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Atmospheric Chemistry and Physics Discussions

ACPD

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Interactive Comment

Interactive comment on "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City" *by* K. Adachi and P. R. Buseck

K. Adachi and P. R. Buseck

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Response to Reviewer #1

RC: reviewer's comments
AC: Author's comments

Referee #1

General comments:

This paper discusses results from an analysis of TEM images of particles collected from aircraft over Mexico City. The paper concludes that most particles measured downwind contain internal mixtures, most of which are internal mix-

tures of soot. The paper reports original measurements and some new conclusions. I recommend publication after the following comments and suggestions are addressed.

AC: We appreciate reviewer #1's comments.

RC1-1: Abstract and throughout text.

The authors use the terms "soot" and "organic matter" separately without really defining either. Soot (from fossil-fuel sources) is a combination of black carbon aggregates coated with lubricating oil (organic matter), unburned fuel oil (organic matter), and some other chemicals (e.g., sulfate, depending on the sulfur content of the fuel). As such, "soot" is emitted as a mixture. The ratio of OM:BC in soot varies with particle size. Particles smaller than the size of an individual BC spherule (e.g., 20 nm) contain no BC but are mostly liquid, containing unburned fuel oil and lubricating oil. Above 20 nm, BC is usually the dominant component. The authors should clarify their definition of soot and what it contains. Similarly, is the OM referred to primary or secondary OM? What is the difference between the OM that is externally mixed from soot and the OM emitted with soot?

AC1-1: We added definitions of soot and OM in the revised abstract and text. We define "soot" as "aggregated carbonaceous spherules with graphitic structures". Our definition follows the IPCC 2007 report and the reference therein, where *"Particles formed during the quenching of gases at the outer edge of flames of organic vapours, consisting predominantly of carbon, with lesser amounts of oxygen and hydrogen present as carboxyl and phenolic groups and exhibiting an imperfect graphitic structure."* and Charlson and Heintzenberg (1995), *"Soot particles are typically present in the atmosphere as aggregate of platelets having diameters of some tens of nanometers. Depending upon the formation process, soot particles can have oily surface coatings or, alternatively, exhibit a high surface density of sites for adsorption of gases."*

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Revised:

Abstract

Soot particles, which are aggregated carbonaceous spherules with graphitic structures, are major aerosol constituents that result from burning of fossil fuel, biofuel, and biomass.

Introduction

Soot particles, which are aggregated carbonaceous spherules a few tens of nanometers in diameter and with graphitic structures, are emitted through incomplete combustion of fossil fuel, biofuel, and biomass carbon together with OM. The latter is amorphous carbonaceous material that, in our samples, mainly formed through condensation and coagulation.

RC1-2: Abstract.

The authors state "More than 50% of the particles consisted of internally-mixed" then state "Moreover, soot occurs in more than 60% of all particles" This is confusing. Please just state something like, "about 55% of all particles contained soot coated by other material and 7% contained uncoated soot, so a total of 62% contained either coated or uncoated soot. The rest did not contain any soot"

AC1-2: we have changed the text.

Revised: Abstract

In the MC plumes, over half of all particles contained soot coated by organic matter and sulfates.

Moreover, about 80% by volume of the particles consisting of organic matter with sulfate also contained soot, indicating the important role of soot in the formation of secondary aerosol particles.

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RC1-3: Section 2.2.

It looks like the smallest particles on the sampler are 50 nm. This means that smaller particles were not picked up. Since small particles coagulate the fastest and faster after they begin to evaporate off the lubricating oil (Jacobson, Kittelson, and Watts, EST, 39, 9486, 2005), this could mean that many particles between 20-50 nm (the smallest BC particles) contain internal mixtures of BC plus smaller lubricating-oil or sulfuric-acid-water particles. Thus, the percentages found are applicable only to a limited size range above 50 nm. The authors should clarify this in the abstract and text and explain how the percentages might change if smaller particles were accounted for and why.

AC1-3: We mentioned their size range in the abstract and added discussion about the smaller particles in the revised text.

Revised: Section 2.2

Particles smaller than 50 nm, which include individual or small clusters of soot spherules and freshly emitted sulfates and OM, can have large number concentrations, especially during particle-formation events (Smith et al., 2008). However, such small particles generally coagulate rapidly after emission (Seinfeld and Pandis, 2006; Jacobson et al., 2005), and the mass and number fractions of soot particles smaller than 50 nm are small (Salcedo et al., 2006; Saathoff et al., 2003). Thus, our underestimate of the number of small particles has minor effects on conclusions based on total volume of particles in the air.

RC1-4:

A map would be useful in addition to or as a replacement for Table 1 since it difficult to visualize where the measurements are being taken relative to MC from the lat/lons alone.

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AC1-4: We added Figure 1.

RC1-5: P. 9184.

"with median about 44 nm." This is below the sampling limit of 50 nm. Please comment.

AC1-5: Here, we mention the sizes of soot spherules but not those of aggregates. As soot spherules aggregate, their aerodynamic diameters become larger than 50 nm, at which size we can collect them by using our sampler. We modified the sentence.

