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Atmospheric Measurement Techniques Discussions

Application of an online ion chromatography-based instrument for gradient flux measurements of speciated nitrogen and sulfur

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Atmospheric Measurement Techniques Discussions

Abstract

The dry component of total nitrogen and sulfur atmospheric deposition remains uncertain. The lack of measurements of sufficient chemical speciation and temporal extent make it difficult to develop accurate mass budgets and sufficient process level detail is not available to improve current air-surface exchange models. Over the past decade, significant advances have been made in the development of continuous air sampling measurement techniques, resulting with instruments of sufficient sensitivity and temporal resolution to directly quantify air-surface exchange of nitrogen and sulfur compounds. However, their applicability is generally restricted to only one or a few of the compounds within the deposition budget. Here, the performance of the Monitor for AeRosols and GAses in ambient air (MARGA 2S), an commercially available on-line ion chromatography-based analyzer is characterized for the first time as applied for air-surface exchange measurements of HNO_3, NH_3, NH_4^+, NO_3^-, SO_2 and SO_4^{2-}. Analytical accuracy and precision are assessed under field conditions. Chemical concentrations gradient precision are determined at the same sampling site. Flux uncertainty measured by the aerodynamic gradient method is determined for a representative 3-week period in fall 2012 over a grass field. Analytical precision and chemical concentration gradient precision were found to compare favorably in comparison to previous studies. During the 3-week period, percentages of hourly chemical concentration gradients greater than the corresponding chemical concentration gradient detection limit were 86%, 42%, 82%, 73%, 74%, and 69% for NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, and SO_4^{2-}, respectively. As expected, percentages were lowest for aerosol species, owing to their relatively low deposition velocities and correspondingly smaller gradients relative to gas phase species. Relative hourly median flux uncertainties were 31%, 121%, 42%, 43%, 67%, and 56% for NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, and SO_4^{2-}, respectively. Flux uncertainty is dominated by

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Atmospheric Measurement Techniques Discussions

uncertainty in the chemical concentrations gradients during the day but uncertainty in the chemical concentration gradients and transfer velocity are of the same order at night. Results show the instrument is sufficiently precise for flux gradient applications.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

1. Introduction

Development of risk assessments and mitigation strategies such as critical load frameworks (Burns et al., 2008) to protect ecosystems from nutrient and acidic deposition requires accurate speciated deposition budgets of nitrogen (N) and sulfur (S) compounds. In the United States, wet deposition has been well characterized by the National Atmospheric Deposition Program (NADP). The U.S. Environmental Protection Agency's (U.S. EPA's) Clean Air Status and Trends Network (CASTNet) was established in 1991 to characterize temporal and spatial trends in atmospheric concentrations and dry deposition of select nitrogen (N) and sulfur (S) compounds in rural locations. Air concentrations of sulfur dioxide (SO_2), nitric acid (HNO_3) ammonium aerosol (NH_4^+), nitrate aerosol (NO_3^-), and sulfate aerosol (SO_4^{2-}) are measured on a weekly time-scale using a filter pack (Sickles et al., 1999), from which dry deposition fluxes are estimated using a multi-layer resistance model. While NADP and CASTNet are, in combination, very useful for estimating deposition of some compounds, the nitrogen budget derived from these measurements is incomplete, particularly the dry deposition fraction. For example, fluxes of ammonia (NH_3) are not quantified. Furthermore, CASTNet dry deposition is not directly measured, rather it is estimated using a resistance model. This model, and others used within regional chemical transport models such as the Community Multi-scale Air Quality Model (CMAQ), have not been rigorously evaluated across the range of chemical, meteorological and canopy characteristics of ecosystems for which deposition budgets are urgently needed. Thus, the dry component of total N and S deposition remains uncertain due to a lack of measurements of sufficient chemical speciation and temporal extent to develop complete annual mass budgets or of sufficient process level detail to improve current air-surface exchange models.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Atmospheric Measurement Techniques Discussions

Over the past decade, significant advances have been made in the development of continuous air sampling measurement techniques with sufficient sensitivity and temporal resolution to directly quantify air-surface exchange of nitrogen and sulfur compounds. With respect to nitrogen, these range from bulk measurements of groups of compounds, such as fast chemiluminescence with thermal conversion for total reactive nitrogen ($\sum N_r$) (Marx et al., 2012), thermal dissociation – laser induced fluorescence (TD-LIF) for total peroxy nitrates ($\sum$PNs) and total alkyl and multifunctional alkyl nitrates ($\sum$ANs) (Farmer et al., 2006). More selective methods for specific compounds have also emerged, including chemical ionization mass spectrometry (CIMS) (Sintermann et al., 2008) and tunable diode laser spectroscopy (TDLS) (Whitehead et al., 2008) for NH_3; thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) for peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN) (Wolfe et al., 2009); and aerosol mass spectrometry for inorganic particles (Farmer et al., 2011; Nemitz et al. 2008). These methods are sufficiently fast such that fluxes may be quantified by the eddy covariance (EC) technique. However, their applicability is generally restricted to only one or a few of the compounds within the deposition budget.

