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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

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Abstract

Effect of the exclusion of crustal ions (Ca^{2+}, Mg^{2+}, and K^{+}) in estimating water content of $PM_{2.5}$ is investigated using a gas/aerosol equilibrium model, SCAPE 2 (Simulating Composition of Atmospheric Particles at Equilibrium 2), (Kim et al., 1993; Kim and Seinfeld, 1995; Meng et al., 1998), for the particles collected at polluted city, Seoul, and clean background offshore, Gosan, Korea. Measurement data show higher concentration of all inorganic species at Seoul, up to 5 times higher in average equivalent concentration especially for volatile species. At both sites there were sufficient equivalent fractions of t-NH_3 (total ammonia = $NH_3 + NH_4^+$ to neutralize acidic species such as t-H_2SO_4 (total sulfuric acid = $H_2SO_4 + SO_4^{2-}$), t-HNO_3 (total nitric acid = $HNO_3 + NO_3^-$) and t-HCl (total hydrochloric acid = $HCl + Cl^-$). t-NH_3 and t-HNO_3 were higher at Seoul while t-H_2SO_4 was higher at Gosan. With respect to the estimated water content differences between with and without crustal ions, all the samples are classified into 3 cases; increased, decreased, and constant water content. We identified that change in inorganic composition contributes to increase of water content for aqueous aerosols. And those inorganic compositions vary differently according to ambient atmospheric composition. Meanwhile, aerosol phase shifting from the aqueous to solid phase is the main contributor to decrease of water content and binary salt composition change in the solid phase appears as no change of water content.

1 Introduction

Water content of aerosol affects mass concentration and size distribution of the ambient particles and, thus aerosol properties such as visibility reduction, radiative forcing, and human health (Haywood and Boucher, 2000; Malm and Day, 2001; Choi and Kim, 2010). Those effects are more significant in fine particles, i.e. $PM_{2.5}$ (particlulate matter with an aerodynamic diameter of less than or equal to a nominal 2.5 µm).

Water occupies significant portion of an aerosol in the higher ambient relative humidity (RH) than the aerosol's deliquescence relative humidity (DRH, relative humidity where the particle starts to absorb water). DRH is a good proxy of aerosol's hygroscopic property and mainly determined by temperature and inorganic composition of the binary slats as they comprise 25–50 % of dry total fine aerosol mass (Heintzenberg, 1989). In general, multicomponent aerosols have lower DRH than respective binary salts comprising the aerosol (Wexler and Seinfeld, 1991).

Inorganic salts found are mainly consisting of sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), and ammonium (NH_4^+). Especially in Northeast Asia, crustal species; calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+) originating from open dry fields, unpaved roads, and biomass burning (Lee et al., 2001) indicate relatively high levels in fine particles in addition to the aforementioned inorganic ions. Also, mineral dusts from arid region such as the Gobi dessert are transported by frontal system (Maxwell-Meier et al., 2004) and aerosol composition might be compromised during the transport due to the interaction with anthropogenic air pollutants (Kim et al., 2009).

Water content of an aerosol and the inorganic composition are hard to measure simultaneously (McMurry, 2000). Although there have been several studies of hygroscopicity measurement utilizing the Tandem Differential Mobility Analyzer (TDMA), they were limited to the submicron size particles (Chan and Chan, 2005). One way to overcome this difficulty is applying computational methods solving thermodynamic equilibrium equations of given inorganic species concentration.

Hygroscopic capacity of aerosols can differ when crustal species are included because of both that inclusion of crustal species affects availabilities of gaseous species forming an aerosol and a number of mineral aerosols are more water-soluble than non-mineral inorganic aerosols (Kim and Seinfeld, 1995; Fountoukis and Nenes, 2007). Notwithstanding the importance of crustal species, only a few models among those estimating the water content of the aerosols consider crustal ions (Zhang et al., 2000).

