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Ammonia, the dominant base in the remote marine troposphere: a review

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ABSTRACT

Ammonia appears to be the dominant base in the remote marine troposphere, yet its rôle in atmospheric acid-base chemistry is not well understood. The physical and chemical interactions of ammonia with acidic species is complicated by its presence in the gas and particle phases and in cloud-, rain- and seawater. This review summarizes the reported ammonia concentration data in these 5 phases as well as existing sampling and analysis methods. An attempt is made to compare these data using equilibrium and scavenging calculations. The lowest measured ammonia gas phase concentrations appear to be consistent with reported sulfate and ammonium concentrations in the particulate phase. The high gas phase concentrations of ammonia found in older data appear to be a result of sampling artifacts. Reported ammonium particle and rainwater data also appear to be consistent with each other. Calculations suggest that ammonia may be in equilibrium between the gas phase and the ocean surface. To confirm or refute these conclusions, the simultaneous measurement of ammonia and relevant acidic species in all 5 phases is needed.

1. Introduction

Acid-base interactions play a large rôle in the chemistry of the atmosphere. The major acidic species, H_2SO_4, HNO_3, CH_3SO_3H, HCOOH, CH_3COOH, $C_2H_2O_4$, and HCl have been and are being studied extensively (Andreae and Raemdonck, 1983; Galloway, 1985; Huebert, 1980; Saltzmann et al., 1983; Galloway et al., 1982; Norton, 1985; Norton et al., 1983). By comparison, little attention has been given to the basic species, and in particular, to ammonia. In this paper, we will focus on the marine troposphere because it provides the simplest case and because it is relevant to understanding the background imposed upon the continental atmosphere.

Ammonia appears to be the dominant base in the remote marine troposphere (Ayers and Gras, 1980; Söderlund, 1982). An important acid-base interaction in cloud and rainwater is the reaction of excess (non-seasalt) H_2SO_4 aerosol with NH_3 to form NH_4HSO_4 and $(NH_4)_2SO_4$. The sensitivity of this atmospheric acid-base system to the concentration of ammonia can be seen by considering this reaction when it occurs in clouds as the titration of a strong acid with a weak base. The calculated titration curves for different amounts of H_2SO_4 in cloud condensation nuclei (CCN) are plotted as pH versus total ammonia concentration in Fig. 1. The steep portions of the curves occur close to where the $[NH_4^+]/[SO_4^=]$ equivalence ratio equals one. This value is near the molar ratio found in rainwater in the remote marine troposphere (Galloway, 1985; Vong, 1985). In the marine case, excess sulfate usually is the dominant anion and H^+ and NH_4^+ are the dominant cations (Vong, 1985). Thus small changes in the concentration of ammonia should affect significantly the acid-base chemistry of the marine troposphere.

Within and in contact with the marine atmosphere, ammonia exists in five phases;

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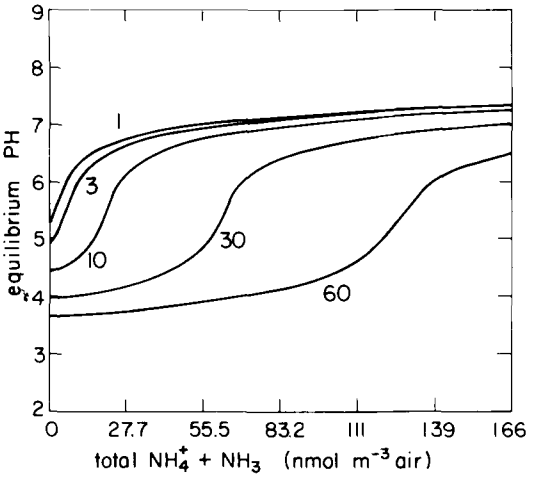

Fig. 1. pH sensitivity to xs $SO_4^=$ and total ammonia for a cloud. Liquid water content = 0.5 g m^{-3}; $(SO_2)_g$ = 50 pptv, T = 278 K. The abscissa shows total ammonia, the ordinate is the resultant equilibrium pH. Each curve represents an aerosol sulfate concentration as H_2SO_4 in nm m^{-3}.

ocean water, the gas phase, the particulate phase, cloudwater, and rainwater. The species in each phase are listed in Table 1. To completely understand the cycle of ammonia through the marine boundary layer, it is necessary to include the acidic species with which ammonia interacts. One reason for this necessity is that vapor pressure relationships of NH_3 (g) are pH dependent (Lau and Charlson, 1977; Tang, 1980). NH_3 (g) can react with H_2SO_4 aerosol to form NH_4^+ (p). Particles containing NH_4^+ can then act as CCN. Alternatively, NH_3 (g) can be dissolved directly into cloud or rainwater. NH_4^+ in a cloud droplet can either be returned to the gas phase as NH_3 (g) when the cloud evaporates or it can be removed from the atmosphere by rain. The cycle of ammonia within and through the marine boundary layer and its interactions with acidic sulfur species are shown in Fig. 2. HNO_3 is also present in the marine troposphere, but it has been omitted from Fig. 2 as its importance is most likely secondary to that of the sulfur species.

