



# Bias in Filter-Based Aerosol Light Absorption Measurements Due to Organic Aerosol Loading: Evidence from Ambient Measurements

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During the 2006 Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMAC-CS 2006) a filter-based (Particle Soot Absorption Photometer, or PSAP) and a photoacoustic-based aerosol light absorption technique were deployed and here the data are compared. The level of agreement between the two techniques with ambient aerosol depended on the abundance of organic aerosol (OA), with the ratio of OA to light absorbing carbon (LAC) mass ( $R_{\text{OA-LAC}}$ ) of particular importance. When OA mass concentration was low the agreement between the methods was within instrumental uncertainties (PSAP measuring 12% higher), however at high ( $R_{\text{OA-LAC}}$ ) ( $\sim 15$ – $20$ ) the difference in agreement was between 50 and 80%. This difference is similar to the bias observed in the laboratory studies of a companion paper using non-absorbing OA and LAC (Cappa et al. 2008a). It was found that most of the OA was oxidized and non-absorbing in nature. We postulate that the observed differences results from a bias in the filter-based measurements due to (a) the redistribution of liquid-like organic particulate matter (PM) around the fiber filters thereby modifying the filter surface and subsequent light scattering, and (b) the possible coating and absorption enhancement of pre-existing absorbing PM (i.e., soot) as OA deposition and redistribution occurs. We stop short or recommending a universal correction using these findings due to the magnitude of the bias showing some dependence on air mass type. Any use of this data for a correction must consider the uncertainties in measuring OA

mass concentrations, LAC mass concentrations and type of OA present. The observed PSAP bias may have a significant impact on the accuracy of aerosol single scatter albedo (SSA) and LAC mass concentrations derived from filter-based aerosol absorption methods from regions impacted by large amounts of OA. Although this study was performed using the PSAP we caution users of other filter-based instrumentation to the possibility of a similar bias in those instruments.

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## INTRODUCTION

Light absorption is a critical component of aerosol optical properties required to determine the radiative forcing by atmospheric aerosol (Schwartz 2004). Absorbing aerosol, unlike purely scattering aerosol, can heat or cool the atmosphere depending on the fraction of absorption relative to scattering and the underlying earth and atmosphere albedo. Absorbing aerosol can contribute to localized heating of clouds and the atmosphere, especially in regions where the underlying surface is highly reflective. Aerosol absorption usually comprises a small fraction of the total light attenuated by the aerosol, and thus can be difficult to measure accurately.

Filter-based techniques for measuring aerosol light absorption, which have been used for decades (Lin et al. 1973), rely on the change in transmission of light through a filter as it is loaded with aerosol to determine the aerosol absorption coefficient ( $b_{\text{abs}}$ ). The filter-based method is integral to the aethelometer (Hansen et al. 1984; Arnott et al. 2005), the particle soot absorption photometer (PSAP) (Bond et al. 1999; Virkkula et al. 2005) and the multi-angle absorption photometer (MAAP)

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(Petzold et al. 2005). The majority of in-situ data for aerosol absorption measured globally is based on these filter measurements (e.g., Global Atmospheric Watch program, ACE—Asia, Baltensperger 2003; Huebert et al. 2003). In addition, they are used in intercomparisons with ground-based and satellite remotely sensed aerosol optical properties (Schmid et al. 2000; Schmid et al. 2006).

A fundamental and serious drawback to the filter-based instruments is that the aerosol is deposited on a filter matrix prior to the light absorption determination, which may change the physical properties of the particles and combined optical properties of the deposit and matrix. Additionally, empirical corrections are required to account for the effect of the deposited PM on radiative transfer on the surface of, and within, the filter itself which can alter the measured change in transmission and apparent  $b_{abs}$ . These corrections limit the accuracy of the measured absorption to between 20–30% (Bond et al. 1999; Weingartner et al. 2003; Virkkula et al. 2005). The MAAP instrument was developed to correct for scattering artifacts in real time and has much improved measurement uncertainty ( $\sim 12\%$ ) for pure soot, compared to other filter-based techniques (Petzold et al. 2005).

Comparisons between filter-based absorption ( $b_{abs,filter}$ ) and various reference methods, such as absorption by difference between aerosol extinction ( $b_{ext}$ ) and scattering ( $b_{scattering}$ ), or absorption by photoacoustic spectroscopy (PAS) ( $b_{abs,ref}$ ), are essential to determine instrument performance. The difference method and PAS are appropriate standards to gauge the performance of the filter-based techniques as they sample the aerosol in suspension, without the need for collection on a filter. Laboratory comparisons of absorption from soot generated within a controlled flame achieve agreement within stated experimental uncertainties (Bond et al. 1999; Arnott et al. 2005; Virkkula et al. 2005). Some studies using ambient aerosol do show good closure. For example, in testing a new multi-wavelength PSAP system, Virkkula et al. (2005) found a PSAP to PAS slope ( $R_{abs} = b_{abs,filter}/b_{abs,ref}$ ), using two days of ambient data, of 1.12, which is within the stated uncertainties for the methods used. Sedlacek and Lee (2007), using a photo-thermal interferometry (PTI) technique to measure aerosol absorption on ambient aerosol, showed good correlations with a PSAP ( $R_{abs} = 1.03$ ) for low RH conditions. However, in addition to these cases, poorer agreement between techniques is regularly observed with ambient aerosol. For example Moosmuller et al. (1998) and Arnott et al. (1999) compared photoacoustic- and aethelometer-measured absorption for ambient samples and found  $R_{abs}$  as low as 0.5 (aethelometer and PAS). It was suggested that the discrepancies could be related to “spatial inhomogeneities in aerosol properties” due to separation of sampling inlets, inaccurate instrument measurements or “temporal changes in the aerosol absorption efficiency” (Moosmuller et al. 1998). Arnott et al. (2003) obtained an  $R_{abs}$  of 1.6 (PSAP and PAS) from an intensive field operation in northern Oklahoma, USA. This study sampled many different air masses, including clean, rural, biomass burning and well-processed air masses, over a 14-day

