10.2

MEASUREMENT OF TRACE GASES AND $PM_{2.5}$ MASS AND COMPOSITION NEAR THE GROUND AND AT 254 M AGL DURING TEXAQS 2000

Karsten Baumann *, Frank Ift, Jing Zhi Zhao, Mike Bergin, Armistead Russell
Georgia Institute of Technology, Atlanta, Georgia

1. INTRODUCTION

Continuous (1 min) measurements of various meteorological parameters, trace gases (NO, NO_x, NO_y, CO, SO_2, and O_3), and discrete, 6 to 24 h integrated filter-based measurements of $PM_{2.5}$ mass and composition, including aerosol gases (NH_3, HONO, HNO_3, HCl, SO_2, and light organic acids), were made at the LaPorte municipal airport (LP), near the Houston ship channel, during TexAQS2000. These discrete measuremnts were made by means of a three-channel Particle Composition Monitor (PCM) used in previous experiments carried out in the Southeastern U.S. within the framework of the Southern Oxidant Study (SOS), and described in greater detail by Baumann et al. (2001). Similar PCM measurements supplemented by semi-continuous (30 min) O_3 and TEOM mass measurements were made on the 62nd floor of the Williams Tower (WT), 254 m agl, and ~12 km west of downtown Houston. The quality of the measurements is briefly assessed here, and the results are compared and investigated for systematic differences induced by the difference in sampling height above ground.

2. METHODS

The measurement principle of our PCM is based on successive separation of particles larger than 2.5 microns aerodynamic diameter, followed by the separation of gaseous species from the particles prior to $PM_{2.5}$ collection on Teflon membrane and quartz fiber filters backed by specifically impregnated filters as backup adsorbers. The sampler operates three channels each controlled at a nominal flow rate of 16.7 lpm. $PM_{2.5}$ separation is achieved by standard, Teflon coated cyclone heads, after the sample air is pulled through 30 cm long, 14 mm ID, Teflon coated inlet tubes. Separation of the gases is achieved by means of appropriately coated denuders. During TexAQS2000 a phosphorous acid coating solution was used in channel 1, which selectively removed NH_3, while a sodium carbonate solution was used in channel 2 capturing the acidic gases HNO_3, HONO, SO_2, HCl, acetic, formic, and oxalic acids. Denuders were 3-annuli edged glass tubes that have a theoretical removal efficiency, based on molecular diffusion assuming 100% adsorption of 99.9% for NH_3, and 99.7% for HNO_3 at 0.1s residence time (Possanzini et al., 1983). The effective denuder efficiencies are actually governed by the adsorption ability and sticking coefficient of the individual species, and were experimentally determined by extraction and analysis of two identical denuders set-up in series; see Table 1. Atmospheric concentrations of all the above gas-phase compounds were determined for each sample collected during the first half of the study, considering the listed denuder efficiencies, with exception of HONO and HNO_3, for which the amounts of nitrite and nitrate found on the second denuder were considered artifact due to heterogeneous reactions involving NO_2, O_3, and water vapor according to Ferm and Sjodin (1985); see Baumann et al. (2001) for details. Therefore, HONO and HNO_3 were reported as differences from the amounts found in the extractions of the second from the first denuder. Correspondingly coated paper filters were placed downstream of the Teflon filters in order to capture volatilization losses

---

* *Corresponding author address:* Karsten Baumann, Georgia Tech, School of Earth and Atmospheric Sciences, Atlanta, GA 30332-0340;
e-mail: kb@eas.gatech.edu

Table 1a: PCM data quality indicators for gaseous species, as retrieved from phosphorous acid and sodium carbonate coated denuders (D(pa) and D(sc), resp): denuder efficiencies (D-eff), detection limits (DL) from blank analysis, bias (precision estimate based on side-by-side runs). SO_2 accuracy has been determined from linear regression with continuous SO_2 UV fluorescence measurements.

