.14	0.31	23	36	0.17	0.29	0.24	0.59
2-methyl -2- Butene	35	23	0.11	0.42	0.29	2.67	47	12	0.20	0.49	0.37	2.81
2-Methyl heptane	10	48	0.05	0.48	0.21	3.13	31	28	0.23	2.80	0.42	72.88
2-Methyl hexane	23	35	0.04	0.72	0.37	4.92	16	43	0.20	0.98	0.29	10.94
2-Methyl pentane	54	4	0.04	1.52	0.93	12.69	49	10	0.46	4.36	1.73	110.32
2-Ni trop propane	NM	NM	NM	NM	NM	NM	5	54	2.15	9.39	4.81	29.51
3-chl oro-1-Propene	NM	NM	NM	NM	NM	NM	0	59
3-methyl -1- Butene	9	49	0.03	0.21	0.09	0.54	11	48	0.14	0.21	0.17	0.46

Compound	Site 1					Site 2						
	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean	Med	Max
3-Methyl pentane	50	8	0.14	0.92	0.56	6.94	47	12	0.35	3.09	1.20	73.31
4-methyl-1-Pentene	3	55	0.03	0.03	0.03	0.03	1	58	0.21	0.21	0.21	0.21
Acetone	NM	NM	NM	NM	NM	NM	58	1	3.64	21.64	8.74	184.97
Acetonitrile	NM	NM	NM	NM	NM	NM	0	59
Acetophenone	NM	NM	NM	NM	NM	NM	7	52	2.46	3.39	3.19	4.91
Acetylene	11	0	0.88	2.53	2.37	4.69	NM	NM	NM	NM	NM	NM
Acrolein	NM	NM	NM	NM	NM	NM	19	40	1.17	3.01	2.75	6.86
Acrylonitrile	NM	NM	NM	NM	NM	NM	0	59
alpha-methyl-Styrene	NM	NM	NM	NM	NM	NM	1	58	0.44	0.44	0.44	0.44
alpha-Pinene	3	55	0.06	0.22	0.28	0.33	6	53	0.28	0.36	0.36	0.50
Benzene	57	1	0.16	2.94	0.83	49.39	59	0	0.51	1.51	1.12	9.14
Benzonitrile	NM	NM	NM	NM	NM	NM	0	59
Benzyl chloride	NM	NM	NM	NM	NM	NM	0	59
beta-Pinene	3	55	0.06	0.63	0.17	1.67	24	35	0.28	6.51	4.85	25.74
Bromodi chloromethane	NM	NM	NM	NM	NM	NM	0	59
Bromoform	7	0	0.72	2.32	1.86	6.20	0	59
Bromomethane	11	53	0.04	0.09	0.04	0.31	3	56	0.19	0.39	0.19	0.78
Carbon disulfide	NM	NM	NM	NM	NM	NM	11	48	1.81	2.23	2.21	2.77
Carbon tetrachloride	55	3	0.06	0.73	0.57	7.99	59	0	0.44	0.60	0.57	1.01
Chlorobenzene	17	41	0.05	2.40	0.74	13.36	1	58	0.69	0.69	0.69	0.69
Chlorodifluoromethane	NM	NM	NM	NM	NM	NM	47	12	0.25	0.64	0.53	4.85
Chloroethane	NM	NM	NM	NM	NM	NM	15	44	0.13	0.20	0.18	0.34
Chloroform	17	41	0.05	0.12	0.10	0.44	2	57	0.34	0.39	0.39	0.44
Chloromethane	8	0	1.34	2.95	2.92	5.18	59	0	1.14	1.60	1.57	2.99
cis-1,2-Dichloroethene	NM	NM	NM	NM	NM	NM	0	59
cis-1,3-Dichloropropene	NM	NM	NM	NM	NM	NM	0	59
cis-2-Butene	24	34	0.02	0.28	0.22	1.31	35	24	0.11	0.22	0.21	0.73
cis-2-Hexene	4	54	0.03	0.19	0.14	0.45	18	41	0.17	0.26	0.22	0.48
cis-2-Pentene	25	33	0.06	0.26	0.23	0.95	29	30	0.14	0.32	0.20	2.81
Cyclohexane	10	48	0.03	0.63	0.14	4.89	19	40	0.17	4.86	0.34	85.02
Cyclohexanone	NM	NM	NM	NM	NM	NM	3	56	4.38	4.78	4.78	5.18
Cyclopentane	20	38	0.03	0.26	0.17	1.86	34	25	0.14	0.65	0.26	10.70
Cyclopentene	NM	NM	NM	NM	NM	NM	10	49	0.14	0.22	0.20	0.47
Di bromochloromethane	NM	NM	NM	NM	NM	NM	0	59
Di chlorodifluoromethane	NM	NM	NM	NM	NM	NM	59	0	1.75	2.56	2.49	4.64
Ethanol	NM	NM	NM	NM	NM	NM	58	1	1.55	62.40	28.08	388.16
Ether	NM	NM	NM	NM	NM	NM	0	59
Ethyl acrylate	NM	NM	NM	NM	NM	NM	0	59
Ethyl tert-butyl ether	NM	NM	NM	NM	NM	NM	0	59
Ethylbenzene	38	20	0.04	0.44	0.39	1.82	58	1	0.26	1.77	0.59	28.57

Compound	Site 1					Site 2						
	n	ND	Min	Mean	Med	Max	n	ND	Min	Mean	Med	Max
Isopentane	57	1	1.24	6.08	4.37	53.76	55	4	1.56	57.11	4.57	486.90
Isoprene	28	30	0.06	0.20	0.14	0.61	23	36	0.14	0.75	0.22	11.28
Isopropyl alcohol	NM	NM	NM	NM	NM	NM	11	48	1.55	3.37	2.53	11.63
Isopropyl benzene	10	48	0.05	0.14	0.10	0.39	15	44	0.44	1.64	1.47	5.21
m, p-Xylene	52	6	0.04	1.09	0.65	6.43	59	0	0.83	4.89	2.21	90.32
Methacrylonitrile	NM	NM	NM	NM	NM	NM	0	59
Methanol	NM	NM	NM	NM	NM	NM	59	0	1.97	221.76	5.44	3053.30
Methyl ethyl ketone	NM	NM	NM	NM	NM	NM	19	40	1.74	20.76	18.96	78.75
Methyl isobut' ketone	NM	NM	NM	NM	NM	NM	0	59
Methyl methacrylate	NM	NM	NM	NM	NM	NM	0	59
Methyl tert-butyl ether	NM	NM	NM	NM	NM	NM	0	59
Methyl cyclohexane	14	44	0.08	1.22	0.24	12.33	35	24	0.20	5.55	0.32	177.91
Methyl cyclopentane	26	32	0.07	0.76	0.45	6.78	55	4	0.17	2.44	0.48	101.89
Methylene chloride	42	22	0.03	0.28	0.21	1.35	58	1	0.21	3.91	0.49	174.72
n-Butane	NM	NM	NM	NM	NM	NM	59	0	1.07	5.48	4.02	19.78
n-Decane	19	39	0.06	0.59	0.52	2.01	NM	NM	NM	NM	NM	NM
n-Heptane	15	43	0.04	0.90	0.33	7.05	59	0	0.25	4.58	0.53	229.52
n-Hexane	47	11	0.14	1.00	0.63	10.50	59	0	0.35	4.39	1.06	173.77
n-Nonane	16	42	0.10	0.39	0.21	3.04	23	36	0.26	4.65	0.63	81.83
n-Octane	11	47	0.09	0.63	0.28	4.25	34	25	0.23	3.87	0.37	113.06
n-Pentane	58	0	0.06	2.23	1.46	21.04	59	0	0.74	12.43	1.98	243.45
n-Propyl benzene	17	41	0.05	0.19	0.15	0.69	27	32	0.25	1.13	0.84	6.98
n-Undecane	19	39	0.07	1.21	0.49	7.12	NM	NM	NM	NM	NM	NM
Nitrobenzene	NM	NM	NM	NM	NM	NM	0	59
o-Xylene	45	13	0.04	0.61	0.48	3.99	58	1	0.43	2.14	0.98	33.83
Perchloroethylene	14	44	0.07	0.47	0.37	1.36	6	53	0.34	1.31	0.47	5.49
Propionitrile	NM	NM	NM	NM	NM	NM	0	59
Propylene	8	0	0.21	0.74	0.64	1.89	59	0	1.02	5.16	4.99	16.97
Styrene	14	44	0.04	0.33	0.15	1.79	22	37	0.21	3.54	3.62	16.83
Tetrahydrofuran	NM	NM	NM	NM	NM	NM	5	54	2.57	3.20	3.42	3.75
Toluene	58	0	0.34	2.46	1.39	16.17	59	0	0.90	4.54	2.68	58.79
trans-1, 2-Dichloroethene	NM	NM	NM	NM	NM	NM	0	59
trans-1, 3-Dichloropropene	NM	NM	NM	NM	NM	NM	1	58	0.27	0.27	0.27	0.27
trans-2-Butene	23	35	0.02	0.32	0.23	1.63	38	21	0.11	0.30	0.21	1.81
trans-2-Hexene	6	52	0.03	0.40	0.21	1.10	0	59
trans-2-Pentene	38	20	0.09	0.38	0.27	1.98	43	16	0.14	0.39	0.34	1.95
Trichloroethylene	1	57	0.05	0.05	0.05	0.05	15	44	0.32	1.29	1.02	3.33
Trichlorofluoromethane	58	0	0.90	1.63	1.52	4.89	59	0	1.07	1.41	1.35	3.65
Vinyl acetate	NM	NM	NM	NM	NM	NM	9	50	1.87	11.84	3.38	60.91
Vinyl chloride	1	57	0.03	0.03	0.03	0.03	0	59