period. Schmid et al. (2006) presented a comprehensive assessment of the performance of an aethelometer and PSAP using a PAS as reference absorption during the LBA-SMOCC 2002 field campaign and found variability in closure that was related to RH, temperature and mixing state of the aerosol. Poor agreement at low absorption levels ( $< 10 \text{ Mm}^{-1}$ ) were observed for a majority of the data. Slowik et al. (2007) found  $R_{abs}$  was consistently 1.2 for aethelometer and PAS absorption, while Weingartner et al. (2003) found discrepancies in aethelometer results when soot particles were coated with organic aerosol (OA) from ozonolysis of  $\alpha$ -pinene. Despite the detailed assessment in the Schmid et al. (2006) study, assessments of the corrections needed for the various filter techniques, and a large body of work assessing the quality of filter-based methods of aerosol absorption, there is no clear explanation for the variable results between the various aerosol absorption measurement techniques. It is clear that under some conditions closure of the aerosol light absorption is achieved between these independent methods. More often, however, this is not the case.

Here we present field measurements that show that  $R_{abs}$  for PSAP and PAS absorption is dependent upon the amount of OA present, with the ratio between the OA mass and light absorbing carbon (LAC) mass [ $R_{OA-LAC}$ ] being of particular importance. These results are supported by laboratory measurements reported in a companion article (Cappa et al. 2008a) and have implications for the utility of filter-based absorption measurements in regions that are strongly influenced by OA as well as for interpretation of long-term measurements.

## MEASUREMENT TECHNIQUES

Data were collected onboard the NOAA research vessel Ronald H Brown (RHB) in the Gulf of Mexico and inland waters near Houston, Texas over 37 days of August and September during the 2006 Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS). The PAS used in this study is similar to that described in Lack et al. (2006) and measured light absorption ( $b_{abs,PAS}$ , in  $\text{Mm}^{-1}$ ) at 532 nm. Aerosol extinction ( $b_{ext}$ ) and gas-phase absorption ( $b_{ext,gas}$ ) at 532 nm were measured using a cavity ring down-aerosol extinction spectrometer (CRD-AES) sampling aerosol-containing and aerosol-free air, respectively (Baynard et al. 2007). The contribution of  $b_{ext,gas}$  was  $\leq 10\%$  of total absorption in the most polluted conditions in this study and was subtracted from  $b_{abs,PAS}$ . A Radiance Research Inc.<sup>1</sup> three wavelength PSAP (467 nm, 530 nm, and 660 nm) was also used and the 530 nm data was converted to 532 nm using an Ångström exponent for absorption ( $\dot{A}_{abs}$ ) of 1. This conversion was based on

<sup>1</sup> Certain commercial equipment, instruments, or materials are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recognition or endorsement by the National Oceanic and Atmospheric Administration, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

results presented in Figure 5 and Equation (1). We present PSAP data ( $b_{abs,PSAP}$ ) corrected using the firmware corrections for the three wavelength PSAP which includes the filter transmission, flow and basic sample area corrections from Bond et al. (1999). An additional filter sample area correction (0.873) according to Sheridan et al. (2005) was applied prior to applying the scattering corrections of Virkkula et al. (2005) (1.3%, 1.6%, and 2.1% for 467 nm, 530 nm, and 660 nm, respectively). This modified PSAP scheme was applied as a result of the commercial three wavelength PSAP having different geometry to the one used in the Virkkula et al. (2005) study. The Bond et al. (1999) correction scheme was also applied although technically only applies to the single wavelength PSAP. The  $R_{abs}$  obtained using the modified PSAP scheme were typically closer to 1 at low OA concentrations than the  $R_{abs}$  obtained using the Bond et al. (1999) correction scheme (e.g., 1.12 compared to 1.17) however the general conclusions of this paper are independent of the choice of PSAP data correction scheme. Aerosol scattering was measured using a TSI<sup>1</sup> nephelometer (model 3563, TSI, Inc., St. Paul, MN), corrected for illumination non-idealities according to Anderson and Ogren (1998) and converted to 532nm using the nephelometer-derived scattering Ångström exponent. Organic aerosol mass concentrations (including oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA)) were determined from an Aerodyne<sup>1</sup> quadrupole aerosol mass spectrometer (Q-AMS) (Allan et al. 2003; Zhang et al. 2005). Uncertainty in the Q-AMS measured OA mass is estimated to be 20% (Quinn et al. 2008) while it is estimated that the OA analysis to obtain OOA + HOA reconstructs 97% of measured OA (Bates et al. 2008). All instruments sampled from a common aerosol inlet mast which extended 5 m above and forward of the aerosol measurement containers onboard the RHB. The inlet was a rotating cone-shaped nozzle that was automatically positioned into the relative wind. Air was pulled through this 5 cm diameter inlet nozzle at  $1 \text{ m}^3 \text{ min}^{-1}$  and down the 20 cm inner diameter mast. The lowest 1.5 m of the mast was heated to reduce the relative humidity (RH) to approximately  $60 (\pm 5)\%$ . Twenty-one 1.6 cm inner diameter conductive tubes extending into this heated zone were used to sub-sample the main air flow for the various aerosol instruments at flows of  $30 \text{ l min}^{-1}$ . The nephelometer and PSAP flow was passed through a  $1 \mu\text{m}$ , 50% cut-diameter impactor. A sub-sample of  $1 \text{ l min}^{-1}$  was taken from the outlet of the nephelometer using an isokinetic probe, passed through a nafion tube diffusion drier (MD-110-12SS, Permapure,<sup>1</sup> Toms River, NJ) and then sampled by the PSAP. The CRD-AES and PAS flow was passed through an identical impactor, sub-sampled at  $6 \text{ l min}^{-1}$  using an isokinetic probe and  $2 \text{ l min}^{-1}$  of this flow was then passed through a similar drier (PD 100T-12SS, Permapure,<sup>1</sup> Toms River, NJ). Losses in these driers have been measured and modeled and shown to be less than 4% for submicron aerosols (Dick et al. 1995; Ojanen 2003). The data from all instruments was converted to standard temperature and pressure conditions and then averaged to 10 min to remove any effect of sample residence time lags (residence