Kim and Seinfeld (1995) pointed out the importance of crustal ions inclusion in the aerosol thermodynamics model in the way to develop SCAPE. They figured out that crustal ions concentration transported by yellow sand phenomenon might be significant especially in the East Asia atmosphere, and investigated their roles in aerosol chemistry. Jacobson (1999) has examined the effects of Ca^{2+} and Mg^{2+} on size-distributed NO_3^- and NH_4^+ using EQUISOLV II. Fountoukis and Nenes (2007) suggested that the absence of crustal species would introduce small under-prediction of water content in the consideration of DRH points of those mixtures using ISORROPIA II.

It is expected that the dust emissions and the ambient concentration of crustal ions of the region be reduced as living standard in Northeast Asia soars. In addition, as suggested in the 4th Intergovernmental Panel on Climate Chage (IPCC, 2007), the future rainfall amount in Northeast Asia region both in winter and summer will be increased. Consequently there is a possibility that dust emissions during the Asian dust season be reduced. Therefore, it is necessary to understand what would be the aerosol composition and resultant aerosol properties for the future development if the concentrations of crustal species were reduced while the concentrations of anthropogenic species are the same. One of the interesting problems is the partitioning of volatile species such as nitric acid (HNO_3), ammonia (NH_3), and hydrochloric acid (HCl) when the crustal ions are removed in the particles. That might affect aerosol composition and water content, and, thus, various aerosol properties.

In this study, we have explored the effect of exclusion of crustal ions (Ca^{2+}, Mg^{2+}, and K^+) in estimating water content using a gas/aerosol equilibrium model, SCAPE 2, for Seoul and Gosan, Korea. We focused on understanding how $PM_{2.5}$ water contents responds to the removal of crustal ions.

2 Measurement data

Table 1 summarizes the data sets used in this study. For Seoul, two data sets from Kang (2003) and Kim and Kim (2007) are used. Kang (2003) and Kim and Kim (2007) applied a sampling system with a denuder and a 3-stage filter-pack to collect gaseous and particulate matters. Use of denuder would quantify the over estimation of aerosol concentration possibly occurred during aerosol collection on a filter-pack by capturing gaseous species prior to the filter-pack. The used data from Kang (2003) are 24 h average concentration and the number of data is 48, collected from April 2001 to February 2002. The data from Kim and Kim (2007) are 24 h average of two 12 h concentrations. The total number of the data is 37, collected from November 2004 to July 2005.

For Gosan, data from annual reports by the National Institute of Environmental Research (NIER) are used. A 3-stage filter-pack was applied. The number of 24 h average data is 118 collected between 1996 and 2007.

Use of denuder does not affect the measured total concentration, but only helps better quantification between gas and particle distribution. Since SCAPE 2, the model we use in this study, needs total concentration as an input, differences between the data sets from Seoul and Gosan originating from use of denuder can be ignored. The filter pack system without denuders at Gosan might be susceptible to the positive artifacts from SO_2. However, the ambient concentration of sulfur dioxide at Gosan is low enough, usually about or less than 1 ppb (Kim et al., 1998), to make the positive artifact or errors negligible.

Figure 1 shows the average fractions of the measured inorganic species in equivalent concentration at Seoul and Gosan, respectively. They show large differences in the fractions of Na^+, t-H_2SO_4, t-HNO_3, and t-NH_3. At the ambient air conditions, practically all t-H_2SO_4 exists in the particle phase (i.e. SO_4^{2-}) due to its low vapor pressure, thus we can assume that t-H_2SO_4 is equal to SO_4^{2-}. SO_4^{2-} is mainly formed by oxidation of sulfur dioxide, mostly emitted from fossil fuel combustion in the region and has longer retention time than t-HNO_3 in the atmosphere. Gosan is located in south of Korean peninsula, west of Japan, east of China, and northeast of Taiwan and has little air pollutant emission sources. Therefore, high SO_4^{2-} concentration observed at Gosan is considered as a result of long-range transport (Lee et al., 2001; Kim et al., 2003; Park et al., 2004). The fraction of t-NH_3 is high enough to neutralize existing acidic species for both sites. In the Northeast Asia, t-NH_3 concentration has been vigorously increasing along with the fast-growing agricultural, livestock-farming and industrial activities

