

The Effects of Sampling Flow Rate on the Concentrations of Dry Acid Deposition Components

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Abstract

One of the most critical problems associated with filter-pack data comparisons from various field networks is the use of different sampling flow rates. In this field study, the effects of various filter-pack (FP) sampling conditions were examined. Experiments were conducted to evaluate the effects of varying sampling flow rates (1.5 to 10 sLpm) on measured concentrations of dry acid deposition species. Collocated FP samples were also collected to determine sampling and analysis data reproducibility. Ambient air samples were collected simultaneously for the seven day durations at various flow rates. The chemical species measured were sulfur dioxide (SO₂), particulate sulfate (P-SO₄²⁻), nitric acid (HNO₃), and particulate nitrate (P-NO₃⁻). The results indicated that the collocated samples can be measured reproducibly and that sampling bias for the species measured is not significant. It was concluded that variations in the flow rates (1.5 to 10 sLpm) did not significantly affect the concentration of the species of interest. Although the results were not significantly different between different flow rates, artifacts were more likely to occur at high flow conditions (>5 sLpm) (e.g., via volatilization of particulate nitrates) than at low flow conditions (<5 sLpm).

Key words : dry acid deposition, ambient concentration, filter pack, sampling flow rate, Nylon filter

1. INTRODUCTION

Acid deposition, resulting from anthropogenic emissions of acid precursors, SO₂ and NO, can be divided into two distinct types, wet acid deposition and dry acid deposition. While not as important as those, cloud/fog impaction is also an important process. Wet acid deposition (i.e. by rain, snow, etc.) has been studied extensively and is well documented compared to dry acid deposition (i.e., in the absence of precipitation) and cloud/fog impaction (Allen *et al.*, 1994). However, dry acid deposition has received increased attention in recent years because of its role in acidifying ecosystems

(Geigert *et al.*, 1994; US EPA, 1991; Chamberlain *et al.*, 1985). As such, measurements of dry acid deposition species have become prerequisite for the studies of regional acid deposition and of oxidant modeling (Novak and Reagan, 1986).

Unlike wet acid deposition, dry acid deposition is found to occur from both indoor and the outdoor environment. Respiratory organs can be impaired via an exposure to fine acid particles (Brauser *et al.*, 1991). The existence of dry acid deposition species can also threaten living creatures through acidification of terrestrial and aquatic ecosystems (Meyers *et al.*, 1991).

A quantitative description of dry acid deposition is important to accurately predict the en-

vironmental impacts and to place suitable controls on the precursors of these acidic species. Two parameters, which include the ambient concentration (Geigert *et al.*, 1994) and specific deposition velocity (Hosker and Lindberg, 1982) of acidic species, are required to estimate dry acid deposition rates (Lindberg and Lovett, 1992). Several techniques are available for measuring the concentrations of dry acid deposition species (Kim, 1992). These methods include: filter packs (FP), annular denuder systems (ADS), transition flow reactors (TFR), and modified dichotomous samplers (MDS). Filter pack methods have been used by scientists from Environmental Protection Agency of the United States (US EPA), the Canadian Atmospheric Environment Service (AES), and other agencies as being most suitable for practical use (Dasch *et al.*, 1989). They have been most frequently used in regional or large scale networks in spite of inherent problems associated with artifact effects and size selective sampling (Sickles *et al.*, 1987).

One of the most significant problems in comparing filter-pack data sets arises from the use of different sampling flow rates and sampling durations. For example, a southeastern commercial forest network (Allen and Sutton, 1991a) used a sampling flow rate of 2 standard liters per minute (sLpm) for the sampling duration of seven days. The US EPA National Dry Deposition Network (NDDN) has been utilizing the filter pack method at flow rate of 1.5~3 sLpm for seven day periods (ESE, 1988). The Canadian Atmospheric Environment Service ran the triple filter pack at a flow rate of about 35 sLpm for a few hours of sampling duration (Anlauf *et al.*, 1985). In comparison, General Motors Research Laboratories used the filter pack at a sampling flow rate of 9~20 sLpm with a sampling time of a few days (Cadle, 1985). All the principal North American dry deposition monitoring networks have employed different sampling flow rates and durations. In

addition, filter types, sorbents, and filter configurations were standardized neither nationally nor internationally (Harrison and Kitto, 1990; Anlauf *et al.*, 1986; Chan *et al.*, 1986; Appel *et al.*, 1980). This situation seriously hampers data assimilation and comparisons, bringing about a lot of confusion in comparing dry acid deposition data at various conditions, locations, and durations from various networks.

Spicer *et al.* (1982) and Appel *et al.* (1984) suggested the potential effects of varying flow rates on the measured concentration of nitric acid. Perrino *et al.* (1988) found that nitrous acid is retained on Nylon filters with efficiency range of 25% (at 12 Lpm) to 80% (at 2 Lpm). According to McDow and Huntzicker (1990), the concentration of organic carbon on quartz fiber filters tend to decrease systematically with increasing flow rates.

