

### *Response to Referee 2's comments*

*The authors thank the reviewer (Anonymous Referee #2) for their helpful comments and suggestions which will help improving the original paper. Please find our itemized responses to comments in bold italic text below.*

#### General Comments:

The analysis essentially applies the calculations found in the chapter on aerosol thermodynamics from Seinfeld and Pandis (1998) to the dataset from Beijing, China. The result of this analysis (p17144-17145) is that the ammonium nitrate aerosol cannot be treated as a pure solid. The analysis and discussion hints at the concepts of deliquescence and crystallization but only dances around the edges. Though not necessary, I think the authors could do a better job of synthesizing these concepts with their observations. Ammonium sulfate, for example, at room temperature deliquesces around 79% RH but once it deliquesces it remains in the aqueous phase until it reaches its crystallization relative humidity, around 33%, due to hysteresis (i.e., Cizco et al, JGR 1997). Ammonium nitrate, on the other hand, once reaching the deliquescence RH (DRH), does not seem to have a crystallization RH (Pauline et al., J. Aero. Sci., 1998).

#### *Response:*

*We will follow your suggestions introducing the following concepts in the discussion paper (p17143, line 25 - p17144, line 5):*

*“Several laboratory and field studies have given attention to the relative humidity (RH) at which solid particles liquefy (deliquescence point), and the RH at which liquid particles form solids (crystallization point), because the phase (wet or dry) of the atmospheric aerosol particles can affect both their optical and radiative properties and gas-aerosol reactions (Dougle et al., 1998, Tang et al. 1995). Cizco et al (1997) carried out laboratory and field experiments on ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and ammonium bisulphate (NH<sub>4</sub>HSO<sub>4</sub>) aimed to determine the phase of the particles as the relative humidity (RH) with which they are in equilibrium is changed. Their results showed that (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at room temperature uptakes water (deliquesces) at a relative humidity (RH) of 79 ± 1% that there is no kinetic inhibition to the uptake of water by dry (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles on the timescales of a few seconds and longer. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol particles remain liquid phase, forming a "metastable" liquid state (supersaturated state), until a very low RH (33 ± 2%, crystallization point) is reached, at which point a highly concentrated liquid aerosol particle nucleates to form a solid. NH<sub>4</sub>HSO<sub>4</sub> particles deliquesce at a 39 % RH, but solid*

*NH<sub>4</sub>HSO<sub>4</sub> particles are difficult to form (Cizco et al., 1997). Pure ammonium nitrate deliquesces at 62% RH (298 K), but laboratory experiments show that they don't reach crystallization point also at 8 % RH (Dougle et a., 1998). The deliquescence relative humidity (RHD) for pure NH<sub>4</sub>NO<sub>3</sub> varies with air temperature and can be modified by particle size and composition under real ambient conditions (Seinfeld and Pandis, 1998). If the ambient RH is less than the RHD, then the equilibrium state of NH<sub>4</sub>NO<sub>3</sub> is modeled as a solid. At relative humidity above that of deliquescence, NH<sub>4</sub>NO<sub>3</sub> is modeled in the aqueous state. During the winter the ambient RH was always lower than RHD (Fig. 3), thus, NH<sub>4</sub>NO<sub>3</sub> will exist in equilibrium with the solid phase. Instead, during the summer the ambient RH was not always lower than RHD (Fig. 4), thus, NH<sub>4</sub>NO<sub>3</sub> will be also in equilibrium with the aqueous phase and deliquescent particles. The explanation could be that NH<sub>4</sub>NO<sub>3</sub> in the atmosphere exists as a mixture of other components such as ammonium sulphate/bisulphate, elemental carbon (soot), organic carbon, crustal material. Impurities can initiate crystallization in bulk salts, inducing crystallization at a higher RH than the crystallization point of the pure salt aerosols. Douglas et al. (1998) found that soot is highly unlikely to promote crystallization in ambient aerosols, and suggested that the crystallization in the ambient aerosols might have been induced by the more abundant organic carbon.”*

*Then, we will follow with the same text in the manuscript from p17144, line 5.*

*In addition we will add that following paper to the reference:*

*Cizco D. J., Nowak J. B., Hu J. H. and Abbatt J. P. D.: Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: observation of deliquescence and crystallization, J. Geophys. Res. 102, D15, 18843-18850, 1997.*