	Site	**NH_3**	**HNO_3**	**HONO**	**SO_2**	**HCl**	**HCOOH**	**CH_3COOH**	**$(COOH)_2$**
Medium		D(pa)	D(sc)	D(sc)	D(sc)	D(sc)	D(sc)	D(sc)	D(sc)
D-eff [%]	LP	91±18	90±22	91±8	87±19	97±6	83±10	81±18	78±17
	WT	92±22	85±23	88±9	91±18	96±17	83±11	89±19	73±21
DL [ppbv]	LP	0.49	0.33	0.03	0.07	0.18	0.08	0.21	0.01
	WT	1.40	0.36	0.04	0.20	0.15	0.11	0.28	0.02
Bias [%]	n/a	10	11		6	14	6	12	20
Accuracy [%]	LP				-27				

Table 1b: Same as Table 1a for particulate species. EC/OC accuracy has been determined from NIST standards, total mass (M_{tot}) accuracy from linear regression with TEOM measurements.

	Site	**NH_4^+**	**NO_3^-**	**SO_4^{-2}**	**EC**	**OC**	**SVOC**	**M_{tot}**
Medium		T+P	T+P	T	Q	Q	XAD-Q	T
DL [ug m^{-3}]	LP	0.23	0.09	0.06	0.42	0.80	0.51	1.1
	WT	0.22	0.10	0.05	0.59	0.93	0.51	1.1
BIAS [%]	LP	12	33	13	7	5	25	12
	WT	13	19	3	7	5	25	12
Accuracy [%]	n/a				-9	+10		+5/+11

	Site	**Na^+**	**K^+**	**Ca^{2+}**	**Cl^-**	**F^-**	**$HCOO^-$**	**CH_3COO^-**	**$C_2O_4H^-$**
Medium		T	T	T	T	T	T+P	Q	Q
DL [ug m^{-3}]	LP	0.15	0.10	0.18	0.07	0.02	0.88	1.71	0.18
	WT	0.10	0.07	0.14	0.07	0.02	0.84	0.84	0.16
BIAS [%]	LP	20	35	17			17	11	25
	WT	22	37	26			17	11	27

(as a result of the altered gas-phase/solid phase equilibrium after removal of gaseous species through the denuders) of the Teflon filters. The chemical analysis followed ion chromatography (IC) using a Dionex DX-500 with EG-40 eluent generator.

The third channel served the measurement of particulate organic and elemental carbon (OC/EC) by the thermal optical transmittance (TOT) (Birch and Cary, 1996). This channel minimizes positive artifacts to occur on the quartz filter by passing the aerosol sample through a 28.5 cm long 8-annuli XAD coated denuder at 0.8 s residence time. If denuders are used that quantitatively remove these gases that are otherwise susceptible to uptake, the positive artifact is in principle eliminated. However, the imposed change in equilibrium between particle and gas phase species can now cause an increased volatility of semi-volatile species associated with the collected particles thus generating a negative artifact and necessitating a backup adsorber (Eatough et al., 1985). An XAD coated quartz filter was used as backup adsorber in PCM channel 3 on an experimental basis. Results of tests adressing positive and negative artifacts associated with quartz filter sampling and subsequent EC/OC analysis, are discussed in Zhao et al. (2001). Since OC represents only pure carbon from the TOT analysis, other organic elements (OOE) bound to carbon in the organic species had to be considered. Assuming an average organics molecular weight to carbon weight ratio of 0.4 (White and Roberts, 1977; Countess et al., 1980; Japar et al., 1984], OOE is calculated to be 0.4*OC.

O_3 was measured using a pressure and temperature compensated commercial UV absorption instrument (model TEI 49-C, TEI, Inc., Franklin, MA), being absolutely calibrated by the known absorption coefficient of O_3 at 254 nm. The linearity and precision of the analyzer at LP was checked on average once every 22 hours by comparison with a primary standard. The O_3 analyzer's detection limit was 1.0 ppbv; and the precision determined from the linear regressions was ±4%. The accuracy is estimated to be the same. The same type analyzer was deployed at WT and was subjected to the primary standard calibration procedure before and after the study yielding similar quality.