(Kim et al., 2006). t-HNO_3 is produced from oxidation of nitrogen oxides, the largest emission source of which is vehicles (Lee and Kim, 2007). There are no significant differences of the crustal ions (Ca^{2+}, Mg^{2+} and K^+) fractions between two sites. Sea-salt species, Na^+ and Cl^- represent higher fractions at Gosan because of its geographical reason locating offshore. Relatively higher concentration of t-HCl to Na^+ at Seoul is due to gaseous HCl emitted from industrial processes. Among the measured inorganic species, t-NH_3, t-HNO_3, and SO_4^{2-} represent a significant fraction at both sites.

For Seoul, RH and T were measured at the nearest station to the aerosol collection site operated by Korea Meteorological Administration (KMA). For Gosan, RH and T were measured by KMA at the same site where the aerosols were collected.

3 Aerosol thermodynamics model, SCAPE 2

To estimate the gas/aerosol distribution, inorganic salts concentration in liquid and solid phase, and water content of aerosols, thermodynamics model SCAPE 2 is used. We refer the readers to Kim et al. (1993), Kim and Seinfeld (1995), and Meng et al. (1998) for the model details.

For a closed multiphase system in chemical equilibrium at constant temperature T and pressure, the total Gibbs free energy of the system should be at a minimum.

$$\sum v_{ij}\mu_i = 0 \tag{1}$$

Where v_{ij} is the stoichiometric coefficient of the ith species in the jth reaction, μ_i is the chemical potential of species i given in Eq. (2):

$$\mu_i = \mu_i^\circ(T) + RT\ln a_i \tag{2}$$

where $\mu_i^\circ(T)$ is the standard chemical potential for the ith species at temperature T in Kelvin, and a_i is the activity of the ith species given in Eq. (3):

$$a_i = \gamma_i m_i \tag{3}$$

where γ_i is its activity coefficient and m_i is the molality of species i. By substituting Eqs. (2) and (3) into (1), Eq. (4) is obtained:

$$\exp[-\frac{1}{RT}\sum \nu_{ij}\mu_i^\circ] = \prod a_i^{\nu ij} \equiv K_j \equiv \prod_i (\gamma_i m_i)^{\nu i} \quad (4)$$

where K_j is the equilibrium constant of the jth reaction (Denbigh, 1981). Therefore, estimating accurate activity coefficient is essential to obtain accurate equilibrium concentration of the species with the given equilibrium constants. In SCAPE 2, three methods are available and the Kusik and Meissner (K-M) method is selected for calculating activity coefficient in this study.

For water content, the Stokes, Robinson, and Zdanovskii (ZSR) method is used in SCAPE 2 because of simplicity.

$$W = \sum_i \frac{M_i}{m_{io}(a_\mathrm{w})} \quad (5)$$

where a_w is water activity, equal to the RH expressed as a fraction. And $m_{io}(a_\mathrm{w})$ is the molality of the binary solution at the desired water activity a_w of the multi-component solution. M_i is the molar concentration of species i in the air (mol m^{-3} air) and W is the mass concentration of water in the aerosol (kg water m^{-3} air). Input data for SCAPE 2 are total ammonia (t-NH_3 = gaseous NH_3 + particulate NH_4^+), t-HNO_3 (gaseous HNO_3 + particulate NO_3^-), t-HCl (gaseous HCl + particulate Cl^-), sulfate (SO_4^{2-}), carbonate (H_2CO_3), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), RH, and ambient temperature. We estimated DRH of aerosols by running the model for different RH conditions from 0 to 95 % with intervals of 5 %.

