7.9 CHARACTERIZATION AND ANALYSIS OF ULTRAFINE AND FINE PARTICLES AT A FOREST SITE NEAR THE GREAT SMOKY MOUNTAINS NATIONAL PARK

Meng-Dawn Cheng[*1] and Roger L. Tanner[2]
[1]Oak Ridge National Laboratory, Environmental Sciences Division, Oak Ridge, TN 37831, USA
[2]Tennessee Valley Authority, Environmental Research Center, Muscle Shoals, AL 35662, USA

1. INTRODUCTION

Most of the ambient particles in urban atmospheres are in the ultrafine size range (Peters *et al.,* 1997*;* Woo *et al*., 2001), that is, with diameters less than 100 nm (=0.1 μm). Ultrafine particles have been observed during photochemical and nitrate radical reactions in outdoor smog chambers (c.f., Heisler and Friedlander, 1977; McMurry and Friedlander, 1979; Flagan *et al*., 1991). Wehner *et al*. (2000) observed high levels of ultrafine particles during the millennium fireworks display in Germany. Ultrafine particles have also been measured in remote areas such as the tropical boundary layer (Clarke *et al*., 1992) and in polar areas (Pirjola *et al*., 1998). On average the chemical composition of fine airborne particulate matter in East Tennessee in summer was approximately 56% ammonium sulfates, 30% organic carbon, 6% elemental carbon, 0.4% ammonium nitrate, and the remaining fraction (≅ 7%) undetermined (Tanner and Parkhurst, 2001). The Great Smoky Mountains National Park (GSMNP) in eastern Tennessee is a Class I region, and has been visited annually by more than 10 million people during the past few years, making it the most popular national park in the continental United States. Mobile source emissions from nearby urban areas (e.g., Knoxville) and interstate highways (I-40, I-75, I-81), and stationary source emissions from industrial activities and coal-fired power plants are potential contributors of pollutants to the park. These sources emit precursor gases such as nitrogen oxides (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO), and possibly hazardous air pollutants. Forested areas in the GSMNP give off a series of biogenic organic compounds (principally isoprene) as well as water vapor. The combination of man-made and biogenic emissions and abundant sunshine and water vapor leads to summertime production rates and levels of ultrafine particles that are relatively high in the vicinity of the GSMNP.

Corresponding Author. Mengdawn Cheng, Oak Ridge National Laboratory, Environmental Sciences Division, Oak Ridge, TN 37831-6038, e-mail address: chengmd@ornl.gov.

2. DESCRIPTION OF DATA

During a 4-week intensive field campaign in the summer of 2000, a number of measurements were made continuously at Look Rock, Tennessee, a sampling site operated by the Tennessee Valley Authority (TVA) and collocated with the IMPROVE network site operated by the National Park Service (NPS). The Look Rock air quality monitoring station is located in a rural area in Blount County, TN (see Fig. 1) at 35.6°N, 83.9°W, and 793 M above mean sea level. The land use pattern at the site is predominantly mixed deciduous forest. On-site meteorological measurements during the field campaign included wind speed, direction, solar radiation, temperature, and precipitation. TVA measurements included the following gaseous species: nitrogen oxide (NO), NO_2, NO_y, SO_2, O_3, and CO. Aerosol mass composition was measured on filter samples collected using 2 collocated Federal Reference Method (FRM) samplers, and by a PC-BOSS sampler (Modey *et al*., 2001; Ding et al., 2002) which quantified semi-volatile as well as non-volatile organic aerosol components. A TEOM continuous $PM_{2.5}$ mass monitor was also operated by TVA personnel during this period. The size distribution of particles of diameter between 15 and 626 nm was taken continuously using a TSI Scanning Mobility Particle Spectrometer (SMPS) equipped with a long differential mobility analyzer and a ultrafine condensation particle counter. The SMPS was operated by Oak Ridge National Laboratory (ORNL) personnel. The observable parameters are listed in Table 1, and the sampling frequencies of these measurements are also described in the same table.

3. RESULTS

Analyzing the relationship of variables in a large multi-variate data set typically requires the use of a technique such as factor analysis (Anderson, 1984). Our intent was to resolve the complex relationships among the measured number concentrations as a function of particle size (from 10 to 626 nm) and the mass concentrations of gaseous species and meteorological variables. A classical factor analysis using the varimax rotation technique was performed using StatGraphics® for Windows® (version 4.0) on the 30-min averaged concentration data from JD230 to JD252. The 8 summed number concentrations [Σ(15-30), Σ(31-40), Σ(41-50), Σ(51-60), Σ(61-100), Σ(101-200), Σ(201-400), Σ(401-626)], CO, NO_2, NO_y, O_3, SO_2, radiation, mean wind speed and $PM_{2.5}$ mass were used in the factor analysis. As shown in Table 3, six (6) factors were resolved using this data set, in which each factor has an eigenvalue greater than 1.0, a cutoff value chosen for distinguishing signal from noise embedded in the measurement data. The 6-factor model accounts for 79.7% of the total variance embedded in the data. Additional tests showed that there to be no advantage in explaining the relationships among the 17 variables by including additional factors in the analysis.

