

## Light scattering by fine particles during the Pittsburgh Air Quality Study: Measurements and modeling

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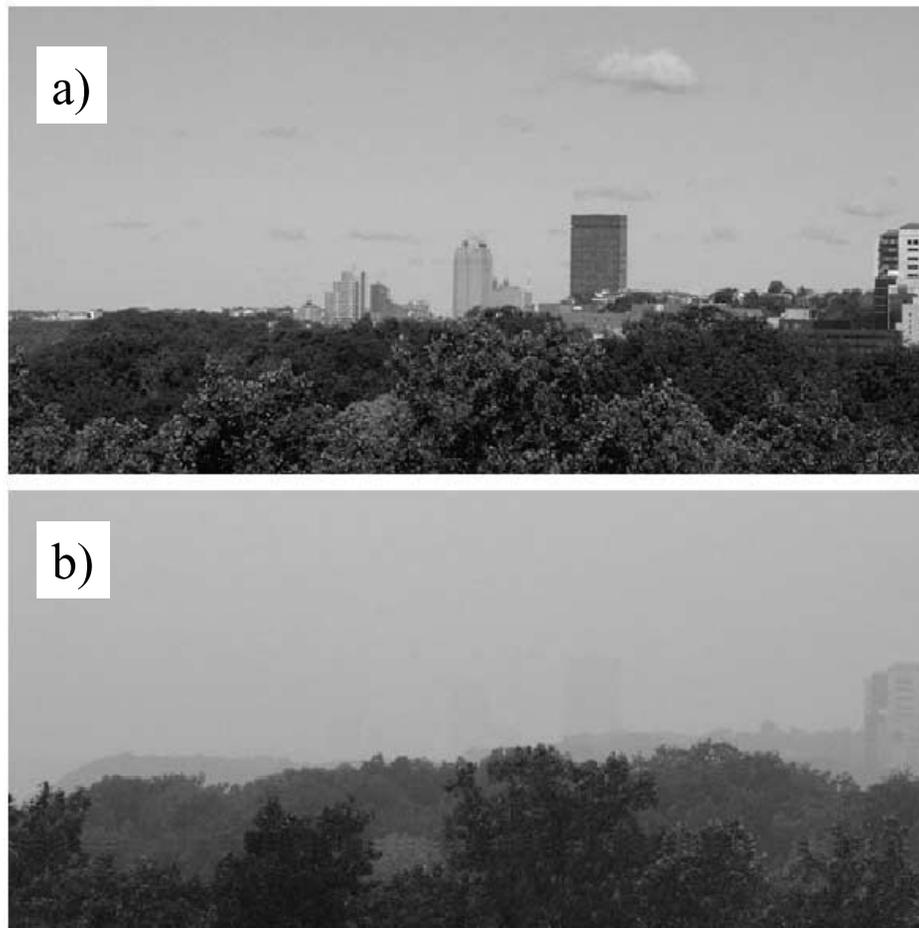
[1] Light scattering by fine particulate matter was measured during the Pittsburgh Air Quality Study (PAQS) as close to ambient conditions as possible. Several approaches are used for the theoretical calculation of the scattering coefficient and the results are compared to the direct measurements. The first approach uses ambient high time and daily resolved PM<sub>2.5</sub> composition concentrations to estimate the scattering coefficient assuming that the aerosol is an external mixture. The second approach uses a thermodynamic model and Mie theory to predict the scattering coefficient of aerosols from daily size composition distributions. The third approach introduces high time and daily resolved ambient aerosol water concentrations and concentrations of sulfate, nitrate, organic material, and soil with fixed scattering efficiencies. During the summer the first two approaches underestimate the measured scattering coefficient by around 20%. Agreement within experimental error is obtained between the measured scattering coefficient and the model, incorporating measured water aerosol concentrations. During the winter the first two approaches tend to overpredict the measured scattering by around 15%. This overprediction is weakly correlated to the organic mass. The modeling approaches suggest that sulfate and the associated water contribute 65–73% to the scattering coefficient during the summer, with organic material contributing 25–30%. During the winter, sulfate accounts for 35–43%, nitrate accounts for 24–32%, and organic material accounts for 30–40% of the scattering coefficient. *INDEX TERMS*: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS*: atmospheric aerosols, optical properties, Pittsburgh Air Quality Study

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### 1. Introduction

[2] Visibility degradation is probably the most readily perceived impact of atmospheric pollution. The protection of good visibility conditions for scenic views and the reduction of haze in rural and urban areas is one of the main goals of the Clean Air Act (U.S. Environmental Protection Agency, 1999). Figure 1 shows the effect of fine particle mass concentrations on visibility impairment for the Pittsburgh metropolitan area. High fine particulate concentrations can deteriorate visibility reducing the visual range to a few hundred meters.

[3] Fine particulate matter (below 2.5 microns in aerodynamic size) is efficient in scattering light in the atmosphere and is the main cause of visibility degradation over urban and remote areas. Light scattering from fine particles depends on various factors such as chemical composition, ambient relative humidity, and size distribution of the aerosol [Ouinette and Flagan, 1982; Sloane, 1984; Seinfeld and Pandis, 1998; Watson, 2002]. Sulfate and organic material are the most common components of the fine particulate matter (below 2.5  $\mu\text{m}$ ) for the eastern United States [Malm, 2000; U.S. Environmental Protection Agency, 2002; NARSTO, 2003]. The mass of these particles tends to accumulate between 0.1 and 1  $\mu\text{m}$ . Scattering by particles of sizes comparable to the wavelength of visible light (0.4–0.7  $\mu\text{m}$ ) is mostly responsible for visibility reduction in the atmosphere.



**Figure 1.** Comparison of visual characteristics during PAQS. View of downtown Pittsburgh from the PAQS main site at Schenley Park. (a) Day with low aerosol concentrations:  $\text{PM}_{2.5} = 6 \mu\text{g}/\text{m}^3$ ,  $b_{\text{sp}} = 5 \text{ Mm}^{-1}$ ,  $\text{RH} = 60\%$ . (b) Polluted day:  $\text{PM}_{2.5} = 70 \mu\text{g}/\text{m}^3$ ,  $b_{\text{sp}} = 255 \text{ Mm}^{-1}$ ,  $\text{RH} = 74\%$ . See color version of this figure at back of this issue.

[4] The presence of water in the aerosol phase increases the ability of these particles to scatter light. Hygroscopic growth of inorganic salts as a function of relative humidity has been thoroughly studied by several authors [Tang *et al.*, 1981; Tang, 1996; Cruz and Pandis, 1998, 2000; Hand *et al.*, 2000]. Thermodynamic models that calculate the equilibrium of the inorganic aerosol with the gas phase have been developed, and the estimates of these models are usually in agreement with the laboratory measurements [Pilinis and Seinfeld, 1987; Wexler and Seinfeld, 1990, 1991; Nenes *et al.*, 1998; Ansari and Pandis, 1999].

[5] The role of organic material in the aerosol water uptake is not well understood. In some cases an increase in aerosol water is observed, while in others a decrease in aerosol water content is reported when organics are added to atmospheric inorganic aerosols [Cruz and Pandis, 1998, 2000; Saxena *et al.*, 1995]. Relatively little theoretical work has been done trying to explain the water uptake from organic aerosol, mainly because of the difficulties in estimating the physical properties of organic aerosols, which are composed of hundreds of different compounds [Saxena and Hildemann, 1997; Jang and Kamens, 1998; Ansari and Pandis, 2000; Hemming and Seinfeld, 2001; Koo *et al.*, 2003]. However, Ansari and Pandis [2000]

reported that the secondary organic aerosol (SOA) fraction of the aerosol could account for around 20% of the aerosol water. Koo *et al.* [2003] reported that SOA increased the water uptake from aerosols by 2–15%, depending on the conditions.

