

The influence of ammonium nitrate equilibrium on the measurement of exchange fluxes of ammonia and nitric acid

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Abstract

Three sets of data with a time resolution of 40 minutes at Leende, Zegveld and Speuld in the Netherlands are used to evaluate atmospheric equilibrium of ammonia and nitric acid with ammonium nitrate. The comparison between the measured concentration products K_m and theoretical values K_e reveals that gaseous ammonia and nitric acid are not in simultaneous equilibrium with ammonium nitrate aerosol, because the ratios of K_m to K_e are far from unity, varying from less than 0.01 to above 100. Kinetic constraints upon the attainment of equilibrium are emphasized strongly by the results obtained at the three sites. The disequilibrium phenomena can be used to explain why HNO_3 can show upward gradients and to obtain indications of the errors, using gradient methods in the measurement of deposition fluxes.

1. INTRODUCTION

In Europe, exchange of NH_3 and HNO_3 between atmosphere and biosphere is of increasing interests. However, it is very difficult to derive their representative dry deposition velocities, especially for HNO_3 , because of the chemical reactions involving HNO_3 , NH_3 and NH_4NO_3 aerosol. Sutton et al. [1] found consistent negative R_c for HNO_3 in Essex, England, while Huebert et al. [2] found a steeper aerosol nitrate gradient than that of its vapor and sometimes an apparent emission of HNO_3 in the USA. According to Kramm and Dlugi [3], if no equilibrium exists, the fluxes can not be calculated by micrometeorological methods without appropriate corrections. Therefore, it is necessary to test whether the chemical equilibrium among HNO_3 , NH_3 and NH_4NO_3 really occurs in the atmosphere.

The hypothesis of atmospheric equilibrium among gaseous HNO_3 , NH_3 and NH_4NO_3 aerosol was first proposed by Stelson et al. [4] in 1979, who tried to analyze field experimental data by application of the equilibrium relationship. Since then, extensive work has been done regarding thermodynamic theory and field experiments [5-17]. Field measurements in the United States, Japan and Europe showed that NH_4NO_3 aerosol was generally in equilibrium with its gaseous precursors [8-17], especially at temperatures above 5°C and a relative humidity less than 80%. Departure from equilibrium was mostly found under conditions of low temperature and high humidity [9,10,15,16], when the concentration product was depressed to values less than 1 ppbv^2 [18].

Meanwhile the validity of this thermodynamic approach was questioned for a long time [18-19]. The large uncertainty in the equilibrium constant under ambient conditions, as it is derived from laboratory experiments, complicates any assessment of its importance. Numerical simulations indicated that significant deviations from equilibrium, both positive and negative, might occur as the reactions are not sufficiently fast to maintain equilibrium under conditions of changes in meteorological, emission and chemical reaction parameters. However, after Jaffe's criticism [19], Mozukewich [7] argued that the available thermodynamic data on this system was much better than was implied by a factor of two range and that the dissociation constant may be determined within $\pm 12\%$ for dry aerosol.

In the Netherlands, equilibrium between HNO_3 , NH_3 and NH_4NO_3 aerosol is not extensively investigated yet. Erisman et al. [14] and Allen et al. [16] reported that the concentration products of the gaseous acids and base were generally in good agreement with theoretical prediction at temperatures higher than 0°C and relative humidity less than 80%. However, large deviations from theoretical values can be observed from the data of Erisman et al. [14] and Allen et al. [16]. Recently, various kinds of denuder techniques were developed to measure NH_3 and HNO_3 with high accuracy [20]. Many good data sets on simultaneously measured gaseous NH_3 and HNO_3 concentrations as well as meteorological data were obtained in recent years with a time resolution of 40 minutes by ECN. Three sites with different characteristics in location, emission and meteorology are chosen to test whether gaseous HNO_3 and NH_3 are in equilibrium with NH_4NO_3 aerosol in the Netherlands. The results obtained indicate complications in the measurement of dry deposition fluxes of NH_3 and HNO_3 .

