

# The effect of ambient ozone and humidity on the performance of nylon and Teflon filters used in ambient air monitoring filter-pack systems

Pamela E. Padgett

USDA Forest Service, Riverside Fire Lab. 4955 Canyon Crest Drive Riverside, CA 92507 USA

## ABSTRACT

Nylon and Teflon filter media are frequently used for monitoring ambient air pollutants. These media are subject to many environmental factors that may influence adsorption and retention of particulate and gaseous nitrogenous pollutants. This study evaluated the effects of ozone and humidity on the efficacy of nylon and Teflon filters used in the US dry deposition monitoring network. Ozone was shown to reduce retention of nitric acid on nylon filters and high humidity was shown to dramatically increase retention on nitrate on Teflon filters.

### Keywords:

Nitric acid  
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### Corresponding Author:

Pamela E. Padgett  
Tel: 951 680 1584  
Fax: 951 680 1501  
E-mail: ppadgett@fs.fed.us

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## 1. Introduction

The Clean Air Status and Trends Network (CASTNET, 2009) is the US Environmental Protection Agency's program for monitoring dry deposition of nitrogen and sulfur containing air pollutants. The network has established about 90 monitoring locations across the continental US with the objective of collecting data on regional trends in air quality, which impacts regional trends in dry deposition. When paired with the wet deposition network – the independent National Atmospheric Deposition Program (NADP, 2009) – the data generated is designed to give researchers and regulators a picture of deposition loads to managed and unmanaged ecosystems.

The heart of the CASTNET monitoring method is the filter pack (FP). The FP is a series of three commercially available filters: The inlet configuration and sampling head exclude particles larger than 2.5  $\mu\text{m}$ . The FP itself is a series of three commercially available filters. Particles smaller than 2.5  $\mu\text{m}$  are captured on a Teflon filter. Behind that is a phosphoric acid coated glass filter that traps ammonia ( $\text{NH}_3$ ), followed by a "Nylasorb" filter (a proprietary nylon product) that traps nitric acid ( $\text{HNO}_3$ ) and sulfur dioxide. There are no denuders or devices for trapping pollutant gases prior to exposure to the Teflon filters. Thus  $\text{NH}_3/\text{NH}_4^+$  and  $\text{HNO}_3/\text{NO}_3^-$  captured by the glass and nylon filters may be from decomposed particulates trapped by the Teflon filter or ambient gaseous pollutants that pass through the Teflon filter. When deployed in the field, the FP is mounted on towers 10 m above the ground. Pollutants are collected by the filters by continuous flow pumps set

at flow rates of 1.5  $\text{L min}^{-1}$  in the east, and 3.0  $\text{L min}^{-1}$  in the west. Filter packs are exchanged weekly, exposed filters are extracted in aqueous solutions, and the resulting solutions analyzed for constituents of interest. This data is then used to calculate dry deposition rates by inferential methods (Clarke et al., 1997, Meyers et al., 1998). The data is made available to the public through the website, <http://www.epa.gov/castnet> (CASTNET, 2009).

The efficacy and representativeness of the FP in atmospheric monitoring is a long-standing debate (Harrison and Kitto, 1990; Sickles et al., 1999). In part, the debate centers around the ability of the filter materials to behave uniformly across environmental conditions that range from the Pacific Northwest to the Gulf of Mexico, and the deserts of the southwest to the north Atlantic coast.

The physico-chemistry of surfaces such as filter media is influenced by temperature, humidity, and the specific combination of atmospheric contaminants (Harrison and Kitto, 1990; Tsai et al., 2004). Dry deposition – the ecological attribute the FPs are designed to estimate – is highly influenced by wind characteristics and vegetation (Clarke et al., 1997; Brook et al., 1997). Measurements or estimates of dry deposition continue to be an elusive and limiting factor in understanding air pollution effects on natural ecosystems (Fenn et al., 2003). Understanding the biases associated with the FP systems is critical to the usefulness of the CASTNET network in assessing ecological responses to dry deposition.

Several research groups have conducted valuable theoretical (Kolb et al., 1997; Stelson and Seinfeld, 2007) and experimental studies (Harrison and Kitto, 1990; Tsai et al., 2004; Keck and Wittmaack, 2005) directed at quantifying the environmental influences and biases of these filters. In particular, Sickles and colleagues (1999, 2002, and 2008) have published several detailed evaluations highlighting potential chemical interactions and losses. In a comparison of annular denuder systems to FP nylon filters, the FP system appeared to be biased high relative to the denuder systems, particularly in the presence of elevated photochemical reactivity (Sickles et al., 1999). When compared to the Interagency Monitoring of Protected Visual Environments (IMPROVE, 2009) sampling method, the FP  $\text{NO}_3^-$  concentrations from the Teflon filters were biased low. Because the protocol for IMPROVE specifies a single 24-hour collection period per FP rather than a week long exposure used by CASTNET, the interpretation of the difference was that the week-long continual exposure at high temperatures and low ambient concentrations resulted in increased losses due to volatilization from the CASTNET Teflon filter (Sickles and Shadwick, 2008). Both of these studies made use of ambient air pollution conditions rather than controlled fumigation exposures for pollutant treatments.