[6] Several authors have used approaches of different complexity to estimate the visibility degradation due to aerosols in the atmosphere [Watson, 2002; Molenaar *et al.*, 1994; White, 1986]. The simpler models are based on bulk concentrations of fine particulate matter (PM) [Trijonis *et al.*, 1988; Charlson *et al.*, 1992; Gebhart *et al.*, 1994; Malm *et al.*, 1994, 2000a]. These models assume an external mixture of the aerosol components and average scattering efficiencies for each individual compound to determine the increase in the scattering efficiency as a function of relative humidity. In more complex models, additional characteristics of the aerosol (i.e., mixing state, size distributions of the different compounds, and the physical shape of the particles) are taken into account, and Mie theory is used to calculate the optical properties [Heintzenberg, 1980; Jaggard *et al.*, 1981; Ouimette and Flagan, 1982; Sloane, 1984; Wu *et al.*, 1996; Hegg *et al.*, 1993; Zhang *et al.*, 1994; Lowenthal *et al.*, 1995; Tang, 1996]. In the most advanced models the aerosol water

content is calculated by thermodynamic models or estimated from semiempirical relationships [Sloane and Wolff, 1985; Sloane, 1983, 1986; Larson et al., 1988; Pilinis, 1989; Nemesure et al., 1995; Pilinis et al., 1995; Quinn et al., 1995; McMurry et al., 1996; West et al., 1998; Koloutsou-Vakakis et al., 1998; Malm et al., 2000a, 2000b].

[7] Most previous studies found that measured scattering was generally consistent with the aerosol composition measurements [White et al., 1994; Pilinis et al., 1995; Malm et al., 1996], assuming that the inorganic aerosol components were responsible for the PM water uptake [Malm et al., 2003]. Discrepancies between predictions and observations have been attributed to PM composition measurement errors or lack of high temporal resolution composition measurements, lack of information about the aerosol size distribution, lack of understanding of the particle hygroscopic growth, and uncertainties in the scattering efficiencies of the different components.

[8] Despite the advances, there are a number of remaining issues. The ability of the more advanced theoretical tools to simulate visibility reduction has rarely been tested in the eastern United States. The few available studies [Sloane and Wolff, 1985; Lowenthal et al., 1995; Malm et al., 2000a; Kreisberg et al., 2001; Malm and Day, 2000] have relied on daily or semidaily average composition measurements and not on higher-resolution information. The causes of the discrepancies between models and measurements are not well understood because the aerosol water concentration has not been measured in any of the previous field campaigns. Finally, the role of organics in the water uptake by aerosols and therefore their contribution to scattering is yet to be elucidated.

[9] In this work, several modeling approaches of varying complexity are used to predict the scattering coefficient of aerosol particles using composition and size distribution measurements during the Pittsburgh Air Quality Study (PAQS) during the summer of 2001 (July–August) and during the winter of 2002 (January). The results of each approach are compared to the measured scattering coefficient from nephelometry. High time resolution (1 hour) and daily measurements of the principal components of the fine particulate matter are used for the estimations of the scattering coefficient for the simplest approach proposed. Daily concentrations and size distributions are used for a thermodynamic model applying Mie theory to estimate the scattering coefficient. Finally, for the first time we use continuous measurements of the aerosol water concentration to directly calculate its contribution to light scattering. We conclude by addressing the role of aerosol water and organics in the optical properties of the aerosol measured at PAQS.

## 2. Experiment

### 2.1. Scattering Coefficient Measurements

[10] An integrating nephelometer (NGN-3, Optec, Inc., Lowell, Michigan) was used to measure the scattering coefficient of PM<sub>2.5</sub> continuously during the summer of 2001 (July–August) and during the winter of 2002 (January) at PAQS. The main sampling site was located on the

top of a hill just outside the Carnegie Mellon University campus, around 5 km from downtown Pittsburgh.

[11] Scatter of light inside the instrument chamber is measured over a 170° angle, from 5° to 175° at a range of wavelengths, peaking near 550 nm for typical atmospheric aerosols [Molenaar, 1997]. A cyclone is used in the sampling inlet for the collection of PM<sub>2.5</sub> from ambient air. Raleigh scattering (clean air) calibrations were performed automatically by the instrument approximately every 12 hours. The nephelometer was operated as close to ambient conditions as possible, without using the heater or any treatment of the incoming sample air. However, small differences in the ambient air temperature and the chamber were still observed. Air temperature inside the chamber was on average 3°C higher than the ambient air temperature for the length of the project. Differences in the chamber and the ambient temperature affect the relative humidity of the sampled air. The chamber relative humidity was estimated on the basis of the Clausius-Clapeyron equation [Gebhart et al., 1994]:

$$\text{RH}_{\text{cham}} = \text{RH}_{\text{amb}} \cdot \exp\left(5210.5 \cdot \left(\frac{T_{\text{amb}} - T_{\text{cham}}}{T_{\text{amb}} \cdot T_{\text{cham}}}\right)\right), \quad (1)$$

where RH<sub>cham</sub> is the relative humidity inside the nephelometer measuring chamber, RH<sub>amb</sub> is the ambient relative humidity, T<sub>amb</sub> is the ambient temperature (°K), and T<sub>cham</sub> is the nephelometer chamber temperature (°K). Relative humidity inside the chamber of the nephelometer ranged from 15 to 92% during the measurements.

[12] Ambient relative humidity (RH) was measured by the meteorological station installed at the main site of the PAQS with a Campbell Scientific HMP45C probe. The probe contained a Vaisala HUMICAP<sup>®</sup> 180 capacitive relative humidity sensor (expected accuracy at 20°C is ±2% from 0 to 90% RH and ±3% from 90 to 100% RH).

### 2.2. Aerosol Sampling

[13] Several samplers were operated during the Pittsburgh Supersite project for the determination and speciation of PM<sub>2.5</sub> aerosol mass. Continuous and semicontinuous instruments were used for the determination of total PM<sub>2.5</sub> mass, organic and elemental carbon, sulfate, nitrate, and ammonium aerosol concentrations from July 2001 to July 2002 [Wittig et al., 2004a]. The uncertainties in the measurements of the major ions are described by Wittig et al. [2004a, 2004b] and the merging of the different data sets for the same parameter to one self-consistent data set in the work of Takahama et al. [2004].

[14] A tamper element oscillating microscale (TEOM, Series 1400a, Rupprecht and Patashnick Co., Inc., Albany, New York) was operated continuously during PAQS, reporting PM<sub>2.5</sub> mass concentrations. The TEOM operated at 30°C and was equipped with a Nafion diffusion dryer sample equilibration system (SES, Rupprecht and Patashnick Co., Inc.). Atmospheric aerosol was collected on quartz fiber filters using several sampler configurations for the determination of the carbonaceous material concentrations [Cabada et al., 2004a; Subramanian et al., 2004]. High time resolution samples were collected with a denuded in situ semicontinuous sampler (Carbon aerosol analysis field instrument, Sunset Lab, Tigard, Oregon),

with 2–4 hour time resolution. The denuder was used to remove gas-phase organics and to minimize the positive organic aerosol sampling artifact. Daily samples were collected using an undenuded sampler with the use of backup filters for the correction of positive and negative artifacts [Subramanian *et al.*, 2004]. The ambient organic and elemental carbon concentrations were determined following the National Institute for Occupational Safety and Health protocol with the thermal/optical transmittance method and a flame ionization detector (FID) [Cabada *et al.*, 2004a]. Concentrations of secondary organic aerosol (SOA) were estimated using the elemental carbon (EC) tracer method [Cabada *et al.*, 2004a]. Aerosol concentrations of sulfate and nitrate were measured on a 10-min basis using Rupprecht and Patashnick (R&P) instrument models 8400N and 8400S, respectively [Wittig *et al.*, 2004b]. High time resolution total (gas + aerosol) ammonium, nitrate, and chloride concentrations were measured using a steam sampler [Khlystov *et al.*, 1995]. The crustal material concentrations were less than 5% of the PM<sub>2.5</sub> concentration [Rees *et al.*, 2004]. The comparison of the aerosol mass concentration (measured using the federal reference method) and the sum of the component concentrations during PAQS are discussed by Rees *et al.* [2004]. After accounting for the water retained on the filters when the aerosol was acidic, mass balance was achieved within 10% for all days, well within experimental error. The aerosol was neutral during the winter but was often acidic during the daytime of the summer days [Rees *et al.*, 2004].

