

We thank the reviewers for careful reading and helpful comments that improve the quality of the manuscript. Reviewer comments have been copied followed by our responses in bold.

Anonymous Referee #2)

This manuscript presents some valuable data and a number of interesting ideas. However, due to some technical issues and an overall lack of cohesion of the different parts of the paper, I don't believe it is publishable in the current form.

The authors made ambient observations of atmospheric chemistry/air quality during a haze episode in South Korea in 2014, which is representative of a situation where poor air quality in Seoul is due to a combination of air pollution coming from China + local emissions and chemical processing.

Measurements were made at a remote site upstream of Seoul, and in Seoul.

R2C1) It is not clear to me what the relationship between the ambient measurement data presented in this manuscript and the data from Seo et al. ACP (2017) from the same group is - the data presented here seem to be a subset of that study. This is very important and should be made more clear in the manuscript.

Response)

Yes, we use the same ambient data from the previous work by Seo et al. 2017. The previous work focused on the synoptic meteorological conditions for the haze episode at Seoul in 2014 occurred by the combination of PM transport from China and local emissions. And this work focuses on chemical and physical processes (atmospheric chemistry) that lead to particle formation under the synoptic meteorological conditions during the haze episode.

We add the following in Line 27 on Page 2:

“... air quality. The previous work (Seo et al., 2017) focused on the synoptic meteorological conditions for the haze episode at Seoul in 2014 occurred by the combination of PM transport from China and local emissions. And this work focuses on chemical and physical processes (atmospheric chemistry) that lead to particle formation under the synoptic meteorological conditions during the haze episode. We hypothesize ...”

R2C2) Although this was not discussed in the manuscript, the calculated aerosol pH at Deokjeok Island presented in Figure 5 (pH 8.9 and pH 9) is very concerning. According to the SI, aerosol pH was calculated using E-AIM. Typical aerosol pH is generally between 0 and 5, so, based on the literature and my experience with aerosol thermodynamic models, I believe there was probably an error in the calculation. The authors need to discuss and defend this result if they believe it is correct. Aqueous chemistry calculations are very sensitive to aerosol pH, and if there was an error in the calculation of aerosol pH it's likely that there was also an error in aerosol liquid water calculations - another critical parameter for this study. The authors should compare their results to results from ISORROPIA, AIOMFAC, or another model, and refer to the current literature regarding pH of Asian haze aerosol (e.g. Chi et al, J. Met. Res. 32 (1) 14-25 2018; Guo et al., Sci. Rep, 7 (1) 12109 (2017)).

Response)

Those high pH values were estimated by E-AIM with the “Batch” mode, in which the amount of OH can be entered directly since the systems are OH⁻ deficit. Through the personal communication with an E-AIM developer (Dr. Simon Clegg), E-AIM is not intended for alkaline systems (it is intended for acidic systems); nonetheless the batch mode still allows OH⁻ deficit systems to estimate pH. To validate pH values from E-AIM, we also ran with ISORROPIA-II with both forward and reverse modes (and metastable option). These ISORROPIA-II simulation results are shown with E -AIM results in Table S3. Based on ion balance, either the forward mode or reverse mode is chosen in this work (i.e., the forward mode for H⁺ deficit systems (pH 2-3 in Table S3) and the reverse mode for OH⁻ deficit systems (pH 7.5 in Table S3)). The chosen mode is then compared with E -AIM results (shown in bold in Table S3). E -AIM

simulated pH is either more acidic or more basic than ISORROPIA-II pH by ± 1.5 . Therefore, with this difference we expect that aqueous chemistry is not too different. *E*-AIM simulated ALW is higher than ISORROPIA-II. However, the values of ALW due to inorganic compounds (W_i), which are shown in parenthesis, from both simulations are very close (within $\sim 9\%$ uncertainty). Note that $ALW = W_i + W_o$, where W_o is organic contribution (Guo et al., 2015). The difference of ALW between *E*-AIM simulations and ISORROPIA-II simulations is mainly due to W_o . In *E*-AIM, organic is assumed to be glyoxal. In ISORROPIA-II, W_o is calculated based on (5) in Guo et al., 2015 and κ_{org} is estimated based on O/C of organics (Fig. 3 in Jimenez et al., 2009). In Fig. 11, we now add simulated pH and mass concentrations from ISORROPIA-II, and in Fig. S7 we show simulation results from ISORROPIA-II. We would like to note that both simulations for pH are not too different (within ± 1.5), and simulations for W_i are very close. Please see our response to R1C2, regarding the uptake of NH_3 and HNO_3 simulations of Deokjeok Island haze particles at Seoul conditions to describe multiphase chemical aging at Seoul using ISORROPIA-II (Fig. S8).

