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WBEA - HNO₃ Passive Sampler Evaluation Study

Final Report

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Executive Summary

Through the Terrestrial Environmental Effects Monitoring (TEEM) program, WBEA (Wood Buffalo Environmental Association) has been measuring ambient NH_3 and HNO_3 concentrations employing passive sampling techniques at remote sites in the Athabasca Oil Sands, since 2005. For NH_3 , the Ogawa sampler (Ogawa & Co., Pompano Beach, FL) has been used, similar to the one here. For HNO_3 , the USDA Forest Service sampler design was used, exposing a Nylasorb 47 mm diameter nylon filter behind a similar diameter 2 μm pore-size Zefluor (PTFE Teflon) filter in an inverted Millipore Petri dish of 50 mm diameter.

To date, performance of the aforementioned passive systems used in TEEM have not been rigorously examined. Therefore, we evaluated the comparability of passive and active (denuder) systems for the measurement of ambient NH_3 and HNO_3 over one year (+ 5 months) at the two most comprehensive WBEA air monitoring stations (Figure 1), Bertha Ganter at Fort McKay (FMK=AMS01) and Patricia McInnes at Fort McMurray (FMM=AMS06), that are also part of TEEM. We compared passive and active (denuder) surfaces coated with citric acid and phosphorous acid for the collection of NH_3 , but sodium chloride (NaCl) and nylon for the collection of HNO_3 . This approach allowed the quantitative assessment of the performance differences and especially in the case of HNO_3 , the difference in effective stoichiometric, specific chemical absorption of HNO_3 onto sodium chloride versus the non-specific physical adsorption of HNO_3 onto nylon (occurring at an unknown rate).

For NH_3 , using citric acid on both denuder and passive collection surfaces yielded the best agreement with lowest bias per site of 8% and 25% at FMK and FMM, respectively. Using phosphorous acid on passive sampling media caused an underestimation of NH_3 relative to citric acid at FMK and FMM by -13% and -54%, respectively.

For HNO_3 , using sodium chloride on passive surfaces yielded HNO_3 concentrations biased towards high relative to using it on active denuder surfaces by 80% and 92%, at FMK and FMM respectively. However, using nylon instead of sodium chloride as passive collection surface caused a consistent and very high bias at both sites by about a factor of 7 to 8 (685% at FMM to 789% at FMK). Using nylon as passive collection surface yielded exceedingly high HNO_3 values relative to all other passive and active collection surfaces, suggesting artifact reactions that are specific to the nylon surface material. Comparison with long-term HNO_3 data collected elsewhere corroborates our finding that the exposed nylon material causes a significant positive artifact. However, it is unclear what reactions drive this specific artifact. Comparison with simultaneously measured NO_2 , O_3 and water vapor, points to the nylon surface being susceptible to heterogeneous hydrolysis reactions involving NO_2 , N_2O_5 and NO_3 radicals.

Therefore, it is recommended that future WBEA studies not use nylon for the passive sampling of HNO_3 concentrations and their atmospheric deposition at remote and pristine locations relevant to ecological effects assessments. We recommend the use of NaCl. Further, there are approaches to correcting and recovering the past long-term, multi-year WBEA nylon data against the NaCl data

that is substantiated by collocated passive sampling and the active collection systems used in the present study.

Introduction

Passive sampling (PS) is based on free flow of analyte molecules (here HNO_3 or NH_3) from the ambient air to a collecting medium as a result of a difference in chemical potentials. The devices used for PS are usually based on gas diffusion through a well-defined diffusion barrier or permeation through a membrane and subsequent deposition onto a physical adsorbent or a chemical absorbent. In contrast to active sampling, PS requires no electricity (for pumps), no moving parts, and no operational support (flow control, calibration, etc.). After sampling, the collected analytes are desorbed off the adsorbent or absorbent by solvent (usually DI or de-ionized water) or thermal desorption (adsorbents only), and analyzed in the laboratory. Thus, the advantages of PS are i) *small size* allowing compact, portable, and unobtrusive operation, ii) *low cost* both for material and labor allowing for sampling at multiple locations combining geographical mapping with long term data trends, iii) *long integration* providing average pollution levels over time periods of weeks and months, iv) *low impact* requiring no supervision, being noiseless and odorless for use in remote environments without attracting wildlife. Its main disadvantages on the other hand are the relatively laborious post-processing of the samples in the laboratory and the low time resolution, preventing any information on the relationships about dynamic atmospheric changes, sensitivities of the analyte and the stochastic receptor response (Krupa and Legge, 2000).

The theory of PS has been extensively reviewed elsewhere (e.g. Bailey et al., 1981; Namiesnik et al., 1984; Krupa and Legge, 2000; Gorecki and Namiesnik, 2002; Kot-Wasik et al., 2007 and references cited therein), so that we focus here primarily on issues related to HNO_3 . In addition to the acidification of the surface on which HNO_3 is deposited, as a member of the reactive nitrogen complex, initially it is part of the nitrate (nitrogen) soil fertilization process leading to increased growth, productivity and reproduction of terrestrial plants, followed by changes in the structure of plant communities (shifts from nitrophobic to nitrophilic species) and bio-diversity. Further, atmospheric nitrate inputs can result in surface water eutrophication, hypoxia and other impacts such as the mortality of animal life (Bell and Treshow, 2002). Nitric acid reacts very rapidly in the atmosphere with ammonia to form highly deliquescent $\text{PM}_{2.5}$ ammonium nitrate aerosol that leads to reductions in visibility and increased cloud nucleation and precipitation on a regional scale.

In the present context of passive air sampling, diffusional mass transfer both through a static layer of the sampled medium (ambient air) and across a membrane can be described by Fick's first law of diffusion. It states that a given analyte's sampling rate (m_i , the volumetric amount of analyte collected by the sampler per unit time at constant concentration in the surrounding medium) is a function of its diffusion coefficient (D_i) and the geometric constant of the sampler ($A/\Delta x$):

$$m_i = D_i * A / \Delta x. \quad (1)$$

The A and Δx are given by the sampler specific geometry. The A/ Δx ratios for the Ogawa and Radiello samplers are specified by the manufacturer as 2.23 cm and 14.2 cm respectively. For NH₃, Radiello (2006) specifies a constant sampling rate m_{NH_3} of 235 ml min⁻¹ for ambient T, RH and wind speeds ranging within 2-39 °C, 10-90 %, and 0.1-10 m/s, respectively. The NH₃ sampling rate for the Ogawa sampler is 32.3 ml min⁻¹ (Ogawa, 2010). Neither the literature nor the manufacturer provides sampling rates for HNO₃ utilizing the Ogawa type PS. Therefore, employing equation 1, we used a value of 15.8 ml min⁻¹ assuming a constant HNO₃ diffusion coefficient of 0.118 cm² s⁻¹ (Durham and Stockburger, 1986) and an A/ Δx ratio of 2.23 cm.

In the present study, assuming that D_i of both HNO₃ and NH₃ vary little within the existing range of ambient temperature and pressure in the WBEA monitoring domain, then m_i depends mainly on the sampler geometry; i.e. the effective diffusive surface (cross section) A and diffusion path length Δx , which is the distance between the diffusive and adsorbing or absorbing surface. If the relationship between the sampling rate and analyte concentration is known, a time-weighted (integrated) average ambient concentration of analyte i can then be easily determined by the difference between the analyte's mass on the exposed sampler (M_i) and a field blank ($M_{i,0}$) divided by the analyte specific air volume the sampler had been exposed to (V_i):

$$C_i = (M_i - M_{i,0}) / V_i \quad (2)$$

Where, $V_i = m_i * t_{exp}$ (sampler exposure time) (3)

As already indicated, this determination can be employed only if at least three main conditions are met: (a) The receiving medium must act as a so-called *zero sink*, that is, it must not release any of the trapped molecules, even if the concentration of the analyte around the sampler decreases to zero, (b) The trapped molecules are either inert to any changes in ambient conditions or chemical species that may react, or change their state to a measurable quantity in a consistent fashion and at 100% efficiency and (c) The sampling rate must remain constant throughout the sampling session. This can be easily accomplished when the analyte is absorbed (for example into a liquid receiving phase) or chemisorbed (such as in the case of HNO₃ on NaCl-coated surface). However, it can be problematic when physical adsorption is responsible for the analyte collection, as is the case for HNO₃ on Nylon. In this instance, only the linear portion of the adsorption isotherm should be utilized throughout the entire sampling process. Typically, this is accomplished by using high-capacity sorbents at low mass loadings (far from thermodynamic equilibrium). However, since adsorption is a competitive process, the linear range of the adsorption isotherm can be easily exceeded whenever other molecules are trapped in large amounts alongside the analyte molecules. The adsorption of HNO₂ and NO₂ onto Nylon is a good example of this mechanism as described below.

Table 1 gives an overview of the most common passive sampling methods for the time-integrated collection of atmospheric NH₃ and HNO₃. While passive NH₃ samplers have been developed and used more widely and successfully, passive sampling of HNO₃ has proven to be more difficult. De Santis et al. (2003) developed one of the first passive samplers to monitor HNO₃ concentrations inside museums. This sampler was a modification of the open-tube design and used an appropriately impregnated filter to trap the pollutant. The filter was placed at the bottom of an inverted glass vial and held in position by a stainless steel ring. To avoid turbulent diffusion inside the vial, the open end was protected using a fine stainless steel screen. Although this sampler was designed for indoor use, attempts to use it outdoors were successful albeit for short periods of time and only under controlled conditions. The development of designs suitable for outdoor sampling appeared to be more difficult. Lan et al. (2004) successfully deployed generic passive diffusion samplers for the measurement of atmospheric HNO₃ over monthly periods. The improved design employed NaCl and glycerin aqueous reagent solution as the impregnating agent on a cellulose filter to collect HNO₃.

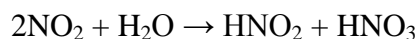
Table 1: Overview of passive sampling methods for NH₃ and HNO₃; adapted from Tang et al. (2001).