2. EXPERIMENTAL

Ammonium nitrate NH_4NO_3 is present either in solid phase or as a solution, dependent upon temperature and relative humidity in atmosphere. NH_4NO_3 is assumed to be in reversible equilibrium with its gas precursors NH_3 and HNO_3 . The equilibrium constant of the reversible reaction is defined as the product of NH_3 and HNO_3 vapor pressure above NH_4NO_3 aerosol. For solid aerosol, temperature dependence of the dissociation constant K_p of ammonium nitrate is given as [7]:

$$\ln K_p = 118.87 - 24084/T - 6.025 \ln T \quad (1)$$

with T in K and K_p in ppbv^2 with an accuracy of $\pm 12\%$. When relative humidity is above the deliquescence point, NH_4NO_3 will exist as droplets. The equilibrium constant K_p' above the droplet is given as [7]:

$$K_p' = [P_1 - P_2 (1 - a_w) + P_3 (1 - a_w)^2] (1 + a_w)^{1.73} K_p \quad (2)$$

$$\ln P_1 = -135.94 + 8763/T + 19.12 \ln T \quad (3)$$

$$\ln P_2 = -122.65 + 9969/T + 16.22 \ln T \quad (4)$$

$$\ln P_3 = -182.61 + 13875/T + 24.46 \ln T \quad (5)$$

Where a_w is water activity and K_p is the equilibrium constant of solid NH_4NO_3 .

Simultaneous measurements of NH_3 and HNO_3 with a time resolution of 40 minutes were made at three sites in the Netherlands: Speuld (coniferous forest) for a whole year in 1989; Leende (heathland) between April 25 and May 10, 1991; and Zegveld (grass pasture) from July 13 to July 20, 1993. A detailed description of the experiments at the three sites is given elsewhere [20-22]. A brief introduction to the experiments is given below.

NH_3 and HNO_3 were measured at two heights at Leende and Zegveld and at one height in Speuld by wet denuders. Combining chemical and meteorological data, in total 240, 400 and 894 samples were obtained at Leende, Zegveld and Speuld respectively. NH_3 concentration showed a diurnal variation with a maximum at nighttime and a minimum in daytime and HNO_3 concentration showed a weak diurnal variation with slightly higher values in the late afternoon at the three sites, shown in figure 1. NH_3 fluxes were generally directed to the surface at Leende and Speuld, while NH_3 showed a bi-directional flux at Zegveld. For HNO_3 , its fluxes were observed to be directed away from the surface at Leende and Zegveld most of the time, as shown in figure 2. As it is believed that any surface is a perfect sink for

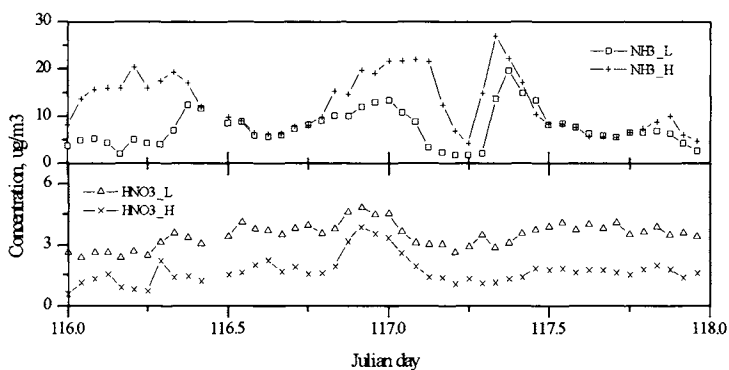


Figure 1. Concentration variations of NH_3 and HNO_3 on April 26-27, 1991 at Leende in the Netherlands (L= lowest level, H= highest level)

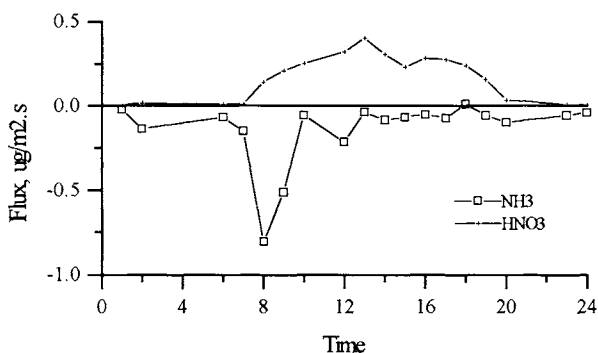


Figure 2. NH_3 and HNO_3 fluxes on April 26, 1991 at Leende in the Netherlands

HNO₃, the upward fluxes of HNO₃ are probably caused by the changes in the NH₃/HNO₃/NH₄NO₃ system.