2. Relationships between excess sulfate and ammonia in the five phases

2.1. Equilibrium considerations

Lau and Charlson (1977), Georgii and Gravenhorst (1977), Ayers and Gras (1980), and Tang (1980), report equilibrium calculations for ammonia under different conditions for various phases and in relation to excess (non-seasalt) particulate sulfate, xs $SO_4^=$ (p). Based on sparse concentration data that were acquired at different places and times, however, it is difficult to say whether ammonia was in equilibrium between the different phases in which it existed. In addition, because the chemical composition of aerosol particles depends on size (Jensen and Charlson, 1984), there may be no unique aqueous phase composition of hydrated aerosol particles. The same result may be true for cloud droplets if coalescence is not rapid and does not completely homogenize the liquid phase composition. As a result, equilibrium calculations of the vapor pressure of ammonia over particles and cloud droplets become less meaningful. Nonetheless, using these reported data in equilibrium calculations helps to reveal whether the system may be near equilibrium and the expected direction of the ammonia flux from phase to phase.

Within the atmosphere, equilibrium conditions depend at least on the relative amounts of ammonia, sulfuric acid, liquid water, and on temperature. Surface sea water with a fixed pH would appear to be the simplest case, but could be complicated by surface chemical effects.

Table 1. *Ammonia species important to acid-base chemistry in the remote marine atmosphere*

Species	Symbol	Concentration notation and units
1. Gaseous NH_3	NH_3 (g)	$(NH_3)_g$, nmol m^{-3}
2. NH_4^+ in solid or liquid phase aerosol particles	NH_4^+ (p)	$(NH_4^+)_p$, nmol m^{-3}
3. NH_4^+ in cloud water	NH_4^+ (c)	$[NH_4^+]_c$, molar
4. NH_4^+ in rainwater	NH_4^+ (r)	$[NH_4^+]_r$, molar
5. Aqueous NH_3 and NH_4^+ in the sea surface	NH_3 (s) + NH_4^+ (s)	$[NH_3]_s + [NH_4^+]_s$, molar or $[NH_3]_{tot\text{-}s}$
6. Total ammonia in non-cloudy air	NH_3 (g) + NH_4^+ (p)	$(NH_3)_{tot\text{-}air}$, nmol m^{-3}

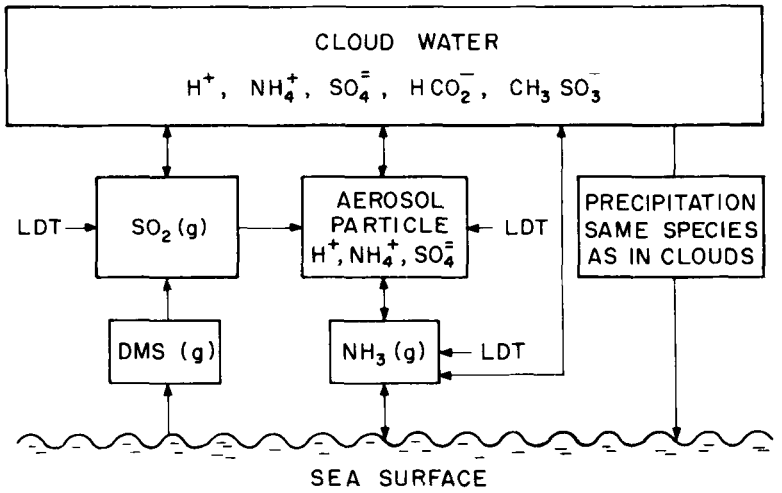

Fig. 2. The cycle of ammonia and its interactions with acidic sulfur species within and through the marine boundary layer. Note, LDT: long distance transport. Key species are indicated for each phase.

2.2. Ammonia in the gas phase, NH_3 (g)

A summary of the published data for gas phase ammonia concentrations in the marine troposphere is given in Table 2. The values range from 1.2 to 530 nmol m^{-3}. It is not clear that all of the air masses studied were of purely marine origin since meteorological analyses were not complete in all cases. Interferences from continental air masses may have contributed to the wide range of values. The lowest values (0.6 to 6 nmol m^{-3}) correspond to purely marine trajectories at Cape Grim, Tasmania. However, the Cape Grim data were not acquired simultaneously with aerosol ammonium and sulfate concentrations, so it is difficult to determine if that system was in equilibrium.