It has been suggested that sampling flow rates may not directly affect the measurements of dry acid deposition species (Anlauf *et al.*, 1986; Spicer and Schumacher, 1979). However, for both studies, experiments were conducted from their laboratories under high flow rates (38.2 and 99.3 Lpm; 5~20 Lpm, respectively) with sampling durations ranging from four to twenty-four hour periods. ESE (1988) performed field experiments at low flow rates (1.5 and 3 sLpm) for seven day periods. In their studies, flow rate effects were not significant on the measured data sets. There might be a critical point, between low and high flow rates, which could affect the data quality of dry acid deposition measurements. Therefore, it is highly desirable to design a set of field experiments during which samples are collected in between low (1.5 to 5 sLpm) and high (2 to 10 sLpm) flow rates for the same sampling duration (e.g., 7 days).

The primary objective of this project was to determine if the measurement of dry acid deposition species (particulate sulfate/nitrate, nitric acid and sulfur dioxide) is affected by as a

function of sampling flow rate (at a fixed sampling duration). It was also intended to evaluate the consistency and reproducibility in collection and analysis of dry acid deposition species. Finally, an ancillary experiment was conducted to test the extent of sulfur dioxide retention on Nylon filters as a function of flow rate.

2. MATERIALS AND METHODS

2.1 Site

The study site, Austin Cary Forest, is located approximately 15 km NE of the downtown business district of Gainesville, Florida, U.S.A. This rural site is within a two hectare cleared area surrounded by commercial slash pine plantations. The relatively flat surrounding terrain is gently rolling; soils are sandy and low in natural fertility. At this site, air quality, meteorology and acid deposition monitoring activities have been conducted routinely by the scientists of University of Florida, Gainesville, Florida since July 1988 (Allen *et al.*, 1994).

2.2 Sampling

The project was conducted during a four-month period covering April 30 through August 20, 1991. Collocated filter-pack samples were collected to evaluate sampling and analysis reproducibility throughout the project period. During this field research, a comparative study for low flow rates (i.e., 1.5 to 5.0 sLpm) was accomplished during the first six weeks. From weeks 7 through 16, another comparison study of similar type was performed at high sampling flow rates from 2.0 to 10 sLpm.

A schematic diagram of the dry deposition sampling system is shown in Fig. 1. Sampling for dry acid deposition was performed following the procedures developed from both Integrated Forest Study (IFS) and National Dry Deposition Network (NDDN). A triple filter

pack (TFP) system was used in the latter case (Allen *et al.*, 1994; Kim, 1992). The system consisted of a four-stage Teflon filter holder (Fig. 2) (Saville Model 0-473-4N) with the following configuration: (1) a 47 mm, 2 μ m Teflon filter (Saville, Minnetonka, MN), (2) a 47 mm, 1 μ m Nylasorb Nylon filter (Gelman, Ann Arbor, MI), and (3) two separate 47 mm, treated cellulose fiber filters (Schleicher and Schuell (S&S) (Keene, NH) #589 Black Ribbon) impregnated with an aqueous solution (10% v/v glycerol and 25% w/v potassium carbonate).

However, during some part of this research, the two separate S&S cellulose filters had to be combined in a filter stage because only three-stage TFPs were available. The Teflon, Nylon, and two S&S cellulose filters were arranged to sequentially and selectively remove particulate matters, gaseous nitric acid and sulfur dioxide, respectively, from ambient air drawn through the filter pack at various flow rates.

A new 10 meter tilt-down sampling tower (Tower *N*) was located and set up on March 31, 1991 in the proximity of (2.3 m) an existing tower (Tower *O*) after considering the prevailing frequency of wind direction (North and South) data obtained during the second and third quarters of 1989 (Allen *et al.*, 1994). As shown in Fig. 1, sample lines made up of thick wall flexible plastic tube (0.95 cm i.d. Tygon) were extended from the inverted filter packs down to a shelter in which the mass flow controllers and vacuum pumps were housed. The filter packs were mounted on the tilt-down towers at a height of ten meters and in an inverted (face down) position. Stainless steel bonnets were used to protect the filter packs from precipitation and solar radiation. Tower *N* consisted of four filter pack assemblies at varying flow rates, while tower *O* supported two filter pack assemblies, including a filter pack and one blank filter pack. Each filter pack assembly in tower *N* was connected to a mass flow controller (MFC) (Tylan Model FC-