4 Results

4.1 Difference in the estimated water content between with and without crustal species

The estimated water contents of $PM_{2.5}$ show differences between with (w/) and without (w/o, when they are set to zero) crustal ions in the model. According to the level of differences, all samples are classified into 3 cases as shown in Table 2. Differences less than 1 % of the average water content of each site are regarded as no change or constant as those amounts of difference can arise from treatment of significant numbers in computation and measurement artifacts. The average water contents of the particles from Seoul are 15.54 $\mu g\,m^{-3}$ (w/) and 15.77 $\mu g\,m^{-3}$ (w/o). Thus the differences (w/o-w/) in the range of ±0.16 $\mu g\,m^{-3}$ are classified as case 2. For the samples from Gosan, the average water contents are 8.91 $\mu g\,m^{-3}$ (w/) and 8.87 $\mu g\,m^{-3}$ (w/o), thus the range of case 2 is in between ±0.09 $\mu g\,m^{-3}$. As indicated in Table 2, only a few samples are not affected by removal of crustal ions and most of samples show differences as a result of the crustal ions removal in the modeling. There are two probable reasons for the differences; (1) phase shift between the solid and aqueous phase and (2) hygroscopicity variation due to the change of inorganic composition remaining in the same phase.

4.2 Phase shift between solid/aqueous phase

If the estimated DRH is lower than the ambient RH, aerosols contain water at least partially and if the estimated DRH is higher than the ambient RH, aerosols are regarded as solid with no water. It has been figured out both theoretically (Wexler and Seinfeld, 1991) and experimentally (Tang and Munkelwitz, 1993) that DRH of a salt mixture is lower than the lowest DRH among each component. However there was no evidence if that property is applicable to aerosols containing crustal species because crustal compounds were not included in the past studies. As a result of crustal ions removal from this study, most of aerosol's DRH increased or remained constant showing that the aforementioned property is valid for crustal aerosols. Only 4 samples collected at Gosan out of total 203 samples show decreased DRH. The change of the DRH and solid salts composition with the removal of crustal ions for the typical samples of each site are shown in Table 3. As crustal ions are removed, the number of constituents is decreased and the DRH of an aerosol increases.

Behavior of case 2 and 3 can be generally explained by the phase shift. Phase shift from the aqueous to solid phase means water content decrease. The aerosol containing water with crustal ions may lose its water by crustal ions removal because of increased DRH at the same ambient RH. Among the samples in case 3, thirty out of thirty-two samples from Seoul and seventeen out of thirty-nine samples from Gosan are the case. If the phase is not changed from solid, the particle contains no water for both w/ and w/o. Among the samples in case 2, five from Seoul and four from Gosan are the case.

4.3 Hygroscopicity variation along with changing inorganic composition

At a given RH, for those of aqueous aerosols showing no phase shift, inorganic salts composition is crucial in determining the hygroscopicity of the particle. Since SO_4^{2-} preferentially combined with cations including crustal ions, removal of crustal ions results in the increase of available SO_4^{2-}. If there are sufficient cations such as t-NH_3 and Na^+ to neutralize increased SO_4^{2-}, then the concentrations of $(NH_4)_2SO_4$ and/or Na_2SO_4 will be increased while remaining NH_4NO_3 concentration being constant. If insufficient, SO_4^{2-} and t-HNO_3 are competing for cations and SO_4^{2-} compounds are preferred form (Ansari and Pandis, 1998). Therefore, NH_4NO_3 and $NaNO_3$ concentrations will be decreased.

On the other hand, it has been assumed that HNO_3 (g) uptake by crustal particles are as following (Jacobson, 1999; Dentener et al., 1996):

$$CaCO_3(s) + 2HNO_3(g) \rightleftharpoons Ca^{2} + + 2NO_3^- + CO_2(g) + H_2O(aq) \qquad \text{(R1)}$$

$$MgCO_3(s) + 2HNO_3(g) \rightleftharpoons Mg^2 + + 2No_3^- + CO_2(g) + H_2O(aq) \tag{R2}$$

$$K_2CO_3(s) + 2HNO_3(g) \rightleftharpoons 2K^+ + 2NO_3^- + CO_2(g) + H_2O(aq) \tag{R3}$$