CO was measured by gas filter correlation, nondispersive infrared absorption (model TEI 48C-TL with a hand-selected PbSe detector matched with an optimal preamplifier, and an absorption cell with gold-plated mirrors). The absorption cell temperature was controlled at 44 ±0.1 ^{o}C during the entire study. A catalytic zero trap kept at 180 ^{o}C quantitatively oxidized CO to CO_2 at an efficiency greater 99 %, and allowed the switching of zero modes every 11 min for 2 min. NIST traceable calibration gas of 405 ±4 ppmv CO in N_2 (Scott-Marrin Inc., Riverside, CA) was introduced into the sample stream by mass flow controlled standard addition and dynamic dilution at the instrument inlet for 2 min approximately every 11 h. The detection limit for a 1 min average based on the 1 Hz data was ~107 ppbv, and ~23 ppbv for a 1 h average. The instrument's precision, determined from the standard addition span checks, was ±9 % at ~570 ppbv. The accuracy was estimated at ±17 % for the entire measuring range based on the RMS error of uncertainties in the individual system components. The instrument's linearity within its 5000 ppbv range was determined from all calibrations performed during the study (zero excluded), and revealed an r^2 of 0.98.

SO_2 was measured by use of a commercial, pulsed UV fluorescence instrument (model TEI 43C-TL) with pressure and temperature compensated signal output. Its response time was ~45 s and therefore, required longer zeroing and calibration periods compared to the CO instrument: zero for 4 min once every 55 min; calibration - via mass flow controlled standard addition of 30.6 ±0.3 ppmv SO_2 in N_2 NIST traceable calibration gas (Scott-Marrin Inc.) and dynamic dilution at the instrument inlet - was performed for 4 min once every 11 hours. Zero [SO_2-free] air was produced by passing ambient air through a HEPA glass fiber in-line filter (Balston) impregnated with a 0.15 molar Na_2CO_3 solution. At a flow rate of 0.9 slm, the filter removed >99 % of the SO_2 in the sample. Calibrations were performed and evaluated analogous to the CO measurements resulting in a detection limit of 4.3 ppbv for 1 min, and 0.08 ppbv for 1 h averages, and a precision of ±4 % at 60-130 ppbv. Since the instrument's measurement principle is known to be sensitive to organic hydrocarbons (HC), the efficiency of the internal HC removal through a semi-permeable wall was enhanced by introducing an activated carbon trap into the flow of the low-[HC]-side of the wall, and thereby further increasing the [HC] gradient across the wall. NO is known to be another interferent, and its level of interference was examined by standard addition of NO calibration gas earlier before the study, resulting in a 2-3 % increase of signal. The reported data were not corrected for this relatively small interference. The accuracy was estimated as the RMS error of uncertainties in the individual system components, yielding ±17 % for the entire measuring range. The instrument's linearity within its 200 ppbv range was determined from all calibrations during the study, and revealed an r^2 of 0.99.

Proto-type Air Quality Design (AQD, Golden, Colorado) NO/NO_y and NO/NO_x analyzers were deployed for the measurement of NO, NO_x, and total reactive nitrogen oxides (NO_y) that include NO, NO_2, NO_3, N_2O_5, HONO, HNO_3, aerosol nitrate, PAN and other organic nitrates. The NO_y measurements were based on the principal method of metal-surface induced reduction of the more highly oxidized species to NO, and its subsequent chemiluminescence detection (CLD) with excess ozone. The metal surface here was a 35 cm long, 0.48 cm ID MoO tube (Rembar Co., Dobbs Ferry, NY), temperature controlled at 350 ±2 ^{o}C, and housed inside an inlet box mounted to the met tower ~9 m above ground. The NOx measurements made 4.5 m agl, utilized a Xe/Hg photolysis system with an average NO_2 conversion fraction of 12 ±3 % at 1 s sample residence time. The data quality of these measurements are summarized on the basis of 1 min averages in Table 2.

Table 2: Detection limits (DL), precision (P), and accuracy (A) of the NO, NO_x, and NO_y measurements.

	DL (ppbv)	**P (%)**	**A (%)**
NO	0.003	10	15
NO_x	0.5	15	25
NO_y	0.4	15	20

3. RESULTS

At both the LaPorte and the Williams Tower site, semi-continuous $PM_{2.5}$ mass measurements were made using a Tapered Element Oscillating Microbalance (TEOM) in addition to and much higher resolved than the discrete filter measurements. The TEOM mass concentrations were systematically low relative to the gravimetric filter mass by 5 amd 11 %, respectively, which is attributed to the active humidity control employed with both TEOM. All Teflon sample filters were dehydrated in a desiccator located in a temperature- (21°C) and humidity- (40%) controlled clean room in order to remove humidity artifacts. The samples remained in the desiccator for at least 4 days, in most cases longer. The final mass was determined gravimetrically from the desiccated channel 1 Teflon filters. Channel 2 Teflon masses were systematically higher by 15 ±13 % (corresponding 3.2 ±4 $\mu g\ m^{-3}$) at LaPorte, and by 17 ±16 % (4.4 ±6 $\mu g\ m^{-3}$) at Williams Tower, which is suspected to be due to artifacts caused by the glycerol-containing sodium carbonate coating solution used in the channel 2 denuders (Finn et al., 2001). The semi-volatile fractions of NH_4^+, NO_3^-, and the organic acids (from paper backup filters, considering corresponding blank levels and denuder efficiencies) are added to the gravimetric mass determined from the Teflon filters.