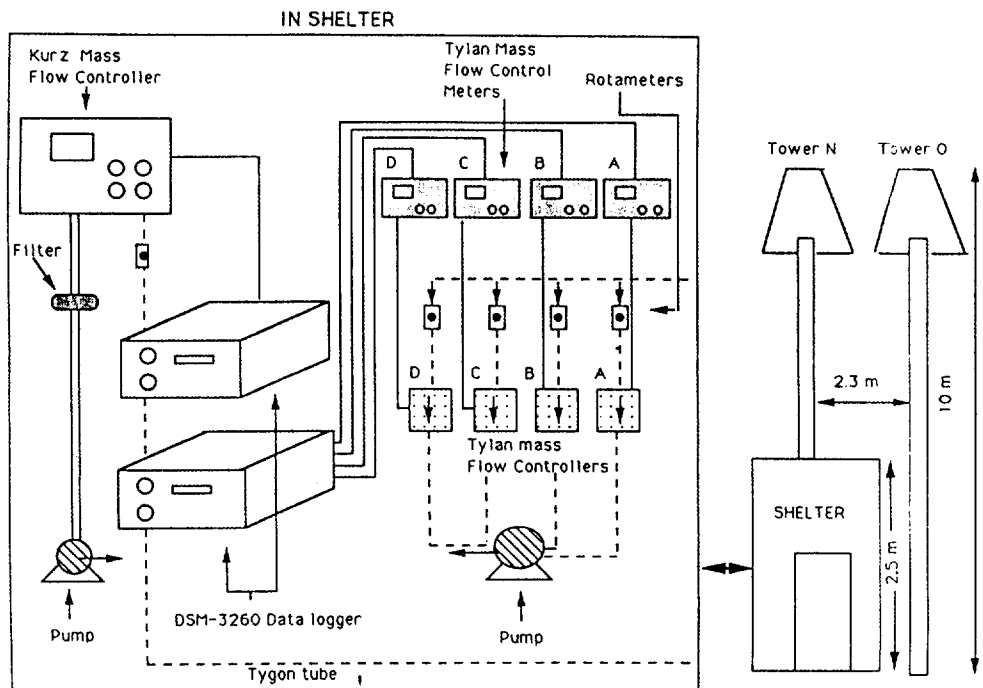


Fig. 1. A schematic diagram of filter pack sampling train arrangement.

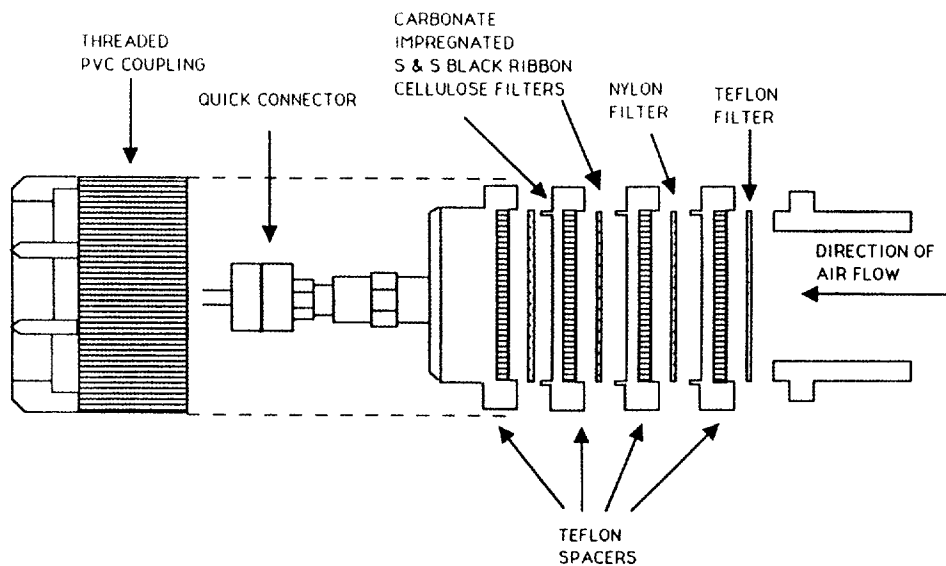


Fig. 2. A schematic diagram depicting a filter pack assembly system for the measurements of dry acid deposition.

280) as shown in Fig. 1. These MFCs were operated in the range of 0 to 20 sLpm. One filter pack system on tower *O* was connected to an MFC (Kurz Model 251-4) with an operation range of 0 to 10 sLpm. A high speed dual diaphragm pump (Air Dimensions, Model 01620N) was interfaced with the Tylan MFCs to maintain the optimal flow rate of 5 to 10 sLpm. For sampling at the Tower *O*, a brushless-motor pump (Kurz Model 251) was combined with another type of MFC (Kurz Model 251-4) to collect samples at flow rate of 2.0 sLpm. Two Odessa DSM-3260 primary data acquisition systems were installed and used to record hourly average flow rates. The filter packs were exchanged every Tuesday. Each time, system performance checks (leakage, etc.) were carried out, and data were downloaded to floppy diskettes from the data acquisition systems. Ambient air samples were collected continuously for seven days. Field blank samples were changed at intervals of 4 to 6 weeks. All filter pack samples and sampling record forms were shipped for analyses to the Air Pollution Analysis Laboratory located in Black Hall, University of Florida, U.S.A..

