OPTICAL PROPERTIES OF AEROSOLS AND THEIR SENSITIVITY TO RELATIVE HUMIDITY AND SIZE DISTRIBUTION IN THE NEW YORK CITY URBAN-COASTAL AREA

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ABSTRACT

Aerosol particles exert important influences on climate and climate change by scattering and absorbing solar radiation and by influencing the properties of clouds. The aerosol life cycle determines the spatial and temporal distribution of atmospheric particles and their chemical, microphysical, and optical properties, which in turn determines the earth radiation budget. In this paper, we investigate the performance of the atmospheric model CMAQ 4.71 (Community Multiscale Air Quality) currently used by the Department of Environmental Conservation (DEC) to provide regional pollution forecasts and analysis. We focus on the use of remote sensing tools to better understand the modifications of the optical properties of aerosols as a function of relative humidity, size-distributed composition and sulphate content. In doing this, a novel technique is used to calculate the comparison of optical parameters, such as extinction, backscatter and aerosol optical depth. This, in turn, is used on the CMAQ 4.7.1 model outputs to be compared with concentrations of PM2.5 (particulate matter less than 2.5 μm in size) measured with TEOM (Tapered element oscillating microbalance), with sunphotometer measurements of AOD (aerosol optical depth) and with multiwavelength lidar-derived backscatter and extinction profiles.

INTRODUCTION

Particles in the atmosphere arise from natural forces, such as windborne dust, seaspray, and volcanoes, and from anthropogenic activities, such as combustion fuels. Measurements of the atmospheric particulates give us only a snapshot of atmospheric conditions (visibility, pollution levels, etc) at a particular time and location (1,2). These measurements alone are difficult to interpret without a clear conceptual model of the atmospheric processes. In addition measurements alone cannot be used directly by policy makers to establish an effective strategy for solving air quality problems. An understanding of the individual processes does not imply an understanding of the system as a whole. Mathematical models provide the necessary framework for integration of our understanding of the system as a whole. One atmospheric mathematical model is the Community Multiscale Air Quality (CMAQ) (3) modelling system which is being developed and maintained under the leadership of the Atmospheric Modeling and Analysis Division of the EPA National Exposure Research Laboratory in Research Triangle Park, NC (4). CMAQ represents over two decades of research in atmospheric modelling and has been in active development since the early 1990's. CMAQ combines current knowledge in atmospheric science and air quality modelling with multiprocessor computing techniques in an open-source framework to deliver estimates of ozone, particulates, toxics, and acid deposition.

In urban areas, such as the NYC (New York City), the aerosols are a mixture of primary emissions from industries, transportation, power generation, and natural sources and secondary material formed by gas-to-particle conversion mechanisms. The number distribution is dominated by particles smaller than 0.1 μm, while most of the surface area is in the 0.1-0.5 μm size range. Atmospheric particulate matter in NYC is regulated by US Environmental Protection Agency. It is considered as major pollutant in an aggregate sense with total PM2.5 standards with limits on daily average and annual average concentrations (4).

Current aerosol models need improvement in several areas: emissions; mechanisms, and rates of new particle formation and their dependence on controlling variables, growth, and aging; distinguishing natural and anthropogenic influences; and computational efficiency of model representation (1,5,6). In addition, the models need to be systematically evaluated not only at ground level but also in the planetary boundary layer (PBL) to determine the cause of differences between simulated and observed aerosol properties.

In assessing the model against optical measurements, it is important to note that the optical parameters of aerosols are sensitive to size distribution and chemical composition as a function of relative humidity. Furthermore, the vertical structure predicted by the CMAQ model is critical in understanding anomalies even in surface parameters such as PM2.5 mass (7). To get a better understanding of not only the surface predictions but the upper air distribution of pollutants, it is critical that active remote sensing techniques are used. However, the conversion of mass properties to optical properties depends strongly on the underlying aerosol models. The humidity and rigorous computation schemes that take these affects into account must be developed (8).

In this paper, we first construct a rigorous Mie theoretical model that accounts for the hygroscopic growth of the aerosols to relative humidity (RH) and the modifications to the refractive index that modifies the optical model (9). The growth factor and the refractive index for the different species and wavelengths are stored within the Optical Properties of Aerosols and Clouds (OPAC) data base (3). Using this algorithm, the outputs of the optical parameters (backscatter, extinction and aerosol optical depth (AOD)) retrieved by CMAQ can be compared with lidar, ceilometers and sunphotometer measurements performed at the City College of the City University of New York (CCNY/CUNY) campus (5). Since the urban area contribution to the atmospheric constituents is much higher when compared to aerosol transported from outside the urban region, the domain of the CMAQ files used in the analysis is 12 km $\times$ 12 km and is based on local emissions only. The model currently used by the Department of Environmental Conservation (DEC) is CMAQ 4.7 which uses the AE5 chemistry module for PM2.5 (9). The level data provided by the model provides the inputs needed for calculation of the optical parameters taking into consideration the hygroscopic growth based on RH at the corresponding levels (10,11,12).

METHODOLOGY

The optical parameters obtained from the multiwavelength elastic-Raman lidar (described in the Instrumentation section) are the backscatter at 355, 532 and 1064 nm and extinction at 355 nm. The data used for comparison and model development is sparse due to unfavourable atmospheric conditions like rain or low clouds that do not allow for correct alignment of the lidar or data collection with the sky radiometer (Cimel sunphotometer).

Our analysis focused on summer days and in particular the months of August and September 2010. The CMAQ model provided mass concentration for different species and size modes alongside with pressure, water vapour and temperature at 22 different layers between surface and 16.000 m. This data allowed for calculation of the optical parameters taking into consideration the hygroscopic growth based on the relative humidity (RH) at the corresponding levels. The growth factor and the refractive index for the different species and wavelengths were obtained from the Optical Properties of Aerosols and Clouds (OPAC) data base (13). After retrieving the extinction and backscatter for each mode and species we added up the results and compared with the lidar Mie channels: 355, 532 and 1064 nm.

A vertical integration of the extinction coefficients also allowed for aerosol optical depth (AOD) comparison with the sunphotometer measurements. To complete the comprehensive assessment of the CMAQ model, we also compared the concentrations of particulate matter less than 2.5um in diameter measured by the TEOM (Tapered Element Oscillating Microbalance) instrument located on the CCNY campus. Along with the extinction calculated by the technique proposed by the authors and the Malm (14) formula we also estimated the integrated extinction over the total atmospheric path, known as aerosol optical depth (AOD). The modelled AOD values were compared then with the sunphotometer AOD.