*Dougle P. G., Veefkind J. P. and Ten Brink H. M.: Crystallisation of mixtures of ammonium nitrate, ammonium sulphate and soot, J. Aerosol Sci. 29, 3, 375-386, 1998.*

*Kim Y. P. and Seinfeld J. H.: Atmospheric gas-aerosol equilibrium I. Thermodynamic model, Aerosol Sci. Technol. 19, 2, 157-181, 1993.*

*Tang I. N., Fung K. H., Irnre D. G., and H. R. Munkelwitz: Phase transformation and metastability of hygroscopic microparticles, J. Aerosol Sci. 23, 3, 443-453, 1995*

*Wexler A. S. and Seinfeld J. H.: Second generation inorganic aerosol model, Atmos. Environ. 25A, 12, 2731-2748, 1991.*

So, it is not just the measured RH that is important but the RH and temperature history of the air parcel along with the aerosol composition. Under these conditions a thermodynamic models such as AIM or ISORROPIA might be more appropriate than unconnected discrete equations. Furthermore, these models are used in regional air quality models and comparing these observations with those model results would be of value to in evaluating regional air quality models, in general, and of Beijing, in specific. I hope the authors with consider this in the future.

**Response:**

*Thank you for your suggestion, which will be certainly considered for our future papers. Equilibrium models of atmospheric aerosols are, certainly, an essential tool in simulating the evolution of both gaseous and aerosol species and in predictive modeling of atmospheric aerosols. Several mathematical gas-aerosol equilibrium models have been developed, varying degrees of computational complexity and thermodynamic approaches, among them the AIM (Aerosol Inorganic Model), and ISORROPIA. Generally, the principal properties considered in these models to estimate gas-aerosol equilibrium are: the equilibrium constants or chemical potentials, the solute activity coefficients, the water activity and the relative humidity of deliquescence (RHD). The first three properties determine the component concentrations and the last one governs the maximum possible RH at which a solid species can exist. AIM and ISORROPIA models differ between them because of considering different methods to calculate the properties, which are listed above. In particular, ISORROPIA is suitable for incorporation into 3-D air quality models due to its computational efficiency, whereas AIM is a theoretically complete and accurate phase equilibrium model, but is very slow and not currently configured for incorporation into 3-D air quality models (Yu et al., 2005).*

There is a tendency in this paper to overuse undefined qualifiers. For example, how are the authors differentiating a good correlation from a strong correlation (i.e., p17145, line 15)? Is an  $r^2$  of 0.40 universally considered 'good' correlation? Also, p17145, line 15, is 40% high relative humidity? In the context of the deliquescence and crystallization of ammonium sulfate or ammonium nitrate aerosol it could be.

**Response:**

*Thank you for your comment, here is the reply given also to comments by referee #1.*

*Despite the fact that  $R^2$  is a unitless statistic, there is no absolute standard for what is a "good" value. Jacob Cohen (1988) has written the most on this topic. In his well-known book he suggested the Cohen scale, for example, in which a correlation greater than 0.5 is large/strong (0.50-1.00), 0.3 is weak/moderate (0.30-0.49) and 0.1 is small, right on the cusp of "medium/modest" (0.30-0.49). However these cutoff criteria are largely arbitrary and shouldn't be applied too strictly. The real answer is that the  $R^2$  is only an indicator of the completeness of the regression model. Only the p-value of the coefficients should be used to determine the goodness or significance of a regression. If the p-value is less than 5% then you should consider the regression to have found a significant relationship.*

*However, we will follow your suggestion using the Cohen scale only the word "significant" and not "good" for the Cohen scale with a  $R^2$  value  $< 0.5$ :*

*p17145, lines 14-15;*

*p17147, line 25.*

Specific Comments:

The writing is very spotty with numerous examples of misuse and over usage of words such as, indeed, besides, thus, however, instead.

