

Characteristics of Gas- and Particle-phase Acids and NH_3 at Urban and Rural Sites in Korea

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(Received 28 April 2004, accepted 27 July 2004)

Abstract

To study the characteristics of ammonia and the related compounds, atmospheric aerosols and gases were collected using a triple filter pack sampler, a low volume air sampler, and a three-stage Andersen air sampler in Seoul and Kangwha Island, Korea from Dec. 1996 to Oct. 1997. Ammonia concentrations showed approximately two times higher in summer than in winter at both sites. The highest HNO_3 levels were generally observed in summertime at two sampling sites. The average mass concentration of $\text{PM}_{2.5}$ in heavily industrialized Seoul was about three times higher than that of Kangwha. In winter, the sum of NH_4^+ and its counter ions (such as Cl^- , NO_3^- , and SO_4^{2-}) comprised 30–41% of $\text{PM}_{2.5}$ mass concentration at each sampling site. Temperature dependence of particulate nitrate was examined at the urban sampling site. The formation of the nitrate in the fine mode was dependent not only on the amount of precursors but also on the variation of temperature. $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 coexisted with NH_4NO_3 and NH_4Cl at each site. According to the summertime backward trajectory analysis, NO_3^- showed higher level with air parcels transported from northeast Asian continent. On the other hand, the concentration of SO_4^{2-} showed significantly higher level when air masses originated from Pacific Ocean, southern part of Japan, and Korea.

Key words : Ammonia, Fine particle, Temporal variation, Backtrajectory, $\text{PM}_{2.5}$

1. INTRODUCTION

Fine airborne particulate matter that is smaller than $2.5 \mu\text{m}$ in diameter is responsible for visibility

impairment and harmful health effects linked to chronic respiratory illness, cancer, and premature death (Eldering and Cass, 1996; White, 1986; Cass, 1979). Therefore numerous investigations about the species that are precursors to fine particle formation have been carried out (Pryor *et al.*, 2001; Johnson *et al.*, 1994; Cadle *et al.*, 1982). As a precursor of fine

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particles, ammonia is the only common alkaline gas in the atmosphere, and thus reacts rapidly with sulfuric and nitric acids, forming aerosols of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . NH_3 is emitted primarily from animal waste with a smaller proportion from fertilizer evaporation (Buisjman *et al.*, 1987). It is necessary to measure NH_3 in ambient air in order to understand the transformation of HNO_3 into particulate nitrate as well as the neutralization of atmospheric acidity ascribed to sulfuric acid. Because of these processes, it can be quickly removed from the atmosphere (Bassett and Seinfeld, 1983). In a polluted environment, the ammonium salts (i.e. NH_4NO_3 and NH_4Cl) account for 10–30% of the fine aerosol mass, and the total inorganic salts account for 25–50% of the fine aerosol mass (Gray *et al.*, 1986; Appel *et al.*, 1981). Aerosol nitrates are important contributors of visibility reduction in cities with photochemical air pollution problems. White and Robert (1977) estimated that aerosol nitrates were responsible for about 40% of the light scattering observed at Riverside in the east Los Angeles Basin. Stelson *et al.* (1979) postulated that these ammonium salts were in thermodynamic equilibria with their respective gas-phase counterparts, NH_3 , HNO_3 , and HCl . This assumption has been supported by ambient measurements, and the equilibrium constants for ammonium nitrate and ammonium chloride in the soil and aqueous phase have been calculated as a function of ambient temperature, relative humidity, and particle composition (Hildemann *et al.*, 1984; Bassett and Seinfeld, 1983; Stelson and Seinfeld, 1982; Tanner, 1982; Doyle *et al.*, 1979). Stelson and Seinfeld (1982) calculated the ammonia and nitric acid partial pressures over ammonium nitrate–nitric acid solutions accounting for nitrate, hydrogen and ammonium ion non-idealities. Their analysis showed the ammonia–nitric acid partial pressure product was sensitive to relative humidity but insensitive to pH (1–7). However, recent studies (Gaydos *et al.*, 2003; Koo *et al.*, 2003) pointed out problems with the accuracy of the equilibrium method to predict $\text{PM}_{2.5}$ nitrate concentrations. By comparison between the hybrid (using both the trajectory–grid method and an ODE

solver) and equilibrium method predictions with measurements at five locations in USA, Gaydos *et al.* (2003) reported that the equilibrium method predictions for PM_{10} and $\text{PM}_{2.5}$ mass were found to be similar to the hybrid method but the size distribution of ammonia and nitrate did not compare as well to measurements. As the problems of the equilibrium method, they pointed out that the equilibrium method was one-dimensional chemical transport method with a poor size distribution, particularly with ammonia and nitrate.

In this study, in order to characterize gas- and particle-phase acids and NH_3 at urban and rural sites in Korea, the simultaneous measurements of atmospheric particles and gaseous materials were made in heavily industrialized Seoul and at rural site on western coast of Korea Peninsula. In relation to the meteorological properties, the seasonal characteristics of ammonia and its related species at both sampling sites are discussed. Also, several attempts were made to investigate the property of ammonia and related species.