INSTRUMENTATION

The most unique and important instrument at our disposal suitable for assessing the vertical predictions of CMAQ is a multiwavelength lidar system (5). A schematic of the CCNY lidar system is illustrated in Figure 1. The transmitting laser is a Q-switched Spectra-Physics Quanta Ray Pro230 Nd:YAG with variable output power up to 475 mJ at 532 nm, 950 mJ at 1064 nm and 300 mJ at 355 nm. The instrument currently has five channels with wavelengths at 1064, 532 and 355 nm, including a Raman channel at 407 nm for water with a second Raman channel at 387 nm for nitrogen.

The laser emits at a pulse repetition rate of 30 Hz with 1-2 ns pulse duration at 532 nm and <0.5 mrad beam divergence. The beam is separated in three components to allow power measurements on separate channels and then regrouped and directed by three dichroic mirrors into the atmosphere above the system. The beam is co-axial with the telescope field-of-view. Due to the different wavelength channels, different detectors are used. An APD (silicon enhanced avalanche photodiode) for the 1064 nm (infrared) channel is used while a PMT (Hamamatsu) is used for the 532 nm (green), 386 nm (Raman) and 355 nm (UV) and 407 nm (Raman) channels.

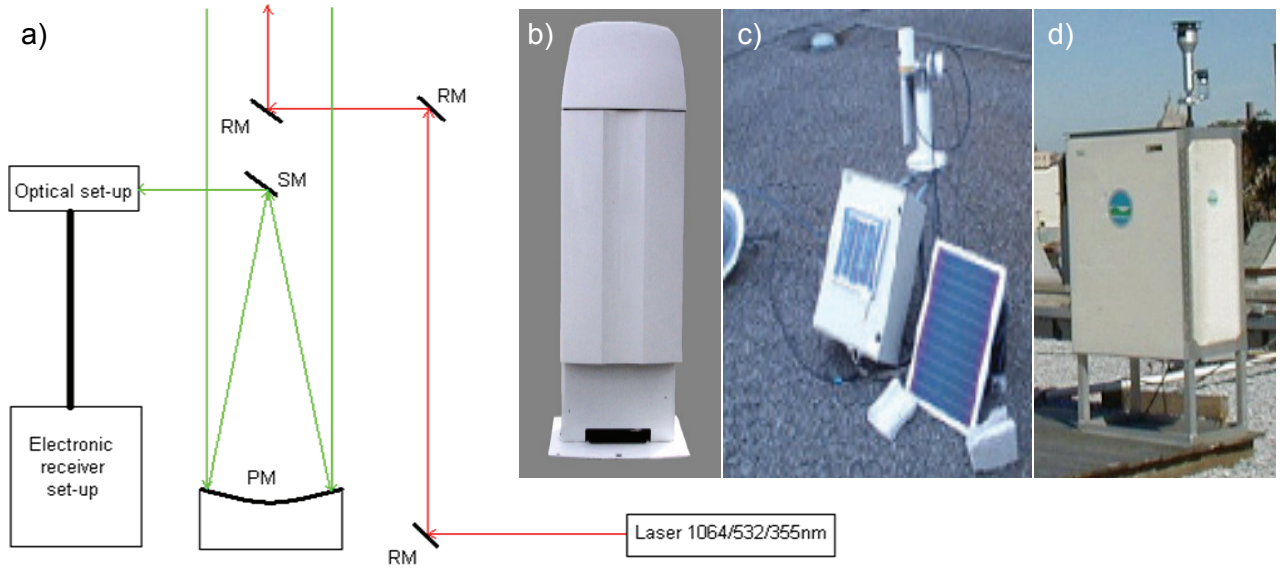


Figure 1: Observation instruments a) multiple wavelength lidar, b) ceilometer, c) Cimel Sunphotometer, d) TEOM (tapered element oscillating microbalance).

A complementary measurement which provides data on column integrated extinction (i.e Aerosol Optical Depth) is a scanning sky radiometer located on the CCNY campus. This instrument is one of the devices that make up the NASA AERONET (AErosol RObotic NETwork.) This microprocessor controlled, stepper motor positioned robot has a two component optical head containing the sun collimator without lens and the sky collimator with lenses and filter wheel. Sun tracking is controlled with a 4-quadrant detector. Data is temporarily stored in memory and once every hour uploaded to NASA via a GOES-E (geosyncronous) satellite uplink. The instrument directly measures the incoming solar energy (sky radiance) at selected wavelengths of 340, 380, 440, 670, 870, 1020 nm (aerosols), and 936 nm (water vapour).

Light is absorbed and scattered by atmospheric gasses, water vapour and aerosols. The concentration of different atmospheric components can be determined by the attenuation at wavelengths which are strongly absorbed or scattered. Total Optical Depth (*TOD*) is the sum of the Rayleigh Optical Depth (from atmospheric gasses, e.g. Nitrogen, Oxygen, Argon), the Ozone Optical Depth, the Mixed Gas Optical Depth (e.g. Carbon dioxide, oxides of Nitrogen), the Water Vapour Optical Depth and the Aerosol Optical Depth (*AOD*). *AOD* is of most interest because it cannot be directly measured by other methods, and is determined by subtraction of the other quantities. Aerosol phase functions and size distribution can also be inferred. The sun photometer measurements are also important as standards for satellite-derived values of *AOD*.

One problem with the lidar is the large non overlap region between transmitter and receiver. To fill in this gap (approx. 500 m), we use the Vaisalla 3000 ceilometer which is capable of seeing in the near field down to 20 meters. Unfortunately, the noise of this instrument makes far range observations difficult. However, by merging the ceilometer to the lidar profiles by using regression fits in regions of overlap, we can get a continuous profile through the PBL.

Finally, we use the TEOM (tapered element oscillating microbalance) instrument to assess the surface PM2.5 predictions. The TEOM Series 1400a Ambient Particulate Monitor deployed in EPA's AirNOW network incorporates an inertial balance that directly measures the mass collected on an exchangeable filter cartridge by monitoring the corresponding frequency changes of a tapered element. The sample flow passes through the filter, where particulate matter collects, and then continues through the hollow tapered element on its way to an active volumetric flow control system and vacuum pump.

The data collected from all the instruments described above are used in the assessment process of the CMAQ model and the technique developed by the authors.