The factor-loading matrix is shown in Table 2 where significant loadings are in bold. The number concentrations of ultrafine particles are grouped into

Factor 1. The loadings for particles smaller than 60 nm were greater than 0.8; the loading for Σ(61-100) was 0.71 statistically significant. Statistically, this factor is independent of the gas variables (i.e., carbon monoxide, nitrogen species, ozone, and sulfur dioxide) included in the factor analysis. The reasons why variability in the concentrations of ultrafine particles ($D_p \leq 100$ nm) appears in a single factor are unclear at this point without, for example, additional data such as the chemical composition of the ultrafine particles. This issue should be pursued in future studies, especially if ultrafine particles are shown conclusively to cause adverse impacts to human health. Factor 2 has significant loadings in CO, Σ(101-200), Σ(201-400) and $PM_{2.5}$ mass (see column 3 of Table 4). $PM_{2.5}$ mass and number concentrations of accumulation mode particles [i.e., Σ(101-200) and Σ(20l1-400)] show up most strongly. The loading for CO was only 0.66—lower than that associated with particles. The variables, accumulation-mode particles, $PM_{2.5}$ and CO, are signatures for regional transport of pollutants. Based on these significant loadings, we assigned this factor to regional transport. Ozone is known to be a regionally transported secondary pollutant, especially in summer and at higher altitudes, but its mean transport distance is not as large as secondary particles. Since its regional transport is not as dominant, it has a lower and statistically not significant loading on this factor. Significant loadings of Factor 3 were found to be associated mainly with gaseous species that included NO_2 and NO_y, both of whose values were ≥ 0.8. There was also a mild CO loading (0.51) and another smaller loading from SO_2 (0.59). Strong loadings in nitrogen species and a mild loading on SO_2 indicated that Factor 3 is associated with the primary gaseous emissions. These emissions likely include point and "immediate area" sources of NO_2, NO_y, and SO_2. It was interesting that CO has mild loadings in Factor 2 (an assigned regional transport factor) and this Factor 3 (an assigned local primary emission factor). Tropospheric CO mixing ratios are ranging from 40 to 200 ppbv (p. 86, Seinfeld and Pandis, 1998). However, the minimum and maximum CO values observed in our campaign were 79 and 441 ppbv, respectively, with a median of 169 ppbv. The median concentration of our CO data is at the higher end of the mixing ratio range reported by Seinfeld and Pandis (1998) indicating possible source contributions additional to the Tropospheric background. Note that ozone is completely absent (loading = 0.00) in Factor 3, and that neither the particle number concentrations nor $PM_{2.5}$ mass has significant loadings. Hence, variability in primary gaseous emissions including point sources and mobile sources in the East Tennessee valley could be the primary contributing sources of Factor 3. A significant loading in Factor 4 includes mean wind speed (loading = 0.85) and a mild loading (0.62) for ozone. This loading pattern suggests that variability in the 30-min mean wind speed could not explain any variability of the particle variables. The ability to use mean wind speed to explain ozone variation was moderate as seen in the loading values. As previously discussed for Factor 2, ozone is a secondary species transported over a sub-regional scale compared to secondary particles (in the accumulation mode).

In Factor 4, ozone was decoupled from particle loadings and other primary gaseous emissions. Since mean wind speed was the single “statistically” significant factor loading, this factor was assigned as a unique factor of mean wind transport, possibly responsible for the ozone variation observed at the site. A single strong loading for Factor 5 is solar radiation (loading = 0.90). Note that although the loading for SO_2 on Factor 5 was 0.44, the second largest on this factor, this loading is statistically insignificant. With the low factor signal on SO_2 and all other variables except solar radiation, we attribute this factor to the variation of solar variation alone. Interestingly, NO (loading = 0.95) was the single significant loading on Factor *6*. We think that this was associated with the data quality of this particular variable. Note that from Table 2 the data recovery rate for this variable was 48%, about 30% lower than other variables. Thus, it is likely this factor simply isolate the variable from others and we should attribute this factor as a unique factor meaning it could not be explained by any physical relationships with other variables we have included.