Table 5.4. Polycyclic Aromatic Hydrocarbon (PAH) concentrations (in ng/m³) from Dual Fine Particle Sequential Sampler (DFPSS). Air pollutants summarized for detected values, only.

PAH	ESL ¹ Max	ESL ² (24 h)	n	ND	Site 1				Site 2				Site 3					
					Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max	n	n-miss	Min	Mean
Acenaphthene	1.5	400	0	19	.	.	.	1.8	2.20	2.30	2.5	1	20	1.5	1.50			
Anthracene	1.50	23.3	4	15	1.6	1.83	1.65	2.4	1.97	1.80	2.8	3	18	1.4	8.73			
Benzo(a)anthracene	6.7	12	0	19	1	20	6.7	6.70			
Benzo(a)pyrene	.	12	0	19	0	21	.	.			
Benzo(b)fluoranthene	5.5	200	0	19	1	20	5.5	5.50			
Benzo(e)pyrene	2.60	200	0	19	1	20	2.6	2.60			
Benzo(g,h,i)perylene	.	12	0	19	0	21	.	.			
Benzo(k)fluoranthene	2.40	2.4	0	19	1	20	2.4	2.40			
Chrysene	9.00	200	0	19	1	20	9.0	9.00			
Di benzo(a,h)anthracene	.	12	0	19	0	21	.	.			
Fluoranthene	2.40	63.2	18	1	1.3	2.75	2.60	6.0	17	2	1.4	3.06	2.70	5.1	8	13	1.4	9.81
Fluorene	2.85	6.8	12	7	1.3	1.90	1.60	4.2	18	1	1.6	2.79	2.30	5.6	10	11	1.3	3.05
Indeno(1,2,3-c,d)pyrene	.	12	0	19	0	21	.	.			
Naphthalene	1.95	4.9	16	3	1.3	2.40	2.05	6.2	17	2	1.3	2.38	2.00	5.0	16	5	1.6	2.31
Phenanthrene	5.10	134.4	19	0	5.8	11.81	10.40	26.2	19	0	3.9	13.29	10.20	26.7	21	0	1.8	12.97
Pyrene	35.8	200	10	9	1.5	2.21	1.80	4.2	14	5	1.4	1.97	1.85	2.8	1	20	35.8	35.80

Table 5.5. Pesticide concentrations (in ng/m³) from Dual Fine Particle Sequential Sampler (DFPSS). Air pollutants summarized for detected values, only.

ESL ¹ Pesticide (24 h) (annual)	Site 1					Site 2					Site 3							
	n	ND	Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max
4, 4' -DDD 400 NA	0	19	0	19	0	21
4, 4' -DDE NA NA	0	19	0	19	0	21
4, 4' -DDT 400 100	0	19	0	19	0	21
Acephate 28000 7000	0	19	0	19	0	21
alpha-Chlordane 2000 500	0	19	0	19	0	21
Atrazine 20000 5000	0	19	0	19	0	21
Azinphos-methyl 800 200	0	19	0	19	0	21
Captan 20000 5000	0	19	0	19	0	21
Carbofuran 400 100	0	19	0	19	0	21
Chlorpyrifos 800 200	0	19	1	18	19.7	19.7	19.7	19.7	0	21
cis-Permethrin 20000 5000	0	19	0	19	0	21
Di azinon 400 100	0	19	0	19	0	21
Dieldrin 1000 250	0	19	0	19	0	21
Ethyl parathion 200 50	0	19	0	19	0	21
gamma-Chlordane 2000 500	0	19	0	19	0	21
Heptachlor 200 50	0	19	0	19	0	21
Lindane	0	19	0	19	0	21

Table 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.

3	Site 1										Site 2										Site
	Measurement	Mean	Median	n	ND	Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max	n	n-mi	ss	Min		
PM _{2.5}	5105	4399	0.01	7.27	5.64	94.35	7335	1995	0.00	8.80	7.02	104.68	6754	2624	0.01						
8.09	6.20	837.59	NA	NA	NA	NA	9053	277	14.00	77.21	80.64	100.00	8027	1351	18.34						
RH	77.88	81.81	100.00	NA	NA	NA	9274	56	-2.48	22.88	24.32	35.13	9333	45	-2.55						
Temp	22.52	23.84	34.96	0.00	157.60	141.00	360.00	9195	135	0.06	161.24	151.34	359.98	9285	93	0.00					
VWD	160.97	149.34	359.99	NA	NA	NA	9198	132	0.03	4.24	4.06	13.60	9291	87	0.05						
VWS	4.32	4.09	12.43																		

Table 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.

3	Site 1										Site 2										Site
	Measurement	Mean	Median	n	ND	Min	Mean	Median	Max	n	ND	Min	Mean	Median	Max	n	n-mi	ss	Min		
PM _{2.5}	265	2	0.22	8.00	7.27	26.07	377	3	0.17	9.30	8.35	27.18	379	2	0.47						
7.82	7.14	42.40	NA	NA	NA	NA	376	0	39.58	77.08	77.19	100.00	342	0	37.91						
RH	77.87	77.20	100.00	0.80	4.90	4.38	15.88	383	0	1.31	4.21	10.04	396	0	1.53						
SWS	4.44	4.18	9.65																		

Table 5.7. Transboundary fine particulate air monitoring and comparison with literature data. Units for $PM_{2.5}$, C_E , and C_V in $\mu g/m^3$, elements in ng/m^3 .