OPTICAL PARAMETER MODEL CALCULATION

In our analysis we use CMAQ-OPAC parameters (density, refractive index, particle mass by size and species, meteorological parameters, size parameters, etc.) as an input to the calculation of the aerosol extinction and backscatter parameters. We then use the size parameters to calculate number and volume size distribution by modes (fine, accumulation and coarse) and species (or classes) which are further used as inputs in the Mie or Malm calculations of extinction and backscatter by species and different size modes.

Given σ^i, $r^i_{\mathrm{mod},V}(RH)$, $m^r_k(RH,\lambda)$, $m^i_k(RH,\lambda)$, V^i_k we calculated from Mie theory the extinction and scattering coefficients

$$\alpha^i_k(\lambda,RH)=\int_{r_{\min}}^{r_{\max}}\frac{3}{4r}\left(\frac{\mathrm{d}V}{\mathrm{d}r}\left(\sigma^j,r^{i,k}_{\mathrm{mod},V}(RH)\right)\right)Q_e\left(q=\frac{2\pi r}{\lambda},m^r_k,m^i_k\right)\mathrm{d}r$$
$$\beta^i_k(\lambda,RH)=\int_{r_{\min}}^{r_{\max}}\frac{3}{4r}\left(\frac{\mathrm{d}V}{\mathrm{d}r}\left(\sigma^j,r^{i,k}_{\mathrm{mod},V}(RH)\right)\right)Q_b\left(q=\frac{2\pi r}{\lambda},m^r_k,m^i_k\right)\mathrm{d}r \quad (1)$$

where Q_e and Q_b are the extinction and respectively backscatter efficiencies as functions of the size parameters q and the real and imaginary refractive indexes m. The volume distributions are functions of the particle size r and standard deviation σ. In the volume distribution we take into account the particle size growth as a function of relative humidity. In Eq. (2) below we indicate the mathematical formula used in the calculation of the volume distribution of particles.

$$\frac{\mathrm{d}V}{\mathrm{d}r}=\frac{V_{2.5}}{\sqrt{2\pi}r\log(\sigma)}\exp\left(-.5\left[\frac{\log(r)-\log(r_{\mathrm{mod},V})}{\log(\sigma)}\right]^2\right) \quad (2)$$

In the end, we sum up over all species and modes for total optical parameters.

$$(\alpha,\beta)(\lambda,RH)=\sum_i\sum_k(\alpha,\beta)^i_k(\lambda,RH) \quad (3)$$

The chemical species used in our model are given in Table 1 by classes and species. The Malm's extinction used for comparison is described by the relation below:

$$\beta_{ext}=0.003f(RH)(SO_4+NO_3)+0.004OM+0.01EC+0.001FS+0.0006CM \quad (4)$$

The relative humidity based aerosol growth factor $f(RH)$ is calculated based on a look up table from Binkowski et al (2003) (8). The importance of the relative humidity on the growth of particles, the

refractive index and implicitly on the optical parameters has been studied extensively (10-12,15,16).

Based on the CMAQ-OPAC meteorological outputs (modelled pressure level, water vapour mixing ratio and temperature) we calculated saturated pressure and *RH*. This *RH* is then used as interpolation base to locate exact humidity factor. All the terms in Malm's equation refer to mass density ($\mu g/m^3$) (see Table 1).

Table 1: CMAQ Aerosol species and physical properties.

Species	Classes (OPAC)	Mass Density	Dry state refractive index at 500 nm (OPAC) [a]	
		g/cm^3	Real	Imaginary
'ASO4J_PM2.5'	Water soluble	1.8	1.430E+00	-1.000E-08
'ASO4I_PM2.5'	Water soluble	1.8	1.430E+00	-1.000E-08
'ANH4J_PM2.5'	Water soluble	1.8	1.530E+00	-5.000E-03
'ANH4I_PM2.5'	Water soluble	1.8	1.530E+00	-5.000E-03
'ANO3J_PM2.5'	Water soluble	1.8	1.530E+00	-5.000E-03
'ANO3I_PM2.5'	Water soluble	1.8	1.530E+00	-5.000E-03
'AORGAJ_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AORGAI_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AORGPAJ_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AORGPAI_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AORGBJ_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AORGBI_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'AECJ_PM2.5'	soot	1.7	1.750E+00	-4.500E-01
'AECI_PM2.5'	soot	1.7	1.750E+00	-4.500E-01
'A25J_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'A25I_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'ACORS_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03
'ASEAS_PM2.5'	Seasalt	2.2	1.500E+00	-1.550E-08
'ASOIL_PM2.5'	Insoluble	2	1.530E+00	-8.000E-03

[a] refractive index as a function of RH and λ from OPAC/optdat

The ammonium sulphate and ammonium nitrate were taken as the sum of ammonium, plus sulphate, plus nitrate $\left(\left[NH_4^+\right]+\left[SO_4^{2-}\right]+\left[NO_3\right]\right)$ and in the model comparison was the sum of the following atmospheric components: ASO4I_PM25, ASO4J_PM25, ANO3I_PM25, ANO3J_PM25, ANH4I_PM25, and ANH4J_PM25. The light absorbing carbon (*EC*) was taken as elemental carbon, available in the CMAQ output as AECI_PM25. Organic mass (*OM*) was taken as the sum of all organic species and is available in the sized resolved CMAQ quantities as the sum of AORGPAI_PM25 and AORGPAJ_PM25. The fine soil (*FS*) was taken as the unspecified anthropogenic mass A25J_PM25 and A25I_PM25 (this term is referred to in (8) as the "unspeciated portion of PM2.5 emitted species"). The coarse mass term was not implemented in CMAQ analysis, however we included it in our analysis as *CM*=ACORS_PM25. The CMAQ aerosol species and physical properties are specified as reference in Table 1.

RESULTS

The lidar permits us to retrieve the optical properties of aerosols over a vertical spatial domain. The light emitted by these instruments is backscattered by atmospheric constituents, collected and interpreted, allowing us to determine PBL height, aerosol backscatter and extinction coefficient, and Ångstrom exponent (15) for aerosol characterisation by type (dust, sand, sea salt, volcanic emissions, etc). As an example, Figure 2 gives aerosol backscatter coefficients at 532 nm retrieved

from lidar measurements on August 31 and September 1, 2010. As it can be seen, strong aerosol backscatters appear in the low altitude (<3 km) which correspond to more aerosol loading.