4. SUMMARY

A varimax-rotation factor analysis was performed to explore the relationship of the fine and ultrafine particle number concentrations, the gaseous species concentration, the mean wind speed, and the solar radiation. A 6-factor model was found to best resolve 79.7% of the variability embedded in the data. The model suggests that 31.4% of the data variability could be explained by ultrafine particles (the diameters smaller than or equal to 100 nm). It was difficult to further elucidate this factor without chemistry information of the ultrafine particles. However, no gas species were loaded on Factor 1, indicating that ultrafine particle concentrations observed in this study were not associated with primary source emissions of NO_x and SO_2. The decoupling of the ultrafine particles from the fine particles also implies that the former ones might have been produced and transported to the site by separated mechanisms from those of fine particles. The second factor included the $PM_{2.5}$ mass concentration and the number concentrations of particles in the diameter range of 101 to 400 nm.

The loading pattern on Factor 2 led to the conclusion that this factor was contributed by regional transport. The third factor includes CO, NO_2, reactive odd nitrogen (NO_y), and SO_2 that were contributed by primary source emissions. The mean wind speed and ozone (with a mild loading) were loaded in Factor 4 that was tentatively labeled as mean wind transport. Identification of this factor led to an observation that ozone transport to the site may be in part decoupled from the regional transport factor of fine particles (i.e., Factor 2). Solar radiation was singly included in the fifth factor indicating this is a unique factor. The quality of

NO data was marginal and this variable was placed by the model into Factor 6.

5. REFERENCES

Aalto, P., K. Hameri, E. Becker, R. Weber, J. Salm, J.M. Makela, C. Hoell, C.D. O'Dowd, H. Karlsson, H. C. Hansson, M. Vakeva, I. K. Koponen, G. Buzorius, M. Kulmala (2001) *Tellus B*., 53(4): 344-358.

Anderson, T. W. (1984) *An Introduction to Multivariate Statistical Analysis*, 2nd Ed., John Wiley & Sons, New York, NY.

Clarke, A. D. (1992) Atmospheric Nuclei in the Remote Free Troposphere, *J. Atmos. Chem*., 14: 479-488.

Ding, Y. M., Y. B. Pang, D. M. Eatough, N. L. Eatough, and R. L. Tanner (2002) High-Volume Diffusion Denuder Sampler for the Routine Monitoring of Fine Particulate Matter: II. Field Evaluation of the PC-BOSS, *Aerosol Sci. & Technol*., 36: 383-396.

Flagan, R. C., S.-C. Wang, F. Yin, J. H. Seinfeld, G. Reischl, W. Winklmayr, and R. Karch (1991) Electrical Mobility Measurements of Fine-Particle Formation during Chamber Studies of Atmospheric Photochemical Reactions, *Environ. Sci. Technol*., 25: 883-890.

Heisler, S. and Friedlander, S. K. (1977) Gas-to-Particle Conversion in Photochemical Smog: Aerosol Growth Laws and Mechanisms for Organics, *Atmos. Environ*. 11:157-168.

Kulmala, M., K. Hämeri, P. P. Aalto, J. M. Mäkelä, L. Pirjola, E. D. Nilsson, G. Buzorius, Ü. Rannik, M. Dal Maso, W. Seidl, T. Hoffman, R. Janson, H.-C. Hansson, Y. Viisanen, A. Laaksonen, and C. D. O'Dowd (2001) Overview of the International Project on Biogenic Aerosol Formation in the Boreal Forest (BIOFOR), *Tellus*, 53B(4): 324-343.

Modey, W. K., Y. Pang, N. L. Eatough, D. J. Eatough (2001) Fine Particulate ($PM_{2.5}$) Composition in Atlanta, USA: Assessment of the Particle Concentration-Brigham Young University Organic Sampling System, PC-BOSS, During the EPA Supersite Study, *Atmos. Environ*., 35: 6493-6502.

McMurry, P. H. and Friedlander, S. K. (1979) New Particle Formation in the Presence of an Aerosol*, Atmos. Environ.* 13:1,635-1,651.

Peters, A., Wichmann, H.E., Tuch, T., Heinrich, J., and Heyder, J. (1997) Respiratory effects are associated with the number of ultrafine particles, *Am. J. Respir. Crit. Care Med.*, 155:1,376-1,383.

Pirjola, L., A. Laaksonen, P. Aalto, and M. Kulmala (1998) Sulfate aerosol formation in the Arctic Boundary Layer, *J. Geophys. Res*., 103: 8,309-8,322

Seinfeld, J. and S. Pandis (1998) *Atmospheric Chemistry and Physics*, John Wiley & Sons, New York, NY.

