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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Variation in Global Chemical Composition of $PM_{2.5}$: Emerging Results from SPARTAN" *by* Graydon Snider et al.

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Responses to Anonymous Referee #2

We thank the referee #2 for these helpful comments. Referee comments are numbered, with our responses, and any changes to the manuscript, subsequently given.

1) line 22: "2-22 month periods", what was the average period for all sites? Whether 2 or 22 months of data were available for a given station is highly relevant with regard to its representativeness. Please clarify in the abstract and in the text.

The text and abstract now note that the average sampling period of sampling is 12 months.

2) line 34: the term "residue" is rather confusing, especially if one sees later on in the

text that it refers mainly to organic matter. I would suggest to find a different term.

We have changed all mentions of 'residue' to 'residual' matter. We follow C. A. Brock et al.: Characteristics, sources, and transport of aerosols, ACP, 2011, figure 7, which notes of an aerosol "residual = un-speciated mass (probably organic)".

3) line 51, treatment of outliers: how were outliers processed? This line refers to a major sulphate event, and in the final section of the MS for several stations the authors describe the impact of dust events, major forest fires... How were these outliers dealt with? Depending on the duration of the sampling (see the first comment above), these outliers may have been not representative and strongly impact the mean aerosol concentration. A section should be added to discuss how frequent these outliers were, and how they were treated.

These major events (e.g. dust storms, annual festivals) affect exposure and are thus included in the averages. These major events are described in detail in Section 5.3. Number of filters and date ranges are included for each site to assess representativeness.

For other instances of outlier data we have added a new section (4.4), which describes major sources of uncertainty for chemical and physical measurements.

4) lines 116-121: please highlight as a limitation that no data are available for Europe. This is a major spatial gap, despite data being openly available (e.g., chemical speciation data and nephelometry from the EMEP stations, stored in the EBAS database).

We have added at the lines 169-171:

"Site selection prioritizes under-represented globally-dispersed, population-dense regions; no SPARTAN sites yet exist in Europe".

5) line 135, what was the diameter of the filters, 47 mm?

Thank you for noting this, we now state the 25mm filter diameter.

6) line 155: were all the filters from all sites shipped to Dalhousie Univ. for analysis? Please describe how filters were stored + transported to guarantee sample conservation, as this could be a major issue. How many filters/month were sampled, and how many in total per site? Please add a Table (even if in Supplementary material).

Added 155-161: “As described by Snider et al (2015), loss rates of ammonium nitrate during passive air flow were an order of magnitude less than during active air flow. Thus the sampling protocol is designed to actively sample for one diurnal cycle and to avoid daytime sampling after collecting nighttime PM. Following the IMPROVE protocol (Hand and Malm, 2006), filters are transported and stored between measurement sites and the central SPARTAN laboratory at Dalhousie University, where analysis is conducted. Filters are stored at room temperature in sealed containers”.

The number of filters at each site is stated in Table 3. Line 151-2 states that one filter is sampled every 9 days. Thus there are typically 3 filters/month per site.

7) line 298: please add a reference for the 0.18 coefficient applied to Na+

We have added the reference Henning et al. (2003) to this line.

8) line 320: please rename the fraction "residue matter" and state clearly from the beginning that it refers mainly to organics

We have modified lines 247-249 to read

“Residual matter, which is treated as mainly organics, is estimated by subtracting dry inorganic mass (IN) and its associated water (referenced to our weighing conditions of 35 5 % RH) from total PM2.5 mass”

9) section 4.10: this entire section is very descriptive, but hardly any interpretation of the results is provided.

We have moved this descriptive overview to section 5.1 to emphasize that it is intended to provide context for interpretation of specific site characteristics in the rest of section

5.

10) line 357: this result is surprising for Beijing: even despite the influence of dust storms, a major urban area like Beijing should have a high Zn/Al ratio (high anthrop. influence). Whys is this not the case? Could it be due to the potential lack of representativeness of the samples, linked to how outliers were dealt with? Please discuss and clarify in the text.

We compared our ratios with previous work (Yang et al. 2011), that found a ratio of Zn:Al 0.67, which remains lower than compared with Hanoi and Dhaka. The moderate Zn:Al ratio could reflect the sampling location to the west of the city, upwind of many traffic sources. We have commented further on this in section 5.3.1 (previously 4.12.1), lines 468-473:

“The mean PM2.5 Zn:Al ratio is lower than other large cities (0.51) likely due to larger fraction of natural dust sources and the sampling location in the northwest quadrant of the city, upwind of many traffic sources. The lowest coarse-mode Zn:Al mass ratios are observed in April 2014 (0.07) and April 2015 (0.06) during the annual Yellow dust storm season. This is balanced by urban dust sources throughout the year, in agreement with Lin et al. (2015) who found evidence of high CM in industrial areas of Beijing”.

11) line 376, 60% in Kanpur: if RM is so high in Kanpur it implies that CM will be very low, which seems surprising for an Indian city. Could this be because sampling took place during the monsoon season, maybe? This refers again to the temporal representativeness of the sampling. Some of the chemical composition results seem unexpected, please include a section discussing the potential sources of uncertainty, e.g. sampling period, filter transport, technical issues during sampling... What could have gone wrong, with such a disperse network of stations?

The RM in Kanpur is consistent with previous measurements of organics and RM in Kanpur. From section 5.3.6 (lines 566- 569):

“Notably the combined OM + unknown fractions from these previous two studies account for two thirds of aerosol mass, 58% for Behera and Sharma (2010) and 63% for Ram et al. (2012), similar to our 59% RM estimate”.

