

The Effects of Varying Sampling Flow Rates on the Measurements of Total Nitrate and Sulfate in Dry Acid Deposition

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Abstract

One technique for determining dry acid deposition fluxes involves measurement of time-averaged ambient concentrations of dry acid deposition species using filter packs (FP) coupled with estimates of mean deposition velocities for the exposure period. A critical problem associated with filter pack data comparisons between various field sampling networks is the use of diverse sampling flow rates and duration protocols. Field experiments were conducted to evaluate the effects of varying sampling flow rates, from 1.5 to 10 standard liters per minute, on total nitrate and sulfate measurements of specific dry acid deposition species. Collocated FP samplers were used to determine sampling and analysis data reproducibility and representativeness. Ambient air samples were simultaneously collected using groups of filter packs operated at various flow rates over identical 7 day periods. The species measured were sulfur dioxide, particulate sulfate, nitric acid and particulate nitrate.

Statistical results (ANOVA; alpha level 5%) showed that neither the low nor high sampling flow rates caused a significant difference in the measurements of total sulfate and adjusted total nitrate (ATN). However, it was concluded that for high flow rate sampling measurements, total nitrate (TN) could be affected during extended sampling durations because of potential nitric acid overloading and breakthrough. Although the previous workers (Costello, 1990; Quillian, 1990) used much higher sampling flow rates (~ 17 sLpm) than employed here, it was assumed that for a high loading (> 50 µg HNO₃) of nitric acid on the Nylon filters, a significant fraction (~ 10%) of nitric acid could pass through the Nylon filters and be collected on the carbonate impregnated filters. It was concluded that even at the highest sampling flow rate employed (10 sLpm) at the Cary Forest site, nitric acid breakthrough was less than 10% of the total HNO₃ collected. However, for a heavily polluted urban airshed or with longer sampling times, higher filter loadings could result in substantial nitric acid breakthrough and HNO₃ concentrations would be underestimated.

Key words : dry acid deposition, wet deposition, filter pack, total sulfate, adjusted total nitrate (ATN)

1. INTRODUCTION

Acid deposition, resulting from anthropogenic emissions of acid precursors, SO₂ and NO_x, can be divided

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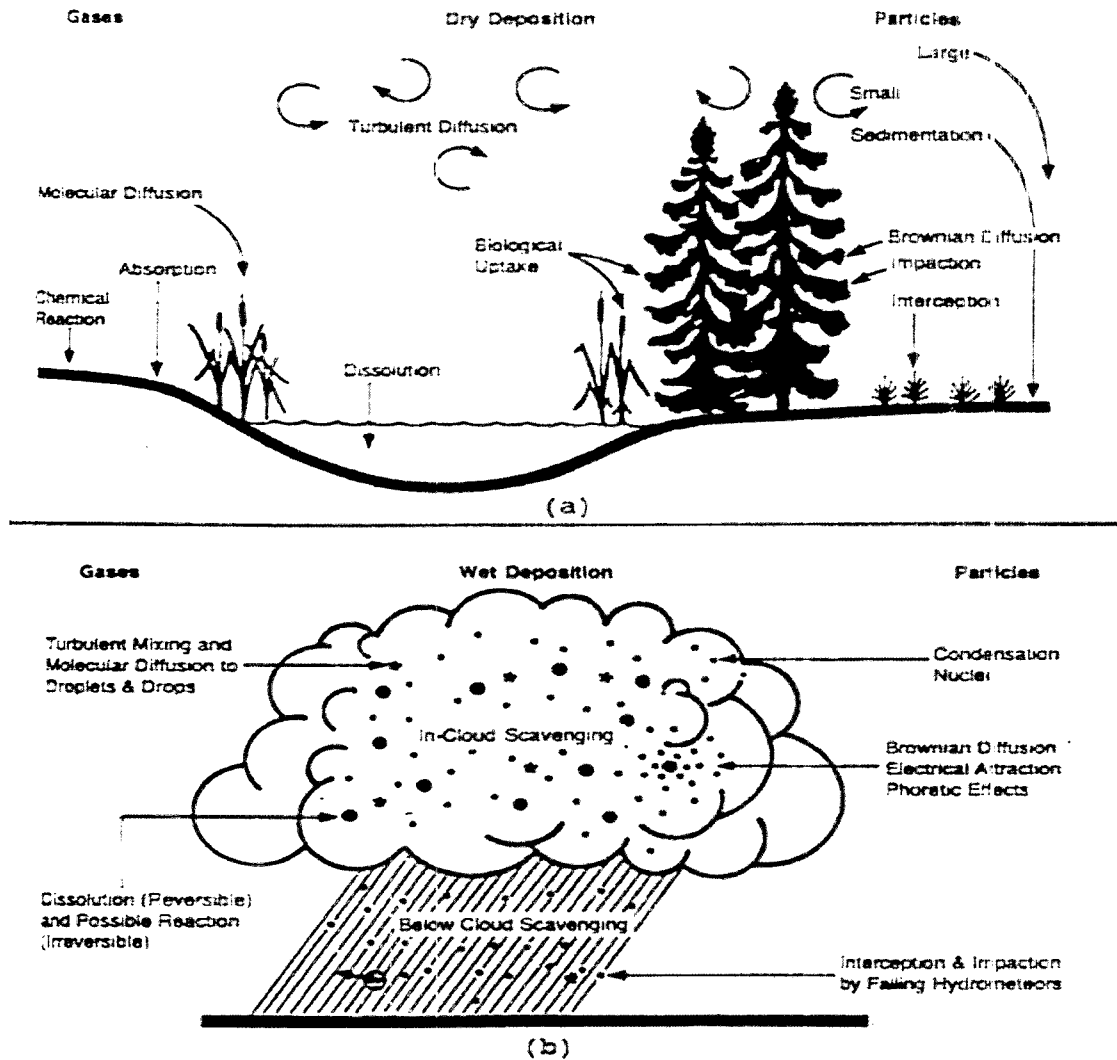