*Response:*

*As also replied to comments by referee #1, we will follow your suggestions deleting the words "Indeed" and "Besides" in all paper.*

*We will delete the word "Indeed" in the following sentences:*

*p17139, line 26;*

*p17140, lines 16 and 27;*

*p17142, lines 20 and 25;*

*p17145, lines 12 and 14;*

*p17147, lines 22 and 24;*

*p17148, line 27;*

*p17149, lines 7 and 15;*

*p17151, line 22;*

*p17152, lines 17 and 21;*

*p17153, lines 21 and 26.*

*We will delete the word “Besides” in the following sentences:*

*p17131, line 9;*

*p17151, line 5.*

*We will delete the word “Thus” in the following sentences:*

*p17140, line 1;*

*p17141, line 2;*

*p17146, line 24;*

*p17150, line 3.*

*We will delete the word “However” in the following sentences:*

*p17128, line 16;*

*p17131, line 21;*

*p17137, line 25;*

*p17138, line 8.*

*We will delete the word “Instead” in the following sentences:*

*p17128, line 13;*

*p17144, line 3;*

*p17148, line 13.*

*We will replace the word “Instead” with “However” in the sentence P17147, line 8.*

- p17129, line 16 add an “s” on the end of “source”.

**Response:**

*As also replied to comments by referee #1, we will add an “s” to the word “source” (p17129, line 16).*

- p17129, line 18 - “in the gas phase”

**Response:**

*As also replied to comments by referee #1, we will add the word “phase” after the word “gas” (p17129, line 18).*

- p17129, line 23 - typically not “tipically”

**Response:**

*As also replied to comments by referee #1, we will replace the word “tipically” with the word “typically” (p17129, line 23).*

- p17130, line 6 - “gases, such as...”

**Response:**

*As also replied to comments by referee #1, we will add the word “such” after “gases” (p17130, line 6) and, thus, we will change the sentence “Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) are formed via reversible phase equilibrium with precursor gases as  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ” with the sentence “Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) are formed via reversible phase equilibrium with precursor gases such as  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ”.*

- p17130, line 23 - reference to HNO<sub>3</sub> formation

**Response:**

*We will add new references about HNO<sub>3</sub> formation such as:*

*Calvert, J. G. and Stockwell, W. R.: Acid generation in the troposphere by gas-phase chemistry. Environ. Sci. Technol. 17, 428–443, 1983.*

*Lin Y. C., Cheng M. T.: Evaluation of formation rates of NO<sub>2</sub> to gaseous and particulate nitrate in the urban atmosphere, Atmos. Environ. 41, 1903–1910, 2007.*

- p17130, line 24 - remove “may”

**Response:**

*We will remove the word “may” before “combines” (p17130, line 24).*

- p17131, line 5 - reference to HCl sources/budget

**Response:**

*We will add new references about HCl sources and emission such as:*

*Andreae M. O., Atlas E., , Harris G. W., Helas G., de Kock A., Koppmann R., Maenhaut W., Manø S., Pollock W. H., Rudolph J., Scharffe D., Schebeske G., Welling M.: Methyl halide emissions from savanna fires in southern Africa, J. Geophys. Res. 101, 23,603-23,613, 1996.*

*Graedel T.E., and Keene W. C.: The tropospheric budget of reactive chlorine, Global Biogeochem. Cycles 9, 47-78, 1995.*

*Keene W.C., Khalil M. A. K., Erickson D. J., McCulloch A., Graedel T. E., Lobert J. M., Aucott M. L., Gong S.-L., Harpe D. B., Kleiman G., Midgley P., Moore R. A., Seuzaret C., Sturges W. T., Benkovitz C. M., Koropalov V., Barrie L. A., Li Y.-F.: Composite global emissions of reactive chlorine from anthropogenic and natural sources: The reactive chlorine emissions inventory, J. Geophys. Res. 104, 8429-8440, 1999.*

- p17131, line 8 - “volcanoes” not vulcanoes

**Response:**

*As also replied to comments by referee #1, we will change the word “vulcanoes” with the word “volcanoes” (P17131, line 8).*

- Table and Figure labels should specify whether the 2hr or 24hr data is being shown.