2. MATERIAL AND METHODS

2.1 Sampling locations

Field measurements were carried out simultaneously on the roof of a five-story building (15 m) of Kon-Kuk University (126° 58' E, 37° 34' E), Seoul and at the top of a tower (10 m) (126° 22' E, 37° 37' E) away about 100 m from sea shore, Kangwha, Korea from Dec., 1996 to Oct., 1997. As the capital city of South Korea, Seoul is located in the central western part of the Korean Peninsula. Seoul has a population of 10.6 million people in 605 km². The annual average temperature is 11.1 degrees Celsius in Seoul but its climate varies drastically with seasons due to monsoon. Annual rainfall is relatively high at 1,295 mm but the precipitation concentrated in summer from June to September. A major source of air pollution in Seoul is motor vehicles which is counted as about 2.5 million. Also, the triangle area which connects Seoul, Incheon, Suwon is one of large industrial zones in South Korea with

several satellite cities such as, Anyang, Puchon, and Uijonbu. Kangwha with 70,300 people is located at the west coast of Korean peninsula and is 45 km west from Seoul. As a mobile source, about 14,000 motor vehicles (diesel: 6,803, gasoline: 7,256) are in Kangwha. Also as a major NH₃ source, farmlands (rice field: 12,700 ha, dry field: 4,045 ha) and cattle shed (chicken yard: 984 ha, pasture land: 1,368 ha, pig pen: 2,107 ha) occupy 21,204 ha. But there is no major industrial NH₃ contributor such as combustion of lignite, NH₃ synthesis, and subsequent mineral fertilizer production near the both urban and rural sampling sites. Locations of both sampling sites indicated by filled circles are given in Figure 1.

2.2 Sampling and analysis

A triple filter pack sampler was used for the sampling of fine particles and gaseous materials at both sampling sites. It consists of a Teflon-coated aluminum cyclone with a cut size of 2.5 μm at a flow rate of 16.7 l min⁻¹ (URG, USA), a Teflon filter holder (Sarvillex, USA), and a critical orifice. In the

triple filter pack, Teflon membrane filters (Gelman, Zefluor) were used at the first stage to collect fine particles. This Teflon filters have been found to have minimum positive artifact with regard to sorption of gaseous species like HNO₃ and SO₂ (Appel *et al.*, 1981). Nylon filters (Gelman, Nylasorb) and 1% oxalic acid impregnated quartz fiber filters (Whatman, QM-A) were used at the second and third stages for acidic gases (HNO₃, HCl) and NH₃, respectively.

Though filter pack method is often used for the measurement of atmospheric components in the gas and particulate phase, both negative and positive interferences are possible with this filter pack method. Negative interference can be caused by losses of NH₃ to particulate matter collected on the prefilter. On the other hand, a positive artifact can result if NH₄NO₃ collected on the prefilter dissociates into NH₃ and HNO₃ due to a shift in the equilibrium (Appel *et al.*, 1981). However, this acid-impregnated filter pack method is still believed to provide a useful measure to the NH₃ concentration (Cadle *et*

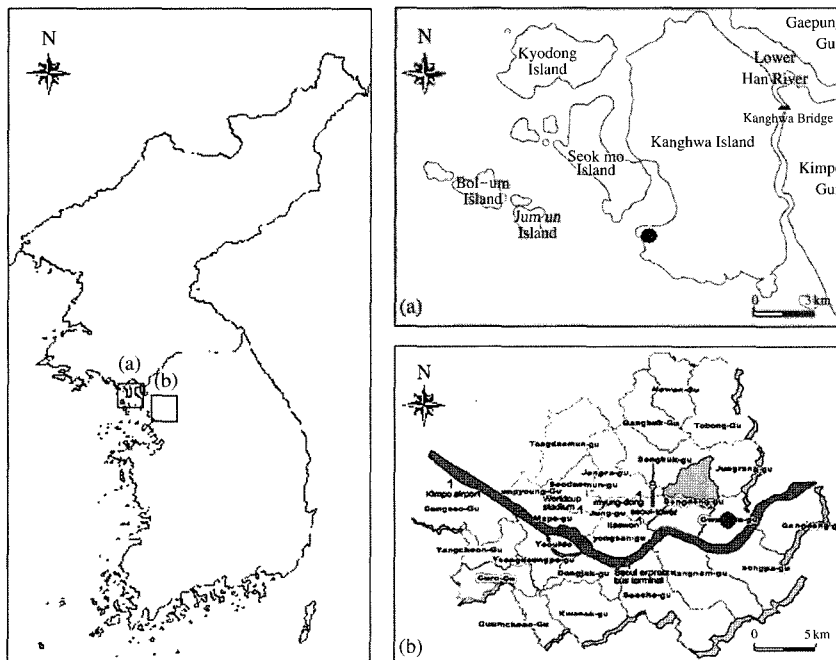


Fig. 1. Location of sampling sites. (a) and (b) are Kangwha and Seoul sampling sites, respectively.

al., 1982). In order to estimate the artifacts of filter pack method, Benner and Eatough (1991) conducted the comparison study of Annular denuder system (ADS) and filter pack collection of several gases and particulate materials in the Southwest desert in U.S. By this field study, they reported that comparisons between ADS and filter pack results were very good for gas-phase HNO_3 and total nitrate. This good agreement between the two sampling system for HNO_3 (g) results from most of the atmospheric nitrate being present as HNO_3 (g). This result suggests that the ratio of HNO_3 (g)-to-particulate nitrate in the sampled atmosphere can be minimized. However, for the particulate-phase nitrate concentration, correlation coefficient was not good with 0.709 due to the loss of HNO_3 (g) from particles collected in the filter pack.

In this study, filter pack sampler was used for the collection of acidic gases and NH_3 because of the restriction of simultaneous sampling at two sites. Furthermore to investigate the size-dependence characteristics of particles, low volume air sampler (PM_{10}) (Hitach, S2) and three-stage Andersen sampler (Kanomax, 3351) were used at urban site. The particle sizes of three-stage Andersen sampler are shown in Table 1. In this study, every sampler was operated once every week for 24 h. 12–14 samples were collected at each site in each season during sampling period. After sampling, all filters were placed in clean polyethylene petridishes. And then, after sealing with Teflon tape and wrapping with aluminum foil, all petridishes were refrigerated until analysis. Blank filters were handled in the same manner as the samples. The pretreatment of filters was carried out before analysis. Teflon filters were wetted by 0.5 ml ultra pure ethanol and were extract-

ed using an ultrasonicator with pure deionized water to analyze water-soluble ionic components. The oxalic acid impregnated quartz filters and nylon filters were extracted with 10 mL pure deionized water and 10 mL of IC eluent solution (1.8 mM Na_2CO_3 , 17 mM, NaHCO_3), respectively. Major water-soluble ionic components in the aqueous extracts were analyzed by IC (Dionex, DX-100). Also water extracts of nylon and oxalic acid-impregnated quartz filters were analyzed by IC for nitrate, chloride, and ammonium, respectively. Cations were analyzed using a CS 12 column, 22 mM MSA eluent solution and anions were analyzed AS 12A column, 1.8 mM Na_2CO_3 /17 mM NaHCO_3 eluent solution. The ranges of detection limits are 0.003–0.042 $\mu\text{g m}^{-3}$ for anions and 0.022–0.026 $\mu\text{g m}^{-3}$ for cation, respectively. Table 1 shows the information of sampler and analyzed components.