Fig. 1. Dry (a) and wet (b) deposition processes. Source: Chamberlain *et al.*, 1985.

into three distinct types, wet and dry acid deposition, and cloud/fog impaction. 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). However, dry acid deposition has received increased attention in recent years because it is believed to be as important as wet acid deposition in acidifying ecosystems in wes-

tern Europe and North America (Geigert *et al.*, 1994; US EPA, 1991; Chamberlain *et al.*, 1985). Estimates of the ambient concentrations and fluxes of dry acid deposition species are considered to be important requirements for regional acid deposition and oxidant modeling (Park and Allen, 2000; Novak and Reagan, 1986). Dry acid deposition, unlike wet acid deposition, is found in indoor as well as outdoor environments (see

Fig. 1). It has been suggested that human respiratory health may be impaired as a result of exposure to fine acid particles (Brauser *et al.*, 1991). Also, dry acid deposition species may threaten living creatures and micro-organisms by acidification of terrestrial and aquatic ecosystems such as forests, vegetation, soils, streams and lakes (Sievering *et al.*, 2001; Meyers *et al.*, 1991).

Quantitative descriptions of dry acid deposition inputs (fluxes) are necessary in order to predict and assess impacts on the environment, and to justify placing suitable controls on the emissions of precursors of these acidic species. Several techniques have been used to estimate dry deposition fluxes including direct micro-meteorological techniques (Dyer, 1974), vertical concentration gradient methods (Park and Allen, 2000; Lee *et al.*, 1989; Seila *et al.*, 1982), deposition to surrogate surfaces, and measurements of ambient concentrations (Geigert *et al.*, 1994; Johnson *et al.*, 1994; Meyers *et al.*, 1991) that are combined with deposition velocity estimates derived from local meteorological and environmental characteristics (Davidson and Wu, 1990; Hosker and Lindberg, 1982). And another some techniques have been used for measuring ambient concentrations of particulate and gaseous dry acid deposition species in rural environments. These methods include; filter packs (FP) (Johnson *et al.*, 1994; Harrison and Kitto, 1990; Sickles *et al.*, 1987; Anlauf *et al.*, 1986; Appel *et al.*, 1984; Cadle *et al.*, 1982; Spicer *et al.*, 1982); annular denuder systems (ADS) (Sickles *et al.*, 1989; Possanzini *et al.*, 1983); transition flow reactors (TFR) (Quillian and Lundgren, 1992; Sickles *et al.*, 1987; Durham *et al.*, 1986; Knapp *et al.*, 1986) and modified dichotomous samplers (MDS) (John *et al.*, 1988). Filter pack sampling combined with deposition velocity estimation has been the preferred method of determining dry acid deposition fluxes by government agencies; US EPA (National Dry Deposition Network, NDDN); Atmospheric Exposure Cooperative (AEC); Clean Air Status and Trends Network (CASTNET) and the Canadian Atmospheric Environment Service, as well as private organizations,

such as the Electric Power Research Institute Integrated Forest Study. This preference is based on the economics and feasibility of widespread use in regional or large scale networks (Dasch *et al.*, 1989) in spite of inherent problems resulting from artifact effects and the lack of size.