NH_3 and HNO_3, which are thought to together dominate the nitrogen deposition budget in many areas (Dennis et al., 2013) are difficult to measure due to their tendency to stick to surfaces within the sampling and analytical components of online measurement systems. For this reason, wet chemical techniques such as the Gradient of Aerosols and Gases Online Register (GRAEGOR) (Thomas et al., 2009; Wolff et al., 2010) Ammonia Measurement by ANnular Denuder sampling with online Analysis (AMANDA) (Wyers et al., 2013) and GRadient Ammonia High Accuracy Monitor (GRAHAM) (Kruit at al., 2007) systems are the preferred

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Atmospheric Measurement Techniques Discussions

methods for air-surface exchange applications. These systems are configured such that the air sample travels only a short distance (~ 0.1 m) before diffusion into solution within a wet rotating denuder. Opportunity for loss to surfaces within the sampling system are therefore minimized. A secondary benefit of the wet chemical techniques is that the use of ion-chromatography or flow injection analysis allows for simultaneous measurement of multiple compounds, thereby minimizing the bias introduced by constructing deposition budgets from multiple measurement systems. For the NH_3-HNO_3-NH_4NO_3 system, simultaneous measurement of gas and aerosol components is essential to assess potential errors in fluxes related to aerosol thermodynamic instability (Wolff et al., 2010; Nemitz et al., 2004). Furthermore, simultaneous measurement of sulfur and nitrogen compounds allows for examination of co-deposition effects between SO_2 and NH_3 related to surface acidity (Erisman and Wyers, 1993) as well as the degree of ammonium sulfate aerosol neutralization. While wet chemical techniques meet the rigorous precision and accuracy requirements of air-surface exchange applications, their temporal resolution is on the order of 30 minutes to an hour. In contrast to the direct EC technique, in which air concentrations are measured at 10 Hz or faster using a single concentration measurement, fluxes must be quantified using the aerodynamic gradient method (AGM), which uses gradient concentrations at a 30 to 60 minute temporal average. Furthermore using gradient concentration measurements requires additional experiments to determine the precision associated with using two sampling collection devices.

The Monitor for AeRosols and GAses in ambient air (MARGA, Metrohm-Applikon, the Netherlands) is a commercially available on-line ion chromatography-based analyzer that semi-continuously measures gases and soluble ions in aerosols (ten Brink et al., 2007; Makkonen et al., 2012; Rumsey et al., 2014) The MARGA is quasi-similar to the GRAEGOR system

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

157 described by Thomas et al. (2009) and Wolff et al. (2010), which has been used for flux
158 measurements. The major difference between the MARGA 2S and GRAEGOR systems is that
159 the MARGA employs ion chromatography for analysis of both anions and cations whereas the
160 GRAEGOR employs ion chromatography for anions and flow injection analysis (FIA) for
161 cations. The MARGA also employs mass flow control to regulate air sampling flow rates, as
162 opposed to control by critical orifice in the GREAGOR. Another difference between the
163 GRAEGOR and the MARGA that may influence the performance of the instruments is the
164 integration of instrument control and chromatography in the MARGA software, which includes
165 real-time instrument performance and data quality indicators for air and liquid flows, sample
166 collection device conditions, and chromatography. The performance of the GRAEGOR in
167 measuring air-surface fluxes has been described by Thomas et al. (2009) and Wolff et al. (2010),
168 however, there has been no evaluation of the performance of the MARGA in measuring air-
169 surface fluxes. Furthermore, neither the Thomas et al. (2009) or Wolff et al. (2010) studies
170 assessed the performance of the GRAEGOR for sulfur compounds in comparison to empirical
171 gradient flux data.

172 In this study, the performance of the MARGA in measuring gradient flux of speciated
173 nitrogen and sulfur is evaluated and described for the first time. This study uses a MARGA 2S
174 system, which is different from the MARGA 1S system described by Rumsey et al. (2014) in
175 two key ways. First, the 2S system employs two sampling boxes interfaced to a single analytical
176 system. The two sampling boxes in this case are positioned at two heights above the terrestrial
177 surface to simultaneously measure the vertical concentration gradient. Second, the MARGA 2S,
178 as configured for this work, draws the air sample through a much shorter length of tubing (30
179 cm) relative to the 1S configuration described by Rumsey et al. (2014).

