Below-cloud scavenging of tropospheric ammonia

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ABSTRACT

Below-cloud scavenging of tropospheric ammonia gas by raindrops was investigated by observing the change in the $NH_3(g)$ concentration measured before and during long precipitation events. The removal was parameterized as a first-order process; the scavenging coefficient, defined here as the first-order rate coefficient, was computed by two different methods:

(1) the average "measured" scavenging coefficient was calculated by taking into account the average "pre-event" and "event" concentrations and the duration of the event,

(2) the average "theoretical" scavenging coefficient was calculated by considering the diffusion of the gas to the raindrop, the intensity of precipitation during each hour of the event, and the raindrop size distribution.

The scavenging coefficient was computed for fourteen precipitation events. The median "measured" scavenging coefficient was 1.3×10^{-4} s^{-1}, which is equivalent to an *e*-folding time of 2.1 hours. Note, however, that these values spanned two orders of magnitude. A comparison of the "measured" to "theoretical" scavenging coefficients showed that these two quantities were within an order of magnitude of each other for most cases. The precipitation-scavenged ammonia was calculated as the difference between the gas concentrations at the beginning and end of the event. For a majority of the events, the scavenged ammonia contributed less than 10% of the total ammonium found in precipitation.

1. Introduction

One of the atmosphere's cleansing processes is the scavenging of trace gases and aerosols by precipitation. The removal of gases and aerosols determines the chemical composition of precipitation. Although many studies have described the relationship between (1) the gas and/or particle concentrations in the atmosphere measured at the surface or at cloud base and (2) the corresponding ion concentrations in the collected precipitation (reported as a scavenging or washout ratio; see Scott, 1981; Misra et al., 1985; Barrie, 1985; Harrison and Pio, 1983; Pratt and Krupa, 1985; Uematsu et al., 1985; Davidson et al., 1985; Hicks and Shannon, 1979), few studies have examined the changes in gas and particle concentrations during individual precipitation events. De Pena et al. (1985) reported on the relationship between the concentrations of tropospheric ammonia gas, the most abundant alkaline gas

present in the atmosphere, and ammonium ion concentrations in precipitation collected on an event basis. In that paper, the equilibrium NH_4^+ concentration, which is dependent on the partial pressure of $NH_3(g)$, the pH of the precipitation, and the temperature, i.e.,

$$[NH_4^+]_{eq} = \frac{K_D K_H}{K_w} [H_3O^+] P_{NH_3}$$ (1)

where

K_D = dissociation constant of aqueous ammonia,

K_H = Henry constant for $NH_3(g)$,

K_w = solubility product of water,

$[H_3O^+]$ = hydronium ion concentration in precipitation,

P_{NH_3} = average $NH_3(g)$ concentration measured at the surface during the precipitation event,

was compared to the observed NH_4^+ concentration. The observed ammonium ion concentrations were between 0.03% and 3% of the calculated equilibrium values (see Table 1). This apparent discrepancy can be explained by realizing that for a highly soluble gas the time required to reach equilibrium is much longer than the time needed for a typical raindrop to fall from cloud base to the ground (Shimshock and de Pena, 1986). So, for the case of NH_3(g) the solubility is sufficiently high enough to ensure that equilibrium will not be attained. However, more information regarding the scavenging of ammonia is desired in order to fully understand this phenomenon.

Thus, the purpose of this paper is to report below-cloud scavenging coefficients for tropospheric ammonia; only removal by raindrops will be considered. The theory of gas scavenging by falling raindrops is reviewed in the next section; the measurement techniques and outline of the project are given in the third section. The results

section describes the distribution of the scavenging coefficients; estimates of the amount of NH_4^+ in the collected precipitation due to below-cloud scavenging of NH_3(g) (percentage basis) are also reported in the results section.

2. Gas scavenging theory

Slinn (1984) has shown that the flux of a gas toward a falling raindrop of diameter D can be described mathematically by the following equation:

$$\frac{d}{dt}\left\{\frac{\pi}{6}D^3[C_{gas}]\right\} = \pi D^2 K_o\left\{P_{gas} - \frac{[C_{gas}]}{\alpha^*}\right\}, \quad (2)$$

where

P_{gas} = partial pressure of the gas,

$[C_{gas}]$ = concentration of gas dissolved in the drop,

K_o = overall transfer velocity of the gas in both the liquid and gas phase,

α^* = overall solubility parameter,

$[C_{gas}]/\alpha^*$ = equilibrium partial pressure of the gas.