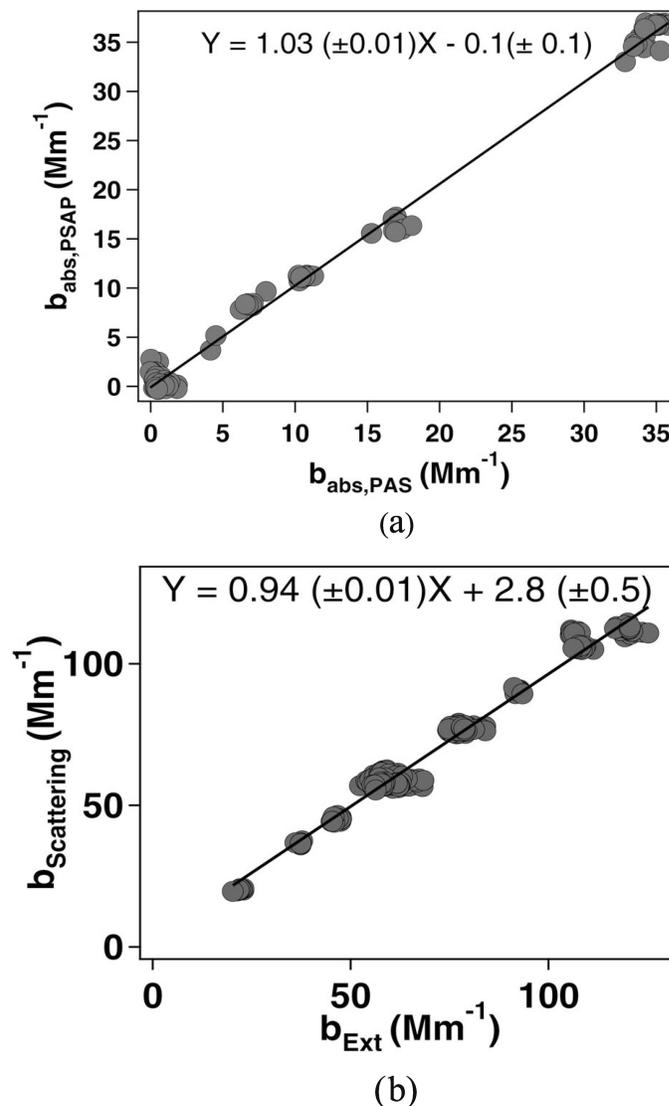


FIG. 1. (a) PSAP vs. PAS measured absorption for absorbing polystyrene test aerosol; (b) Nephelometer versus CRD-AES measured scattering for ammonium sulfate, sucrose, and polystyrene test aerosol. All test aerosol were run using the inlet configuration used in the TexAQS/GoMACCS study.

times: CRD-AES = 2 seconds, PAS = 10 seconds, PSAP = 6 seconds). All tubing connecting instrumentation was routed with stainless steel or conductive silicon tubing and minimal sharp bends to avoid sample losses. Absorbing and non-absorbing test aerosol used during the experiment were atomized, dried, introduced to the inlet mast and sampled with all instruments using the sampling configuration described above. These aerosol were used to test the optical measurement system and investigate aerosol losses due to differences in the flow systems. Figure 1a shows an  $R_{abs}$  of 1.03 between PSAP and PAS measured absorption on absorbing polystyrene spheres (300 nm, Duke Scientific Corp.,<sup>1</sup> Palo Alto, CA), which is well within measurement uncertainties (PSAP: 20%, PAS: 5%). Figure 1b shows