Thus, if crustal ions are removed, NO_3^- that has been combined with crustal ions in the particle phase will be evaporated into the gas phase to maintain the charge balance in Reactions (R1–R3) NH_4NO_3 will be formed if the product of the mixing ratios of the HNO_3 (g) and NH_3 (g) is higher than its equilibrium constant (K_{eq}) at the given RH and T for the reaction of Reaction (R4), (Kim et al., 1993). Dissociated form of the reaction is,

$$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4^+ + NO_3^- \tag{R4}$$

Temperature dependent equilibrium coefficient, $K_{eq}(T)$ for the Eq. (6) is,

$$\frac{\{NH_4^+\}\{NO_3^-\}}{\{NH_3(g)\}\{HNO_3(g)\}} = \frac{m_{NH_4^+} m_{NO_3^-} \gamma_{NH_4^+,NO_3^-}{}^2}{\rho_{NH_3}(g)\rho_{HNO_3}(g)} = K_{eq}(T)(\text{mol}^2\,\text{kg}^{-2}\,\text{atm}^{-2}) \tag{6}$$

where $\{X\}$ is the thermodynamic activity of species X, m is the molality (mol kg^{-1}), ρ_x is the gas phase partial pressures (atm) of the species x, and $\gamma_{NH_4^+,NO_3^-}$ is the mean mixed activity coefficient of NH_4NO_3. The value of $\gamma_{NH_4^+,NO_3^-}$ becomes higher when crustal ions are included than removed. If crustal ions occupied considerable fractions, $m_{NH_4^+}$ and $m_{NO_3^-}$ need to be increased to offset the decrease of $\gamma_{NH_4^+,NO_3^-}$ when they are removed (Jacobson, 1999). In other words, HNO_3 (g) and NH_3 (g) need to be transformed into the particle phase from the gas phase (i.e. NO_3^- and NH_4^+).

Taken together, when crustal ions are removed, SO_4^{2-} and HNO_3 (g) are released to the system. Released SO_4^{2-} will form compounds with cations taking from nitrate or chloride compounds. If the system has sufficient NH_3 (g) then $(NH_4)_2SO_4$ will be formed. When system's NH_3 (g) is insufficient NH_4^+ will be taken from NH_4NO_3 or NH_4Cl and the form of sulfate salts can be acidic ones such as $(NH_4)_3H(SO_4)_2$ or NH_4HSO_4.

Therefore, at first, concentrations of nitrate and chloride compounds will be decreased and sulfate compounds will be increased. Then, remaining NH_3 (g) will combine with HNO_3 (g) or HCl (g) to form NH_4NO_3 or NH_4Cl if the concentration products exceed respective equilibrium constants. If the system's RH is high enough for the compounds to be dissolved at the moment the particle will contain water. Since each compound's water uptake capacity and the DRH are varying along with their inorganic composition, the water content of the particle is determined by inorganic composition. To sum up, there are two reasons in varying hygroscopicity; (1) changing total concentration of dissolved ions (2) their fractions.

For the samples of case 1 (increased water content), water content of the samples increases by different mechanisms for Seoul and Gosan. At Seoul, total concentration of dissolved ions is increased when crustal ions are removed. All samples have shown the change of the composition in the aqueous phase. As more gaseous species are condensed into the particle phase, the condensed ions absorb more water. Compare to Gosan, Seoul has about 1.5 times more t-H_2SO_4, 3.5 times more t-NH_3, and 5 times more t-HNO_3 in equivalent concentrations. And as shown in Fig. 1, Seoul has higher fraction of t-HNO_3 and lower fraction of t-H_2SO_4. Therefore not like at Gosan, NH_4NO_3 can attribute to absorb water at Seoul. At Gosan, sulfate and ammonia compounds mainly determine water content. Gosan has higher fractions of t-H_2SO_4 and crustal ions. Released SO_4^{2-} by crustal ions removal are abundant so that Na^+ and NH_4^+ are taken from nitrate compounds. If the system still has enough NH_3 (g) and HNO_3 (g) or HCl (g) it is likely to form NH_4NO_3 or NH_4Cl. Water content is increased when additional formation of these salts are available and is decreased when gaseous species concentrations are insufficient. Notable feature of the samples involving case 3 (decreased water content) is that total particulate concentration is significantly decreased (more than 10 % of its concentration before the crustal ion removal). Decrease of particulate formation means decrease of water absorption potential.