Tanner, R. L. and W. J. Parkhurst (2001) Sources of PM2.5 Carbonaceous Aerosols at a Site near the Great Smoky Mountains National Park, poster paper presented at the 20th National Meeting of the American Association for Aerosol Research held in Portland, OR, in October.

Wehner, B., A. Wiedensohler, and J. Heintzenberg (2000) Submicrometer Aerosol Size Distributions and Mass Concentration of the Millennium Fireworks 2000 in Leipzig, Germany, *J. Aerosol Sci*., 31:1,489-1,493.

Woo, K. S., D. R. Chen, D. Y. H. Pui, and P. H. McMurry (2001) Measurement of Atlanta Aerosol Size Distributions: Observations of Ultrafine Particle Events*, Aerosol Sci. and Technol.*, 34: 75-87.

6. ACKNOWLEDGEMENT

The authors acknowledged the assistance of Thomas Wainman of the Oak Ridge Associated Universities and Solomon Bairai, Elizabeth Gray, Ken Olszyna, David Phillips, Larry Shelton, Myra Valente, Ray Valente, and Mark Wolfe of TVA in acquiring the data. Thomas Wainman was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education.

The DOE/Fossil Energy/Natural Gas and Oil Technology Program, DOE's National Energy Technology Laboratory, EPRI, and TVA's Public Power Institute provided partial funding of this work. The authors acknowledge the thorough and in-depth comments of two anonymous reviewers who helped improve the quality of this manuscript. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

Table 1. Summary of Continuous Measurements

PARAMETERS	INTERVAL	INSTRUMENT	COMMENTS
Ozone, O_3	1 min. avg.	TEII 49	Full scale range: 0 - 200 ppb; Zero: Clean, dry air; Span: 160 ppb; Precision: 40 ppb; Time Constant: 30 sec
NO/NO_2	1 min. avg.	TEII 42S	Full scale range: 0 – 50 ppb; Span (w/NO): 20 ppb; Addition (w/NO) 3x: 5 ppb; Zero: Night readings; Time Constant: 10 sec
NO_y	1 min. avg.	TEII 42S	Full scale range: 0 – 100 ppb; Span (w/NO): 40 ppb; Addition (w/NO) 3x: 10 ppb; Addition (w/NPN)3x: 50 ppb; Zero 4x: Clean dry air; Time Constant: 10 sec
CO	1 min. avg.	TEII 48S	Full scale range: 0 - 1000 ppb; Span: 800 ppb; Addition (w/CO) 2x: 200 ppb; Zero 12x: Ambient native zero gas Time Constant: 20 sec
SO_2	1 min. avg.	TEII 43S	Full scale range: 0 – 100 ppb; Addition (w/SO_2) 2x: 20 ppb; Zero 2x: Clean dry air; Time Constant: 20 sec Full Scale Voltage Output: 10V
Wind Speed	1 min. avg.	R.M. Young	10 Meters above ground
Wind Direction	1 min. avg.	R.M. Young	10 Meters above ground
Air Temperature	1 min. avg.	Platinum RTD	10 Meters above ground
Humidity	1 min. avg.	Rotronics	10 Meters above ground
Total UV Radiation	1 min. avg.	Eppley	9 Meters above ground
Particle size distribution	6 min. average	TSI SMPS 3080LDMA	Inlet at 10 Meters above ground, *data* in # cm^{-3}.
PM2.5 mass concentration	5 min. average	RP TEOM	

Table 2. Factor Loading Matrix after Varimax Rotation

Variable	F1	F2	F3	F4	F5	F6	Communality
CO	0.00	**0.66**	0.51	0.12	0.09	-0.21	0.75
Mean Wind Speed	0.04	0.00	0.14	**0.85**	-0.09	0.01	0.75
NO	0.00	-0.06	0.05	-0.01	0.08	**0.95**	0.91
NO_2	0.17	-0.07	**0.91**	-0.09	-0.18	-0.01	0.90
NO_y	0.19	0.17	**0.81**	0.26	0.13	0.22	0.85
Ozone	0.15	0.48	0.00	**0.62**	0.24	-0.18	0.73
Radiation	-0.06	0.02	0.02	-0.03	**0.90**	0.09	0.82
SO_2	0.18	0.21	0.59	0.05	0.44	-0.09	0.63
Σ(101-200)	0.33	**0.86**	0.14	-0.05	0.06	-0.01	0.88
Σ(15-30)	**0.81**	-0.07	0.12	0.11	0.12	-0.06	0.71
Σ(201-400)	0.08	**0.94**	0.02	0.11	-0.01	0.02	0.91
Σ(31-40)	**0.94**	-0.02	0.08	0.06	0.04	-0.04	0.90
Σ(401-600)	-0.02	0.49	-0.06	0.44	-0.03	0.20	0.48
Σ(41-50)	**0.96**	0.06	0.06	0.03	-0.05	0.00	0.92
Σ(51-60)	**0.91**	0.13	0.10	0.00	-0.10	0.04	0.86
Σ(61-100)	**0.71**	0.41	0.21	-0.09	-0.04	0.07	0.73
$PM_{2.5}$ Mass	-0.06	**0.90**	0.03	0.08	0.03	-0.06	0.82