Type	Dimensions L(cm)xA(cm ²)	Inlet	Collection surface	Collection medium	NH ₃ Spl Rate ml min ⁻¹	HNO ₃ Spl Rate ml min ⁻¹	Comment, Reference
Ogawa Badge	0.6 x 0.79 (25 holes/0.2cm dia)	Open	Glass fiber or Cellulose filter on stainless grid	Citric acid	31.2-32.8	-	Protective cover used outdoors; Mulik et al., 1989; Roadman et al., 2003; Ogawa, 2010
Sigma-Aldrich Radiello	1.8 x 25.6 (via 1.6 x 6 cyl.)	cylindrical microporous PE membr.	5.8 x 60 mm adsorbing cartridge	Phosphorous acid	198-235	-	Protective cover used outdoors; Radiello, 2006; NADP, 2009
USDA Petri Dish	0.12 x 13.7	Zefluor membrane	47mm Nylon filter behind membrane	Nylon	-	179.1* - 239.8 [#]	*rel. to denuders; [#] lab controlled environ; Bytnerowicz et al., 2005
Teflon Pack	0.7 x 7.9*	Open	Cellulose 25/47 mm NH ₃ /HNO ₃	Citric acid / NaCl for NH ₃ /HNO ₃	6.6 [#]	12.1 [#]	*assumed 1/3 of filter A; [#] from ppb/ug/day; Lan et al., 2004
Palmer Diff. Tube	7.1 x 0.95	Open	Stainless steel grids	Sulphuric acid	1.6	-	With protective cover; Palmer et al., 1976; Atkins & Lee, 1992
Palmer Diff. Tube	3.5 x 0.95	Membrane	Stainless steel grids	Sulphuric acid	3.4	-	With protective cover; Thijsse et al., 1996; Sutton et al., 1997
Blatter Diff. Tube	0.7 x 0.64	Open	Absorbent behind Teflon membrane	Ethylene glycol, HCl	114.0	-	Protective cover used outdoors; Blatter et al., 1992
Ferm Badge	1.0 x 3.14	Steel grid + Teflon	Whatman 40	Citric acid	39.3	-	Ferm 1991; Ferm & Rodhe, 1997; Ferm & Svanberg, 1998
Willems Badge	0.2 x 5.31	PTFE membrane	Glass fiber filter	Tartaric acid	333.3	-	Addl. 0.8 cm inlet in front of membrane; Willems, 1993
CEH ALPHA	0.6 x 3.46	PTFE membrane	Schleicher & Schuell 595	Citric acid	72.3	-	Protective cover used for outdoor sampling; Tang et al., 2001
CSPSS Badge	8.0 x 17.35	PTFE membrane	Absorbent behind PTFE membrane	-	271.7	-	Not tested for NH ₃ ; protective cover needed; Tang et al., 1999
Krochmal Badge	1.0 x 4.91	PP membrane	Whatman 1 or Stainless steel grids	-	61.5	-	Not tested for NH ₃ ; Krochmal & Kalina, 1997
UC Davis Badge	1.03 x 8.50	Zefluor membrane	Whatman 41	Citric acid	103.5	-	Raubaud et al., 2001
Kasper & Puxbaum	0.90 x 8.04	Teflon membrane	Stainless steel grids	Phosphoric acid	112.0	-	Protective cover used outdoors; Kasper & Puxbaum, 1994

The USDA Forest Service and University of California (Riverside) researchers have developed a simple and inexpensive passive sampler for monitoring atmospheric HNO₃ (Bytnerowicz et al., 2001). The sampler is based on HNO₃ diffusion through a 47 mm diameter Teflon membrane with 2 μm pore size and adsorption onto a 47 mm Nylon backup filter (Nylasorb, Pall Corporation). Bytnerowicz et al. (2005) showed that HNO₃ concentrations determined with the passive nylon samplers closely corresponded with those measured with collocated CaCO₃ (behaves like Na₂CO₃ discussed below) coated honeycomb annular denuders both under ambient and controlled conditions of exposure. The filter pair was housed in a 50 mm commercially available polycarbonate Petri dish, kept in place by Teflon rings, and protected from wind and rain by a polycarbonate cap. The original design provided insufficient protection as high winds cause uncontrolled turbulent flow and disrupt the laminar airflow controlling HNO₃ deposition onto the nylon filter.

Most passive samplers described in the literature and listed in Table 1 are planar or axial in shape with limited sampling rates and sampling capacity. A radial coaxial design in the Radiello sampler for NH₃ (Radiello, 2006) provides an improved geometry, which helps to circumvent limitations in sensitivity during short-term sampling (improved sampling rates) and long-term sampling (no analyte back-diffusion/loss to high capacity). This is superior to the planar or axial design because the NH₃ uptake rate is proportional to the height of the diffusive cylinder and inversely proportional to the logarithm of the ratio of diffusive over adsorbing cylinder radius. The radius of the diffusive cylindrical surface can only be determined empirically via exposure experiments, which have not yet been performed successfully for HNO₃ due to difficulties associated with the physical and chemical properties of the micro-porous layer of the tubular diffusive membrane (www.radiello.com).

Table 2 gives an overview of the most common active sampling methods for the time-integrated collection of HNO₃ and other inorganic gas and aerosol species. The filter-pack method, usually with Teflon, nylon or impregnated filters in series, is the least accurate, but simplest and most commonly used sampling procedure. This technique is labor intensive, and suffers possible interference due to oxidation of nitrites (or other reactive N species) collected on nylon filters by adsorption, positively biasing HNO₃ collection. This positive bias was first discovered by Perrino et al. (1988), who found that nitrite retained on Nylon from HNO₂ or NO₂ adsorption is oxidized to nitrate at near 100 % conversion efficiency, during photochemically active sampling periods. NO₂ adsorption on Nylon follows the heterogeneous surface reaction with H₂O according to



with a removal constant of about $1 \times 10^{-4} \text{ ms}^{-1}$ at a H₂O concentration of 2 % v/v. The Teflon-nylon sampling configuration also suffers from evaporation of aerosol nitrate from the Teflon filter up front (Appel et al., 1981).

In a study first described by Perrino et al. (1990), that was later confirmed by Bari et al. (2003), a sodium carbonate impregnated surface allowed similar artifact reactions like nylon but at a significantly lower rate; i.e. N-containing species (such as NO_x and Peroxyacetyl nitrate, PAN) were interfering agents, producing albeit relatively small amounts of nitrite and nitrate on sodium carbonate. They also found artifact contributions to the measured nitrite and nitrate levels, produced by the above heterogeneous reaction of NO₂ and water vapor but at much lower levels than for nylon. Perrino et al concluded overall, based on penetration efficiency and measured interference from NO₂⁻: “It has been demonstrated that this phenomenon occurs on both the nylon surface and on Na₂CO₃ coatings (but at a much lower level), and that during photochemical smog events up to 100% of the NO_x amount may be converted to NO₃. As a consequence, all the species which are retained on the denuder coating yielding NO_x should be considered as potential indirect interferents in the measurement of HNO₃”.

In the atmosphere, HNO₃ is mainly formed from reaction of NO₂ with the hydroxyl radical. Hydrolysis reactions involving N₂O₅ and NO₃ radicals, as well as NO₂ and NO₃ reactions with O₃ and certain NMHC also yield HNO₃. All these reactions may also take place heterogeneously on reactive surfaces such as nylon or sodium carbonate impregnated surfaces, but at different extents.

Table 2: Overview of active sampling methods for NH₃ and HNO₃ (adapted from Trebs et al., 2004).

Method	Measured Species	References
Impregnated, Teflon and Nylon filters in series	NH ₃ , HNO ₃ , PM: NH ₄ ⁺ , NO ₃ ⁻ , Cl ⁻ , SO ₄ ⁼	Appel et al., 1980; Appel et al., 1981; Cadle et al., 1982; Parrish et al., 1986; Galasyn et al., 1987; Solomon et al., 1988; Appel et al., 1991
Denuder - Filter Pack	NH ₃ , HNO ₃ , HONO, HCl, SO ₂ , PM: NH ₄ ⁺ , NO ₃ ⁻ , Cl ⁻ , SO ₄ ⁼	Kitto and Harrison, 1992; Harrison et al., 1996; Danalatos and Glavas, 1999; Possanzini et al., 1999
Dry Coated Denuder	NH ₃ , HNO ₃ , HONO, HCl, SO ₂	Eatough et al., 1985; Durham et al., 1987; Marshall and Dimmock, 1992
Wet Effluent Denuder	NH ₃ , HNO ₃ , HONO, HCl, SO ₂	Simon et al., 1991; Vecera and Dasgupta, 1991; Taira and Kanda, 1993; Buhr et al., 1995; Zellweger et al., 1999
Parallel Plate Denuder	NH ₃ , HNO ₃ , HONO, HCl, SO ₂	Simon and Dasgupta, 1993; Boring et al., 1999; Genfa et al., 2003
Thermo-Denuder	NH ₃ , HNO ₃	Keuken et al., 1989; Klockow et al., 1989
Wet Annular Denuder	NH ₃ , HNO ₃ , HONO, HCl, SO ₂	Keuken et al., 1988; Wyers et al., 1993; Allegrini et al., 1994; Slanina and Wyers, 1994; Oms et al., 1996; Jongejan et al., 1997
Diffusion Scrubber and Mist Chamber	NH ₃ , HNO ₃ , HONO, HCl, SO ₂	Matusca et al., 1984; Cofer et al., 1985; Philips and Dasgupta, 1987; Lindgren, 1992; Lefer et al., 1999; Sanhueza and Garaboto, 2002

Various inter-comparison experiments (e.g. Spicer et al., 1982; Hering et al., 1988; Williams et al., 1992) revealed significant discrepancies between different HNO₃ measurement techniques, which emphasized the need of artifact-free measurement methods for an accurate determination of

HNO₃ and particulate nitrate in the atmosphere. The most widely used approach for sampling a gas in the presence of corresponding aerosol particles is the denuder technique. Dry-coated denuders are reliable, but labor intensive and provide only long time-averaged concentrations on the order of 24 hours (Dasgupta, 1993). These drawbacks were overcome by various other developments. Simon et al. (1991) have proposed four different designs for wet effluent diffusion denuders coupled to ion chromatography (IC) with continuously renewed collection surfaces. It should be noted that ion chromatography allows the quantification of the total, water soluble nitrate, but does not allow the identification of the source of nitrate, HNO₃ versus the contribution of other reactive N species. Nevertheless, efficient retention of trace gases and higher time resolution measurements may be achieved by parallel-plate denuders coupled to on-line analysis. Keuken et al. (1989) developed an automated thermo-denuder system for the determination of NH₃ in ambient air. A device that enjoyed some popularity is the Wet Annular Denuder (WAD) that has the ability to maintain near-quantitative collection efficiencies at high sampling rates in a compact design (Dasgupta, 1993; Wyers et al., 1993). Diffusion scrubber and mist chamber techniques also provide measurements with higher time resolution and lower sensitivity towards artifacts.