Figure 2 shows the particle compositions and their variation over RH for a typical sample of case 1. When the system contains crustal ions (w/), NH_4NO_3 is the most abundant component and crustal compounds also represent major proportions. When crustal ions are removed (w/o), the most relevant change is the increment of $(NH_4)_2SO_4$ while NH_4NO_3 concentration is also increased. Even though this graph is in molar concentration if we think of it in equivalent concentration, the amount of $(NH_4)_2SO_4$ is comparable to NH_4NO_3. We can see that the water content is increasing along with dissociation of nitrate and sulfate compounds, but not significantly affected by crustal compounds. Therefore it can be inferred that the increment of $(NH_4)_2SO_4$ and NH_4NO_3 with the crustal ions removal is mainly contributing to the increased water content since the water contents of these two salts are higher than corresponding crustal salts.

Figure 3 shows the variation of particle composition over RH for sample of Gosan collected at 23 June 1999, which is a typical example of case 3. Even though Na_2SO_4 concentration is increased, the total concentration is lowered notably. With the crustal ions (w/), there are several compounds in considerable concentrations. Upon the crustal ions removal (w/o), as the number of constituent compounds are decreasing, the proportion of Na_2SO_4 gets higher contributing to less water content of the particle.

Withstanding the fact that the aerosol water content is determined largely by relative humidity and that the relative humidity varies dramatically over the course of 24 h, it is hard to be seen that the result from this study represents the bulk composition at any one time during the day. Although it is a limitation of a time integrated sampling system, our result is valid for the purpose of predicting future trend change.

5 Summary

Independently collected $PM_{2.5}$ at Seoul and Gosan show different characteristics in RH and inorganic species concentrations, the crucial factors in determining particle water content. As a result of crustal ions removal in the modeling, water content of more than 85 % of total samples are increased or decreased. The differences are from; (1) phase shift between solid/aqueous phase and (2) variation of inorganic composition. About

15 % of samples show no change of estimated water content with the removal of crustal ions due to negligible amount of crustal ions and/or too low RH to reach DRH of the particle. Clearly, when an aerosol containing water has changed its phase from liquid to solid because of increased DRH by removal of crustal ions, the water content is decreased.

For an aerosol containing water in both w/ and w/o, water uptake behavior is different between at Seoul and Gosan. Major inorganic species found at both sites are t-NH_3, t-HNO_3, and t-H_2SO_4, and t-NH_3 is sufficient to neutralize t-HNO_3 and t-H_2SO_4. Differences between two sites are; (1) Seoul has higher concentrations of all inorganic species and higher fraction of t-HNO_3 and (2) Gosan has higher fraction of t-H_2SO_4 and has higher RH than Seoul about 12 % in average.

At Seoul, increased sulfate, nitrate, and ammonium compounds as a result of the crustal ions removal are contributing to water content increment. Meanwhile at Gosan, sulfate compounds mainly determine water content variation. Water contents are increased when released SO_4^{2-} combined with t-NH_3 forming ammonium sulfates. However, when released SO_4^{2-} forms Na_2SO_4 by breaking relatively hygroscopic $NaNO_3$ and NaCl (Seinfeld and Pandis, 2006), water contents are decreased because it is hard to form additional particulate through the reactions between gaseous species with its low mixing ratio at Gosan. Moreover in this case, the DRH of the particle is increased due to reduction in variety of binary slats comprising the aerosols. It makes water uptake capacity over RH slowed down so that many compounds remain in solid phase at the same RH.

To sum up, removal of crustal ions affect not only in water content but also inorganic salts composition. Moreover the effects are different from site to site according to the atmospheric level of chemical species. With expected reduction of crustal ions in the Northeast Asia, it is likely that ambient particles might have more water for a major portion of cases and, thus, $PM_{2.5}$ mass concentration increases. Based on the fact that atmospheric ammonia is in excess in the region, major contributor to such water content increment is anthropogenic nitrate at Seoul and transported sulfate at Gosan.