The K_o term incorporates the overall transfer resistance to gas absorption by the raindrop, and is equal to the sum of the resistances in the air-phase, liquid-phase, and to the surface resistance. As outlined by Peters (1983), a surface resistance can be due to the existence of a surface film and to the "non-sticking" of gas molecules which impinge the drop (i.e., accommodation coefficients, the probability of impinging gas molecules sticking to the drop, less than one). Internal circulations which develop in falling raindrops tend to disrupt the surface film, thus minimizing this effect. The contact time for gas molecules which impinge the drop is expected to be "relatively long" so this factor should not introduce a significant surface resistance as well. In the absence of better information, we will assume the accommodation coefficient has a value of one, and assume the surface resistance is negligible.

The internal circulations also accelerates the transfer of the dissolved gas in the liquid phase. For highly soluble, low molecular weight gases like ammonia, we will neglect the liquid phase transfer in comparison to the gas phase transfer.

Table 1. *Precipitation data: Comparison of the observed vs. equilibrium NH_4^+ concentration*

Date	$\bar{T}$ ambient (°C)	$[H_3O^+]$[a] (μeq/l)	$[NH_4^+]$[a] (μeq/l)	$\frac{[NH_4^+]}{[NH_4^+]eq}$ (%)[b]
26 Aug 85	18.2	47.9	18.7	2.4
30 Sept 85	14.0	8.1	5.4	0.3
02 Oct 85	12.4	75.9	20.1	1.5
13 Nov 85	7.3	56.2	11.6	>0.5
15 Nov 85	15.7	57.5	8.0	>1.2
17 Nov 85	2.0	27.5	2.1	>0.4
23 Nov 85	0.0	33.9	2.4	0.03
05 Feb 86	1.0	41.7	8.8	>1.0
02 July 86	16.5	36.3	12.0	0.07
27 Oct 86	8.3	46.8	15.0	0.1
06 Nov 86	1.2	53.7	2.8	0.03
23 Nov 86	0.0	19.5	1.8	>0.1
11 Dec 86	3.7	42.7	16.0	>2.7
19 Dec 86	2.0	91.2	38.0	>1.2

[a] Data supplied by Multi-State Atmospheric Power Production Pollution Study (MAP3S); units are microequivalents per liter.

[b] P_{NH_3} values found in Table 3 under "event" column; for P_{NH_3} values below the detection limit of the denuder, a minimum $[NH_4^+]/[NH_4^+]eq$ ratio was computed.

Hence K_o can be approximated by the following expression:

$$K_o = \frac{2 D_c (Sh)}{D}, \qquad (3)$$

where

D_c = diffusion coefficient,

Sh = Sherwood number = $1 + 0.4 \ (Re)^{1/2}(Sc)^{1/3}$,

Re = Reynolds number,

Sc = Schmidt number (Slinn, 1984).

We used equation (2) to calculate $[C_{NH_3}]$ as a function of time for a falling raindrop. The results, expressed as a percentage of the equilibrium NH_4^+ concentration, are shown in Fig. 1. Note that for a raindrop, characterized by an initial pH of 4.0 and initially containing no dissolved $NH_3(g)$ or NH_4^+, falling through air containing 1 ppbv each of $NH_3(g)$ and $SO_2(g)$ at $0°C$, the time needed to reach just 1% of its equilibrium value is at least ten minutes. This time is comparable to the time it takes a drop to fall from cloud base to ground. Varying any of the parameters, i.e., the ambient $NH_3(g)$ or $SO_2(g)$ partial pressure, initial pH of the drop, initial quantity of $NH_x(NH_x = NH_3 \cdot H_2O + NH_4^+)$ in the drop (provided $[NH_x]_i < 50 \ \mu mol/l$), or the temperature will not change this result (Shimshock and de Pena, 1986). Therefore, we submit that it is reasonable to say that chemical equilibrium between the NH_4^+ concen-

tration in the drop and P_{NH_3} will not be established, i.e., $P_{NH_3} \gg [C_{NH_3}]/\alpha^*$.

