A Preliminary Analysis of Chemical Characteristics of Atmospheric Pollutants and Their Deposition Budget on the Fu-shan Forest in Taiwan

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ABSTRACT

This paper presents the chemical characteristics of atmospheric pollutants measured at the Fu-Shan forest (620 m MSL) during two two-weeks field experiments held in the summer and winter of 1993. Chemical compositions of these atmospheric pollutants in solid, gaseous and liquid phases were analyzed. The deposition budget of S and N compounds through dry and wet deposition pathways were particularly assessed. As a result, aerosol mass spectra were found to be bimodal, having the 50% cut size < 1.0 μm and around 3.2 μm for fine and coarse modes, respectively. In summer, fine and coarse modes were primarily composed of ammonium sulfate and nitrate, respectively. But, in winter the coarse mode was dominated by sea salts due to the influence of northeast monsoon flows. Our average HNO_2 (~ 0.10 ppb) was appreciably higher than those observed in clean troposphere, whereas HNO_3 was at a comparable level. Meanwhile, ammonia gas and particulate ammonium were at a lower concentration level compared with those generally observed on the continental grounds. The SO_2 (< 1 ppb) was comparable with those frequently observed in the free troposphere, while SO_4^{2-} was close to the lowest level typically obtained in urban areas. In addition, NO_3^- which is thought to be associated with local pollution was limited. Therefore, we believe that excessive SO_4^{2-}, to a larger extent, was transported to the site via long-range transport, particularly in winter. With regard to the deposition budget, wet deposition pathway (>

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90%) was the most effective mechanism for delivering atmospheric S and N compounds to the Fu-Shan forest during the periods of our field experiments.

(Key words: Dry deposition, Wet deposition, Sulfate, Nitrate, Aerosol particle)

1. INTRODUCTION

The importance of atmospheric inputs onto an ecosystem depends on their net fluxes and duration of existence. They can become either harmful pollutants or vigorous nutrients. For instance, most unpolluted terrestrial environments are N-limited (Vitousek and Matson, 1988). In nature, primary productivity is partially controlled by the amount of N which is made through soil microbial processes, mineralization and immobilization. The input of anthropogenic N through various atmospheric processes has the potential to alter the natural balance of many ecosystems. Although a small increase in N deposition can produce a moderate increase in productivity, excessive N loading may have several adverse effects on both ecosystem health and water quality (Ollinger et al., 1993). In a forest ecosystem, high N deposition can increase foliar N concentrations and decrease foliar Mg and Ca concentrations, possibly resulting in foliar imbalances or a loss of forest hardness (McNulty et al., 1991). Therefore, assessing the total atmospheric N deposition is particularly important for understanding the dynamics of nutrient cycling and of the entire N budget for a forest ecosystem.

Based on measurement data collected during July 12-23, 1993 (hereafter, this period is denoted as "P1"), and December 24, 1993-January 5, 1994 (hereafter, this period is denoted as "P2") at the Fu-Shan Forest, this paper focuses on investigating the exposure of the Fu-Shan forest to atmospheric pollutants, as well as on estimating deposition fluxes of above pollutants on this forest and, subsequently, determining relative contribution of various deposition pathways to total deposition budget.

The Fu-Shan site (24°46'N and 121°43'E) is located in the Fu-Shan Research Station of the Taiwan Forest Research Institute (TFRI) in northern Taiwan, as illustrated in Fig. 1. The Station is about 25 km away from the nearest urban area. There are no heavy industries, just agriculture and fisheries in the surrounding region. The site is about 620 m in elevation and its surrounding area of around 1100 ha has been preserved as a natural conservation zone for animals and forests. In the Fu-Shan forest, about 90% of the total area exceeds 600 m in elevation. The highest elevation is 1419 m. Inside the Station, a natural garden for plants, the first one of its kind in Taiwan, has been managed. This area is largely forested by chinkapin, red machilus, yellow basket willow, Chinese meliosma, litsea, narrow leafed oak, gold colored neolitsea and *Pyrenaria* shinkoensis (King and Hsia, 1997).

The Station is bathed in warm and humid weather conditions in summer, but experiences cool and wet northeast monsoon flows in winter. The temperature at this site ranges between 12 and 27 °C with a mean value of 19 °C (King and Hsia, 1997). The annual rainfall is about 3300 mm, and the relative humidity is above 75% all the year round, having a mean value of 88%. It is noted that mountain-valley circulations were frequently observed during the experi-
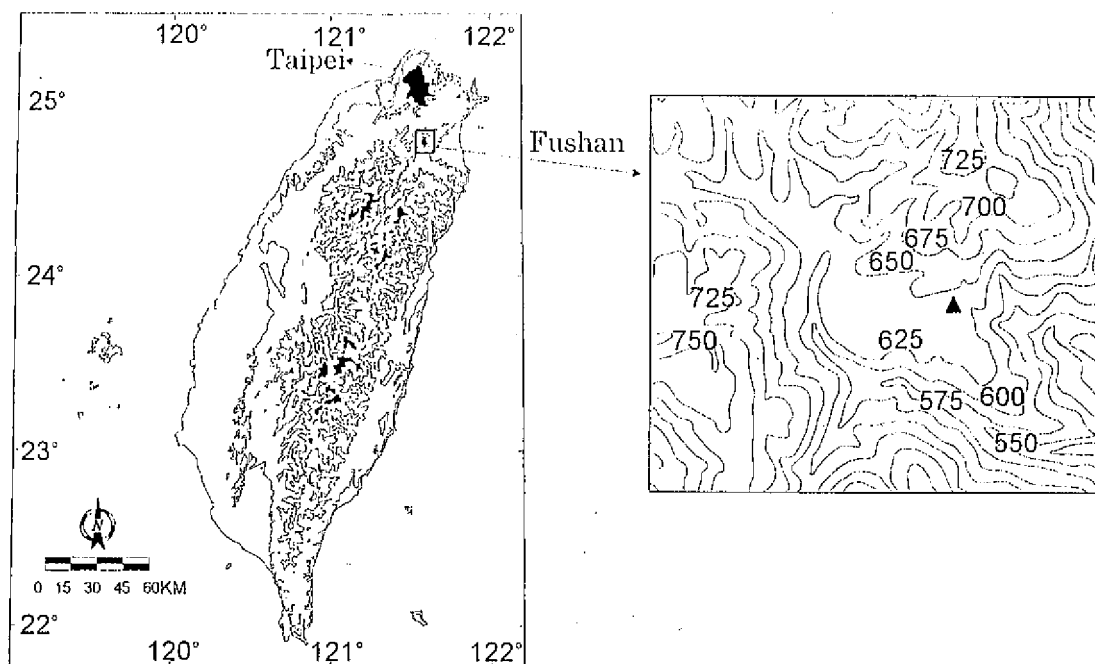
Fig. 1. Location and topography of the Fu-Shan site. The "▲" marks the site.