The gas phase plays a central rôle in the environment since it interacts with all of the other phases (see Fig. 2). Therefore, NH_3 (g) will be related to NH_4^+ (p) and aqueous species in clouds, rain, and seawater. These relationships will be discussed in the following sections.

2.3. Ammonia in the ocean, NH_3 (s) + NH_4^+ (s)

If the air/sea interface is in equilibrium with respect to ammonia species, then Henry's Law as given in eq. (1) should apply,

$$(NH_3)_g = K_{hN}[NH_3]_s. \quad (1)$$

A net flux of NH_3 (g) could exist from the ocean to the atmosphere or vice versa depending on the concentration gradient between the two phases (Liss, 1983). Georgii and Gravenhorst (1977) reported concentrations of NH_3 (g) of 100 to 500 nmol m^{-3} over the Sargasso Sea with no apparent influence from continental sources. They suggested that, in this case, the ocean could be acting as an ammonia source.

Assuming the existence of an Henry's Law equilibrium for ammonia between the gas and ocean phases, $(NH_3)_g$ over the ocean can be calculated following the method of Georgii and Gravenhorst (1977) and Ayers and Grass (1980). At 15°C, the Henry's Law constant for NH_3, K_{hN}, is 0.0105 atm l mol^{-1} (Liljestrand and Morgan, 1981). K_w, as defined in eq. (2), is 4.5×10^{-15} mol l^{-2} (Harned and Owen, 1958),

$$K_w = [OH^-]_s[H^+]_s. \quad (2)$$

K_b, as given by eq. (3), is 1.6×10^{-5} mol l^{-1} (Bates and Pinching, 1950),

$$K_b = \frac{[NH_4^+]_s[OH^-]_s}{[NH_3]_s}. \quad (3)$$

An expression for $(NH_3)_g$ given in terms of $[NH_4^+]_s$ can be obtained by combining eqs. (1), (2), and (3),

$$(NH_3)_g = \frac{K_w K_{hN}[NH_4^+]_s}{K_b[H^+]_s}. \quad (4)$$

In calculating $(NH_3)_g$ from eq. (4), the fact that $[NH_4^+]_s$ and $[NH_3]_s$ are measured together so that

Table 2. *Summary of gas phase ammonia concentrations in marine air*

Site/date	(nmol m^{-3}) mean	range	Method	Reference
Hawaii coast, 1954	144	98–192	acid solution	Junge (1957)
Mauna Kea	63	37–159		
S. Pacific, 1967	10		acid solution	Tsunogai and Ikeuchi (1968)
N. Pacific, 1968–1969	4	1.2–13	acid solution	Tsunogai (1971)
Mid-Pacific	1.9	1.3–4.8		
S. Pacific	4.4	1.2–9.6		
N. Atlantic, 1973	60	44–190		Georgii and Gravenhorst (1977)
Mid-Atlantic		12–60		
Sargasso Sea		100–500		
Cape Grim, continental air, 1978–1980	20	0.6–50	tandem filter	Ayers and Gras (1983)
Marine air	3.3	0.6–6.0		
Bermuda, 1982	20		WO_3 denuder system	LeBel et al. (1985)

For NH_3, 1 μg m^{-3} = 58.8 nmol m^{-3} = 1.32 ppbv.

both contribute to reported bulk seawater concentrations must be taken into account. This can be done by substituting

$$a = [NH_3]_s + [NH_4^+]_s \quad (5)$$

into eq. (3). Solving the new K_b expression for $[NH_4^+]_s$ and substituting the result into eq. (4) yields

$$(NH_3)_g = \frac{aK_w K_{hN}}{K_w + K_b[H^+]_s}. \quad (6)$$

Eq. (6) is plotted over a range of temperatures and concentrations of total seawater ammonia in Fig. 3. Reported total seawater ammonia concentrations, $[NH_3]_s + [NH_4^+]_s$, vary from 0.23 to 0.55 μmol l^{-1} (Ayers and Gras, 1980; Söderlund and Svensson, 1976). At 15°C, this range yields equilibrium $(NH_3)_g$ of 3.6 to 8.7 nmol m^{-3}, which correspond to the lowest values of $(NH_3)_g$ reported in Table 2. At 25°C, the same seawater concentrations yield equilibrium $(NH_3)_g$ an order of magnitude higher. At 15°C, approximately 4% of NH_3 (s) + NH_4^+ (s) should exist as NH_3 (s). At 25°C, 9% of total seawater ammonia should be in the form NH_3 (s). Apparently, the effects of temperature on the distribution of ammonia between the gas phase over the ocean and the ocean surface waters are significant. To improve the accuracy of these calculations, a correction for K_{hN} in the presence of CO_2 (Hales and Drewes, 1979) as well as activity corrections for the ionic strength of seawater may be necessary.