Assuming that the total amount of gas in the air and gas dissolved in the drop remains constant (i.e., no advection of gas into the column of air being scavenged), equation (2) can be reduced to a simple first-order expression:

$$P_{NH_3} = [P_{NH_3}]_i \exp[-\Lambda t] \qquad (4)$$

where

$[P_{NH_3}]_i$ = initial ammonia gas concentration,

Λ = scavenging coefficient

$$= \int 2\pi D_c [Sh] DN(D) \, dD, \qquad (5)$$

$N(D)$ = raindrop number distribution,

t = time.

Lambda, Λ, defined as the scavenging coefficient, can be computed provided $N(D)$ is known. The Marshall–Palmer raindrop distribution, i.e.,

$$N(D) = 0.08 \exp(-41 \, DI^{-0.21}),$$

where

$N(D)$ = no. drops/volume air/length (cm^{-4}),

D = diameter of drop (cm),

I = rain intensity $(mm \ h^{-1})$,

was used to compute the quantity we call the "theoretical" Λ. As suggested by Levine and
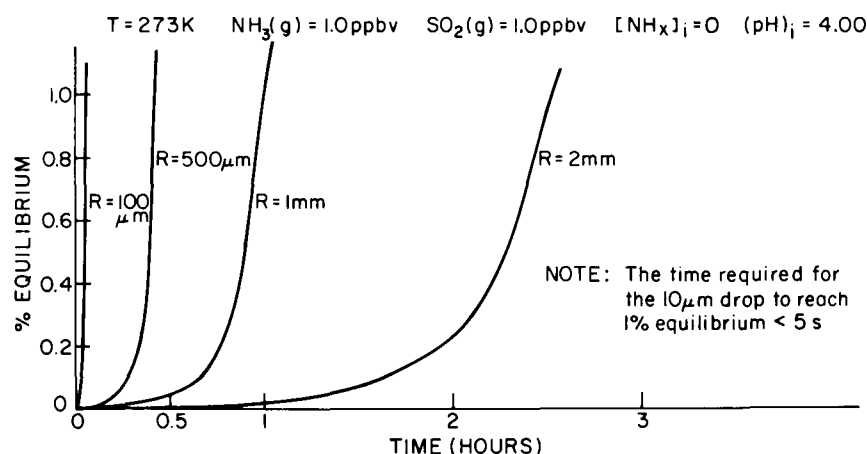

Fig. 1. Plot of the percentage of equilibrium reached versus time for drops of radius R (range is 0–1% of the equilibrium value).

Schwartz (1982), we reduced the number of drops in the size range $0.02 \text{ cm} \leqslant D \leqslant 0.12 \text{ cm}$ by 50% since this distribution tends to overestimate the number of small drops. (We assumed that there is no height dependence of the precipitation intensity.)

The scavenging coefficient can also be determined from measurements of ammonia; this is outlined in the next section.

3. Experimental methods

Ammonia gas was collected with an oxalic acid-coated denuder at a rural central Pennsylvania (USA) site from 1985–1987. The site (latitude 40°43′N, longitude 77°56′W, elevation ~400 m above MSL) was located in an agricultural field used for growing corn, soybean and grain crops, and was operated by The Pennsylvania State University. Information regarding the climatology, particulate and pollutant levels of this area are given in Table 2. Detailed descriptions of the denuder and analytical methods have been reported elsewhere (Lewin et al., 1986; Shimshock and de Pena, 1986). A few salient features of the denuder system, however, are worth repeating:

1. We estimate the accuracy of the denuder measurements to be ±10% (combination of both sampling and analytical errors).

2. The collection efficiency was determined to be greater than 90%.

3. The major drawback of the system was that long sampling times were needed (hours) in order to measure concentrations sufficiently larger than the blank value.

In addition, the precipitation was collected on an event basis for the Multi-State Atmospheric Power Production Pollution Study (MAP3S) at a nearby site (Penn State site). The site description and protocol for precipitation sample collection and analysis are well documented (Bowersox, 1980; MAP3S/RAINE Research Community, 1982).

