15 January 2015

To: Prof. Ken Carslaw,
Executive Editor, Atmospheric Chemistry and Physics

Re: Revisions for “Estimating sources of elemental and organic carbon and their temporal emission patterns using a Least Squares Inverse model and hourly measurements from the St. Louis-Midwest Supersite” by B. de Foy, Y. Y. Cui, J. J. Schauer, M. Janssen, J. R. Turner, C. Wiedinmyer, Atmospheric Chemistry and Physics Discussion, 2014.

Dear Ken,
Thank you for the re-reviews of our paper and for your suggestions to better quantify the limitations in our modeling, which we believe we have now done to the best of our ability. This included performing new simulations to quantify the impact of wet and dry deposition, and using estimates of secondary organic aerosol calculated from past studies of the same data. Please find a list of the changes along with the new text shown in italics below.

As requested, the conclusions have been augmented with 2 new paragraphs, one for the question of deposition and one for the question of secondary organic aerosol formation:

"There are two important limitations in our modeling. The first is that we do not include deposition in the FLEXPART back-trajectories. This means that we cannot obtain emissions directly from the Residence Time Analysis grids but instead we obtain results for the contributions of sources towards EC or OC concentrations at the measurement site. For EC, which is a passive tracer, we performed a sensitivity test on the impact of deposition using forward simulations with CAMx. The emissions based on the FLEXPART inversion were used as input into CAMx and two sets of simulations were performed: one set without deposition, and a second set with both wet and dry deposition. Wet and dry deposition in the model reduced the EC concentration at the site by 4% on average over the whole year. The main reason this number is low is that most of the impacts are due to fairly local emissions (within 100 to 200 km). Overall, this shows that neglecting deposition in FLEXPART has a minor impact on the results.

The second limitation in our modeling is that we do not include secondary formation of OC. There is considerable formation of OC in the atmosphere (Jimenez et al., 2009; Robinson et al., 2007) and also significant uncertainties in simulations of secondary organic aerosols (Napelenok et al., 2014). These uncertainties include the complex behavior of semi-volatile and intermediate volatility organic precursors involving the evaporation of primary OC and recondensation after oxidation (Hodzic et al., 2010). In our inverse model, the OC emission results need to be interpreted as the combination of emissions and inplume formation. To estimate the contribution of secondary formation to OC in our time series, we consider three lines of evidence. First, using the same data as our paper, Bae et al. (2006) estimate that 20 to 40 % of OC at ESTL was secondary organic aerosol on an annual average (see their Fig. 2). Second, Fig. 8 shows that the primary OC simulated using the LADCO inventory (2 ug m-3) is 40 % lower than the average OC at the measurement site (3.5 ug m-3). It would be reasonable to expect that a significant fraction of this 40 % is due to secondary formation: whereas the average concentration of OC is significantly higher than the primary OC contribution from the LADCO inventory, the reverse is true for EC where the average concentration of EC is lower than the primary EC contribution. Third, Fig. 13 shows large excess peaks of OC in the summer and during the daytime which can be interpreted as consisting mainly of secondary organic aerosol. We further note that the seasonality in Fig. 13 (minimal secondary OC in the winter increasing to a majority of OC in the summer), is similar to the seasonality shown in Fig. 2 in Bae et al. (2006). Overall, these three

items suggest that 40 % would be a reasonable estimate of the OC that could be due to secondary formation in the atmosphere. Consequently, the OC emissions estimates such as in Table 1 should be interpreted as being the sum of somewhat over half of primary emissions (~60 %) and a little under half of secondary formation (~40 %)."

In addition, we have adjusted the text in the results and discussion sections as follows:

Sec 3.2 Inverse Model results: time series and impacts:
"Whereas EC behaves as a tracer species from source to receptor, OC is due to the combination of transport from source to receptor and formation in the atmosphere during transport. Because this paper only considers transport, we expect the model results to underestimate average concentrations: the prior time series represents 60 % of the average OC concentration. As discussed in Sec. 4, this suggests that 40 % of OC at the measurement site is from secondary formation, in line with the estimate provided in Bae et al. (2006)"

3.3.2 Non-Road emissions:
"For OC, the summer peak in the posterior is double that in the prior. We also see an enhancement of around 50 % during daylight hours. An estimate of 40 % of OC at the site being due to secondary formation (Bae et al., 2006) would account for most of the excess in OC, as discussed further in Sec. 4."

3.5 Inverse model results: Residence Time Analysis impact:
"Note that the FLEXPART-WRF simulations do not include deposition, and that secondary OC formation is not included either. Both of these limitations would impact the estimation of actual emission amounts from the inverse model. In this section, we therefore report only impacts of different source regions on concentrations at the measurement site, which are not affected by deposition and include estimated impacts of both primary emissions and in-plume secondary formation. As will be discussed in Sec. 4, deposition is estimated to account for a 4 % loss of EC, and secondary formation is estimated to account for around 40 % of OC."

3.6 Inverse model results: emission totals:
"This suggests that the inverse results are in agreement with the inventory, bearing in mind that the model does not distinguish between primary and secondary OC. As around 40 % of OC is estimated to be secondary (see Sec. 4), this is a significant source of uncertainty."

We have added the following caveat to the captions for Tables 1 and 2, and for Figure 10:
"Note that OC Inverse totals combine primary emissions and secondary formation."

In the process of revising the manuscript we further made a few minor cosmetic changes to the text: one correction of the use of "the", expanded an ambiguous "this", repositioned the sub-section header "3.3.1 On-Road emissions", and eliminated a sentence fragment that had been introduced in the LaTeX file by mistake.

We are very grateful for your time and for your consideration of the reviews, and hope that we have responded to your concerns.
Sincerely,
Ben

Benjamin de Foy and Jamie J. Schauer