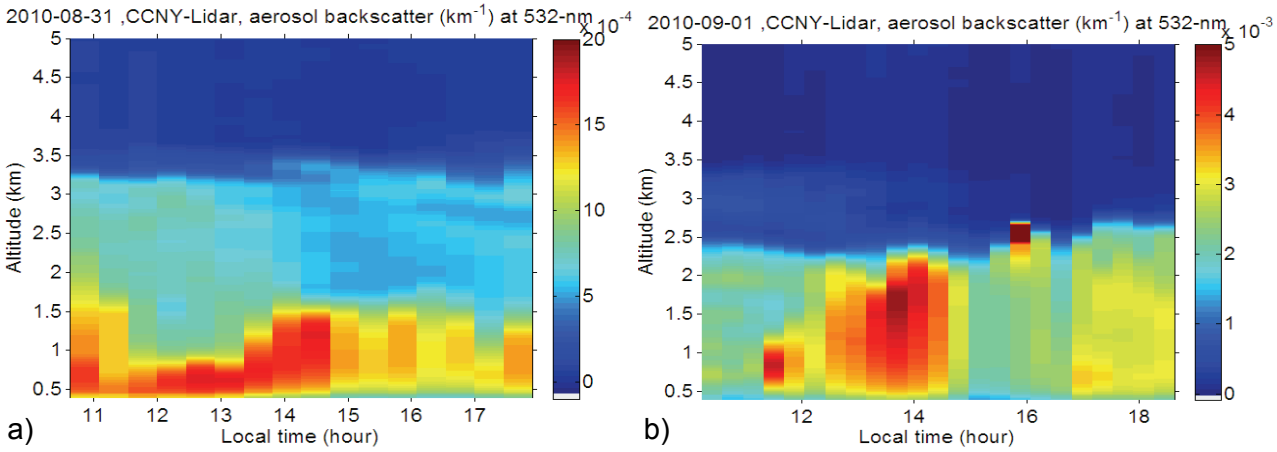


Figure 2: Lidar-derived aerosol backscatter coefficients on a) 2010-08-31 and b) 2010-09-01.

The comparisons of aerosol extinction coefficients between the lidar retrievals and CMAQ model are illustrated in Fig 3. These vertical profiles of the optical parameters indicate good agreements in the trends of the CMAQ model. Note that the lidar ratio (extinction to backscatter ratio) is taken to be 50 for regular urban sites in order to convert the aerosol backscatter to extinction coefficient.

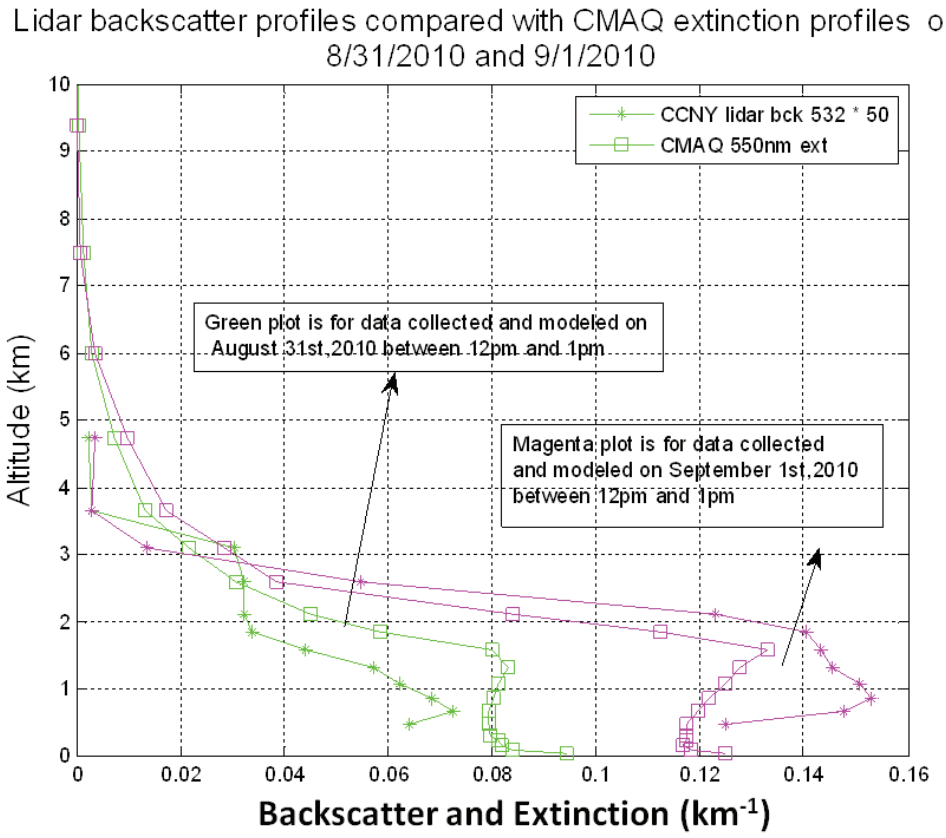


Figure 3: Aerosol extinction vertical profiles measured by the lidar and calculated with CMAQ-model outputs at 12:00-13:00 local time on 2010-08-31 and 2010-09-01.

In the comparisons shown in Figure 4, PM2.5 mass in CMAQ is obtained by simply summing the mass of all particulate components of the Aitken mode (i-mode) and accumulation mode (j-mode) (4). For summer 2010, the CMAQ version used was 4.7.1 with PREMAQ as emission input and the “aero4” aerosol sub-module. Again, in our averages, we restrict ourselves to cases where only clear and sunny sky conditions occur (5 days for summer 2010). To assure quality matchups of the

PM2.5 mass from the TEOM data, representative of a 12km x 12km footprint, only cases where the deviation of the observations between three urban sites within the CMAQ model pixel were less than 20% of the mean were used. In the work of (6), the direct source of this overbias was not clear but it was suggested that error in the PBL height could play a significant part of this anomaly, too.

However, in the lidar backscatter measurements the vertical structure of the optical profiles are very similar. In particular, we see no evidence of the enhanced spiking behaviour that leads to the PM2.5 over estimates. This is reasonable since that reference was focused on pre dawn and post sunset conditions where the PBL height is seen to collapse strongly within the models. In our case, we focus only on daytime conditions where convective processes dominate. This observation seems to indicate that the most likely causes are model overestimations of emissions.