3. RESULTS AND DISCUSSION

Figure 3 presents the measured concentration products $[\text{NH}_3][\text{HNO}_3]$ in Leende, together with theoretical curves calculated for equilibrium between aerosol and gaseous compounds, expressed as a function of temperature and relative humidity. The measured products in Leende show a tendency to exceed the equilibrium condition generally (figure 3). Below a relative humidity Rh of 60%, the measured products fit theoretical prediction for solid aerosol qualitatively with a slightly systematic positive bias (positive and negative bias are defined as measured products higher or lower than the equilibrium value), while they greatly exceed theoretical predictions for droplets. In contrast to Leende, the measured products for $[\text{NH}_3][\text{HNO}_3]$ in Zegveld are generally lower than theoretical prediction when Rh is below 60%. As Rh increases, the measured concentration products exceed the theoretical prediction increasingly. In Speuld, the measured concentration products can be higher or lower than

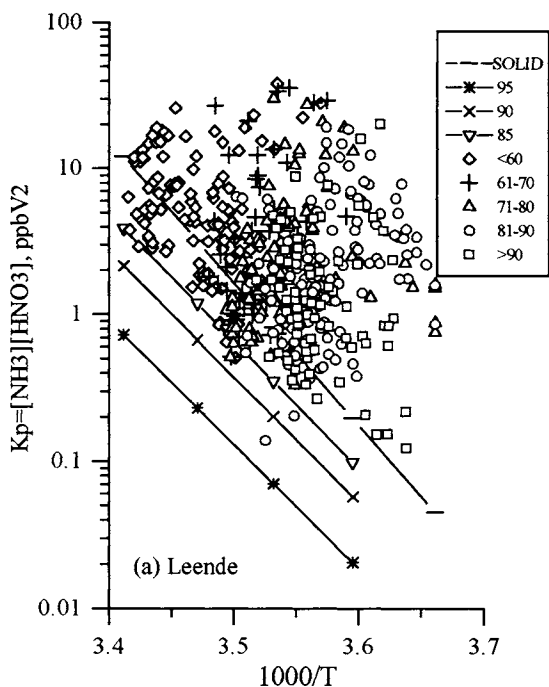


Figure 3. Measured concentration products $[\text{NH}_3][\text{HNO}_3]$ and theoretical equilibrium curves as a function of temperature and humidity at Leende.

theoretical predictions regardless of the fact that the aerosol was in solid or in aqueous phase. The significant characteristic in Speuld is that the measured concentration products tend to be smaller than theoretical predictions at lower relative humidity. The discrepancies from equilibrium are still large if the data with relative humidity $> 80\%$ and temperature $< 5^\circ\text{C}$ are rejected. Lewin et al. [13] obtained a good agreement between measured concentration products and theoretical equilibrium constants between HNO_3 , NH_3 and NH_4NO_3 at a temperature higher than 0°C at a rural site in the Northeastern U.S. on a 24 hours basis, although their data set was relatively small. In Speuld, a rural site in the Netherlands, disequilibrium was generally observed.

Recently, Mozukewich [4] offered a model to calculate the dissociation constant of NH_4NO_3 aerosol as an explicit function of temperature and relative humidity, allowing a more precise evaluation of the equilibrium in different temperature and relative humidity. The ratio of measured concentration product $K_m = [\text{NH}_3][\text{HNO}_3]$ to the value K_e predicted by theory is defined as a measure of whether the system is in equilibrium. If the system is in equilibrium, the ratio should be near unity. Any ratio larger or smaller than unity means that system is not in equilibrium.