mental periods. Easterly winds prevail during the daytime period, generally traveling through the valley along an east-west direction. In summer, the weather is primarily dominated by the Pacific high. Warm and humid airmasses typically intrude into the region along the outflow of the high pressure system. Afternoon thunderstorms in the mountain areas frequently occur due to local convections. In winter, cool and wet northeast monsoon flows prevail in region, generally enriched by marine aerosols and sulfates (Lin et al., 1999).

Table 1. lists the parameters measured and instruments utilized in this work. Aerosol particles (AP) were collected using the Micro-Orifice Uniform Deposit Impactor (MOUDI, see Marple et al., 1991). The pressure drop of MOUDI was routinely checked and manually maintained at a certain level based on their calibration curves. The MOUDI consists of eight stages for collecting particles with aerodynamic diameters of 50% cut points ranging from 0.185 to 10 μm (as shown in Fig. 2). The first stage after inlet and last stage after filter collect AP between 10 and 18 mm and AP < 0.185 μm, respectively. In consideration of relatively clean air in the mountain environments, the samples were taken on a 48-hour basis during summer measurements, compared with 24-hour or less sampling time which is often adopted in urban areas. In winter, the sampling duration was shortened to 24 hours since the summer measurements suggested an affordability of analytical techniques.

Gaseous pollutants including nitrous acid (HNO_2), nitric acid (HNO_3), sulfur dioxide (SO_2) and ammonia (NH_3) were collected using the annular denuder of four tubes (Perrino et al., 1990). A flow rate of 10 l min^{-1} was adopted. The samples were mostly taken on a 24-hour basis except for the first run of 48-hour sampling on July 13, 1993.

Table 1. Parameters measured and instruments used at the Fu-Shan site during
P1 (summer) and P2 (winter).

Parameter	Instrument
Meteorological measurements	
Wind speed	Handar-555 portable meteorological tower
Wind direction	
Air temperature	
Barometric pressure	
Relative humidity	
Solar radiation	
Precipitation	
Sample collection	
Liquid phase	
Rain water	Acid Precipitation Sampler Model-APS
Solid phase	
Particle mass spectrum	MSP MOUDI
Gaseous phase	
NH_3, HNO_2, HNO_3 and SO_2	Annular denuder
Chemical analysis	
pH	Electrode probe
Anion	Ion Chromatography
Cation	Ion Chromatography and Atomic Absorption Spectrometry

Rainwater was collected on a daily basis utilizing the wet/dry collector (Acid Precipitation Sampler-Model APS) which is identical to the one deployed by the USA National Atmospheric Deposition Program/National Trends Network (NADP/NTN). The TFRI was responsible for rainwater collection. The rainfall amount was recorded using a conventional tipping bucket gauge.