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Atmospheric Measurement Techniques Discussions

The objective of this paper is to comprehensively evaluate and describe the performance of the MARGA in the measurement for air-surface exchange measurements of HNO_3, NH_3, NH_4^+, NO_3^-, SO_2 and SO_4^{2-}. This requires two sets of experiments, one set to describe the performance of the MARGA as an analytical instrument and another to determine the performance of the MARGA as a gradient flux system. The analytical performance of the instrument is assessed by determining the accuracy, precision and analytical detection limit of the instrument using liquid standards in field conditions. To assess the performance of the MARGA as a gradient flux system, the precision of the concentration gradient which can also be defined as the gradient detection limit is determined in field conditions. The concentration gradient precision (uncertainty) and overall flux uncertainty (concentration gradient uncertainty + transfer velocity uncertainty) are then examined for a representative 3-week period over an unfertilized grass surface during the fall of 2012. A companion paper focusing on the air-surface exchange processes of individual compounds over a longer period of study is forthcoming.

2. Methods

2.1. Study site

Measurements were conducted in an unfertilized 15 ha grass field in the Blackwood Division of Duke Forest, Orange County, North Carolina, USA (35.97_ N, 79.09_ W). Vegetation is primarily tall fescue (Festuca arundinacea Shreb.), with less common species consisting of a mixture of C3 and C4 grasses, herbs, and forbs (Fluxnet, 2014). The field is generally cut twice per year, once in summer and fall, and the clippings are removed for use as animal feed at local farms.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Atmospheric Measurement Techniques Discussions

203 *2.2. Description of MARGA gradient system*

204 As previously mentioned, the MARGA is a commercially available on-line ion
205 chromatography-based analyzer that semi-continuously measures gases and soluble ions in
206 aerosols. The 2S version used in this study employs two sampling boxes interfaced to a single
207 analytical system. The two sampling boxes (SB1 and SB2) are positioned at two heights above
208 the surface to measure simultaneous concentration gradients from which the vertical chemical
209 fluxes are calculated. Air is sampled through a short length (30 cm, 0.5" O.D.) of PFA Teflon
210 tubing with a coarse Teflon screen over the inlet to exclude large material such as insects and
211 entrained vegetation.

212 Each sample box contains a wet rotating denuder (WRD) and steam jet aerosol collector
213 (SJAC). The sample air first flows (as laminar flow) into the WRD (Wyers et al., 1993; Keuken
214 et al., 1990) which rotates continuously so that the walls of the denuder are coated with
215 absorption solution (double de-ionized (DDI) water with 10 ppm hydrogen peroxide), ensuring
216 that the gases diffuse into the liquid film. The level of the bulk liquid within the WRD is kept
217 constant using a level sensor and pump connected to the absorbance solution. Particles pass
218 through the WRD and are collected directly downstream in the SJAC (Khlystov et al., 1995).
219 Within the SJAC, a supersaturated environment is created in which particles grow by
220 deliquescence, allowing them to be collected by inertial separation. The supersaturated
221 environment is created using a temperature-controlled steamer continuously supplied with
222 absorbance solution. Air is drawn through the WRD and SJAC at 16.7 Lpm using a vacuum
223 pump (KNF Model N840FT.18, KNF Neuberger, Inc., Trenton, NJ) and mass flow controller
224 (Brooks Smart Mass Flow Controller, Brooks Instrument, Hatfield, PA). The liquid samples
225 from the WRD and SJAC are collected in a syringe pump module located in the detector box.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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226 The syringe pump module consists of three sets of syringes: one set for the WRD, another for the
227 SJAC and a third for the internal standard. The syringe pumps operate in tandem such that while
228 a set of samples is being collected, the set collected during the previous hour is being analyzed.
229 Prior to analysis, each sample (volume = 25 ml) is mixed with an internal standard (LiBr)
230 solution, which uses two smaller syringes (volume = 2.5 ml). Further information on the internal
231 standard, the absorption solution and other chemical solutions used for MARGA ion
232 chromatography system is included in the supporting information. The samples are analyzed
233 using cation and anion ion conductivity detectors (IC, Metrohm USA, Inc., Riverview, FL,
234 USA). For the cation chromatography, the MARGA uses a 500 µL injection loop and a Metrosep
235 C4 150mm column (Metrohm USA, Inc.) in conjunction with a methanesulfonic acid (MSA)
236 eluent. For the anion chromatography, the MARGA uses a 250 µL injection loop and a Metrosep
237 A Supp-10 75mm column (Metrohm USA, Inc.) in conjunction with an eluent containing sodium
238 carbonate monohydrate and sodium bi-carbonate anhydrous.
239 Software integrated within the MARGA calculates atmospheric concentrations based on
240 air sample flow rate, syringe speed during injection (relatively constant) and ion concentrations
241 (corrected for internal standard) in the collected solutions. These results, as well as the anion and
242 cation chromatograms and various hardware parameters, are recorded by the MARGA software.
243
244 *2.3. Analytical Experiments*
245 *2.3.1. Accuracy*
246 To verify the analytical accuracy of the MARGA as controlled by the internal LiBr
247 standard and to assess potential contamination in the liquid solutions and in the liquid flow path
248 of the MARGA system, an experiment was conducted during field deployment using a liquid