**Response:**

*We will follow your suggestion, thus we will change:*

*- the label of Table 1 “Statistics of concentrations ( $\mu\text{g m}^{-3}$ ) of some gas species and ions in  $\text{PM}_{2.5}$ , during the winter and the summer periods at Beijing.” with the label “Statistics of concentrations ( $\mu\text{g m}^{-3}$ ) of some gas species and ions in  $\text{PM}_{2.5}$ , measured on a 24-h basis, during the winter and the summer periods at Beijing.” (P17166);*

*- the label of figure 1 “Temporal trends of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$ , and temperature (T) during the winter and summer measurements at Beijing.” with the label “Temporal trends of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$ , and temperature (T) during the winter and summer measurements, carried out on a 24-h basis, at Beijing.” (P17168);*

*- the label of figure 2 “Relationship between molar concentrations of fine particulate ammonium ( $\text{NH}_4^+$ ) and the sum of the molar concentrations of fine particulate sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and chloride (Cl) on the Teflon filters during the winter and summer measurements at Beijing.” with the label “Relationship between molar concentrations of fine particulate ammonium ( $\text{NH}_4^+$ ) and the sum of the molar concentrations of fine particulate sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and chloride (Cl) on the Teflon filters during the winter and summer measurements, carried out on a 24-h basis, at Beijing.” (P17169);*

*- the label of figure 3 “Temporal trends of temperature (T), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium ( $\text{NH}_4^+$ ), sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and chloride (Cl) during the winter measurements at Beijing.”*



*with the label “Temporal trends of temperature (T), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium (NH<sub>4</sub><sup>+</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and chloride (Cl) during the winter measurements, carried out on a 24-h basis, at Beijing.” (P17170);*

*- the label of figure 4 “Temporal trends of temperature (T), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium (NH<sub>4</sub><sup>+</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and chloride (Cl) during the summer measurements at Beijing.” with the label “Temporal trends of temperature (T), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium (NH<sub>4</sub><sup>+</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and chloride (Cl) during the summer measurements, carried out on a 24-h basis, at Beijing.” (P17171);*

*- the label of figure 5 “Thermodynamically predicted equilibrium dissociation constant K<sub>n</sub> (black solid line) for pure NH<sub>4</sub>NO<sub>3</sub> and measured concentration product K<sub>mn</sub> = [HNO<sub>3</sub>][NH<sub>3</sub>] as a function of temperature for winter (right side) and summer (left side) seasons at Beijing.” with the label “Thermodynamically predicted equilibrium dissociation constant K<sub>n</sub> (black solid line) for pure NH<sub>4</sub>NO<sub>3</sub> and measured concentration product K<sub>mn</sub> = [HNO<sub>3</sub>][NH<sub>3</sub>] as a function of temperature for winter (right side) and summer (left side) seasons at Beijing. The K<sub>n</sub> and K<sub>mn</sub> constants have been determined by data collected on a 24-h basis.” (P17172);*

*- the label of figure 6 “Thermodynamically predicted equilibrium dissociation constant K<sub>n</sub> (black solid line) for pure NH<sub>4</sub>NO<sub>3</sub>, K<sub>n</sub><sup>\*</sup> (grey solid line) for NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> mixtures, and measured concentration product K<sub>mn</sub> = [HNO<sub>3</sub>][NH<sub>3</sub>] as a function of temperature for summer period at Beijing.” with the label “Thermodynamically predicted equilibrium dissociation constant K<sub>n</sub> (black solid line) for pure NH<sub>4</sub>NO<sub>3</sub>, K<sub>n</sub><sup>\*</sup> (grey solid line) for NH<sub>4</sub><sup>+</sup>/NO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> mixtures, and measured concentration product K<sub>mn</sub> = [HNO<sub>3</sub>][NH<sub>3</sub>] as a function of temperature for summer period at Beijing. The K<sub>n</sub>, K<sub>n</sub><sup>\*</sup> and K<sub>mn</sub> constants have been determined by data collected on a 24-h basis.” (P17173);*

*- the label of figure 7 “Thermodynamically predicted equilibrium dissociation constant K<sub>c</sub> (black solid line) for pure NH<sub>4</sub>Cl and measured concentration product K<sub>mc</sub> = [HCl][NH<sub>3</sub>] as a function of temperature for winter (right side) and summer (left side) seasons at Beijing.” with the label “Thermodynamically predicted equilibrium dissociation constant K<sub>c</sub> (black solid line) for pure NH<sub>4</sub>Cl and measured concentration product K<sub>mc</sub> = [HCl][NH<sub>3</sub>] as a function of temperature for*

winter (right side) and summer (left side) seasons at Beijing. The  $K_c$  and  $K_{mc}$  constants have been determined by data collected on a 24-h basis.” (P17174);