The denuder system was employed in the following manner: when rain was forecasted to fall fairly steadily for a period of several hours (usually the storm was a well developed cyclone, not individual localized showers), sampling was started approximately 12–24 h before the onset of the precipitation. When the precipitation began to fall, the denuder was collected, and a new denuder was set-up and run. This second denuder collected ammonia from the air during the time precipitation was falling; the sampling ended as soon as the rain stopped. Thus, the average "pre-event" and average "event" ammonia concentration were measured. We hypothesized that if the air was being cleansed by the hydrometeors, then the event concentration should be less than the pre-event ammonia concentration. Any decrease in the ammonia concentration was then assumed to be due to the scavenging by the raindrops. Essentially we thought of the removal of the gas in terms of a simple "box model" in which drops falling at a constant velocity through a well-mixed (i.e., no gradients of $NH_3(g)$) column of air scavenge the gas.

This is not to say that changes in the $NH_3(g)$ concentration during the event were due solely to below-cloud scavenging by the raindrops. Transport of $NH_3(g)$-laden or $NH_3(g)$-deficient air into the sampling area would obviously alter the quantity of gas removed. In support of this hypothesis, ancillary measurements of sulfur dioxide, ozone, condensation nuclei and winds (~6 m height) were made; this data was recorded as one-half hour averages (background values of sulfur

Table 2. *Climatology, particulate and pollutant levels at the sampling site*

Variable	Range (average)
temperature[a]	−3°C Jan to 22°C July
precipitation[a]	62 mm Feb to 100 mm May
NH_4^{+}[b]	1 μg m^{-3} Apr to 4 μg m^{-3} June
SO_4^{-}[b]	3 μg m^{-3} Apr to 15 μg m^{-3} June
condensation nuclei	30,000 cm^{-3}[c]
sulfur dioxide	10 ppbv[c]
ozone	30 ppbv[c]

[a] Data is for University Park, PA, which is located 11 km northeast of the site; data obtained from Department of Meteorology, The Pennsylvania State University.

[b] Data obtained from weekly filter pack data collected at our site from 21 January 86 to 03 June 86 for the National Oceanic and Atmospheric Administration/Air Resources Laboratory/Atmospheric Turbulence and Diffusion Division (NOAA/ARL/ATDD).

[c] Typical background value.

dioxide, ozone, and condensation nuclei are listed in Table 2). We examined the behavior of these variables as a function of time and noted the time periods during the event when "unusual" behavior occurred. We defined "unusual" behavior in the following manner:

● sulfur dioxide concentration increases greater than 5 ppbv
● ozone concentration increases greater than 5 ppbv
● condensation nuclei concentration increases greater than 5000 cm^{-3}
● wind direction shifts greater than 90° occurring over a maximum three hour period with sustained wind speeds greater than 1 m s^{-1}.

If at least three of the four conditions were met during the event, then we assumed that an air mass change occurred. Subsequently we submit that for those cases there is evidence that below-cloud scavenging may not be the dominant process responsible for the changes in the $NH_3(g)$ partial pressure.

Only one rain storm met the criteria outlined above; this case was not considered further. Yet it was obvious that for other storm cases the transport effects (horizontal and/or vertical) dominated the scavenging effects despite the fact these cases did not meet the rejection criteria (see below). A possible explanation why these cases were not rejected may be found by examining a typical pre-event $NH_3(g)$ partial pressure. For the storm cases in which the pre-event partial pressure was greater than that of the event, the average pre-event partial pressure was 0.71 ppbv; for the storms in which the reverse case was true, the average pre-event partial pressure was 0.22 ppbv. For these later cases, perhaps the transport effects became dominant only because the initial quantity of gas present was low. In the absence of better information, we assumed the scavenged effects dominated the transport effects unless the cases were eliminated by the criteria already described.

Changes in ambient temperature and humidity could alter the distribution of ammonia in both the gas and condensed phases (Martin Ferm, personal communication, 1987). In particular, the equilibrium between ammonium nitrate, ammonia gas, and nitric acid gas

$$NH_4NO_3(s) \rightleftharpoons NH_3(g) + HNO_3(g)$$

is both temperature and humidity dependent. Earlier simultaneous measurements of $NH_3(g)$ and $HNO_3(g)$ at our site were used to show that this equilibrium can exist (Lewin et al., 1986). However, evidence that the $NH_3(g)$ concentration changes were due in part to alterations in the equilibrium of ammonia in the gas and condensed phases was not acquired. Despite the fact that we could not isolate the scavenging effects from these other effects, we submit that when the gas concentration decreased during the event, scavenging by the raindrops was the dominant process.

