Atmos. Chem. Phys. Discuss., 13, C5957–C5961, 2013
www.atmos-chem-phys-discuss.net/13/C5957/2013/

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Water-soluble organic carbon over the Pearl River Delta region during fall–winter: spatial variations and source apportionment" *by* X. Ding et al.

Anonymous Referee #3

Received and published: 18 August 2013

This manuscript analyzes 24-hr filter measurements of OC, EC, WSOC and selected organic tracer compounds at three sites in the Pearl River Delta (PRD) region during the fall-winter season in 2008. The authors attempted to attribute the sources of WSOC based on concentrations of tracers for different sources, i.e., biomass burning and different types of secondary organic aerosols.

Unfortunately, there are many issues with the analysis method adopted by the authors, making the conclusions drawn from the data highly questionable. I recommend a rejection of the manuscript and urge the authors reanalyze their data. Specifically, my comments are elaborated as follows.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

Major comments:

1) Their methods of splitting WSOC and deriving POC and SOC have fundamental flaws. In Equation 4 (POC = OC - SOCtotal = WIOC + WSOCBB) and the related text, the authors mixed up the two terms SOCtotal and WSOCSOA (WSOC that is not from BB, which is another source of error that will be discussed later). The fact that SOA formation is a major source of WSOC does not mean that all SOA are water-soluble. Comparisons between field observations of WSOC and oxygenated organic aerosol (OOA) measured by AMS suggest that WSOC is only ∼40-80% of SOC, depending on sampling locations and dominant aerosol source/SOA formation pathways [Kondo et al., 2007; Zhang et al., 2013]. In addition, chamber studies have revealed that SOA formed from various anthropogenic and biogenic precursors have different hygroscopicity [e.g., Varutbangkul et al., 2006]. SOA formed through aqueous phase reactions are thought to be highly water-soluble [Ervens et al., 2011 and references therein]. Likewise, SOA may have a considerable contribution to WIOC in PRD, which might explain the higher WIOC/EC ratio in PRD than Tokyo (Page 13781, Line 1-5). Thus, it is fundamentally wrong to apportion WSOC into SOCprecursor, WSOCBB and unexplained WSOC. SOCprecursor calculated by the authors that contain non water-soluble compounds will also lead to an underestimation of the unexplained WSOC fraction. In order to make this method valid, the authors need to calculate WSOCSOA using a different set of parameters.

2) To help the reviewers (and the readers) better assess the robustness of the analysis, the authors should discuss explicitly the (substantial) uncertainty associated with the tracer-based method, specifically the uncertainty due to the over-simplification of applying laboratory-derived single parameters to calculate SOA mass from the ambient samples. Moreover, it is highly possible that many other SOA precursors that contribute to the WSOC (and OC) concentration sampled at PRD are not considered in their method. How would this affect the outcome and the subsequent analysis?

3) One of the major conclusions of this study is that the "unexplained" WSOC by the

SOA tracer method is likely from photochemical aging of POA in the atmosphere, supported by the "strong" correlation between the "unexplained" WSOC and POC (Figure 5). First of all, an r2 value of the fit based on three data point is problematic. Further, as discussed above, the invalid approach to deriving unexplained WSOC and POC makes the relationship between the two not meaningful. Finally, there are many possible mechanisms other than POA aging can be used to explain the discrepancy (if any) in the WSOC closure calculation, for example, missing SOA precursors (IVOC/SVOC) [de Gouw et al., 2011] and aqueous SOA formation. The authors should explore these and other mechanisms and provide more evidence that this unexplained fraction is due to POA aging and not other processes.

4) The authors used the correlation between WSOC and EC as one and the only piece of evidence that WSOC is mainly associated with biomass burning throughout the manuscript. However, a strong correlation between WSOC and EC does not necessarily indicate a biomass-burning source to WSOC since vehicular emissions also contribute to both WSOC and EC concentrations. Influences due to meteorology further confound the picture. It is also unclear why the authors didn't correlate WSOC with levoglucosan, a biomass burning tracer that is commonly used and was also quantified in the study.

Minor comments:

Page 13780, Line 13-15: The observation of high WIOC at WQS is somewhat contradicting with the site description on Page 13777, Line 9-12. Why is WQS considered a rural site with rare traffic and representing "regional background" when both WIOC and POC concentrations were almost as high as those at the sub-urban site? The authors need to better reconcile their knowledge about the site and the observations.

Page 13781, Line 9: SOCtotal also includes WSOC and WIOC from vehicle emissions.

Page 13783, Line 28: Can the authors provide some explanation of why SOC from anthropogenic sources exhibit little spatial variation whereas POC does?

Page 13785, Line 5: Splitting WSOC into WSOCBB and SOC based on levoglucosan concentration is not a new analytical method.

Page 13785, Line 8: The high fraction of WSOCBB in the total WSOC is not evidence that WSOC is mainly from BB since WSOCBB is calculated using levoglucosan with the assumption that BB contributes to WSOC concentration.

Technical corrections:

Page 13774, line 11-13: This sentence needs rewording.

Page 13774, line 18: totally → in total

Page 13775, line 7: add “formation” after “SOA”

Page 13775, line 23: short the gap → close the gap

Page 13776, line 3: overestimate → overestimation

Page 13776, line 21: delete “with the purpose”

Page 13778, line 12: filtered → filtration

Page 13779, line 17: shares → share; were → was

Page 13779, line 26: major → mainly

Page 13780, line 2: deeply → strongly, greatly or largely

Page 13783, Equation 5: change “SOC” to “SOCprecursor”

Page 13783, line 6: SOCtoluene is probably more precise than SOCaromatics

Page 13783, line 26: I believe PAHs are included in the aromatics

Page 13785, line 7: OC contribution → contribution to OC

Reference

de Gouw, J. et al., Science, 331, 1295-1299, 2011.

Ervens, B. et al., Atmos. Chem. Phys., 11, 11069–11102, 2011.

Kondo, Y. et al., J. Geophys. Res., 112, D01203, doi:10.1029/2006JD007056, 2007.

Varutbangkul, V. et al., Atmos. Chem. Phys., 6, 2367–2388, 2006.

Zhang, X. et al., Environ. Sci. Technol., 47, 3685-2693, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 13773, 2013.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper