5.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The Texas $PM_{2.5}$ Air Sampling and Analysis Study objectives were to acquire a $PM_{2.5}$ mass and chemical composition data base of specified accuracy, precision, and validity, and to examine spatial and temporal variations of $PM_{2.5}$ concentrations for five major cities in Texas, with the focus on the city of Houston. These objectives have been attained as described in the previous sections of the report. This section summarizes the conclusions from the measurement efforts and provides recommendations for future study.

5.1 Summary

5.1.1 Data Validity

Mass, ions (e.g., nitrate, sulfate, ammonium), crustal-related species (e.g., aluminum, silicon, potassium, calcium, manganese, iron, zinc) combustion-related species (e.g., organic carbon, elemental carbon, soluble potassium, chlorine, bromine), and trace elements (e.g., arsenic, selenium, cadmium, mercury, beryllium) were measured at the Texas sites with specified precision, accuracy, and validity for the period between 03/11/97 and 03/12/98.

Comparison of collocated $PM_{2.5}$ samplers (DRI MEDVOL fitted with a Bendix $PM_{2.5}$ cyclone) were made at three of outdoor sites, HT, H3 and HC, as well as between samplers placed indoors (HS) and outdoors (HW) at the Shell Westhollow Technology Center. The average difference in $PM_{2.5}$ mass measurements between the collocated and primary samplers at the three outdoor sites ranged from –0.3 to 0.8 $\mu g/m^3$. Collocated precisions are comparable to or better than collocated measurements from other studies (Chow, 1995).

Comparison of sampler data from the indoor and outdoor sites at the Shell Westhollow Technology Center showed the indoor samples to be on average about 8.0 $\mu g/m^3$ lower than the samples simultaneously taken outdoors.

The sum of measured chemical concentrations accounted for approximately 70% of the $PM_{2.5}$ mass with a correlation coefficient of 0.95. Tests for physical consistency were performed for: 1) sulfate versus total sulfur, 2) soluble potassium versus total potassium, 3) ammonium balance, and 4) anion and cation balance. These comparisons identified a few outliers that were explainable by the previously applied flags. The sulfate versus total sulfur comparison gives a ratio of 2.8, which implies that nearly all of the $PM_{2.5}$ sulfur was present as sulfate. The soluble versus total potassium comparison showed that the water soluble fraction accounts for 60% of the total potassium.

Calculated and measured $PM_{2.5}$ ammonium were consistent with each other, with correlation coefficients exceeding 0.96. The comparison also implies that the majority of the sulfate was neutralized and in the form of ammonium sulfate. The anion and cation balance demonstrate that all of the ionic measurements were highly correlated ($r = 0.98$) with a slope of 0.89. A majority of the cations can be balanced with anions on molar equivalent basis with ± 13% of unity.

5.1.2 Characteristics of PM Mass and Chemistry

Only one exceedance of the 24-hour average National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ of 65 $\mu g/m^3$ was found during the study period from 03/11/97 to 03/12/98, occurring at the El Paso (EP) site on 12/18/97. Annual average of the scheduled days shows $PM_{2.5}$ mass ranging from 9.6 ± 4.5 $\mu g/m^3$ at the HT collocated site (denuder on) to 18.0 ± 8.4 $\mu g/m^3$ at the HC collocated site (denuder on).

Only two sites H3 and HC have scheduled days annual average concentrations exceeding the annual NAAQS of 15 $\mu g/m^3$, but most of the sites (except CC, HG and SA) have average concentrations within 20% of the standard. At least three years of $PM_{2.5}$ monitoring with federal reference methods are needed to determine attainment or non-attainment of the $PM_{2.5}$ standards.

The comparison of indoor versus outdoor samples at the Shell Westhollow Technology Center showed that on average $PM_{2.5}$ mass concentrations indoors was about one-third the outdoors concentration.

The most abundant chemical species (>1 $\mu g/m^3$) were ions (e.g., nitrate, sulfate, ammonium) and carbon (e.g., organic and elemental carbon). Nitrate concentrations ranged from 0.0 ± 0.03 (H3, 09/01/97) to 9.5 ± 0.6 $\mu g/m^3$ (EP, 12/18/97), while sulfate ranged from 0.5 ± 0.04 (H7, 09/13/97) to 13.5 ± 0.9 $\mu g/m^3$ (HC, collocated with denuder on, 09/01/97), and ammonium ranged from 0.1 ± 0.03 (HG, 07/27/97) to 4.9 ± 0.3 $\mu g/m^3$ (H3, 03/23/97).

Total carbon (organic carbon + elemental carbon) was the most abundant species, accounting for over 27% of the mass. Organic carbon ranged from 0.0 ± 0.9 (H3, 06/21/97) to 20.1 ± 1.5 $\mu g/m^3$ (EP, 12/18/97) and elemental carbon ranged from 0.1 ± 0.04 (H7, 09/13/97) to 7.9 ± 0.5 $\mu g/m^3$ (EP, 12/18/97). The indoor site (HS) had an even larger percentage of mass attributable to total carbon, nearly 52%.