During the last decade, filter-based methods were replaced by continuous denuder devices and optical measurement techniques limited to measuring either a single compound or species of the same physical state (i.e. either gas or aerosol). These techniques evolved into samplers combining aqueous phase aerosol collectors with the denuder technique for the simultaneous collection of gas and aerosol species. In 1999 USEPA-sponsored the Atlanta Super Site Experiment providing a breakthrough in the development of new semi-continuous aerosol measurement techniques with on-line IC analysis of the resulting aqueous solution (Solomon et al., 2003). The Atlanta Super Site Experiment also provided a quantitative assessment of the performance of the combined denuder-filter techniques for time-integrated aerosol measurement. Acknowledging the semi-volatile character of HNO₃, the recommendation was to use sodium carbonate impregnated denuders to effectively remove HNO₃ upstream from the Teflon filter collecting fine PM, and to place a nylon or sodium carbonate impregnated backup filter, collecting the volatile fraction of the nitrate aerosol from the front filter, in order to accurately measure the nitrate content in PM_{2.5}.

In order to put our HNO₃ results into greater spatial context, we compared the results from other long-term measurements in the United States and overseas. Considering sodium chloride being the reference absorbent, our 15-month average HNO₃ concentration is 0.23 and 0.44 μg m⁻³ from active and passive samplers, respectively. SEARCH network measurements made in the southeastern U.S. (Hansen et al., 2003) during the same period, show overall HNO₃ averages ranging from 0.53 μg m⁻³ in rural areas to 1.09 μg m⁻³ in urban environs. Ferm et al. (2005) reported a similar urban-rural gradient in HNO₃ for various locations in Europe, tropical Africa and tropical Asia. Interestingly, Ferm et al. (2005) also observed a gradient at much greater

spatial scales; that is, tropical low latitudes exhibited an average annual HNO₃ level of about 1.4 μg m⁻³ versus roughly 0.3 μg m⁻³ at high European latitudes close to the WBEA domain.

All these levels are well below the 15-month average concentrations of 2.5 and 3.2 μg m⁻³ measured with the Ogawa nylon sampler at FMM and FMK, respectively. In other words, not only does nylon yield HNO₃ concentrations higher than other collocated samplers, it also yielded HNO₃ concentrations much higher than urban centers in the U.S. and Europe. Taken together, these results indicate there is a significant, but as yet unexplained, positive bias to passive nylon measurements of HNO₃.

Background and Objectives of the Present Study

As noted previously, investigating long-term effects of air emissions on terrestrial ecosystems by means of passive sampling is an important task of WBEA and is performed through its Terrestrial Environmental Effects Monitoring (TEEM) program. TEEM reports annual average ambient concentrations of various reactive gases including ammonia (NH₃) and nitric acid (HNO₃) from a number of different locations within their geographic domain (<http://www.wbea.org/air-monitoring/passive-monitoring>). In 2010, the annual averages for NH₃ ranged from 0.5 to 3.4 μg m⁻³ yielding a domain-wide average of 1.3 ±0.6 μg m⁻³, while for HNO₃ a range of 0.26 to 1.55 was reported with average 0.53 ±0.27 μg m⁻³. The 2010 averages were based on data from 39 stations, whereas values from only 27 stations were reported in 2011, which were generally higher: NH₃ averaged 1.8 ±1.9 μg m⁻³, ranging from 0.5 to 10.0 μg m⁻³, and HNO₃ averaged 1.3 ±0.5 μg m⁻³, ranging from 0.5 to 2.6 μg m⁻³.

Thus, the objective of this study was to determine the comparability (i.e., detection limit, precision and accuracy) of several active and passive sampling measurement techniques for the two reactive atmospheric gases (NH₃ and HNO₃). This report provides data and results for a 17-month study (i.e. June 2011 through October 2012) keeping in mind its application in environmental impact assessments.

Materials and Methods

Since 2005 WBEA has been measuring both ambient NH₃ and HNO₃ concentrations employing passive sampling techniques at remote sites. For NH₃, the Ogawa sampler (*Ogawa & Co., Pompano Beach, FL*) has been used, similar to the one here. For HNO₃, the USDA Forest Service sampler design has been used, exposing a Nylasorb (*Pall Corporation, Port Washington, NY*) 47 mm diameter nylon filter behind a same diameter 2 μm pore-size Zefluor, PTFE Teflon (*Pall Corporation*) filter in an inverted Millipore Petri dish of 50 mm diameter, as described in Bytnerowicz et al. (2005).

To date, performance of the aforementioned passive sampling systems used in TEEM have not been rigorously examined. Therefore, our study quantitatively compared the performance of passive and active (annular denuder system, *URG, Chapel Hill, NC*) surfaces in collecting atmospheric NH₃ and HNO₃ during monthly intervals at two sites within the WBEA monitoring

network (Figure 1 and also for details, see Percy et al., in Percy, 2012), Bertha Ganter at Fort McKay (AMS01=FMK) and Patricia McInnes at Fort McMurray (AMS06=FMM). The passive samplers (PS) tested were the Ogawa PS-100 and the Radiello RAD-168 (*Padova, Italy, also www.radiello.com*). Surfaces coated with citric acid (Ogawa) and phosphorous acid (Radiello) served to collect NH₃; sodium chloride and Nylon filters collected HNO₃. The Annular Denuder System (ADS) consisted of URG 242 mm long annular diffusion tubes (*University Research Glassware, Chapel Hill, NC*) coated with sodium chloride (SCL) for HNO₃ and with phosphorous acid (PA) or citric acid (CA) for NH₃. The different collection techniques and surface types are summarized in Table 3.

The ADS operates two channels with the denuders positioned downstream from a PM_{2.5} impactor and upstream of a single-stage filter pack loaded with a Teflon filter. Sample volume for each channel was measured by a dry gas flow meter and during the first 8 months of the campaign, flow rate was controlled by needle valves, which were replaced by individual mass flow controllers for the last five months.

Table 3: Active and passive sample media deployed for the study.

Sampler Type	Collection Surface	Abbrev. ID	Target Gas
Active-ADS	SCL: sodium chloride on denuder wall	SCLD	HNO ₃
Active-ADS	CA: citric acid on denuder wall	CAD	NH ₃
Active-ADS	PA: phosphorous acid on denuder wall	PAD	NH ₃
Passive-Ogawa	SCL: sodium chloride on cellulose pad	OgaSCL	HNO ₃
Passive-Ogawa	NYL: nylon filter 13mm 0.2µm Whatman	OgaNYL	HNO ₃
Passive-Ogawa	CA: citric acid on cellulose pad	OgaCA	NH ₃
Passive-Radiello	PA: phosphorous acid on cartridge	RadPA	NH ₃

Passive samplers (PS) tested for NH₃ collection, were the Ogawa PS-100 (*Ogawa Inc. USA, Pompano Beach, FL*) equipped with CA impregnated cellulose pads and the Radiello RAD-168 (*Padova, Italy, www.radiello.com*) equipped with a PA sample cartridge. Passive samplers (PS) tested for HNO₃ collection, were the Ogawa PS-100 equipped with either SCL impregnated cellulose pads or Nylon (NYL) filters. The cellulose pads were provided by Ogawa Inc and the NYL pads were 13 mm diameter Whatman filters with nominal 0.2 µm pore size. They were washed prior to sampling with a 1% sodium carbonate solution followed by triple DI water rinse and dried under a HEPA-filtered contaminant-free laminar flow hood together with the other coated pads. Potential effects of the nylon washing on the derived HNO₃ results were investigated during the last two sampling periods. All coating solutions applied to either denuders or pads were 1% (w/w) in DI water.

All samplers were deployed in duplicate at two WBEA monitoring sites (Figure 1) (Bertha Ganter, Fort McKay, FMK=AMS01, and Patricia McInnes, Fort McMurray, FMM=AMS06) for nominal 1-month exposure periods. Sampling points of both PS and ADS units were comparable between the units and sites; that is, the PS collection surfaces and ADS inlets were mounted at approximately the same height above ground and at consistent distances between each other. We

attempted to avoid sampling in the wake of eddy effects by considering the site specific preferred wind direction and mounting the much more bulky ADS units “downwind” from the PS units.

Figure 2 illustrates the sampler locations at FMK and FMM. This layout also allowed the investigation of a potential systematic influence by the local operators using the stairs during their regular maintenance visits. Sampling started on June 7, 2011 at both sites and sample media were exchanged simultaneously (i.e. within a few hours on the same day) within the first 10 days of each following month. The only deviations from this schedule occurred in 2012, when media were exchanged on May 2 and on May 7 at FMM and FMK, respectively. These samples were also exposed for two months instead of one, i.e. until July 5, 2012. No sampling occurred during rest of July 2012 but sampling resumed in August for three more periods including October 2012.

During the first two months of the study, denuder breakthrough and artifact on the 2-channel ADS “reference” was investigated by using duplicate SCL or CA denuders in series. Upon validation (see Results section) and for the remaining measurement period, each ADS operated tandem denuder channels, one with a SCL-coated followed by a CA-coated denuder, the other with a SCL-coated followed by a PA-coated denuder; see Figure 3. Monthly sample volume was determined from the ADS flow control system and related to the total mass of NH_3 and HNO_3 extracted from each denuder, yielding the respective ambient concentrations as “reference” for the different PS units.

The two PS types (Ogawa and Radiello) provide turbulence-free diffusion of the target gas into the cavity housing the specific absorbing material. The construction of both PS types prevents particle collection and thus the measured gas concentration is not biased by the collection of ammonium nitrate aerosol. However, as the results will show, physical adsorption onto nylon material seems to entail numerous gas-phase reactions leading to a large nitrate artifact. This artifact seems to be slightly enhanced when washing nylon prior to exposure.

The duplicate exposure of passive and active sample media was used to assess measurement precision. Each sampling medium was accompanied by a field blank providing a measure for overall detection limit. Lab blank duplicates were further restricted by not being shipped outside the laboratory, and therefore served to capture measurement uncertainties introduced by the sample media preparation itself. Samplers were deployed for about 1 month, then returned to ARA, extracted with DI water and analyzed for NH_4^+ and NO_3^- via ion chromatography (IC). The ambient air concentration of NH_3 and HNO_3 was calculated from the respective mass adsorbed, the duration of exposure, the specific diffusion coefficient, and sampler geometry, as discussed below.