The major species of interest in dry acid deposition estimates are sulfur dioxide (SO₂), particulate sulfate (P-SO₄²⁻), nitric acid vapor (HNO₃) and particulate nitrate (P-NO₃⁻). Although the measurement of nitric acid vapor can, in principle, be performed accurately, separation and collection of HNO₃ from ambient air is subject to several problems including artifact formation effects (Cadle, 1985; Larson and Taylor, 1983; Forrest *et al.*, 1982; Stelson and Seinfeld, 1982; Appel *et al.*, 1981). Adsorption of gaseous compounds on filter media have been shown to depend on pressure drop (i.e. flow rate) across the medium, surface area, etc., (Cooper and Alley, 1986). Thus, collection of vapors at different flow rates may disproportionately contribute to artifact effects. Previous research has shown that variations in sampling flow rate do not directly affect measurements of concentrations of dry acid deposition species, however, these laboratory studies were primarily conducted at relatively high flow rates; 38.2 and 99.3 Lpm (Spicer and Schumacker, 1979), and from 5 to 20 Lpm (Anlauf *et al.*, 1986) for short durations in the range from 4 to 24 hours. Field comparison studies at low flow rates (1.5 and 3 sLpm) have been reported for the US EPA NDDN (ESE, 1988) which suggested that estimated mean concentrations of dry acid deposition species were unaffected by use of either of these low flow rates. Spicer *et al.* (1982) and Appel *et al.* (1984) suggest that there are potential artifact effects on the measurement of nitric acid due to varying filter pack sampling flow rates. Perrino *et al.* (1988) have shown that nitrous acid vapor (HNO₂) is retained on Nylon filters with efficiencies varying from 25% at 12 Lpm to 50% at 2 Lpm. This problem, however, is prevalent at night when HNO₂ concentrations are much greater than in day time, as a result of HNO₂ photodissociation.

Another problem arises from the stability of the ammonium nitrate (NH_4NO_3) fraction of the particulate nitrate collected by filter packs. It is well established that particulate ammonium nitrate stability depends on temperature and tends to dissociate into gaseous ammonia and nitric acid vapor at higher ambient temperatures. Such dissociation of NH_4NO_3 could be enhanced at higher sampling flow rates used by high volume samplers and may lead to underestimation of ambient particulate nitrate and overestimation of nitric acid vapor concentrations. Also, McDow and Huntzicker (1990) reported that the concentration of organic carbon, as determined by collection on quartz fiber filters, exhibited a significant decrease with increasing sampling flow rates.

The overall objective of this field project is to determine whether or not varying simultaneous sampling flow rates for a fixed sample duration will significantly affect the measurements of total nitrate and total sulfate in ambient air using filter packs.

2. EXPERIMENTAL METHODS

2.1 Site

The field sampling site at Austin Cary Forest is located approximately 15 km northeast (29.75°N , 82.21°W) of Gainesville, Florida. This inland rural site is situated within a two hectare cleared area surrounded by mature slash pine plantations. In general, the summer seasons are long, warm and relatively humid at this location. There is little day to day temperature variation. Afternoon temperatures reach 32°C (90°F) or higher with great regularity during the summer, but temperatures of 38°C (100°F) or higher seldom occur, typically only once or twice each year. The summer season, especially, June through September, is the rainy season, which on the average accounts for about half the total annual rainfall (134 cm). The larger portion of the summer rainfall results from frequent, short duration afternoon or early evening local thunderstorms, which occur on about half of the days (Park

and Allen, 2000; Allen, 1991; Allen and Sutton, 1991). Routine air quality, meteorology and acid deposition monitoring activities were conducted at this site from July 1988 through June 1991.