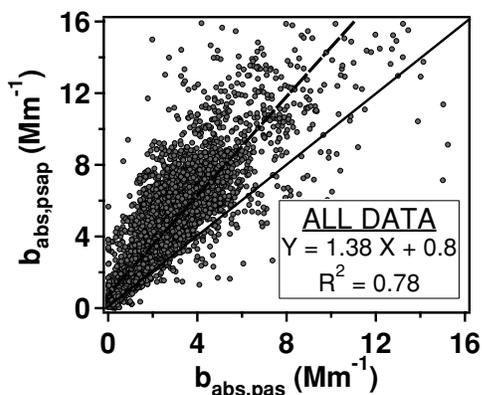


FIG. 2. Ambient PSAP and PAS aerosol absorption data from the Tex-AQS/GoMACCS study. 1:1 line = Solid. Least-square fit to data = Dashed.

the comparison of nephelometer measured  $b_{scattering}$  and CRD-AES measured  $b_{ext}$  for purely scattering aerosol (poly-disperse submicron ammonium sulfate and succinic acid and 300 nm polystyrene spheres [Duke Scientific Corp.,<sup>1</sup> Palo Alto, CA]). These data shows that, for a variety of aerosol composition, the two scattering instruments agree within 6% (for non absorbing aerosol  $b_{ext} = b_{scattering}$ ). The results presented in Figure 1 shows that relative aerosol losses between the instrumentation are equivalent and should not present any loss artifacts to this dataset.

## RESULTS

Over the course of the study ambient  $b_{abs,PSAP}$  and  $b_{abs,PAS}$  were linearly correlated, with an average slope ( $R_{abs}$ ) of 1.38 ( $\pm 0.01$ ) and an  $R^2$  of 0.78 (Figure 2). However,  $R_{abs}$  was found to depend on the mass concentration of OA, as determined by the Q-AMS ( $R_{abs}$  did not show any dependence on Q-AMS sulfate, nitrate or ammonium mass concentrations). We investigated the  $R_{abs}$  dependence on OA by binning the absorption data according to the mass concentration of OA (Figure 3 and Table 1). The first three bins were selected based on the range of OA mass concentrations expected for different regions of the globe (rural/remote, urban downwind, and urban) defined by Zhang et al. (2007) while the fourth bin is representative of heavily polluted regions, such as the Houston shipping channel within the current study area. At the lowest OA loadings (OA  $< 2.5 \mu\text{g m}^{-3}$ ), the PSAP was systematically 12% higher than the PAS (Figure 3a), which is within the uncertainties of the instrumentation. At the highest OA mass concentrations ( $> 12.5 \mu\text{g m}^{-3}$ ) the PSAP absorption was  $\sim 1.7$  times that of the PAS (Figure 3d). Table 1 provides details regarding the comparisons shown in Figure 3. Assuming a linear relationship between  $R_{abs}$  and OA (Figure 4a) we found that  $R_{abs}$  increased by ca. 8% for every  $1 \mu\text{g m}^{-3}$  increase in OA. However, the data in Figure 4a also indicate that combined Urban/Downwind and Urban categories constituted one, larger population with an  $R_{abs}$  of about 1.6 and the Houston Shipping Channel another population with  $R_{abs}$  of 2 to 3.

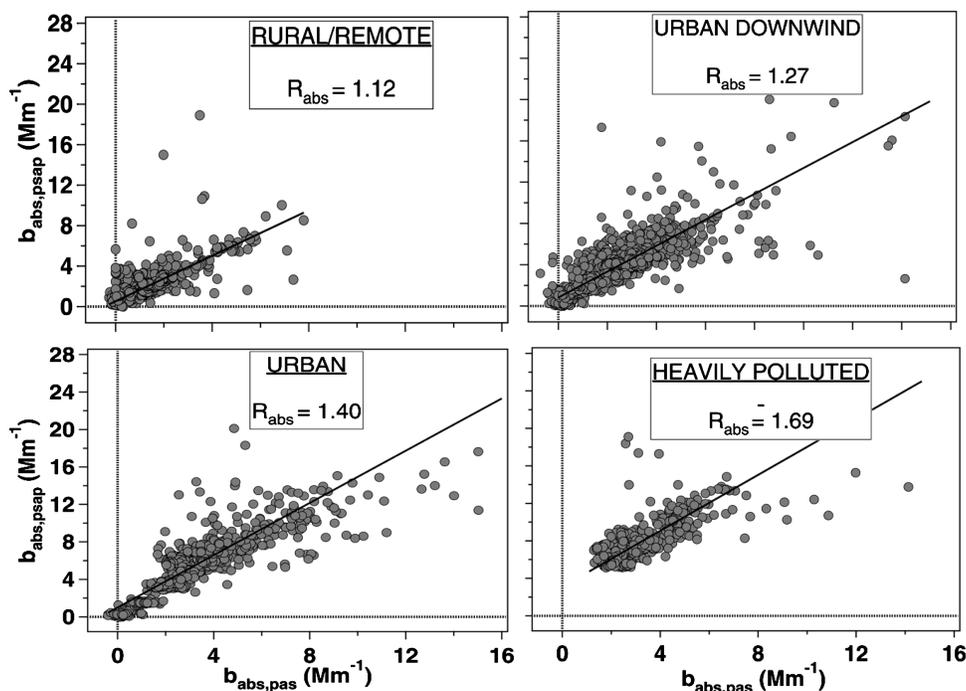


FIG. 3. PSAP aerosol absorption as a function of PAS aerosol absorption for different OA concentration ranges. Solid lines are least-squares regressions to the data. Rural/Remote, Urban Downwind, and Urban labels correspond to the definitions given in Zhang et al. (2007). Further details of this figure are provided in Table 1.