We add the following at the end of Text S1 in Supplementary Material:

“Concentrations of organic/inorganic constituents, ALW, and pH of haze particles in the atmosphere are also estimated by using ISORROPIA-II with the metastable option. Both the forward mode and the reverse mode were performed. Based on ion balance, either the forward mode or reverse mode is chosen in this work (i.e., the forward mode for H^+ deficit systems (pH 2-3 in Table S3) and the reverse mode for OH^- deficit systems (pH 7.5 in Table S3)). The chosen mode is then compared with *E*-AIM results (shown in bold in Table S3). *E*-AIM simulated pH is either more acidic or more basic than ISORROPIA-II pH by ± 1.5 . Therefore, with this difference we expect that aqueous chemistry is not too different. *E*-AIM simulated ALW is higher than ISORROPIA-II. However, the values of ALW due to inorganic compounds (W_i), which are shown in parenthesis, from both simulations are very close (within $\sim 9\%$ uncertainty). Note that $ALW = W_i + W_o$, where W_o is organic contribution (Guo et al., 2015). The difference of ALW between *E*-AIM simulations and ISORROPIA-II simulations is mainly due to W_o . In *E*-AIM, organic is assumed to be glyoxal. In ISORROPIA-II, W_o is calculated based on (5) in Guo et al., 2015 and κ_{org} is estimated based on O/C of organics (Fig. 3 in Jimenez et al., 2009).”

We modify the sentence (Line 22, Page 5):

“... using aerosol thermodynamic models (Wexler and Clegg, 2002; Fountoukis and Nenes, 2007).”

We modify the sentence (Line 23, Page 5):

“Estimated ALW fraction of particles using *E*-AIM (Fig. 5) and ISORROPIA-II (Fig. S7) is substantial. Note that two methods of estimating ALW fraction and pH of particles by using *E*-AIM and ISORROPIA-II are described in Supplementary Material S1 and listed in Table S3.”

We modify the sentence (Line 16, Page 9):

“... with the haze PM measurement in Seoul using both *E*-AIM and ISORROPIA-II.”

We add the following at the end of the caption for Figure 5:

“... estimated. Note that SO_4^{2-} is total sulfates. Values in the parenthesis are simulated results by using ISORROPIA-II. For more ISORROPIA-II results, see Fig. S7 and S8 and Table S3.

R2C3) Based on the ambient observations, the authors hypothesize that the particles coming in to Seoul from upwind are hygroscopic and undergo multiphase chemical processing. This is an interesting hypothesis but the basis for this hypothesis is not well-articulated, and it is not apparent to me when looking at Figures 4 and 5.

Response)

In Figure 4, high O/C ratios for Seoul/Deokjeok haze particles (A and B) are mainly driven by dicarboxylic acids, which are considered evidence of aqueous chemistry (Line 16-17, Page 6). Furthermore, Seoul/Deokjeok haze particles are inorganic rich; therefore, they are hygroscopic (Figure 5) (Line 21-22, Page 5). At high RH in Seoul the ALW component is the most dominant (Figure 5). So aqueous chemistry together with gas-phase chemistry (therefore, multiphase chemistry) is expected to play an important role in particle formation/aging at Seoul. To validate the hypothesis and to understand the chemical insights of this multiphase chemistry smog chamber experiments were then performed.

We add the following at the end of Section 3.1:

“The high O/C and the dominant fraction of dicarboxylic acids in OM are evidence of aqueous chemistry. Hygroscopic inorganic-rich particles at high RH form ALW, which provides a medium for aqueous chemistry. So aqueous chemistry together with gas-phase chemistry of NO_x (therefore, multiphase chemistry) is expected to play an important role in particle formation/aging at Seoul. To validate the hypothesis and to understand the chemical insights of this multiphase chemistry smog chamber experiments were then performed (next section).”