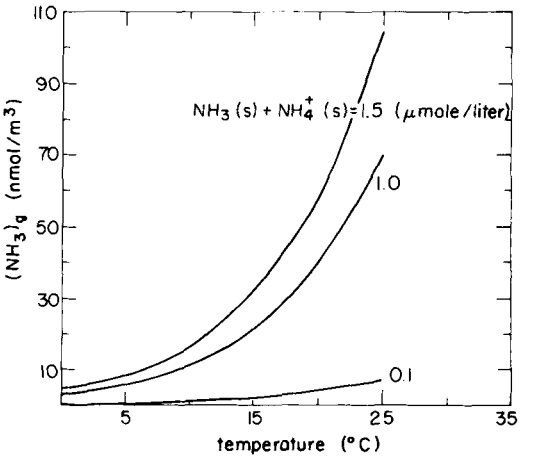

Fig. 3. $(NH_3)_g$ over the ocean surface as a function of temperature and $[NH_3]_s + [NH_4^+]_s$ (Georgii and Gravenhorst, 1977).

However, it appears that there may be instances when purely marine air masses are in equilibrium with the ocean surface with respect to ammonia.

2.4. Ammonium in aerosol particles, NH_4^+ (p)

In the simplest case of H_2SO_4 aerosol particles which are partially neutralized by NH_3, the concentration of NH_4^+ (p) depends on the $(NH_3)_g$, the NH_4^+ (p)/xs $SO_4^=$ (p) molar ratio, the relative humidity, RH, and temperature. Even though there are limitations in applying simplified theoretical calculations to actual situations, it is useful

to consider Fig. 4, adapted from Tang (1980) for the remote marine troposphere. This figure illustrates the effect of $(NH_3)_g$, $(NH_4^+)_p$, and $(xs\ SO_4^=)_p$ on the partitioning of NH_3 between the gas and particulate phases.

Consider a realistic situation in which the NH_4^+ (p)/xs $SO_4^=$ (p) molar ratio is about one, the RH is 85%, and the temperature is fixed at 25°C. When the xs $SO_4^=$ (p) concentration is 1 nmol m^{-3}, NH_3 is distributed equally between the gas and particulate phases (point A in Fig. 4). When the xs $SO_4^=$ (p) concentration is increased to 10 nmol m^{-3}, the amount of NH_4^+ in the particulate phase is increased by a factor of 10 (point C in Fig. 4). Temperature also affects the partitioning of ammonia between the gas and particulate phases. Partitioning between aqueous particles or cloud droplets and the gas phase depends on K_{hN}, K_w, and liquid water content. Since each of these parameters is temperature dependent, partitioning should be a strong function of temperature. Corrections of Tang's work may be necessary when non-ideal, concentrated solutions are considered; however, we expect the general results to remain the same.

The concentration of NH_4^+ (p) has been found to range between 1 and 32 nmol m^{-3} on the Hawaiian coast (Junge, 1957) and between 0.6 and 12 nmol m^{-3} in the central and southern Pacific Ocean (Huebert and Lazrus, 1980). If $(NH_4^+)_p$ of 0.6 nmol m^{-3} and $(NH_3)_g$ of 1 nmol m^{-3} (Tsunogai, 1971) are put into Fig. 4, an $(xs\ SO_4^=)_p$ near 1.0 nmol m^{-3} results. This value corresponds well with typical measured $(xs\ SO_4^=)_p$ of 3 nmol m^{-3} (see, for example, Savoie, 1984). This correlation between theoretical calculations and experimental values indicates that ammonium and sulfate may behave as predicted by the equilibrium model represented by Fig. 4. Simultaneous observations of all of the parameters involved in the partitioning of ammonia between the gas and particulate phases are needed for further verification of the model.