Pollutant	Emission ⁴	TAPP (Mean)	TAPP (Maximum)	PTEAM (Mean ⁵)	PTEAM (Maximum ⁶)	El Paso ⁷ (Mean)	Houston ⁸ (Mean)
$PM_{2.5}$		10.37 ¹ 7.55 ² 6.72 ³	34.25 ¹ 21.58 ² 21.81 ³	50	110	27.2	36.2
C_E	combustion, refineries, botanical, tire wear, diesels	0.13 ¹ 0.13 ² 0.11 ³	0.22 ¹ 0.20 ² 0.12 ³				1.4 ^{8a}
C_V	combustion, industrial, refineries, diesels, paved road dust	0.6 ¹ 0.6 ² 0.4 ³	2.2 ¹ 1.7 ² 1.0 ³				5.7 ^{8a}
Al	soil, paved & unpaved roads, construction, limestone production, cement, fly ash, slag, field burning	283.6 ¹ 125.0 ² 94.1 ³	1264.2 ¹ 614.4 ² 355.1 ³	487.6		155	107.5

Pollutant	Emission ⁴	TAPP (Mean) (Maximum)	PTEAM (Mean ⁵) (Maximum ⁶)	El Paso ⁷ (Mean)	Houston ⁸ (Mean)
As	coal combustion, glass & wood preservatives, pesticides	1.7 ¹ 1.5 ² 1.4 ³	1.9 ¹ 1.8 ² 2.7 ³	25	
Ba	brake lining material	23.3 ¹ 27.8 ² 32.5 ³	71.3 ¹ 68.0 ² 76.8 ³	41	
Br	leaded gasoline combustion (non-USA), diesels	3.4 ¹ 3.0 ² 3.1 ³	12.3 ¹ 9.5 ² 8.5 ³	11.2	19.5
Ca	soil, paved & unpaved roads, construction, limestone production, cement, fly ash, slag	172.7 ¹ 35.5 ² 36.4 ³	1413.3 ¹ 186.7 ² 448.0 ³	235	415
Cl	marine, wood combustion, field burning	221.5 ¹ 37.6 ² 33.9 ³	822.9 ¹ 166.3 ² 374.9 ³	140.4	256.5
Cr		1.9 ¹ 3.8 ² 1.2 ³	3.1 ¹ 4.3 ² 1.8 ³	1	1.5

Pollutant	Emission ⁴	TAPP (Mean) (Maximum)	PTEAM (Mean ⁵) (Maximum ⁶)	El Paso ⁷ (Mean)	Houston ⁸ (Mean)		
Cu	copper smelter	3.0 ¹ 2.2 ² 1.5 ³	12.4 ¹ 13.3 ² 5.2 ³	12	16	36	16.5
Fe	soil, steel production, paved & unpaved roads, construction, limestone prod. cement, fly ash, slag, brake lining material	85.2 ¹ 31.1 ² 23.7 ³	751.6 ¹ 351.4 ² 187.8 ³	324.6	590	134	121
K	soil, wood combustion (soil-corrected), field burning, paved & unpaved construction, limestone production, cement, fly ash, slag	88.9 ¹ 61.4 ² 60.2 ³	467.6 ¹ 362.0 ² 202.5 ³	181.2	300	127	102
Mg	marine, brake lining material	45.6 ¹ 24.5 ² 16.9 ³	89.4 ¹ 97.1 ² 57.3 ³				
Mn	steel production	3.0 ¹ 2.2 ² 1.6 ³	13.9 ¹ 8.0 ² 4.8 ³	12.9	19.5	4	9

Pollutant	Emission ⁴	TAPP (Mean) (Maximum)	PTEAM (Mean ⁵) (Maximum ⁶)	El Paso ⁷ (Mean)	Houston ⁸ (Mean)
Na	marine	272.3 ¹ 92.1 ² 57.0 ³	596.8 ¹ 200.3 ² 193.8 ³		
Ni	industrial	2.4 ¹ 1.7 ² 1.5 ³	6.5 ¹ 10.5 ² 3.5 ³	1	8
P		16.0 ¹ 16.0 ² 18.6 ³	42.4 ¹ 16.0 ² 18.6 ³	110.5	
Pb	leaded gasoline combustion (non-USA), incinerator, diesels	4.4 ¹ 4.2 ² 3.7 ³	16.1 ¹ 12.9 ² 9.9 ³	24.2 37	481 435
Rb		1.1 ¹ 0.9 ² 0.9 ³	1.8 ¹ 1.2 ² 1.4 ³		<2
S	sulfates (anthropogenic & marine), tire wear, coal combustion	864.1 ¹ 849.6 ² 752.1 ³	3621.3 ¹ 3205.1 ² 3046.3 ³	1555.5 2950	823
Se	coal combustion	1.0 ¹ 1.0 ² 1.1 ³	1.4 ¹ 1.6 ² 1.8 ³	2	<2

Pollutant	Emission ⁴	TAPP		PTEAM		E1 Paso ⁷ (Mean)	Houston ⁸ (Mean)
		(Mean)	(Maximum)	(Mean ⁵)	(Maximum ⁶)		
Si	soil	312.2 ¹ 115.6 ² 109.2 ³	2854.3 ¹ 1223.9 ² 798.6 ³	534.2	925	436	170
Sn		12.9 ¹	18.6 ¹				<2
Sr		2.3 ¹ 1.8 ² 1.4 ³	8.6 ¹ 5.3 ² 3.3 ³	7.8			<1
Ti	soil	27.3 ¹ 20.2 ² 13.2 ³	88.0 ¹ 39.1 ² 23.5 ³	58.6		3	<8
V	electric utility oil combustion	4.1 ¹ 4.7 ² 4.2 ³	23.3 ¹ 28.3 ² 13.1 ³				<2
Zn	incinerator, tire wear	4.9 ¹ 4.2 ² 4.2 ³	43.5 ¹ 35.4 ² 102.4 ³	40.6	75.5	55	73.5

¹ Site 1

² Site 2 (An "a" superscript in the maximum column indicates only one measurement detected.)

³ Site 3 (An "a" superscript in the maximum column indicates only one measurement detected.)

⁴ Emissions represent air emission sources or processes that usually form such air emissions. **NOTE: Elements may be present in other sources, as well.** Emission source information from: Graedel (1978), Hopke (1985), Dzuby et al. (1984), Lewis and Einfield (1985), Hildemann et al. (1991), Shields (1991), Ozkaynak et al. (1996) and USEPA (1996a).
⁵ Particle Total Exposure Assessment Methodology Study (PTEAM). Consecutive, 12 h day-night PM_{2.5} mean values from Ozkaynak et al. (1996) converted to 24-h mean values.
⁶ Particle Total Exposure Assessment Methodology Study (PTEAM). Consecutive, 12 h day-night PM_{2.5} maximum values are the 90th percentile from Clayton et al. (1993) converted to 24-h mean values.

⁷ Mean PM_{2.5} values from Davis et al. (1984).

⁸ Consecutive, 12 h day-night mean PM_{2.5} values from Dzuby et al. (1982) converted to 24-h mean values.

^{8a} 12 h mean PM_{2.5} values from Dzuby et al. (1982), Houston study; data presented in USEPA (1996a).

Table 5.8a. Transboundary VOC air monitoring and comparison with literature data. Units in $\mu\text{g}/\text{m}^3$. Dominant emission sources are indicated in **bold**.

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
1,1,1-Trichloroethane	waste water, vapor degreasers	0.76 ¹ 0.61 ²	2.67 ¹ 1.04 ²	11 ⁴ 2.0 ⁹ 4.00 ⁹ 6.48 ⁹ 7.73 ⁹	40 ⁴ 3.6 ⁹ 46 ⁹ 281 ⁹ 492 ⁹
1,2,4-Trimethylbenzene	graphic arts	1.05 ¹ 2.08 ²	3.59 ¹ 29.89 ²	3.5 ⁵	33617 ⁵
1,3-Butadiene	auto, diesel, forest fire, petroleum mfr., plastics mfr., syn. rubber mfr.	0.24 ¹ 0.29 ²	1.39 ¹ 0.97 ²	0.4 ⁵ 2.3 ⁹ 5.68 ⁹	525 ⁵ 321 ⁹ 332 ⁹
1,3,5-Trimethylbenzene	auto, diesel, gasoline vapor, graphic arts, plant volatile, solvent, turbine	0.52 ¹ 0.89 ²	3.20 ¹ 11.70 ²	1.0 ⁵	608 ⁵
1-Butene	auto, diesel, forest fire, microbes, petrol. mfr., polymer comb., turbine	0.81 ¹ 0.83 ²	5.30 ¹ 2.71 ²	1.7 ⁶	16.4 ⁶
1-Pentene	auto, diesel, gasoline vapor, polymer comb., turbine	0.40 ¹ 0.39 ²	1.75 ¹ 1.29 ²	0.6 ⁶	11.2 ⁶