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

blank and four liquid external standards with different concentrations. Furthermore, the relationship between the expected and observed external standard concentrations as well as the blank concentrations were used to adjust the raw concentration data prior to flux calculations. Both the blanks and the external standards experiments were conducted with the air pumps disconnected and denuder inlets sealed. A blank was assessed using the absorption solution for a period over 24 hours. The external standard test was conducted by replacing the absorption solution with a known liquid standard containing SO_4^{2-}, NH_4^+, NO_3^-, Na^+ and K^+. Although Na^+ and K^+ atmospheric concentrations are the not the focus of this particular study, the analytical performance of the MARGA for these compounds is included to give additional information on the performance of the MARGA for a range of compounds. The ranges of concentrations for the external standard were chosen to represent the typical ambient concentrations observed at the study site. Additional information on the external standard liquid solutions is provided in the supporting information. The external standard experiments were conducted for a minimum of 12 hours.

2.3.2. Analytical Detection Limit

The detection limit of an analytical instrument is defined as the lowest concentration that can be determined to be statistically different from a blank at a certain level of statistical confidence. In this study, the MARGA detection limit is calculated using a method from Currie (1995) where

$$D_L = 2t_{1-\alpha,\nu}\,\sigma_o \quad (1)$$

where σ_o is the standard deviation of the distribution of concentration when the concentration is just above the detection limit, v is the degrees of freedom, α is the level of statistical significance

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Atmospheric Measurement Techniques Discussions

and *t* is the Student's t-statistic. The analytical detection limits of the MARGA were calculated using an observed liquid concentration after being adjusted for the internal standard.

The detection limit was determined by combining data from all analytical channels (in this study, there are four different channels including denuder and SJAC samples from both sample boxes) into a single data set. From this single data set, the standard deviation and number of analyses are used to determine the detection limit. However, using this approach means that the standard deviation may reflect a combination of random error plus systematic error between channels. To investigate this possibility, the detection limit methodology was conducted in conjunction with the Dunn's test (Dunn, 1964) and the Brown-Forsythe test (Brown and Forsythe, 1974) to compare differences across channels. Additional information on the detection limit methodology as well as descriptions of the Dunn's test and Brown-Forsythe test methodologies are provided in the Supporting Information.

When quantifying the detection limit using an external standard, the aim is to use a concentration that is slightly above the detection limit as variance may increase with increasing concentration. Therefore an appropriate external standard level was selected for each compound. In addition, two different solutions used to determine SO_4^{2-} and Na^+ detection limits allow an opportunity to investigate the relationship between concentration level and variance and thus its potential impact on the detection limit.

2.4. Gradient flux experiments

2.4.1. Aerodynamic gradient method

Air-surface exchange fluxes were quantified using the aerodynamic gradient method (AGM). The AGM is based on the application of Fick's Law to turbulent diffusion, which relates

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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the flux of heat, mass, and momentum to the vertical gradient and turbulent transfer coefficient (eddy diffusivity) of the particular scalar of interest**,** in this case air concentration (C). Following Thomas et al. (2009), which is an adaptation from Thom (1975), the flux may be expressed as:

$$F_x = -C_* u_* \tag{2}$$

where u_* is friction velocity, calculated from the momentum flux measured by EC and C_* is the concentration scale calculated as:

$$C_* = \frac{k}{\ln\left(\frac{z_2 - d}{z_1 - d}\right) - \psi_H\left(\frac{z_2 - d}{L}\right) + \psi_H\left(\frac{z_1 - d}{L}\right)} \cdot \Delta C \tag{3}$$

Here ψ_H is the integrated stability function for sensible heat (Thom, 1975), z_1 and z_2 are the measurement heights above ground between which the concentration gradient (ΔC) is measured, L is the Monin-Obukhov length calculated from the EC derived sensible heat flux, and k is the von Karman constant (k = 0.41), d is the zero plane displacement height, which is determined by canopy height using the relationship provided by Stanhill (1969). During the period for which fluxes are presented average grass height within the field was 1.2 m and gradient sampling heights were 1.25 and 4.0 meters above ground.