The objectives of the work presented here were to evaluate two environmental factors that have not, yet, been addressed experimentally: (1) The interaction of ozone ( $\text{O}_3$ ) with adsorption and retention of  $\text{NO}_3^-$  and  $\text{HNO}_3$ . (2) The effect of relative humidity, specifically the rapid change in humidity associated with dewfall, on particulate sorption and retention by Teflon and nylon filters.

Ozone is usually a co-contaminant when atmospheric  $\text{HNO}_3$  levels are high as both are produced by the same photochemical processes (Seinfeld and Pandis, 1998). One key difference is, however,  $\text{O}_3$  continues to participate in the atmospheric reactions, while  $\text{HNO}_3$  does not. Once formed,  $\text{HNO}_3$  is, however, very reactive with aqueous and solid surfaces resulting in very high deposition velocities and a short atmospheric lifespan of a week or less (Sanhueza, 1982). Because of ozone's reactivity, the question arises whether the presence of  $\text{O}_3$  causes secondary reactions by  $\text{NO}_3^-$  containing pollutants trapped by filters.

The preferential partitioning of  $\text{HNO}_3$  into water droplets has been well established and continues to be one of the confounding factors in calculating dry deposition from atmospheric concentrations (Kolb et al., 1997; Stelson, and Seinfeld, 2007). In many regions of the US, particularly in the west, sunset is accompanied by a rapid drop in temperature, which triggers a rapid rise in RH and dewfall. This phenomenon may have significant consequence for the behavior of both  $\text{NO}_3^-$  containing particles and  $\text{HNO}_3$  vapor. Controlled experiments using open top chambers (OTC) and continuously stirred tank reactors (CSTR) were established to evaluate these two environmental factors on sorption and retentions of  $\text{NO}_3^-$  by Teflon filters and  $\text{HNO}_3$  by nylon filters.

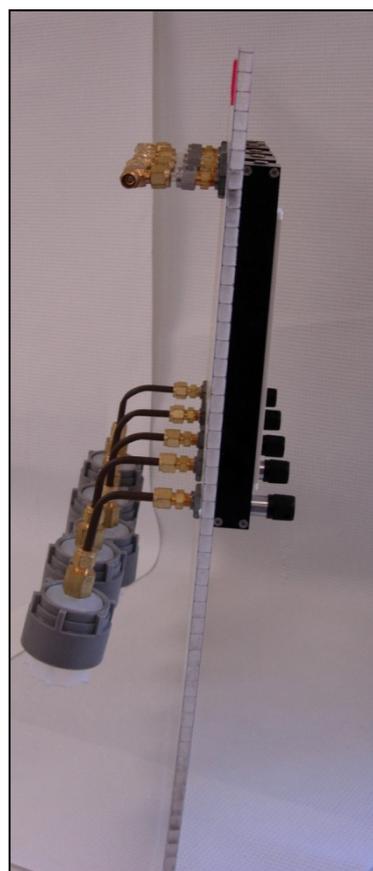
## 2. Materials and Methods

All experiments were conducted using the same batch of Nylasorb filters (Nylon [1 micron] Pall Nylasorb #66509 Lot #427601) and Teflon filters (Millipore LSWP04700 Lot #H9BM51884). Each batch was tested (and passed) for residual contamination and pressure drop prior to use.

Filters were loaded in Teflon US EPA CASTNET-supplied FP. The FPs were used without the stainless steel outer casing. All components were washed in soap-water, rinsed in distilled deionized water and air dried between uses. Handling of filters and FP was conducted using clean forceps and nitrile gloves.

Plexiglas panels were constructed to hold 5 FP, each FP was connected to a high accuracy flowmeter, FM-1050 series (Matheson Tri-Gas, Montgomeryville, PA). The flowmeters were

linked together and attached to a single continuous flow pump (Sierra Instruments Inc, Monterey, CA) (Figure 1). Air flow at each FP was adjusted independently to  $1.5 \text{ L min}^{-1}$ , the CASTNET standard for the east coast. Although the experiments were conducted in the west where the standard practice is  $3 \text{ L min}^{-1}$ , ambient air pollution in Riverside, CA is very high (Padgett et al., 1999) and  $3 \text{ L min}^{-1}$  was not representative of typical filter loading for the network. Preliminary studies have shown that exposures at these conditions were well below the saturation levels for the filters and denuders. During the experiments air flow at each FP was monitored daily and adjusted as needed to maintain a constant flow (although adjustments were rarely needed). All experiments included a panel of five replicates for each treatment, a panel set-up but not deployed to serve as a field blank, and a set of filters extracted directly from the box.