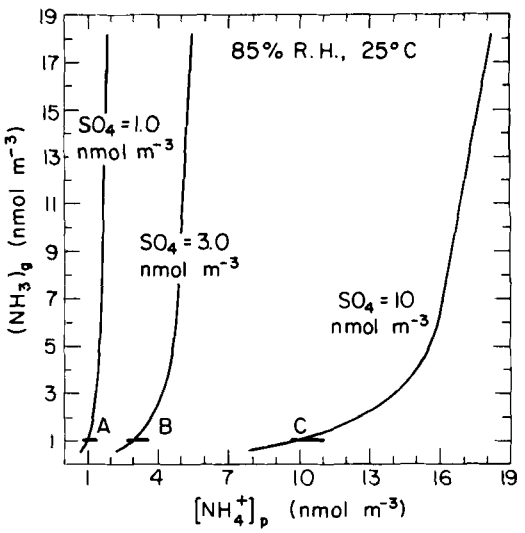

Fig. 4. $(NH_3)_g$ as a function of $(NH_4^+)_p$ and $(xs\ SO_4^=)_p$ at 85% RH (adapted from Tang, 1980). Points A, B, and C referred to in the text correspond to solution droplets of a fixed NH_4^+/xs $SO_4^=$ molar ratio. Moving from A to C, the $(NH_3)_g$ remains fixed but the $(NH_4^+)_p$ increases.

2.5. *Ammonium in clouds, NH_4^+ (c)*

There are at least two processes that incorporate NH_4^+ and $SO_4^=$ into cloudwater. Aerosol particles containing NH_4^+ and $SO_4^=$ can act as CCN. SO_2 (g) can be oxidized to $SO_4^=$ and dissolved and NH_3 (g) can be dissolved yielding cloudwater that contains sulfate and ammonium ions. Table 3 lists the available data for $[NH_4^+]_c$ in marine and continental cloudwater. The values range from 30 to 860 μmol l^{-1}. Petrenchuk and Drozdova (1966) reported that the cloudwater samples from the northern European Territory of the USSR were free of significant industrial pollution and reflect the atmosphere over the Baltic Sea. The low value of 30 μmol l^{-1} compared to the higher values from continental upper regions supports this assertion. Further measurements of $[NH_4^+]_c$ in the marine troposphere need to be made to confirm or refute existing data.

If equilibrium exists between the gas and liquid phases for ammonia in a cloud, the relative amount of NH_3 (g) and NH_4^+ (c) will be given by eq. (4) where $[NH_4^+]$ and $[H^+]$ are concentrations within the liquid droplets (Lau and Charlson, 1977). Because of the high solubility of ammonia in cloudwater, most of the ammonia in clouds should be in the liquid droplets. Thus, it may not be possible to measure $(NH_3)_g$ between cloud droplets with currently available techniques (Taylor et al., 1983).

2.6. *Ammonium in rain, NH_4^+ (r)*

Assuming that rain is an efficient removal

Table 3. *Summary of ammonium concentrations in cloudwater*

Site/date	(μmol l^{-1}) mean	range	Method	Reference
N. ETU*, 1961–1964	30		bulk samples	Petrenchuk and Drozdova (1966)
Muskegon, MI, 1971	860		bulk samples; supercooled droplets collected on nylon wand	Scott and Laulainen (1979)
Whiteface Mtn., 1982		150–425	ground-based collector; Teflon filaments	Kadlecek et al. (1983)

* European Terrority of the USSR.

Table 4. *Summary of ammonium concentrations in rainwater and in snow in a marine atmosphere*

Species	Site/date	(μmol l^{-1}) mean	range	Method	Reference
NH_4^+ (r)	N. Pacific Ocean, 1968–1969	0.2	0.03–0.7	Event-only collection	Tsunogai (1971)
	Pacific Ocean				
	RV Korolev, 1983	2.9			Galloway (1985)
	RV Discoverer	2.8			
	Amsterdam Island, 1980–1982 (in excess)	1.8		Event-only collection	Galloway and Gaudry (1984)
	W. Atlantic Ocean, 1981	3.2	0–8.9	Event-only collection	Galloway et al. (1983)
	Bermuda	2.4		Event-only collection	Galloway (1985)
	Bermuda, 1955	0.5			Junge (1963)
NH_4^+ (snow)	Greenland, 1974–1975	0.3			Busenberg and Langway (1979)
	Antarctic, 1959–1969	0.2			Legrand and Delmas (1984)
	Antarctic	0.4			Parker and Zeller (1980)

mechanism for NH_3 from the remote marine troposphere and that $[NH_4^+]_c$ is equal to $[NH_4^+]_r$ for a raining cloud, it is possible to estimate $[NH_4^+]_r$ from the total concentration of NH_3 in the atmosphere using the Junge scavenging formalism given in eq. (7) (Charlson and Rodhe, 1982; Vong and Charlson, 1985).

$$[NH_4^+]_c = \frac{\varepsilon (NH_4^+)_p}{ML}, \tag{7}$$

where $(NH_4^+)_p$ is in g m^{-3}, ε is the activation efficiency and is assumed to equal one, M is the molecular weight of ammonium, and L is the liquid water content of the cloud in l m^{-3}.