We also added a new section 4.4 (lines 339-346) to describe our sources of uncertainty regarding loss of semivolatiles:

“Of concern is the loss of semivolatiles after sampling. In the laboratory we reduce semivolatile loss by storing filters in closed containers. For time spent in the field, we examined the trend in PM2.5 mass and ANO3 from the first filter sampled (54 day residence time in instrument) through the last filter sampled (negligible residence time in instrument). Statistically insignificant trends were found for both PM2.5 (-0.09 0.46 g m-3/position) and ANO3 (0.06 0.15 g m-3/position) providing confidence in retention of semivolatiles on filters in the cartridge”.

12) line 394, strong correlation between ASo4 and ANO3: this is unexpected due to the thermal instability of ANO3 in summer (when formation of ASO4 is highest). On an annual basis both components might correlate, but not on a monthly basis. Please clarify.

We clarify that ammonium and sulfate correlate well, but make no claims that ammonium nitrate correlates well with ammonium sulfate. ($r2 < 0.15$).

13) section 4.11: this section is very unclear, what studies are the authors comparing their SPARTAN results with? Please specify. What are "study A" and "Study B" in the Figure?

We have removed the terms “Study A” and “Study B”. The first sentence of this section (lines 433-434) was modified to read:

“We compare SPARTAN PM2.5 speciation with one or two previous studies available from the literature (Prior Study in figure 3) and focus on collocated relative PM2.5 composition of major species within the last 10 years.”

14) line 417: "expectation that RM is organic", this is not an expectation, it is a definition of the SPARTAN methodology (given that all other components are already accounted for)

We modified lines 450-451 to now read:

“SPARTAN measurements of RM appear to be predominantly organic in nature”.

15) line 410: "10-30%", this is an overall limitation of the work: because such a broad range of station types, geographical regions and locations is used, the results also become rather broad and non-specific. E.g., stating that ASO4 contributes with 10-30% to PM2.5 mass is not a very specific result, it could represent almost anywhere in the world. Therefore, please state this limitation in the intro or results section, and extract the use of this kind of very global data, e.g. probably (in my opinion) for modelling studies, etc. What is the ultimate purpose of this work? Otherwise it becomes simply a descriptive manuscript.

The ultimate purpose of work is to describe the initial results about PM2.5 concentrations from around the world. Due to the variability of PM components at each location, we provide broad concentration ranges when describing the SPARTAN project as a whole. We are developing modelling studies to further interpret the measured composition.

We have modified Lines 18-21 of the Abstract to read:

“The Surface PARTiculate mAtter Network (SPARTAN) is a long-term project that includes characterization of chemical and physical attributes of aerosols from filter samples collected worldwide. This manuscript discusses the ongoing efforts of SPARTAN to define and quantify major ions and trace metals found in fine particulate matter (PM2.5)”.

Lines 122-123 in the Introduction now reads:

“We discuss the ongoing efforts of the SPARTAN project to quantify major ions and

trace metals found in aerosols worldwide".

16) section 4.12.1: same issue as above, please discuss the relative contribution of natural and anthropogenic dust in Beijing. The large number of samples available (100) should allow for this kind of interpretation.

We elaborate on the Zn:Al ratio to understand the relative contribution of natural and anthropogenic dust. We are currently preparing a manuscript that characterizes source attribution of different chemicals and elements. Lines 470-475:

"The mean PM2.5 Zn:Al ratio is lower than other large cities (0.51) likely due to larger fraction of natural dust sources and the sampling location in the northwest quadrant of the city, upwind of many traffic sources. The lowest coarse-mode Zn:Al mass ratios are observed in April 2014 (0.07) and April 2015 (0.06) during the annual Yellow dust storm season. This is balanced by urban dust sources throughout the year, in agreement with Lin et al. (2015) who found evidence of high CM in industrial areas of Beijing"

17) line 445: due to volatilzation but also to the fact that the authors are comparing their results with those from different periods in time, in the other studies.

We now note different sampling periods. Lines 478-480:

"SPARTAN ANO3 concentrations (8.5%) are relatively higher than most other locations, though lower than either previous study (11-12 %), possibly due to different sampling periods".

18) line 520, "organic matter burning": this is another example of a potential outlier. In addition, it would be useful if the authors could add somewhere in the text a brief assessment of major common emission sources, e.g., biomass combustion, agriculture, natural dust... This would help to integrate the results from the different sites rather than simply state ranges of chemical components (e.g., ASO4 = 10-30%) which don't provide much specific information.

These major common emission sources are described at the start of Section 2. We are

preparing a modelling comparison manuscript to more quantitatively assess emission sources.

19) line 572: festival in Israel, another probable outlier

We agree this festival is an unusual event. However, it is an event that affects ambient PM. We moved discussion of this event into a separate paragraph.

20) line 691: black carbon should be equivalent black carbon

Updated and corrected, thank you.

21) line 697: "3-year span", please clarify that this is not a continuous monitoring period in all sites, but instead a sequence of consecutive 4-month (approx) periods in different stations. This is a very big difference.

We have modified this to read:

"We report ongoing measurements of fine particulate matter (PM2.5), including compositional information, in 13 locations in two month or greater intervals all within a three-year span (2013-2016)"

22) Conclusions: the conclusions section is again very descriptive, it is rather a summary. Actual conclusions and applications for their data should be extracted by the authors.

We have revised this section to further develop specific conclusions.

23) As proposed above, a reference to major common emission sources could be added (this is slightly hinted at in paragraph 7369-744).

We attempt to tailor emission sources to each SPARTAN location. More general land use references include Latham et al (2014) and O:C characteristics from Canagaratna et al. (2015).

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