Particulate absorption and its variation with mixing status

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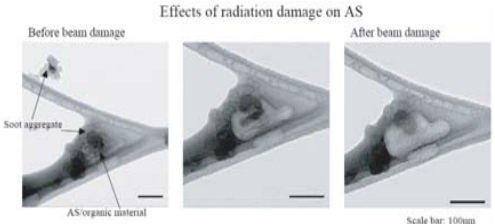
This study supported by NSF ATM05-11521, NASA NNG-06GA90G and NASA ESSF 05-0000-0186.

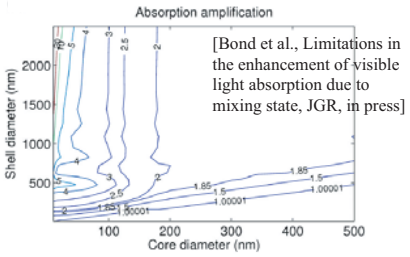
Introduction

Atmospheric particles of strongly light absorbing carbon alter Earth's radiative balance. This direct effect is difficult to model primarily because of the non-spherical shape of refractory carbon and the internal mixing with volatile material. Our main objective is to estimate the absorption amplification for urban and biomass burning aerosols collected from aircraft.



[Peter R. Buseck and Kouji Adachi, Arizona State University]

(top) Electron microscopy of particles collected during MIRAGE. Ammonium sulfate (AS) and organic material coexisted with soot aggregates, but some of them were volatilized with energy beam. These volatile coatings are expected to increase the soot absorption, the so-called lens effect.

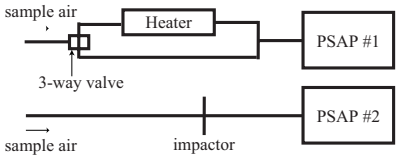


[Bond et al., Limitations in the enhancement of visible light absorption due to mixing state, JGR, in press]

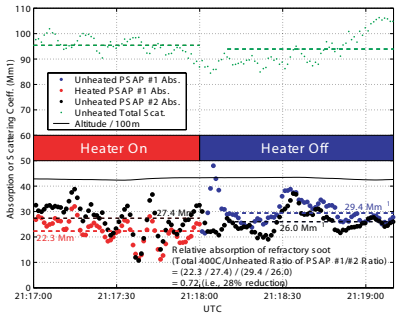
(bottom) Absorption amplification calculated using Mie theory for concentric shell aerosols with strongly absorbing core (refractive indices n = 1.85 - 0.71i) and weakly absorbing shell (n = 1.55 - 10^{-6}i). For a 100-nm core, for example, the absorption increases by factors of 1 - 3 depending on the thickness of the coatings.

PSAP Measurement of Heated Particles

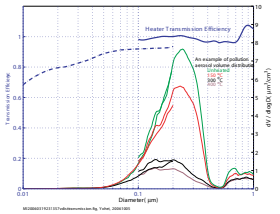
Light absorbing particles of urban and rural origin were measured in-situ from C-130 aircraft in the troposphere over Mexico during MIRAGE. Thermal analysis of aerosol size distributions and direct measurements of mutiwavelength visible light scattering and absorption enabled evaluation of optical properties of the strongly light absorbing carbon with and without volatile coating material.



(top) Thermal absorption analyzer. When sample air path was switched to the heater set at 400 ^{o}C, refractory particles deprived of volatile coatings were fed to one of the Particle Soot Absorption Photometers (PSAP). The other PSAP, set behind a 1 um impactor, always sampled unheated particles to observe the ambient aerosol fluctuations.



(middle) Time series of absorption coefficients measured during 22:17:00 – 22:19:10 UTC on March 8, 2006. With the heater in line, PSAP #1 averaged 22.3 Mm^{-1} (red) for the minute preceeding the valve switch at 22:18. After a 10 second transient generated by the valve, PSAP #1 absorption increased to 29.4 Mm^{-1} (blue). Meanwhile, the unheated PSAP #2 (black) decreased from 27.4 Mm^{-1} to 26.0 Mm^{-1}. After normalizing with the PSAP #2 absorption, the PSAP #1 absorption ratio with heater on/off, 0.72 for this example, indicates the relative absorption of refractory soot.