Table 4 summarizes the existing NH_4^+ data in rainwater and in snow for marine environments and remote continental areas, respectively. The measured concentrations range from 0.2 to 8.9 μmol l^{-1}. The rainwater values are within a factor of two of estimates made using the above mentioned scavenging calculation. This correlation suggests that reported total concentrations of ammonia in air and rainwater are consistent with each other and that rain is an efficient removal mechanism for ammonia. The different washout ratios, $[NH_4^+]_{snow}/[NH_4^+]_p$ and $[NH_4^+]_r/[NH_4^+]_p$, for snow and rain may make the comparison meaningless between $[NH_4^+]_r$ and $[NH_4^+]_{snow}$.

2.7. *Existing data versus equilibrium considerations and time scales*

The previous sections have shown cases in which existing ammonia data both agree and disagree with values predicted by equilibrium models. For example, the calculated equilibrium $(NH_3)_g$ over the ocean based on measured concentrations of NH_3 (s) + NH_4^+ (s) is about 7.5 nmol m^{-3}. This value is significantly lower than the majority of measured NH_3 (g) concentrations listed in Table 2. Such inconsistencies may be due to sample contamination, sampling of continental rather than marine air, or a lack of simultaneous measurements of all ammonia species present. Alternatively, it may be that in some instances,

Table 5. *Required detection limits for the measurement of ammonia in the 5 relevant phases*

Species and phase	Required detection limit	Reference
NH_3 (g)	0.5 nmol m^{-3}	Tsunogai (1971)
NH_4^+ (p)	0.1 nmol m^{-3}	Huebert and Lazrus (1980)
NH_4^+ (c)	30 μmol l^{-1}	Petrenchuk and Drozdova (1966)
NH_4^+ (r)	0.03 μmol l^{-1}	Tsunogai (1971)
NH_3 (s) + NH_4^+ (s)	0.2 μmol l^{-1}	Ayers and Gras (1980)

the ammonia species in different phases are not in equilibrium.

Processes that determine how rapidly an atmospheric system may attain equilibrium include the relative reaction times and turnover times of the chemical constituents. One step in the cycle of NH_3 through the atmosphere is the reaction of NH_3 (g) with H_2SO_4 aerosol particles. These aerosol particles, as well as some NH_3 (g) are then scavenged by cloud or rain droplets. The atmospheric turnover times of NH_3 (g), NH_4^+ (p) and xs $SO_4^=$ (p) may be defined as their burden in the atmosphere (g m^{-2}) divided by their respective fluxes (g m^{-2} yr^{-1}) out of the atmosphere. Based on a total ammonia concentration of 3 nmol m^{-3} (0.05 μg m^{-3}), a scale height of 7 km, and a wet deposition rate of 0.06 gN m^{-2} yr^{-1} (Galloway, 1985), the turnover time of total ammonia is about 1.6×10^5 s (1.8 days). This short turnover time suggests that once an air mass is several days from a continent, the primary source of ammonia should be the ocean itself. Using a sulfate concentration of 3 nmol m^{-3} (0.3 μg m^{-3}), scale height of 7 km, and wet deposition rate of 0.15 gS m^{-2} yr^{-1} (Granat et al., 1976; Galloway, 1985) yields a sulfate turnover time of 1.5×10^5 s (1.7 days), comparable to that of NH_3 (tot). For comparison, the turnover time of nitrate based on a flux of 0.03 gN m^{-2} yr^{-1} (Galloway, 1985) and a burden of 1.2 nmol m^{-3} (Savoie, 1984) is about 1.7 days. If scale height is reduced to 3.5 km, the turnover times become less than 1×10^5 s (<1 day). The turnover time of particles that act as CCN in the lowest 1.5 km of the troposphere is about 1 day (Wallace and Hobbs, 1977; Pruppacher and Klett, 1980), which suggests that a common meteorological factor may control the removal from the atmosphere of these substances. It also suggests that the CCN may be composed mainly of H_2SO_4 that is partly neutralized by NH_3.

The reaction time of NH_3 (g) with an H_2SO_4 aerosol droplet should be controlled by the frequency of collision of the two reactants (Cupitt, 1975; Huntzicker et al., 1980). For a droplet with a radius of 0.1 μm and an NH_3 (g) concentration of 0.5 nmol m^{-3}, the time of the reaction is found to be 2×10^4 s. For $(NH_3)_g$ of 5 nmol m^{-3}, the time constant is 2×10^3 s. The short turnover times of ammonia and sulfate when compared to these reaction times suggest that the aerosol system may not always be able to attain equilibrium.