Sulfate was the second most abundant species, accounting for slightly less than 27% of the mass. However, if all sulfate were assumed to be ammonium sulfate, ammonium sulfate would be the largest constituent, accounting for approximately 35% of the mass.

5.2 Conclusions

Several conclusions can be drawn from the analysis of $PM_{2.5}$ concentrations in the study area. With respect to ambient measurements, a validated data base with specified precision, accuracy, and validity has been established for the 03/11/97 to 03/12/98 study period.

Annual average mass concentrations at most of the sites are at or near (within 20%) the annual NAAQS of 15 $\mu g/m^3$.

A majority of the nitrate is lost due to volatilization during warm non-winter periods. The fraction of total particulate nitrate contributed by volatilized nitrate did not show a

significant difference with the aluminum denuder on or off, indicating that the sampler surface is acting as an efficient denuder.

Total carbon is the largest single contributor to $PM_{2.5}$ mass in Texas, accounting for about 27%. Sulfate was the second largest contributor, also accounting for about 27%. If all sulfate were presumed to be ammonium sulfate, then ammonium sulfate would be the largest contributor, accounting for about 35%.

5.3 Recommendations

Two more years of $PM_{2.5}$ mass data will be necessary to determine attainment or non-attainment of the $PM_{2.5}$ NAAQS. With most states setting up monitoring programs to comply with the new $PM_{2.5}$ standard, these data should be available in the future.

To better understand the contribution of volatilized nitrate to total particulate nitrate and the effectiveness of the aluminum denuder, further study with collocated comparisons of denuded versus non-denuded samples would be needed. Retrieval and refrigeration of the samples immediately after sampling would provide the most accurate concentration information.

To better characterize the carbonaceous aerosol and more accurately determine its contribution to the percentage of the measured mass, organic speciation analysis should be performed on the samples in addition to the analyses currently undertaken.

6.0 BIBLIOGRAPHY

Berkson, J. (1950) Are there two regressions? *J. Am. Stat. Assoc.* **45,** 164-180.

Bevington, P.R. (1969) *Data Reduction and Error Analysis for the Physical Sciences.* McGraw Hill, New York, NY.

Chow, J.C., Liu, C.S., Cassmassi, J.C., Watson, J.G., Lu, Z., and Pritchett, L.C. (1992a) A neighborhood-scale study of PM_{10} source contributions in Rubidoux, California. *Atmos. Environ.* **26A,** 693-706.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., and Richards, L.W. (1992b) PM_{10} source apportionment in California's San Joaquin Valley. *Atmos. Environ.* **26A,** 3335-3354.

Chow, J.C., Watson, J.G., Bowen, J.L., Gertler, A.W., Frazier, C.A., Fung, K.K., and Ashbaugh L. (1993a). A sampling system for reactive species in the western U.S. In *Sampling and Analysis of Airborne Pollutants,* E. Winegar and L.H. Keith, Eds. American Chemical Society, Washington, D.C., pp. 209-228.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., and Richards, L.W. (1993b) PM_{10} and $PM_{2.5}$ compositions in California's San Joaquin Valley. *Aerosol Sci. Technol.* **18,** 105-128.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., and Purcell, R.G. (1993c) The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, evaluation and applications in U.S. air quality studies. *Atmos. Environ.* **27A,** 1185-1201.

Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z., Lawson, D.R., and Ashbaugh, L.L. (1994a) Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California Air Quality Study. *Atmos. Environ.* **28,** 2061-2080.

Chow, J.C., Fujita, E.M., Watson, J.G., Lu, Z., Lawson, D.R., and Ashbaugh, L.L. (1994b) Evaluation of filter-based aerosol measurements during the 1987 Southern California Air Quality Study. *Environmental Monitoring and Assessment* **30,** 49-80.

Chow, J.C. (1995) Critical review: Measurement methods to determine compliance with ambient air quality standards for suspended particles. *JAWMA* **45,** 320-382.

Chow, J.C., Watson, J.G., Lowenthal, D.H., and Countess, R.J. (1996a) Sources and chemistry of PM_{10} aerosol in Santa Barbara County, CA. *Atmos. Environ.* **30,** 1489-1499.

Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H., and Magliano, K.L. (1996b) Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. *Atmos. Environ.* **30,** 2079-2112.

Chow, J.C. and Watson, J.G. (1998a) Ion chromatography. In *Elemental Analysis of Airborne Particles,* Landsberger, S. and Creatchman, M., Eds. Gordon and Breach, Newark.

Chow, J.C. and Watson, J.G. (1998b) Guideline on speciated particulate monitoring. Prepared for U.S. EPA, Research Triangle Park, NC, Desert Research Institute, Reno, NV.

Chow, J.C., Zielinska, B., Watson, J.G., Fujita, E.M., Richards, H.W., Neff, W., Dietrich, D., and Hering, S.V. (1998) Northern Front Range Air Quality Study. Volume A: Ambient measurements. Prepared for Colorado State University, Cooperative Institute for Research in the Atmosphere, Fort Collins, CO, Desert Research Institute, Reno, NV.