**Figure 1.** Filter pack panels used for testing environmental effects on filter adsorption and retention. Each panel consisted of five Teflon filter packs provided by US EPA each individually connected to a flow meter for independent adjustment.

At the end of the exposures, filters were removed from the FP, transferred into vials for extraction, and sent to the Canadian Air and Precipitation Monitoring Network (CAPMoN) Laboratory in Toronto, Ontario for analysis. Preliminary studies were conducted to compare the results of duplicate and split samples between the CAPMoN Lab and the contract Lab (MACTEC Engineering and Consulting, Newberry Fl) used by the CASTNET operation. Results for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were within 5% of each other. All data shown here were produced by the CAPMoN laboratory.

### 2.1. Honeycomb denuders as secondary methods

Honeycomb denuders (Slanina et al., 1992; Koutrakis et al., 1993) were used as secondary monitoring systems for both the  $\text{O}_3$  and humidity experiments. Denuders were placed in each of the chambers (open top and continuously stirred) without duplication.

Airflow for each denuder was set at  $10 \text{ L min}^{-1}$  using constant flow pumps (Sierra Instruments Inc., Monterey CA). Denuders were exchanged every 24 hours and the exact numbers of minutes were recorded. Denuders and filters were extracted by standard method (Koutrakis et al., 1993) and analyzed by ion chromatography in-house at the Riverside Fire laboratory.

## 2.2. Experiment 1: Ozone effects on nitrate/nitric acid sorption and retention

The experimental system for the  $\text{O}_3$  experiments was open top chambers (Musselman and Hale, 1997). The OTC facility is on site at the Riverside Fire Laboratory in Southern California and consists of 8 plastic covered cone-top chambers. Monitoring instrumentation includes a Campbell meteorology station, a Daisibi ozone monitor, a Monitor Labs nitrogen oxide monitor, and portable particulate monitors (DataRam 4, MEI, Thermo instruments). Portable temperature/relative humidity sensors (Onset, Pocasset MA) were deployed in each of the chambers to evaluate differences between chamber and outside conditions. Ozone and nitrogen oxides were measured and recorded electronically in each chamber, in addition to deployment of honeycomb denuders.

Each chamber is equipped with 6 inch (15 cm) activated charcoal filters and a series of particulate filters. Activated charcoal is effective in removing  $\text{O}_3$  chemically and most ambient particulates and aerosols physically, but not generally effective in removing nitrogen oxides. The ground surface inside the chambers is covered with coarse gravel, which reduces, but does not eliminate, local dust.

Ozone is generated by a Griffen  $\text{O}_3$  synthesizer (Griffin Technics Corp. Lodi, NJ, USA). Synthesized  $\text{O}_3$  was added back to the filtered air stream at controlled concentrations that reflected typical diurnal patterns. The levels were set for 0, 75 and 150 ppb peak afternoon concentrations, which is at the higher end of the pollution spectrum, but not unrealistic in Southern California. The experiment was conducted for 7 days.

## 2.3. Experiment 2: The effects of humidity on uptake and retention of nitric acid on Teflon and nylon filters

There were two components to these experiments. The first was to evaluate retention of atmospheric moisture by nylon filters and the second was to quantify the effect of atmospheric moisture on retention of nitrate/nitric acid by Teflon and nylon filters.

For the water retention experiment forty nylon filters were weighed using a microbalance. Fifteen were placed in desiccators with desiccant for a 0% RH. Fifteen were placed in desiccators containing distilled water for a 100% RH. Ten were set aside as controls. The thirty treated filters were allowed to equilibrate for five days in the 0% and 100% pretreatments. Filters were reweighed following the pretreatment before being divided into five groups of three. Each group of three (three from the dry treatment and three from the wet treatment) were placed into one of five desiccators containing solutions with equilibrium water content of 31% (saturated  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , 280 g in 100 mL), 51% (saturated  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 266 g in 100 mL), 81% (saturated  $(\text{NH}_4)_2\text{SO}_4$ , 71 g in 100 mL), and back into the 0% and 100% RH treatments. The filters were allowed to equilibrate a second time at the new RH treatments for three days before being weighed for a third time. The water content lost or gained was calculated from the difference between the weights following treatment in 100% and 0% RH and the weights following the 0%, 31% 51%, 81% and 100% RH treatments.

The  $\text{HNO}_3$  exposure experiments were conducted in CSTRs modified for  $\text{HNO}_3$  fumigations from the original design by Heagle and Pillbeck (1979). The CSTRs are housed in a temperature controlled greenhouse on the University of California, Riverside

campus. The fumigation system consists of 10 clear Teflon covered chambers 1 m in diameter and 1.5 m tall. A  $\text{HNO}_3$  generator in an attached headhouse synthesizes  $\text{HNO}_3$  vapor that is delivered to each chamber in controlled concentrations. Each chamber is monitored independently using a standard NO monitor. To avoid losses of  $\text{HNO}_3$  between the chambers and the monitor, a molybdenum converter is installed at each chamber which reduces  $\text{HNO}_3$  to NO for transport to the monitoring system. The details of the system can be found in Padgett et al. (2004). Ammonia gas and ammonium particulates are a contaminating by-product of the greenhouse activities.