The four Tylan MFCs and the Kurz (Model 251-4) MFC with operating ranges 0 to 20 sLpm were calibrated both prior to and subsequently to the field sampling against a National Institute of Standards and Testing (NIST) traceable primary standard (Gilian model D-800268).

2.3 Analytical Methods

Upon receipt of sampled filter packs, they were disassembled under clean laboratory conditions. Initially, each filter was placed in a labeled (US EPA approved) 40 mL glass vial and sealed with a Teflon-sealed screw cap. The filter samples were extracted by the addition of 1) 35 mL deionized water to the vials containing the Teflon filters, 2) 25 mL anion IC eluant diluted four times (i.e., 0.45 mM

$\text{Na}_2\text{CO}_3/0.43 \text{ mM NaHCO}_3$) to the vials containing Nylon filters, and 3) 25 mL deionized water plus 10 microliters (μL) of 30% hydrogen peroxide (H_2O_2) to the vials containing the carbonate-impregnated filters. All vials containing filters were sealed and solutions were agitated for 30 minutes in an ultrasonic bath (Branson Model B 22-4) and allowed to stabilize to ambient temperature for ion chromatography (IC) analysis. The Air Pollution Analysis Laboratory has participated in internal and external audit programs and followed the standard operating procedures (SOPs) for quality assurance in dry acid deposition analyses.

A Dionex Model 4000i ion chromatograph (IC) (Sunnyvale, CA) was used for the analysis of nitrate and sulfate ion concentrations. The operating conditions for the IC were as follows: 1.7 mM $\text{NaHCO}_3/1.8 \text{ mM Na}_2\text{CO}_3$ anion eluant was pumped at 2.0 mL/min through a guard and a separator anion column (Dionex AG4A and AS4A, respectively) and an anion micromembrane suppressor column (Dionex AM-MS). The analytical procedure was computer-automated for multiple sample analyses using Baseline software (Waters Chromatography, Medford, MA) loaded on a computer. A Dionex automated sampler was used in conjunction with the Baseline automated sample program enabling sequential runs up to 56 samples in unattended mode.

3. RESULTS AND DISCUSSION

3.1 Study of Sampling Reproducibility

In order to evaluate the reproducibility of measurements made by filter packs at the similar location, two samples collected on a weekly basis at the identical flow rate of 2 sLpm from towers *N* and *O* were compared (Fig. 1). In Table 1 and Fig. 3 are compared the paired filter pack data for particulate sulfate and nitric acid as being representative of dry deposition species. Generally more frequent rain

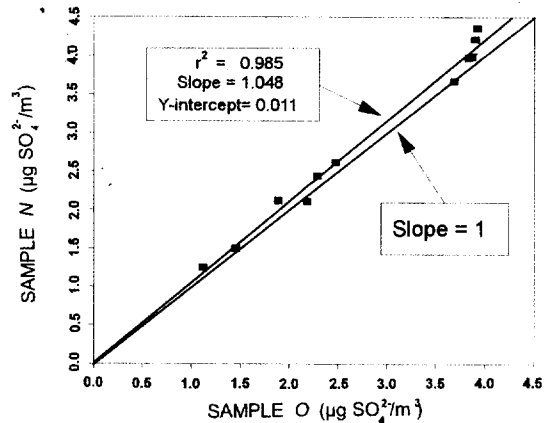
Table 1. The results of nitric acid measurements from collocated sampling with a flow rate of 2.0 sLpm.

Component	HNO ₃ ($\mu\text{g HNO}_3/\text{m}^3$)		Relative Ratio
	Sampler Tower N	Sampler Tower O	
Week 2	0.59	0.62	0.95
Week 3	0.82	0.82	1.00
Week 4	0.12	0.15	0.80
Week 5	0.89	0.89	1.00
Week 6	0.50	0.42	1.19
Week 7	1.10	1.07	1.03
Week 8	0.42	0.40	1.05
Week 9	0.61	0.54	1.13
Week 10	0.16	0.14	1.14
Week 11	0.99	0.90	1.10
Week 13	1.01	0.97	1.04
Mean=	0.66	0.63	1.04
SD=	0.31	0.31	0.10

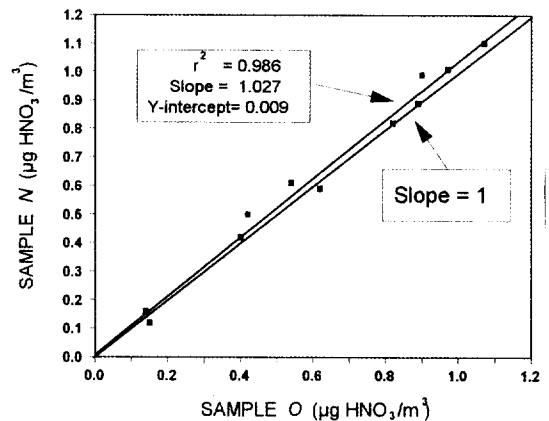
Relative Ratio is defined by the concentration ratio between the two sites *N* and *O*. SD denotes standard deviation.

events during the summer months may help scavenge acidic gaseous and particulate species in the atmosphere, thus serving as the principal factor in establishing the relatively low levels of those species in the atmosphere (as seen in Fig. 3). During our field study periods, the daily temperature and relative humidity were 24.4°C and 72.3%, respectively.