In the present study, denuder breakthrough was determined from the use of tandem pairs during the first two months at both sites. The average breakthrough of both NH_3 and HNO_3 was less than 10%. Therefore, no correction was needed in the calculations outlined below. Furthermore, the average ammonium mass found in extracts of exposed SCL denuders was less than the amount found in SCL field blanks, which did not warrant any additional correction of the

calculations. Therefore, arriving at ambient NH_3 and HNO_3 concentration values from the ADS samples (C_{ADS_i} , $I = \text{NH}_3, \text{HNO}_3$) is straightforward following equation 4:



Figure 1: Location of sampling sites in the WBEA (Athabasca Oil Sands) study region.

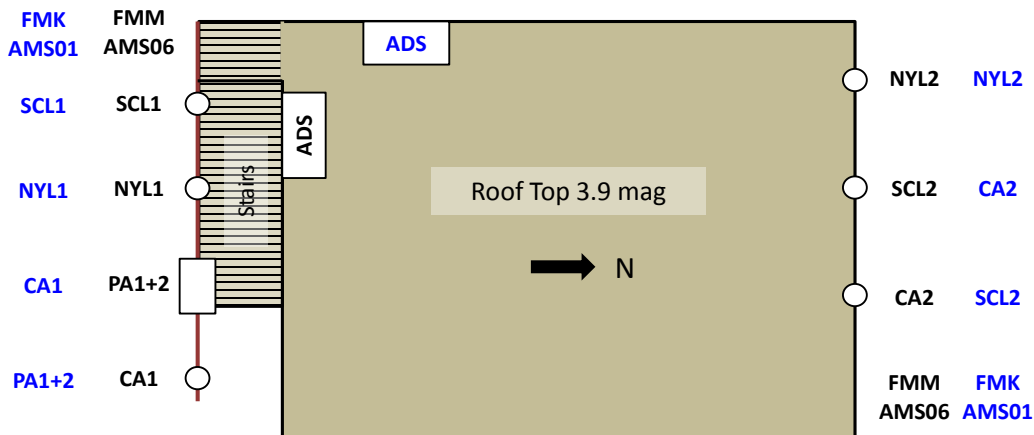


Figure 2: Location of samplers on the station rooftop at FMM (black) and FMK (blue).

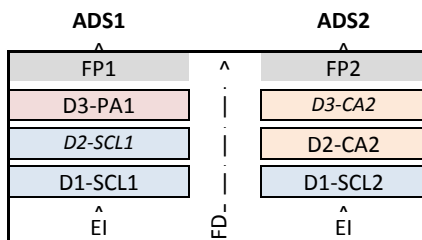


Figure 3: The ADS operates two flow-controlled channels with an elutriator-impactor (EI) inlet allowing $PM_{2.5}$ to pass through a denuder train from the bottom up (see flow direction FD) for collection in a filter pack (FP) downstream. The backup denuders *D2-SCL1* and *D3-CA2* were used to assess denuder breakthrough and specificity only during the first 2 months.

$$C_{ADSi} = (M_{DI} - M_{D0}) / V_D \quad (4)$$

M_{DI} ... mass of NH_3 or HNO_3 on sampled denuder

M_{D0} ... mass of NH_3 or HNO_3 on field blank

V_D ... measured ambient air sample volume drawn through denuders (DGM).

A similar approach was followed for the PS data, per equation 5:

$$C_{PSi} = (M_{PI} - M_{P0}) / V_P \quad (5)$$

M_{PI} ... mass of NH_3 or HNO_3 on exposed PS

M_{P0} ... mass of NH_3 or HNO_3 on field blank

V_P ... calculated air volume the PS has been exposed to.

Determination of V_P is more complex and can be approximated by:

$$V_P = m_i * t_{exp} \quad (6)$$

$$m_i = D_i * A / \Delta x$$

- m_i ... diffusion flow rate or sampling rate in $l \text{ min}^{-1}$
- D_i ... diffusion coefficient for NH_3 or HNO_3
- A ... effective diffusion cross section
- Δx ... effective diffusion path length
- t_{exp} ... PS exposure time.

As mentioned previously, A and Δx are determined by the specific geometries of each PS, and the $A/\Delta x$ ratios are given by the corresponding manufacturer as 2.23 cm and 14.2 cm for Ogawa and Radiello, respectively. Furthermore, Radiello specifies a constant NH_3 sampling rate m_{NH_3} of 235 ml min^{-1} for a wide range in ambient T , RH and wind speed. We used 235 ml min^{-1} for all our RadPA samples. Ogawa's NH_3 sampling rates provided in the literature vary between 31.19 ml min^{-1} (NADP, 2009) and 32.3 ml min^{-1} (Ogawa, 2010). We consistently used 32.3 ml min^{-1} , acknowledging that values in the cold winter months will likely be more uncertain as the very low ambient temperatures experienced at FMM and FMK are outside the tested and calibrated specifications of these samplers. Neither the literature nor the manufacturer provides sampling rates for HNO_3 utilizing the Ogawa type PS. Therefore, employing equation 1, we used a value of 15.8 ml min^{-1} assuming a constant HNO_3 diffusion coefficient of 0.118 $\text{cm}^2 \text{ s}^{-1}$ (Durham & Stockburger, 1986) and an $A/\Delta x$ ratio of 2.23 cm.

Results and Discussion

Results can be considered as final, as active denuder sampling ended on July 5, 2012, while passive sampling continued on until November 2, 2012. Thus, the presented data roughly reflect monthly averages encompassing the period June 7, 2011 through November 2, 2012, whereby one sampling period included two months (May 7 to July 5, 2012). In addition, during the first eight sampling periods, the ADS values suffered greater than usual uncertainty due to problems in determining the correct sample volume at both sites. The following compares the data quality indicators such as detection limit and precision for NH_3 and HNO_3 , before we compare differences in active and passive sampling results.

Detection Limits (DL)

Neglecting the field blanks from the first sampling period, the detection limits (DL) were calculated as two times the standard deviation (four times for unwashed OgaNYL, Ogawa nylon, at the corresponding same level of confidence) of the IC values obtained from the field blank extracts relative to the actual sample volumes of the exposed ADS and PS samples. Thus, the DL values summarized for the different sampling media and each site separately in Table 4 are in $\mu\text{g m}^{-3}$. The effective DL for ADS is about 3-25 times lower than the PS due to the vastly larger sample volume for active versus passive samples. Similarly, the RadPA (Radiello phosphorous acid) sampler yielded a lower detection limit thanks to the inherently larger sample volume. The

washed and unwashed nylon material tested in the Ogawa sampler yielded similar detection limits.

Again, Table 3 is provided for ready reference:

Table 3: Active and passive sample media deployed for the study.

Sampler Type	Collection Surface	Abbrev. ID	Target Gas
Active-ADS	SCL: sodium chloride on denuder wall	SCLD	HNO3
Active-ADS	CA: citric acid on denuder wall	CAD	NH3
Active-ADS	PA: phosphorous acid on denuder wall	PAD	NH3
Passive-Ogawa	SCL: sodium chloride on cellulose pad	OgaSCL	HNO3
Passive-Ogawa	NYL: nylon filter 13mm 0.2µm Whatman	OgaNYL	HNO3
Passive-Ogawa	CA: citric acid on cellulose pad	OgaCA	NH3
Passive-Radiello	PA: phosphorous acid on cartridge	RadPA	NH3

Table 4: NH₃ and HNO₃ detection limits in µg m⁻³ based on field blank values and actual sample volumes. SCLD, CAD, and PAD are ADS field blanks with SCL, CA and PA coatings. Bottom row shows average sample volume in liters.

DL ug/m3	HNO3				NH3			
	SCLD	OgaSCL	OgaNYL	unwashed	CAD	PAD	OgaCA	RadPA
FMK	0.010	0.288	0.171	0.305	0.014	0.019	0.163	0.074
FMM	0.016	0.210	0.243	0.021	0.036	0.064	0.203	0.082
V_l	99,829	729	729	664	92,601	107,057	1,489	10,834

Precision (Bias) in NH₃ Measurements

Figure 4 shows scatter plots of ambient NH₃ concentrations at FMK (left) and FMM (right) derived from PS unit 2 versus unit 1 for the Ogawa and Radiello samplers. Since same configuration of denuders were not deployed, denuder derived NH₃ is depicted as CAD versus PAD. The tables below the plots summarize the linear regression statistics R², slope and intercept. Excluding one point (in blue) from each FMK and FMM data set, the CAD vs. PAD relationship was significant at the 95% confidence interval (p-value < 0.05). The slopes however, indicated significant site-to-site differences: CAD-derived NH₃ was 12% higher than PAD at FMK, but was 67% lower than PAD at FMM. Although the Radiello samplers were physically closer to each other than the Ogawa samplers (see Fig. 2), the slope deviated much farther from 1 at both sites. The Ogawa CA pads, in contrast, captured ambient NH₃ to within 6% and 8% of each other at FMK and FMM, respectively. This proves that visitors, including local operators using the stairs up to the shelter platform, do not systematically bias our measurements in any statistically significant way.

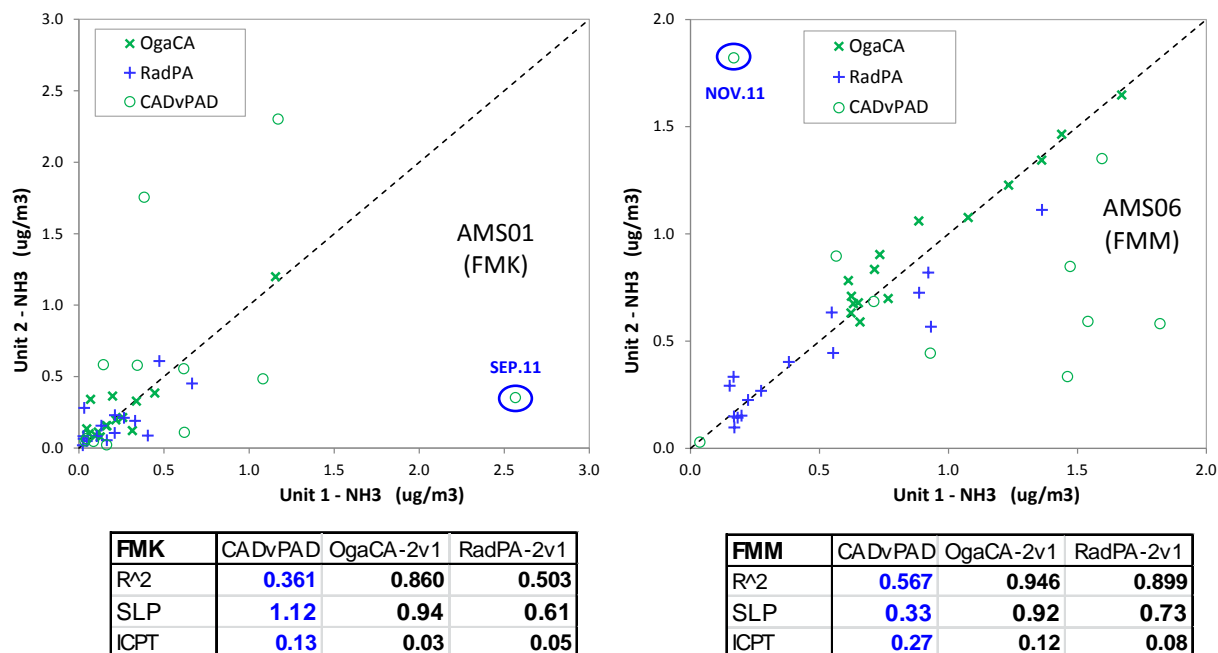


Figure 4: Performance of NH₃ collection media at FMK (left) and FMM (right) based on sample duplicates. Blue circles indicate “outliers” that were excluded in the regression statistics listed in the tables below.