Figure 4 depicts relative humidity and temperature dependence of this ratio K_m/K_e at Leende. The ratios K_m/K_e are mostly larger than unity, but some are slightly lower than unity at low humidity and high temperature. As Rh increases, the ratio increases and discrepancy from theory also increases (figure 4a). As temperature increases, the ratio decreases with a strong linear relationship (figure 4b). At $\text{Rh} < 80\%$, the ratios are ranging generally between 0.1 and 100. Figure 4 clearly shows that maximum disequilibrium occurs under conditions of high humidity and low temperature, while the concentration products are slightly under equilibrium at high temperature and low humidity. The same relations between humidity, temperature and the ratio K_m/K_e are obtained in Zegveld and Speuld.

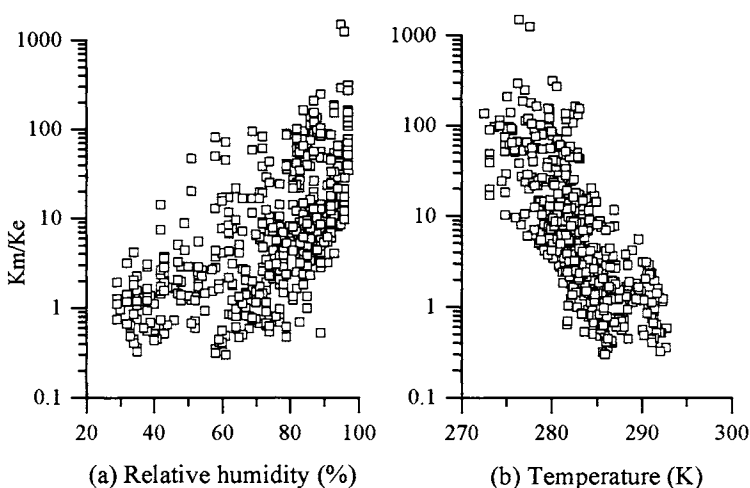


Figure 4. The ratio of measured concentration product to equilibrium value predicted by thermodynamics as a function of relative humidity (a) and temperature (b) at Leende.

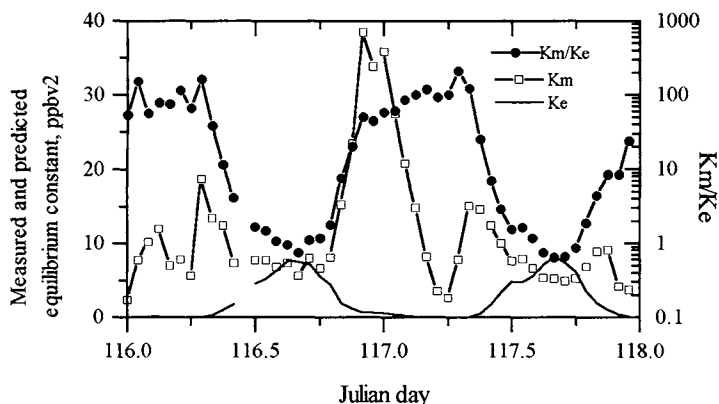


Figure 5. Diurnal variation of the ratio of measured concentration product K_m to theoretical prediction K_e at Leende from April 26-27, 1991.

The ratio K_m/K_e shows strong diurnal variation at Leende, as shown in figure 5. The ratios are much higher than unity in the night and the early morning and slightly lower than unity in the late afternoon. This variation is consistent with NH_3 concentration changes (figure 1), showing the major role of NH_3 in the disequilibrium. If the accuracy of the theoretical prediction is taken into account, the conclusion is that the system of NH_3 , HNO_3 and NH_4NO_3 is strongly above equilibrium in the night and nearly in equilibrium or under equilibrium at daytime in Leende.