2.2 Sampling

A schematic diagram of the ambient air dry deposition component sampling system was shown elsewhere (Kim and Allen, 1997). Dry acid deposition sampling was performed following a combination of Integrated Forest Study (IFS) and National Dry Deposition Network (NDDN) sampling protocols using independently operated triple filter pack (TFP) systems (Kim, 1992; Allen, 1991; Allen and Sutton, 1991). A filter pack system consisted of a three or four stage Teflon filter holder (Model 0-473-4N Savillex, Minnetonka, MN) which contained a 47 mm, $2\ \mu\text{m}$ Teflon filter (Savillex, Minnetonka, MN), a 47 mm, $1\ \mu\text{m}$ Nylon filter (Gelman, Ann Arbor, MI), and two combined or separated 47 mm, treated cellulose fiber filters (#589 Black Ribbon Schleicher and Schuell (S&S) Keene, NH), impregnated with an aqueous solution containing 10% v/v glycerol and 25% w/v potassium carbonate. The Teflon, Nylon, and two S&S cellulose filters were arranged to sequentially and selectively remove particulate matter, gaseous nitric acid and sulfur dioxide, respectively, from ambient air drawn through the filter pack at flow rates varying from 2 to 10 sLpm.

The original 10 m tilt-down sampling tower (Tower O) has been used to collect ambient air samples for dry deposition species estimation from July 1988. It was located approximately 10 m from the 3 m high shelter that contained monitoring instrumentation. Typically, two filter packs were vertically mounted in an inverted position at the top of the tower inside a stainless steel bonnet. The bonnet served to protect the filter packs from precipitation, solar radiation and strong winds. One of these filter packs was operated by drawing air at a constant flow rate (2 sLpm) through a leak-free heavy wall flexible plastic hose, that was connected to the filter pack via a quick-connect fitting, using a mass flow controller (Model 251-4 Kurz, Carmel Valley,

CA) and brushless motor driven pump (Model 251 Gast, Benton Harbor, MI). The second filter pack mounted on this tower was used as a static background sampling device. No air was drawn through the latter pack.

A new 10 meter tilt-down tower (Tower N) was set up adjacent (2.3 m apart) to the original tower (Tower O) on a line perpendicular to the seasonal prevailing winds to minimize interference with the air parcels being sampled. The second tower filter pack holder was configured to independently operate up to four filter packs at similar or different flow rates. The latter filter packs were operated by four separate mass flow controllers (Model FC-280 Tylan General, Torrance, CA) and a high speed dual diaphragm pump (Model 01620N Air Dimensions, Deerfield Beach, FL). Hourly averaged flow rates were simultaneously recorded on a data logger (Model DSM-3260 Odessa, Austin, TX).

Filter packs were simultaneously changed out on a weekly basis, following continuous collection of ambient air samples for seven days. Field blank (static) samplers were changed out every 4 weeks. Filter pack samples and corresponding sampling conditions and flow rate data, downloaded from the data logger, were transferred to the UF Air Pollution Analysis Laboratory for analysis and evaluation. Mass flow controllers (MFCs) were calibrated in the range from 1 to 15 sLpm prior to, during and subsequent to use in the field against a NIST-traceable electronic bubble meter (Model D-800268 Gilian, Wayne, NJ). Indicated flow rates and output voltages of the MFCs were accurate (>99% recovery) and precise (rel. std. dev. = 0.5%). System leak checks were performed before and after sampling to ascertain that there were no observable leaks in tubing or fittings. All flow systems except one showed negligible leak rates, less than 0.05 sLpm. One sampling line developed a serious leak (~0.45 sLpm) during the twelfth week of operation consequently this line was shut down for the remainder of the project. Correction factors for MFC flow rates were derived from the averaged calibration data sets.

2.3 Analytical methods

Upon receipt of used filter packs at the laboratory, the packs were disassembled under clean conditions and each filter was placed in a separately labeled (US EPA-approved) 40 mL glass vial and sealed with a Teflon-seated screw cap. The individual filter samples were treated by the addition of 1) 35 mL deionized water to the vials containing Teflon filters, 2) 25 mL anion IC eluant diluted 4 times (i.e., 0.45 mM Na₂CO₃ /0.43 mM NaHCO₃) to the vials containing Nylon filters, and 3) 25 mL of deionized water plus 10 microliters (μL) of 30% hydrogen peroxide (H₂O₂) to the vials containing the carbonate-impregnated filters. All sealed vials containing filters and extract solutions were agitated for 30 minutes in an ultrasonic bath (Model B 22-4 Branson) and allowed to stabilize to ambient temperature prior to analysis by ion chromatography (IC). The UF Air Pollution Analysis Laboratory has participated in internal and external audit programs and follows written standard operating procedures (SOPs) for quality assurance of dry acid deposition sample analyses.