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
2,2-Dimethylbutane	auto, forest fire, gasoline vapor, petroleum mfr.	0.41 ¹ 1.17 ²	1.73 ¹ 17.59 ²	1.3 ⁶	42.7 ⁶
2,2,4-Trimethylpentane (Iso-octane)	auto, gasoline, refinery, natural gas, turbine	0.55 ¹ 0.95 ²	4.34 ¹ 2.85 ²	2.0 ⁵ 22.5 ⁹	824.7 ⁵ 230 ⁹
2,3,4-Trimethylpentane	refinery, gasoline, auto	0.26 ¹ 0.54 ²	1.12 ¹ 3.69 ²	1.8 ⁷	3.5 ⁷
2,3-Dimethylbutane	auto, forest fire, gasoline vapor, refinery	0.52 ¹ 1.49 ²	2.04 ¹ 55.34 ²	6.2 ⁶	286.1 ⁶
2,3-Dimethylpentane	gasoline, auto, natural gas, gas, turbine	0.41 ¹ 1.62 ²	1.15 ¹ 29.22 ²	1.0 ⁶	14.1 ⁶
2,4-Dimethylpentane	auto, gasoline vapor, refinery, architectural coatings	0.30 ¹	1.09 ¹	1.8 ⁸	4.1 ⁸
2-Methylheptane	auto, gasoline vapor, natural gas, turbine	0.48 ¹ 2.80 ²	3.13 ¹ 72.88 ²	1.6 ⁵	125 ⁵
2-Methylhexane	auto, turbine	0.72 ¹ 0.98 ²	4.92 ¹ 10.94 ²	5.9 ⁸	12.9 ⁸

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
2-Methylpentane	gasoline, gasoline vapor, auto, petrol. mfr., refinery, natural gas, plant volatile, turbine	1.52 ¹ 4.36 ²	12.69 ¹ 110.32 ²	6.5 ⁷	13.5 ⁷
2-Methyl-1-Pentene	auto, turbine	0.17 ¹ 0.29 ²	0.31 ¹ 0.59 ²	0.3 ⁶	6.8 ⁶
2-Methyl-2-Butene	auto, diesel, forest fire, gasoline vapor, turbine	0.42 ¹ 0.49 ²	2.67 ¹ 2.81 ²	1.0 ⁶	12.3 ⁶
3-Methylhexane	gasoline, auto, gasoline vapor, natural gas, turbine	0.94 ¹ 2.90 ²	4.22 ¹ 88.53 ²	4.1 ⁷	7.0 ⁷
3-Methylpentane	gasoline, petrol. mfr., gasoline vapor, refinery, auto, natural gas, forest fire, plant volatile	0.92 ¹ 3.09 ²	6.94 ¹ 73.31 ²	4.7 ⁸	9.4 ⁸
3-Methyl-1-Butene	auto, diesel, turbine	0.21 ¹ 0.21 ²	0.54 ¹ 0.46 ²	0.2 ⁶	12.6 ⁶
4-Methyl-1-Pentene	auto, diesel, turbine	0.03 ¹	0.03 ¹ 0.21 ^{2a}		

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
Acrolein	auto, diesel, forest fire, lacquer mfr., litho. coater, plastics comb., spray painting, syn. rubber mfr., turbine, etc.	3.01 ²	6.86 ²	14.3 ⁹	24.6 ⁹
"-Pinene	biogenic , solvent, veneer drying, wood pulping	0.22 ¹ 0.36 ²	0.33 ¹ 0.50 ²		
Benzene	auto, solvent , waste water , coke ovens, refinery, chemical mfr., diesel, forest fire, gasoline vapor, landfill, lacquer mfr., petrol. mfr., plant volatile, polymer comb. & mfr., refuse comb., etc.	2.94 ¹ 1.51 ²	49.39 ¹ 9.14 ²	7.1 ⁴ 1.56 ⁹ 2.56 ⁹ 2.68 ⁹ 4.77 ⁹ 10.1 ⁹	25 ⁴ 5.30 ⁹ 6.75 ⁹ 21.7 ⁹ 67.3 ⁹ 206 ⁹
β-Pinene	biogenic , wood pulping	0.63 ¹ 6.51 ²	1.67 ¹ 25.74 ²		
Carbon Tetrachloride	chemical mfr., fumigating agent, petroleum stor., plant volatile, refuse comb., solvent	0.73 ¹ 0.60 ²	7.99 ¹ 1.01 ²	0.73 ⁴ 0.64 ⁹ 0.77 ⁹ 0.96 ⁹ 1.60 ⁹	1.8 ⁴ 0.83 ⁹ 1.09 ⁹ 38.8 ⁹ 27.8 ⁹

Pollutant	Emission ³	TAPP (Mean)	(Maximum)	Comparison Data (Typical)	(High)
Chloroform	waste water , chemical mfr., landfill, plant volatile, refuse comb., solvent, etc.	0.11 ¹ 0.39 ²	0.44 ¹ 0.44 ²	0.47 ⁴ 0.16 ⁹ 0.55 ⁹ 2.68 ⁹	7.5 ⁴ 0.89 ⁹ 115 ⁹ 145 ⁹
cis-2-Pentene	auto, diesel, gasoline vapor, turbine	0.26 ¹ 0.32 ²	0.95 ¹ 2.81 ²	0.4 ⁶	0.5 ⁶
Cyclohexane	gasoline, auto, solvent , petrol. mfr., plant volatile, turbine	0.63 ¹ 4.86 ²	4.89 ¹ 85.02 ²	2.3 ⁷	4.0 ⁷
Cyclopentane	auto, gasoline vapor, natural gas, petrol. mfr., turbine	0.26 ¹ 0.65 ²	1.86 ¹ 10.70 ²	6.0 ⁶	279.4 ⁶
Ethanol	animal waste, auto, fat subst. plant, forest fire, insects, petrol. stor. plant volatile, plastics comb., printing, refuse comb., wood pulping, etc.	62.40 ²	388.16 ²		

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
Ethylbenzene	auto, chemical mfr., diesel, gasoline vapor, polymer mfr., solvent, turbine	0.44 ¹ 1.77 ²	1.82 ¹ 28.57 ²	3.2 ⁴ 1.1 ⁹ 1.10 ⁹ 1.68 ⁹ 2.04 ⁹ 7.9 ⁹	16 ⁴ 3.0 ⁹ 5.56 ⁹ 18.5 ⁹ 36.7 ⁹ 1248 ⁹
Hexane	gasoline, gasoline vapor, propane-rich, auto, building mtls., chemical mfr., diesel, forest fire, petrol. mfr., plant volatile, etc.	1.00 ¹ 4.39 ²	10.50 ¹ 173.77 ²	6.5 ⁸ 12.6 ⁹	14.1 ⁸ 273 ⁹
Isobutane	gasoline vapor, petrol. mfr., refinery, auto, diesel, forest fire, microbes, natural gas, propellant, turbine, etc.	2.50 ¹ 5.42 ²	36.87 ¹ 14.26 ²	5.4 ⁸	11.9 ⁸
Isopentane	gasoline vapor, petrol. mfr., auto, refinery, building mtls., diesel, forest fire, natural gas, plant volatile, turbine	6.08 ¹ 57.11 ²	53.76 ¹ 486.90 ²	17.3 ⁵	3202 ⁵

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
Isoprene	biogenic	0.20 ¹ 0.75 ²	0.61 ¹ 11.28 ²	4.0 ⁶	33.8 ⁶
m,p-Xylene	gasoline, auto, solvent, diesel, fish oil mfr., polymer comb., turbine	1.09 ¹ 4.89 ²	6.43 ¹ 90.32 ²	18 ⁴ 3.62 ⁹ 3.9 ⁹ 5.54 ⁹	90 ⁴ 17.1 ⁹ 11.3 ⁹ 127 ⁹
Methanol	animal waste, auto, charcoal mfr., fat subst. plant, forest fire, insects, petrol. stor., plant volatile, plastics comb., printing, refuse comb., wood pulping, etc.	221.76 ²	3053.30 ²	11.4 ⁹ 22.0 ⁹ 23.1 ⁹	20.9 ⁹ 41.1 ⁹ 62.3 ⁹
Methylcyclohexane	gasoline, auto, natural gas, turbine	1.22 ¹ 5.55 ²	12.33 ¹ 177.91 ²	1.7 ⁷	3.4 ⁷
Methylcyclopentane	auto, gasoline vapor, natural gas, petrol. mfr., plant volatile, turbine	0.76 ¹ 2.44 ²	6.78 ¹ 101.89 ²	2.9 ⁷	5.7 ⁷