3. RESULTS AND DISCUSSION

3.1 Temporal variation

Seasonal mean concentrations of major water-soluble ionic components in fine particles, gaseous species, and mass of $\text{PM}_{2.5}$ are shown in Table 2. At Kangwha sampling site, NO_3^- concentrations showed the wintertime maximum and summertime minimum. Also, NH_4^+ concentrations were found to be similar seasonal variation. On the other hand, though the temporal variation of NO_3^- and NH_4^+ at Seoul is different from those of Kangwha, the maxima levels for two ions were still observed in wintertime. Though the detailed information like the emission inventory of gaseous materials such as NO_x , NH_3 and HNO_3 , the source profiles, and

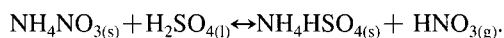
Table 1. The employed sampling apparatuses with their cut-off sizes and flow rates. The measured gases and ionic compounds are also listed.

Sampler	Particle size	Flow rate (l min^{-1})	Analyzed components	Sampling site
Triple filter pack	$\text{PM}_{2.5}$	16.7	NH_3 , HNO_3 , HCl , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^-	Seoul, Kangwha
Low-vol. air sampler	PM_{10}	20	NH_4^+ , SO_4^{2-} , NO_3^- , Cl^-	Seoul
Andersen air sampler	$11 \mu\text{m}^a$, $2.1 \mu\text{m}^a$, $0.08 \mu\text{m}^a$	28.3	NH_4^+ , SO_4^{2-} , NO_3^- , Cl^-	Seoul

^a 50% effective cut-off diameter

the local movement of air parcel around sampling sites are needed, the high atmospheric loading for pollutants was frequently observed in wintertime because of the large amount of pollutant emission from domestic heating and the characteristic wintertime meteorological condition like the low mixing height and the high atmospheric stability (Ma *et al.*, 2004). Moreover one of the possible reasons of the winter maximum for NO₃⁻ and NH₄⁺ can be explained by the fact that the fine particle nitrate is formed mainly by the homogeneous reaction between HNO₃ and NH₃ during the low temperature period of winter. In here, the formation of ammonium nitrate requires nitric acid and free ammonia and the formation reaction is favored at low temperature (night and winter) and high relative humidity.

The maximum HNO₃ levels were generally observed in summertime at both sampling sites, presumably due to the temperature dependence of NH₄NO₃ (HNO_{3(g)} + NH_{3(g)} ↔ NH₄NO_{3(s)}). In addition, greater HNO₃ is produced in the summer because of larger hydroxyl radical concentration (Danalatos and Glavas, 1999). Furthermore, HNO₃ can be released in the gas phase through the following reaction



The similar seasonal variation has been reported for HNO₃ in other sites: Patras, Greece (Danalatos

and Glavas, 1999), Athens (Kirkitsos and Sikiotis, 1991) and California (Solomon *et al.*, 1992). Atmospheric HNO₃ has a short lifetime and is removed by both wet and dry deposition. HNO₃ should originate much closer to the sampling site due to the short lifetimes of NO_x and HNO₃ (Logan, 1983). Therefore, though we have no definite information, a large amount of NO_x, which was emitted from transportation like ships and cars as well as unknown other local sources, can be responsible for the relatively high HNO₃ concentrations at rural site.

There was the winter maximum and summer minimum for chloride at both sites, too. As discussed earlier, this seasonal variation in fine Cl⁻ concentration can be equally explained in terms of the characteristics of seasonal pollutant emission and meteorological condition. In addition, the high volatility of ammonium chloride, which decomposes to gaseous NH₃ and HCl, can contribute the seasonal variation of HCl, too. The highest HCl concentration in summertime at the two sites can support this explanation. A similar seasonal variation in fine chloride concentration was observed during an aerosol study using dichotomous sampler in six U.S. cities (Spengler and Thurston, 1983).

Mass concentrations of PM_{2.5} were 32.4 μg m⁻³, 23.1 μg m⁻³, 16.1 μg m⁻³, and 19.8 μg m⁻³ in winter, spring, summer and fall, respectively, at Kangwha. The mass concentration of PM_{2.5} at Kangwha was about two times higher in winter than in summer.

Table 2. Concentration of major ionic components in fine particles (PM_{2.5}), gaseous species, and mass concentration of PM_{2.5} seasonally measured at Seoul and Kangwha sites.