An ion chromatograph (IC : Model 4000i Dionex, Sunnyvale, CA) was used for analyses of soluble nitrate and sulfate ions in aqueous solution following protocols recommended in EPA Method 300.6 (Peden *et al.*, 1986). The IC operating conditions were: 1.7 mM NaHCO₃ 1.8 mM Na₂CO₃ anion eluant was pumped at 2.0 mL/min through guard and separator anion columns (Dionex AG4A and AS4A, respectively), and an anion micromembrane suppressor column (Dionex AMMS). 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 to run up to 56 samples in unattended mode. More details on anion analysis were reported elsewhere (Kim and Allen, 1997).

3. RESULTS AND DISCUSSION

3.1 Quality control measurements

Ion chromatograph calibrations for nitrate and sulfate ions were performed initially, during and subsequent to sample analyses to observe instrument response. It was concluded from comparisons of these calibration curves that there were no significant differences between the initial, intermediate and final calibration data. Quality control (QC) checks for nitrate (NO_3^-) and sulfate (SO_4^{2-}) anions were performed using independently prepared calibration standards. Aliquots (5 mL) of these QC solutions were analyzed with each batch of samples. The calibrations checks were made frequently and routinely to check for trends in instrument operation and to ensure that the analyzer was working within control limits during analyses of the field samples. The method limits of detection for nitrate and sulfate anions by IC were 0.02 and 0.03 ppm (g/mL), respectively. Percent recovery, standard deviation, and coefficient of variation (CV) were calculated using QC check solutions for each species. The average recoveries (accuracy) of nitrate and sulfate anion measurements were 98.1% (CV = 0.93%, n = 25) and 98.8% (CV = 0.67%, n = 25), respectively. These data demonstrate that there was little or no bias in the analytical results. Calibration check replicates were run twice per batch. Excellent precisions in nitrate (CV = 1.51%) and sulfate (CV = 1.25%) data were achieved. Laboratory studies have suggested that similar sample extraction and analytical factors contribute less than 5 percent to the measurement imprecision (Anlauf *et al.*, 1986). On the basis of the results obtained here for quality control of filter sampling and analyses, it may be concluded that the flow-control and analytical systems were performing satisfactorily during the sampling and analysis periods.

3.2 Sampling reproducibility study

In order to evaluate the precision (reproducibility) of ambient concentration measurements made with filter

packs at the same location, two samples, one each from towers N and O were collected at the same flow (2 sLpm). The samples collected at the same elevation (10 m) but 2.3 m apart, presumably were from the same air parcel. Data from weeks 1 and 12 were not included in statistical calculations because of potential contamination of samples and larger than normal experimental errors. Fig. 2 illustrates the relationship between P- SO_4^{2-} (and HNO_3) values obtained by simultaneously sampling ambient air using filter packs on towers N and O under the same conditions and flow rates (2 sLpm). Frequent rain events, that occurred during the summer months, scavenged acidic gaseous

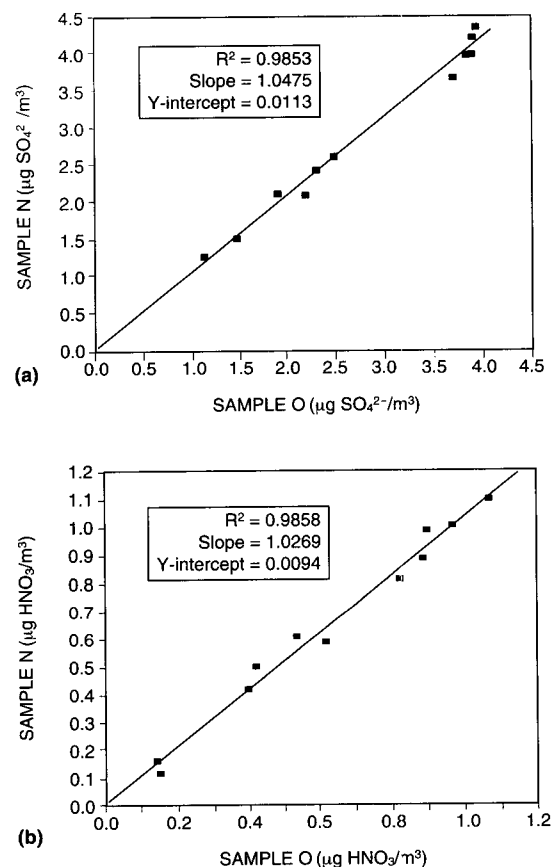


Fig. 2. Representative plots of (a) P- SO_4^{2-} and (b) HNO_3 collected by collocated filter pack samples on towers N and O at the same conditions.

and particulate species in the atmosphere and these events may be the principal factor in establishing the relatively low weekly averaged levels of species observed. However, the weekly mean concentration values obtained appeared to be highly reproducible. During the duration of the field study, the averages of the daily temperatures and relative humidities (RH) were 24.4°C and 72%, respectively.