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
Methylene Chloride	chemical mfr., foaming agent, landfill, solvent	0.27 ¹ 3.91 ²	1.35 ¹ 174.72 ²	0.88 ⁹ 1.70 ⁹ 2.90 ⁹ 3.91 ⁹	10.7 ⁹ 59 ⁹ 112 ⁹ 83 ⁹
n-Butane	gasoline vapor, propane-rich, natural gas, auto, coke ovens, gasoline, building mtls., diesel, forest fire, microbes, petrol. mfr., polymer comb. propellant, turbine, water treatment	5.48 ²	19.78 ²	20.3 ⁸	43.5 ⁸
n-Propylbenzene	auto, gasoline vapor, graphic arts, plant volatile, turbine	0.19 ¹ 1.13 ²	0.69 ¹ 6.98 ²	0.8 ⁵	912 ⁵
o-Xylene	gasoline, auto, fish oil mfr., gasoline vapor, phthalic anhydride mfr., plant volatile, polymer comb.	0.61 ¹ 2.14 ²	3.99 ¹ 33.83 ²	6.5 ⁴ 1.37 ⁹ 1.5 ⁹ 2.68 ⁹ 8.5 ⁹	29 ⁴ 5.38 ⁹ 4.1 ⁹ 64.1 ⁹ 391 ⁹

Pollutant	Emission ³	TAPP (Mean)	TAPP (Maximum)	Comparison Data (Typical)	Comparison Data (High)
Pentane	gasoline vapor, auto, gasoline, propane-rich, refinery, coke ovens, building mtls., diesel, forest fire, natural gas, petrol. mfr., polymer comb., water treatment, etc.	2.23 ¹ 12.43 ²	21.04 ¹ 243.45 ²	9.5 ⁸	18.9 ⁸
Propylene	auto, diesel, forest fire, microbes, natural gas, petrol. mfr., polymer comb., refuse comb., turbine, wood pulping	0.74 ¹ 5.16 ²	1.89 ¹ 16.97 ²	1.6 ⁶	13.2 ⁶
Styrene	building resins, chemical mfr., glue vapor, polymer mfr. river water odor, solvent	0.45 ¹ 3.54 ²	3.02 ¹ 16.83 ²	1.7 ⁴ 0.19 ⁹ 0.58 ⁹ 3.7 ⁹	13 ⁴ 3.55 ⁹ 35.1 ⁹ 279 ⁹

Pollutant	Emission ³	TAPP (Mean)	(Maximum)	Comparison Data (Typical)	(High)
Toluene	auto, gasoline, graphic arts, architectural coatings, solvent, chemical mfr., diesel, fish oil mfr., forest fire, gasoline vapor, landfill, petrol. mfr., plant volatile, polymer comb. & mfr., turbine, wood pulping, etc.	2.46 ¹ 4.54 ²	16.17 ¹ 58.79 ²	16.77 5.17 ⁹ 5.78 ⁹ 9.9 ⁹ 19.9 ⁹ 24.2 ⁹	32.4 ⁷ 20.6 ⁹ 16.5 ⁹ 561 ⁹ 750 ⁹ 965 ⁹
Trans-2-Butene		0.32 ¹ 0.30 ²	1.63 ¹ 1.81 ²	0.6 ⁶	13.0 ⁶
Trans-2-Pentene		0.38 ¹ 0.39 ²	1.98 ¹ 1.95 ²	0.4 ⁶	8.7 ⁶
Trichloroethylene	vapor degreasers, waste water, chemical mfr., dry cleaning, landfill, solvent, etc.	1.29 ²	0.05 ^{1a} 3.33 ²	0.22 ⁴ 0.42 ⁹ 0.71 ⁹ 2.08 ⁹ 2.63 ⁹	1.6 ⁴ 17.8 ⁹ 17.6 ⁹ 376 ⁹ 162 ⁹
Vinyl Acetate	forest fire, industrial	11.84 ² 60.91 ²		<7	

¹ Site 1 (An "a" superscript in the maximum column indicates only one measurement detected.)

² Site 2 (An "a" superscript in the maximum column indicates only one measurement detected.)

³ Emissions represent air emission sources or processes that usually form such air emissions. Sources listed in **bold** are dominant sources for the given compound. **NOTE: VOCs are ubiquitous and may be present in other sources, as well.** Emission source information from: Graedel (1978), Doskey et al. (1992), Kenski et al. (1991), Kenski et al. (1992), Scheff and Wadden (1993), and Wadden et al. (1995).

⁴ The typical value is the arithmetic average and the high value is the 12-h maximum from Wallace et al. (1991).

⁵ The typical value is the median and the high is the maximum value; units in ppb converted to µg/m³ from Shah and Joseph (1993); data summarized in U.S. EPA (1994).

⁶ The typical value is the arithmetic average and the high is the maximum value; units in ppb converted to µg/m³ from Purdue et al. (1992).

⁷ The typical value is the arithmetic average and the high is the maximum value; units in ppb converted to µg/m³ from Lewis (1991).

⁸ The typical value is the arithmetic average and the high is the maximum value; units in ppb converted to µg/m³ from Lewis and Zweidinger (1992).

⁹ The typical value is the mean and the high is the maximum value from Kelly et al. (1993).

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

Ambient VOC Literature	Site 1					Site 2					U.S. EPA National Data Base		
	n	Min	Mean	Med	Max	n	Min	Mean	Med	Max	Min ²	Mean	Med
Lower Upper 1, 1, 1-Trichloroethane 0.15 ¹ 1.2 ¹	68	0.05	0.145	0.110	0.49	59	0.07	0.112	0.110	0.19			0.44 ¹
1, 1, 2, 2-Tetrachloroethane 0 ¹ 0.009 ¹	NM	NM	NM	NM	NM	0			0.911 ³ 0.162 ³
1, 1, 2-Trichloroethane 0 ³ 0.008 ³ 0.0062 ¹ 0.034 ¹	0	0			0.101 ³ 0 ³
1, 2, 4-Tri chlorobenzene 0.100 ³ 0.200 ³	NM	NM	NM	NM	NM	4	0.23	0.498	0.495	0.77			0.172 ³ 0.100 ³
1, 2, 4-Tri methyl benzene 0.59 ¹ 1.4 ¹	34	0.03	0.214	0.145	0.73	59	0.07	0.423	0.280	6.08			1 ¹
9.3											0.1	1.2 ²	
1, 2-Di chl orobenzene 0 ³ 0.038 ³	1	0.01	0.010	0.010	0.01	1	0.08	0.080	0.080	0.08			1.3 ⁴ 0 ³
1, 2-Di chl oroethane 0 ¹ 0.67 ¹	7	0.01	0.066	0.070	0.18	1	0.05	0.050	0.050	0.05			0.2 ¹
1, 2-Di chl oropropane 0.045 ¹ 0.068 ¹	0	0			0.384 ³ 0 ³
1, 3, 5-Tri methyl benzene 0.011 ³ 0.065 ³	28	0.01	0.106	0.060	0.65	41	0.05	0.181	0.100	2.38			0.160 ³ 0.022 ³

	Site 1			Site 2			U. S. EPA National					
	Min	Mean	Max	Min	Mean	Max	Min ²	Mean	Med			
Ambient VOC												
Literature												
VOC												
Max ² Quartiles												
Lower	18	0.01	0.055	0.040	0.24	0.22	0.05	0.115	0.075	0.79	0.337 ³	0.228 ³
Upper												
2, 3, 4-Tri methyl pentane	8	0.02	0.101	0.050	0.28	0.23	0.05	0.394	0.080	7.13	1.797 ³	0.487 ³
0.104 ³												
2, 3-Di methyl pentane	54	0.01	0.431	0.265	3.60	49	0.13	1.236	0.490	31.30		2.5 ¹
0.141 ³												
2-Methyl pentane												
2.4 ¹												
1.140 ³											3.325 ³	2.194 ³
3-Methyl hexane	18	0.03	0.228	0.115	1.03	45	0.08	0.707	0.200	21.60	1.736 ³	0.785 ³
0.414 ³												
3-Methyl pentane	50	0.04	0.262	0.160	1.97	47	0.10	0.877	0.340	20.80		1.8 ¹
1.8 ¹												
0.845 ³											2.550 ³	1.525 ³
Acetone	NM	NM	NM	NM	NM	58	1.48	8.811	3.560	75.30		0.35 ¹
0.27 ¹												
0.93 ¹												
Acetonitrile	NM	NM	NM	NM	NM	0	0.024 ³	0 ³
0 ³												
0.048 ³												
alpha-Pi nene	3	0.01	0.040	0.050	0.06	6	0.05	0.065	0.065	0.09		0.07 ¹
0.02 ¹												
0.16 ¹												
0.023 ³												
0.264 ³												
Benzene	71	0.05	0.784	0.250	15.46	59	0.16	0.473	0.350	2.86		2.8 ¹
1.4 ¹											0.8	5.8 ²
4.6 ¹												
37.7												
0.630 ³											2.800 ³	1.665 ³
3.343 ³												2.7 ⁴
Carbon tetrachloride	62	0.01	0.118	0.090	1.27	59	0.07	0.095	0.090	0.16		0.15 ¹