[15] Size distributions of the major inorganic and carbonaceous material were measured using a micro-orifice uniform deposit impactor (MOUDI). Daily samples were collected for 15 days during the summer (July 2001) and for 8 days during the winter intensive (January 2002) [Cabada *et al.*, 2004b]. Samples were collected on aluminum foils for analysis of carbonaceous material and on Teflon filters for analysis of particle mass and inorganic compounds. Carbonaceous concentrations from the MOUDI samples were determined by the thermal/optical method (same as the filter-based samplers), and the inorganic compound concentrations were determined by ion chromatography. During the summer, around 50% of the organic material was lost from the aluminum foils as compared to a filter-based sampler. The organic aerosol losses were negligible during the winter. The corrected MOUDI values (uniform correction for all stages), based on the artifact corrected filter measurements, were used in the present study. Cabada *et al.* [2004b] showed that these corrections satisfy the mass balance of all MOUDI stages.

[16] The comparison of the inorganic aerosol measurements is discussed by Wittig *et al.* [2004a], the comparison of the organic aerosol measurements is discussed by Subramanian *et al.* [2004] and Cabada *et al.* [2004a], and the comparison of the MOUDI results with the bulk measurements is discussed by Cabada *et al.* [2004b]. The results of all of these approaches with different time and size resolutions were merged into one self-consistent data set [Takahama *et al.*, 2004; Cabada *et al.*, 2004b] using the artifact-corrected traditional filter measurements as the basis. When more than one continuous method was used, the average of the corrected values was used for each hour. In the present study the daily average values of the

continuous measurements are the same as these of the daily filter measurements, and the sum of the MOUDI concentrations are equal to the artifact corrected bulk measurements.

### 2.3. Aerosol Water Content

[17] A dry-ambient aerosol size spectrometer (DAASS) system [Stanier *et al.*, 2004] operated during PAQS reporting number, surface area, and volume distributions of aerosols. The system consists of two scanning mobility particle sizers (SMPS, TSI 3936N25 and TSI 3936L10) and an aerodynamic particle sizer (APS, TSI APS 3320) that measure the aerosol size distribution between 3 nm and 10 μm in diameter. The inlets of the instruments and their sheath air lines were equipped with computer controlled valves that direct air through Nafion dryers or bypass them. The Nafion dryers reduce the RH to below 30%, at which ambient particles are expected to lose most or all of the water. The instrument cycles between dried and the ambient conditions every 7 min and is synchronized with the scan times of the aerosol spectrometers. The aerosol water concentrations measurements are described in detail by A. Khlystov *et al.* (Water content of ambient aerosol during the Pittsburgh Air Quality Study, submitted to *Journal of Geophysical Research*, 2004, hereinafter referred to as Khlystov *et al.*, submitted manuscript, 2004). The amount of aerosol water can be found from the difference of the integrated dry and wet aerosol volumes. Owing to malfunctions in the APS system, aerosol water concentrations are only calculated from this approach for July and August 2001.

## 3. Scattering Coefficient Calculation

### 3.1. Approach 1a: Use of Bulk PM<sub>2.5</sub> Composition (High Time Resolution)

[18] The scattering coefficient was calculated assuming external mixing of the aerosol components and utilizing bulk PM<sub>2.5</sub> concentrations of the different compounds with the ability to scatter light, using the relationship proposed by Malm *et al.* [2000a]:

$$\text{Bsp} = 4.125 \times [\text{SO}_4^{2-}] \times f(\text{RH})_{\text{salt}} + 3.87 \times [\text{NO}_3^-] \times f(\text{RH})_{\text{salt}} + 4 \times [\text{OM}] \times f(\text{RH})_{\text{org}} + 1 \times [\text{SOIL}], \quad (2)$$

where  $[\text{SO}_4^{2-}]$  is the sulfate concentration ( $\mu\text{g}/\text{m}^3$ ),  $[\text{NO}_3^-]$  is the nitrate concentration ( $\mu\text{g}/\text{m}^3$ ),  $[\text{OM}]$  is the organic mass concentration ( $1.8 \times [\text{OC}]$ ) ( $\mu\text{g}/\text{m}^3$ ) and  $[\text{SOIL}]$  is the crustal material ambient concentration, estimated here to be 4% of the TEOM fine mass ( $\mu\text{g}/\text{m}^3$ ). The dry scatter efficiency of sulfates and nitrates is assumed to be 3 m<sup>2</sup>/g, 4 m<sup>2</sup>/g corresponds to the organic material dry scattering efficiency, and 1 m<sup>2</sup>/g corresponds to the crustal material scattering efficiency [Trijonis *et al.*, 1988; Gebhart *et al.*, 1994]. The above parameters were estimated from measurements mainly in the western United States. Sulfate was assumed to be fully neutralized (i.e., ammonium sulfate) for both summer and winter, and the 4.125 factor in equation (2) accounts for both the scatter efficiency and the ammonium corresponding to the sulfate. The increase in scattering efficiency as a function of relative humidity for the inorganic hygroscopic aerosols,  $f(\text{RH})_{\text{salt}}$ , was calculated

**Table 1.** Average Conditions Used to Calculate the Scattering Efficiency Curves During Summer and Winter

	Summer	Winter
Temperature, K	300	280
Total NH <sub>3</sub> , <sup>a</sup> μg/m <sup>3</sup>	2.6	1.6
Total HNO <sub>3</sub> , <sup>a</sup> μg/m <sup>3</sup>	1.4	2.0
Total HCl, <sup>a</sup> μg/m <sup>3</sup>	0.4	0.3
Size range, μm	Sulfate, μg/m <sup>3</sup>	Sulfate, μg/m <sup>3</sup>
0.056–0.10	0.1	0.0
0.10–0.18	0.5	0.2
0.18–0.32	1.3	0.6
0.32–0.56	2.2	0.6
0.56–1.00	3.9	0.9
1.00–1.80	0.6	0.1
1.80–2.50	0.1	0.0

from Mie theory and the average size distribution of sulfate (Table 1) in PAQS using the model described by *Pilinis* [1989] (see also the description of approach 2). For the summer the aerosol was assumed to be always liquid based on the PM water concentration measurements of *Khlystov et al.* (submitted manuscript, 2004). For the winter the particles were assumed to be solid below approximately 60% RH and liquid for higher RH based on the same measurements. The same  $f(\text{RH})_{\text{salt}}$  was used both for sulfate and nitrate since the scattering efficiency curves are very similar for these two compounds [*Tang, 1996*]. Figure 2 shows the calculated scattering efficiencies for the two seasons. A higher scattering efficiency at high RH is calculated for the winter. During the winter the geometric mean diameter of the aerosol is smaller than during the summer [*Cabada et al., 2004b*]. For this approach the contribution of the organic matter to aerosol water is considered to be negligible; therefore  $f(\text{RH})_{\text{org}}$  is set to 1.

[19] Most mass balance studies use a value of 1.4 for the organic carbon (OC) multiplier. Recent work by *Turpin and Lim* [2001] examines this factor, recommending values ranging from 1.1 for fresh emissions to 1.6–2.1 for an aged aerosol. Comparison of PAQS main site data with satellite sites indicates that the air quality in Pittsburgh is dominated by regional transport [*Tang et al., 2004*]. We therefore used a multiplication factor of 1.8, which is representative of an aged, regional aerosol to estimate total organic mass from OC measurements. Our choice of the 1.8 for the conversion of the OC to organic aerosol concentration is supported by the mass closure study of *Rees et al.* [2004].

### 3.2. Approach 1b: Use of Bulk PM<sub>2.5</sub> Composition (Daily Resolution)

[20] For this approach the scattering from particles was also calculated from equation (2), but daily averaged concentrations were used. Since the effect of relative humidity on the scattering from particles is nonlinear, daily averaged values need to account for this to avoid biasing the calculations of the model low. To estimate the effect, the daily average of  $f(\text{RH})$  is calculated from hourly resolved data (from approach 1a). From the daily average value of  $f(\text{RH})$ , the effective value of relative humidity is estimated. On average, this effective relative humidity value is 4%

higher than the arithmetic average of relative humidity for each day. Therefore the  $f(\text{RH})_{\text{salt}}$  is calculated at the daily averaged RH plus 4% for all days.