In order to estimate whether the paired samples obtained from the two different towers were statistically similar or not, a two-sample paired t-test (5% two tail test) was performed. However, the t-test does not show how closely the paired samples are related. Therefore, correlation analyses were also conducted at the 5% level (two-tail test). The statistical results suggested that all the paired samples were similar and very closely related at the 5% level (two-tail test) (Kim, 1992).

Field studies (US EPA, 1990) have been conducted to verify the precision of collected species of interest using collocated filter packs. Collocated FP samples collected using identical flow rates were compared at West Point, NY during 1988 (first through third quarter). In general, good agreement was found between the paired samples for particulate and gaseous species. However, particulate nitrate data showed appreciable scatter over the range of observed concentrations and generally much more scatter than was observed for the other chemical species. The results for nitric acid during the third quarter of 1988 appeared to be anomalous compared to those for the previous quarter and for other sites for subsequent quarters (US EPA, 1990). In addition, collocated filter pack samples from four different sites (Parsons, WV; Georgia Station, GA; Alhambra, IL; Chiricahua, AZ) were collected on a weekly basis and compared during 1989. In general, good agreement was found between samples analyzed from collocated filter packs. It was reported that the single western collocation study site showed uniformly better data precision than those for the three eastern sites (US EPA, 1991).

A recent comparative study of dry acid component

collection systems at the Cary Forest site (Quillian and Lundgren, 1992) using TFR (at 5 m) and TFP (at 10 m) systems showed remarkably similar concentrations for HNO₃ vapor, despite the different sampler inlets, collections and flow rates.

3.3 Total nitrate and total sulfate concentration comparison

Total nitrate consists of the soluble nitrate associated with Teflon and Nylon filters. Adjusted total nitrate is the total nitrate and any nitrate found on the carbonate-impregnated filters. Nitrate ion (NO₃⁻) associated with carbonate filters has been detected by ion chromatography. Anlauf *et al.* (1986) found from laboratory experiments that conversion of NO and NO₂ to nitrate on the Teflon filter was much less than 0.2% of the gas concentration. That is to say, Teflon filters are inert to gaseous pollutants such as NO, NO₂, and HNO₂. Therefore, these nitrogen oxides can pass through the Teflon filters. Appel *et al.* (1984) have reported similar results. Perrino *et al.* (1988) reported that HNO₂ is retained on Nylon (1 µm, 47 mm, Nylasorb Gelman) filters with efficiencies varying from 25% at 12 Lpm to 80% at 2 Lpm yielding NO₂⁻ ion. Relative humidity (RH) was varied from 40 to 70% during these experiments. In the case where oxidant concentration is high, NO₂⁻ is oxidized to NO₃⁻ with a conversion efficiency up to 100%. NO₂ passed through the Nylon filters with less possibility for interference than HNO₂. It was assumed in the studies reported here that NO₂ and some HNO₃ might pass through the Nylon filter and be collected on the carbonate-impre-

Table 1. Total nitrate comparison at low flow rates.

	Total nitrate	Adjusted total nitrate
F	0.0320	0.660
p-value	0.810	0.590
d.f. (F)	3	3
d.f. (E)	16	16

Note : d.f. (F) = Degrees of freedom for treatments (factors).

d.f. (E) = Degrees of freedom for errors.

p-value = Significance probability for rejecting the null hypothesis (alpha level = 5%, two-tail test).

Low Flow Rates include sampling at 1.5, 2.0, 3.0, and 5.0 sLpm.

Table 2. Total nitrate comparison at high flow rates.

	Total nitrate	Adjusted total nitrate
F	4.420	3.190
p-value	0.028	0.063
d.f. (F)	2	2
d.f. (E)	21	20

Note : High flow rates include sampling at 2.0, 5.0, 10 sLpm.

gnated filters. However, the identity of the source of NO_3^- associated with the carbonate-impregnated filters is not certain. NO_2 , HNO_2 , HNO_3 , peroxyacetyl nitrate (PAN), or their mixtures could contribute to the former observation.