TABLE 1

Analysis of closure between PSAP and PAS-derived absorption binned by Q-AMS OA mass concentration from Figure 3

	Figure 3a	Figure 3b	Figure 3c	Figure 3d
Classification	Rural/Remote	Urban Downwind	Urban	Heavily Polluted
AMS OA Mass ( $\mu\text{g m}^{-3}$ )	0–2.5	2.5–5.0	5.0–12.5	>12.5
Slope	1.12	1.27	1.40	1.69
Intercept ( $\text{Mm}^{-1}$ )	0.5	0.8	0.9	2.0
$R^2$	0.75	0.82	0.80	0.80

### Comparison with Laboratory Data

In an effort to further understand the field observations, a laboratory study was conducted, the results of which are presented in a companion article (Cappa et al. 2008a). This study investigated the PSAP bias under controlled conditions using  $\alpha$ -pinene-derived secondary OA (SOA), soot produced from a methane flame and absorbing Nigrosin dye. These laboratory experiments confirm that a significant PSAP bias can result from non-absorbing OA interacting with the PSAP filter previously loaded with absorbing material. The mass concentrations used by Cappa et al. (2008a) were much higher than those found in the atmospheric measurements reported here. Nonetheless we can make a brief comparison to the laboratory results by presenting the absorption bias ( $R_{abs}$ ) as a function of  $R_{OA-LAC}$  ( $R_{OA-LAC} = [\text{OA}]/[\text{LAC}]$ ) (Figure 4b). The mass concentration of LAC for the ambient data, was estimated from the measured  $b_{abs,PAS}$  using a mass absorption coefficient (MAC) of  $7.75 \text{ m}^2 \text{ g}^{-1}$  (literature value converted to 532 nm from 550 nm using  $A_{abs} = 1$ , Kirchstetter et al. 2004) from Bond and Bergstrom (2006). The LAC mass concentration is likely an upper limit as the MAC used is for fresh soot and can increase by a factor of  $\sim 1.5$  as the aerosol ages (Bond et al. 2006). The laboratory and field data both indicate that  $R_{abs}$  increases with the  $R_{OA-LAC}$  (or  $R_{OA-Nigrosin}$ ; ratio OA mass concentration to Nigrosin mass concentration) and are quantitatively consistent within experimental uncertainties. Interestingly, when considering  $R_{abs}$  from the field data as a function of the  $R_{OA-LAC}$  instead of as a function of LAC alone (Figure 4b) the scatter in the data was reduced indicating that the impact of OA on the PSAP measurement is a stronger function of  $R_{OA-LAC}$  rather than just OA. These results indicate that changes to  $R_{OA-LAC}$  could influence time-series measurements of  $b_{abs}$  made using filter-based methods. Interpretation of such measurements should be made with this in mind.

## DISCUSSION

### Potential Mechanisms of Bias

Recent theoretical and laboratory studies suggest that complex mixtures of organic compounds that exist as particles are predominantly liquid-like (Marcolli et al. 2004; Subramanian et al. 2007; Cappa et al. 2008b). We postulate that the observed

PSAP bias and relation between  $R_{abs}$  and OA abundance results from redistribution of liquid-like OA PM on the filter fibers via two possible mechanisms. The first is a physical change in the shape of the OA particles as they deposit and then coat the individual filter fibers (e.g., Subramanian et al. 2007) that changes the PSAP scattering artifact beyond the degree accounted for by commonly used corrections which are based on solid aerosol such as ammonium sulfate and soot (Bond et al. 1999; Virkkula et al. 2005). This mechanism may account for the dependence of the bias on the abundance of OA alone (Figure 4a), particularly if non-absorbing OA is present. The second possible mechanism is via a coating with OA of absorbing material that was already present on the filter (e.g., soot particles). This could explain the dependence of  $R_{abs}$  on  $R_{OA-LAC}$ . However, without detailed imaging and optical analysis of loaded filters it is difficult to fully establish the physical origin of the PSAP bias. An important consideration in the mechanism is whether the absorbing material is internally mixed with OA prior to deposition on the filter. Freshly emitted soot will be fractal and have a different absorption capability than if the fractal aggregates are already collapsed. It is likely that soot internally mixed with OA (e.g., as a coating on the soot aggregate; Bond et al. 2006) compared to externally mixed fresh soot will behave differently when loaded onto a filter with OA. Certainly there was the potential for time separation of soot and OA deposits on the filter during the TexAQS/GoMACCS study given the variability of sources which could permit such a deposition and subsequent coating process.