In order to estimate whether the data from the paired samples between the two towers were statistically similar or not, a two-sample paired t-test (5% two-tail test) was performed. The t-test did not show how closely the paired samples were related. Hence, correlation analyses were conducted at the 5% confidence level (two-tail test). Both statistical results suggested that all the paired samples were similar and very closely correlated at the 5% confidence level (two-tail test) (Kim, 1992). It was also assumed that the different sampling configurations (Fig. 1) did not affect the overall precision in our measurements of sulfur dioxide or any of the other concurrently measured



(a)



(b)

Fig. 3. Plots of particulate sulfate (a) and nitric acid (b) concentrations determined by collocated samplers from towers *N* and *O*. Note: 'slope =1' indicates an arbitrary case wherein sample *O* is equal to sample *N*.

species.

Different types of studies (US EPA, 1990) had also been conducted to verify the analytical precision of our methods. The collocated FP samples collected under identical flow conditions from West Point, NY, U.S.A. during 1988 (first through third quarter) were investigated for this purpose (US EPA, 1990). A good agreement was found for particulate and gaseous species between the paired samples. How-

ever, particulate nitrate data showed appreciable scatter over the range of observed concentrations relative to the other chemical species. The nitric acid results during the third quarter of 1988 appeared to be anomalously high compared to those acquired during the previous quarter and for other sites during subsequent quarters (US EPA, 1990). In addition, collocated filter packs were collected on a weekly basis during 1989 from the four different sites in the United States (Parsons, WV; Georgia Station, GA; Alhambra, IL; Chiricahua, AZ). In most cases, a good agreement was found between different studies. It was reported that the single western collocated site showed uniformly good data precision relative to those three sites located in the Eastern US (US EPA, 1991).

An intersite comparison of dry acid components was conducted using the two datasets from two nearby locals between the one previously used as Integrated Forest Study network (IFS) and our present study site in Austin Cary Forest (Allen 1991; Allen and Sutton, 1991b). The former site is located approximately 2 km northeast of the Cary Forest site but sampling was made above the forest canopy. The triple filter pack (TFP) system employed at the IFS site was identical to that used at the Cary Forest site. The main differences between the two were that FP was mounted at 10 m (27 m above ground) above the top of the mature forest canopy in the IFS site, whereas the Cary Forest filter pack was mounted 10 m above ground in a cleared area. A comparison of the data from the high (27 m) and low (10 m) elevation from 4/88 to 2/89 showed that the levels of particulate sulfate, nitric acid, and particulate nitrate were similar and that they were not readily distinguishable by elevation or location. However, it was seen that in the fall and winter months, sulfur dioxide concentrations at the IFS site exceeded those of the Cary Forest site (by 20 to 30%).

A recent comparative study of collection systems for the dry acid component (Quillian and Lundgren, 1992) also conducted from the Cary Forest site using TFR (Transition Flow Reactor) (at 5 m) and TFP (at 10 m) systems showed remarkably similar results for HNO₃ vapor despite different inlet elevations for sampling.

3.2 The Effects of Flow Rate on Measured Data

The reproducibility study suggested that the collocated sampling for dry acid components can be made quite precisely. In this section, the effects of flow rate on measured concentrations were carefully examined using the data collected from both high and low flow rates. For the first 6 weeks, samples of row flow rate were collected weekly at flow rates of 1.5, 2.0, 3.0, and 5.0 sLpm. This comparison was performed to evaluate the effect of flow rate variation (1.5 to 5.0 sLpm) on the collection of the individual dry acid deposition species. In Fig. 4a, the 5-week mean concentration data collected at varying flow rates are presented as a histogram. The results of ANOVA tests suggest that both sampling and analysis were not significantly affected by variation of sampling flow rates (at the 5% confidence level), since all p-values were greater than 0.05 (Table 2).

Only a few comparisons have been made to directly compare possible differences in the sampling efficiency of filter pack methods.

Table 2. The results of ANOVA test on the concentrations determined at low sampling flow rate (1.5~5.0 sLpm).