Season	Site	Ionic components (μg m ⁻³)				Gases (ppb)			PM _{2.5} mass conc. (μg m ⁻³)	Temp. (°C)	R.H. (%)
		NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₃	HCl	HNO ₃			
Winter (96/12/13 -97/02/23)	Seoul	3.44 ± 1.53	3.46 ± 1.39	9.49 ± 1.96	7.27 ± 1.99	4.52 ± 1.05	0.24 ± 0.05	0.29 ± 0.11	79.19 ± 9.31	-4.8-8.0	35-63
	Kangwha	3.07 ± 1.12	0.43 ± 0.24	3.63 ± 0.31	6.06 ± 1.09	5.19 ± 0.86	0.12 ± 0.04	0.46 ± 0.14	32.43 ± 3.74	-4.3-6.5	50-75
Spring (97/03/01 -97/05/18)	Seoul	1.69 ± 0.59	0.79 ± 0.41	5.79 ± 1.21	10.53 ± 2.23	12.03 ± 1.22	0.65 ± 0.22	0.53 ± 0.18	77.26 ± 5.14	2.9-24.6	43-61
	Kangwha	2.16 ± 0.16	0.2 ± 0.04	1.76 ± 0.78	5.63 ± 0.72	9.89 ± 0.96	0.17 ± 0.05	0.36 ± 0.08	23.11 ± 2.05	2.3-21.0	48-68
Summer (96/07/12 -97/08/18)	Seoul	2.46 ± 0.85	0.69 ± 0.19	1.23 ± 0.33	3.78 ± 0.78	9.38 ± 1.33	1.64 ± 0.16	0.7 ± 0.31	45.01 ± 4.67	22.2-25.8	59-71
	Kangwha	0.51 ± 0.17	0.19 ± 0.06	0.46 ± 0.16	1.23 ± 0.33	9.91 ± 1.01	0.37 ± 0.21	0.64 ± 0.27	16.08 ± 2.32	21-26.1	69-85
Fall (97/09/29 -97/10/03)	Seoul	1.59 ± 0.62	2.39 ± 1.08	4.32 ± 0.54	8.28 ± 1.45	11.56 ± 2.99	1.44 ± 0.87	0.33 ± 0.16	59.15 ± 7.78	17.3-19.7	59-67
	Kangwha	2.55 ± 0.28	0.39 ± 0.58	1.76 ± 0.38	6.92 ± 0.96	7.04 ± 1.41	0.19 ± 0.06	0.15 ± 0.67	19.77 ± 2.47	15.1-17.3	71-73

And those in Seoul show the maximum value in winter and followed by spring, fall, and summer. The average mass concentration of PM_{2.5} in heavily industrialized Seoul was about three times higher than that of Kangwha. It is suggested that the high concentration of PM_{2.5} at winter in both sites is due to emission from domestic heating apparatus and the phase changes of gaseous materials to particulate ammonium. In winter (from December to February), the sum of ammonium and its counter ions such as Cl⁻, NO₃⁻, and SO₄²⁻ increased to 23.57 μg m⁻³ and 13.19 μg m⁻³ in Seoul and Kangwha, respectively. And they comprise 30–41% of PM_{2.5} mass concentration at both sampling sites. Stagnant air conditions occurring during cold days would, of course, result in the maximum concentration of fine particles.

Concentration of NH₃ is likely to be highly variable due to seasonal changes in natural sources and reaction with acidic species. Therefore, the results

from each site will be discussed in more detail below.

Figure 2 shows the seasonal variation of NH₃ and NH₄⁺ in Kangwha and Seoul, respectively. At Kangwha site, NH₃ concentration clearly showed the seasonal variation with significantly higher concentrations in the spring and summer periods compared to those in winter and fall times. On the other hand, the maximum value of NH₃ is shown in springtime and followed by fall, summer, and winter at Seoul site. The NH₃ concentrations were approximately two times higher in summer than in winter at both sites. The reason for high NH₃ concentration in summer may be the phase change from NH₄NO₃ to NH₃ and NO₃⁻ and activity of bacteria that contribute to NH₃ generation in soil. And high concentration in springtime is due to increasing soil emission and fertilizer volatilization (Cadle *et al.*, 1982). And the seasonal varia-

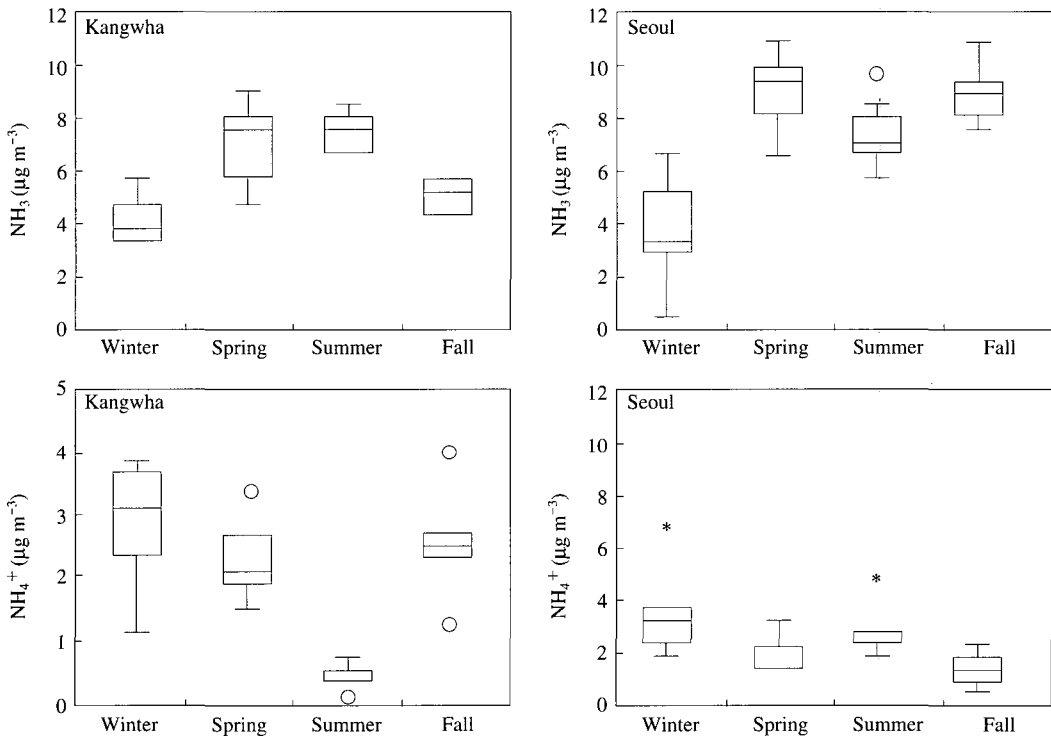


Fig. 2. Seasonal variation of NH₃ and NH₄⁺ at Kangwha and in Seoul. The rectangle, top bar, bottom bar, circle and asterisk represent case of 50%, maximum, minimum, outlier and extreme data, respectively.