Dzubay, T.G., Morosoff, N., Whitaker, G.L., Yasuda, H. (1981) Evaluation of polymer films as standards for x-ray fluorescence spectrometers. In *Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis.* Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Hidy, G.M. (1985) Jekyll Island meeting report. *Environ. Sci. Technol.* **19,** 1032-1033.

Hildemann, L.M., Markowski, G.R., and Cass, G.R. (1991) Chemical composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **25,** 744-759.

Kendall, M.G. (1951) Regressions, structure and functional relationship, Part I. *Biometrika* **39,** 96-108.

Kendall, M.G. (1952) Regressions, structure and functional relationship, Part II. *Biometrika* **39,** 96-108.

King, D.E. (1977) Evaluation of interlaboratory comparison data on linear regression analysis. In *Methods and Standards for Environmental Measurement,* Kirchoff, W.H., Ed. NBS Publication 464, Gaithersburg, MD.

Lee, K.W. and Ramamurthi, M. (1989) *Aerosol Measurement: Principles, Techniques and Applications.*

Lippmann, M. (1989) Calibration of air sampling instruments. In *Air Sampling Instruments For Evaluation of Atmospheric Contaminants,* Hering, S.V., Ed. American Conference of Governmental Industrial Hygeinists, Cincinnati, OH, pp. 73-111.

Madansky, A. (1959) The fitting of straight lines when both variables are subject to error. *J. Am. Stat. Assoc.* **54,** 173-205.

Turpin, B.J., Huntzicker, J.J., and Adams, K.M. (1990) Intercomparison of photoacoustic and thermal-optical methods for the measurement of atmospheric elemental carbon. *Atmos. Environ.* **24A,** 1831-1835.

U.S.EPA (1997a) National ambient air quality standards for particulate matter - final rule. *Federal Register* **62,** 38651-38760.

U.S.EPA (1997b) Compilation of air pollutant emission factors. Volume I: Stationary point and area sources. U. S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC.

Watson, J.G., Lioy, P.J., Mueller, P.K. (1989) The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants,* Hering, S.V., Ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 51-57.

Watson, J.G. and Chow, J.C. (1993) Ambient air sampling. In *Aerosol Measurement: Principles, Techniques and Applications,* Willeke, K. and Baron, P.A., Eds. Van Nostrand, Reinhold, New York, NY, pp. 622-639.

Watson, J.G. and Chow, J.C. (1994) Particle and gas measurements on f ilters. In *Sampling of Environmental Materials for Trace Analysis,* Markert, B., Ed. VCH-Publisher, Weinheim, New York, Tokyo, pp. 83-175.

Watson, J.G., Lioy, P.J., Mueller, P.K. (1995) The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants,* Cohen, B. and Hering, S.V., Eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 187-194.

Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B., Richards, L.W., Neff, W., and Dietrich, D. (1998) Northern Front Range Air Quality Study. Final report. Prepared for Colorado State University, Cooperative Institute for Research in the Atmosphere, Fort Collins, CO, Desert Research Institute, Reno, NV. XRF

CITATIONS IN TEXT

Berkson, 1950 3-12
Bevington, 1969 3-3
Chow and Watson, 1998a 2-6
Chow and Watson, 1998b 2-6
Chow et al., 1992a 4-28
Chow et al., 1992b 4-28
Chow et al., 1993 1-1
Chow et al., 1993a 2-6, 3-1
Chow et al., 1993b 4-28
Chow et al., 1994b 3-10
Chow et al., 1994c 4-28
Chow et al., 1996a 4-28
Chow et al., 1996b 4-28
Chow et al., 1998 3-6
Chow, 1995 ..... 2-6, 5-1
Dzubay et al., 1981 3-6
Hidy, 1985 3-1
Hildemann et al., 1991 4-32
Kendall, 1951 3-12
Kendall, 1952 3-12
King, 1977 3-10
Lee and Ramamurthi, 1993 2-6
Lippmann, 1989 2-6
Madansky, 1959 3-12
Turpin et al., 1990 4-32
U.S. EPA, 1997a 1-1
U.S. EPA, 1997b 1-1
Watson and Chow, 1993 2-6
Watson and Chow, 1994 2-6
Watson et al., 1989 3-1
Watson et al., 1995 ..... 3-1, 3-3
Watson et al., 1998b 2-6, 3-6

Energy and Environmental
Engineering Center

From Jim Price
1/27/1999 SWC
For NARSTO Archiving

Final Report for the Texas $PM_{2.5}$ Sampling and Analysis Study

(March 11, 1997, through March 12, 1998)

Document No. 6570-685-7770.1F

December 15, 1998

PREPARED BY:

Dr. Richard J. Tropp
Mr. Steven D. Kohl
Dr. Judith C. Chow
Mr. Clifton A. Frazier

Desert Research Institute
P.O. Box 60220
Reno, NV 89506

and

TRC Environmental Corporation
6340 Quadrangle Dr., Suite 200
Chapel Hill, NC 27514

PREPARED FOR:

Manuel Aguirre, Jr., Monitoring and Analysis Coordinator
Bureau of Air Quality Control
City of Houston
7411 Park Place Blvd.
Houston, TX 77087