The above collected samples in three phases were chemically analyzed. Rainwater samples were analyzed for concentrations of Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}. The H^+ concentration was converted from the pH of rainwater. The samples collected by annular denuder were analyzed to determine the concentration levels of gases NH_3, HNO_2, HNO_3, and SO_2. Ion compositions of water soluble aerosol particles collected by MOUDI were analyzed
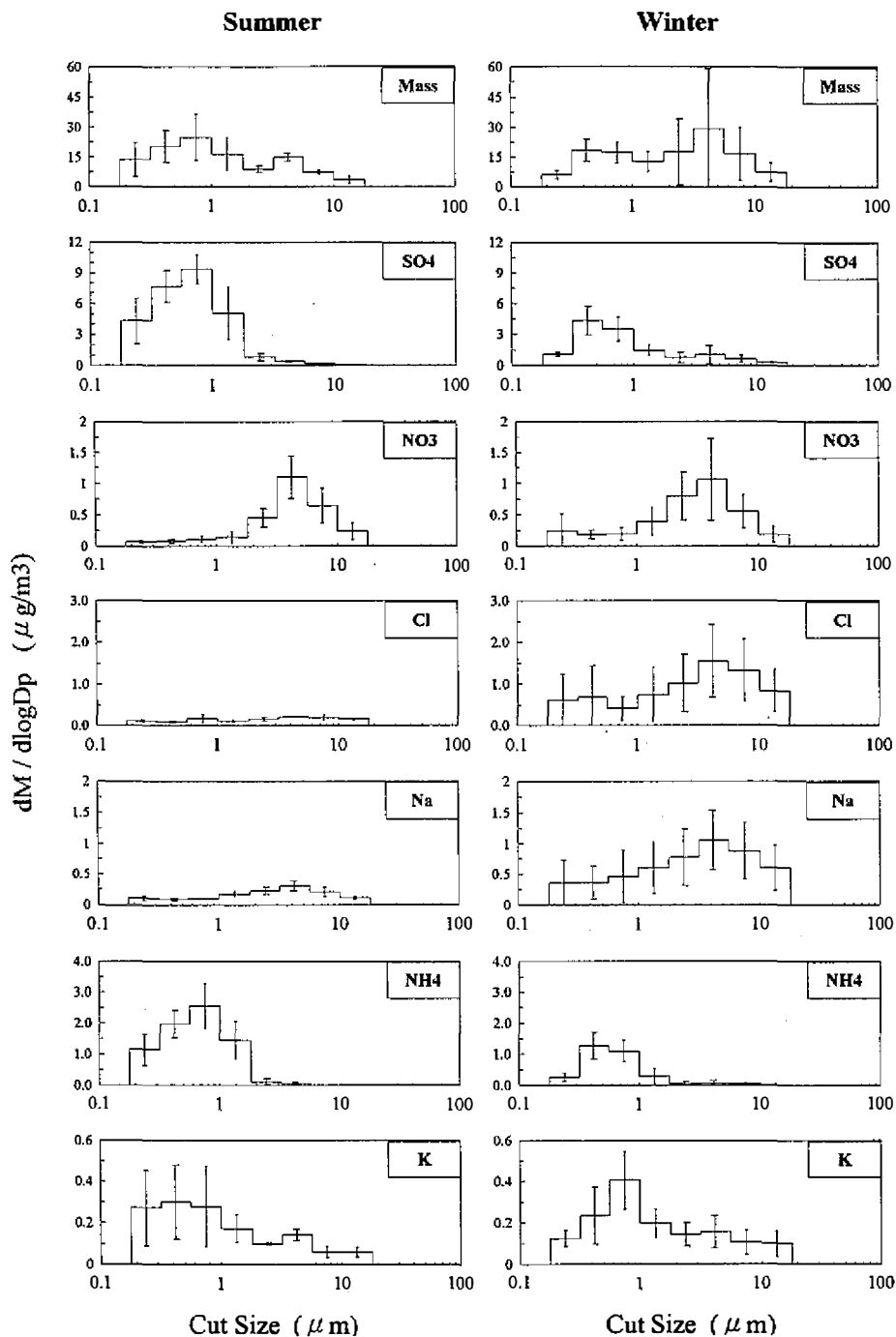
Fig. 2. Average mass spectrum of aerosol particles and corresponding water soluble compositions collected at the Fu-Shan site during P1 (summer) and P2 (winter).

for Cl⁻, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, Na⁺ and K⁺. Detailed analytical procedures are not given here since they are generally common.

2. AEROSOL PARTICLES

The aerosol particles (AP) with a cut size ≤10 μm are categorized as PM_{10}. They are further divided into FP (Fine particle) and CP (Coarse particle) with the cutting diameter at 2.5 μm as conventionally used. However, the MOUDI does not have a clear cutting point at 2.5 μm. Hence, aerosols with cutting diameters less than and greater than 2.5 μm are attributed to FP and CP, respectively. Detailed discussion is given below.

2.1 Aerosol Mass Spectra

Figure 2 depicts the average mass spectra of AP and their water-soluble ions, as annotated in the legends, over the entire sampling periods P1 and P2. Evidently, the bimodality in AP mass concentration can be found. The modes of FP and CP were at the diameters < 1.0 μm (0.56 and 0.32 μm during P1 and P2, respectively) and 3.2 μm, respectively. During P1, average mass concentration of the fine mode (6.27 μg m⁻³) was 74% higher than that of the coarse mode (3.60 μg m⁻³). The fine mode mostly consisted of ammonium sulfate (see Fig. 2), indicating a possible influence of local production of ammonia. By contrast, the coarse mode was largely composed of nitrate salts. However, the average mass concentration of water-soluble ions for the fine mode (3.16 μg m⁻³) was approximately six times that for coarse mode (0.56 μg m⁻³). These undetermined compositions of coarse particles may be attributed to crustal materials from natural processes (Seinfeld, 1986). But, the fine particles of high solubility to water were mainly the secondary products (e.g., SO_4^{2-}). Unlike the results of summer measurements during P1, average mass concentration of the fine mode (4.46 μg m⁻³) was about 63% of that of coarse mode (7.07 μg m⁻³) for winter measurements during P2. This contrast can be attributed to the abundance of sea salts in the coarse mode, as illustrated in Fig. 2. Obviously, wintertime northeast monsoon flow brought higher marine aerosols to our site. Still, ammonium sulfate in fine mode during P1 was more than twice that during P2, indicating a relatively lower formation rate of fine particles in winter due to colder temperatures.

2.2 PM_{10}

Table 2 lists average mass concentrations of chemical compositions for FP, CP and PM_{10} during P1 and P2. During P1, PM_{10} ranged from 16.2 to 43.1 μg m⁻³ (which is not shown in Table) with an average of 29.1 μg m⁻³. As to the chemical composition of aerosol particles, the water soluble ions including Cl⁻, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, Na⁺, and K⁺, weighed 11.2±2.3 μg m⁻³ (mean ± standard deviation), accounting for 40.2±6.1% of PM_{10} mass. Meanwhile, SO_4^{2-} alone can account for 66.1±0.8% of total ions. The secondary ion was NH_4^+ (17.2±0.8%), followed by NO_3^- (6.6±0.9%). The SO_4^{2-} contributed about 10 times the NO_3^- to PM_{10} mass. Sea salts, including Cl⁻ and Na⁺, were only 3.0±0.6% and 3.3±0.5% of total ions, respectively. Potassium was at about the same level as sea salts. The above results indicated that SO_4^{2-}

Table 2. Average mass concentrations of FP, CP and PM_{10}, as well as the water-soluble ion compositions and their fractions of total ions, collected by MOUDI at the Fu-Shan site during P1 and P2 (Unit: $\mu g\ m^{-3}$).

