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## ***Interactive comment on* “Chemical and microphysical properties of the aerosol during foggy and nonfoggy episodes: a relationship between organic and inorganic content of the aerosol” by D. S. Kaul et al.**

**Anonymous Referee #1**

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The study addresses the analysis of a data set that describes chemical and microphysical aerosol properties acquired during an extensive field experiment in the Indo-Gangetic Plain. Particular focus was (1) the source apportionment of pollution and (2) the potential impact of fog on the modification of aerosol properties. While such analyses are clearly of high interest to improve our understanding of the pollution sources and the role of aqueous phase processing, the study's conclusions are not very convincing. This might be largely ascribed to poor language that makes it very hard to understand several sections of the text and to a very lengthy style that lacks some

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clear structure of the manuscript.

If the authors consider submitting a revised manuscript that considers my comments below I strongly suggest using a professional editing service in order to improve language and understandability. In my comments I do not list all places where incorrect English is used but only those where I did not understand the meaning of complete sentences.

#### General comments

1) What are your conclusions on the role of aqueous phase processing in modifying aerosol? While you state in the abstract that it changed the mean diameter of aerosol size distributions, throughout the manuscript your findings keep changing and you ascribe increase in aerosol mass to varying boundary layer heights or possibly some aqueous phase processes.

2) The use of the term 'interstitial particles' is misleading. Interstitial particles are usually those that are not activated into droplets. I have the impression that the authors imply that 'interstitial particles' are the particles that acted as condensation nuclei and are immersed in droplets.

3) There seems to be a conceptual misunderstanding of SOA formation in the aqueous phase. The authors discuss at several places that inorganics (ammonium, sulfate) are required to form SOA mass in the aqueous phase. The processes that are referred to here are all processes that occur in the aqueous phase of very concentrated, deliquesced aerosol particles. Chemical processes in the aqueous phase of much more dilute fog droplets do not require any inorganics. There is a huge body of literature that shows that e.g. oxalic acid or related acids are formed by such processes (e.g., (Crahan et al., 2004; Sorooshian et al., 2006; Ervens et al., 2011)). Both oxalate and sulfate are formed in droplets and thus appear in the same mode (droplet mode) but there is no chemical interaction required.

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4) Given the fact that the authors conclude that SOA formation in fog might have been rather negligible and that individual compounds have not been identified anyway, the review-like text in the introduction of detailed processes can likely be condensed. In fact it seems that the authors have heavily used the review article by Ervens et al., 2011, ACP, for this text. Thus, it can be significantly shortened with the appropriate reference.

5) Unfortunately you do not show any concentrations of VOCs for the duration of the measurements. Could differences in aerosol composition (partially) ascribed to different emissions?

6) The source apportionment seems to have been associated with large uncertainties (e.g., K+). In addition, the four identified factors are mostly characterized by species rather than by specific sources. Some discussion is needed in order to link these species to sources.

## Specific comments

p. 14485, l. 6/7: reword this sentence.

p. 14485, l. 17: how does sulfate get attached to BC?

p. 14485, l. 25: that is very vague: how can scavenging be identified by measuring the listed constituents?

p. 14487, l. 20: There are several studies that show that SOA in the aqueous phase might be composed of photochemically produced compounds without any heteroatoms, e.g., (De Haan et al., 2009; Lim et al., 2010)

p. 14488, l. 3-5: Most of these references do not refer to ambient studies as implied by the text.

p. 14488, l. 6: how does SOA formation in the aqueous phase change number concentration? (here and at other places throughout the manuscript)

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- p. 14488, l. 7: do you mean surface and volume distributions?
- p. 14489, l. 1: There are numerous studies that have explored the absorptive properties of SOA, e.g., (Shapiro et al., 2009; Trainic et al., 2011; Nguyen et al., 2012)
- p. 14492, l. 17: O<sub>3</sub> is barely soluble. Has the study by Herrmann et al (or others) indeed shown that the aqueous phase can be an efficient sink for O<sub>3</sub>?
- p. 14493, l. 17: Can you give a rough estimate (<1%, <10%, 50% ...?) of how much uncertainty was introduced by these additional factors?
- p. 14493, l. 28: Does the fact that all species were categorized as ‘weak’ mean that they concentrations were roughly on the same order of magnitude,. Some explanation might be useful here for readers who are not familiar with PMF.
- p. 14494, l. 8ff: If the aerosol is dominated by biomass burning – shouldn’t PMF simply show one factor? Why were these period excluded? How certain is your source apportionment considering these large uncertainties in K<sub>+</sub>?
- p. 14494, l. 21: what does the refractory factor tell you about possible sources?
- p. 14495, l. 6: can you speculate on what this large identified fraction might have included?
- p. 14495, l. 10-13: This sentence combines two completely different facts (‘ionic species affect visibility and ‘organic mass formation in the aqueous phase’)
- p. 14495, l. 26: NH<sub>4</sub><sup>+</sup> is not oxidized – it simply dissolves. NH<sub>3</sub> is usually taken up by droplets in order to neutralize the present excess of anions.
- p. 14496, l. 1: do you mean that sulfate and ammonium can be directly emitted from specific sources?
- p. 14496, l. 7: what does the ‘higher water solubility’ refer to? (higher than what?) Did Pratt et al. identify the same factor as you did in your study? Do you have any measure-