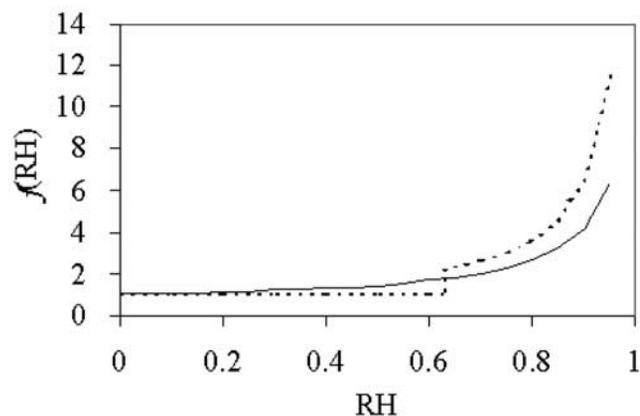
### 3.3. Approach 2: Use of Mie Theory, Size Composition Distributions, and a Thermodynamic Model

[21] In this approach the scattering coefficient was calculated using a thermodynamic model and Mie theory. The model is described in detail by *Pilinis* [1989]. Briefly, the thermodynamic model uses as inputs the measured size distributions of sulfate, sodium, organic material, elemental carbon, crustal material (Tables 2 and 3), and total concentrations (gas + aerosol) of ammonium, nitrate, and chloride together with the ambient temperature and RH. The model finds the appropriate form of the sulfate in the particulate phase (sulfate, bisulfate, or sulfuric acid), partitions the total inorganic semivolatile species (nitrate, ammonium, chloride) between the gas and aerosol phases, calculates their size distribution, and also calculates the aerosol water size distribution. Therefore the thermodynamic model provides the full size composition distribution of the particles including water. After the thermodynamic calculation, Mie theory is used to estimate the scattering coefficient of the aerosol. The relative humidity used is the effective relative humidity used in approach 1b. The performance of one size-resolved equilibrium calculation per day reduces significantly the computational cost and the potential numerical problems of this method. For the days where no size/composition measurements were available (e.g., August 2001, second half of January 2002), the average distribution for the month was used together with the bulk concentrations measured during that day.

### 3.4. Approach 3a: Use of Measured Aerosol Water Concentrations (High Time Resolution)

[22] Since ambient aerosol water concentrations are available from the DAASS system, the contribution of water to the scattering coefficient can be directly estimated. For this analysis, equation (2) is modified to account for the water aerosol as an ambient concentration as follows:

$$\text{Bsp} = 4.125 \times [\text{SO}_4^{2-}] + 3.87 \times [\text{NO}_3^-] + 4 \times [\text{OM}] + 1 \times [\text{SOIL}] + 3 \times [\text{WATER}]. \quad (3)$$



**Figure 2.** Scattering efficiency curve,  $f(\text{RH})$ , as a function of relative humidity for the summer (solid line) and winter (dashed line) during PAQS.

**Table 2.** Summer Average Size Distributions ( $\mu\text{g}/\text{m}^3$ ) of Compounds Used and Predicted by the Thermodynamic Model

Size Range, $\mu\text{m}$	Sodium	Sulfate	OM	EC	Dust	Nitrate	Ammonium
0.056–0.10	0.00	0.1	0.4	0.0	0.00	0.00	0.03
0.10–0.18	0.01	0.5	0.7	0.1	0.00	0.01	0.1
0.18–0.32	0.01	1.3	1.1	0.1	0.01	0.01	0.3
0.32–0.56	0.01	2.2	1.7	0.1	0.01	0.01	0.6
0.56–1.00	0.01	3.9	1.4	0.1	0.02	0.02	1.0
1.00–1.80	0.01	0.6	0.7	0.1	0.02	0.02	0.1
1.80–2.50	0.01	0.1	0.4	0.0	0.05	0.05	0.03

The terms used in this equation are the same as in equation (2), with the introduction of the water aerosol concentration [WATER] ( $\mu\text{g}/\text{m}^3$ ). Note that for equation (3) the dependence of the scattering efficiency as a function of relative humidity,  $f(\text{RH})$ , is not needed. The aerosol water scattering coefficient is assumed to be  $3 \text{ m}^2/\text{g}$ . The choice of the water mass scattering efficiency is based on the similarity of the optical properties and size distribution of water with that of the sulfates and nitrates [Seinfeld and Pandis, 1998]. The use of the same scattering efficiency for the inorganic salts and water is implicitly consistent with the previous studies of aerosol optical properties that calculated  $f(\text{RH})$  on the basis of the measured PM hygroscopic growth.

### 3.5. Approach 3b: Use of Measured Aerosol Water Concentrations (Daily Resolution)

[23] For this approach, daily averaged concentrations of sulfate, nitrate, organic mass, and water were used to estimate the scattering coefficient from equation (3).

## 4. Results and Discussion

### 4.1. Approach 1a: Use of Bulk $\text{PM}_{2.5}$ Composition (High Time Resolution)

[24] The time series of measured and estimated scattering coefficient using this approach is shown in Figure 3. For both seasons the model predictions track the actual measurements with the exception of localized episodes mostly during the summer. Figure 4 depicts the comparison between the measured scattering coefficient from the nephelometer and the estimated value from equation (2) for the high time resolution measurements. Good correlation between the measured and the reconstructed scatter is shown during the summer, and a weaker correlation is observed during the winter due to lower values (Table 4). The uncertainty of the predicted values because of the PM composition measurement uncertainty is estimated to be around 15% and can explain most but not all the discrepancies between predictions and measurements.

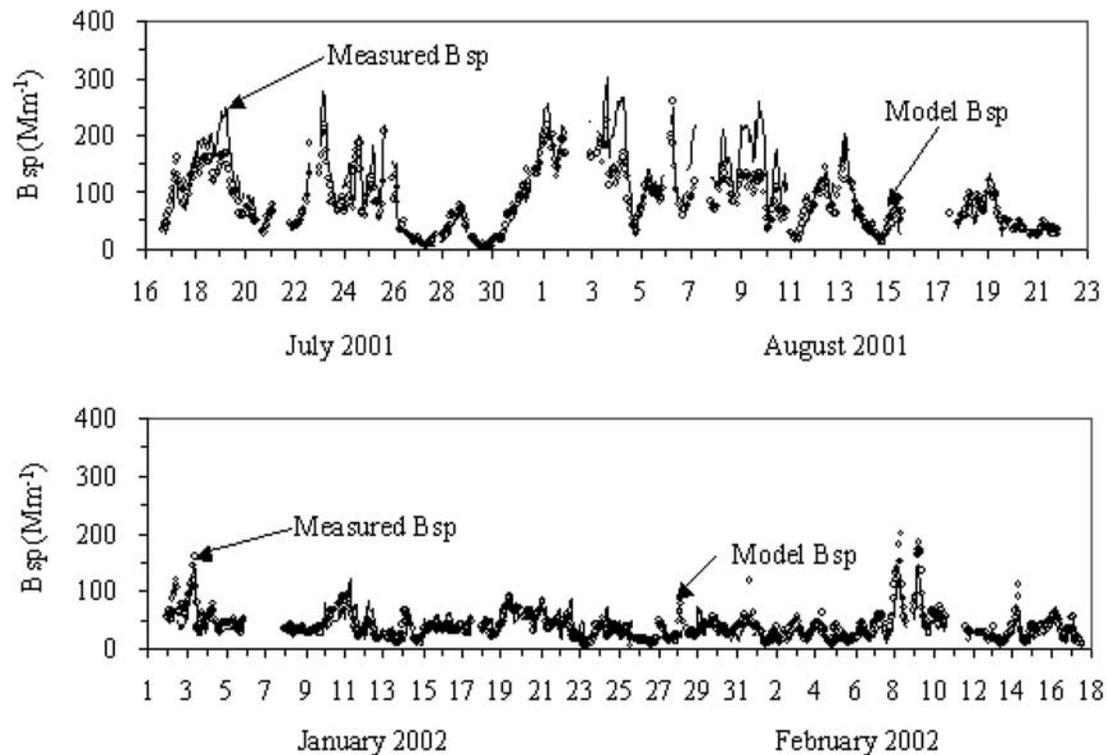
[25] During the daytime of the summer months, Pittsburgh aerosol is often acidic, whereas for the other seasons the aerosol is mostly neutralized [Rees *et al.*, 2004]. During periods when the aerosol is acidic, the assumption of neutralized particles may introduce errors. Malm *et al.* [2000a] showed that errors in the assumed degree of neutralization can explain some of the discrepancies between predictions and observations. However, for our case, these errors are expected to be less than 5% on a daily average basis because of the small difference in the mass between ammonium sulfate and bisulfate and because aerosol was acidic only during the daytime when the RH was low. This is consistent with the weak correlation ( $R^2 = 0.08$ ) of the model error for scattering to the sulfate concentrations. The error was also not correlated with the nitrate ( $R^2 = 0.12$ ) and the organic aerosol ( $R^2 = 0.14$ ) concentrations. However, a relatively high and statistically significant correlation (at the 99.5% level) was found between this error and the measured concentration of ambient aerosol water ( $R^2 = 0.53$ ). The link of the error to the aerosol water indicates a potential limitation of the model used to deal with the effect of hygroscopic growth on the scattering from particles.