Season		mass	ION[*]	Cl⁻	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+
P1 (*Summer observations*)										
FP	$\mu \pm \sigma$	22.82 ± 8.75	10.07 ± 2.15	0.18 ± 0.03	0.03 ± 0.03	0.23 ± 0.03	7.19 ± 1.52	1.91 ± 0.48	0.20 ± 0.02	0.33 ± 0.16
	% of ION			1.9 ± 0.4	0.3 ± 0.3	2.4 ± 0.6	71.4 ± 0.6	18.8 ± 0.8	2.1 ± 0.4	3.1 ± 0.9
CP		6.27 ±1.03	1.08 ± 0.20	0.14 ± 0.02	0.03 ± 0.03	0.49 ± 0.15	0.18 ± 0.03	0.02 ± 0.01	0.16 ± 0.03	0.07 ± 0.01
				13.1 ± 2.1	2.5 ± 2.7	44.6 ± 6.4	16.9 ± 1.5	1.8 ± 1.5	14.7 ± 0.8	6.3 ± 1.9
PM_{10}		29.09 ± 9.64	11.15 ± 2.33	0.32 ± 0.05	0.05 ± 0.05	0.72 ± 0.15	7.37 ± 1.55	1.93 ± 0.47	0.36 ± 0.04	0.39 ± 0.15
				3.0 ± 0.6	0.5 ± 0.5	6.6 ± 0.9	66.1 ± 0.8	17.2 ± 0.8	3.3 ± 0.5	3.40 ± 0.6
P2 (*Winter observations*)										
FP	$\mu \pm \sigma$	19.24 ± 6.06	6.30 ± 0.61	1.04 ± 0.67	0.07 ± 0.07	0.49 ± 0.12	2.86 ± 0.63	0.76 ±0.23	0.77 ± 0.47	0.32 ± 0.07
	% of ION			16.0 ± 9.8	1.1 ± 1.0	7.7 ± 1.6	46.0 ± 12.0	12.3 ± 4.1	11.7 ± 6.5	5.0 ± 1.0
CP		13.15 ± 10.89	2.62 ± 1.06	0.93 ± 0.44	0.01 ± 0.01	0.44 ± 0.19	0.49 ± 0.30	0.03 ± 0.03	0.63 ± 0.29	0.09 ± 0.04
				34.8 ± 10.0	0.4 ± 0.6	17.8 ± 7.1	18.3 ± 7.5	1.4 ± 1.4	23.7 ± 4.9	3.6 ± 1.4
PM_{10}		32.39 ± 16.15	8.92 ± 1.42	1.97 ± 0.89	0.08 ± 0.08	0.93 ± 0.28	3.34 ± 0.83	0.79 ± 0.24	1.40 ± 0.63	0.41 ± 0.09
				21.6 ± 9.1	0.9 ± 0.9	10.4 ± 2.5	38.2 ± 10.3	9.2 ± 3.6	15.2 ± 5.9	4.6 ± 1.0

[*] The total mass concentration of water soluble ions.

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played a more dominant role in ion composition of PM_{10} collected at our site in P1.

During P2 measurements, SO_4^{2-} was still the principal component ($38.2 \pm 10.3\%$ of total ions) in PM_{10}, but it was less than half of that observed during P1. In addition, sea salts (Cl⁻ and Na⁺), accounting for about 37% of total ions, became another dominant component. Meanwhile, by mass, they were almost five times that during P1, indicating a strong influence of marine aerosols associated with monsoon flows. NO_3^- during P2 was at about the same level as that during P1. Photochemical products (NO_3^-) were relatively limited at our site, indicative of a lack of local sources of their precursors (e.g., NO_x).

In summary, SO_4^{2-} was comparable with other rural sites (Dasch and Cadle, 1985; Lindberg et al., 1986; Muller and Weatherford, 1988; Ohta and Okita, 1990; Sopauskiene and Budvytyte, 1994), and significantly less than the lowest limit of around 10 µg m⁻³, generally measured in urban areas (Tanner, 1990). On the other hand, NO_3^- was evidently lower than those in other rural areas. These findings suggested that the Fu-Shan site was relatively less influenced by anthropogenic pollutants, such as sulfate and nitrate aerosols.

2.3 Fine and Coarse Particles

As seen in Table 2, during P1, the FP and CP were 22.8±8.8 and 6.3±1.0 µg m⁻³, respectively. Meanwhile, they accounted for 78.4% and 21.6% of PM_{10}, respectively. On average, 44.1% and 17.3% of FP and CP mass, respectively, were determined as water soluble ions. In comparison with FP mass, the above decrease in water soluble ions of CP mass was probably due to undetermined cations such as Mg^{2+} and Ca^{2+}, since they were generally favored with CP. For FP, SO_4^{2-} alone can account for 71.4% of total ions, compared with only 16.9% for CP. Ammonium (18.8%) was the secondary component of FP. In contrast, NO_3^- can account for about half of total ions for CP, whereas sea salts and sulfate were at about the same level and both approximately accounted for the other half of total ions. As to the partition of individual ions to FP and CP, it was equivalent for Cl⁻, Na⁺ and NO_3^-. Nitrate was favored in CP (68%), whereas more than 95% of SO_4^{2-} fell into FP, as well as NH_4^+. The above observations are consistent with the general knowledge that gaseous nitric acids tend to deposit on coarse particles to form nitrate particles. By contrast, the sulfates form as fine particles through a gas-to-particle conversion mechanism.