We unfortunately encountered two major problems when we conducted this experiment. The first problem was that the precipitation did not fall steadily throughout the lifetime of every storm. Some of the storms had quite complicated storm-tracks and precipitation patterns (areal and temporal), and so some of the sampling periods did not coincide exactly with the hours of rain. The second problem, in violation of our basic assumption, occurred when the event concentration was larger than the pre-event ammonia concentration. Obviously, for these cases the transport effects dominated the scavenging effects. (This phenomenon could not be due to alteration of the $NH_4NO_3/NH_3,HNO_3$ equilibrium since the ambient conditions during the event sample were cooler and more humid compared to the pre-event sample. The equilibrium product of $P_{NH_3} \cdot P_{HNO_3}$ decreases with decreasing temperature and increasing humidity; see Stelson and Seinfeld (1982a, b).) This situation occurred for about one third of the events sampled, and has been noted by other researchers (Sperber and Hameed, 1986).

Nevertheless, we were able to compile data for 14 storm cases. Note that in half of these cases, the event ammonia concentration was below the limit of detection of the denuder, so for these cases we assumed that the event concentrations were equal to this value (about 0.02 ppbv). The average scavenging coefficient was calculated from the $NH_3(g)$ measurements as shown below:

$\bar{P}_{NH_3}$ = average event concentration,

$(\bar{P}_{NH_3})_i$ = average pre-event concentration,

$$\bar{P}_{NH_3} = \frac{\int P_{NH_3} dt}{\int dt} = \frac{\int [P_{NH_3}]_i \exp[-\Lambda t] dt}{\int dt},$$

$$\overline{P}_{NH_3} = \frac{[P_{NH_3}]_i \{1 - \exp[-\overline{\Lambda}[\text{measured}]t]\}}{\overline{\Lambda}[\text{measured}]t},$$

t = duration of the "event" sample (hours).

We define $\overline{\Lambda}$(measured) as the average scavenging coefficient computed from the measurements of $NH_3(g)$.

4. Results

A listing of the average measured scavenging coefficient, $\overline{\Lambda}$(measured), is given in Table 3. The median value is 1.3×10^{-4} s⁻¹ which is equivalent to an e-folding time of about 2.1 h. Sperber (1985) has also calculated scavenging coefficients for ammonium from the measurements of the NH_4^+ concentration in sequential precipitation samples. For samples which met his criteria of storm homogeneity (criteria discussed in Sperber and Hameed, 1986), the mean and standard deviation of the scavenging coefficient computed from 292 sample pairs in which the precipitation intensity for the sequential samples was within $\pm 50\%$ of each other were 1.2×10^{-4} s⁻¹ and 0.2×10^{-4} s⁻¹ respectively (these numbers include 43 snow samples, but the mean and standard deviation for the snow samples were not significantly different from the overall numbers). Note, however, that Sperber's values represent the total removal, both in-cloud and below-cloud, of $NH_3(g)$ and ammonium-containing particles.

Both groups observed wide variations in the scavenging coefficients, although the range observed by Sperber ($< 1.0 \times 10^{-5}$ s⁻¹ to $\sim 4.0 \times 10^{-4}$ s⁻¹) was less than the range of values seen here (6.6×10^{-6} s⁻¹ to 8.5×10^{-4} s⁻¹). Neither group found any correlation between scavenging coefficients and average precipitation rate (Sperber: 0.1 mm h⁻¹ to ~ 5 mm h⁻¹).

A comparison of the average measured to theoretical scavenging coefficients, $\overline{\Lambda}$(measured) versus $\overline{\Lambda}$(theory) (the theoretical value was calculated by knowing the intensity of rain for each hour of every storm), is shown in Table 3. For most cases the two values are within an order of magnitude of each other. This agreement, while remarkable in light of the simplifications made in the scavenging model, is evidence that the scavenging coefficient can indeed be estimated by eq. (5).