- the label of figure 8 “Diurnal trends of fine particulate  $Cl$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$ , and gaseous  $HNO_3$ ,  $HCl$  and  $NH_3$ , and temperature ( $T$ ), relative humidity ( $RH$ ), wind speed and direction during the intensive winter measurements at Beijing.” with the label “Diurnal trends of fine particulate  $Cl$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$ , and gaseous  $HNO_3$ ,  $HCl$  and  $NH_3$ , and temperature ( $T$ ), relative humidity ( $RH$ ), wind speed and direction during the intensive winter measurements, carried out on a 24-h basis, at Beijing.” (P17175);

- the label of figure 9 “Diurnal trends of fine particulate  $Cl$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$ , and gaseous  $HNO_3$ ,  $HCl$  and  $NH_3$ , and temperature ( $T$ ), relative humidity ( $RH$ ), wind speed and direction, and natural radioactivity (Stability) during the intensive summer measurements at Beijing.” with the label “Diurnal trends of fine particulate  $Cl$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and  $NH_4^+$ , and gaseous  $HNO_3$ ,  $HCl$  and  $NH_3$ , and temperature ( $T$ ), relative humidity ( $RH$ ), wind speed and direction, and natural radioactivity (Stability) during the intensive summer measurements, carried out on a 24-h basis, at Beijing.” (P17176);

- Figures 5, 6, and 7 – Range (error) bars should be added to the measured concentration products.

**Response:**

We will follow your suggestion adding range (error) bars to the measured concentration products in the figures 5, 6 and 7 (see below).

The uncertainty (error bars) have been calculated as percentage relative error, by error propagation theory (Taylor, 1982). The relative error associated to the measured concentration product  $K_{mn} = [HNO_3]/[NH_3]$  was determined by the following equation 1 (eq. 1)

$$\left( \frac{\sigma_{K_{mn}}}{K_{mn}} \right) = \left( \sqrt{\left( \frac{\sigma_{HNO_3}}{[HNO_3]} \right)^2 + \left( \frac{\sigma_{NH_3}}{[NH_3]} \right)^2} \right) \quad (\text{eq. 1})$$

Where  $\sigma_{HNO_3}$  is the uncertainty associated to nitric acid ( $HNO_3$ ) concentration, which is 8.6 % of the measured  $HNO_3$  concentration (Perrino et al., 2001);  $[HNO_3]$  is the measured  $HNO_3$  concentration (as ppb);  $\sigma_{NH_3}$  is the uncertainty associated to ammonia ( $NH_3$ ) concentration,

which is 6.1% of the measured  $NH_3$  concentration (Perrino et al., 2001)) and  $[NH_3]$  è is the measured  $NH_3$  concentration (as ppb). We have calculated that the percentage relative error associated to  $K_{mn}$  is 10.54 %.

The relative error associated to the measured concentration product  $K_{mc} = [HCl][NH_3]$  was determined by the following equation 2 (eq. 2)