During P2, the FP and CP were 19.2±6.1 and 13.1±10.1 µg m⁻³, contributing 59.4% and 40.6% of PM_{10}, respectively. On average, 32.7% and 19.9% of FP and CP, were water soluble ions, respectively. The CP during P2 was more than twice that during P1, whereas the FP during P2 was only about 60% of that during P1. As discussed in the preceding subsection, this result was attributed to the enhancement of CP by marine aerosols during P2. Table 2 shows that sea salts in CP during P2 were much higher than those during P1. However, NO_3^- remained at the same level (0.4-0.5 µg m⁻³) during both periods of field experiments, suggesting that stable photochemical conditions persisted at our site, resulting in no excess of NO_3^- formed on the surface of marine aerosols. Regarding the relative contribution of individual ions to total ions, for FP, SO_4^{2-} decreased 25% from P1 to P2, compared with a slight increase for CP. This result was primarily attributed to a dramatic increase of Cl⁻ and Na⁺, as well as to a decrease of SO_4^{2-}, in FP during P2. Similarly, NO_3^- in CP decreased from 44.6% during P1

to 17.8% during P2. The nitrate during P2 was no longer dominant in CP, as it was during P1. The above results indicated that the characteristics of aerosol particles during P2 were significantly altered due to the addition of marine aerosols, strongly depending upon the meteorological conditions.

3. GASEOUS MEASUREMENTS BY ANNULAR DENUDER SYSTEM

Table 3 lists average concentration levels of nitrous acid (HNO_2), nitric acid (HNO_3), sulfur dioxide (SO_2) and ammonia (NH_3) gases measured during P1 and P2 using the annular denuder. Our average HNO_2 concentration of 0.17 and 0.31 ppb during P1 and P2, respectively, were appreciably higher than those in the clean troposphere, which is on the order of 10^{-3} ppb (Harris et al., 1982). HNO_2 during P2 was almost twice that during P1.

Our concentration level of HNO_3 during P1, 0.28 ± 0.02 ppb, was comparable with, but slightly higher than, those observed in the clean troposphere (Hanst et al., 1982), which were generally measured at 0.02-0.30 ppb. By contrast, during P2, our HNO_3 was on the order of 10^{-2} ppb. In the boundary layer troposphere, the oxidation of NO_2 by OH radicals is the major routine of HNO_3 formation during daylight hours. A second mechanism, involving NO_3 chemistry, for HNO_3 formation is also important at night. In the presence of H_2O, the HNO_2 and HNO_3 can be formed through the heterogeneous reactions of NO_2 with aerosol particles and fog droplets (Warneck, 1988). Our HNO_3 during P1 could result from active photochemistry during this favorable season.

Previous observations (Warneck, 1988) indicated that, by and large, HNO_3 and aerosol nitrate were present in the atmosphere with comparable concentrations. Most of ground-based measurements showed a moderate excess of particulate nitrate, so that the HNO_3/NO_3^- mass ratio was generally less than unity. In the free atmosphere, the relation was reversed. It can be no doubt that in the ground-level atmosphere such a ratio is strongly influenced by the losses of HNO_3 resulting from its very high dry deposition velocity of 2-3 cm s^{-1} (Huebert and Robert, 1985). Table 3 shows that our HNO_3/NO_3^- mass ratio during P1 averages as unity as expected for ground atmosphere. However, our average NO_3^- of 0.72 μg m^{-3} (Table 2) was comparable with those observed in free atmosphere (Huebert and Lazrus, 1980). During P2, this ratio was much less than unity, indicative of inactive photooxidation chemistry of NO_x during the experimental period, perhaps, a high deposition rate of HNO_3 on the surface as well. Combining gaseous with particulate nitrates as total nitrates, they averaged 1.44 and 1.03 μg m^{-3} during P1 and P2, respectively.

For another N-originated species, ammonia gas and particulate ammonium during P1 were 1.40 ± 0.21 ppb, and 1.93 ± 0.47 μg m^{-3}, respectively. A great excess of particulate NH_4^+ over NO_3^- obviously had neutralized SO_4^{2-}, as revealed by the molar ratio of NH_4^+/SO_4^2 (which can be calculated to be 1.40 as converted from the mass ratio). Our result suggested that the ammonium salt of sulfuric acid co-existed with that of nitric acid. During P2, ammonia gas and particulate ammonium were less than 50% of those during P1, indicating that ammonia production became less in a colder environment.

In addition, our average mass ratio of NH_3/NH_4^+ was found to be significantly less than

Table 3. Gaseous pollutants measured by the annular denuder at the Fu-Shan site.

Season		Gaseous matters (ppb)				Concentration ratio ($\mu g \, \mu g^{-3}$)[a]			Total nitrate ($\mu g \, m^{-3}$)
		HNO_2	HNO_3	SO_2	NH_3	NH_4^+ / SO_4^{2-}	HNO_3 / NO_3^-	NH_3 / NH_4^+	$HNO_3 + NO_3^-$
P1 (*Summer observations*)	μ	0.17	0.28	0.25	1.40	0.26	1.00	1.05	1.44
	σ	0.04	0.02	0.03	0.21				
	n	5	5	5	5	5	5	5	5
P2 (*Winter observations*)	μ	0.31	0.04	0.63	0.37	0.24	0.11	0.68	1.03
	σ	0.10	0.01	0.14	0.14				
	n	8	3[b]	11	10	11	3	10	11

a. Mean concentrations of aerosol particles (PM_{10}) were adopted from Table 2.

b. Only 3 samples were above the detection limit.

unity during P2, indicating a preference of atmospheric ammonia in particulate phase. Our value was comparable with those found elsewhere (for example, Georgii and Lenhard, 1978). The NH_3/NH_4^+ ratio should be determined by the rate at which ammonia is tied to aerosol particles following the production of sulfuric acid and nitric acid, relative to the rates of ammonia supply and its removal from the atmosphere by precipitation. By inspecting the ratio of NH_3/NH_4^+, it was found that particulate ammonium existed preferably during the winter season, because of a lower temperature.