The results obtained here are slightly different from those of Erisman et al. [14] who found that a reasonable agreement existed between measured products and theoretical calculation for a temperature $> 0^\circ\text{C}$ and $R_h < 80\%$ at Cabauw in the Netherlands. The explanation for the disequilibrium between aerosol and gaseous compounds is believed to be kinetic constraints preventing rapid attainment of equilibrium. Gas-particle transformation processes are not governed by thermodynamic law only and kinetic constraints play an important role on the transformation. At the three sites, NH_3 concentrations are higher at night and lower at daytime with a peak in the early morning while HNO_3 concentrations shows a weak diurnal variation. Thus the concentrations products of NH_3 and HNO_3 do not show a strong diurnal variation with a peak in the afternoon, which is predicted by thermodynamic theory based on the variation of temperature and relative humidity, as shown in figure 5. The diurnal changes in temperature and humidity alter the dissociation constant at a rate which is sufficiently rapid to prevent equilibrium between NH_4NO_3 aerosol and its gas precursors. Similarly, changes in precursor gas concentrations can not be accommodated sufficiently rapid to maintain equilibrium conditions [18]. As shown in figure 5, it seems that kinetic constraints for gaseous reactions at low temperature and for aerosol evaporation at high temperature offer a reasonable explanation for the disequilibrium.

In addition to kinetic constraints, high NH_3 concentrations reduce HNO_3 concentrations to such a low level that large measurement uncertainties may occur, resulting in departure from theory especially at high humidity. However, the measurement uncertainties are not the main reason for the disequilibrium because the measured products do not fit the theory well at

temperatures above 5°C, relative humidity less than 80% and measured concentration products larger than 1 ppbv². In Zegveld and Speuld, interference by dissociation followed by deposition of the products could cause a negative departure, because the sampling height is low and the wet surface of the canopy is a strong sink for HNO₃ and NH₃. The formation of hydrated gases, which are not accounted for in the theoretical model, may result in underestimation of the HNO₃ concentration especially at low temperatures and high humidity.

4. A FIRST ORDER ESTIMATION OF THE INFLUENCE OF THE NH₃/HNO₃/NH₄NO₃ SYSTEM ON THE FLUXES OF HNO₃ AND NH₃

In Leende, the interference on NH₃ and HNO₃ fluxes by dissociation of NH₄NO₃ is obvious and large, especially for HNO₃, shown in figure 2. NH₃ is deposited, while HNO₃ fluxes are directed away from the surface. Since HNO₃ shows a very weak peak in the late afternoon, the photochemical formation of HNO₃ is not a reasonable explanation to the upward gradient of HNO₃. In Zegveld, NH₄NO₃ and HNO₃ were measured by thermodenuder in July, 1992. Although the precision of the data can not allow calculation of aerosol flux, they reveal that the HNO₃ gradient and NH₄NO₃ concentration show an anti-correlation, see figure 6. At high NH₄NO₃ concentrations, apparent HNO₃ emissions are observed and at low NH₄NO₃ concentrations, HNO₃ depositions are observed. In Manddorf, Germany where high ammonium sulfate and low NH₄NO₃ concentration were observed, HNO₃ usually showed a deposition flux. In Leende, nitrate concentration was very high and about 70% of the nitrate existed as NH₄NO₃. As figure 5 shows, in daytime, especially in the late afternoon, the system is nearly in equilibrium or under equilibrium. Decreasing nitrate aerosol concentrations were observed in Leende, as shown in figure 7. In daytime, NH₄NO₃ aerosol dissociation is favored at low level compared to higher levels due to the influence of the dissociation followed by deposition. Equal amounts of NH₃ and HNO₃ are produced this way. The HNO₃ gradient is easily changed from downward to upward direction by this mechanism because HNO₃ concentrations and gradients are small. At the night, the NH₃, HNO₃ and NH₄NO₃ are strongly above equilibrium and the system has shifted to aerosol formation. HNO₃ upward gradient usually did not change very much, implying that aerosol formation rate was slow, otherwise, the strong NH₃ deposition gradient would change the