Humidity in the CSTR chambers was amended by installation of a mist valve in the bulk air supply. Water to the mister was supplied from a deionized water source. The water supply was control by a timer-relay set-up that opened the valve at about sunset to mimic dewfall as air temperatures rapidly drop at sunset.

The diurnal pattern of  $\text{HNO}_3$  in the chambers was designed to reproduce the ambient conditions in the lower elevations of Southern California: no  $\text{HNO}_3$  after dark, an increase in concentrations with sunrise and automobile traffic reaching a peak concentration mid-afternoon and subsequently declining until the  $\text{HNO}_3$  delivery system was shut off prior to sunset. In these experiments "dewfall" was timed to occur when atmospheric concentrations of  $\text{HNO}_3$  were at a minimum (see Figure 5 in Section 3).

The experiment ran for 4 days. Nitric acid was monitored continuously using a Thermo Nitrogen Oxide monitor. Ammonia,  $\text{HNO}_3$  and particulate  $\text{NH}_4^+$  and NO was monitored using honeycomb denuders. The protocol for the denuders was 24 h sampling period at  $10 \text{ L min}^{-1}$  flow rate. Calculations reflect the average ambient air concentrations over the 4 day exposure period. Because the experiments were conducted using the standard operating procedures specific to each monitoring method, direct comparisons between the FP and the denuders are not possible. Consistency analysis suggested that particulate capture was similar between the two systems, but that gases captured by the glass denuders were far greater than gasses captured by the nylon of glass filters of the FP and that there was no statistical relationship between the two systems for the gasses.

## 2.4. Data analysis

Each panel of 5 FP was analyzed as a single treatment of 5 replicates. Treatment effects were evaluated using one-way ANOVA using Sigma-Stat V2.0 (Jandel Scientific Software San Rafael, CA). Chamber effects and the appropriate (or misappropriate) use of "replicate" chambers has been described by several authors (Potvin, 1993; Peterson and Mickler, 1994). The conclusion of these studies is that each chamber must be evaluated as a unique treatment. True replication among different chambers is not really possible.

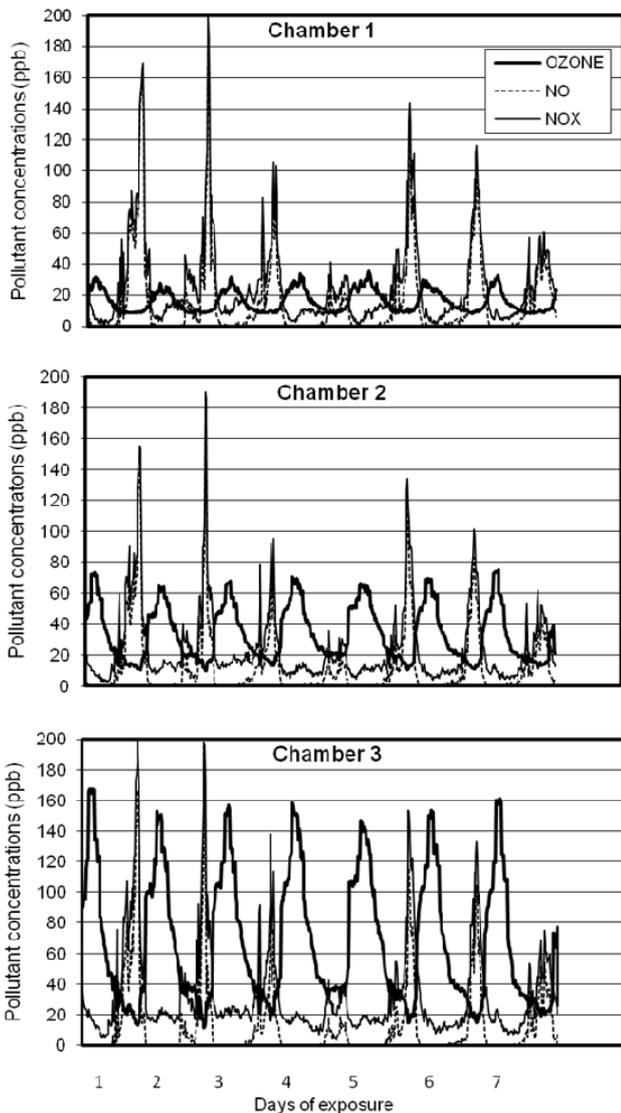
Data is presented as accumulation and extraction of analytes on a per filter basis without further modeling as would be used for presentation by CASTNET.