The results shown in Table 1 indicate that variation in low flow rates did not significantly affect the total nitrate (TN) or adjusted total nitrate (ATN) concentrations at the 95% confidence level (two-tail test), since the p-values (0.810 and 0.590, respectively) are greater than 0.05. However, total nitrate comparisons at high flow rates (Table 2) suggested that the mean values at 2.0, 5.0, and 10 sLpm were significantly different at the 5% level (p-value is 0.028.). The latter observations suggest that at high flow rates total nitrate measurements are significantly affected by the choice of flow rate. In order to determine which of the data series are different, an ANOVA test (5% two-tail test) was performed.

The results using 2.0 and 10 sLpm sampling flow rates indicated that these results were significantly different at the 5% level, since the p-value (0.025) was less than 0.05. However, comparisons for 2.0 and 5.0 sLpm and 5.0 and 10 sLpm data series suggest that they were not significantly different at the 5% level since p-values (0.269 and 0.089, respectively) were greater than 0.05. These statistical results suggested that the possibility of HNO_3 breakthrough may be greater on the Nylon filters (Nylasorb) due to either higher loading of HNO_3 (greater than $50 \mu\text{g HNO}_3$) or to a lowered collection efficiency as a result of shorter residence time at high flow rates. Several researchers have suggested that using Nylon filters, as a collection medium for HNO_3 , has some limitations. Anlauf *et al.*

(1986) found that Nylon filters ($1 \mu\text{m}$, Membrana Corp.) collect greater than 90% of the HNO_3 at loadings up to $435 \mu\text{g}/\text{filter}$ (47 mm). The tests were conducted at 22°C and 40°C and at controlled relative humidities in the range from 50 to 100 percent. At higher loadings the efficiency decreased, e.g., to about 60% at $1,450 \mu\text{g}/\text{filter}$. Costello (1990) tested collection efficiencies of Nylon filters (Nylasorb and Sartolon) under heavy nitric acid loads. Most of the Nylasorb filter tests were conducted using a TFR system which was operated at a flow rate of 17 sLpm in the range from 6 to 95% RH and at room temperature. These tests showed a decreased nitric acid retention with loads over about $100 \mu\text{g}$ nitric acid for both types of Nylon filters. At loads from 25 to $35 \mu\text{g}$ of nitric acid the average collection efficiency was about 94%. When the loading was increased to about $100 \mu\text{g}$, the collection efficiency was variable with an average efficiency of about 90%. Quillian (1990) observed the same trend as seen in the laboratory work by Costello (1990).

Four runs were performed with the TFR containing two Nylon filters in series after the Teflon filter, during the field study at ESE. The two Nylon filters, which were exposed to loadings higher than about $50 \mu\text{g}$ of HNO_3 in the field showed a collection efficiency of 90%. Also, sixteen 24-hour samples were taken by ESE, Inc. with two Nylon filters in the filter pack run at 18 sLpm. The mean HNO_3 vapor found on the second Nylon filter was about 8% of the total (Quillian, 1990). Therefore, adjusted total nitrate (ATN) was considered here assuming that only HNO_3 which could pass through the Nylon filters at high loadings greater than $50 \mu\text{g HNO}_3$ could be retained on the carbonate impregnated filters (refer to Table 2). In order to demonstrate the possibility of the HNO_3 breakthrough, HNO_3 mass (μg) on Nylon filter detected by IC was listed in Table 3. The results shown in Table 4 show that CV of the total nitrate increased abruptly corresponding to week 11. This observation implies that there was a possibility of a significant HNO_3 breakthrough ($\sim 10\%$) at 10 sLpm since HNO_3 loadings

Table 3. Mass (μg) of HNO_3 collected on Nylon filter.

Week	Sampling flow rate		
	2.0 (sLpm)	5.0 (sLpm)	10.0 (sLpm)
8	8.87	19.7	38.5
9	13.0	30.8	69.5
10	3.43	6.86	16.1
11	21.3	46.7	67.6
13	19.5	48.7	61.0
14	15.6	35.2	56.3
15	17.0	36.7	54.9
16	18.0	40.0	63.4

Table 4. Statistical total nitrate comparison at high flow rates.