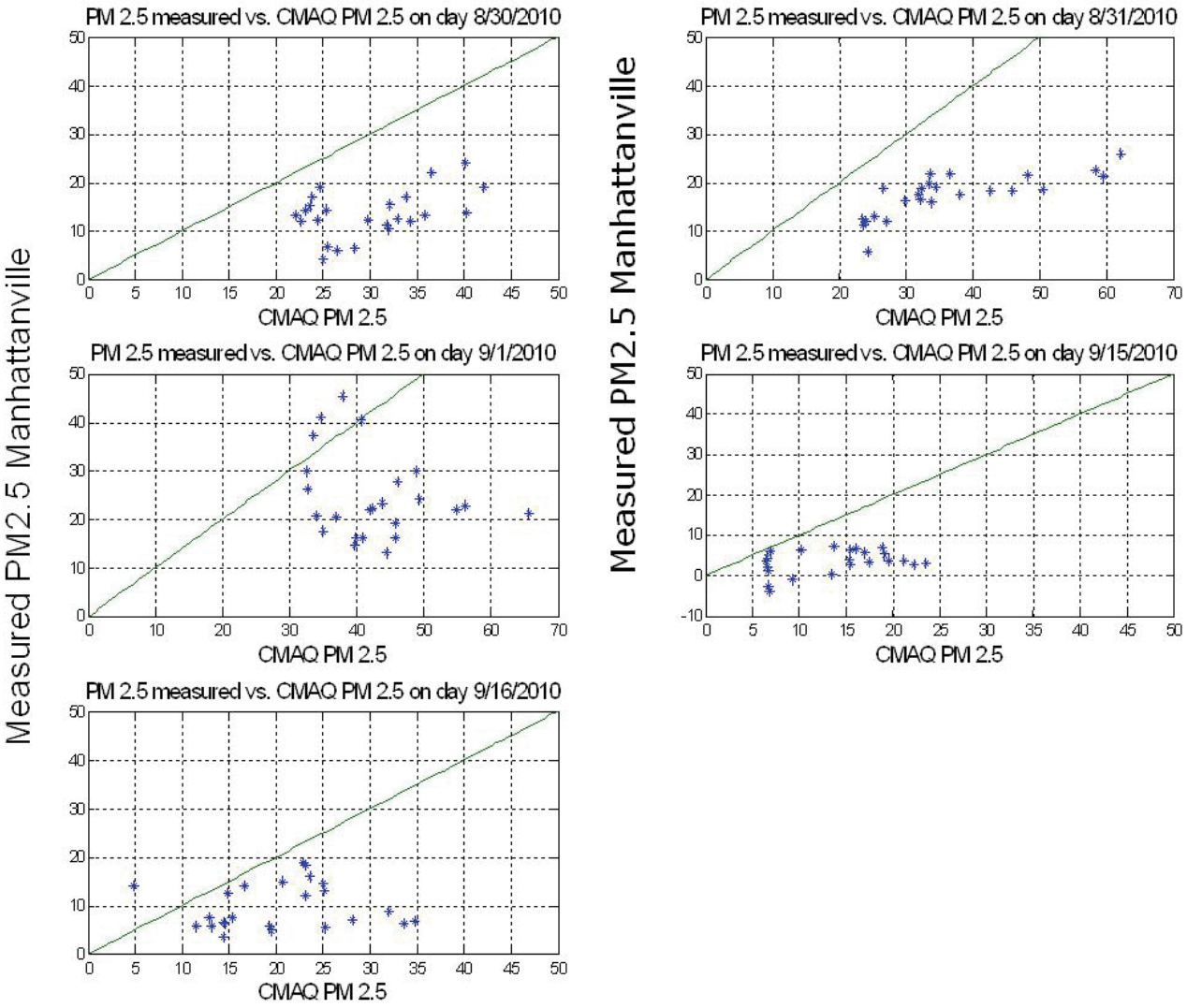


Figure 4: Correlations between measured and modelled PM2.5 values over 5 days of analysis during August and September 2010. The green lines represent the one to one correlation. Units are µg/m^3.

The aerosol optical depth (AOD) values measured at 500 nm by the sunphotometer and available on the AERONET website[1] were compared with the CMAQ retrieved AOD. The results indicate good agreement on days with low PBL variability. However, on days with high PBL variability, the measured aerosol optical depth tends to be higher than the modelled AOD both from the CMAQ model and our technique. However, it should be pointed out that our technique is closest to the measured values of aerosol optical depth on all days.

[1] http://aeronet.gsfc.nasa.gov/new_web/data.html

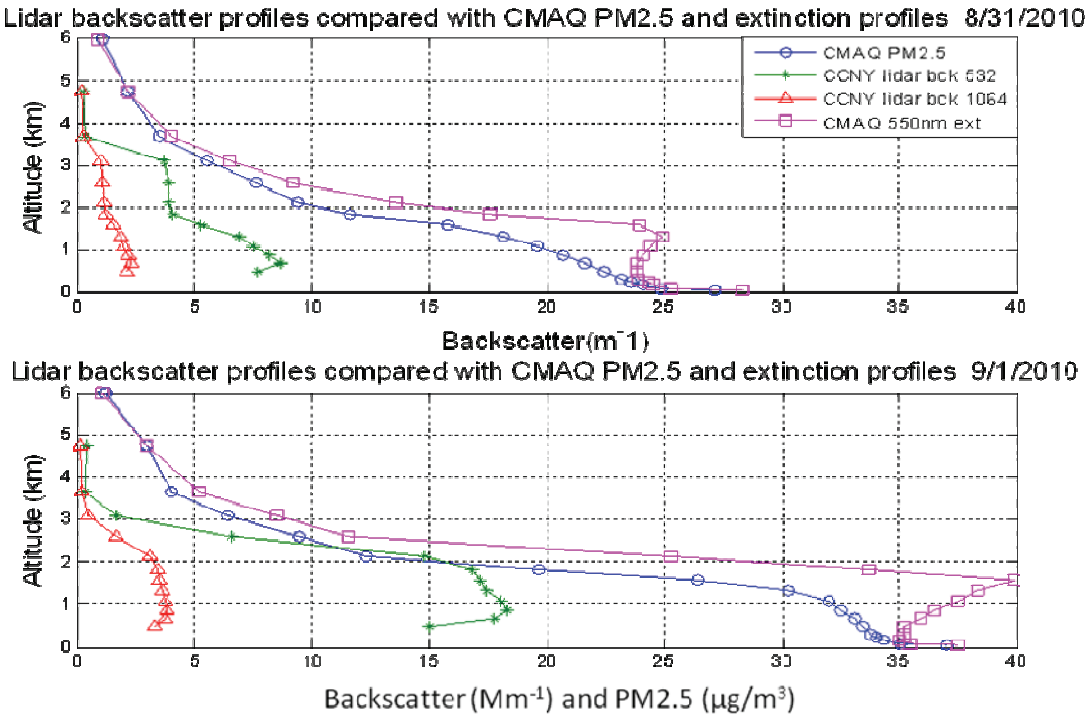


Figure 5: Trends in the lidar backscatter profiles compared with CMAQ extinction and PM2.5. for 2 days of analysis 2010-08-31 and 2010-09-01.