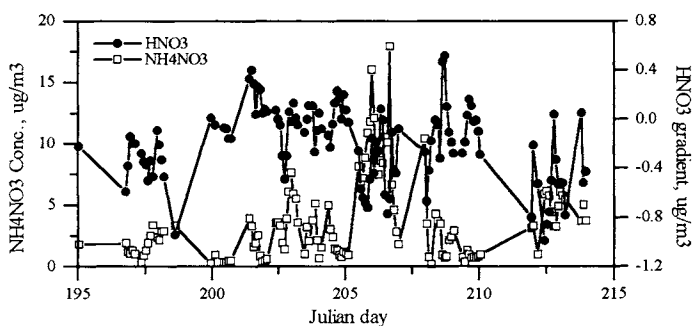


Figure 6. Anti-correlation between NH₄NO₃ concentration and HNO₃ gradient in July, 1992 at Zegveld in the Netherlands

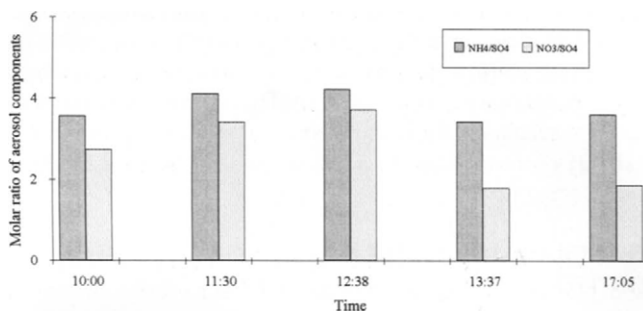


Figure 7. Aerosol $\text{NH}_4^+/\text{SO}_4^{2-}$ and $\text{NO}_3^-/\text{SO}_4^{2-}$ changes on April 26, 1991 in Leende

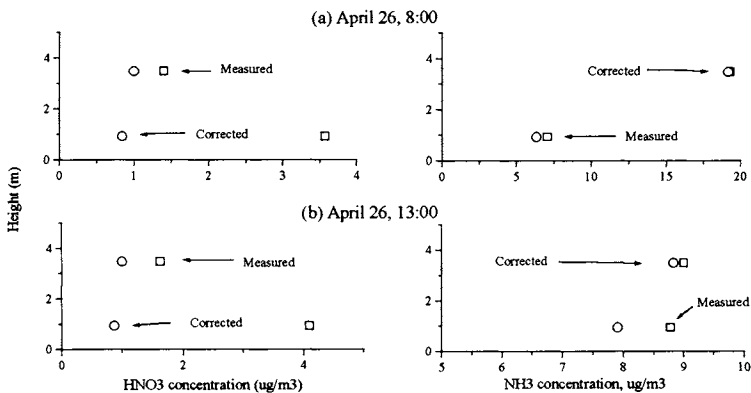


Figure 8. Diagram of the influence of NH_4NO_3 dissociation on NH_3 and HNO_3 fluxes on April 26, 1991 at Leende in the Netherlands

HNO_3 gradient greatly.

At present, the kinetics of the NH_3 , HNO_3 and NH_4NO_3 equilibrium system are not well understood and NH_4NO_3 aerosol deposition is not measured precisely. It is very difficult to analyze quantitatively how the equilibrium influences the fluxes of the species involved in the system. Even though large uncertainties exist, the measurements of HNO_3 and NH_3 concentrations do indicate that the $\text{NH}_3/\text{HNO}_3/\text{NH}_4\text{NO}_3$ system influences NH_3 and HNO_3 fluxes and the upward fluxes of HNO_3 are probably caused by NH_4NO_3 dissociation. Based on the assumption that the HNO_3 upward gradient is caused by NH_4NO_3 dissociation, a first order estimate can be made of the influence of the NH_4NO_3 dissociation to NH_3 flux.