Component	P-SO ₄ ²⁻	P-NO ₃ ⁻	HNO ₃	SO ₂
F	0.03	0.32	0.09	0.55
p-value ¹⁾	0.99	0.81	0.97	0.66
d.f. (F) ²⁾	3	3	3	3
d.f. (E) ³⁾	16	16	16	16

¹⁾ α -level=5%, two-tail test

²⁾ Degrees of freedom for treatments

³⁾ Degrees of freedom for errors

During the entire year of 1987, collocated filter-pack samplers at West Point, New York, U.S.A. were operated at flow rates of 1.5, and 3.0 sLpm. The high/low flow ratios (3.0 sLpm/1.5sLpm) of the yearly averaged results are shown in Table 3. At both sites, the re-

sults were gene-rally in good agreement.

After the initial six-week comparison study at low flow rate, samples were collected weekly at higher flow rates (at 2.0, 5.0, and 10 sLpm). This comparison was intended to test the effects of high flow rate on the precision of measured concentration. In Fig. 4b, the mean concentrations determined concurrently under different flow rate conditions is presented as a histogram. In order to see if enhanced flow rates have an effect on concentration measurements of each species concerned, an one-way analysis of variance (ANOVA) test (5%, two-tail test) was performed. The overall results of ANOVA tests suggest that both sampling and analysis were not significantly affected as a function of sampling flow rates (at the 5% confidence level, since all p-values were greater than 0.05 (refer to Table 4)).

Anlauf *et al.* (1986) conducted a laboratory study for high flow rate sampling using several different types of filter media for a short period of time (i.e., Teflon, Nylon, Whatman 40 filters, and Whatman 41 filter impregnated

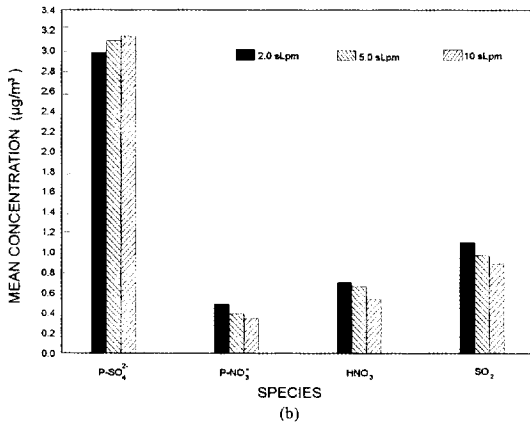
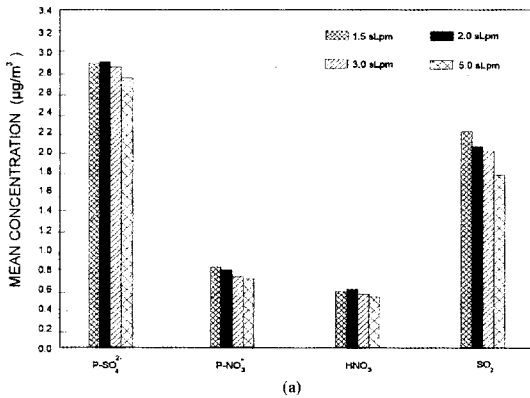


Fig. 4. Comparison of mean species concentration determined under low (a) and high (b) flow rate sampling conditions.

Table 4. The results of ANOVA test on the concentrations measured at high flow rates (2.0~10 sLpm).

Component	P-SO ₄ ²⁻	P-NO ₃ ⁻	HNO ₃	SO ₂
F	0.05	1.92	1.51	0.29
p-value ¹⁾	0.95	0.17	0.24	0.75
d.f. (F) ²⁾	2	2	2	2
d.f. (E) ³⁾	24	24	24	24

¹⁾ α-level=5%, two-tail test

²⁾ Degrees of freedom for treatments

³⁾ Degrees of freedom for errors

Table 3. A comparison of experimental conditions and the resulting data sets between the two different field studies.

Site	Flow Rate (sLpm)	Period (month)	P-SO ₄ ²⁻ (µg/m ³)	P-NO ₃ ⁻ (µg/m ³)	HNO ₃ (µg/m ³)	SO ₂ (µg/m ³)
Austin Cary Forest	3.0	4	1.02	1.19	0.97	0.98
West Point*	1.5	12	0.98	0.87	0.96	0.91

* ESE (1988)

with NaCl). They reported that varying flow rates within the range of 8.0 to 20 Lpm did not affect the measured concentrations of dry acid deposition species (i.e., nitric acid, sulfur dioxide, and atmospheric particles). Spicer and Schumacher (1979) also found that nitrate collection efficiency on four different types of filters was not affected by different flow rates (e.g., between 38.2 and 99.3 Lpm).