In making comparisons to the Malm model, we can also assess when the models agree with the rigorous Mie Calculations. In Figure 7, we see that largest error at higher extinction coefficients, which are almost always associated with higher *RH*. This is consistent with the discrepancies we see in the column *AOD* measurements of Figure. 6. This means that care must be taken in applying the Malm algorithm to heavy polluted cases.

As it can be seen in Figure 7 there is not a major difference in the extinction correlation for the different classes.

A typical urban aerosol size/composition distribution (17) indicates that sulphate, nitrate, and ammonium have two modes in the 0.1 to 1 μm range (the condensation and droplet modes) and a third one over 1μm (coarse mode). This distribution varies considerably in space and time. The variability of the aerosol concentration field is determined by meteorology and the emission of aerosols and their precursors. For example the annual average concentration of PM2.5 in North America varies by more than an order of magnitude as one moves from clean remote to the polluted urban areas (18). Sulphate dominates the fine aerosol composition in the eastern USA, while organics are major contributors to the aerosol mass everywhere (19,20).

Finally, it is interesting to see how the microphysical properties and optical properties of the aerosol are modified as the sulphate contribution varies. In particular, we are most interested in sulphates since in the northeastern United States, they lead to high fine aerosol concentrations, increased extinction values and therefore low visibility. In this regard, we analyse the particle size standard deviation and mean values as function of extinction in Figure 8. These plots indicate that slight variations in the distribution parameters are accompanied by major differences in the optical parameters.

Furthermore, Figure 9 illustrates the significant changes that occur in the optical properties as the total volume of the sulphate distribution is increased. In particular, we note a very clean increase of the refractive index, which we attribute to the sulphate dry state properties. As the sulphate volume decreases the water component dominates.

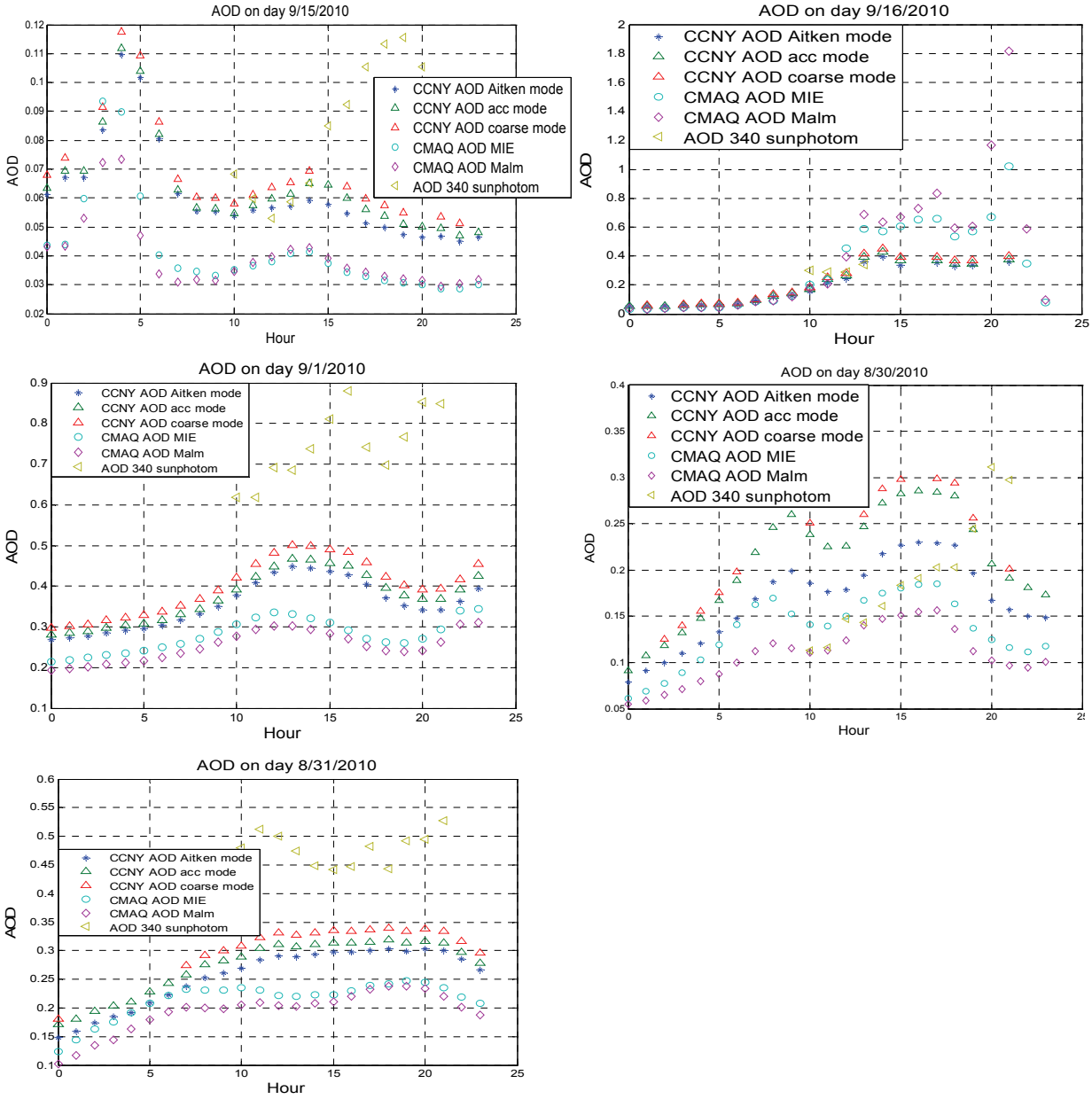


Figure 6: AOD comparisons between CMAQ, sunphotometer and the technique proposed by authors using CMAQ-OPAC input parameters for calculation of the optical parameters.