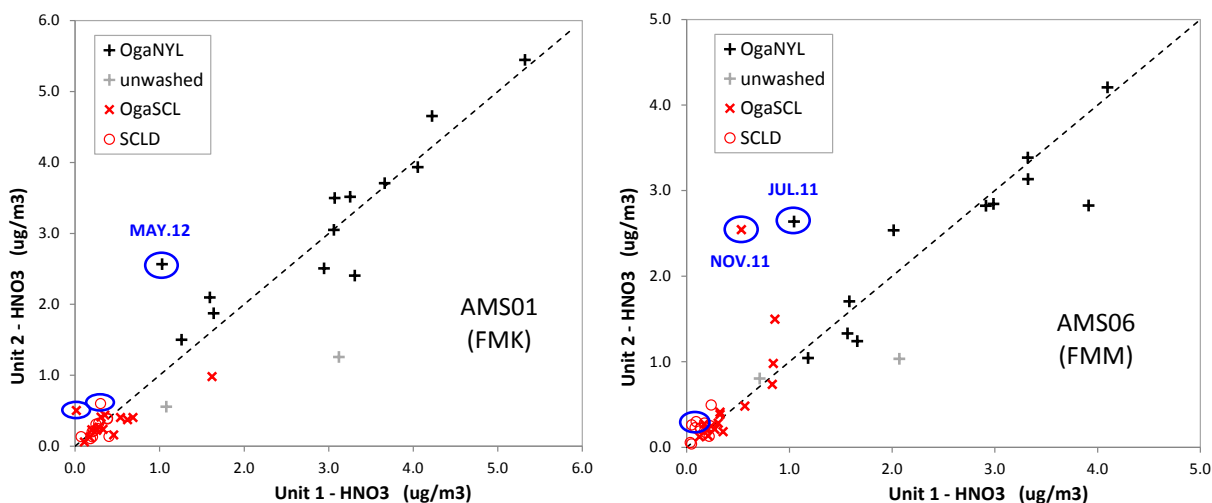
Table 5 compares ambient NH₃ and HNO₃ concentrations derived from passive and active duplicate sample media used at FMK and FMM. The agreement is expressed as average bias between the two identical units exposed simultaneously, yielding positive values when the concentration from unit 1 (close to stairs) exceeded that from unit 2. In general, passive data agree to within ±10 % at both sites. The unwashed nylon material showed low bias in HNO₃ at both sites, albeit based on only the last two sampling periods. Denuder data showed relatively poor agreement at FMM, where problems with ADS flow rate monitoring were more severe.

Table 5: Bias expressed as percent difference (i.e., $200 * (\text{unit 1} - \text{unit 2}) / (\text{unit 1} + \text{unit 2})$). Ogawa unit 1 samplers were exposed close to the staircase (see Figure 2). Since PAD and CAD were not run in duplicates, here PAD was assumed as unit 1 and CAD unit 2.

Bias %		HNO ₃				NH ₃		
		SCLD	OgaSCL	OgaNYL	Unwashed	PAD-CAD	OgaCA	RadPA
FMK	AVG	4	10	-10	-74	13	-10	5
	STD	46	64	27	15	102	55	75
FMM	AVG	-43	-9	-1	-27	37	-5	7
	STD	55	46	29	56	80	11	34

Precision (Bias) in HNO₃ Measurements

Figure 5 shows scatter plots of ambient HNO₃ concentrations at FMK (left) and FMM (right) derived from PS unit 2 versus unit 1 for the Ogawa PS loaded with either two SCL or two NYL adsorbing pads (both pads extracted together). Bias in ADS denuder derived HNO₃ is depicted as values derived from the first SCL denuder in channel 1 (D1-SCL1 in Figure 3) versus those from the first SCL denuder in channel 2 (D1-SCL2). Excluding a few outliers in blue from each FMK and FMM data sets, yielded significant regressions at the 95% confidence interval (p-value < 0.05). Except for NYL, the slopes indicated largely different agreement between sites, suggesting SCL-derived HNO₃ being highly precise within 1% at FMK but with much poorer precision of 32% at FMM. As mentioned before, this lack of agreement is mainly attributed to the greater uncertainty in the ADS sample volumes at FMM. At both sites the Ogawa SCL data deviated significantly from the 1:1 line but on different sides with unit 1 being ~45 % higher at FMK and unit 2 being ~30 % higher at FMM, which translated into +10 % and -9 % average bias per Table 5, respectively. NYL values yielded the highest correlation and best precision (slopes closest to 1) at both sites, however, at concentrations markedly elevated above all other samplers. This tendency for NYL to yield higher HNO₃ is discussed later.



FMK	SCLD-2v1	OgaSCL-2v1	OgaNYL-2v1
R ²	0.783	0.842	0.886
SLP	0.99	0.54	0.94
ICPT	0.00	0.09	0.27

FMM	SCLD-2v1	OgaSCL-2v1	OgaNYL-2v1
R ²	0.516	0.825	0.937
SLP	1.32	1.29	0.96
ICPT	0.00	-0.07	0.00

Figure 5: Performance of HNO₃ collection media at FMK (left) and FMM (right) based on sample duplicates. Blue circles indicate “outliers” that were excluded from the regression statistics in the tables below.

The grey “+” symbols in Figure 5 indicate the effect of using unwashed nylon pads in unit 2 of the OgaNYL samplers during the last two months of the study. At both sites, the unwashed nylon

collected on average less HNO₃ than the routinely washed. However, this missed fraction was significantly larger at FMK than FMM, with 54 ±8 % versus 18 ±45 %, respectively. It can be speculated that the almost three times higher ambient NH₃ levels at FMM may compensated the effect that washing the nylon pads had, or in other words, besides an apparent decrease in effectively adsorbing HNO₃-nitrate, washing with 1% sodium carbonate may have also reduced alkalinity of the adsorbing nylon surface in the presence of atmospheric NH₃, which was significantly higher at FMM. This may explain the near zero concentration of residual sodium on the washed nylon pads from FMM compared to the significant levels found at FMK.

Accuracy in NH₃ Measurements

Table 6 and Figure 6 compare average NH₃ values from each sampling medium pair for FMK and FMM. Based on OgaCA, the study period's average NH₃ concentration at FMM was 0.93 ±0.34 µg m⁻³, significantly greater than 0.26 ±0.27 µg m⁻³ at FMK. Note, that ADS operation ended by the end of the May 12 period; i.e. on July 5th, 2012. Assuming that CAD served as *reference* for PAD and OgaCA, which in turn served as *reference* for RadPA, the percentages in the 3 right hand columns in Table 6 indicates the magnitude of the challenged sampler's bias away from the respective *reference* to either higher (positive %) or lower (negative %) values. Here, the bias is expressed as 100*(X_i/CAD-1); X_i = PAD or OgaCA, and 100*(X_i/OgaCA-1) for RadPA. Using PA as the denuder coating yielded NH₃ concentrations biased high on average of 89% and 96% at both FMK and FMM, respectively. However, using PA on passive sampling media caused an average low bias relative to OgaCA at both sites with -13% and -54%, respectively. Using the same CA coating solution on both denuder and PS collection surface yielded the best agreement per site with lowest bias of 8% and 25% at FMK and FMM, respectively.

Table 6: Comparison of monthly average NH₃ derived from active and passive samplers at FMK and FMM with individual biases relative to the CA *reference*. Bias values in italic were excluded because the CAD reference was at or below DL.

Month	FMK							FMM						
	CAD ug/m3	PAD ug/m3	OgaCA ug/m3	RadPA ug/m3	PAD v.CAD	OgaCA v.CAD	RadPA v.OgaCA	CAD ug/m3	PAD ug/m3	OgaCA ug/m3	RadPA ug/m3	PAD v.CAD	OgaCA v.CAD	RadPA v.OgaCA
JUN.11	2.30	1.17	1.18	0.56	-49%	-49%	-53%	0.45	0.93	1.23	0.75	107%	174%	-39%
JUL.11	0.72	0.62	0.20	0.24	-14%	-71%	17%	0.69	0.71	0.67	0.27	4%	-3%	-59%
AUG.11	1.75	0.38	0.24	0.25	-78%	-87%	5%	0.85	1.47	0.63	0.22	74%	-26%	-64%
SEP.11	0.35	2.57	0.11	0.26	628%	-68%	131%	1.46	3.28	1.66	0.81	125%	14%	-51%
OCT.11	0.11	0.62	0.08	0.16	463%	-28%	98%	1.39	3.40	1.45	1.24	144%	4%	-15%
NOV.11	0.05	0.04	0.21	0.09	-28%	320%	-55%	0.90	0.56	0.77	0.39	-37%	-14%	-49%
DEC.11	0.02	0.16	0.22	0.16	652%	905%	-28%	0.33	1.46	0.73	0.13	338%	119%	-82%
JAN.12	0.58	0.14	0.09	0.02	-75%	-84%	-76%	0.59	1.54	0.62	0.22	161%	5%	-64%
FEB.12	0.07	0.04	0.16	0.05	-32%	141%	-70%	0.03	0.04	0.82	0.16	30%	2809%	-80%
MAR.12	0.05	0.09	0.10	0.05	84%	118%	-53%	1.82	0.17	0.70	0.16	-91%	-62%	-77%
APR.12	0.58	0.34	0.16	0.14	-41%	-72%	-10%	0.58	1.82	0.97	0.50	213%	67%	-49%
MAY.12	0.48	1.08	0.33	0.22	124%	-31%	-33%	1.35	1.60	1.35	0.59	18%	0%	-56%
AUG.12			0.42	0.54			30%			0.65	0.87			33%
SEP.12			0.28	0.11			-61%			1.08	0.25			-77%
OCT.12			0.09	0.06			-39%			0.67	0.17			-74%
AVG	0.59	0.60	0.26	0.18	89%	8%	-13%	0.87	1.42	0.93	0.45	96%	25%	-54%
RSD	123%	120%	116%	79%	266%	1604%	-464%	61%	75%	37%	74%	126%	269%	-56%

Figure 6 also includes TEEM data from the first 7 months of the study period. At both sites, monthly TEEM averages of NH_3 ranked among the highest of all sampler types. AIM data depicted for the first three months stemmed from hourly averages generated by the Ambient Ion Monitor Ion Chromatography (AIM-IC). The AIM-IC consists of an AIM 9000D air sampler (*URG Corp., Chapel Hill, NC*) fitted with a $2.5 \mu\text{m}$ cyclone inlet, a wet parallel-plate denuder for the collection of gases (including NH_3 and HNO_3), a particle super-saturation chamber and two ICS-2000 ion chromatographs (*Dionex Corp., Sunnyvale, CA*) for anions and cations.