## 3. Results and Discussion

### 3.1. Experiment 1: Ozone effects on nitrate/nitric acid adsorption and retention

Chamber concentrations of  $\text{O}_3$ , NO, and  $\text{NO}_x$  are shown in Figure 2. There were no significant differences in NO and  $\text{NO}_x$  concentrations among the three chambers. Ozone concentrations were significantly different, however, as planned. The no ozone-added treatments (designated "low" rather than "0", chamber 1) had low, roughly global background concentrations of 30 ppb peak

daytime levels. The O<sub>3</sub> added chambers were targeted for 75 ppb (medium, chamber 2) and 150 ppb (high, chamber 3).

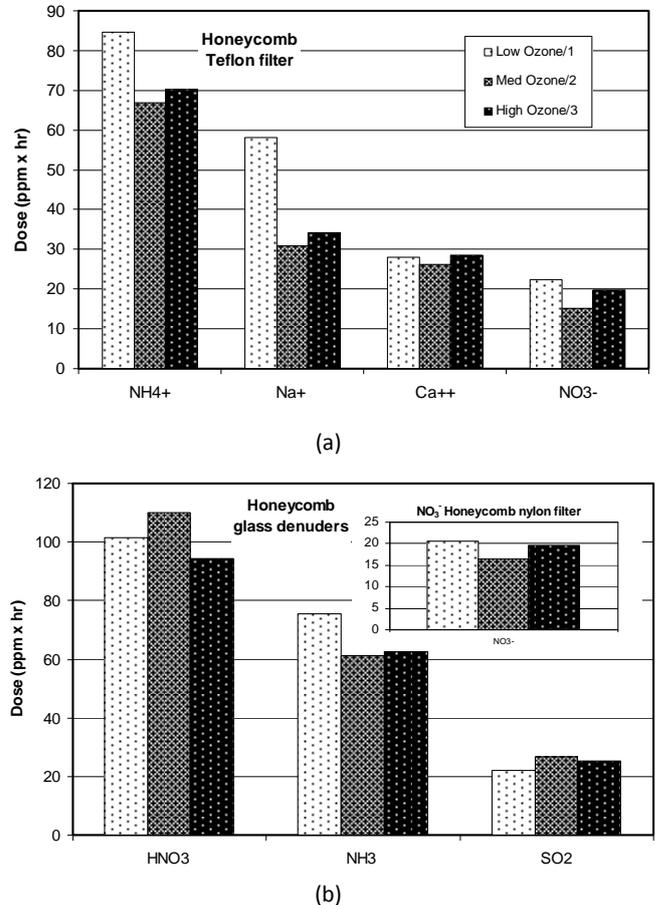


**Figure 2.** Ozone, NO, and NO<sub>x</sub> concentrations during filter pack exposure in Open Top Chambers. Data was collected from continuous monitors using a Dasibi Ozone monitor and a Monitor Labs Nitrogen Oxide monitor. Ambient air was scrubbed by activated charcoal to remove O<sub>3</sub> before being pumped into the chambers. Ozone was synthesized by a Griffen O<sub>3</sub> synthesizer and added back at the concentrations shown. Nitrogen oxides are not removed by charcoal so were provided by ambient atmospheric concentrations.

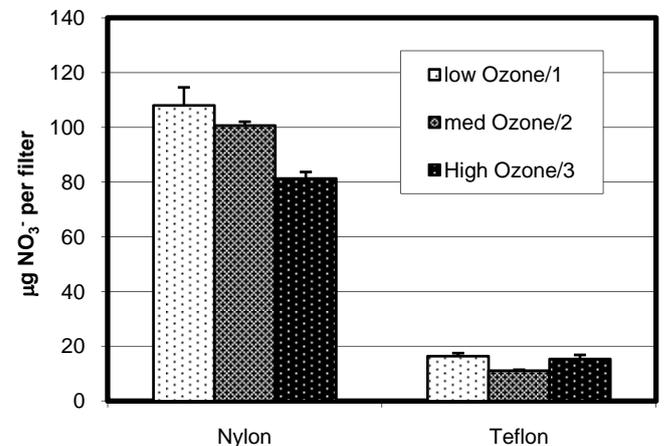
The honeycomb denuders/filter packs were used as secondary monitors to evaluate particulate NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup> and Ca<sup>+2</sup>, and NH<sub>3</sub> and HNO<sub>3</sub> vapor concentrations in each of the OTCs (Figure 3). Particulate NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> were higher in the low chamber, but Ca<sup>+2</sup> and NO<sub>3</sub><sup>-</sup> containing particles were similar among the three treatment chambers. Gaseous HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub> as determined by the glass honeycomb denuders, were also similar across chambers. Nitrate extracted from the nylon filters (designed to capture HNO<sub>3</sub> evolving from degradation of particles) was also similar among the three chambers (inset Figure 3b).