tion pattern of NH₃ concentration in Seoul was different from that of Kangwha. This different pattern of seasonal variation at both sites can be explained by NH₃ generated by human activity and vehicles at metropolitan city. In previous study, similar seasonal variation of NH₃ concentration in metropolitan city of northeast America was reported (Möller and Schieferdecker, 1985). Though there is a wide range of emission rates for vehicle sources NH₃, NH₃ emissions from vehicles may be greater than the current emission inventory (Geertler *et al.*, 2002; Kean *et al.*, 2000; Moekli *et al.*, 1996). Also in recent, Chitjian *et al.* (2000) reported that NH₃ emission from vehicle sources are the third-largest source and account for ~18% of the inventory in the South Coast Air Basin, which include Los Angeles and the surrounding metropolitan area. There was a tendency towards relatively higher NH₃ concentration in spring and fall seasons than summer. Unfortunately, with the exception of the episodic local emission event, it is difficult to fully understand the higher NH₃ level in falltime for lack of reliable inflow information. With respect to the high concentration of springtime NH₃, one of possible reasons might be that the inflow of NH₃ generated in the suburbs farmlands of Seoul highly affected the high concentration in spring.

Seasonal variation of NH₄⁺ concentration at Kangwha were 3.07 µg m⁻³, 2.16 µg m⁻³, 0.51 µg m⁻³, and 2.55 µg m⁻³ in winter, spring, summer and fall, respectively. As might be expected, there was a tendency towards higher concentration in the wintertime sample. Average concentration of NH₄⁺ falls right down to the lowest point in summertime. This result might be caused by volatilization of particulate ammonium salt to gaseous NH₃ in summer because of the higher temperature. Though in order to diminish the effect of precipitation, the sampler was not operated in rainy day, the scavenging of particulate components including ammonium can be more frequently occurred through the full summer season. The average rainy days per season are 28 days in summer and 7 days in winter. Unlike Kangwha, the temporal variation of NH₄⁺ concentration is not shown in Seoul. Also there is no

marked decrease in the concentration NH₄⁺ in summertime at Seoul sampling site.

As mentioned above, by the field measurements at coastal site (Danalatos and Glavas, 1999) and urban sites (Solomon *et al.*, 1992; Kirkitsos and Sikiotis, 1991), many researchers reported that seasonal variation with higher concentrations in the summer was observed for nitric acid. Also a similar significantly higher value in the summertime for ammonia and particulate ammonium was mentioned in the coastal site study by Danalatos and Glavas (1999). Though the summertime maximum for nitric acid shows the good agreement with the result of this study, the different seasonal variations for ammonia in Seoul and particulate ammonium in Seoul and Kangwha were shown in this study. Therefore the seasonal trends of these species would be expected to be affected by the transformation of gaseous materials into particulate salts as well as the various factors such as characteristic local sources and long-range transportation for long-lived species.

3.2 Characteristics of nitrate

For the purpose of estimating the temperature dependence of particulate nitrate, the concentration ratios of particulate nitrate (C_{Fn} ≤ 2.1 µm) + C_{Cn} (≥ 2.1 µm), fine particle nitrate (C_{Fn}) and coarse particle nitrate (C_{Cn}) to total nitrate (C_{Fn} + C_{Cn} + C_{Gn} (gaseous nitrate)) are plotted in Figure 3. Unfortunately this temperature dependence of particulate nitrate was examined only at urban sampling site. Because size-segregate aerosol samplings using Andersen air sampler were not performed by at Kangwha sampling site. As shown in Figure 3 (a), the ratio of nitrate in fine mode to total nitrate decreased remarkably when temperature increased. It might be that nitrate in the fine mode was volatilized to HNO₃ with increasing of temperature. While on the other, there was no change in the ratio of coarse mode nitrate to total nitrate with the temperature and it led a slight decrease in the ratio of particulate nitrate to the total nitrate with the temperature. NH₃ mediated interplay between HNO₃ and aerosol nitrate appears to involve the fine particle nitrate, with the coarse particle nitrate

involved very little if at all. The probable explanation is that the fine nitrate was NH_4NO_3 as intimated above, connected with HNO_3 through reversible NH_4NO_3 dissociation, while the coarse particle nitrate comprised not only NH_4NO_3 but also NaNO_3 formed by reaction of HNO_3 with sea-salt NaCl (White and Robert, 1977). Fine nitrate predominated with high HNO_3 and low sea-salt concentrations. It is generally concluded that coarse particle nitrate is associated with alkaline particulate material such as sea-salt or soil dust. It seems to be generally agreed that the fine nitrate in Seoul exists predominantly as NH_4NO_3 from reaction of HNO_3 with NH_3 , while coarse particle nitrate results from HNO_3 reaction with pre-existing soil and sea-salt particles.

Matsumoto and Tanaka (1996) investigated the formation and dissociation of atmospheric particulate nitrate and chloride. They introduced an *Y*-value. It is defined as the logarithm of the concentration product of the total nitrate (sum of gaseous and particulate nitrates) and excess ammonia beyond that necessary for the complete neutralization of sulfuric acid. This *Y*-value can be regarded as the amount of precursors potentially capable of generating particulate ammonium nitrate. The excess is calculated by subtracting the ammonium equivalent of sulfate in the fine mode ($(\text{NH}_4)_2\text{SO}_4$) from the total ammonium. *Y*-value is defined by the

following equation.

$$Y\text{-value} = \log [C_{GN} + C_{PN}] [C_{GA} + (C_{PA} - C_{FS} \times (36/96))] \quad (1)$$

where, C_{GN} is the concentration of gaseous nitrate, C_{PN} is the concentration of particulate nitrate in fine mode, C_{GA} is the concentration of gaseous ammonia, C_{PA} is the concentration of particulate ammonium in fine mode, C_{FS} is the concentration of sulfate in fine mode, $C_{PA} - C_{FS} \times 36/96$ is the excess ammonia.