LaPorte was influenced predominantly by a strong land-sea breeze circulation with veering wind directions, causing periodic short-term impacts of plumes from nearby sources with significantly reduced (titrated) nighttime ozone levels. The combination of this air flow pattern and the relative vicinity of various emission sources led to vertically confined ozone plumes, which caused the highest ozone readings of the study at LaPorte on August 30 and 31, with maximum hourly averages of 219 and 196 ppbv, respectively, while the elevated site at Williams Tower, only saw ~50% lower ozone maxima, which can be seen in Figure 1. With exception of this episode, the $PM_{2.5}$ mass and sulfate concentrations generally followed the trends in daily ozone maxima, which points to very rapid ozone production in these plumes as suggested by other investigators. The occasional deviation from this agreement between $[PM_{2.5}]$ and $[O_3]_{max}$ also indicates that ozone is formed much faster than $PM_{2.5}$ under these specific conditions, which stands in contrast to the conditions typically leading to O_3 and $PM_{2.5}$ pollution in the southeastern U.S., where regional stagnation leads to simultaneous buildup of these pollutants as in a 'rising tide'.

A charge balance based on the sulfate-nitrate-ammonium system indicates slightly acidic conditionswith 16 ±17 ne m^{-3} at LaPorte and 25 ±47 ne m^{-3} at Williams Tower, as illustrated in Figure 2. In the context of aerosol acidity, it is important to note that $[NH_3]$, the only neutralizing species measured during the first half of the study, averaged 3.2 ±1.5 ppbv at LaPorte, and 2.9 +1.9 ppbv at Williams Tower. Figure 2 compares the $PM_{2.5}$ mass and charge balances from LaPorte and Williams Tower with previous measurements made in the Southeastern U.S. within the framework of SOS, at sub-urban and rural sites in TN, and at metropolitan Atlanta, GA, during the Atlanta Supersite Experiment in August 1999.

4. REFERENCES

Baumann K., F. Ift, J.Z. Zhao, and W.L. Chameides, under review: Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta Supersite Experiment. *J. Geophys. Res.*

