Atmos. Chem. Phys. Discuss., 13, C7837–C7840, 2013
www.atmos-chem-phys-discuss.net/13/C7837/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Physical-chemical characterization of the particulate matter inside two road tunnels in the São Paulo Metropolitan Area" *by* J. Brito et al.

Anonymous Referee #2

Received and published: 8 October 2013

Brito et al present measurements of aerosol concentration and composition in two traffic tunnels in Sao Paolo, Brazil. Overall the results are organized well and presented clearly. The findings are appropriate for Atmospheric Chemistry & Physics. However, significant revisions are required before the manuscript is ready for final publication. Below I outline major and minor comments for the authors to consider. Comments are in chronological order, not necessarily in order of importance.

MAJOR COMMENTS -The authors offer no discussion of background corrections for their measurements. The ventilation of the tunnel is not described explicitly, but we know that outside (background) air enters the tunnel through some mechanism (e.g.,

by fans or by the motion of traffic). I am unsure of typical PM2.5 concentrations in Sao Paolo, though it is reasonable to assume that, at least for the RA tunnel, the PM2.5 measurements are significantly above background levels. However, even if PM2.5 in the tunnel is well above concentrations outside of the tunnel, the presence of non-vehicular particles could have significant impacts on measured OC/EC ratios, the apportionment of specific ions, and measured optical properties. All of these are presented without background correction, and without discussion of background concentrations.

-Page 20846 - You need to justify how the Angstrom exponent of particles collected on a filter in the MAAP is applicable to suspended aerosol. There are numerous studies that are highly critical of using particles trapped on a filter to infer optical properties. One such reference: Subramanian et al (2007), Yellow beads and missing particles: Trouble ahead for filter-based absorption measurements, Aerosol Sci. Technol., vol 41, p 630-637.

-Page 20846, Line 17 - How variable is the MAC of the MAAP filter substrate? Kirchstetter and coworkers showed that for the aethalometer, which works under similar principles, the "default" MAC did not describe their data obtained from a propane burner and they introduced a scaling factor of 0.6 to account for this difference. Also the calculation in equation 2 assumes no change in particle morphology when it is captured on the filter tape.

-Section 3.2 and Figure 7 - I have several concerns about this section. First, while the temperature steps in the OC/EC analysis should give some information about the RELATIVE volatility of the OC fractions from each tunnel, the authors do not provide much information to give context to Figure 7. Were any calibration runs, with known material, conducted in order to determine that a volatility difference exists between the JQ and RA samples, and is driving the differences in thermograms? The sucrose recommended as a calibration standard for the Sunset OC/EC can desorb during multiple temperature steps, depending on the specific desorption program used. This suggests

that OC desorption temperatures are not directly correlated to volatility. No convincing argument is made that the thermograms are truly indicative of organic aerosol volatility. The differences in thermograms could be due to differences in aerosol loading on the different filters, or could be the result of artifacts (which could be indirectly related to loading). Since these are bare quartz filters, there should be substantial vapor-phase artifacts, especially for the lower concentration conditions in the JQ tunnel, and these artifacts are not discussed.

-Figure 11 and related discussion on page 20857 - I disagree that the changes in aerosol optical properties are the result of gas/particle partitioning. A more likely explanation is that changes in these quantities over the course of the day are driven by the number of vehicles in the tunnel, and therefore the dilution ratio of fresh exhaust. During the overnight hours, when vehicle volumes are low, there will be a high fraction of background air in the tunnel. As the vehicle volumes climb during the day, there is a higher fraction of exhaust in the tunnel and less background air. The diurnal changes you are observing are likely the differences in optical properties between exhaust (at midday) and regional background air (overnight).

MINOR COMMENTS -Page 20843, Lines 1-5: biomass burning is a globally important source of OC and EC. I think that this text is trying to state that in megacities EC is usually dominated by vehicle emissions, but instead it seems to imply that biomass burning is not an important source.

-Page 20843, Line 14 - what does "Tunnel 3" of the RA tunnel mean?

-Page 20845 - Is there any impact of running the MAAP at reduced flow? My understanding is that the default flow rate for this instrument is 16.7 LPM. It seems like lowered flow rate would increase your detection limit (reduce sensitivity) for measurements collected at 1 minute resolution.

-Page 20850, Line 9 - It is probably more appropriate to say that samples with enrichment factors close to 1 are assumed to be crustal. It's not clear that the enrichment

factor can positively identify the sources, as it would depend on the representativeness of the element ratios in UCC relative to the crustal composition in Brazil.

-PAHs are determined from PM10, not PM2.5 filters. Does this bias the results? Since the fresh emissions in the tunnel are mostly in the fine range, are you mostly measuring background PAHs from the air carried into the tunnel by the motion of traffic?

-The discussion of the PAH ratios is lacking. Eg., Page 20851, Line 24-25 notes the InP/(InP+BPe) ratio from Rogge. The current measurements of this ratio are significantly different, but the difference is not discussed.

-Page 20853 - what is the basis for the OM/OC of 1.6 for gasohol? This is not clearly explained.

-Page 20853 - Does the sulfate concentration in the tunnel make sense based on vehicle volumes, typical fuel consumption rates and fuel sulfur contents, and typical conversions of SO2 to SO3 during combustion? There are numerous reference values that can be used to estimate sulfate in the tunnel.

-Figure 10 - The data seem to have much more scatter than an R^2 of 0.95 would indicate. To the naked eye the correlation does not appear that strong, and the fit seems to be influenced by the point with EC of 18 ug/m3.

Grammar notes -Page 20841, Line 19 "considerably amount" -Page 20851 - first paragraph of section 3.1.2 is thoroughly confusing. Are PAHs emissions the result of PAHs in the fuel or the combustion process itself? -Page 20856, Line 23 - "particles" instead of "particulated"

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 20839, 2013.