To evaluate the relationship between precursors such as gaseous nitrate, particulate nitrate, gaseous ammonia and particulate ammonium, and amount of ammonium nitrate, *Y*-value was calculated from urban sampling data.

In Figure 4, the various sizes of circles indicate the concentration ratios of nitrate in fine mode to total nitrate (the sum of fine, coarse and gaseous nitrate) according to the legend. As shown in the figure, the size of circles gradually decline in proportion to the increasing of temperature. On the other hand, there is a marked increase in the size of circles attendant upon the increasing of the *Y*-value. As a consequence, although more detailed information on the source profiles and meteorological conditions are desirable, the formation of the nitrate in fine mode was dependent on the amount of the precursors (*Y*-value), which could potenti-

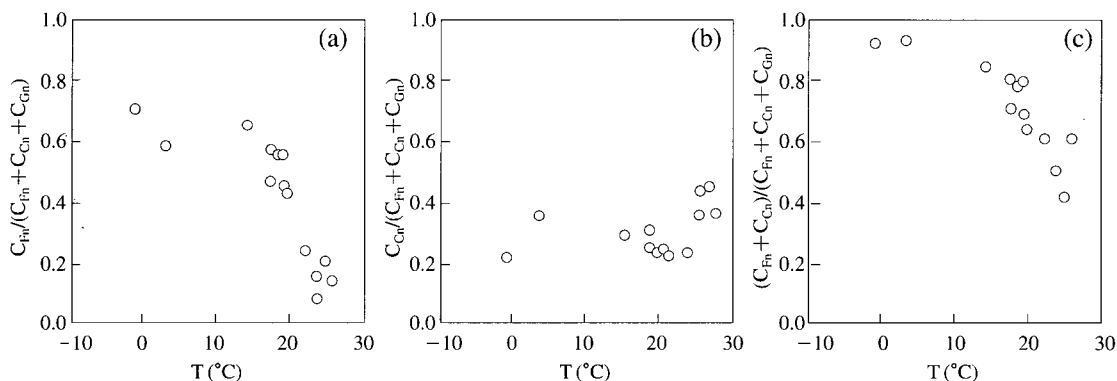


Fig. 3. Temperature dependence of the concentration ratio of fine mode nitrate (a), coarse mode nitrate (b), and particulate nitrate (c) to total nitrate. C_{Fn} , C_{Cn} , and C_{Gn} mean the concentration of fine mode nitrate, the concentration of coarse mode nitrate, and the concentration of gaseous nitrate, respectively.

ally generate ammonium nitrate. Simultaneously this Y-value can be subjected to the change of the temperature, which effects on the phase change of fine mode nitrate. Also it is generally concluded that the nitrate in coarse mode is associated with alkaline particulate materials such as sea salt and soil dust.

Furthermore, we evaluated the existence forms of ammonia at both sites. Though NH₄⁺ and SO₄²⁻ can exist in all proportions; $0 \leq [\text{NH}_4^+]/[\text{SO}_4^{2-}] \leq 2$, it seems reasonable to suppose that main existence forms of ammonium sulfate can be classified into two types such as (NH₄)₂SO₄ and NH₄HSO₄ in the ambient air. Therefore we adopted two assumption as follows.

Assumption [1] : combined forms of NH₃ were NH₄Cl, NH₄NO₃, and (NH₄)₂SO₄

Assumption [2] : combined forms of NH₃ were NH₄Cl, NH₄NO₃, and NH₄HSO₄

On the assumption [1], NH₄⁺ concentration was theoretically calculated by $[(\text{Cl}^- \text{ conc.} \times \text{NH}_4^+ \text{ M.W.}) + (\text{NO}_3^- \text{ conc.} \times \text{NH}_4^+ \text{ M.W.}) + (\text{SO}_4^{2-} \text{ conc.} \times 2\text{NH}_4^+ \text{ M.W.}) / \text{SO}_4^{2-} \text{ M.W.}]$. While on the other hand, on the assumption [2], NH₄⁺ concentration was theoretically calculated by $[(\text{Cl}^- \text{ conc.} \times \text{NH}_4^+ \text{ M.W.}) / \text{Cl}^- \text{ M.W.}] + (\text{NO}_3^- \text{ conc.} \times \text{NH}_4^+ \text{ M.W.}) / \text{NO}_3^- \text{ M.W.}] + (\text{SO}_4^{2-} \text{ conc.} \times \text{NH}_4^+ \text{ M.W.}) / \text{SO}_4^{2-} \text{ M.W.}]$. In here, conc. and M.W. mean concentration and molecular weight, respectively.

Theoretically predicted concentrations of ammonium based on the above two assumptions were compared with those of actually measured in this work. Figure 5 shows the plots of calculated ammonium concentration vs. measured ammonium concentration. There was slight difference of determination coefficient between Assumption [1] and Assumption [2] in both sites. This result indicates that (NH₄)₂SO₄ and NH₄HSO₄ coexisted with NH₄NO₃ and NH₄Cl at both sites. Gaseous ammonia easily reacts with sulfuric acid, which abundantly exists in the atmosphere, and forms ammonium bisulfate by following reaction: H₂SO_{4(l)} + NH_{3(g)} → NH₄HSO_{4(s)}. If the excess NH₃ exists, ammonium bisulfate reacts with NH₃ and forms ammonium sulfate by the following reaction: NH₄HSO_{4(s)} + NH_{3(g)} → (NH₄)₂SO_{4(s)}. Hence, the good correlations between the calculated ammonium concentration and the measured ammonium concentration at the Assumption [1] and [2] in both Seoul and Kangwha suggest that ammonia gas was continuously reacting with sulfuric acid and ammonium bisulfate during our measurement periods at both sampling sites. Moreover, as pointed out earlier, since ammonium bisulfate can be released through the reaction between sulfuric acid and ammonium nitrate, the correlations in Figure 5 might be affected by this ammonium bisulfate.

