**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Effect of the exclusion of crustal ions (Ca^{2+}, Mg^{2+}, and K$^+$) in estimating water content of PM$_{2.5}$ at polluted and clean areas" by Hyung-Min Lee and Yong Pyo Kim

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Thank you for the review. In this reply, we have discussed major issues and detailed item-by-item response will be given later with the revised manuscript.

1. English problem:

The manuscript has been checked by a native English speaker before submission. Still, following the reviewer's suggestion, we will have the manuscript checked again.

2. No water content measurement data for validation of the modeling result:

A major goal of this research is to estimate the new chemical equilibrium state be-

tween the gas and particle phase including aerosol water content if crustal species are removed in the system. To accomplish the research goal, we have collected and compiled various measurement data sets. However, there are few data sets that satisfy our requirements; (1) a sizable fraction of particles being crustal species, (2) long-term data (at least one year) to see seasonal variation, (3) both gas and particle phase data to run an gas/particle equilibrium model, and (4) data from multiple locations (at least two), preferably from polluted and clean sites, to understand the general characteristics of the region. Thus, the data set we could use was limited.

There have been a few researches to develop and apply aerosol water content measurement instruments. Still, it is hard to measure aerosol water content and chemical composition simultaneously (McMurry, 2000), especially, for PM2.5. For example, a Tandem Differential Mobility Analyzer (TDMA) has been used to measure aerosol water content both in the field and laboratory measurements (Chan and Chan, 2005). However, TDMA measurement has been limited to sub-micron size particles. Since a major fraction of crustal species are in super-micron size particles, these data are not useful. In addition, these data are rather short-term measurements.

3. Limited usefulness of the used measurement data:

With all due respect to the reviewer, we do not agree with the reviewer. First of all, what kind of the data and/or modeling methodology should be used in a study is dependent on the question we ask. Evidently, the data sets we used have limitations. In addition, the model we used has limitations as clearly stated in the manuscript. Still, we think the data and modeling tool are suitable for our research goal. Furthermore, if all the points the reviewer has raised be satisfied for a modeling study, we think no modeling work can be carried out. The point is that the suitability of the used data and methodology is determined by what kind of question you ask.

3.1. Validation of the data, at least for Seoul: The measurement data well represent the seasonal variations of chemical composition from two sites and those characteristics

has been dealt with in another paper published earlier (Lee and Kim, 2010) including validation of the data with the modeling result. For the sake of highlighting the effect of crustal species' influence in estimating water content of the particle, we decided not to mention about various factors other than inclusion of crustal species. As long as the actual data exist, we believe that it is better to use actual data than arbitrarily chosen values because actual data can represent at least the time and location of the measurement, whereas the latter has none of such representatives.

3.2. On the limitations of the filter samples and the SCAPE model including the assumption of internally mixed particles: The reviewer is correct that we have treated the particles as internally mixed. As mentioned earlier, we could not obtain size-segregated measurement data which is a long-term data set with a sizable fraction of crustal species. Thus, we have only one particle size (PM2.5) data sets. With those data sets, the assumption of the internally mixed particles is more reasonable than artificially dividing the data into several externally mixed particles. The question is whether the internally mixed particles assumption is valid for the estimation of water content.

In Kim and Moon (1996), a similar approach was used to simulate the aerosol composition with and without crustal species for PM2.5, PM10, and TSP for Seoul and Gosan. They found that the effect of crustal elements on the chemical composition was large for TSP but the effect was small for PM2.5 at Gosan. But the effect was not large at Seoul for all three size particles. Thus, as suggested by the reviewer, ammonium and sulfate might not be with crustal species in TSP, it is likely that these be with crustal species in PM2.5.

3.3. On the problem of no carbonate measurement: We have not analyzed carbonate in the particle phase as point out by the reviewer. In addition to carbonate, we have not analyzed organic ionic species which might constitute a sizable fraction of ionic species in spring and summer at Gosan (Park et al., 2004). To make up lack of carbonate measurement data, constant ambient CO_2 mixing ratio was used. It means we only treated dissolved carbonate. Thus, there might be errors in the simulation. However, since

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we are dealing with water soluble ionic species, the lack of carbonate concentration in the particle phase might not significantly affect the simulation result, especially, in PM2.5. In other words, in a chemically equilibrium system, we assume that the carbonate concentration in the particle phase is in equilibrium with carbon dioxide in the air.

Lack of the organic ionic species data might affect the result significantly. According to Park et al. (2004), the concentrations of carbonate and organic ionic species at Gosan were less than 30% of the total anionic concentrations. Thus, we have applied a quality assurance/quality control (QA/QC) criterion of the ratio of the sum of the cation concentrations to the sum of the anionic concentration be less than 30%. Still, there might be errors for the simulation due to it.

3.4. Problems with a 24-h sampling interval: This is similar argument which the reviewer pointed out in (2), that is about the model capability of estimating size segregation. As clearly stated in the manuscript, a 24-h time resolution data has its limitations. However, there are few measurement data with less time resolution that satisfies our data selection criteria stated earlier. In addition, we believe, as a first step toward this research direction, the result shown in the manuscript is a valuable one with reasonable accuracy.

We will more clearly state the limitations of this modeling work in the revised manuscript.

4. Clear presentation in Figure 1: As stated in the part describing Figure 1, the fraction is based on equivalent concentration. Equivalent is the amount of a substance that reacts with or supplies one mole of hydrogen ions (H+) in an acid–base reaction; or reacts with or supplies one mole of electrons in a redox reaction. Therefore, Figure 1 can be understood as the 'effective' molar ratio that can react 1:1 with each other.

5. Charge balance in the historical data samples: Since we consider this study being not a measurement study but a modeling study using the published data, we have

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not given details on the data. All data used here are checked by our QA/QC criteria. One of them is the charge balance stated earlier. In addition, the modeling result was compared with the measurements (Lee and Kim, 2010). We will give more detailed explanation on the data in the revised manuscript.

6. The authors have not explained how they remove the crustal ions in the model and maintain charge balance: This point is the key of this study. When you remove crustal species from the measurement data, a new chemical equilibrium will be established including satisfying the charge balance. In other words, a charge balance is a necessary condition of a system being in equilibrium. We will state more explicitly on the conditions for the chemical equilibrium.

7. Table 3 – why is KNO3 the only salt that has a (s) subscript?: Because it is always in the solid phase whereas other compounds can exist as both solid and liquid. The authors agree that we should have mentioned about it.

8. It is confusing that the authors choose different symbols for the data in Figures 2 and 3: Sorry about it. We will match them.

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