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ments of hygroscopicity (e.g., growth factors or hygroscopicity based on AMS-derived composition) that would support your conclusions on the higher solubility of biomass burning aerosol as compared to the other factors? How much does the hygroscopicity differ between the factors? Is it significant and sufficient to cause any effects on water condensation and fog properties (e.g. droplet number)?

p. 14496, l. 14: There are many studies that show this drop size dependence and discuss size-dependent sulfate formation rates. Some of the references should be added here, e.g., (Collett et al., 1994; Rao and Collett, 1998)

p. 14497, l. 22: What do you mean by secondary production of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{NH}_4^{+}$ ? These are primary species that are not formed in the atmosphere.

p. 14497, l. 22ff: Figure 5 shows that these species rather increase during fog. I suggest highlighting and discussing this fact rather than implying that these species were removed by the fog and thus decrease upon dissipation (or is this what you mean?)

p. 14498, l. 27ff: are you implying that it is actually not the fog but different emissions that causes differences in aerosol composition?

p. 14499, l. 6ff: I don't understand this section. Sulfate and nitrate are both nearly completely scavenged, i.e. the  $\text{H}_2\text{SO}_4$  concentration is negligible in the gas phase whereas there might be small concentrations of  $\text{HNO}_3$  indeed present. The hygroscopicity of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  is comparable.

p. 14499, l. 24: This header should be reworded according to my general comment 3).

p. 14499, l. 3 (and Table S6a): How does an single value give information about processing? It would be more meaningful to compare values at the beginning and at the end of a fog event.

p. 14500, l. 17: An increase of SOA (OC) in smaller droplets might point to formation processes that occur in a concentrated aqueous phase as often referred to as 'aerosol water' (Lim et al., 2010). Do the aqueous phase concentrations (organic mass/water

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volume) support such speculation?

p. 14500/14501: The mass accommodation coefficient is not dependent on drop size (unless there is some organic coating that is more enriched on smaller droplet which would lead to a decrease of this coefficient). However, the phase transfer rate is inversely proportional to drop size

p. 14501, l. 14: Your previous study (Kaul et al., 2011) reported on clear SOA formation in fogs in the same region and time. What is different in your current study that you conclude that SOA formation in fogs was negligible?

p. 14502, l. 16: Are you implying that new particles form during fog events? This cannot happen in fog droplets since each droplet already includes one (or more upon scavenging) particle and additional mass is imply added. Is there any evidence from lab and/or field studies that enhanced RH – such as during fog events - facilitates new particle formation?

p. 14502, l. 16: Separate clearly here which effects are due to changing boundary layer and which ones can be ascribed to particle growth. Some guidance could be possibly given by {Eck, 2012 #2985}.

p. 14503, l. 3: what is meant by 'leave aqueous oxidized organic compounds behind that form new particles'? New particle formation is usually referred to as the process of forming small clusters of gas molecules (e.g. H<sub>2</sub>SO<sub>4</sub> or possibly organics). These particles have sizes of a few nanometers. – Is this indeed the process you refer to?

p. 14503, l. 23: Could the fact that you see poor correlation of particles < 40 nm with photooxidation be explained by the fact that particles grow to larger sizes and thus are those that indeed show a better correlation?

Figure captions: There seem to be random numbers in all figure captions (e.g. 4, 5 in Figure 1).

Figure 1: It might be helpful to add the total masses to the pie charts.

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Figure S2-5: What does the % refer to? I tried to add up the contributions from the single compounds from the four factors or adding up the contributions of all species within each factor and none of them seems to make sense (> 100%).

Table S7: What was the contribution of the three drop size classes to the total drop populations? Could there be some statistical issue that biases the correlations?

Figure S9 and S10: I assume that unit on the axes should be nm. Could you show an additional figure that shows the evolution of the size distribution over a foggy period (i.e. two curves: initial and processed size distribution)?

Technical comments

p. 14490, l. 11: 'surface' instead of 'diameter' or 'diameter of 2.11 cm'?

p. 14491, l. 29: Fig. 1?

p. 14503: semi-VOC should be 'semivolatile VOCs'

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