With regard to sulfur compounds, the continental background of SO_2 in regions not directly influenced by anthropogenic emissions has remained largely unexplored (Warneck, 1988). Our SO_2 varied within 0.25 ± 0.03 and 0.63 ± 0.14 ppb during P1 and P2, which were about one order in magnitude lower than those generally found in nonurban areas (for example, Altshuller, 1976, 1980), but were comparable with those observed (for example, Ryaboshapko, 1983) in the free troposphere (outside the boundary layer). By contrast, SO_2 in polluted air was frequently observed to be greater than 10 ppb. As to secondary pollutants, SO_4^{2-} particles measured at our site averaged 7.37 ± 1.55 µg m^{-3} during P1, which was close to the lowest level of around 10 µg m^{-3}, in general, obtained in urban areas (Tanner, 1980). However, during P2, our SO_4^{2-} of 3.34 ± 0.83 µg m^{-3} showed a smaller range of fluctuation, indicating that relatively clean air masses arrived at the site. According to Muller and Weatherford (1988), average SO_2 and SO_4^{2-} measured at the Whitetop Mt. were 1.4 ppb and 4.0 µg m^{-3}, respectively, as well as 1.5 µg m^{-3} for total HNO_3 and NO_3^-. Our measurements for the aforementioned species, except SO_2, were comparable with those measured in the above study. We suggested that our site experienced a higher level of sulfates during the sampling period,. Meanwhile, primary sources such as SO_2 were in a limited amount. In addition, most of the SO_2 may have converted to SO_4^{2-} before it arrived at the site. Notably, there were no major sources of SO_2 in the vicinity of the site, even from the nearest urban areas. The SO_4^{2-} originated from somewhere else.

4. DEPOSITION OF SULFUR AND NITROGEN COMPOUNDS ON THE FU-SHAN FOREST

4.1 Estimation of Deposition Fluxes of S and N Compounds

The deposition flux (F_i) for a species (i) can be calculated by the following equation,

$$F_i = I \cdot C_i, \tag{1}$$

where I is the dry deposition velocity (in cm s^{-1}) and precipitation intensity (in mm hr^{-1}), and C_i is the concentration of species i in the air and precipitation, respectively, for dry and wet deposition.

In this study, dry deposition velocities were calculated using the ATDD (Atmospheric Turbulence and Diffusion Division, National Oceanic and Atmospheric Administration, see Hicks et al., 1987). Primary input meteorological parameters of ATDD are the wind speed

(U), wind direction deviation (σ_θ), temperature (T), relative humidity (RH), and solar radiation (PAR). Table 4 lists the seasonal averages of above parameters. In addition, the leaf area index (LAI) is assumed to be 8.93, based on earlier measurements (King and Hsia, 1997). Detailed discussion can be found in Hicks et al. (1987) and Lin (1997).

Table 4. Meteorological parameters as inputs for ATDD model, measured at the Fu-Shan site during the summer (June - August) and winter (December - February) of 1993.

Season	U (m s^{-1})	σ_θ (deg.)	T (°C)	RH (%)	PAR (W m^{-2})
Summer	1.44 ± 0.83*	16.0 ± 12.7	24.7 ± 3.4	99.2 ± 2.3	206.7 ± 294.3
Winter	1.57 ± 1.17	16.4 ± 12.5	14.9 ± 5.0	99.2 ± 5.4	138.1 ± 187.3

* mean ± standard deviation

4.2 Dry Deposition

Based on ATDD model, Table 5 summarizes the average dry deposition velocities (V_d) of HNO$_3$, SO$_2$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$, and their seasonal dry deposition fluxes (F_d). The results are discussed below.

The V_d of above pollutants in winter were commonly greater than those in summer, primarily resulting from higher wind speeds during the former season. For gaseous HNO$_3$ and SO$_2$, their average V_d ranged 0.79-0.90 and 0.19-0.20 cm s^{-1}, respectively. Walcek et al. (1986) obtained 2.5 and 0.8 cm s^{-1} for daytime HNO$_3$ and SO$_2$, respectively, at an altitude of 40 m above ground for eastern USA and southeastern Canada, based on model calculations. They also found that the V_d was strongly dependent on meteorological conditions. Regarding particulate nitrogen compounds, our average V_d of NH$_4^+$ and NO$_3^-$ ranged between 0.11-0.13 and 0.15-0.18 cm s^{-1}, respectively. Our average V_d fell into the lower bounds of the above studies. Table 6 further compares our V_d of SO$_4^{2-}$ and NO$_3^-$ with other studies in Taiwan. In summary, for southern Taiwan the V_d of SO$_4^{2-}$ and NO$_3^-$ ranged in 0.27-0.81 and 0.10-0.45 cm s^{-1}, respectively. Our V_d of SO$_4^{2-}$ was generally no more than half of that measured in other studies. The V_d of SO$_4^{2-}$ and NO$_3^-$ in our study was less than half of those obtained in Kaohsiung (Chen et al., 1996) and Taichung (Jeng et al., 1996), but comparable with those observed in Tainan (Chen and Wu, 1994) and Pingtung (Chen et al., 1996). Based on above comparison, our V_d of particulate pollutants were found to be generally lower than those of other studies, primarily attributed to low wind speeds at the Fu-Shan site. Meanwhile, our V_d of and SO$_2$ was comparable with other studies, whereas our V_d of and HNO$_3$ was evidently lower since the latter gas is more sensitive to the wind speed (Lin, 1997).

Using the average concentrations (see Tables 3 and 4) and V_d of the above pollutants as representative values for the entire season, their seasonal F_d were therefore extrapolated from average deposition fluxes over the 10-day sampling duration during both P1 and P2, as listed in Table 5. In addition, we calculated the seasonal F_d for individual pollutants by summing the

Table 5. Average deposition velocities (V_d, cm s^{-1}) and seasonal deposition fluxes (F_d, kg ha^{-1}) of primary gaseous and particulate pollutants inferred by ATDD, based on the measurements at the Fu-Shan site during P1 and P2.