The volatilization of particulate nitrate may occur as chemical reaction such as decomposition of NH_4NO_3 on front filters made of Teflon or quartz (Cadle *et al.*, 1982; Spicer *et al.*, 1982; Stelson and Seinfeld, 1982a, b). Spicer

et al. (1982) reported that the greatest losses were observed under high temperature and low relative humidity conditions (<60%) as might be expected from equilibrium considerations. During this current field study, the average daily temperature and relative humidity (RH) were 24.4°C and 72.3%, respectively. It is quite possible that evaporation might have been suppressed by high relative humidity or that the extent of evaporation was not affected greatly by varying sampling flow rates during the flow comparison studies (Tables 2 and 4). In addition to the occurrence of similar results, two other statistical results summarized in

Table 5. A statistical comparison of the concentration data determined at low flow sampling rate.

Species Week	P-SO ₄ ²⁻		P-NO ₃ ⁻		HNO ₃		SO ₂	
	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)
2	4.19	2.95	1.14	5.68	0.59	15.3	1.91	10.4
3	2.70	8.01	0.62	18.4	0.78	6.70	2.44	8.73
4	1.42	4.98	0.67	9.04	0.13	13.4	2.11	19.2
5	3.43	6.44	0.63	3.81	0.75	12.6	2.32	5.45
6	2.45	5.20	0.68	12.2	0.49	2.58	1.11	23.0
MEAN(%)		5.52		9.83		10.1		13.4

CV denotes coefficient of variation (%).

* MEAN indicates the average concentration at the four flow rates (1.5, 2.0, 3.0, and 5.0sLpm).

Table 6. A statistical comparison of the concentration data obtained at high flow rates.

Species Week	P-SO ₄ ²⁻		P-NO ₃ ⁻		HNO ₃		SO ₂	
	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)	MEAN* (µg/m ³)	CV (%)
7	4.02	5.29	0.39	28.0	1.00	14.1	1.46	2.90
8	2.06	3.59	0.73	6.85	0.40	5.25	1.31	4.32
9	2.27	6.73	0.23	28.5	0.63	6.04	1.17	19.3
10	1.23	4.02	0.53	9.62	0.15	7.53	0.71	11.4
11	4.36	1.04	0.31	29.0	0.85	20.2	2.32	4.09
12**	2.43	3.88	0.63	12.1	0.58	6.45	1.09	20.8
13	4.17	4.30	0.31	22.9	0.87	25.0	1.09	6.62
14	4.04	3.52	0.27	31.9	0.66	14.4	0.94	12.3
15	2.62	6.36	0.46	20.7	0.71	18.8	1.09	19.4
16	3.81	3.44	0.40	16.2	0.77	14.8	0.89	4.90
MEAN(%)		4.25		21.5		14.0		9.48

CV denotes coefficient of variation (%).

* MEAN indicates the average concentration at the three flow rates (2.0, 5.0, and 10sLpm).

** Data for the week 12 were not included in statistical calculations due to another type of flow rate sampling comparison.

Tables 5 and 6 showed that the particulate nitrate values (CV=9.83%) obtained at high flow rates were much more variable than those (CV=25%) obtained at low flow rates (Tables 5 and 6). This observation suggests that the extent of experimental uncertainties increases under high flow conditions (>5 sLpm) (e.g., volatilization of P-NO₃⁻) relative to low flow conditions (<5 sLpm).

Another type of comparison study was conducted during the week 12 in order to check the effects of flow rate variations in intermediate ranges (i.e., 2.0, 4.0, 5.0, and 8.0 sLpm); therefore, only the data from week 12 were not included in the statistical calculations (Tables 4 and 6). The results from a precision-check comparison of sampling flow rates (2.0, 4.0, 5.0, and 8.0) also suggested that variations in flow rates from 1.5 to 8.0 sLpm did not affect significantly the precision of our measurements.

3.3 The Extent of SO₂ Retention on Nylon Filters

The data from the field study generally indicated that there was a significant retention of ambient SO₂ on the Nylon filters. With increase in the sampling flow rate, the amount of SO₂ adsorbed on Nylon filter decreased (as shown in Table 7). This decrease may result either from a saturation effect for SO₂ or from a reduced retention time of SO₂ at the Nylon filter surface (as the superficial velocity throu-

Table 7. The extent of sulfur dioxide retention on Nylon filter as a function of flow rate.

Flow Rate	Nylon Filter	
	MEAN ($\mu\text{g SO}_2/\text{m}^3$)	SD ($\mu\text{g SO}_2/\text{m}^3$)
2.0 sLpm	0.41	0.07
5.0 sLpm	0.19	0.04
10 sLpm	0.10	0.06

This is a summary for weeks 2 through 16, data for the week 12 is omitted.
SD denotes standard deviation.

gh the filter media increased).