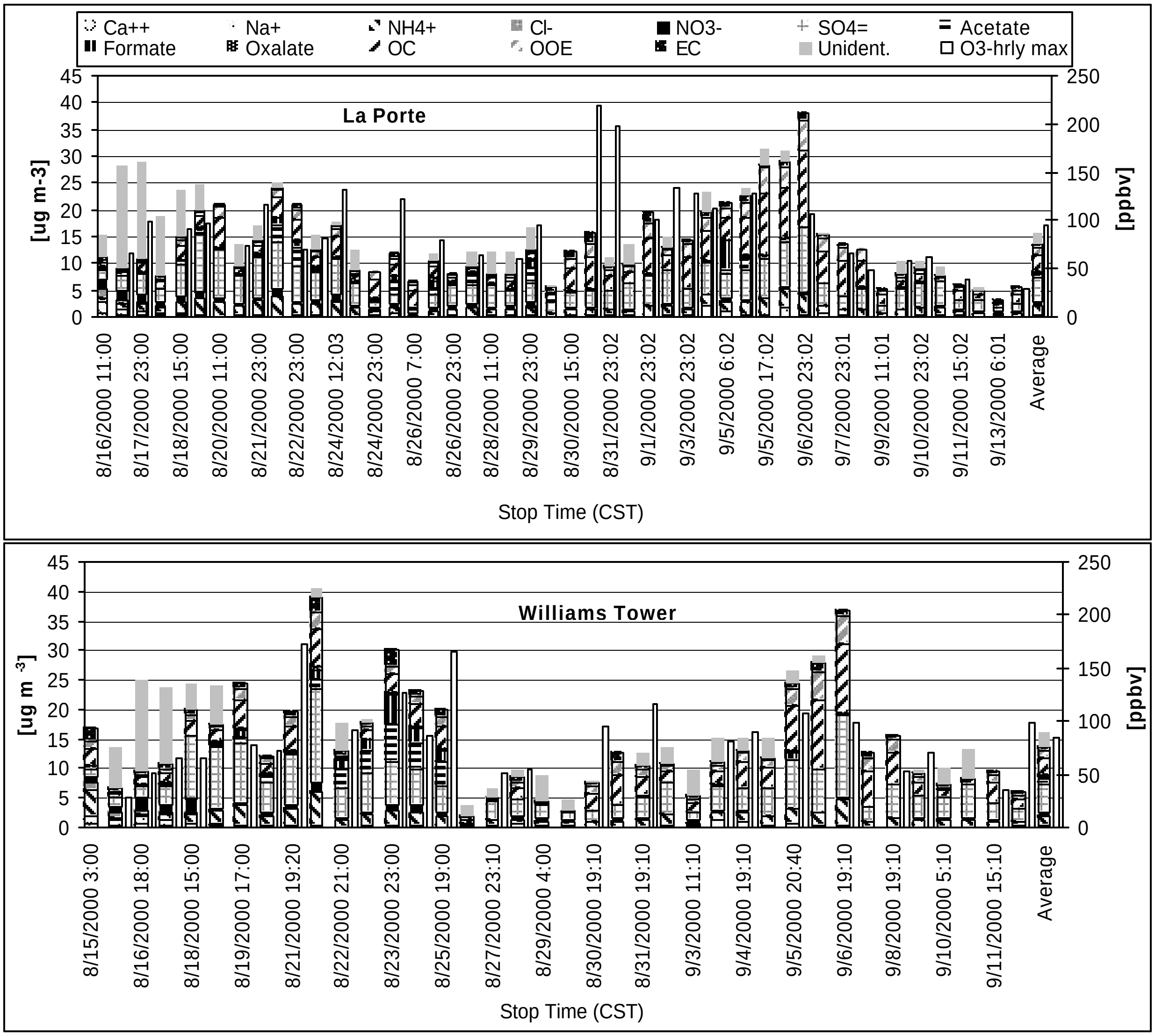

Figure 1 top and bottom: $PM_{2.5}$ mass balance and max. hourly O_3 concentrations for sample periods ranging from 6 to 24 hours in La Porte (top) and at Williams Tower (bottom).

Birch, M.E., and R.A. Cary, 1996: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology*, **25**, 221-241.

Countess, R.J., G.T. Wolff, and S.H. Cadle, 1980: The Denver Winter Aerosol: A Comprehensive Chemical Characterization. *J. Air Pollut. Control Assoc.*, **30**, 1194-1200.

Eatough, D.J., V.F. White, L.D. Hanson, N.L. Eatough, and E.C. Ellis, 1985: Hydration of nitric acid and its collection in the atmosphere by diffusion denuders. *Anal. Chem.*, **57**, 743-748.

Finn, D., B. Rumburg, C. Claiborn, L. Bamesberger, W.F. Siems, J. Koenig, T. Larson, and G. Norris, 2001: Sampling Artifacts from the Use of Denuder Tubes with Glycerol Based Coatings in the Measurement of Atmospheric Particulate Matter. *Environ. Sci. Technol.*, **35**, 40-44.

Japar, S.M., A.C. Szkarlat, R.A. Gorse Jr., E.K. Heyerdahl, R.L. Johnson, J.A. Rau, and J.J. Huntzicker, 1984: Comparison of Solvent Extraction and Thermal-Optical Carbon Analysis Methods: Application to Diesel Vehicle Exhaust Aerosol. *Environ. Sci. Technol.*, **18**, 231-234.