The NH_3 and HNO_3 fluxes on April 26, 1991 in Leende are used as an example. The assumption is that the background HNO_3 concentration at 3.47 m is $1 \mu\text{g}/\text{m}^3$, which is consistent with the HNO_3 concentration on May 3-4, 1991 when HNO_3 showed a deposition flux. The dry deposition velocity V_d of HNO_3 at 3.47 m can be obtained by the inverse of the

sum of R_a and R_b , assuming R_c to be zero. From V_d and the HNO_3 concentration at 3.47 m, the corrected concentration of HNO_3 at 0.93 m can be estimated, as shown in figure 8. The corrected NH_3 concentrations at both levels can be estimated from the measured and corrected concentration of HNO_3 . Figure 8 shows two extreme cases: (a) high NH_3 deposition flux and (b) high HNO_3 upward flux. In both cases, NH_4NO_3 dissociation has an enormous influence on the HNO_3 gradient and sometimes changes its direction. When the NH_3 gradient is large, NH_4NO_3 dissociation has little influence on the NH_3 flux. In figure 8a, where the NH_3 flux is high, the measured NH_3 flux is estimated only about 5% lower than without the correction for NH_4NO_3 dissociation. In figure 8b where the HNO_3 upward flux is high and the NH_3 gradient is small, NH_4NO_3 dissociation has a greater influence on both HNO_3 and NH_3 fluxes. The measured NH_3 deposition flux is estimated 76% lower than without this correction. Figure 9 shows diurnal variations of HNO_3 and NH_3 fluxes before and after the correction for NH_4NO_3 dissociation. Since HNO_3 usually shows an upward gradients at Leende, NH_3 deposition fluxes are underestimated or NH_3 emission fluxes are overestimated in the late afternoon because NH_4NO_3 dissociation influences the NH_3 gradient to a large extent during that period.

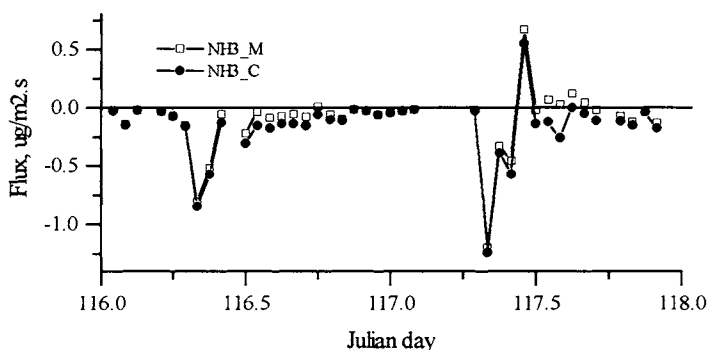


Figure 9. The influence of NH_4NO_3 dissociation on NH_3 flux on April 26-27, 1991 in Leende (NH_3_M : measured NH_3 flux, NH_3_C : corrected NH_3 flux)

5. CONCLUSION

The three data sets collected in 1989, 1991 and 1993 in Speuld, Leende and Zegveld in the Netherlands are investigated to evaluate the atmospheric equilibrium of NH_3 , HNO_3 and NH_4NO_3 aerosol. A very poor agreement between measured gaseous concentration products $K_m = [\text{NH}_3][\text{HNO}_3]$ and theoretical predicted equilibrium values K_e is found at low relative humidity. The comparison between the measured K_m and theoretical K_e reveals that NH_3 and HNO_3 are generally not in equilibrium with NH_4NO_3 aerosol, because the ratios of K_m to K_e are far from unity, varying from less than 0.01 to above 100. The ratio increases with increasing relative humidity and decreasing temperature. The maximum positive departure from equilibrium usually occurs at low temperature and high relative humidity, which is consistent with most field measurement. The maximum negative deviation usually happens at

high temperature and low relative humidity. Kinetic constraints upon the attainment of equilibrium for the $\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3$ system are emphasized by the results obtained at the three sites. Disequilibrium between NH_3 , HNO_3 and NH_4NO_3 can be used to explain why HNO_3 upward gradients in Leende are observed. The dissociation of NH_4NO_3 is responsible for the upward gradient of HNO_3 and results in a slight underestimation of the NH_3 deposition flux during the night. Large errors in the estimation of NH_3 emission or deposition fluxes are caused by the influence of NH_4NO_3 dissociation in the late afternoon when NH_3 gradients are small.

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