R2C4) They then performed some ambitious chamber studies of photochemistry of aqueous aerosols containing glyoxal, H₂O₂, and other inorganic components. The connection between the ambient data and these chamber studies is really not clear. How are the experimental conditions connected to the ambient observations? Why use glyoxal? Why H₂O₂ and not, say, O₃, which may be participating in some chemistry based on Figure 3? What happens to aerosol containing these species when they are dried in a diffusion drier then rehumidified, and are these representative of the local aerosol? The lab study raises more questions than it answers, and I think it should be analyzed more carefully and presented as its own manuscript rather than being framed as having direct relevance to the field data.

Response)

Again, smog chamber studies were performed to validate the hypothesis and to understand the chemical insights of multiphase chemistry responsible for the haze episode at Seoul in 2014. Concentrations of NO_x, wet particle mass, and RH are relevant to the haze episode. Glyoxal has been extensively used as organic surrogates/precursors for aqueous chemistry due to high solubility, a photochemical product of isoprene and toluene (the most dominant biogenic and anthropogenic volatile organic compounds), capability of representing both radical and non-radical chemistry in the aqueous phase (Lim et al., 2010; Ervens et al., 2011). And at Mexico City glyoxal is a main precursor of aqueous chemistry leading to SOA (Volkamer et al., 2007). Since we would like to run photochemistry in the aqueous phase we use H₂O₂ as the source of OH radicals. The concentration of H₂O₂ in the aqueous phase is atmospherically relevant (2 ppb of H₂O₂ in the gas phase). With the glyoxal concentration atmospherically relevant concentrations of OH radicals are generated from photolysis of H₂O₂ (Line 10-13, Page 4). O₃ participates in NO_x chemistry, not in aqueous phase chemistry. O₃ is formed from NO_x. The low concentration of O₃ at Seoul and the high concentration at Deokjeok Island represent that Seoul is NO_x saturated (or VOC limited). The diffusion dryer is used to remove excess water that can be formed from the atomizer. It is expected that water amount is formed based on thermodynamics (hygroscopicity of particles and RH) when particles are introduced in the chamber and rehumidified. Mass concentrations (~ 100 μg/m³) and the dominance of inorganics in particles are relevant to local aerosols at Seoul. Initially, nitrates in chamber particles are lacking. So, from that we clearly observe the uptake of HNO₃ and hygroscopic growth under photochemical NO_x conditions. We believe the chamber experiments are well controlled, relevant to the haze episode at Seoul and certainly provide the chemical insights of multiphase of particle formation/aging, particularly the formation of nitrates in particles and the hygroscopic growth.

We add the following at the end of the paragraph (Line 22, Page 4):

“Concentrations of O₃ and NO_x in a chamber ([NO_x] = 3-83 ppb, [O₃] = 0-34 ppb) are relevant to haze conditions in Seoul. And mass concentrations (~ 100 μg/m³) and the dominance of inorganics in particles are relevant to local aerosols at Seoul.”

We modify the line 1 on page 3:

“... sulfuric acids. Note that glyoxal has been extensively used as organic surrogates/precursors for aqueous chemistry due to high solubility, a photochemical product of isoprene and toluene (the most dominant biogenic and anthropogenic volatile organic compounds), capability of representing both radical and non-radical chemistry in the aqueous phase (Lim et al., 2010; Ervens et al., 2011), and at Mexico City glyoxal is a main precursor of aqueous chemistry leading to SOA (Volkamer et al., 2007). Finally, we validate ...”

We add the following in the line 9 on page 4:

“... at 359 nm). In order to run photochemistry in the aqueous phase, we use H₂O₂ as the source of OH radicals. The concentration of H₂O₂ in the aqueous phase is atmospherically relevant (2 ppb of H₂O₂ in the gas phase). With the glyoxal concentration atmospherically relevant concentrations of OH radicals are generated from photolysis of H₂O₂. During the irradiation, ...”

We add the following in the line 20 on page 5:

“... in a local scale. It should be noted that O₃ participates in NO_x chemistry, not in aqueous phase chemistry. O₃ is formed from NO_x. The low concentration of O₃ at Seoul and the high concentration at Deokjeok Island (Fig. 3D) represent that Seoul is NO_x saturated (or VOC limited). High fractions of NO₃⁻, ...”

We modify the line 7 on page 4:

“ ... residence time of ~ 5 s to remove excess water that can be formed from the atomizer. It is expected that water amount is formed based on thermodynamics (hygroscopicity of particles and RH) when particles are introduced in the chamber and rehumidified. Then, ...”

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