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Table 1. Summary of data used as the input of SCAPE 2.

	Seoul	Gosan
Period	2001.04–2002.02 2004.11–2005.07	1996.03–2007.01
Site (No. of Data)	Konkuk University (48) KIST[1] (37)	Gosan super site (118)
Reference	Kang (2003) Kim and Kim (2007)	NIER[2] (2007)
Particle Size	$PM_{2.5}$	$PM_{2.5}$
Method	Denuder + Filter-pack	Filter-pack
Analyzed Species	Gas (NH_3, HNO_3, HCl) Particle(Mass, Na^+, SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, K^+, Ca^{2+}, Mg^{2+})	Gas (NH_3, HNO_3, HCl Particle (Mass, Na^+,SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, K^+, Ca^{2+}, Mg^{2+})
Meteorological Data	Jongno-gu (KMA[3])	Gosan (KMA[3])

[1] KIST: Korea Institute of Science and Technology

[2] NIER: National Institute of Environmental Research

[3] KMA: Korea Meteorological Administration

Table 2. Case classification for the samples with respect to water content variation (w/-w/o crustal ions.

	Case	Seoul	Gosan
1	Water content increases when removing crustal ions	43 (50 %)	60 (51 %)
2	No change	10 (12 %)	19 (16 %)
3	Water content decreases when removing crustal ions	32 (38 %)	39 (33 %)
	Total	85 (100 %)	118(100 %)

Table 3. Changing DRH and solid compositions due to crustal ions removal for the typical samples.

Site	Sample No.	*T* (K)	Crustal ions	DRH	Case	Composition						
Seoul	4	289.4	w/	0.40	3	$(NH_4)_2SO_4$	Na_2SO_4	NH_4Cl	NH_4NO_3	K_2SO_4	$CaSO_4$	$MgSO_4$
			w/o	0.55		$(NH_4)_2SO_4$	Na_2SO_4	NH_4Cl	NH_4NO_3			
	71	268.4	w/	0.40	3	$(NH_4)_2SO_4$	Na_2SO_4	NH_4Cl	NH_4NO_3	K_2SO_4	$CaSO_4$	$MgSO_4$
			w/o	0.60		NH_2SO_4	Na_2SO_4	NH_4NO_3				
Gosan	42	283.6	w/	0.40	3	NH_2SO_4	NaCl	$NaNO_3$	KNO_3 (s)	$CaSO_4$	$MgSO_4$	
			w/o	0.65		NH_2SO_4	$NaNO_3$					
	108	279.7	w/	0.45	2	$(NH_4)_2SO_4$	NH_2SO_4	K_2SO_4	$CaSO_4$	$MgSO_4$		
			w/o	0.60		$(NH_4)_2SO_4$	NH_2SO_4					

w/: crustal ions are included in the modeling
w/o: crustal ions are set as zero in the modeling

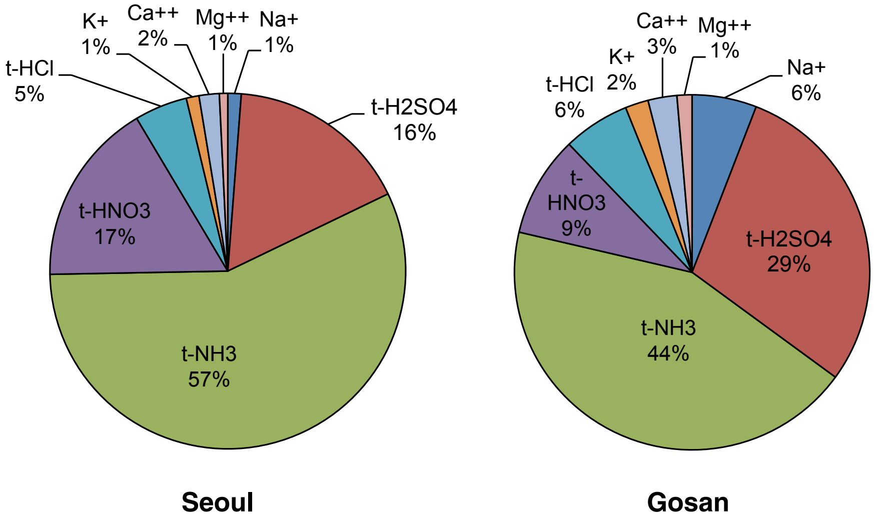

Fig. 1. The average equivalent concentration fractions of all measured data at Seoul and Gosan, respectively (Lee and Kim, 2011).