Japar and Brachaczek (1984) suggested that the conversion efficiency of SO₄²⁻ from SO₂ on Nylon filters is dependent on RH, being higher at higher RH. Chan *et al.* (1986) observed that SO₂ conversion on Nylon filters varied significantly. The rate of conversion depended on the ambient SO₂ concentration such that enhanced conversion occurred at lower SO₂ concentrations. Anlauf *et al.* (1986) also observed that the adsorption of SO₂ on Nylon was significant (10.8%) and that it became greater during summer than during the other seasons. The Cary Forest field study was carried out during the summer (May-August). During the study periods, the average daily relative humidity was 72.3%, and the ambient average SO₂ concentration was 1.62 $\mu\text{gSO}_2/\text{m}^3$. Therefore, it is possible to expect that a significant SO₂ retention on the Nylon filters might have occurred during the field campaign due to the summer weather conditions characterized by high relative humidities and low SO₂ concentrations.

4. SUMMARY AND CONCLUSIONS

A comparative field study was conducted to evaluate the effect of sampling flow rates (1.5 to 10 sLpm) on measured concentrations of the dry acid deposition components. The species measured by the filter pack method include sulfur dioxide (SO₂), particulate sulfate (P-SO₄²⁻), nitric acid (HNO₃), and particulate nitrate (P-NO₃⁻). All samples were collected on a weekly basis. The results of statistical analysis showed that the paired samples (from the two towers N and O) were comparable without any substantial sampling bias for the species measured. An intersite comparison study also showed that the levels of the dry acid deposition species of interest were comparable between study sites, regardless of elevation and location during the summer months (Allen *et al.*, 1994)

The flow rate effects were tested under low

flow rate conditions during the first 6 weeks of this project (April~June). Samples were collected simultaneously on weekly basis at various flow rates of 1.5, 2.0, 3.0, and 5.0 sLpm. According to statistical analyses of our data, no significant differences were apparent for measured concentrations among these low flow rates. Subsequently to the first 6 weeks of study, a same type of study was carried out under high flow rate conditions. In this study, samples were also collected simultaneously at weekly intervals at flow rates of 2.0, 5.0, and 10 sLpm. It was found out that flow rate variations at these ranges did not cause any significant differences in the measured concentration of most species investigated. Comparison of precision at varying flow rates (2.0, 4.0, 5.0, and 8.0) also suggested that variations in the range of 1.5 to 8.0 sLpm did not affect the concentration estimates of particulate and gaseous species. The results of these flow rate effect studies indicate that the differences in the measured data were not affected significantly within the range of 1.5 to 10 sLpm. Although the data obtained between different flow rates exhibited similar trends (Tables 2 and 4), it was suspected that sampling artifacts were more liable to occur with increasing flow rates (e.g., volatilization of particulate nitrates).

In line with the findings of previous studies, a retention of ambient sulfur dioxide on the Nylon filters was noted under low flow rate conditions. When the sampling flow rate increased (to 10 sLpm), however, the quantity of SO₂ adsorbed on the Nylon filter was reduced. It is suspected that this decrease might be due either to a saturation effect for SO₂ adsorption or to a reduced retention time for SO₂ on the Nylon filter.

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산성 건성침적물 샘플링에 따른 유량변수가 그 대기중 농도측정에 미치는 영향

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초 록

산성 건성침적물은 산성비침적만큼 생태계에 중요한 영향을 미친다고 사료된다. 여러 실측소로부터 필터팩 데이터를 비교하는 과정에서 발생하는 가장 중요한 문제들 가운데 하나는 서로 다른 샘플채취 유량의 사용에 있다고 본다. 본 연구에서는 다양한 시료채취 조건이 비교되었는 바, 시료채취 유량의 변화 (1.5~10 sLpm)가 건성침적물의 농도측정에 어떠한 영향을 주는 지를 평가하기 위해 밀도 있는 연구가 이루어졌다. 샘플링과 분석의 재현성을 결정하기 위해 한 쌍의 필터팩시료가 동시에 채취되었다. 대기 중 시료들은 또한 다양한 유량변화 조건하에서 일주일동안 동시에 채취되었는 데, 그 시료 물질들은 아황산 가스, 질산 가스, 질산염 및 황산염 분진물질들이었다. 동시 측정된 한 쌍의 필터팩 시료는 재현성이 있는 것으로 나타났고 언제나 거의 유사한 대기농도 값을 나타내어 주었다. 결론적으로 대기중 산성 건성침적물들의 채취를 위한 유량변화는 그 물질들의 농도측정에 거의 영향을 주지 않는 것으로 나타났다. 그러나, 상대적으로 낮은 유량(<5 sLpm)과 높은 유량만(>5 sLpm)을 비교하였을 때에는, 높은 유량의 경우에 오차의 도입소지가 높다는 것을 알 수 있었다. 또한, 필터물질 자체만을 고려해 볼 때, 시료 유입량의 증가에 따라 나일론 필터에 흡착된 아황산가스의 양은 상당히 감소되는 것으로 나타났다.

주제어 : 산성 건성침적, 대기농도, 필터 팩, 샘플 채취유량, 나일론 필터