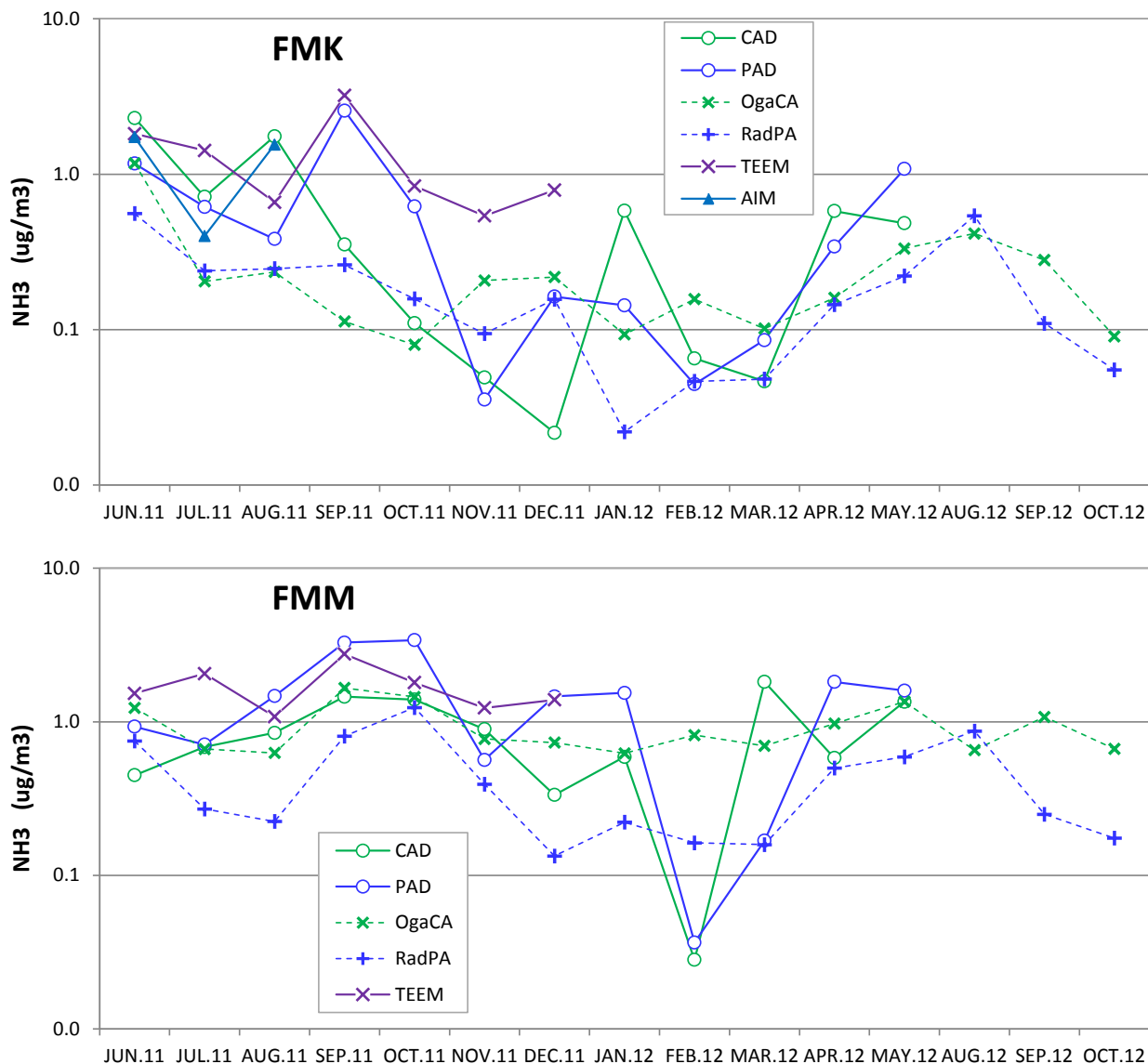


Figure 6: Time series of monthly average NH_3 from active and passive samplers at FMK (top) and FMM (bottom) and available TEEM and AIM data.

The overall impression from Figure 7 was that NH_3 seemed to trend down during the colder winter months and maintain higher average values in spring and summer for both active and

passive collection surfaces, more clearly so at FMK than FMM. Comparing the difference in passive sampling by means of Figure 7, both OgaCA and RadPA values collected at FMK clustered consistently lower relative to those from FMM. Overall, the OgaCA sampler collected ~64 % more NH₃ than the RadPA sampler, when no offset was allowed. Excluding the June 2011 data point from FMK, when the site was impacted by smoke from nearby forest fires, the cluster showed good agreement at a slope of 0.92 ± 0.12 (standard error) and an R^2 of 0.814, under the zero intercept assumption. Conversely, FMM data showed much poorer agreement with a slope of 1.61 ± 0.21 but similar R^2 .

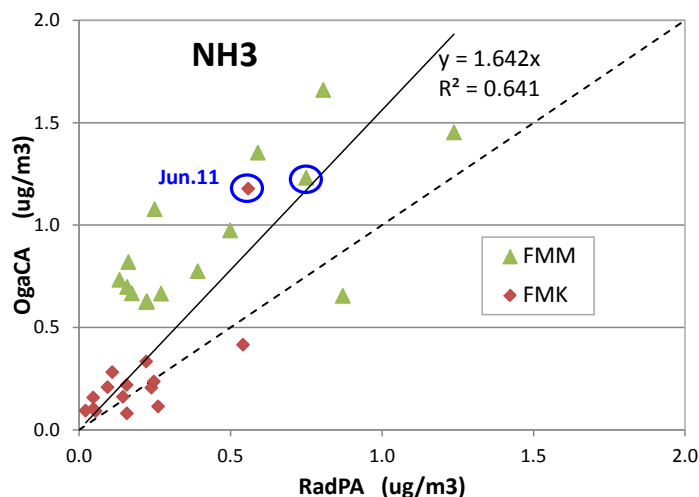
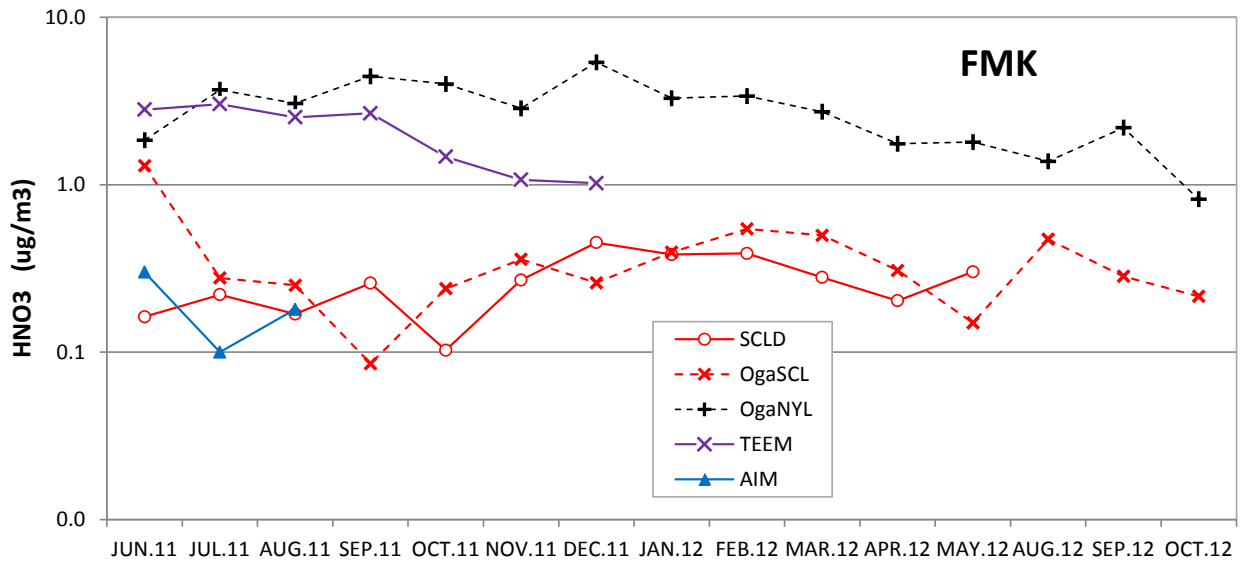