The most significant result was the strong effect O<sub>3</sub> had on NO<sub>3</sub><sup>-</sup> extracted from the nylon filters in the CASTNET FP system (Figure 4). The higher O<sub>3</sub> treatments resulted in significantly

(p<0.05) lower quantities of NO<sub>3</sub><sup>-</sup> measured in the extraction solutions and presumably trapped by the filters. The NO<sub>3</sub><sup>-</sup> extracted from the Teflon filters, on the other hand, indicated no difference among chambers, although total NO<sub>3</sub><sup>-</sup> containing particulate loads on the Teflon filters were much smaller than on the nylon filters.



**Figure 3.** Total particulate and vapor dose during open top chamber experiments as determined by honeycomb denuder. Upper panel shows the dominant ions extracted from the Teflon filter. Lower panel shows the gases extracted from the anion honeycomb denuder (HNO<sub>3</sub> and SO<sub>2</sub>) and the cation denuder (NH<sub>3</sub>).



**Figure 4.** Filter-pack nitrate concentrations from the ozone treatment chambers. Error bars are 1SE.

Interference and secondary reactions of particles by continuous exposure of 1 week has been a long standing concern for the CASTNET system. In a detailed study of FP and annular denuder systems Sickles et al. (1999) proposed that oxidation of ambient  $\text{HNO}_2$  may cause  $\text{HNO}_3$  extracted from nylon filters to be biased high, in comparison to annular denuder systems. During that 14 week study, the first 2 weeks featured very high  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$  and  $\text{H}^+$  concentrations. The speculation was that the high oxidant levels caused increased  $\text{HNO}_3$  by oxidation of  $\text{HNO}_2$ . The data indicated that the bias was not thought to be caused by volatilization of particulate  $\text{NO}_3^-$ .

The results of these controlled  $\text{O}_3$  exposures where all other factors were consistent across treatments indicate that elevated  $\text{O}_3$  depressed the accumulation of  $\text{NO}_3^-$  on the nylon filters. But, like Sickles et al. (1999) had little effect on particles trapped by the Teflon filter. The honeycomb denuders showed no differences in  $\text{HNO}_3/\text{NO}_3^-$  atmospheric concentrations among the chamber suggesting that the events causing depression of  $\text{NO}_3^-$  extracted from nylon filters in the FP occurred at the filter surfaces rather than in the chamber atmospheres.

The mechanism for this observation is not known, and it is unclear whether the effect is due to a reduction in adsorption from the air stream or recovery during extraction. However, since it is thought that nylon, a polyamine, binds  $\text{NO}_3^-/\text{HNO}_3$  on free amine groups, and  $\text{O}_3$  is known to attack non-protonated amines, it is reasonable to hypothesize that the presence of  $\text{O}_3$  reduces the ability of the Nylasorb filter to adsorb  $\text{HNO}_3$  vapor by eliminating binding sites.

### 3.2. Experiment 2: The effects of humidity on uptake and retention of nitric acid on Teflon and nylon filters

**Water gain/loss.** The nylon filters absorbed and desorbed water vapor in response to changes in relative humidity, particularly at higher relative humidity (Table 1). The filters that were initially equilibrated at 0% RH and then transferred to the 100% RH treatment gained 5.6 mg of water over the 3 day exposure period. The moisture gained by the filters transferred into the 31% and 51% RH treatments were not significantly different from one another, but were significantly lower than the 81% RH treatment, which in turn was significantly lower than the 100% RH treatment. The relationship between treatment RH (%) and water gained was not linear suggesting that the nylon filters have a threshold of hydrophilicity.

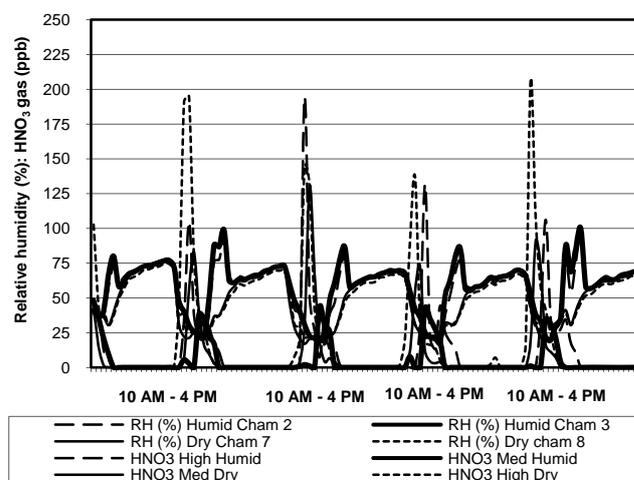
**Table 1.** Water gained and lost by nylon filters after equilibration in 5 different relative humidity levels

Secondary Treatment RH (%)	0% Initial Treatment		100% Initial treatment	
	Water gained	SE	Water lost	SE
0	-0.304	0.090	2.936	0.933
31	0.249	0.363	3.337	1.721
51	0.185	0.117	3.828	0.888
81	1.499	0.282	3.720	1.066
100	5.578	0.683	-2.693	1.089

The pattern of water loss from nylon filters was quite different than the pattern shown for water gain. After 5 days in the initial 100% RH treatment, filters maintained at 100% RH continued to gain water (-2.7 is a "negative", loss in this context). The filters transferred into the lower RH treatments lost moisture at the same rate, regardless of the treatment RH. The adsorption and retention of water by the nylon filters would be expected to strongly affect the adsorption and retention of  $\text{HNO}_3$ .