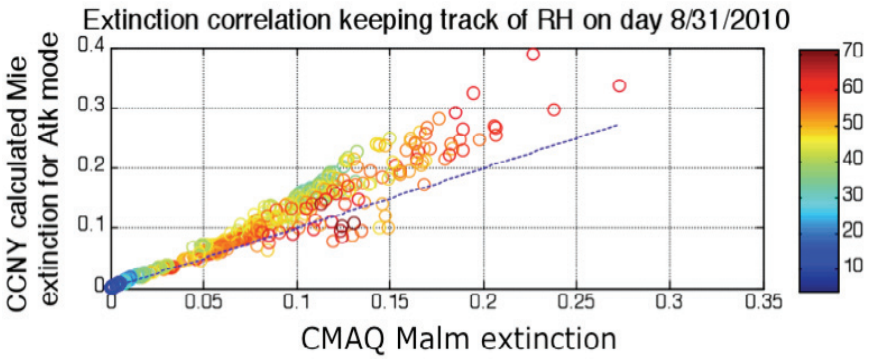
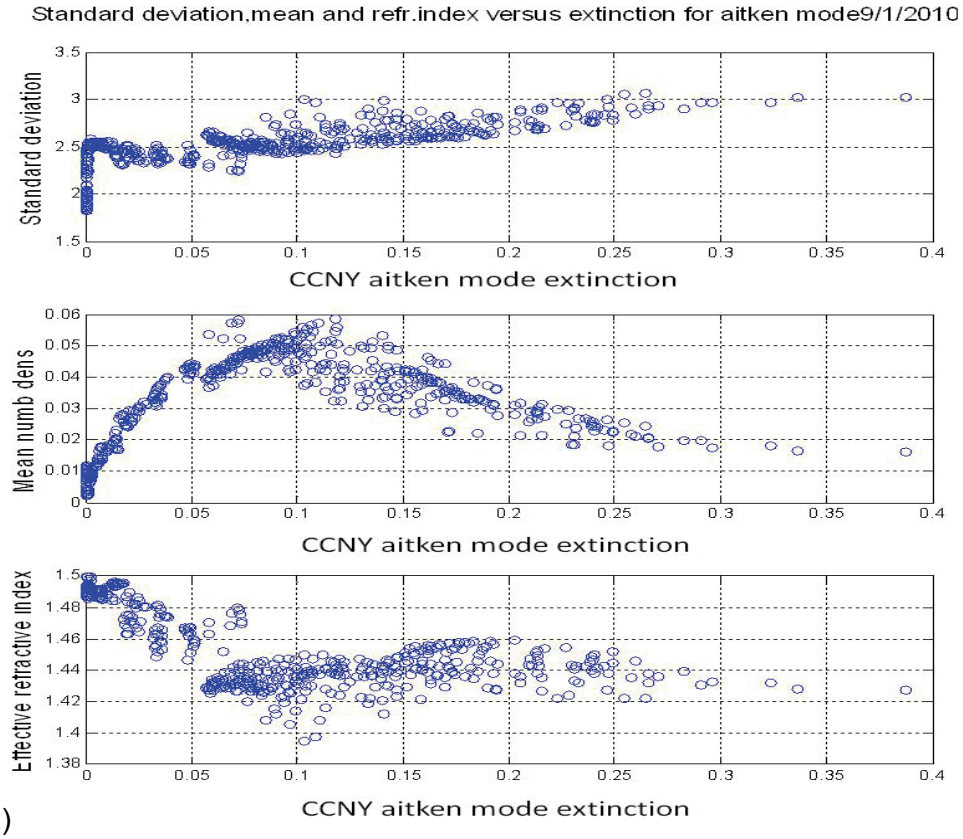
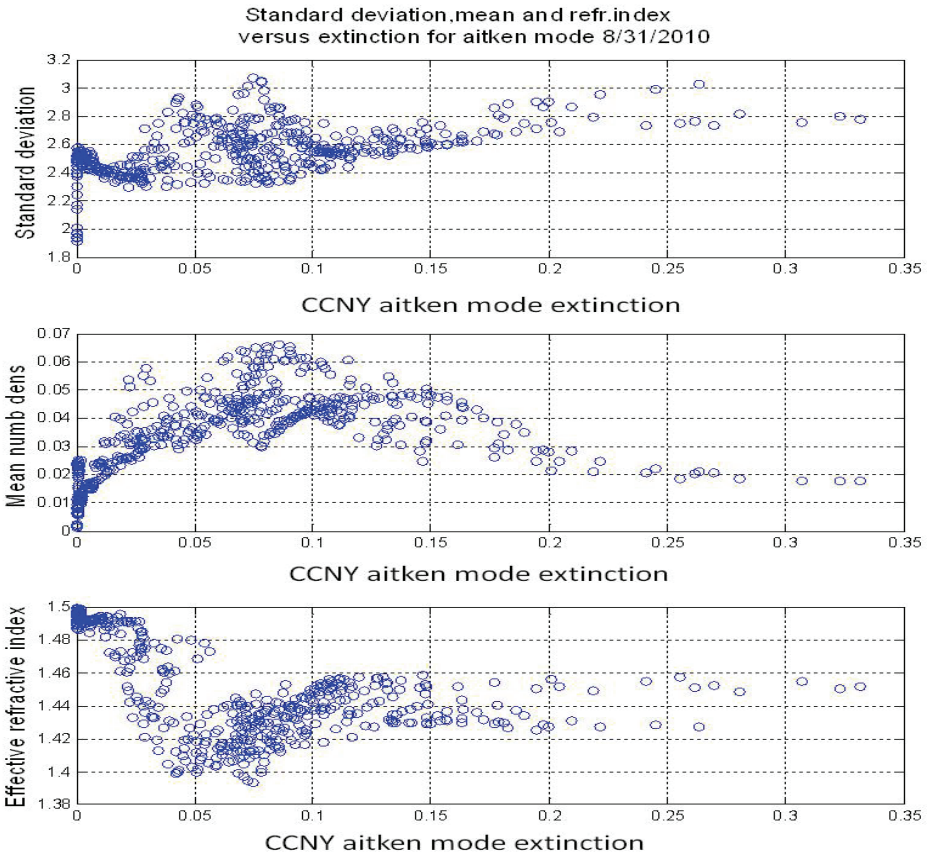


Figure 7: AOD comparisons between CMAQ, sunphotomer and the technique proposed by authors using CMAQ-OPAC input parameters for calculation of the optical parameters.



a)



b)

Figure 8a) and b): Statistical parameters of size distribution (mean and standard deviation of radius of aerosols) and effective refractive index as a function of extinction as calculated using the technique proposed by authors using CMAQ-OPAC input parameters for calculation of the optical parameters.