[26] In relative terms, greater discrepancies between the model and the measurements are observed for the winter (Table 4). There is practically no correlation between the ambient concentrations of the different compounds and the error although there is a downward trend in all of them. The organic mass seems to inversely correlate weakly ( $R^2 \approx 0.2$ ) with the error. This could be due to an overestimation of the organic mass since the mass conversion factor used ( $1.8 \times [\text{OC}]$ ) might be too high for the winter carbonaceous aerosol. The hydrophobic organics could also have a negative effect on the ability of the inorganics to absorb water.

[27] The assumption of an externally mixed aerosol is not physically realistic but provides a good approximation of the scattering properties of atmospheric aerosol. The error in the scattering coefficient introduced by neglecting the

**Table 3.** Winter Average Size Distributions ( $\mu\text{g}/\text{m}^3$ ) of Compounds Used by the Thermodynamic Model

Size Range, $\mu\text{m}$	Sodium	Sulfate	OM	EC	Dust	Nitrate	Ammonium
0.056–0.10	0.00	0.0	0.2	0.0	0.02	0.0	0.0
0.10–0.18	0.00	0.2	0.7	0.1	0.04	0.2	0.1
0.18–0.32	0.01	0.6	0.8	0.1	0.05	0.4	0.25
0.32–0.56	0.01	0.6	1.0	0.1	0.03	0.4	0.25
0.56–1.00	0.01	0.9	0.8	0.1	0.06	0.8	0.4
1.00–1.80	0.02	0.1	0.3	0.0	0.08	0.1	0.05
1.80–2.50	0.02	0.0	0.1	0.0	0.08	0.1	0.02



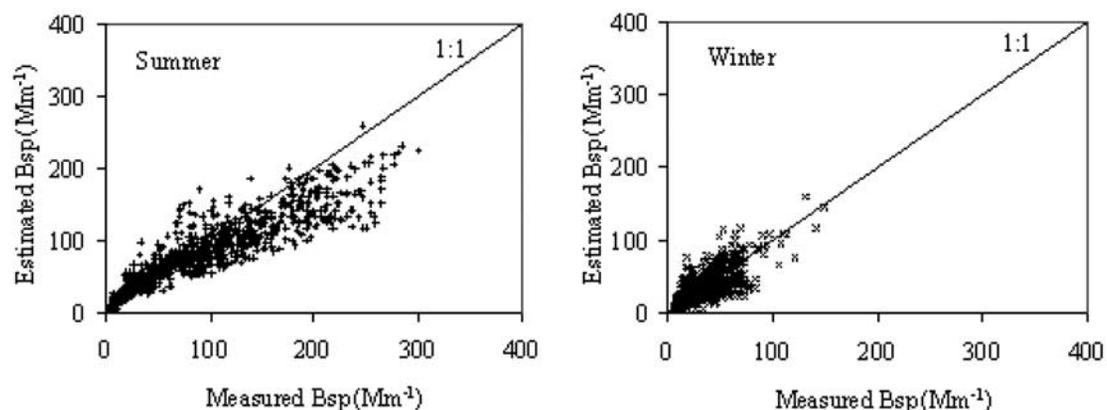
**Figure 3.** Time series of measured scattering coefficient (line) and estimated scattering coefficient (symbols) from approach 1a. Each point corresponds to 1-hour average.

interactions among the different aerosol species coexisting in the same particle is only a few percent [Seinfeld and Pandis, 1998]. One of the advantages of this approach is the direct apportionment of the scattering to the aerosol components [White, 1986]. On average, for the summer, 70% of the estimated scattering is due to sulfate, followed by the organic material with 25% and the remaining fraction is due to nitrates and soil. During the winter, sulfate accounts for 43% of the scattering, organics account for 31%, and nitrates contribute 24% on average. Changes in one of the aerosol components may result in changes in the other components (e.g., an increase in nitrate may accompany a decrease in sulfate), so these results should be used with

caution [Seinfeld and Pandis, 1998]. The reported contributions are based on the external mixture assumption neglecting these interactions.

#### 4.2. Approach 1b: Use of Bulk $PM_{2.5}$ Composition (Daily Resolution)

[28] Figure 5 shows time series of measured and estimated scattering coefficient applying equation (2) with daily averaged measurements. Model predictions for scattering track the measurements both for summer and winter. The scatterplot of measurements versus predictions for the two seasons analyzed is shown in Figure 6. The effect of averaging the concentrations over 24-hour periods reduces



**Figure 4.** Comparison of measured scattering coefficient versus the calculated value approach 1a for two seasons during PAQS.

**Table 4.** Model Performance Statistics for the Different Approaches Used to Estimate Scattering

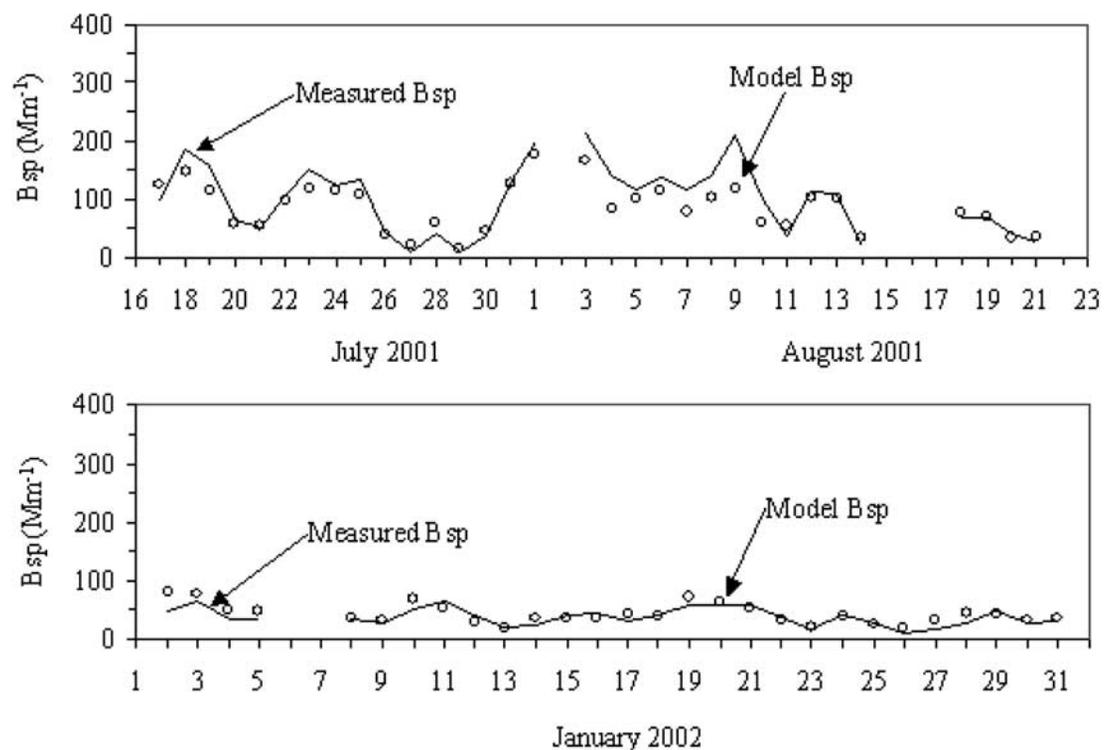
Summer	N	Average, $\text{Mm}^{-1}$	$R^2$	Error, $\text{Mm}^{-1}$	Bias
Measured	690	99			
Approach 1a	690	84	0.80	23.7	-15.1
Approach 1b	32	89	0.87	19.1	-10.4
Approach 2	32	89	0.83	19.6	-10.6
Approach 3a	690	98	0.89	16.0	-1.1
Approach 3b	32	104	0.95	11.6	4.9
Winter	N	Average, $\text{Mm}^{-1}$	$R^2$	Error, $\text{Mm}^{-1}$	Bias
Measured		39			
Approach 1a	639	34	0.44	12.2	-1.5
Approach 1b	28	37	0.61	9.2	1.0
Approach 2	28	40	0.47	9.0	2.3