### Other Instrumental Artifacts

We have so far assumed that the discrepancy between  $b_{abs,PSAP}$  and  $b_{abs,PAS}$  results entirely from a bias in the PSAP measurement. However, it has been suggested that the PAS technique may have a measurement artifact associated with the evaporation of semi-volatile material (e.g., water) which decreases the PAS absorption below the actual absorption, although we note that experimental evidence for this effect for water is not definitive (Arnott et al. 2003). In these experiments such a bias is unlikely given that the system was operated at low RHs ( $\leq 30\%$ ) and also since the OA has a significantly lower volatility than water. In laboratory studies using absorbing polystyrene spheres coated in oleic acid (a semi-volatile organic with a vapor pressure 9 orders of magnitude lower than water [Cappa et al. 2008c] and representative of atmospheric liquid-like material), the negative

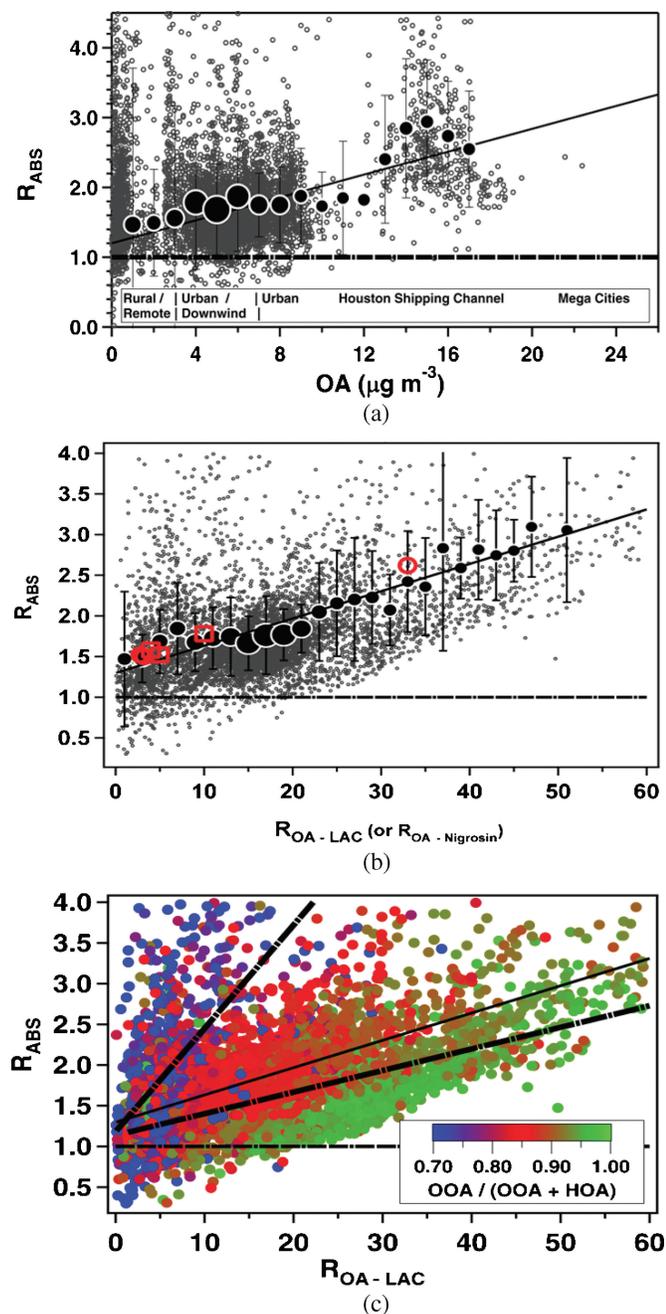


FIG. 4. (a) Ratio of PSAP to PAS measured aerosol absorption coefficient as a function of Q-AMS OA mass. OA mass concentrations measured for different regions of the globe are included from data from Zhang et al. (2007) and this study. (b) Ratio of PSAP to PAS absorption versus ratio of OA to estimated LAC mass. The laboratory data of Cappa et al. (2008a) are included as red circles (LAC) and squares (Nigrosin). For both Figure 4a and Figure 4b graphs the solid black line is a least-square fit to the data, the dashed line is the expected 1:1 agreement between PSAP and PAS, the grey points are individual data points from which bin averages are obtained. Size of the binned data points relates to abundance of data in each OA mass bin and uncertainty bars are  $1\sigma$ . (c) A reproduction of Figure 4b showing the individual data points color coded by fraction of OOA to total OA. Black solid line is the linear fit to all data, dashed black lines are linear fits to the 25% of data having the lowest and highest fractions of OOA. Expected 1:1 line is also included.

bias (due to evaporation or otherwise) was found to be small compared to the total absorption (Cappa et al. 2008a).

### The Optical Nature of Organic Aerosol

When considering the nature of OA, it is important to understand the extent to which the OA is light absorbing in nature, which is currently not well established at the mid-visible wavelengths considered here. The PSAP data were used to determine the Ångström exponent of absorption ( $\mathring{A}_{abs}$ ), defined as:

$$\mathring{A}_{abs} = \frac{\ln(b_x/b_y)}{\ln(x/y)} \quad [1]$$

where  $b_x$  and  $b_y$  are the measured absorption at wavelengths  $x$  and  $y$  (467 nm and 660 nm). Kirchstetter et al. (2004) showed that some compounds in OA emitted by biomass combustion (termed  $C_{BROWN}$  due to their brown or yellow appearance) have a spectral dependence of light absorption that is stronger than that due to soot (i.e.,  $\mathring{A}_{abs}$  for soot = 1;  $\mathring{A}_{abs}$  for  $C_{BROWN}$  > 1). Subramanian et al. (2007) showed that OA containing particles from biomass combustion (including  $C_{BROWN}$ ) are often liquid-like and can form beads and coatings around the filter fibers after deposition. They suggested that this could alter absorption and scattering by the deposited OA compared to its in-situ state and affect filter-based measurement of absorption. If the deposition and spreading of  $C_{BROWN}$  is the source of the bias we might expect to see  $\mathring{A}_{abs} > 1$  for much of the data. For  $OA > 2 \mu g m^{-3}$  (majority of data)  $\mathring{A}_{abs}$  was near 1 (Figure 5), which suggests that the influence of OA on the PSAP absorption is not from  $C_{BROWN}$ . At lower OA concentrations, where HOA was a larger fraction of the OA, the  $\mathring{A}_{abs}$  is noisy due to lower absorption levels but does display a small upward trend to a  $\mathring{A}_{abs}$  of  $\sim 1.5$ , suggesting that the HOA measured may be mildly absorbing. However, the OA in this study appears to be dominated by non-absorbing OOA.

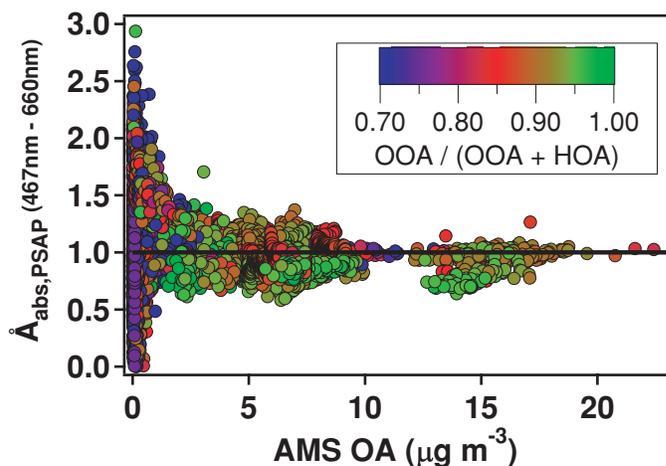


FIG. 5. Ångström exponent ( $\mathring{A}_{abs}$ ) measured by the PSAP (476 nm–660 nm) as a function of OA mass concentration. Data classified by color using the mass fraction of OOA to OOA + HOA.

TABLE 2  
Fit parameters to the analysis presented in Figure 4

Analysis type	Slope ( $\pm$ SD, $1\sigma$ )	Intercept ( $\pm$ SD, $1\sigma$ )
$R_{abs}$ vs. $R_{OA-LAC}$ (Figure 4a)	0.08 ( $\pm$ 0.01) ( $\text{m}^3\mu\text{g}^{-1}$ )	1.20 ( $\pm$ 0.1)
$R_{abs}$ vs. $R_{OA-LAC}$ [All Data] (Figure 4b)	0.032 ( $\pm$ 0.002)	1.30 ( $\pm$ 0.1)
$R_{abs}$ vs. $R_{OA-LAC}$ [High OOA] (Figure 4c)	0.027 ( $\pm$ 0.002)	1.14 ( $\pm$ 0.1)
$R_{abs}$ vs. $R_{OA-LAC}$ [Low OOA] (Figure 4c)	0.127 ( $\pm$ 0.007)	1.20 ( $\pm$ 0.1)

### Potential Correction

The bias presented for this dataset leads to an assessment of the possibility of a correction factor that could be applied to the PSAP. Table 2 shows the statistics of the fits to the data presented in Figure 4a and Figure 4b, as a basis for a potential correction. The use of these numbers for any correction assumes that the bias can be universally applied under all conditions. However, using the ratio of OOA to OOA + HOA as a marker for the age of the aerosol and/or air mass differences we found that the nature of the bias depended on the fraction of OOA within the OA. Figure 4c presents this analysis where we performed linear fits to the 25% of data containing the lowest fractions of OOA, and to the 25% of data containing the highest fractions of OOA. These fits show that the bias is substantially different for different fractions of OOA, indicating that the average bias presented in Figure 4b may not be universally applicable to all air masses. Table 2 also contains the statistics of these lower and upper quartile fits. Given this variability of the bias we recommend caution in applying any correction based on this data. We also point out that this dataset did not contain significant sampling of biomass burning aerosol, a known source of absorbing OA (Kirchstetter et al. 2004), and therefore this dataset may not represent this significant source of LAC (soot and OA).

### Implications for Climate Forcing Calculations

The significance of the PSAP bias identified here will depend on the OA and LAC mass concentration for a particular region. Zhang et al. (2007) summarized AMS OA measurements from 37 Northern Hemisphere locations into urban, urban downwind and rural/remote classifications. The OA mass bins in Figure 3 used these classifications and thus give an indication of the magnitude of the potential PSAP bias for these air mass types. For example, based on the average OA mass concentration measured in urban regions (Zhang et al. 2007) absorption, as determined by the PSAP, could be overestimated by at least 50%. In heavily polluted regions positive biases of  $\geq 100\%$  are possible.