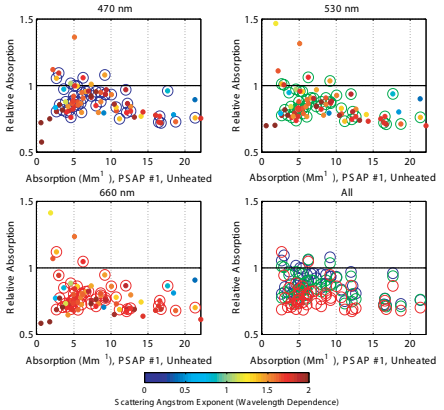
(bottom) Heater transmission efficiency test. Sea salt particles were measured with an optical particle counter behind the PSAP heater. The ratio to unheated sea-salt size distribution (solid blue curve) revealed little (<4%) loss. A similar test with an older heater, used for a differential mobility analyzer, demonstrated a greater thermophoretic loss (dashed curve). Typical pollution aerosol size distributions measured on March 19, 23:14 - 23:27 UTC are plotted for reference.

Summary

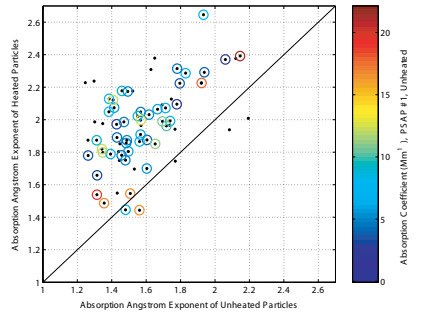
- Soot absorption was reduced by 0 - 30% upon heating.
- Effects of volatile coating "lens", pyrolysis of organics, thermal decomposition and ageing are being investigated.

Soot Absorption Reduction upon Heating

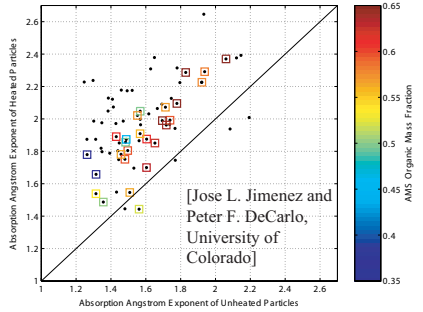
Absorption was reduced by 0 - 30% as particles were heated to 400 ^{o}C to evaporate the coatings. This preliminary analysis is being extended to identify effects of pyrolysis, thermal decomposition and ageing.



(top) The relative absorption of refractory soot ranges from 0.7 to 1.0 for most of the 82 heating tests made during MIRAGE. Outliers disappear as the particle absorption increases (horizontal axis) improving the signal to noise ratio. Circles identify samples with low variability in scattering coefficient and aircraft altitude during each test. The apparent 0 - 30% reduction in absorption probably includes not only the lens effect but also such consequences of heating as pyrolysis and decomposition. In fact, the 660-nm data (bottom left panel), least affected by pyrolysis, consistently shows greater reduction in absorption than the other wavelengths (bottom right). In the presence of dust hinted by low scattering Angstrom exponent (blue dots), the absorption change is small at all wavelengths, as expected.



(middle) Particulate absorption became more wavelength-dependent after heating, presumably due to pyrolysis of organics. Compared to the absorption Angstrom exponent for the unheated particles plotted on the horizontal axis, that for the heated particles on the vertical axis are larger mostly by 0.3 - 0.7. There are exceptions where the Angstrom exponent remained below 1.6 with negligible changes upon heating. The low wavelength dependence suggests that they are urban pollution. The amount of volatile organic material coating such particles may be insufficient to brown the surface. However, this hypothesis alone does not explain other data points with low Angstrom exponent that increased significantly. Pyrolysis, if it did occur, may not have increased absorption beyond the maximum limit per particle. This may be why the Angstrom exponent only increased from low absorption, indicated by blue and green colors of circles put for low ambient aerosol fluctuations.



(bottom) Organic mass fraction shows a weak trend with the absorption Angstrom exponent, consistent with our hypotheses mentioned above. Where aerosol mass spectrometry measurements are available, the color of squares indicates the mass ratio of organic material to the sum of organic and inorganic (e.g., sulfate, nitrate). With several blue squares as exceptions, higher organic fraction is associated with higher Angstrom exponent indicative of biomass burning. For moderate organic fractions, the wavelength dependency remained almost unchanged, perhaps due to lack of pyrolysis. These hypotheses are under investigation.