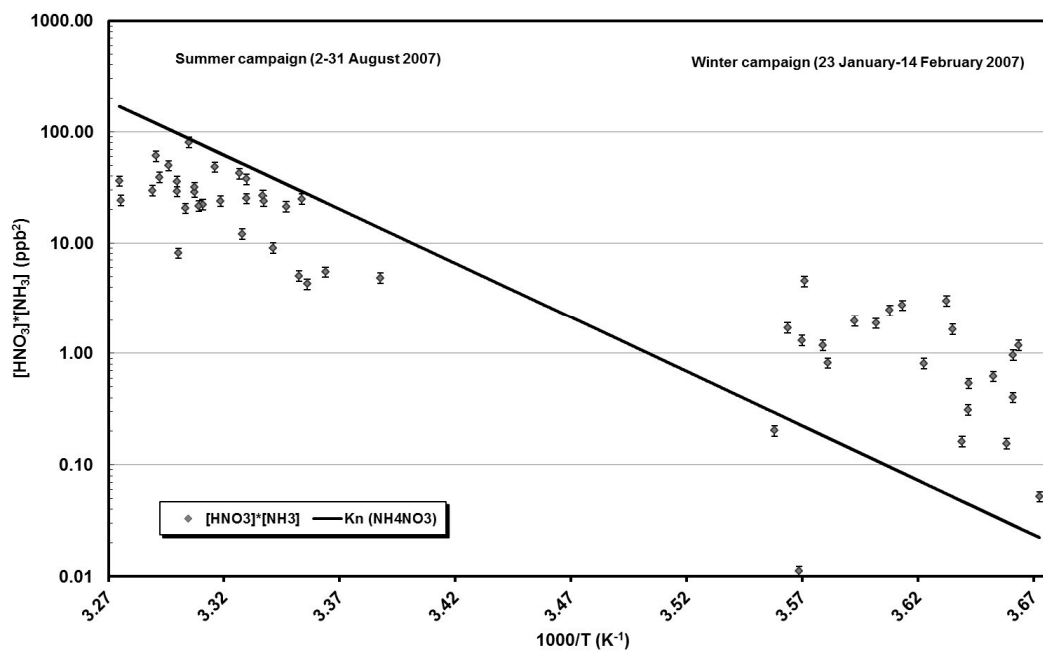
$$\left( \frac{\sigma_{K_{mc}}}{K_{mc}} \right) = \left( \sqrt{\left( \frac{\sigma_{HCl}}{[HCl]} \right)^2 + \left( \frac{\sigma_{NH_3}}{[NH_3]} \right)^2} \right) \quad (\text{eq. 2})$$

Where  $\sigma_{HCl}$  is the uncertainty associated to hydrochloric acid (HCl) concentration, which is 6.7 % of the measured HCl concentration (Perrino et al., 2001) and  $[HCl]$  is the measured HCl concentration (as ppb). We have calculated that the percentage relative error associated to  $K_{mc}$  is 8.91 %.

#### Reference:

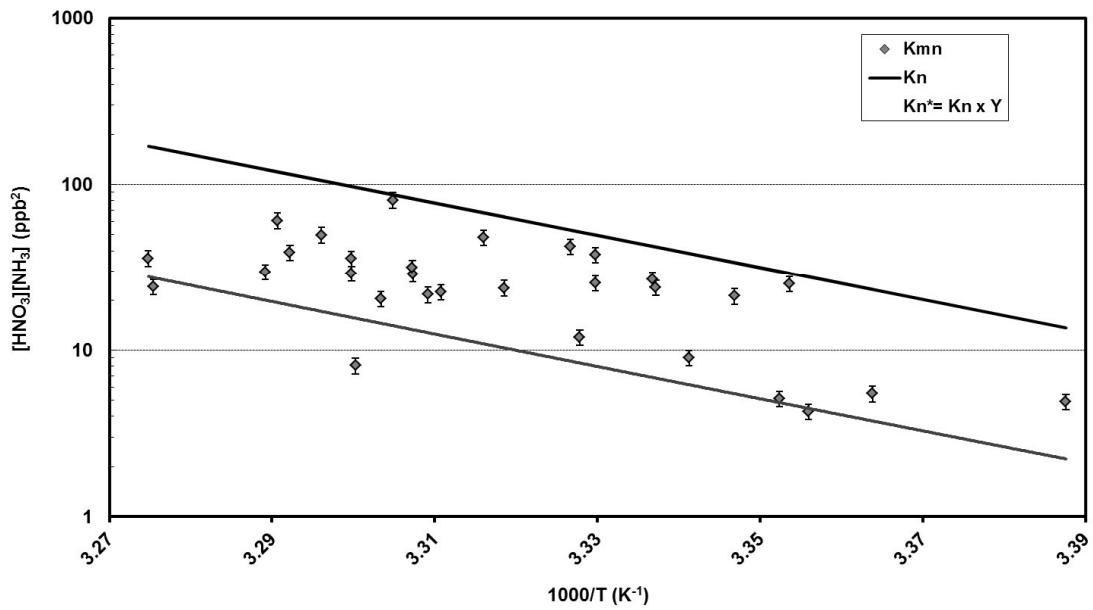
Perrino C., Ramirez D., Allegrini I.: Monitoring acidic air pollutants near Rome by means of diffusion lines: development of a specific quality control procedure, *Atmos. Environ.*, 35, 331-341, 2001.