These measurement biases could have substantial impact on the estimated radiative forcing of aerosol if the PSAP-derived

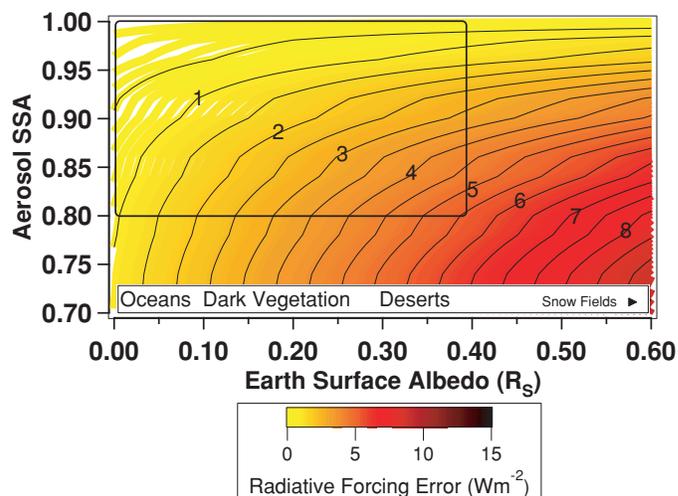


FIG. 6. Additional positive radiative forcing (warming) ( $\text{Wm}^{-2}$ ) estimated due to a PSAP bias of 1.5 as a function of the aerosol and surface albedo. Color contours and line + number contours are radiative forcing error. Aerosol single scatter albedo (y axis) represents that calculated using  $b_{abs,PSAP}$ . Aerosol single scatter albedo (SSA) and earth surface albedo ( $R_s$ ) ranges seen during this study shown within the box. Regional surface albedo examples also shown (Russell et al. 2002).

absorption is used to calculate the aerosol single scatter albedo ( $SSA = b_{scattering}/b_{ext}$ ). We consider this using a simplified estimate of the localized aerosol-induced change in upward radiation flux at the top-of-atmosphere (TOA), as described in Russell et al. (2002) and shown by Equation (2).

$$\Delta_a F \uparrow = \frac{1}{2} F_T T^2 (1 - A_C) \times [SSA \bar{\beta}_a (1 - \bar{R}_s)^2 - 2(1 - SSA) \bar{R}_s] AOD \quad [2]$$

We estimate the TOA forcing ( $\Delta_a F \uparrow$ ) using a solar constant ( $F_T$ ) of  $1366 \text{ Wm}^{-2}$  (Dewitte et al. 2004), atmospheric transmission ( $T$ ) of 0.76 (Russell et al. 2002), aerosol optical depth (AOD) and aerosol backscatter fraction ( $\beta_a$ ) of 0.2 and 0.14, respectively (TexAQS/GoMACCS campaign averages) and a cloud free sky ( $A_C = 0$ , note: this will produce a maximum forcing).  $R_s$  is the surface albedo. We calculate the error in  $\Delta_a F \uparrow$  due to an artifact in the absorption component of the SSA corresponding to an  $R_{abs}$  of 1.5, representing a PSAP bias for urban locations (cf. Figure 4a and b). The error in TOA forcing is shown in Figure 6. Over the course of the TexAQS/GoMACCS study the surface albedo ranged from 0.1–0.4 (given the dark ocean and land surfaces), and the SSA was as low as  $\sim 0.8$ . Under these conditions, the PSAP bias leads to an overestimation of the local warming under cloud free conditions of up to  $5 \text{ Wm}^{-2}$ .

### SUMMARY

During the 2006 TexAQS/GoMACCS field study, aerosol absorption was measured using filter-based (PSAP) and in-situ photoacoustic (PAS) techniques. The PSAP reported

systematically more absorption than the PAS; the magnitude of this bias was found to depend on the abundance of organic aerosol (OA) and light absorbing carbon (LAC). These results are consistent with the laboratory results presented in the companion paper (Cappa et al. 2008a), which suggest that non-absorbing OA can produce a bias that is consistent with the field observations. This bias is likely due to coating of the filter fibers by OA (Subramanian et al. 2007), thereby changing the filter scattering artifact. Coating of absorbing material already present on the filter may also occur as OA is deposited on the filter and spreads across the fibers, thus enhancing absorption. Further research including filter imaging in combination with optical measurements is needed to elucidate the mechanism of the bias.

The PSAP may introduce up to 50% positive bias in measured absorption in urban locations and up to 100% positive bias in heavily polluted areas based on average OA mass loadings reported for these locations (Zhang et al. 2007). Our results also suggest that the bias is dependant on the air mass type, defined by the extent of OA oxidation. It was observed that, within instrument and measurement uncertainties, the PSAP can provide good absorption measurement capabilities in regions having low OA mass loadings. We have conducted this study using one of the commercially available filter-based absorption instruments. It is unknown if this effect would be observed with other instruments, however, given they operate with very similar methodology we caution all users of filter-based instrumentation to be aware of the possibility of such a bias. The observed bias may introduce errors in LAC mass concentrations derived from filter-based measurements, calculated localized heating rates and calculated radiative forcing due to absorption of aerosol. Further investigations, in particular field observations, of filter-based absorption measurements relative to the presence of OA are needed to confirm the magnitude and frequency of the effect. We stop short of recommending a universal correction using these findings due to the magnitude of the bias showing some dependence on air mass type. Any use of this data for a correction must consider the uncertainties in the PSAP correction applied, measurement of OA and LAC mass concentrations and type of OA present.

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