**CSTR humidity experiment.** Nitric acid concentrations in the treatment chambers (as measured by a real-time nitrogen oxide monitor) are shown in Figure 5. Two chambers were established as

"high", one with added humidity, and one without; and two chambers were established as "medium" also with, and without, humidity. Ultimately, the integrated  $\text{HNO}_3$  levels were similar enough that they were combined into two chambers with humidity and two chambers without humidity. The data from control chamber is not shown. The RH patterns in the non-humidified chambers were typical of semi-arid environments, between 20% and 30% during the day and increasing as temperatures cooled after sunset (Figure 5). The dewfall chambers were designed to exaggerate that pattern with a rapid and increase in relative moisture content to nearly 100% followed by quasi-equilibrium of 70% to 80%. Sunrise and warming of the greenhouse caused a rapid decline in RH. The relationship between  $\text{HNO}_3$  presence and RH is also shown in Figure 5. Nitric acid concentrations were at the detection limit (assumed to be 0) when dewfall was initiated and RH was back to background levels before  $\text{HNO}_3$  was re-introduced to the chambers.

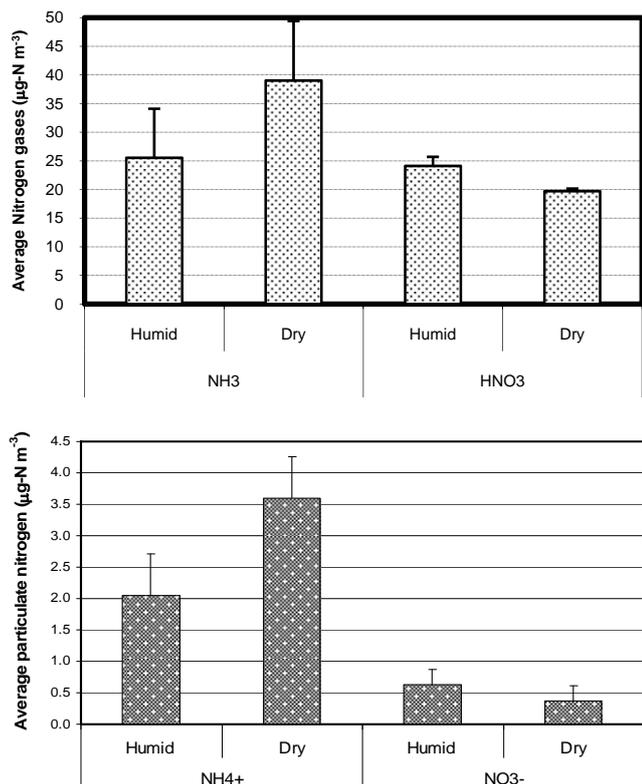


**Figure 5.** Relative humidity and nitric acid concentrations in the continuously stirred tank reactors during exposure of the filter packs.

Denuder measurement of  $\text{NH}_3$  and  $\text{HNO}_3$  vapor indicated no significant differences in  $\text{HNO}_3/\text{NO}_3^-$  between the humid and dry chambers (Figure 6). Ammonia and particulate  $\text{NH}_4^+$  concentrations were highly variable in both the humid and dry chambers as indicated by the large SE bars. There was a trend for higher ammonia vapor in the dry chamber, and a greater amount of  $\text{NH}_3\text{-N}$  relative to  $\text{HNO}_3$ , but neither trend were statistically significant. Particulate  $\text{NH}_4^+$  was, however, significantly higher in the dry chamber ( $p < 0.1$ ) and both humid and dry chambers had significantly greater  $\text{NH}_4^+$  containing particulates than  $\text{NO}_3^-$  particulates. The reasons for this behavior of reduced N are not clear, but may have something to do with other components in the dry fractions that were not captured in this analysis.