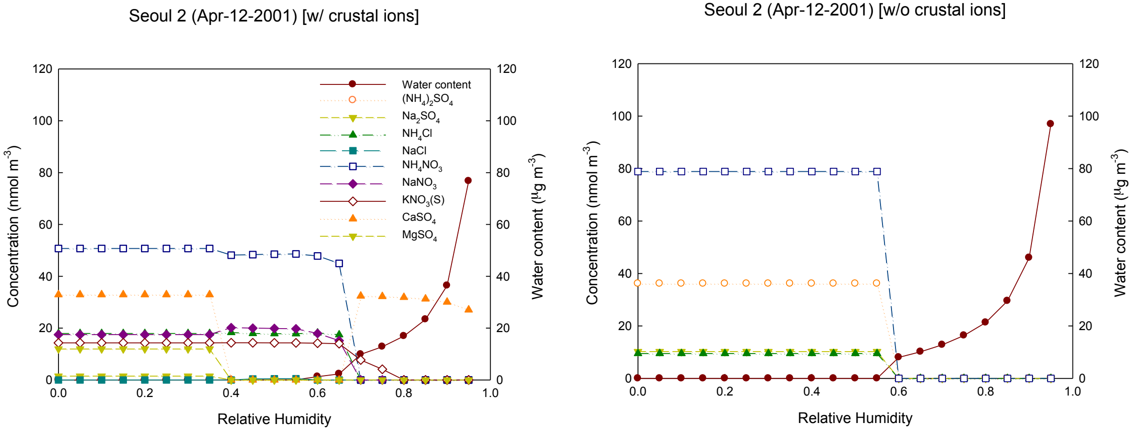

Fig. 2. Estimated particle composition over relative humidity for a typical sample of case 1 for the with (left) and without (right) crustol ions.

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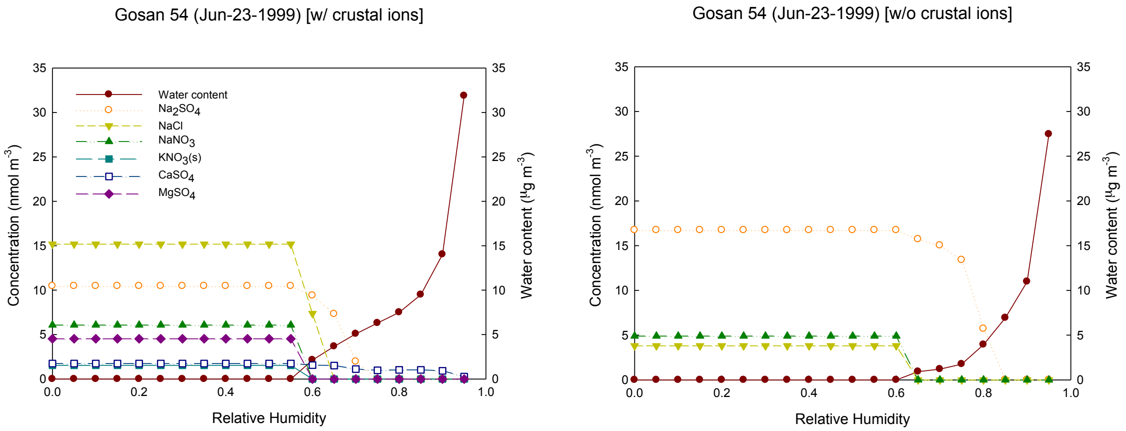

Fig. 3. Estimated particle composition over relative humidity for a typical sample of case 3 for the with (left) and without (right) crustal ions at Gosan.

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