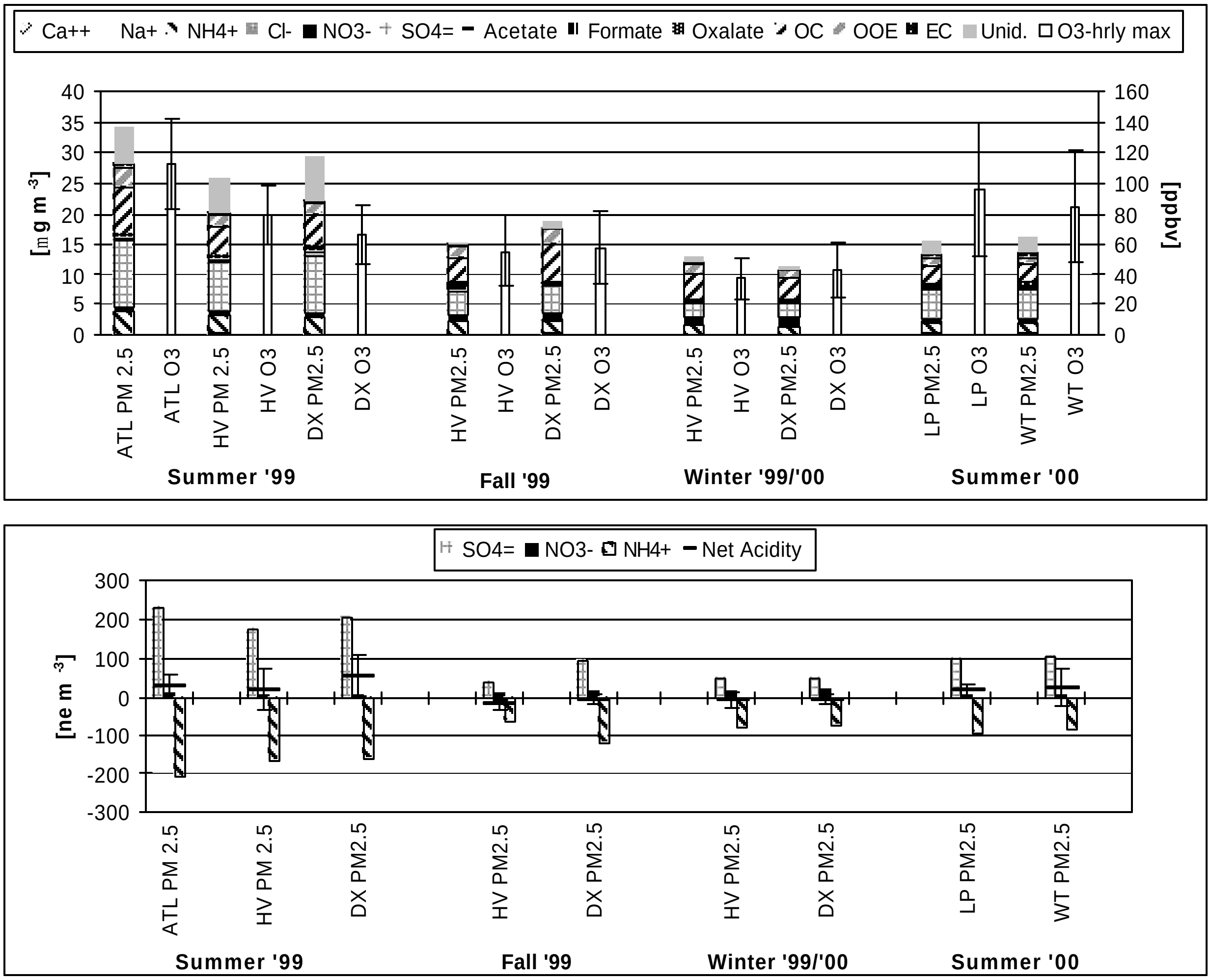

Figure 2 top and bottom: Seasonal averages of $PM_{2.5}$ and O_3 concentrations (top) and charge balance (bottom) for Atlanta, GA (ATL), Dickson, TN (DX), Hendersonville, TN (HV), La Porte (LP), and Williams Tower (WT).

Possanzini, M. et al., 1983: New design of a high-performance denuder for the sampling of atmospheric pollutants. *Atmos. Environ.*, **17**, 2605-2610.

White, W.H. and P.T. Roberts, 1977: On the Nature and Origins of Visibility-Reducing Aerosols in the Los Angeles Air Basin. *Atmos. Environ.*, **11**, 803-812.

5. ACKNOWLEDGEMENTS

The authors gratefully acknowledge Prof. J. Lester from the University of Houston, Clearlake, for laboratory support. This study was carried out as part of the Southern Oxidants Study (SOS), sponsored by EPA and TNRCC.