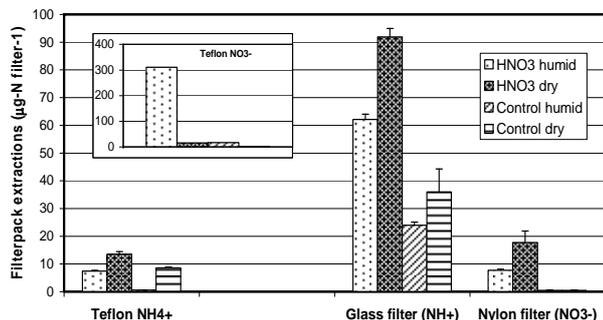
The average 24 h  $\text{HNO}_3$  concentrations in the humid and dry chambers, as measured by the denuders, were similar at 20 to 24  $\mu\text{g-N m}^{-3}$  over the 4 day experiment. Particles containing  $\text{NO}_3^-$  were much lower than the ammonia-containing particles at a 24 h average of about 0.5  $\mu\text{g-N m}^{-3}$ .

The CASTNET FP data indicates that the  $\text{NH}_4^+$  patterns were similar to those measured by the denuder systems, with significantly higher  $\text{NH}_4^+$  containing particulates in the dry chambers. But, without the denuders to strip gaseous  $\text{HNO}_3$ , the FP results were quite different (Figure 7). The most important finding was that  $\text{NO}_3^-$  captured by the Teflon filter was much higher in the humid chamber at over 300  $\mu\text{g-N filter}^{-1}$  compared to the  $\text{NO}_3^-$  extracted from Teflon filters in the dry chambers (Figure 7, inset).



**Figure 6.** Honeycomb denuder measurements of particulates and gases in the continuously stirred tank reactors. Data shown are the mean atmospheric concentrations over the 4 day exposure period in the four treatment chambers. Ammonia vapor and particulates are useful contamination products of the greenhouse environment. Error bars are 1 SE.

Atmospheric moisture has strong influences over HNO<sub>3</sub> physico-chemical behavior. It is well established that HNO<sub>3</sub> will preferentially diffuse into water droplets. The theoretical and physical chemistry has been nicely described by Stelson and Seinfeld (2007). The practical applications are shown here in these simple experiments.



**Figure 7.** Ammonia and nitric acid concentrations extracted from the filter packs after four days of exposure to HNO<sub>3</sub> vapor in continuously stirred tank reactors.

The nylon filters are somewhat hygroscopic as demonstrated by their accumulation and loss of water as a result of changes in relative humidity. As opposed to the hydrophobic nature of Teflon. However, the effect of RH (%) on FP performance was most notable by NO<sub>3</sub><sup>-</sup> extracted from the Teflon filters. Since Teflon does not adsorb water, the results do not suggest solubilization of HNO<sub>3</sub>

vapor in absorbed water. An initial interpretation was the “dewfall” created NO<sub>3</sub><sup>-</sup> aerosols, thus the significant accumulation of apparent particulate-N on the Teflon filters. Although this cannot be totally ruled out, the experiment was repeated twice and the timing of HNO<sub>3</sub> synthesis and moisture addition was carefully monitored to avoid overlap.

The data from the honeycomb denuders shows that once gaseous HNO<sub>3</sub> was removed from the sampling stream, here were not significant differences in atmospheric particles.

#### 4. Summary and Conclusions

The ozone study seriously draws into question the usefulness of nylon filters under high HNO<sub>3</sub> and O<sub>3</sub> conditions. It is important to note that most of the CASTNET sites are in rural or remote locations and this study was clearly at the upper end of typical ambient air concentrations in North America. However, many other monitoring efforts are using the same technology both as active systems such as CASTNET, IMPROVE or denuder systems, or in passive systems such as the ones devised by Bytnerowicz et al. (2001). Since O<sub>3</sub> and HNO<sub>3</sub> are almost always co-contaminants it is almost impossible to get around this. Perhaps a better understanding of the dose - response would be helpful. Since most, if not all of the CASTNET monitoring stations have continuous O<sub>3</sub> monitors there may be a way of incorporating that information into the inferential model. However, the Nylasorb product is proprietary to the manufacturer. Formulation appears to have changed over the years so there appears to be no guarantee that it will not again.

The accumulation of NO<sub>3</sub><sup>-</sup> on the Teflon filter because of dewfall is also a serious problem for interpretation of filter pack data. Differences in humidity, precipitation, and precipitation patterns are probably the biggest environmental variable among the roughly 90 CASTNET sampling sites. Although the physical chemistry leading to the very high NO<sub>3</sub><sup>-</sup> may be a little less obvious, the solution may be easier to find. The honeycomb denuder data suggests that stripping the gasses out of the air stream prior to impacting the Teflon filter reduces the accumulation on that filter. But there are other differences between the two systems including the inlet and the impaction plates, so testing under various environmental conditions is, obviously recommended.

In the end it may be that there is no single system, active, passive, or a hybrid of both, that will function equally in all environments. But at the very least, both researchers and regulators need to understand the biases of these systems.

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#### Disclaimer

Mention of trade names and products is for information only and does not imply endorsement by either the US Department of Agriculture or the US Environmental Protection Agency.

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