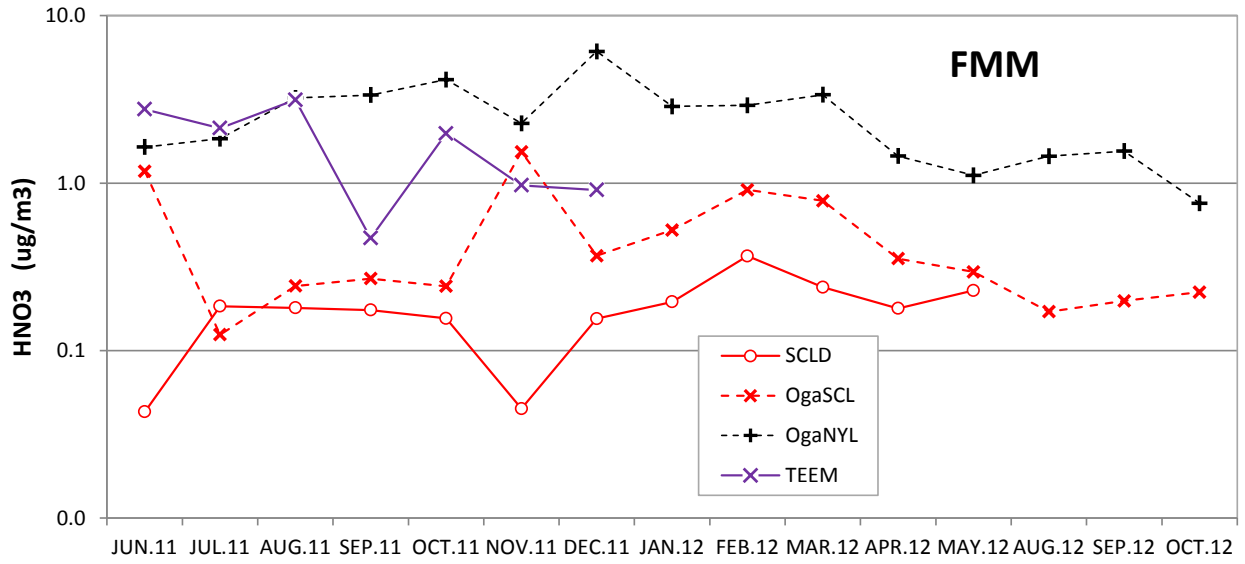
Figure 7: Comparison of ambient NH₃ collected by the two different PS types with linear regression of data from both sites combined.

Table 7 and Figure 8 compare average HNO₃ values from each sampling medium pair for FMK and FMM. SCLD yielded the lowest averages at both sites with a combined value of $0.23 \mu\text{g m}^{-3}$, while SCL as passive collection surface yielded a combined average of $0.44 \mu\text{g m}^{-3}$. Assuming here that SCLD served as *reference* for the OgaSCL, which in turn served as reference for the OgaNYL, the percentages in the 2 right hand columns indicate the magnitude of the challenged sampler bias away from the respective SCL *reference* to either higher (positive %) or lower (negative %) values. Using SCL on the Ogawa pads yielded HNO₃ concentrations biased high at both FMK and FMM by 80% and 92%, respectively. Although the agreement was better at FMK on average, fluctuations between high and low biases were bigger than at FMM (seen in RSD of 256% versus 85%). However, using NYL instead of SCL inside the Ogawa PS, caused a consistently high bias at both sites by about a factor of 7 to 8 (685% at FMM to 789% at FMK).

Table 7: Comparison of monthly average HNO₃, with individual %-biases relative to the SCL (denuder or passive) reference.

FMK	SCLD	OgaSCL	OgaNYL	OgaSCL	OgaNYL	FMM	SCLD	OgaSCL	OgaNYL	OgaSCL	OgaNYL
	ug/m3	ug/m3	ug/m3	v.SCLD	v.OgaSCL		ug/m3	ug/m3	ug/m3	v.SCLD	v.OgaSCL
JUN.11	0.16	1.30	1.85	700%	42%	JUN.11	0.04	1.18	1.64	2630%	40%
JUL.11	0.22	0.28	3.69	26%	1229%	JUL.11	0.18	0.12	1.84	-32%	1380%
AUG.11	0.17	0.25	3.06	49%	1118%	AUG.11	0.18	0.24	3.23	35%	1229%
SEP.11	0.26	0.09	4.44	-67%	5100%	SEP.11	0.17	0.27	3.35	54%	1146%
OCT.11	0.10	0.24	4.00	133%	1569%	OCT.11	0.16	0.24	4.15	56%	1615%
NOV.11	0.27	0.36	2.86	33%	697%	NOV.11	0.05	1.54	2.28	3314%	48%
DEC.11	0.45	0.26	5.38	-42%	1973%	DEC.11	0.16	0.37	6.12	137%	1560%
JAN.12	0.38	0.40	3.29	3%	731%	JAN.12	0.20	0.52	2.87	168%	447%
FEB.12	0.39	0.54	3.39	40%	521%	FEB.12	0.37	0.91	2.92	149%	220%
MAR.12	0.28	0.50	2.73	78%	447%	MAR.12	0.24	0.78	3.37	228%	329%
APR.12	0.20	0.31	1.76	52%	471%	APR.12	0.18	0.35	1.45	98%	310%
MAY.12	0.30	0.15	1.80	-50%	1101%	MAY.12	0.23	0.30	1.11	29%	277%
AUG.12		0.47	1.38		193%	AUG.12		0.17	1.45		748%
SEP.12		0.28	2.19		672%	SEP.12		0.20	1.55		683%
OCT.12		0.22	0.82		280%	OCT.12		0.22	0.76		239%
AVG	0.27	0.39	3.18	80%	789%	AVG	0.18	0.50	2.54	92%	685%
RSD	39%	81%	35%	256%	69%	RSD	47%	85%	55%	85%	81%





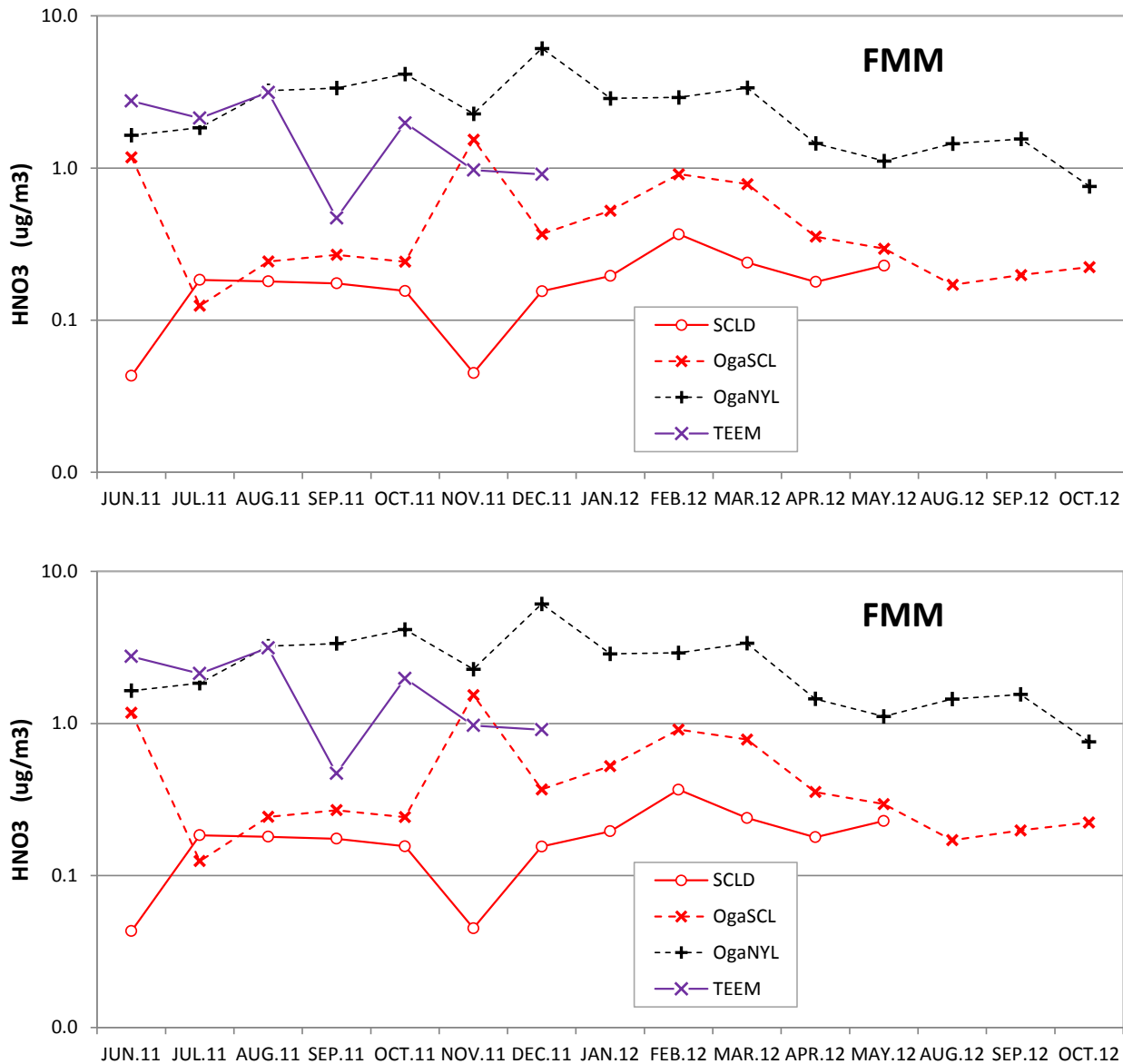


Figure 8: Time series of monthly average HNO₃ from active and passive samplers deployed at FMK (top) and FMM (bottom) compared to available TEEM and AIM data.

As seen in Figure 8, during the first three months, the TEEM-HNO₃ data agreed well with the highly biased NYL data at both sites, but dropped subsequently to within a factor of 3 of the significantly lower Ogawa-SCL data. The AIM data collected at FMK during the first three months agreed with the SCLD *reference* data to within a factor of 2. Similar to NH₃, the scatter plot presented in Figure 9 compares PS-derived HNO₃ when employing different collection surfaces. Here we compared the effective stoichiometric chemical absorption of HNO₃ onto SCL coated collection pads inside the Ogawa sampler (on y-axis) with physical adsorption of HNO₃ onto NYL at unknown rate (on x-axis). Since both collection surfaces were employed in the same type sampler with identical geometries and thus identical diffusion paths and resistances, effects

from these two different processes are directly reflected in the Fig.8 scatter plot. Overall, the NYL surface seemed to cause roughly a factor 10 positive artifact in HNO_3 relative to the SCL surface at significant correlation when linear regression is forced through zero ($n=27$ excl. circled data points). The individual FMK and FMM subsets alone each yielded an apparent positive artifact by a factor of 11.3 ± 2.1 and 8.6 ± 1.8 , respectively.