Taylor J. R.: *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*. University Science Books, 1982.

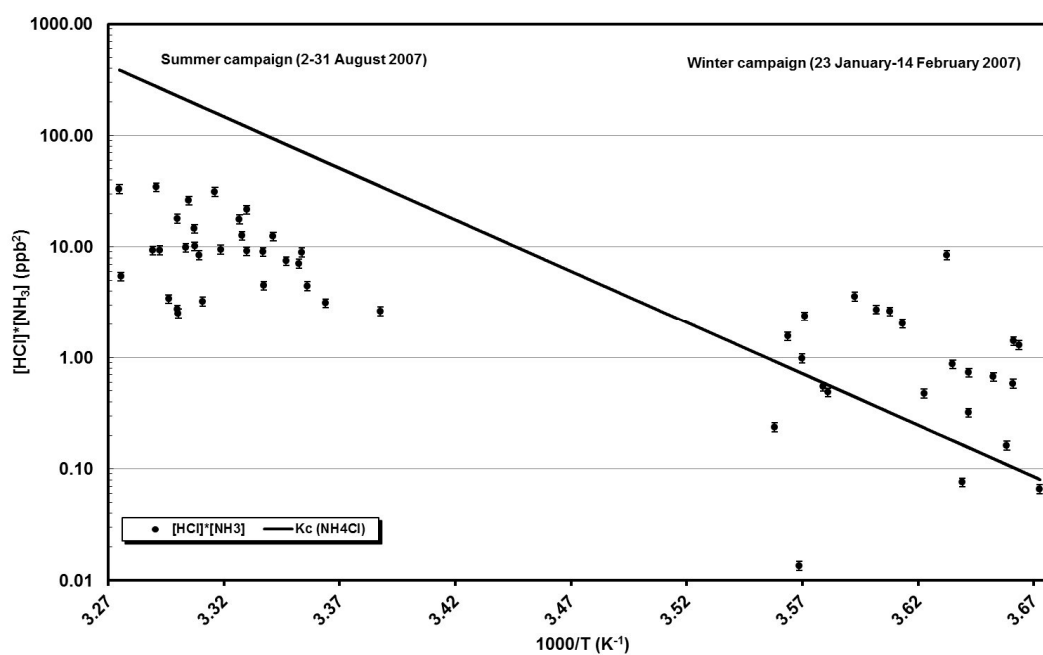


*Fig. 5. Thermodynamically predicted equilibrium dissociation constant  $K_n$  (black solid line) for pure  $NH_4NO_3$  and measured concentration product  $K_{mn} = [HNO_3][NH_3]$  as a function of temperature for winter (right side) and summer (left side) seasons at Beijing. The  $K_n$  and  $K_{mn}$  constants have been determined by data collected on a 24-h basis.*

Summer measurements (2-31 August 2007, PKU, BEIJING)



**Fig. 6.** Thermodynamically predicted equilibrium dissociation constant  $K_n$  (black solid line) for pure  $\text{NH}_4\text{NO}_3$ ,  $K_n^*$  (grey solid line) for  $\text{NH}_4^+/\text{NO}_3^-/\text{SO}_4^{2-}$  mixtures, and measured concentration product  $K_{mn} = [\text{HNO}_3][\text{NH}_3]$  as a function of temperature for summer period at Beijing. The  $K_n$ ,  $K_n^*$  and  $K_{mn}$  constants have been determined by data collected on a 24-h basis.



*Fig. 7. Thermodynamically predicted equilibrium dissociation constant  $K_c$  (black solid line) for pure  $\text{NH}_4\text{Cl}$  and measured concentration product  $K_{mc} = [\text{HCl}][\text{NH}_3]$  as a function of temperature for winter (right side) and summer (left side) seasons at Beijing. The  $K_c$  and  $K_{mc}$  constants have been determined by data collected on a 24-h basis.*