the random errors of the measurements used as input by the model and therefore reduces model errors in both summer and winter (Table 4). *McMurry et al.* [1996] reported that significant uncertainty is introduced by this type of models when the scattering efficiencies are assumed constant for long periods of analysis since the characteristics of the aerosol populations are likely to vary within hours. This uncertainty is present in all approaches using daily average values.

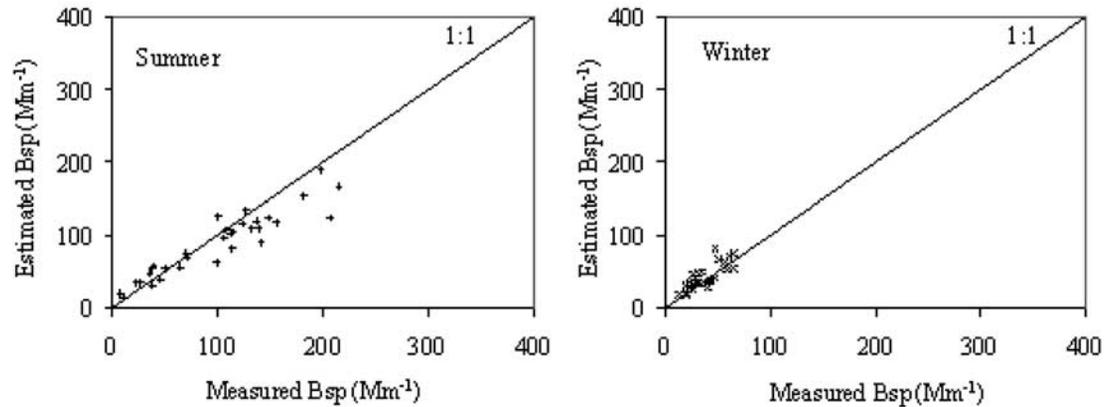
#### 4.3. Approach 2: Use of Mie Theory, Size Composition Distributions, and a Thermodynamic Model

[29] The measured and calculated scattering coefficients for the summer and winter seasons during PAQS are shown in Figure 7. The model predictions and the measurements are in good agreement with the exception of the period of 4–9 August. Figure 8 shows the scatterplot of measure-

ments versus predictions from the model for the two different seasons analyzed. Relatively good correlation is shown between the measurements and the predictions for the summer and the winter (Table 4). During the summer the model tends to under-predict the measured scattering coefficient, although this model shows better agreement between the measurements and the predictions. The errors once more is only weakly correlated to sulfate ( $R^2 = 0.17$ ), nitrate ( $R^2 = 0.06$ ), and organics ( $R^2 = 0.10$ ). The error of this model shows a weak correlation with ambient aerosol water ( $R^2 = 0.22$ ) and  $\text{PM}_{2.5}$  mass concentrations ( $R^2 = 0.37$ ). The weak correlation of the model and  $\text{PM}_{2.5}$  from the TEOM, which also includes some water, suggests that at least part of the error may be related to the hygroscopic properties of the aerosol. Water aerosol concentrations are calculated from the model assuming that only the inorganic material uptakes water at high relative humidity. In the case



**Figure 5.** Time series of measured scattering coefficient (line) and estimated scattering coefficient (symbols) from approach 1b. Each point corresponds to 24-hour averages.

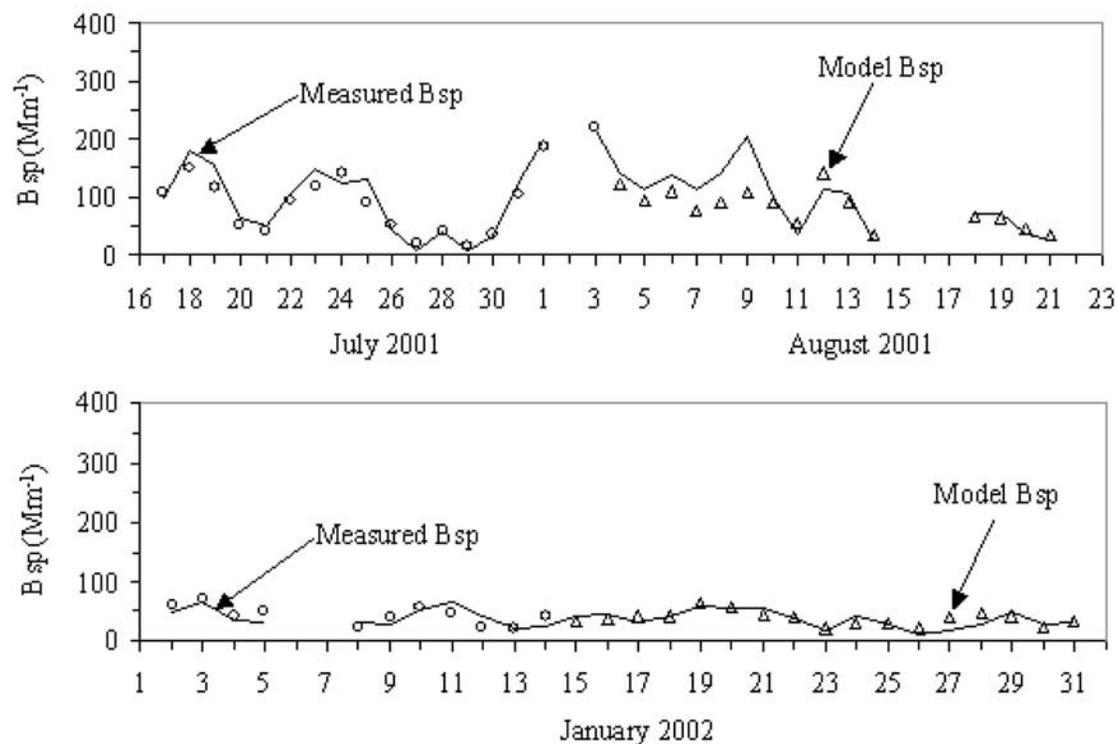


**Figure 6.** Comparison of measured scattering coefficient versus the calculated value from approach 1b for two seasons during PAQS.