Table 3. *Ammonia gas data: measured concentrations, scavenging coefficients, contributions to NH_4^+ in precipitation*

Date	Pre-event conc. (ppbv)	Event conc. (ppbv)	Duration of event sample (h)	Precip intensity (mm/h)	$\overline{\Lambda}$(meas) (s⁻¹)	$\frac{\overline{\Lambda}(\text{meas})}{\overline{\Lambda}(\text{theory})}$	Amount of rain during event sample (mm)	Cloud base height (m)	$\frac{NH_3(g)\ \text{scavenged}}{[NH_4^+]\ \text{precip}}$ (%)
26 Aug 85	1.01	0.08	23	1.2	1.5–04*	1.5	27.2	335	2.8
30 Sept 85	1.20	0.71	13	2.4	2.5–05	0.1	31.1	365	7.6
02 Oct 85	0.56	0.04	8	1.7	5.0–04	3.0	13.2	1005	9.2
13 Nov 85	0.55	<0.05	7	1.2	4.4–04	3.8	8.6	305	7.4
15 Nov 85	1.09	<0.04	9	1.0	8.5–04	8.4	9.1	460	29.1
17 Nov 85	0.51	<0.01	22	2.1	6.6–04	3.5	46.0	365	8.6
23 Nov 85	0.49	0.10	14	0.6	9.9–05	1.3	8.1	460	52.5
05 Feb 86	0.02	<0.01	28	0.7	1.6–05	0.2	19.8	335	0.2
02 July 86	2.76	1.85	12	1.8	2.0–05	0.1	21.6	700	18.1
27 Oct 86	0.47	0.40	14	0.5	6.6–06	0.09	7.4	365	1.9
06 Nov 86	0.98	0.08	19	0.6	1.8–04	2.7	10.7	305	44.6
23 Nov 86	0.19	<0.03	8	1.4	2.3–04	1.8	10.9	400	17.8
11 Dec 86	0.05	<0.01	29	0.4	4.8–05	0.9	11.9	400	0.4
19 Dec 86	0.08	<0.02	15	0.5	7.3–05	1.0	7.9	400	0.5

* The notation 1.5–04 represents 1.5×10^{-4}.

With the values of $\overline{\Lambda}$(measured), the amount of gas removed by the precipitation was computed (derived from the usage of eq. (4) and knowledge of the amount of rain that fell during each storm case and the average cloud base height). In all but three cases (30 September 85, 02 July 86, 27 October 86) the concentration of NH_3(g) at the end of the event was less than 0.01 ppbv, so for these cases we assumed all the gas initially present was removed. This number, which is the quantity of NH_4^+ found in the precipitation due to below-cloud scavenging of NH_3(g), was compared to the total NH_4^+ concentration in the collected rainwater. The results are given in Table 3. For the majority of the cases, the removal of tropospheric NH_3(g) by the hydrometeors contributed 10% or less of the total NH_4^+. This is in good agreement with the results of Lazrus et al. (1983), who reported that below-cloud scavenging of NH_3(g) or NH_4^+-containing particles did not make an important contribution to the composition of the surface rain. Note, however, that their result was based on observations from one storm case only.

In contrast to our and Lazrus' results, Mészáros and Szentimrei (1985) concluded that below-cloud scavenging of NH_3(g) at a site in Hungary was responsible on average for 46% of the NH_4^+ content in the precipitation. Mészáros and Szentimrei derived this number from a regression equation which related the measured deposition of NH_4^+ in precipitation to the daily precipitation amounts and to the measured concentrations of ammonia gas and ammonium ion in particles. This equation is listed below:

$$D_{WT} = 0.38P_d[NH_3-N]$$
$$+ 0.21P_d[NH_4^+-N] + 0.77,$$

where

D_{WT} = total deposition of NH_4^+ in precipitation (mg m^{-2} day^{-1});

P_d = daily precipitation amount (mm day^{-1});

$[NH_3-N]$ = ammonia gas concentration (μg-N m^{-3});

$[NH_4^+-N]$ = ammonium ion concentration (μg-N m^{-3}).