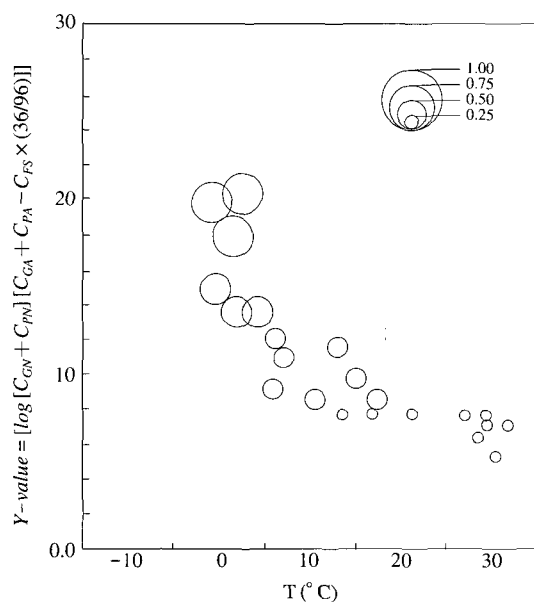


Fig. 4. Effect of Y-value and temperature on the concentration ratio of fine mode nitrate to total nitrate. The various sized circles indicate the ratios of fine mode nitrate to total nitrate according to the legend.

3.3 Backtrajectory analysis

Over the past few decades a considerable number of studies have been made on the effect of pollutants emitted from China continent on East Asia and Pacific Basin (Ma *et al.*, 2001a., Wang *et al.*, 2000; Chung, 1992; Duce *et al.*, 1980). Because these

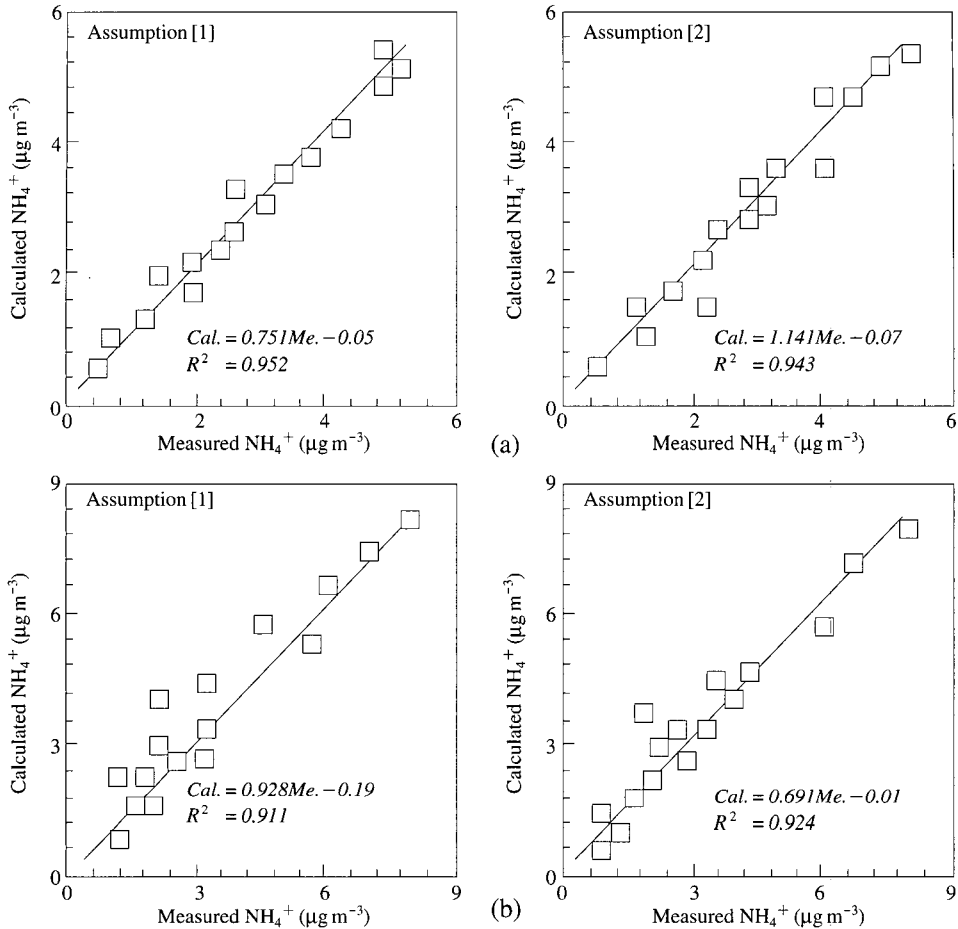


Fig. 5. Comparison between calculated and measured ammonium concentrations at Kangwha (a) and in Seoul (b).

natural and artificial pollutants have led to the significant environmental change in the receptor areas (Lin, 2001; Ma *et al.*, 2001b; Song and Carmichael, 1999). In this study, based on backward trajectory analyses of air parcel that arrived at our Kangwha sampling site, the concentrations of aged particle components were compared. To study long-range transport of pollutants one cannot neglect the pollutant's lifetime, meteorological condition, and the origin of the air masses that arrived at receptor site. Considering the short lifetime of NH₃ and HNO₃, particulate nitrate and sulfate as a long-lived species with a lifetime about a week-ten days (Luria *et al.*, 1996; Danalatos and Glavas, 1999)

would be expected to be affected by long-range transport. The examples of backward trajectories for air parcels that arrived at our Kangwha site calculated from National Oceanic Atmospheric Administration (NOAA, <http://www.arl.noaa.gov/ready/hysplit4.html>) are shown in Figure 6. The concentrations of atmospheric pollutants have strong seasonal variation because of different meteorological conditions and human activities such as domestic heating, biomass combustion, agricultural affairs, etc. It can therefore be suggested that a pair of air parcels with different route in the same season can be reasonably compared. The nearly all of prevailing winds in springtime were originated from