Season	HNO$_3$		SO$_2$		NH$_4^+$		SO$_4^{2-}$		NO$_3^-$	
	V_d	F_d	V_d	F_d	V_d	F_d	V_d	F_d	V_d	F_d
Summer	0.79 ± 0.75	0.44	0.19 ± 0.22	0.09	0.11 ± 0.22	0.16	0.12 ± 0.25	0.73	0.15 ± 0.31	0.09
Winter	0.90 ± 0.80	0.07	0.20 ± 0.24	0.26	0.13 ± 0.21	0.08	0.14 ± 0.24	0.37	0.18 ± 0.29	0.13

Table 6. Comparison of our concentration (C, μg m^{-3}), V_d (cm s^{-1}) and seasonal F_d(kg ha^{-1}) of SO$_4^{2-}$ and NO$_3^-$ with other studies in Taiwan.

Investigator	Period	Location	SO$_4^{2-}$			NO$_3^-$		
			C	V_d	F_d	C	V_d	F_d
Chen et al. (1996)	12/1995-5/1996	Kaohsiung	3.55 - 29.03	0.38	1.05 - 8.58	1.03 - 7.24	0.45	0.34 - 2.54
Jeng et al. (1996)	12/1995-1/1996	Taichung	11.02 ± 2.29	0.27	1.35 - 2.32	7.37 ± 2.72	0.41	1.48 - 3.22
Chen and Wu (1994)	12/1993-2/1994	Tainan	5.8	0.81	1.49 - 4.24	11	0.17	0.57 - 1.90
Chen et al. (1996)	12/1995	Pingtung	35.17	0.29	7.93	17.8	0.10	1.38
This study	Summer 1993	Fu-Shan	7.37 ± 1.55	0.12	0.73	0.72 ± 0.15	0.15	0.09
	Winter 1993	Fu-Shan	3.34 ± 0.83	0.14	0.37	0.93 ± 0.28	0.18	0.13

product of their average concentrations and corresponding hourly V_d over the entire season. By comparing both methods for F_d, except for SO_2 that the former F_d was 40-60% higher than the latter, the relative errors between both F_d were generally within 20%. This significant difference between both F_d for SO_2 was attributed to a larger fluctuation of its V_d.

Consequently, F_d of total NO_3^- in summer (0.53 kg ha^{-1}) was more than twice that in winter (0.20 kg ha^{-1}). In the former season, HNO_3 accounted for most of total deposition, whereas NO_3^- contributed about half in the latter season. The above results support the previous point that active photochemsitry in summer made more products of NO_3^- at our site. Similarly, F_d of SO_4^{2-} in summer (0.73 kg ha^{-1}) was approximately twice that in winter (0.37 kg ha^{-1}); yet, the F_d of total SO_2 for the former (0.09 kg ha^{-1}) was only 35% of that for the latter (0.26 kg ha^{-1}), as attributed to higher SO_2 observed in winter. Table 6 shows that F_d of SO_4^{2-} and NO_3^- from Taichung to Pingtong varied in 0.29-8.10 and 0.34-3.22 kg ha^{-1}, respectively. As to NH_4^+ dry deposition, it was associated with SO_4^{2-} and NO_3^-, as discussed previously. Comparison with other studies indicated that the Fu-Shan forest received substantially low S and N inputs through dry deposition pathway, either due to lower ambient concentration levels of pollutants and/or relatively stable meteorological conditions (to decrease the dry deposition velocities).

4.3 Wet Deposition

Regarding wet deposition (F_w), the deposition fluxes of S and N compounds for each event were directly computed as the product of precipitation intensity and their concentrations in rainwater. Furthermore, seasonal deposition fluxes were accumulated as the sum of individual contribution from each event during the field season. Consequently, Table 7 shows the average NH_4^+, SO_4^{2-} and NO_3^- concentrations in rainwater collected at the Fu-Shan site, as well as their seasonal F_w during the summer and winter field seasons of 1993. The average pH of rainwater in winter was 0.58 units lower than that in summer, indicating that the acidity of the former was approximately 3.8 times higher than that of the latter. This result was apparently attributed to much higher SO_4^{2-} and NO_3^- in rainwater in winter, which were more than twice the continental baseline concentrations measured for Colorado (Hidy, 1994). By contrast, our SO_4^{2-} and NO_3^- in summer was comparable with national average of Japan (Hara et al., 1995). Seasonal baseline F_w of both SO_4^{2-} and NO_3^- for Colorado (Hidy, 1994) were generally as low as 1.5 kg ha^{-1}, as attributed to low annual rainfall of around 40 mm only. Seasonal average F_w of above two ions in Japan (Hara et al., 1995) were approximately 7.5 and 3.0 kg ha^{-1}, respectively. The maximum seasonal F_w of SO_4^{2-} and NO_3^- in the eastern USA during 1985-1987 (NAPAP, 1991) were around 11 and 7 kg ha^{-1}, respectively. Our F_w of these two ions in summer was comparable with those of the above other studies, but substantially higher in winter. Chen et al. (1996) and Lin et al. (1999) have pointed out that relatively high SO_4^{2-} in rainwater and its wintertime F_w at our site which were primarily associated with northeast monsoon flows, to a greater extent resulted from the long-range transport.