Revised: Section 2.4

Soot particles from MC typically consist of aggregated carbonaceous spherules ranging in diameter from 20 to 100 nanometers, with median value about 44 nm.

RC1-6: P. 9184.

"from vehicles, but some come from biomass burning" What about biofuel burning? Which is more prevalent, biomass or biofuel burning? Soot also comes from aircraft; this should be distinguished from surface vehicles.

AC1-6: We changed the sentence to include biofuel burning and aircraft as possible sources of soot particles.

Revised: Section 2.4

Soot particles in MC are mainly from vehicles, but some come from biomass burning (Moffet et al., 2008; Jiang et al., 2005), residential combustion of wood (biofuel burning), and aircraft (Bond et al., 2004; Mexico National Emissions Inventory 1999, 2006).

RC1-7: P. 9185.

“soot with coating of OM”. Since soot contains an OM coating when it is emitted, this category needs to be redefined. Also, please distinguish between primary and secondary OM.

AC1-7: Please see our comment AC1-1.

RC1-8: P. 9186.

Is this method of determining radii (fitting ellipses) standard? If so, please provide a reference. If not, it would seem that a more standard method of defining radii should be used so that results here can be compared consistently with results from other studies.

AC1-8: This method is widely employed when using microscopy. We added two references here (Pósfai et al., 2003; Mogo et al., 2005).

Revised: Section 2.7

Averaged particle radii were determined by fitting ellipses to the particle outlines and taking the geometric mean of the semi-minor and semi-major axes (Pósfai et al., 2003; Mogo et al., 2005).

RC1-9: P. 9188.

It looks like the fractal dimension was specified. Can’t it be calculated using additional information from the TEM images?

AC1-9: By using electron tomography (Adachi et al., 2007) and TEM two-dimensional images (e.g., Katrinak et al., 1993; Gwaze et al., 2006), it is possible to determine the fractal dimensions. However, the method is time consuming (from hours to a day per particle), and we used more than 2800 coated soot particles for the analysis. Also, we aim to calculate the ranges of the volumes but did not try to determine the exact fractal dimensions. Thus, we used the fixed values assuming two cases. In the revised

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paper, we added the sensitivity analysis that shows how fractal dimension and radius of monomers affect the results.

Revised: Section 3.3

For simplification, we divided the soot particles into their end values of either open or compact. For soot particles that have aspect ratios $>$2.0 (open clusters), we used $D_f = 2.4$ and $k_a = 0.7$ (Adachi et al., 2007). For the compacted soot particles (aspect ratios $\leq$ 2.0), we used $D_f = 2.6$ and $k_a = 2.1$ (Adachi et al., 2007; Liu and Mishchenko, 2005).

Approximately 80% and 50% by volume of the OM-S particles collected from MC and outside of MC, respectively, contained soot particles. The median value of soot volume fractions for internally mixed particles is 15% when the median value of *a*=22 nm is used and goes from 7 to 24% for our range of *a* values (from 10 to 50 nm) and for D_f $\pm$ 0.2 from the D_f values shown above.

RC1-10: P. 9189.

“they were compacted slightly during aging (Abel et al., 2003)”. What is this reference being used to refer to? The fact that particles compact during aging in general or that the particles found in the present study compacted. This latter statement seems contradicted by p. 9188, where the text states “those in our samples are not highly compacted” Please clarify.

AC1-10: We took out the sentences as reviewer #2 suggested (RC 2-8).

RC1-11: P. 9190.

“Biomass burning” Again, what about biofuel burning? Which one is more important in MC? There must be an emission inventory estimate for this.

AC1-11: About 36% of PM2.5 came from residential wood combustion in the MC

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area (Mexico National Emissions Inventory 1999, 2006). Yokelson et al., (2007) estimated that about half of the fine particles in the MC area outflow, which is a mixture of MC emissions and those from nearby areas, were from biomass burning. Thus, the biomass-burning emissions were likely a more important source for our samples than biofuel burning. However, biofuel burning is also an important source of aerosol particles in this area. We added sentences to mention biofuel-burning contributions (residential wood combustion).

Revised: Section 4.2

Locally, residential wood combustion (biofuel burning) is another source of K-bearing particles (Moffet et al., 2008; Mexico National Emissions Inventory 1999, 2006).

RC1-12: P. 9191.

How much sulfur is in MC diesel? Please provide approximate percentage of sulfur in diesel fuel in MC.

AC1-12: Diesel fuel in Mexico contains 0.0322% sulfur (Molina and Molina, 2002). We added gasoline and diesel fuel as possible sulfur sources.

Revised: Section 2.4

The S that forms the sulfate comes from regional sources such as petrochemical and power plants, volcanic emissions (Grutter et al., 2008; Johnson et al., 2006; de Foy et al., 2007; DeCarlo et al., 2008), and gasoline and diesel fuel, both of which contain $>$300 ppm of S in Mexico (Molina and Molina, 2002).

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