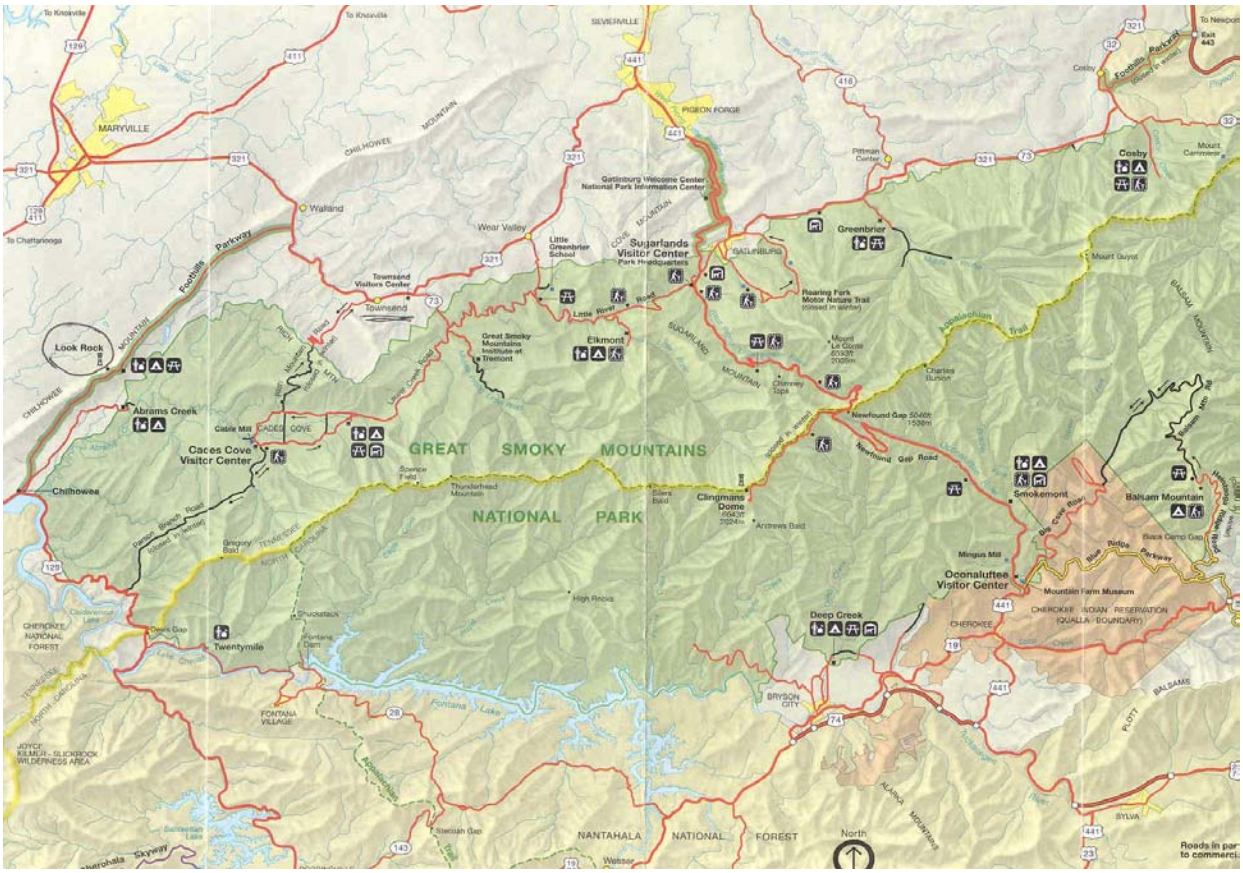

Fig. 1. Map of the Great Smoky Mountains National Park, surrounding areas, and location of the Look Rock Sampling Station