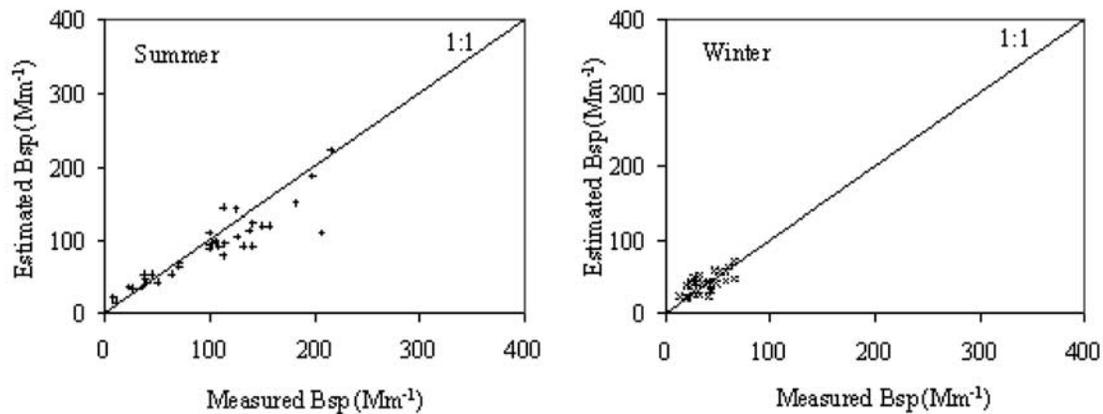
that carbonaceous material contributes to the water uptake into the aerosol phase, this could not be predicted from the model, and the actual scattering would be underestimated. Khlystov et al. (submitted manuscript, 2004) also reported that during certain periods in the summer the measured aerosol water was underestimated from theoretical thermodynamic calculations. The effect of using averaged size distributions during the summer does not seem to affect significantly the overall performance of the thermodynamic model. The corresponding scattering efficiencies for the major aerosol components were approximately the same as those used in approach 1.

[30] Winter estimates from this model tend to overpredict the measured scattering coefficient. The model shows a weaker correlation with the measurements as compared to the other approaches used, but the overall error is smaller (Table 4). No correlation was observed between the aerosol components and the error. The organic mass showed a weak anticorrelation ( $R^2 \approx 0.2$ ), which indicates either an overestimation of the organic mass from the organic carbon measurements or a negative effect of the organics on the water absorption by the inorganics.

[31] Summer contribution of sulfates and nitrates to the scattering coefficient from this model is 67%, followed by



**Figure 7.** Time series of measured scattering coefficient (line) and estimated scattering coefficient from approach 2. Each point corresponds to 24-hour averages. Open circles point correspond to model calculations using actual size distributions. Open triangles were calculated used the average size distributions.

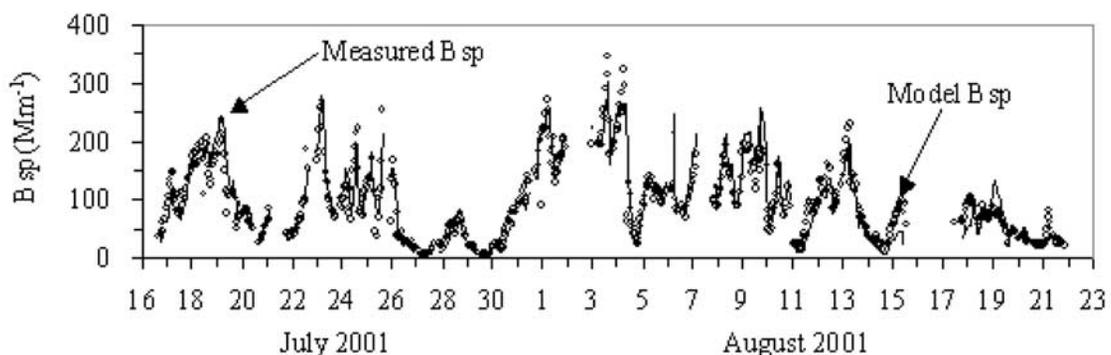


**Figure 8.** Comparison of measured scattering coefficient versus the calculated value from a thermodynamic model using Mie theory for two different seasons during PAQS. Each point corresponds to a 24-hour sampling period.

the organic material with 30%. Negligible contributions are estimated from the other components. These contributions are estimated comparing the base case with the case where the component is not present. For winter, sulfates and nitrates account for 56% of the estimated scattering followed by 39% from the organic material. Other inorganic material and elemental carbon contribute 4% of the estimated scattering for the winter.

#### 4.4. Approach 3a: Use of Measured Aerosol Water Concentrations (High Time Resolution)

[32] Figure 9 shows the time series of measured scattering coefficient and the estimated scattering coefficient for equation (3). The model does a good job in reproducing the observations including the higher peaks. The scatterplot of the measurements and the estimates for the scattering coefficient is shown in Figure 10. Good correlation ( $R^2 = 0.89$ ) is observed between the model predictions and the measurements (Table 4). This model has the lowest absolute error (less than 10%) and a low absolute bias (5%). The consistency of the results is encouraging and indicates that the aerosol water content measurements by the DAASS are quite accurate. The improved agreement also suggests that a large fraction of the error of the previous approaches is indeed due to the estimation of the water uptake of the particles.



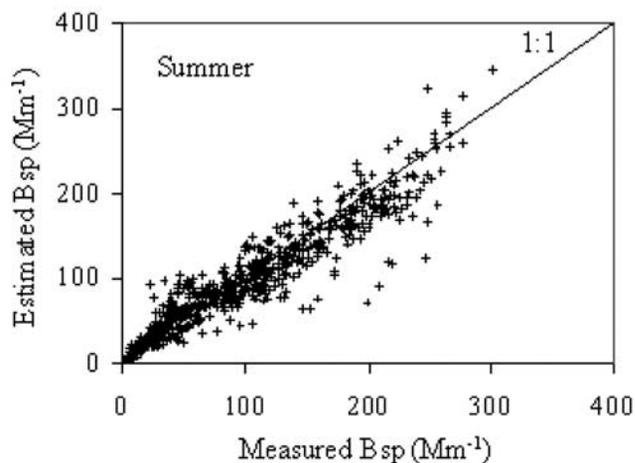
**Figure 9.** Time series of measured (line) and estimated scattering coefficient (symbols) from approach 3a. Aerosol water concentrations are only available for July and August 2001 during PAQS. Each point corresponds to 1-hour average sampling times.

[33] A small source of error in this approach is that the water aerosol is measured with the DAASS system at slightly different conditions of relative humidity than the nephelometer. The measurements of aerosol size distributions and scattering coefficient are done at slightly lower than ambient relative humidity because of heating of the sample in both instruments. This difference in RH is a source of discrepancy between the model predictions and the corresponding scattering coefficient measurements. The magnitude of the discrepancy depends on the ambient RH and is on average around 10%. The error introduced by this RH difference is similar in magnitude to the model error.

[34] The scattering budget estimated from this model indicates that, for the summer, sulfates account for around 38% of the estimated scattering coefficient, water aerosol accounts for 35%, and organic material contributes with 24%. Negligible contributions from nitrate and soil are estimated. In this approach the sulfates, organics, and the corresponding water are decoupled.

#### 4.5. Approach 3b: Use of Measured Aerosol Water Concentrations (Daily Resolution)

[35] Time series of predictions from the model and daily measurements are shown in Figure 11. The model predicts values closely to the measurements (Figure 12). A high correlation ( $R^2 = 0.95$ ) exists between the model and the

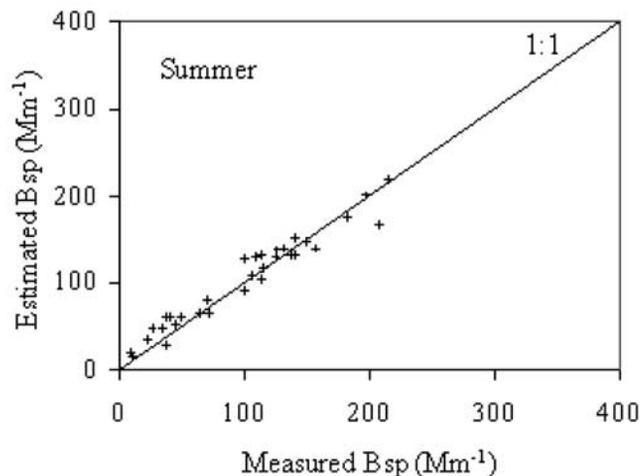


**Figure 10.** Scatterplot of measured scattering coefficient versus predicted values from approach 3.

measured scattering (Table 4). The absolute error of the model is less than 10% for the summer and can be easily explained by the experimental errors. The model slightly overpredicts the scattering coefficient by around 5% (Table 4). The good agreement and performance of this model indicates that the other approaches do not describe accurately the water uptake by fine particles in Pittsburgh.