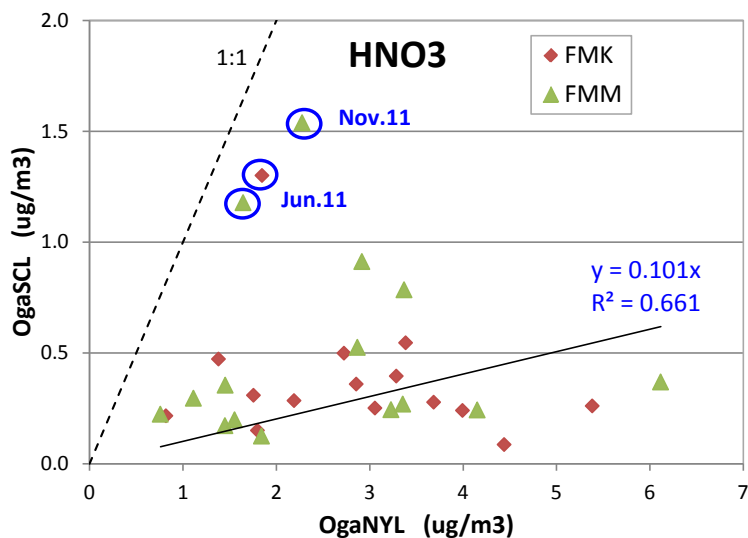


Figure 9: Comparison of ambient HNO_3 collected by the two different PS types.

In order to better understand the possible reasons for the obvious NYL artifact, we correlated the SCL-derived HNO_3 values as well as the net artifact values (HNO_3 from OgaNYL minus HNO_3 from OgaSCL) with ambient NO_2 , O_3 and H_2O vapor measured simultaneously at FMM and FMK. Figure 10 shows the averages of these three parameters with the various HNO_3 measurements from FMK. While NO_2 levels were high in winter and low in summer, O_3 peaks in late spring and early summer, and H_2O showed the expected seasonal profile with winter lows and summer highs. OgaDIFF indicated the trace of the net HNO_3 artifact calculated from the difference measured between the OgaNYL and OgaSCL. No significant correlation was found for any of these three parameters with the entire SCL-derived HNO_3 data from FMM. Only a sub set from FMK of 8 measurement periods between November 2011 and September 2012 yielded significant correlations with the net artifact (NYL – SCL) as depicted in Figure 10, showing a strong 5% molar increase of HNO_3 (NYL-SCL) per mole NO_2 , but an equally strong decrease of about 0.4 ppb HNO_3 artifact per % water vapor increase. No significant correlation existed with ozone. Using the SCL values from the FMK subset, yielded a much weaker molar ratio of $\text{HNO}_3(\text{SCL})/\text{NO}_2$ 0.4% ($R^2=0.15$), and also a weaker relationship with H_2O vapor of -0.03 ppb HNO_3 per % water vapor increase ($R^2=0.1$).

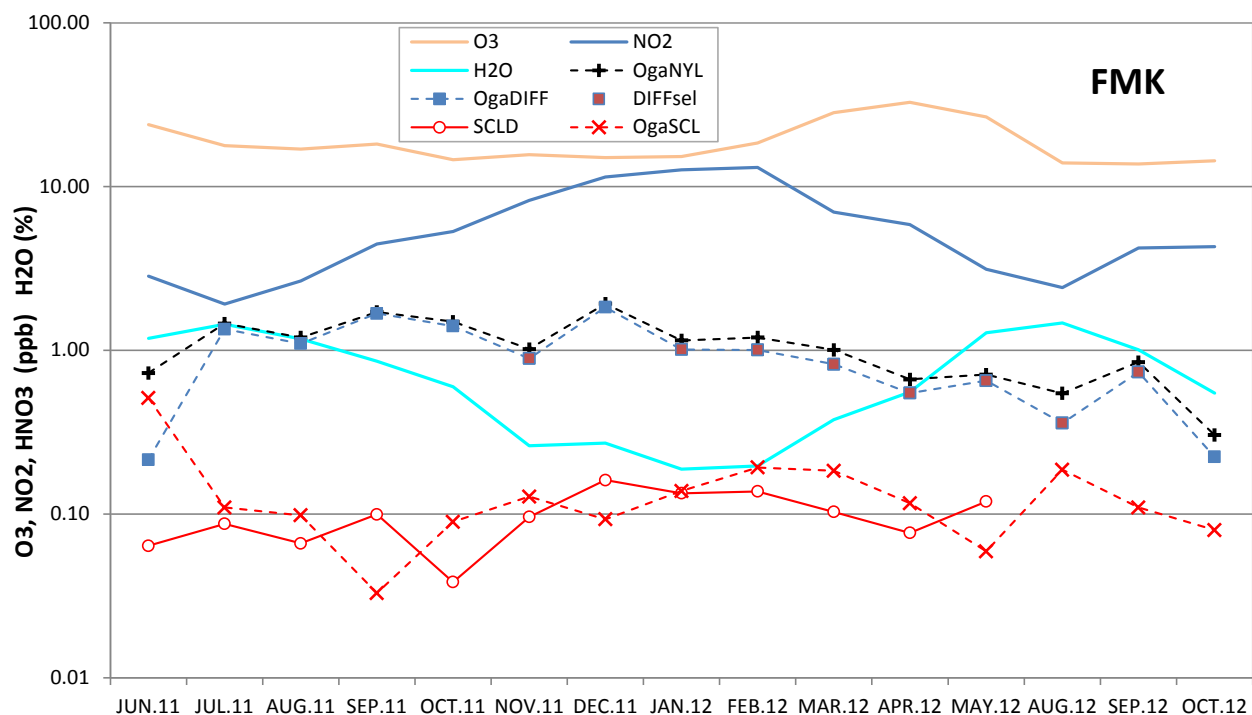


Figure 10: Time series of this study’s HNO₃ measurements compared to NO₂, H₂O and O₃ averages from continuous measurements by WBEA at FMK. OgaDIFF is apparent HNO₃ artifact from OgaNYL-OgaSCL difference, and DIFFsel is subset selected for correlations below.

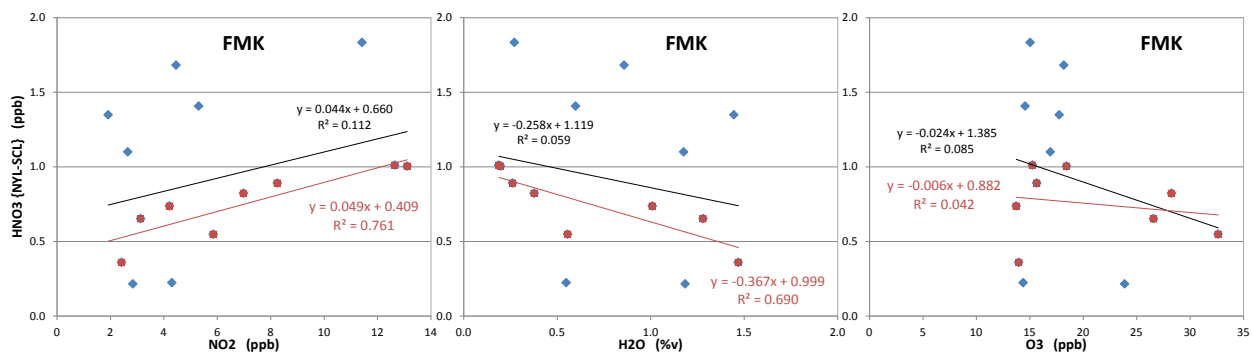


Figure 11: Correlations of HNO₃ artifact on NYL with NO₂ (left), water vapor (middle), and ozone (right). Dark red indicates the selected subset between November 2011 and September 2012.

In the atmosphere, HNO₃ is mainly formed from reaction of NO₂ with the hydroxyl radical. Hydrolysis reactions involving N₂O₅ and NO₃ radicals, as well as NO₂ and NO₃ reactions with O₃ and certain NMHC also yield HNO₃. All these reactions may also take place heterogeneously on the NYL surface.

In order to put our HNO₃ results obtained from SCL surfaces (0.23 μg m⁻³ from active samplers and 0.44 μg m⁻³ from passive samplers) into greater spatial context, we compared them with other long-term measurements in the United States and overseas. For example, SEARCH network measurements made in the southeastern U.S. (Hansen et al., JAWMA 53(12), 2003) during the same period showed HNO₃ averages ranging from 0.53 μg m⁻³ in rural areas to 1.09 μg m⁻³ in urban environs. Ferm et al. (2005) reported a similar urban-rural gradient in HNO₃ for various locations in Europe, tropical Africa and tropical Asia. Interestingly, Ferm et al. (2005) also observed a gradient at much greater spatial scales; that is, tropical low latitudes exhibited an average annual HNO₃ level of about 1.4 μg m⁻³ versus roughly 0.3 μg m⁻³ at high European latitudes similar to the WBEA domain.

Ferm et al. (2005) also reported an increasing urban-rural gradient in the molar HNO₃/NO₂ ratio (from 2.7% urban up to 18% rural), which they attributed to the slow formation of HNO₃ during transport away from its precursor sources. It is interesting to note that our HNO₃ artifact (NYL-SCL) is 5% of NO₂ for the period November 2011 to September 2012 at FMK (see Figure 10 left).

Conclusions:

1. Using nylon (unspecific physical adsorption) as passive (PS) collection surface yielded exceedingly high HNO₃ values relative to all other passive and active (ADS) collection surfaces, suggesting artifact reactions that are specific to the nylon surface material.
2. Comparison with long-term HNO₃ data collected elsewhere corroborates our finding that the exposed nylon material causes a significant positive artifact. However, it is unclear what reactions drive this specific artifact.
3. Sodium chloride (NaCl, SCL) on either collection surfaces (cellulose or nylon) yielded relatively good agreement in ambient HNO₃ concentrations from both active and passive samplers.
4. Citric acid (CA) on either collection surface yielded a good agreement in ambient NH₃ concentrations from active and passive samplers.
5. Overall, the Radiello PS with phosphorous acid inside a cylindrical diffuser collected ~61% less NH₃ than the Ogawa PS equipped with citric acid pads.
6. Moving forward, in order to correct potential HNO₃ artifact on nylon passive samplers, a multi-linear empirical relationship is needed involving ambient temperature, water vapor, O₃ and especially NO₂ to express the nylon artifact in terms of a factor or difference over the SCL (sodium chloride) reference. If artifact reactions are assumed to be stoichiometric, then the relationship should explain the apparent HNO₃ difference.

Clearly this effort will be of great value in the utility of applying the long-term HNO₃ data collected by WBEA using the nylon samplers, in effects assessment and FHM.

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