Week	Total nitrate (2.0, 5.0, 10 sLpm)		Adjusted total nitrate (2.0, 5.0, 10 sLpm)	
	mean ($\mu\text{gNO}_3^- \text{m}^{-3}$)	CV (%)	mean ($\mu\text{gNO}_3^- \text{m}^{-3}$)	CV (%)
8	1.12	5.85	I.D.	I.D.
9	0.85	6.66	1.29	12.9
10	0.68	9.64	0.95	18.6
11	1.15	22.2	1.78	5.33
13	1.16	23.8	1.50	9.89
14	0.91	19.3	1.14	21.7
15	1.16	19.4	1.52	17.0
16	1.15	14.6	1.43	9.56
mean=	1.02	15.2	1.37	13.6

Note : I.D = Invalid data

were greater than $50 \mu\text{g}$ from weeks 11 through 16. The ANOVA test (Table 3) for adjusted total nitrate (ATN) according to the high flow rates (2.0, 5.0, 10 sLpm) indicates a good agreement in ATN measurement at the 5% level (p -value is 0.063).

It can be concluded, therefore, that high flow rates may not affect ATN measurements. If some nitric acid passed through the Nylon filters and was collected on the carbonate filters, it would be expected to be less than 10% of total HNO_3 loading on the basis of Costello's (1990) research. However, the amount of nitrate collected on carbonate filters was always greater than 20% of adjusted total nitrate. This difference suggests that other gaseous nitrogenous compounds could be collected on the carbonate filter and detected as NO_3^- after H_2O_2 -DI water extraction.

Table 5. Total sulfate comparison at high and low flow rates.

	Total sulfate at low flow	Total sulfate at high flow
F	0.330	0.010
p-value	0.804	0.992
d.f. (F)	2	2
d.f. (E)	20	20

Note : d.f. (F) = Degrees of freedom for treatments (factors).
 d.f. (E) = Degrees of freedom for errors.
 p-value = Significance probability for rejecting the null hypothesis (alpha level = 5%, two-tail test).

The results shown in Table 5 suggest that the total sulfate measurements were not affected by low and high flow rates at the 5% level (two tail test) since both p -values (0.804 and 0.992, respectively) are greater than 0.05. The average coefficient of variation (CV = 3.84%) for high flow rates was lower than that (CV = 8.22%) for low flow rates indicating that higher precision was obtained with high flow rates compared to that obtained with low flow rates.

4. SUMMARY AND CONCLUSIONS

This field sampling comparison study was conducted to evaluate the effect of using various sampling flow rates (1.5 to 10 sLpm) on estimates of total nitrate and sulfate concentrations in dry acid deposition. All samples were collected on a weekly basis. Statistical analyses of data showed that the paired samples were reproducible, without any substantial sampling bias for the species measured. Also, a Cary Forest-Florida IFS intersite comparison study showed that the levels of the dry acid deposition species of interest appeared to be similar and independent of elevation and location during summer months.

Statistical results (ANOVA; alpha level 5%) showed that neither the low nor high sampling flow rates caused a significant difference in the measurements of total sulfate and adjusted total nitrate (ATN). However, it was concluded that for high flow rate sampling measurements, total nitrate (TN) could be affected during

extended sampling durations because of potential nitric acid overloading and breakthrough. TN refers to the sum of the nitrate concentrations from the Teflon and Nylon filters. ATN refers to the sum of TN and the nitrate concentration from the carbonate-impregnated filters. Total sulfate refers to the sum of particulate sulfate and sulfur dioxide-sulfate. A laboratory study (Costello, 1990) suggested that the collection efficiency of the Nylon filters can average around 90% at loadings greater than about 35 μg of HNO_3 . Quillian (1990) also observed that the Nylon filters (Nylasorb) exposed to loadings higher than about 50 μg of HNO_3 in the field resulted in a collection efficiency of 90%. Although the previous workers used much higher sampling flow rates (~ 17 sLpm) than employed here, it was assumed that for a high loading (> 50 μg HNO_3) of nitric acid on the Nylasorb Nylon filters, a significant fraction ($\sim 10\%$) of nitric acid could pass through the Nylon filters and be collected on the carbonate impregnated filters. It was concluded that even at the highest sampling flow rate employed (10 sLpm) at the Cary Forest site, nitric acid breakthrough was less than 10% of the total HNO_3 collected. However, for a heavily polluted urban airshed or with longer sampling times, higher filter loadings could result in substantial nitric acid breakthrough and HNO_3 concentrations would be underestimated. Although, at higher concentrations, HNO_3 overloading and breakthrough could be avoided by reducing the sampling duration.

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