## 5. Conclusions

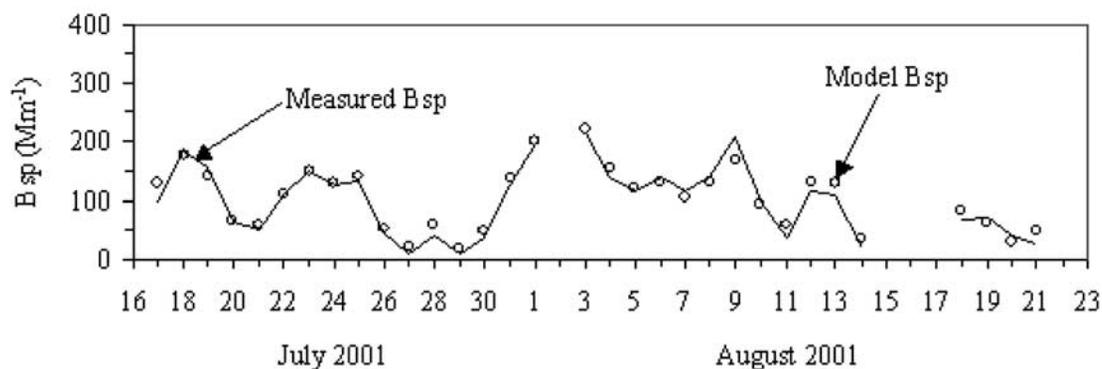
[36] The three modeling approaches used for the calculation of the scattering coefficients (bulk composition and average scattering coefficients, size-resolved composition with Mie theory and a thermodynamic model, and use of the measured water) were able to reproduce the hourly observations with an absolute error less than 25% and a bias of less than 15%. The approach using the measured aerosol water concentration reduces the error to 15% and the bias to 1%. This error is similar to the uncertainty of the predictions due to the PM composition measurement uncertainty. These results suggest that while our water measurements are consistent with the observed optical properties, the current models have still some difficulties predicting the aerosol



**Figure 12.** Scatterplot of measured scattering coefficient versus predicted values from approach 3.

water content. The fact that the thermodynamic model is underestimating the scattering coefficient during the summer is an indication that organics may be contributing to water uptake into the aerosol phase. However, the weak correlation between the error and the organic PM mass suggests that the effect is complex and is probably related not to the total organic matter (OM) but to the hydrophilic fraction of the organic component.

[37] The simplest of the approaches used, bulk  $PM_{2.5}$  composition and average scattering efficiencies, was relatively successful in reproducing the observations even if its parameters were derived from measurements in other parts of the United States [Malm *et al.*, 2000a], and the aerosol acidity during the summer was neglected. This indicates that the model is relatively robust in describing aerosol scattering over not only the western but also the northeastern United States. The use of high time resolution measurements did not result in a significant improvement of the scattering coefficient prediction over using daily resolved concentrations. However, a correction has to be made to the daily relative humidity to account for the nonlinear effect in the scattering coefficient. Also, the relative success (and sometimes failure) of the approach to reproduce hour by



**Figure 11.** Time series of measured (line) and estimated scattering coefficient (symbols) from approach 3b. Aerosol water concentrations are only available for July and August 2001 during PAQS. Each point corresponds to 1-hour average sampling times.

hour variations of the scattering coefficient provides an excellent test for our ability to perform accurate semi-continuous measurements of PM<sub>2.5</sub> composition and of our understanding of the PM<sub>2.5</sub> properties.

[38] A size-resolved thermodynamic model, using daily averaged concentrations, has practically the same performance during the summer as the simpler bulk composition-based model of approach 1. The fact that the growth curves,  $f(\text{RH})$ , in the bulk model were calculated from Mie theory and a thermodynamic model for the average conditions over the two seasons explains part of its success. During the winter the use of size-resolved thermodynamic model marginally improves the estimates of the scattering coefficient.

[39] The summer scattering budget indicates that sulfates and the associated water contribute around 70% and organic material contributes with around 30%. Negligible contributions are estimated for nitrate and soils. During the winter, sulfates are responsible for around 40%, organics for 30%, and nitrates for 25% of the scattering. Negligible contributions to scattering are estimated from the soil ambient concentrations. The budget estimates of the different modeling approaches are within a few percent of each other.

[40] **Acknowledgments.** This research was conducted as part of the Pittsburgh Air Quality Study that was supported by U.S. Environmental Protection Agency under contract R82806101 and the U.S. Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This paper has not been subject to EPA's required peer and policy review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.

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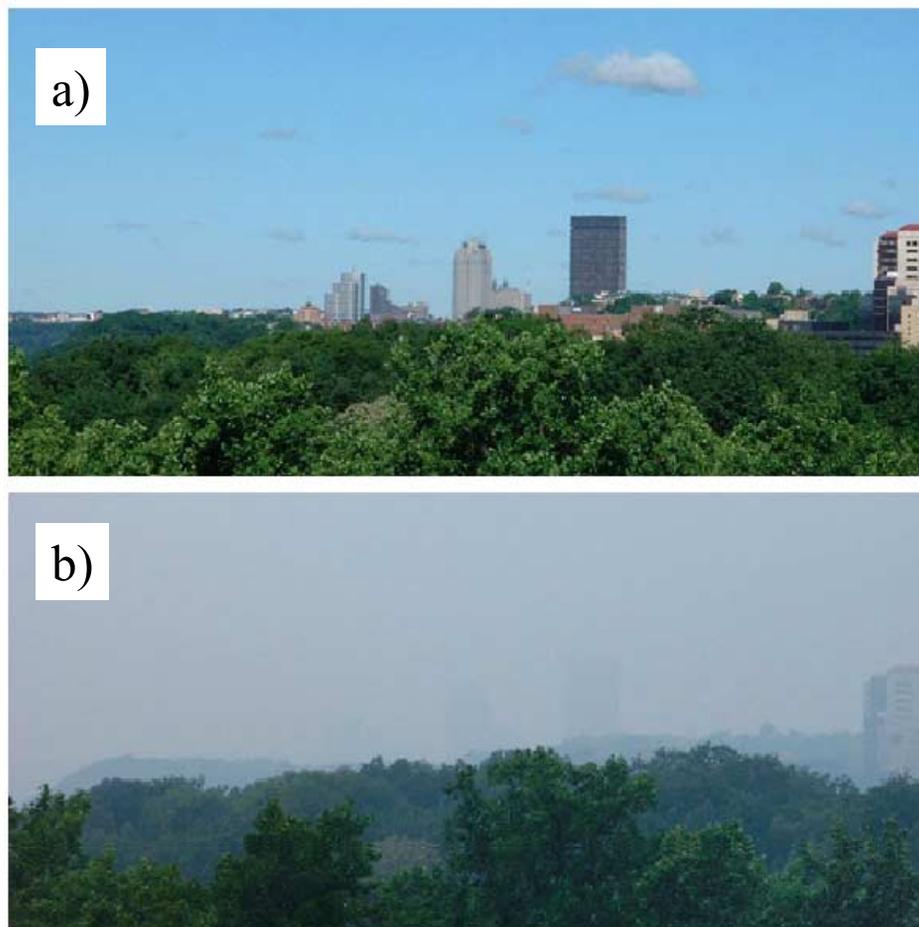
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**Figure 1.** Comparison of visual characteristics during PAQS. View of downtown Pittsburgh from the PAQS main site at Schenley Park. (a) Day with low aerosol concentrations:  $\text{PM}_{2.5} = 6 \mu\text{g}/\text{m}^3$ ,  $b_{\text{sp}} = 5 \text{ Mm}^{-1}$ ,  $\text{RH} = 60\%$ . (b) Polluted day:  $\text{PM}_{2.5} = 70 \mu\text{g}/\text{m}^3$ ,  $b_{\text{sp}} = 255 \text{ Mm}^{-1}$ ,  $\text{RH} = 74\%$ .