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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Determination of OM/OC ratios and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in southern Ontario: implications for emission sources, particle aging, and radiative forcing" *by* T. W. Chan et al.

Anonymous Referee #2

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Chan et al. describe an interesting study with surprising results. However, I feel that several of the conclusions drawn are not supported by the data as analyzed and presented in the paper, and cannot recommend publication. In particular, the authors need to provide more evidence to support their conclusion that the spectral attentuation coefficient (SAC) is linearly related to aging, and that at zero-aging, primary soot particles have a given SAC. In the abstract, the authors describe a daunting 50% difference between global models and the Egbert measurements, but a.) the uncertainties in the

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measurements need to be more carefully considered, and b.) this number and the measurement-model comparison is not explained in the manuscript. The authors further claim that significant differences exist in aerosol composition between the northerly and southerly wind directions, and that these differences are due to different sources. However, for the most part, the statistics presented in the paper do not support this (with notable exceptions in b_asp), and I question whether temperature, which is significantly different between the two wind classifications, is instead the dominant driver of differences in organic aerosol (OA) processing.

Specific Comments The study divides airmasses into two wind direction classifications, north and south. However, these two wind directions are apparently accompanied by very different meteorology, with southerly winds being much hotter. The authors have not convinced this reviewer that wind direction is the appropriate classification scheme rather than meteorological conditions: the chemical implications of these two approaches on aerosol processing are potentially significant, particularly with respect to aging.

The Introduction and Sampling sections are well-written and complete.

The presentation of statistics is misleading in the number of significant figures presented: uncertainties (presumably standard deviations? or standard error of the mean? please specify in table captions) are given to at least two significant figures, which is incorrect: uncertainties are considered valid to one significant figure, and the mean should only be presented to that level of precision. For example, the authors present numbers in the format of 0.51 +/- 0.19. This is properly described as 0.5 +/- 0.2. Further, upon close examination of the numbers, the authors claim that there are significant differences between, for example, the OC_tot/TC ratio between north and south wind directions. However, these two numbers are 74+/-6 and 67 +/- 6, respectively, which are not statistically different (overlapping confidence intervals). The authors need to either perform statistically valid and robust tests on the data, or rewrite the sections of the paper describing supposed differences between OC/EC and OC/TC between the

ACPD

9, C4151–C4154, 2009

different wind directions.

The authors use datasets from 2005 and 2007; however, I am unclear as to what the 2005 datasets add to the analysis, and think it unnecessarily complicates the paper.

I am confused as to why the Northerly wind directions are not included in the aerosol aging analysis? The OM/OC ratios appear to be in the same range, and may have larger error bars, but should still fit the trend.

p14431, the authors point out that on the 17 May 2007, the OM and OC are near detection limits - however, the error bars in the figure show very small uncertainties: these uncertainties must be underestimates, and the authors should check their calculations. The authors also carefully describe potential sources of error in the OM/OC ratio, but do not ascribe negative, positive or random biases to these sources of errors, which would be helpful.

I am concerned that the authors claim that the OM/OC ratios cannot be compared between 2005 and 2007 because different instruments were used: it suggests that not only is there a significant methodological problem, but that the numbers are in and of themselves worthless. If you can't compare the OM/OC numbers for 2005 and 2007, then how can you compare 2005 data to OM/OC ratios in other studies? This suggests that the authors don't trust the 2007 OM/OC numbers, and either they should not be included, or that the numbers are trust-worthy and the differences between 2007 and other studies are process-driven and should be explained. The figure describing the relationship between estimated oxygen mass and POC mass is good, but including the 2005 and 2007 data on the same plot seems inconsistent given that the OM/OC ratios are inconsistent.

I am confused as to why the authors describe the comparisons between the benzene-toluene photochemical clock and the OM/OC ratio (an interesting and relevant comparison), and then use POC as an indicator of aging in the SAC section of the paper. Either OM/OC should be consistently used as an aging indicator, or the case for POC

ACPD

9, C4151–C4154, 2009

as an indicator could be made. However, I object to the sentence that the relationship between POC and SAC 'appear to be wind direction dependent' (p14334, l21-22). Could this also be a temperature-dependent or sulphate-dependent relationship?

The use of a linear regression and the scientific interpretation of the derived intercept between SAC and POC assumes a linear relationship between POC and aging, which has not been demonstrated. It should also be noted that the least-squares method of linear regression assumes no uncertainty in the x-axis coordinate, which is clearly not the case between SAC and POC, and another regression approach should be used. The regressions in Figure 8 are questionably significant by eye: if not separated by wind direction, the slope would be near-zero; uncertainty bars around the regression lines would be helpful. It may also be helpful to plot the SAC and POC data against sulphate, which appears correlated with both components.

Technical corrections. The paper needs to be proofread as there are numerous grammatical errors. Examples of problems include l.16 in the abstract (sentence starting with 'whereas' doesn't make grammatical sense) p14322, l 24 should read 'lasted'

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14315, 2009.