The reaction time of NH_3 (g) with acidic cloud droplets containing xs H_2SO_4 in the cloudy, marine case should be much faster due to the larger surface area of the droplets. This faster reaction time implies that the system has a fast response time in relation to changes in NH_3 (g) and NH_4^+ (p) concentrations within clouds. As a result, in clouds it is more likely for ammonia to be in equilibrium between the two phases. However, different compositions of droplets due to different growth rates as a function of size make it difficult to predict the overall behavior in detail.

3. Sampling and analysis methods for ammonia

The required detection limits to measure ammonia in the 5 phases are listed in Table 5. These values are based on the lowest reported concentrations of NH_3 and NH_4^+. Lower concentrations of ammonia may exist but have not been measured due to limitations of the methods used. Therefore, detection limits of at least an order of magnitude lower may be necessary. Methods that exist for the sampling and analysis of ammonia are listed in Table 6.

The first samples for analysis of gas phase

Table 6. *Summary of existing methods for measurement of ammonia (IC = ion chromatography)*

Phase/species	Methods of sampling and analysis	Detection limit	Sampling time	Interference constraints	References
Gas phase NH_3 (g)	Oxalic acid denuder IC	0.5 nmol m^{-3}	24-h flow rate = 3 lpm	NH_4^+ (p), evaporation of oxalic acid	Ferm (1979)
	WO_3 denuder/converter/NO_x detector	2.9 nmol m^{-3}	20-min flow rate = 1 lpm	Alkylamines	McClenny et al. (1982)
	Oxalic acid filter ring oven technique	2.8 nmol m^{-3}	200-min flow rate = 5 lpm	Absorption/desorption of NH_3 (g) on prefilter	Gillet and Ayers (1979)
	Fluorescence derivatization	4.5 nmol m^{-3}	2 min	Gaseous primary amines	Abbas and Tanner (1981)
	Photofragmentation laser-induced fluorescence	0.04 nmol m^{-3}	30 min	None known	Halpern et al. (1979)
	IR heterodyne radiometry	9.0 nmol m^{-3}	1 min	Does not detect small volume variability	Hoell et al. (1980)
	Long-path FTIR spectroscopy	90 nmol m^{-3}	10-min 1-km path-length	None known	Tuazon et al. (1978)
	Tunable diode laser absorption	4 nmol m^{-3}	1 min	None known	Reid et al. (1978)
Aerosol NH_4^+ (p)	Filter sampling			Reactions on matrix	Tanner et al. (1977)
	Teflon filters			None known	
	Diffusion sampling			Reactions during dissolution	Brosset and Ferm (1978)
	Wet chemical identification IC				
	Thermal analysis; flame photometry			No specidation between NH_4HSO_4 and $(NH_4)_2SO_4$ Qualitative	Huntzicker et al. (1978)
	Humidity and temperature controlled nephelometry	$0 < \frac{NH_4^+/SO_4^=}{\text{molar ratio}} < 2$ xs $SO_4^=$ (p) > 0.1 nmol m^{-3} NH_4^+ (p) > 0.03 nmol m^{-3}	15 min	Interferences of coexisting species yet to be defined	Larson et al. (1982); Vong (1985)

Table 6—*continued*

Phase/species	Methods of sampling and analysis	Detection limit	Sampling time	Interference constraints	References
	IR spectroscopy		12 hr	Qualitative	Blanco and McIntyre (1972)
	Laser Raman spectroscopy	3×10^4 nmol m^{-3}	20 min	Not portable Lacks sensitivity	Rosen and Novakov (1978)
Cloud NH_4^+ (c)	Liquid water collector IC			Samples are an average over a large volume	Mohnen (1980)
	Fog water collector				Pade (1985)
	Droplet to aerosol converter Nephelometer Condensation nuclei counter			Liquid phase composition assessed only via calculation	Ogren et al. (1985)
Rain NH_4^+ (r)	Bulk collector			Dry deposition	Galloway (1978)
	Wet/dry collectors				Galloway (1978)
	Wet collectors IC Ion specific electrode Colorimetry				
Ocean NH_3 (s) + NH_4^+ (s)	Bulk collection Colorimetry				Ayers and Gras (1980)

ammonia were collected by bubbling ambient air through an acidic solution (Junge, 1957; Tsunogai and Ikeuchi, 1968; Tsunogai, 1971). Since then, two sampling methods have been developed that are able to separate the gas and particle phases. One method employs a denuder tube to collect NH_3 (g) followed by a Teflon filter to collect NH_4^+ (p). The other method uses a tandem (i.e., series) filter arrangement. A Teflon prefilter is used to collect NH_4^+ (p) followed by an acid-coated paper filter to collect NH_3 (g).