Mészáros and Szentimrei stated that the three terms on the right-hand side of the equation represent the contributions to the total deposition from below-cloud scavenging of NH_3(g), below-cloud scavenging of NH_4^+ in particles, and the total in-cloud removal of both gas and particles, respectively. While a total of 89 cases were used to derive this equation, the authors only listed the average values of P_d, $[NH_3-N]$, and $[NH_4^+-N]$ in their paper. These values were used to calculate the average NH_4^+ deposited due to below-cloud scavenging of NH_3(g). A measure of the variability of this number can be deduced by looking at the 90% confidence intervals for the regression coefficients. As noted by Mészáros and Szentimrei, the intercept term was not significantly different from zero at a significance level of 0.1, so for the computations here we assumed that the minimum value of the intercept term was zero. By using the appropriate combinations of the minima and maxima of the confidence intervals of the regression coefficients, we estimated that the percent contribution to the total NH_4^+ deposited by precipitation from below-cloud scavenging of NH_3(g) ranged from 26% to 74%. Obviously, our result and that of Mészáros and Szentimrei differs substantially.

In order to understand this apparent discrepancy, we examined the factors which determine the contribution of below-cloud scavenging of NH_3(g) to the NH_4^+ concentration in precipitation. These factors are listed below:

● average pre-storm NH_3(g) concentration;
● average NH_4^+ concentration in precipitation;
● the average rainfall intensity;
● the raindrop distribution (smaller drops scavenge the gas faster than the larger ones—see Fig. 1);
● the average cloud base height.

Mészáros and Szentimrei reported a daily average ammonia concentration (determined from daily measurements over a two year period) of 1.0 μg NH_3 (as N)/m^3, and a mean monthly volume-weighted NH_4^+ concentration in precipitation of 0.86 mg NH_4^+ (as N)/l (measured over roughly the same time period). Although ammonia gas measurements have not been made continuously throughout an entire year at our site, we estimate that the daily average NH_3(g) concentration is approximately one half the concentration measured in Hungary. The mean monthly volume-weighted NH_4^+ concentration is, for our site, about one third as large as the average NH_4^+

concentration in Hungary. Thus, both ammonia gas and ammonium ion concentrations are larger at the Hungarian site, and so the larger gas concentrations can explain at least part of the larger amount of ammonium in Hungary's precipitation.

Although Mészáros and Szentimrei listed a daily average precipitation rate of about 6 mm/day, the average storm duration was not listed, so a storm precipitation intensity cannot be determined (larger precipitation rates could imply that more drops were available to scavenge the gas, and thus faster scavenging rates). Information regarding the raindrop distribution and the average cloud base height is also not available. Perhaps the difference between our result and Mészáros and Szentimrei's result could be due to the variations of these factors.

We should point out that there were some cases in our data set in which the scavenged gas contributed more than 10% of the total NH_4^+. For these cases, either the pre-event $NH_3(g)$ concentration was large (>1.0 ppbv), or the NH_4^+ concentration in the rainwater was low (<3.0 μeq/l). Note, however, that the converse of this statement is not true: the existence of high pre-storm gas amounts or low ion concentrations did not imply that the contribution of the scavenged gas was greater than 10%. In addition, we cannot attribute any of these particular cases to unusual values of precipitation intensity, difficulty in deciding when to measure the gas concentrations, or to the season of measurement. There is no correlation between the quantity of gas scavenged and the NH_4^+ content in precipitation. The paucity of data, however, limits the amount of statistical analyses that can be performed.

Obviously, the remaining NH_4^+ not due to below-cloud removal of $NH_3(g)$ has to be ex-plained by the scavenging of NH_4^+-containing particles and by in-cloud scavenging of both particles and gas. While acknowledging that the separation between in-cloud and below-cloud processes is artificial since there are updrafts and downdrafts associated with each storm (Slinn, 1982), the establishment of liquid-gas phase equilibrium and the dominant particle capture mechanisms are quite different for cloud droplets and raindrops. The study of the scavenging of NH_4^+-containing particles by raindrops will be reported at a later date.

5. Conclusions

Measurements of tropospheric ammonia were made immediately prior to and during long precipitation events. Gas scavenging coefficients were computed by assuming the gas concentration decreased exponentially during the event. The median value of $\overline{\Lambda}$(measured) is $1.3 \cdot 10^{-4}$ s^{-1}; there is good agreement between $\overline{\Lambda}$(measured) and $\overline{\Lambda}$(theory). For most cases, the quantity of $NH_3(g)$ removed by the raindrops contributed less than 10% of the total NH_4^+ found in the collected precipitation.

6. Acknowledgements

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