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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Unraveling the role of silicon in atmospheric aerosol secondary formation: A new conservative tracer for aerosol chemistry" *by* Dawei Lu et al.

Anonymous Referee #2

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This manuscript (acp-2018-914) describes the use of Si to estimate the contribution of secondary aerosol to PM2.5 in the urban environment in Beijing, China. The approach relies on Si content from PM2.5 arising from primary sources only. Secondary aerosol concentrations are estimated by the inferred dilution of expected Si mass. This dilution is calculated by comparing measured Si concentrations in PM2.5 to estimated values based on sources of primary emission. This approach is compared to another approach where concentrations of several secondary species (NH4+, NO3-, SO2-2, secondary organic carbon) are used as tracers for secondary aerosol production. The Si dilution approach gives a value in line but slightly higher than those given by the approach using chemical components associated with secondary aerosols. The authors

argue the Si approach is more direct and has a lower uncertainty associated with it compared to the other approach. Moreover, the authors correlate secondary aerosol components in PM2.5 (SO4-2, NO3-, NH4+, and secondary organic carbon) with Si isotopic composition and observe some correlations that suggest some sources for secondary aerosol.

This manuscript represents a new approach to estimate secondary aerosol formation and is within the scope of Atmospheric Chemistry and Physics. However, several important issues, detailed below, must be carefully addressed by the authors before this manuscript is suitable for publication.

Comments:

1. The authors examined PM2.5 collected on "random haze days" (see page 3, line 3; page 5, line 4). It is unclear what "random haze day" means. Were the analysis days randomly selected? Were the selected days the ones with the highest PM2.5 concentrations, or days where PM2.5 concentrations were above some arbitrary threshold? It is unclear whether the specific days collected are representative of the Beijing region or were chosen specifically for other purposes. Why were not all days with available PM2.5 measurements analyzed? The authors must clarify in revision their methodology for selection of the days that were analyzed. The apparent arbitrary selection of studied days may affect interpretation of the results in Fig. S1 and S2, for example.

2. The authors state that the mean contribution of secondary particles to PM2.5 by the Si tracer method was 79.2% and refer to the reader to Fig. 4b (page 7, line 13). However, the bar graph in Fig. 4b shows a mean secondary concentration that appears to be closer to 70% rather than 80%. The authors should ensure the results they report in the text match those in the corresponding figures. Moreover, the clarity of Fig. 4a would be enhanced by labelling what boxes come from experimental measurements, what are estimations from inventories, etc.

3. The authors should enhance their discussion of uncertainties as well as clarify their

wording. For example, there are no lower error bounds on the values shown in Fig. 4. Error is discussed only for the annual average, but not for the seasonal or daily averages. The authors provide Table S1, which contains concentrations for chemical components indicative of secondary aerosols, but no similar table exists for the Si concentrations. Moreover, there are no uncertainties provided in Table S1. The manuscript would be substantially improved by a clear demonstration of a smaller uncertainty range for the Si approach. In addition, the authors suggest that the two methods being in close agreement is "proving the accuracy of the Si-dilution method" (page 8, lines 2-3). This is an odd statement as the authors spend most of the paper discussing the large uncertainties associated with the secondary tracer approach: could the agreement just be coincidental?

4. Lastly, this approach relies on Si not participating in secondary aerosol formation. The authors reference two previous studies on page 6, lines 7-9, to suggest that organosilicons do not contribute to aerosol formation. However, these studies are 15-25 years old and our understanding of Si chemistry has significantly advanced (as acknowledged in other portions of Section 3.3). In fact, volatile organic compounds like siloxanes are likely to become increasingly significant as aerosols of fossil fuel origin become less important over time (see: McDonald et al., "Volatile chemical products emerging as largest petrochemical source of urban organic emissions", Science, 2017, 359, 760-764, doi: 10.1126/science.aaq0524). In light of these trends, the authors should enhance discussion of the limitations of their approach. Is this approach only valid in heavily polluted urban environments with a large fossil fuel contribution (i.e. where Si contribution to secondary aerosol mass is minimal)?

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