	Site 1					Site 2					U. S. EPA National				
	Min	Mean	Med	Max	n	Min	Mean	Med	Max	n	Min ²	Mean	Med	Max	n
Ambient VOC															
Literature															
VOC	0.163 ³	0.730 ³	0.321 ³	0.346 ³		0.01	0.183	0.040	1.42	19	0.05	1.412	0.100	24.70	1.047 ³
Di chlorodi fluoromethane						NM	NM	NM	NM	59	0.35	0.514	0.500	0.93	0.438 ³
Ethylbenzene						51	0.01	0.094	0.090	0.42	58	0.06	0.407	0.135	6.58
7.3															0.6 ⁴
0.230 ³	1.244 ³														4.495 ³
Hexachlorobutadiene						NM	NM	NM	NM	0					0.036 ³
0.001 ³	0.006 ³					66	0.01	0.281	0.230	1.48	59	0.19	1.125	0.510	20.80
m, p- Xylene															0.088 ¹
0.013 ¹	0.38 ¹														0.3
23.8															3.8 ²
Methylcyclohexane						14	0.02	0.304	0.060	3.07	35	0.05	1.381	0.080	44.30
0.207 ³	0.806 ³					26	0.02	0.222	0.130	1.97	55	0.05	0.710	0.140	29.60
Methylcyclopentane						42	0.01	0.082	0.060	0.39	58	0.06	1.125	0.140	50.30
0.581 ³	0.729 ³														0.62 ¹
Methylene chloride															1.619 ³
0.33 ¹	1.8 ¹														0.774 ³
0.314 ³	1.809 ³														0.4 ⁴
n-Hexane						47	0.04	0.284	0.180	2.98	59	0.10	1.246	0.300	49.30
1.5 ¹	5.3 ¹														2.8 ¹
0.827 ³	2.945 ³					58	0.02	0.755	0.495	7.13	59	0.25	4.211	0.670	82.50
n-Pentane															3.684 ³
5.0 ¹	14 ¹														1.656 ³
															7.6 ¹
															6.894 ³
															3.811 ³

Ambient VOC	Site 1					Site 2					U. S. EPA National Data Base				
	n	Min	Mean	Med	Max	n	Min	Mean	Med	Max	Min ²	Mean	Med		
Lower	72	0.09	0.676	0.370	4.62	59	0.24	1.204	0.710	15.60	1.0	10.3 ²	9.3 ¹		
Upper	14 ¹														
Toluene	58	0.16	0.290	0.270	0.87	59	0.19	0.251	0.240	0.65	7.775 ³	1.889 ³	4.8 ⁴		
65.7													0.196 ³		
Trichloroethylene	1	0.01	0.010	0.010	0.01	15	0.06	0.239	0.190	0.62			0.5 ⁴		
0.025 ¹													0.13 ¹		
0.010 ³	1	0.01	0.010	0.010	0.01	0			0.495 ³		
0.470 ³													0.158 ³		
0.010 ³													3.283 ³		
0.010 ³													0 ³		

NM = not measured

. = data below detection

¹Brodzinsky and Singh (1983)

²Singh et al. (1985)

³Shah and Heyerdahl (1988); Shah and Singh (1988). Both from same data base update. Lower and upper quartiles represent 25% and 75% values; while they are not minimum or maximum values, they represent lower and upper ranges of the summarized data.

⁴Measurements taken in Houston, TX (Edgerton et al., 1989).

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

Pollutant	Emission ⁴	TAPP		Columbus, Ohio ⁵		Houston ⁶		Other Comparison Data	
		(Mean)	(Maximum)	(Mean)	(Maximum)	(Mean)	(Max)	(Mean)	(Max)
Acenaphthene	biomass burning, diesel exhaust	2.2 ²	2.5 ²	4.2	10	22.8	31.1 ⁷	4.7 ⁷	31.1 ⁷
Anthracene	aluminum mfr., asphalt mfr.,	1.8 ¹	2.4 ¹	1	2.0	2.2	39.8 ⁷	6.7 ⁷	39.8 ⁷
	auto, biomass burning, coal	2.0 ²	2.8 ²						
	comb., diesel exhaust, petrol. mfr., refuse comb.	8.7 ³	23.3 ³						
Benzo(a) - anthracene	aluminum mfr., auto, biomass burning, coal			6.7 ^{3a}	0.4	0.7	18.5 ⁷	2.6 ⁷	18.5 ⁷
	comb., diesel & gasoline soot								
Benzo(b) - fluoranthene	biomass burning, diesel & gasoline soot			5.5 ^{3a}	1.1	2.3	14.8 ⁷	1.0	14.8 ⁷
	asphalt mfr., auto, biomass burning, coal							29.7 ⁸	1.7 ⁷
Benzo(e) pyrene	aluminum mfr., asphalt mfr., auto, biomass burning, coal			2.6 ^{3a}	0.5	0.9	0.4	0.4	0.4
	comb., diesel & gasoline soot, petrol. mfr., refuse comb.								
Benzo(k) - fluoranthene	biomass burning, diesel & gasoline soot			2.4 ^{3a}	1.1	2.3	16.5 ⁷	1.8 ⁷	16.5 ⁷
	auto, biomass burning, coal							29.7 ⁸	1.7 ⁷

Pollutant	Emission ⁴	TAPP		Columbus, Ohio ⁵		Houston ⁶		Other Comparison Data	
		(Mean)	(Maximum)	(Mean)	(Maximum)	(Mean)	(Maximum)	(Mean)	(Maximum)
Chrysene	aluminum mfr., auto, biomass burning, diesel & gasoline soot, refuse comb.			9.0 ^{3a}	1.1	2.2	1.0	3.0 ⁷	24.1 ⁷
Fluoranthene	aluminum mfr.,	2.8 ¹	6.0 ¹	5.6	9.4	10.2	13.3 ⁷	62.4 ⁷	
	asphalt mfr.,	3.1 ²	5.1 ²				78.6 ⁸		
	auto, biomass burning, coal comb., diesel, petrol. mfr., oceans, refuse comb.	9.8 ³	63.2 ³						
Fluorene	auto, coal comb., diesel exhaust	1.9 ¹	4.2 ¹			24.2		31.6 ⁷	161 ⁷
		2.8 ²	5.6 ²						
		3.0 ³	6.8 ³						
Naphthalene		2.4 ¹	6.2 ¹	170	330	671			
		2.4 ²	5.0 ²						
		2.3 ³	4.9 ³						
Phenanthrene	aluminum mfr.,	11.8 ¹	26.2 ¹	31	54	50.1		82.0 ⁷	492 ⁷
	auto, biomass burning, coal comb., diesel exhaust, petrol. mfr., oceans, refuse comb.	13.3 ²	26.7 ²						
		13.0 ³	134.4 ³						
Pyrene	aluminum mfr.,	2.2 ¹	4.2 ¹	4.4	9.4	11.8		12.3 ⁷	64.4 ⁷
	asphalt mfr.,	2.0 ²	2.8 ²					68.9 ⁸	
	auto, biomass burning, coal comb., diesel exhaust, petrol. mfr., refuse comb.		35.8 ^{3a}						

- 1 Site 1
- 2 Site 2
- 3 Site 3 (An "a" superscript in the maximum column indicates only one measurement detected.)
- 4 Emissions represent air emission sources or processes that usually form such air emissions. NOTE: PAHs are ubiquitous
in all combustion processes and may be present in other sources, as well. Emission source information from: Graedel (1978),
Marty et al. (1984), Freeman and Cattell (1990), Li and Kamens (1993), Rogge et al. (1993), Lowenthal et al. (1994),
Westerholm and Li (1994), and Jenkins et al. (1996).
- 5 Mean and maximum outdoor air values in Columbus, OH from Chuang et al. (1991).
- 6 Mean values in Boston/Houston from Lewis et al. (1992).
- 7 Mean value and maximum (highest of range) value from Halsall et al. (1994).
- 8 Maximum value from Yamasaki et al. (1982).

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

Pesticide	Use (crop) ¹	TAPP	NOPEs (Mean) ⁴ (Maximum) ⁵	NEFOES ⁶ (Mean)	AHPS ⁷ (Detected Values)	Other Comparison Data (Mean) (Maximum)
Chlorpyrifos	Insecticide (corn, cotton, sorghum, soybeans, etc.)	19.7 ^{2a}	16.7 206	0.8	3.44 1.04 3.09	
Malathion	Insecticide (cotton, fruits & vegetables)	2.2 ^{2a}	0.8 6			
Methyl Parathion	Insecticide (cotton)	8.1 ^{2a}				4.8 ⁸ 26 ⁸
Pendimethalin	Herbicide (corn, cotton, small grain cereals, sugarcane, sorghum, soybeans, etc.)	2.9 ^{3a}				
Trifluralin	Herbicide (carrots, cotton, sorghum, sugarcane, fruits & vegetables)	2.3 ^{2a} 3.0 ^{3a}		0.1	1.27 8.08	0.27 ⁹ 3.4 ⁹ 2.05

¹ These are crops commonly grown in the Lower Rio Grande Valley and may be applied with these pesticides according to Norman and Sparks (1997) and Texas Department of Agriculture (1988); additional information on crop use from Farm Chemicals Handbook (1996). **NOTE: These pesticides can be used on other crops and/or may not be used as intended.**

² **Site 2** (An "a" superscript indicates only one measurement detected.) **NOTE: Caution must be exercised in interpreting one value with the mean comparison data.**

³ **Site 3** (An "a" superscript indicates only one measurement detected.) **NOTE: Caution must be exercised in interpreting one value with the mean comparison data.**

⁴ Non-Occupational Pesticide Exposure Study (NOPEs). Data from Jacksonville, Florida from Summer 1986. Maximum values are the 99th percentile from U.S. EPA (1990a).

⁵ Data from Jacksonville, Florida from Summer 1986. Maximum values are the 99th percentile from U.S. EPA (1990a).

⁶ NC/EPA Farm Occupational Exposure Study (NEFOES) in Camann et al. (1993).

⁷ Agricultural Health Pilot Study (AHPS). Detected values only from five farms; 24-h outdoor air sample collected on application days (Streicher, 1997).

⁸ Mean and maximum ambient air values from Baker et al. (1996); units converted from µg/m³ to ng/m³.

⁹ Mean and maximum ambient air values from Hoff et al. (1992); units converted from pg/m³ to ng/m³.

Table 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.

Metal	TAPP	Other Comparison Data					
		Urban Areas		Rural Areas		Remote Areas	
		Min	Max	Min	Max	Min	Max
Ba	5.4 ² 2.0 ³ 3.2 ⁴	S)))))	S)))))	S)))))	S)))))	S)))))	S)))))
Cd	0.1 ¹	0.5 ⁵	2.3 ⁵	0.15 ⁵	46 ⁵	0.09 ^{6a} 0.034 ^{6b} 0.016 ⁷	0.29 ^{6a} 0.155 ^{6b} 0.208 ⁷
Cu	0.7 ³ 0.9 ⁴	6.8 ⁵	120 ⁵	0.4 ⁵	150 ⁵	0.27 ^{6a} 0.27 ^{6b} 0.07 ⁷ 0.8 ⁹	1.58 ^{6a} 0.53 ^{6b} 0.91 ⁷ 0.9 ⁹
Fe	15.2 ² 52.1 ³ 441.0 ⁴				83 ⁸	5.5 ^{6a} 0.99 ^{6b} 1.7 ⁷	29.2 ^{6a} 7.86 ^{6b} 63.5 ⁷
Pb	0.9 ⁴	5.4 ⁵	147 ⁵	0.96 ⁵	51 ⁵	1.48 ^{6a} 0.61 ^{6b} 0.091 ⁷ 0.7 ⁹	4.76 ^{6a} 1.34 ^{6b} 1.03 ⁷ 1.1 ⁹
Mg	19.9 ¹ 636.0 ² 91.5 ³					80 ⁷	1540 ⁷

Metal	TAPP	Other Comparison Data					
		Urban Areas		Rural Areas		Remote Areas	
		Min	Max	Min	Max	Min	Max
Mn	2.1 ² 6.8 ³ 0.7 ³ 14.2 ⁴	1.9 ⁵	80 ⁵	0.2 ⁵	84 ⁵	0.36 ^{6a} 0.06 ^{6b} 0.11 ⁷ 2.6 ⁹	2.63 ^{6a} 0.506 ^{6b} 3.43 ⁷ 3.0 ⁹
Ni	12.0 ² 10.3 ³ 75.9 ⁴	2.4 ⁵	114 ⁵	<2 ⁵	48 ⁵	0.5 ^{6a} 0.023 ^{6b} 0.63 ⁷ 0.3 ⁹	1.47 ^{6b} 0.32 ^{6b} 1.42 ⁷ 0.4 ⁹
V	0.8 ⁴	16 ⁵	68 ⁵	1.1 ⁵	23 ⁵	0.2 ^{6a} 0.049 ^{6b} 0.1 ⁹	1.16 ^{6a} 0.111 ^{6b} 0.2 ⁹
Zn	2.6 ¹ 4.1 ² 6.4 ³ 4.9 ⁴	18 ⁵	280 ⁵	3 ⁵	311 ⁵	2.39 ^{6a} 0.28 ^{6b} 0.359 ⁷ 4.5 ⁹	13.9 ^{6a} 3.49 ^{6b} 3.93 ⁷ 5.9 ⁹

¹TAPP rain event November 1, 1996
²TAPP rain event November 18, 1996
³TAPP rain event December 21, 1996
⁴TAPP rain event December 27, 1996 (TAPP rain event December 26, 1996 measured but no metals detected)
⁵From a compilation of precipitation studies presented in Galloway *et al.*, 1982. Only rain or rain/snow study results are presented for comparison.
^{6a}From Church *et al.* (1984); results from Middle Atlantic Coast (Lewes, DE).
^{6b}From Church *et al.* (1984); results from Midwestern Atlantic Ocean (Beirmuda).
⁷From Helmers and Schrems (1995); shipboard samples in Tropical North Atlantic.
⁸Data based on one rainfall sample in Austin, TX (considered rural by Galloway *et al.* [1982]); analysis by X-ray fluorescence (Cooper *et al.*, 1976).
⁹Annual averages from summer 1993 to summer 1994 in the Great Lakes (Sweet *et al.*, 1998).

Table 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 $\mu\text{g}/\text{m}^3$.