The first denuder tube for collecting NH_3 (g) was developed by Ferm (1979). He used a 50 cm $\times$ 3 mm ID glass tube coated with 1.5% oxalic acid. The first 15 cm of the tube was left uncoated to promote laminar flow. Gras (1983) used this design for sampling NH_3 (g) in the Antarctic. He placed a 47 mm, 0.2 μm Fluoropore filter directly behind the tube to collect NH_4^+ (p). Phosphorus acid also has been used as a tube coating (Stevens et al., 1978) but because of its low deliquescence point is not as convenient as oxalic acid. A third coating, WO_3, has also been used (Braman et al., 1982; LeBel et al., 1985). The NH_3 (g) is thermally desorbed, oxidized to NO, and detected with a chemiluminescence analyzer.

Ayers and Gras (1983) used the tandem filter method to sample NH_3 (g) at Cape Grim, Tasmania. They used a pre-filter to separate out particles followed by an oxalic acid coated paper filter to collect NH_3 (g).

Both of these sampling methods have major disadvantages. Denuder tubes perform poorly at high and low relative humidities. At high RH, the coating tends to deliquesce and at low RH, the coating may volatilize. Sampling artifacts resulting from the use of the tandem filter method include adsorption and desorption of NH_3 (g) onto the Teflon prefilter.

Because of the low concentrations of NH_3 (g) and NH_4^+ (p) in the remote marine troposphere, it is necessary to collect samples over long periods of time. Sampling times should be shorter than the relevant meteorological time scale. For example, with diurnal meteorological or biological source variation, sampling times should be less than 12 h. In the future, it may be possible to make real-time measurements using spectroscopic or optical waveguide methods (Giuliani et al., 1983) thus avoiding long sampling times and possible sources of contamination. Vertical profiles of ammonia have been measured with an infrared heterodyne radiometer (Hoell et al., 1980) but the method does not appear to be sensitive enough yet to be used in the remote marine troposphere. Measurements of real-time NH_4^+ (p)/xs $SO_4^=$ (p) molar ratios have been made with the thermidograph as a compliment to filter sampling (Larson et al., 1982; Vong, 1985).

Ammonium in cloudwater has been sampled with various liquid water collectors (Mohnen, 1980). These samples have the disadvantage that they are averages over a large volume of cloudwater and droplet size. A droplet-to-aerosol-particle converter (Ogren et al., 1985) is able to size-segregate cloud droplets and assess the composition of aerosol particles within cloud droplets (Noone, pers. comm., 1986). Liquid composition must be inferred from calculation, however. Ideally, a liquid water collector and a droplet to aerosol particle converter should be used together to resolve the relationships between the phases and droplet size.

Ammonium in rainwater has been collected in bulk or with wet/dry collectors (Galloway, 1978). Bulk collectors sample both wet and dry deposition while wet/dry collectors segregate the two. Oceanic ammonium has been collected in bulk. With bulk samples, NH_3 (s) and NH_4^+ (s) are analyzed together (Ayers and Gras, 1980). It would be desirable to measure concentrations of NH_3 (s) separately since it is the species involved in the air/sea exchange of NH_3.

4. Conclusions

Measurements of the concentration of ammonia species have been attempted in the gas and particulate phases, in cloudwater, rainwater, and in the ocean in the marine troposphere. Rarely have any observations of different phases been made simultaneously. The lowest measured $(NH_3)_g$ values are consistent with measured $[\text{xs } SO_4^=]_p$ and $[NH_4^+]_p$ according to the theoretical model of Tang (1980). Simultaneous measurements of at least these three species as well as RH are needed to verify the model further. When the lowest $(NH_3)_g$ are combined with measured $[NH_3]_s + [NH_4^+]_s$ in equilibrium calculations, NH_3 appears to be in equilibrium between the

gas phase and the ocean surface. Separate measurements of $[NH_3]_s$ should be made to investigate whether or not this equilibrium exists. Scavenging calculations indicate that reported $[NH_4^+]_p$ and $[NH_4^+]_r$ data are consistent with each other and that rain is the major removal mechanism for ammonia from the marine atmosphere. The reported $[NH_4^+]_c$ data for the marine troposphere is not sufficiently plentiful to make possible comparisons between cloudwater and the other phases.

This review has shown that data exist for ammonia species in at least four of the five relevant phases shown in Fig. 2. An attempt has been made to check the internal consistency of these data using equilibrium calculations. A lack of agreement has demonstrated the need for improved sampling techniques, perhaps real-time measurement, and above all else, for simultaneous measurement of ammonia and all other relevant species in the 5 phases.

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