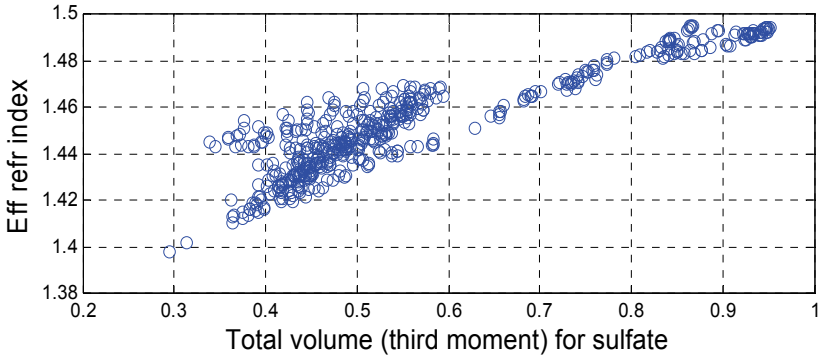


Figure 9: Refractive index variation with total volume for sulphate.

CONCLUSIONS

In this paper, we use a number of remote sensing instruments to assess some of the upper atmospheric properties measured in the CMAQ aerosol profiles. In doing this comparison, we first show that the popular Malm parameterisation often underestimates the true optical extinction especially for higher pollutant levels. This is clearly demonstrated when making comparisons to the total column extinction measurements of AERONET. Furthermore, we use the combined passive and active data to assess over predictions in the TEOM PM2.5 mass. In particular, we show that the vertical structure of the profiles is in reasonable qualitative agreement so that the overestimation occurs over the entire profile. This seems to give evidence that this is primarily an emission overestimation effect and not a PBL height artefact.

In addition, we also explored the modifications of the extinction as a function of the different microphysical size parameters and refractive index and illustrate that very small changes in these parameters can make significant changes to the optical coefficients making more precise modelling of these parameters critical to wider comparisons.

REFERENCES

1 Schwartz S E, 2010. Why hasn't Earth warmed as much as expected? Journal of Climate, 23: 2453-2464

2 New York State Energy Research and Development Authority, 2008. Assessment of Carbonaceous PM 2.5 for New York and the Region, Final Report, 08-01, Volume II, March 2008, 383 pp.. (last date accessed: 8 Mar 2012)

3 CMAQ Center, 2008. Operational Guidance for the Community Multi Scale Air Quality (CMAQ) Modeling System, Aerosol Notes (last date accessed: 8 Mar 2012)

4 US Environmental Protection Agency. PM Standards (last date accessed: 8 Mar 2012)

5 Vladutescu V, Y Wu, B Gross, F Moshary, S Ahmed, M Razani & R Blake. Remote sensing instruments used for measurement and model validation of optical parameters of atmospheric aerosols. IEEE Transactions on Instrumentation and Measurements, to be published, DOI: 10.1109/TIM.2011.2178664

6 Doraiswamy P, C Hoegrefe, W Hao, K Civerelo, J Y Ku & G Sistla, 2010. A retrospective comparison of model based forecasted PM2.5 concentrations with measurements. Journal of Air and Waste Management Association, 60(11): 1293-1308; doi: 10.3155/1047-3289.60.9.1

7 Gan C M, Y Wu, B L Madhvan, B Gorss & F Moshary, 2011. Application of active optical sensors to probe the vertical structure of the urban boundary layer to assess anomalies in air quality model PM2.5 forecasts. Atmospheric Environment, 45: 6613-6621

8 Binkowski F S & S J Roselle, 2003. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component: 2. Model description. Journal of Geophysical Research, 108(D6), 4183, doi:10.1029/2001JD001409

9 NYSDEC Bureau of Air Quality Surveillance. PM2.5 Monitoring, Fine Particulate Matter Monitoring (last date accessed: 8 Mar 2012)

10 Hanel G, 1976. The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air. Advances in Geophysics, 19: 73-188

11 Tang I N, A C Tridico & K H Fung, 1997. Thermodynamic and optical properties of sea salt aerosols. Journal of Geophysical Research, 102(D19): 23269-23275

12 Tang I N, 1994. Chemical and size effects of hygroscopic aerosols on light scattering coefficients. Journal of Geophysical Research, 101(D14): 19245-19250

13 Hess M, P Koepke & I Schult, 1998. Optical properties of aerosol and clouds. The software package OPAC. Bulletin of the American Meteorological Society, 79(5): 831-844

14 Malm W C, J F Sisler, D Huffman, R A Eldred & T A Cahill, 1994. Spatial and seasonal particle concentration and optical extinction in the United States. Journal of Geophysical Research, 99(D1): 1347-1370

15 Mikhailov E, S Vlasenko, R Niessner & U Poschel, 2004. Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement. Atmospheric Chemistry and Physics, 4: 323-350

16 Pahlow M, G Feingold, A Jefferson, E Andres, J A Ogren, J Wang, Y-N Lee, R A Ferrare & D D Turner, 2006. Comparison between lidar and nephelometer measurements of aerosol hygroscopicity at the Southern Great Plains Atmospheric Radiation Measurement site. Journal of Geophysical Research, 111, D05S15, 8pp,doi: 10.1029/2004JD005646

17 Wall S M, W John & J L Ondo, 1988. Measurement of aerosol size distribution for nitrate and major ionic species. Atmospheric Environment, 22: 1649-1656

18 McMurry P, M Shepherd & J Vickery, 2003. Particulate Matter Science for Policy Makers: A NARSTO Assessment. Electric Power Research Institute, Palo Alto, CA (Cambridge University Press) 509 pp. (last date accessed: 8 Mar 2012)

19 Cabada J C, A Khlystov, A E Wittig, C Pilinis & S N Pandis, 2004. Light scattering by fine particles during the Pittsburgh Air Quality Study: Measurements and modelling. Journal of Geophysical Research-Atmospheres ,109(D16S03), 13 pp.

20 Wittig AE, S N Pandis, S V Hering, B W Kirby, A K Khlystov, S Takahama & C I Davidson, 2004. Semi-continuous PM2.5 inorganic composition measurements during the Pittsburgh Air Quality Study. Atmospheric Environment, 38: 3201-3213