<u>April 9, 1993)</u>		<u>TAPP (March 11 - April 16, 1996)</u>			<u>LRGVSS (March 18 -</u>		
<u>Compound</u>		<u>n</u>	<u>Minimum</u>	<u>Median</u>	<u>Maximum</u>	<u>n</u>	<u>Minimum</u>
<u>Median</u>	<u>Maximum</u>						
<u>cis-2-Pentene</u>		2	0.2	0.3	0.4	20	0.1
0.4	0.8						
<u>iso-Butane</u>		6	0.5	1.0	3.5	22	1.0
2.5	6.6						
<u>iso-Pentane</u>		6	2.4	3.1	8.0	22	1.3
6.2	17.9						
<u>m-Xylene & p-Xylene</u>		8	0.3	1.0	1.6	22	0.5
2.6	6.3						
<u>n-Butane</u>		22	1.4
5.8	19.9						
<u>n-Pentane</u>		6	0.4	1.3	3.4	22	0.8
3.1	10.8						
<u>n-Propyl benzene</u>		3	0.1	0.1	0.7	17	0.1
0.3	0.7						
<u>o-Xylene</u>		7	0.3	0.5	4.0	22	0.2
1.0	2.4						
<u>trans-2-Butene</u>		2	0.2	0.3	0.4	20	0.1
0.4	1.1						
<u>trans-2-Pentene</u>		2	0.3	0.4	0.5	17	0.1
0.6	1.7						
<u>Benzene</u>		9	0.4	0.7	1.6	22	0.6
1.3	3.2						
<u>Carbon Tetrachloride</u>		5	0.3	0.5	0.7	.	.
.	.						
<u>Cyclohexane</u>		1	0.3	0.3	0.3	19	0.1
0.4	0.9						
<u>Cyclopentane</u>		2	0.1	0.1	0.1	20	0.1
0.3	0.6						
<u>Ethyl benzene</u>		7	0.2	0.3	0.6	22	0.2
0.8	1.7						
<u>Isoprene</u>		1	0.1	0.1	0.1	4	0.2
0.3	0.4						
<u>Methyl cyclohexane</u>		1	0.2	0.2	0.2	21	0.1
0.5	1.1						
<u>Methyl cyclopentane</u>		3	0.3	0.6	0.6	22	0.2
0.7	1.7						
<u>Styrene</u>		1	0.6	0.6	0.6	11	0.4
0.7	2.5						
<u>Toluene</u>		9	0.5	1.4	2.8	22	0.8
2.9	7.8						
<u>1-Butene</u>		6	0.3	0.4	0.8	14	0.1
0.4	1.1						
<u>1-Pentene</u>		3	0.3	0.3	0.3	19	0.1
0.4	0.8						
<u>1, 1, 1- Trichloroethane</u>		9	0.4	0.6	1.3	.	.
.	.						
<u>1, 2, 4- Trimethyl benzene & sec- Butyl benzene</u>		4	0.7	1.1	2.4	19	0.3
1.3	3.5						

1, 3- Butadiene	0	.	.	.	15	0.1
0.3 0.7						
1, 3, 5- Trimethyl benzene	4	0.2	0.5	0.7	17	0.2
0.6 1.9						
2- Methyl - 1- pentene	0	.	.	.	8	0.1
0.2 0.5						
2- Methyl - 2- butene	3	0.2	0.4	0.7	21	0.1
0.7 2.0						
2- Methyl heptane	2	0.1	0.1	0.1	22	0.1
0.7 2.3						
2- Methyl hexane	2	0.2	0.3	0.4	22	0.2
0.8 1.7						
2- Methyl pentane	6	0.3	0.8	2.5	22	0.4
1.7 4.9						
2, 2- Dimethyl butane	2	0.2	0.3	0.5	22	0.1
0.5 1.6						
2, 2, 4- Trimethyl pentane	4	0.1	0.4	0.6	.	.
.						
2, 3- Dimethyl butane	5	0.1	0.7	1.8	22	0.1
0.5 1.3						
2, 3- Dimethyl pentane	0	.	.	.	15	0.1
0.4 0.9						
2, 3, 4- Trimethyl pentane	1	0.2	0.2	0.2	18	0.1
0.7 1.6						
2, 4- Dimethyl pentane	0	.	.	.	19	0.1
0.3 0.7						
3- Methyl - 1- butene	0	.	.	.	15	0.1
0.2 0.3						
3- Methyl hexane	2	0.3	0.4	0.4	22	0.5
1.0 2.3						
3- Methyl pentane	6	0.2	0.6	1.8	22	0.3
1.2 3.3						

Compound Median Maximum	<u>TAPP (July 14 - August 10, 1996)</u>			<u>LRGVES (July 21 - August 3, 1993)</u>		
	n	Minimum	Median	Maximum	n	Minimum
<u>cis</u> - 2- Pentene	1	0.1	0.1	0.1	14	0.1
0.1 0.2						
<u>iso</u> - Butane	5	0.1	0.4	1.5	14	0.5
0.8 1.4						
<u>iso</u> - Pentane	5	1.2	2.4	3.6	14	1.2
2.0 3.7						
<u>m</u> - Xylene & <u>p</u> - Xylene	6	0.04	0.6	3.3	14	0.6
1.0 4.1						
<u>n</u> - Butane	14	1.3
1.7 2.6						
<u>n</u> - Pentane	5	0.6	1.0	1.2	14	1.0
1.3 1.9						
<u>n</u> - Propyl benzene	2	0.1	0.1	0.1	10	0.1
0.2 0.4						
<u>o</u> - Xylene	5	0.2	0.6	1.3	14	0.2
0.5 1.3						
<u>trans</u> - 2- Butene	2	0.02	0.1	0.3	14	0.1
0.2 0.4						
<u>trans</u> - 2- Pentene	3	0.1	0.1	0.2	14	0.1
0.2 0.4						

Benzene	6	0.3	0.5	0.9	14	0.5
0.7	1.0					
Carbon Tetrachloride	6	0.5	0.7	1.1	14	0.6
0.7	0.7					
Cyclohexane	0	.	.	.	7	0.1
0.1	0.5					
Cyclopentane	1	0.03	0.03	0.03	14	0.1
0.1	0.2					
Ethylbenzene	3	0.4	0.4	0.5	14	0.2
0.4	1.0					

Compound	TAPP (July 14 - August 10, 1996)				LRGVES (July 21 -			
	August 3, 1993)		n	Minimum	Median	Maximum	n	Minimum
	Median	Maximum						
Isoprene	4	0.1	0.1	0.2	14	0.3		
0.5	0.7							
Methylcyclohexane	1	0.1	0.1	0.1	14	0.2		
0.3	0.5							
Methylcyclopentane	1	0.2	0.2	0.2	14	0.2		
0.3	0.5							
Styrene	2	0.1	1.6	3.0	8	0.4		
0.6	0.9							
Toluene	6	0.5	1.4	17.4	13	1.0		
1.4	2.2							
1-Butene	5	0.2	0.6	0.9	14	0.1		
0.4	0.5							
1-Pentene	1	0.1	0.1	0.1	14	0.1		
0.2	0.3							
1,1,1-Trichloroethane	6	0.4	0.7	1.5	14	0.9		
1.1	1.9							
1,2,4-Trimethylbenzene & sec-Butylbenzene	2	0.5	1.0	1.5	14	0.3		
0.5	1.0							
1,3-Butadiene	2				14	0.1		
0.1	0.2							
1,3,5-Trimethylbenzene	2	0.1	0.3	0.4	10	0.1		
0.2	0.4							
2-Methyl-1-pentene	1	0.1	0.1	0.1	6	0.1		
0.1	0.2							
2-Methyl-2-butene	5	0.1	0.2	0.2	14	0.1		
0.2	0.5							
2-Methylheptane	1	0.3	0.3	0.3	14	0.1		
0.2	2.5							
2-Methylhexane	1	0.1	0.1	0.1	14	0.5		
0.7	0.9							
2-Methylpentane	5	0.4	0.5	0.9	14	0.6		
0.9	1.6							
2,2-Dimethylbutane	1	0.1	0.1	0.1	12	0.1		
0.1	0.3							
2,2,4-Trimethylpentane	4	0.1	0.2	0.3	14	0.2		
0.4	0.9							
2,3-Dimethylbutane	5	0.1	0.1	0.4	14	0.1		
0.2	0.4							
2,3-Dimethylpentane	1	0.1	0.1	0.1	2	0.2		
0.2	0.2							
2,3,4-Trimethylpentane	1	0.1	0.1	0.1	8	0.1		
0.2	0.2							

2, 4- Dimethyl pentane	0	.	.	.	3	0. 1
0. 2 0. 2						
3- Methyl - 1- butene	1	0. 1	0. 1	0. 1	10	0. 1
0. 1 0. 1						
3- Methyl hexane	1	0. 2	0. 2	0. 2	14	0. 7
1. 0 1. 2						
3- Methyl pentane	5	0. 2	0. 2	0. 6	14	0. 2
0. 4 0. 8						