China during the springtime measurements. Also we did not find the ideal cases in the fall and winter sampling durations. Hence, the summertime data were compared to estimate the effect of different path of air parcels. The concentrations of NO₃⁻ and SO₄²⁻ at Kangwha when air parcels were coming from northeast Asian continent were higher than those of other summertime. Especially, NO₃⁻ shows roughly two times higher concentration (0.9 μg m⁻³) than summertime average (0.46 μg m⁻³). Also higher SO₄²⁻ concentration on northwesterly wind days may indicate that a significant amount of SO₂ emitted from combustion of fossil fuel in China converted to nss-SO₄²⁻ during the long-range transport. On the other hand, when air masses were originated from Pacific Ocean, southern part of Japan, and Korea, the concentration of SO₄²⁻ (3.45 μg m⁻³) shows significantly higher (about three times) levels than that of summertime average (1.23 μg m⁻³). These remarkably higher levels of SO₄²⁻ concentration may be formed by photochemical reaction of SO₂ emitted from the large-scale industrial zones in South Korea. Though to mention the photochemical reaction of SO₂, one have to consider the detailed information such as SO₂ concentration,

atmospheric humidity, and intensity of UV rays, about half of SO₂ emitted from sources is oxidized in the plume of ambient atmosphere to sulfuric acid aerosols or sulfate by reactions occurring in the gas phase, in the liquid phase, and on the aerosol surface (Finlayson-Pitts and Pitts, 1986). Oceanic emissions of dimethyl sulfide (DMS: CH₃SCH₃) are known to be a major primary source of natural sulfur in the remote marine atmosphere (Shon *et al.*, 2001; Bates *et al.*, 1987). Though at present, the efficiency with which DMS forms SO₂ is still problematic, one of its oxidation products, SO₂, is known to be a major precursor of sulfate aerosol (Shon *et al.*, 2001). Though the limited number of case was compared, it can be thought that one of possible reasons for high level of SO₄²⁻ concentration at Kangwha sampling site when air masses were originated from Pacific Ocean is SO₂ originated from DMS in the remote marine area and known to be a fine mode sulfate aerosol. From their summertime study at the region of Yellow Sea (between Korea and China), Zhang *et al.* (2001) reported that the sea and regional originated aerosols become dominant fraction in coastal atmosphere in summer when the dust storms are expired in source region and southeast monsoon

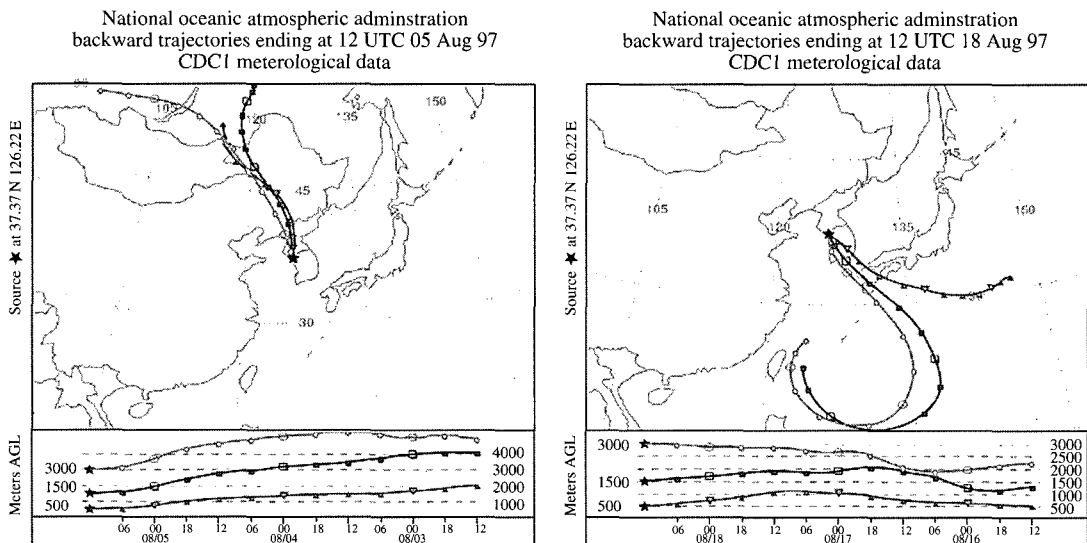


Fig. 6. Examples of backward trajectories for air parcels that arrived at our Kangwha site calculated from NOAA (NOAA, <http://www.arl.noaa.gov/ready/hysplit4.html>).

starts in the Pacific Ocean.

4. CONCLUSIONS

The regional and seasonal characteristics of ammonia and its related species that simultaneous measured at urban and rural sites, Korea were discussed. Also, several attempts were made to investigate the property of gas- and particle-phase acids and ammonia. Concentration of NH_3 is likely to be highly variable due to seasonal changes in natural sources and reaction with acidic species. The characteristics and origins of airborne particles in Seoul and Kangwha seem to be very variable with season on account of domestic heating in winter, increasing soil emission and agricultural affairs in spring, and volatilization and photochemical reaction in summer. The ratio of nitrate in fine mode to total nitrate showed the strong temperature dependence. The existence forms of ammonium at both sites were determined by the intercomparison between theoretically predicted concentrations of ammonium salts and those of actually measured. By means of backward trajectory analysis, the concentrations of aged particle components were discussed. Though the significant differences between previous studies and this work for the characteristics and behaviors of ammonia and related components were not found, the obtained results from this study should be helpful to better estimation of the atmospheric environment in the East Asia.

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