4.4 Budget of S and N Deposition

In order to investigate the relative importance of atmospheric inputs via various deposi-

tion pathways onto the Fu-Shan forest, total S and N depositions were calculated as the sum of all S (SO_2 and SO_4^{2-}) and N (HNO_3, NO_3^- and NH_4^+) compounds by dry and wet depositions, respectively. Table 8 lists the results of deposition budgets of S and N compounds for the summer and winter field seasons. The F_d of N compounds in summer was more than twice that in winter, and *vice versa* for F_w. For total S deposition, the F_d pathway contributed only 6.5 and 1.5% in summer and winter, respectively. With regard to S compounds, F_d in summer and winter were at the same level, whereas F_w in summer was less than half of that in winter. For total S deposition, the F_d pathway contributed only 5.1 and 2.0% in summer and winter, respectively. Evidently, F_w was the dominant pathway for delivering both S and N compounds from the atmosphere to the Fu-Shan forest in summer and winter. By contrast, in a hardwood forest in Tennessee, USA, F_d can account for 56 and 63% of SO_4^{2-} and NO_3^- deposition, respectively (Lindberg et al., 1986). In addition, the fraction of SO_4^{2-} and NO_3^- through dry deposition ranged between 0.2-0.5 and 0.30-0.45, respectively at the CORE sites (Sisterson et al., 1990). Lindberg and Lovett (1992) reported that the F_d pathway contributed 15-48% of SO_4^{2-} in 11 forested sites in USA. According to NAPAP (1991) in the eastern USA 30-60 and 30-70% of total S and N depositions resulted from F_d, respectively.

Comparison of other studies (Lindberg et al., 1986; Sisterson et al., 1990; NAPAP, 1991; Lindberg and Lovett, 1992) with the present study indicated that at our site wet deposition became an extremely important pathway to remove gaseous and particulate pollutants from the atmosphere to forest canopies and collecting surfaces, primarily resulting from higher rainfall received by the Fu-Shan forest. In addition, relatively high SO_4^{2-} and NO_3^- loading in raindrops can be merely attributed to below-clouds scavenging to a lesser extent since ambient concentration levels of these pollutants were significantly low. Therefore, we believe that atmospheric wet inputs to the Fu-Shan forest should largely derive from the long-range transport rather than local emissions, particularly in winter.

5. CONCLUDING REMARKS

In this study chemical constituents of atmospheric pollutants in solid, gaseous and liquid phases, in particular, for S and N compounds, at the Fu-Shan forest during the field experiments (around two weeks for each experiment) in summer and winter of 1993, were investigated. The budget of S and N inputs to the Fu-Shan forest through dry and wet deposition pathways was assessed as well. Our major findings are highlighted below:

- The bimodality in AP mass spectra was found. For the observations in summer, the fine (a cut size < 1.0 μm) and coarse (a cut size ~ 3.2 μm) modes were primarily composed of ammonium sulfate and nitrate, respectively. But, for the observations in winter, sea salts became dominant composition in coarse mode due to the influences of the northeast monsoon flows.
- By mass, SO_4^{2-} was the principal water soluble composition (66.1±0.8% and 38.2±10% for the observations in summer and winter, respectively) in AP, followed by NH_4^+ and NO_3^-. In terms of the ion equivalent concentration, SO_4^{2-} and NH_4^+ were the principal components

Table 7. Precipitation chemistry and estimated seasonal wet deposition (F_w) of NO_3^-, SO_4^{2-} and NH_4^+ at the Fu-Shan site during the summer and winter field seasons of 1993.

Season	N		pH	Concentration (μeq l^{-1})			Rainfall (mm)	F_w (kg ha^{-1})		
				NO_3^-	SO_4^{2-}	NH_4^+		NO_3^-	SO_4^{2-}	NH_4^+
Summer	12	$\mu \pm \sigma$	4.93 ± 0.54	17.15 ± 13.3	49.08 ± 23.00	17.59 ± 14.77	731.5	7.79	16.23	2.17
Winter	10		4.35 ± 0.26	65.55 ± 54.4	123.63 ± 67.11	41.61 ± 29.33	633.0	17.00	36.56	4.51

Table 8. Deposition budget of S and N compounds on the Fu-Shan forest during the summer and winter field seasons of 1993 (Unit: kg ha^{-1}).

Season	F_d		F_w		$F_T (F_d + F_w)$		F_d / F_T (%)	
	N	S	N	S	N	S	N	S
Summer	0.24	0.29	3.45	5.41	3.69	5.70	6.5	5.1
Winter	0.11	0.25	7.35	12.19	7.46	12.44	1.5	2.0

for the observations in summer. However, instead of NH_4^+, Na^+ and Cl^- became the secondary ions for the observations in winter.

- Our average HNO_2 (~ 0.10 ppb) was appreciably higher than those observed in clean troposphere, whereas HNO_3 was at a comparable level. Mean concentration of total nitrates ($HNO_3 + NO_3^-$) was higher than background value in troposphere. Ammonia gas and particulate ammonium were at a lower concentration level, compared with those generally observed on the continental grounds. The SO_2 (<1 ppb) was comparable with those frequently observed in the free troposphere, while SO_4^{2-} was close to the lowest level typically obtained in urban areas. We believe that SO_4^{2-}, to a larger extent, was transported to the site via the long-range transport, particularly in winter. Meanwhile, ammonium production became less in winter due to lower temperatures.

- Dry S and N depositions in summer were appreciably higher than in winter. In contrast, wet S and N depositions in winter were more than twice those in summer, primarily attributed to high SO_4^{2-} and NO_3^- loading in raindrops in wintertime precipitation. For total S deposition, dry deposition pathway contributed only 5.1 and 2.0% in summer and winter, respectively. For total N deposition, dry deposition pathway accounted for 6.5 and 1.5% in summer and winter, respectively. Uncertainties in estimating dry deposition can be on an order of 10 in magnitude owing to several factors primarily including the topographic complexity, and profiles of boundary layer parameters above and within forest canopy. Nevertheless, wet deposition pathway was evidently the most effective deposition mechanism to deliver atmospheric S and N compounds to the Fu-Shan forest during the field seasons.

Our investigations have resulted, for the first time, in quantitative assessment of atmospheric chemical inputs to a rural mountain forest in the subtropical Taiwan. Although the data coverage is only for two field experiments, the results may elucidate, to some extent, a typical chemical condition encompassed at our site in summer and winter. In conclusion, our study provides very useful information for future investigations on S and N nutrient cycles in the biosphere-atmosphere system, as well as on the carrying capacity of the soil for the above two compounds.

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