AGM fluxes were calculated from hourly average concentration gradients and hourly EC momentum and sensible heat fluxes measured above the canopy. EC momentum and sensible heat fluxes were measured with a sonic anemometer (R.M. Young Model 81000V, Traverse City, MI) placed approximately 2.6 m above the ground. EC fluxes were calculated off-line from 10 hz data using SAS (SAS Institute, Cary, NC) software following standard approaches EC. Hourly average concentration gradients were based on adjusted air concentration data. Air concentration measurements were adjusted using the internal lithium bromide (LiBr) standard, external liquid standard calibrations and air flow quality control (QC) checks. Air flow rates

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Published: 22 January 2016

were independently measured at the denuder inlet at least weekly using a National Institute of Standards and Technology (NIST)-traceable primary standard (Bios DryCal DC-Lite flowmeter, Mesa Laboratories, Inc., Lakewood, CO). If the measured airflow rate was > 5% different from the target airflow rate of 16.7 Lpm, the MARGA mass flow controllers were recalibrated using the MARGA calibration feature, which consists of a 3-point calibration at 0, 15, and 18 Lpm. The MARGA software continuously records the air flow rate, which is used to calculate air concentrations from liquid concentrations. Air concentrations were also adjusted for the systematic difference in gas and aerosol concentration measurement between the sampling boxes, during colocated sampling in which the two sample boxes are positioned side-by-side. The systematic difference is determined by plotting the concentrations during the colocation against each other and calculating the slope and intercept by orthogonal least squares regression (Wolff et al., 2010) Slope and intercepts significantly different from 1 and 0, respectively, indicate systematic error between the two boxes, which, if present, is subsequently removed prior to calculation of the concentration gradient.

2.4.2. Flux uncertainty and concentration gradient uncertainty

The flux uncertainty σ_F is calculated as (Wolff et al. 2010):

$$\sigma_F = F \cdot \sqrt{\left(\frac{\sigma_{v_{tr}}}{v_{tr}}\right)^2 + \left(\frac{\sigma_{\Delta C}}{\Delta C}\right)^2} \quad (4)$$

where F is the flux, ΔC is the concentration gradient and $\sigma_{\Delta C}$ is the precision (uncertainty) of the concentration gradient, and v_{tr} and $\sigma_{v_{tr}}$, are the transfer velocity and precision (uncertainty) of the transfer velocity, respectively. Equation (4) is used to assess the uncertainty in the measured fluxes and to quantify the relative contributions of uncertainty in chemical and meteorological

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

measurements. In addition, each observation may be assigned a data quality indicator as being above or below the flux detection limit. v_{tr} is taken as:

$$v_{tr} = \frac{u_* \cdot k}{\ln\left(\frac{z_2 - d}{z_1 - d}\right) - \psi_H\left(\frac{z_2 - d}{L}\right) + \psi_H\left(\frac{z_1 - d}{L}\right)} \quad (5)$$

The transfer velocity and thus the uncertainty in the transfer velocity is a function of friction velocity (u_*), the measurement (z_1 and z_2) and displacement (d) heights, and the integrated stability function at each height (ψ_H), which is a function of u_*, the sensible heat flux (H), buoyancy parameter (g/T), air density (ρ), specific heat (c_p), and von Karman's constant (k) (e.g., Arya et al., 2001). As noted by Wolff et al. (2010), there are no published estimates of the full uncertainty in v_{tr}. Here we approximate the uncertainty in the transfer velocity (σv_{tr}) by calculating v_{tr} using measurements of L and u_* from six colocated R.M. Young Model 81000V sonic anemometers. The standard deviation of this population ($n = 6$) of measurements of v_{tr} represents a lower limit of its transfer velocity uncertainty (σv_{tr}), as uncertainty in d and ψ_H are not explicitly considered. In this case, the precision of v_{tr} was quantified as the standard deviation of the residuals of orthogonal least squares regression of v_{tr} from individual sonic anemometers against the mean for the corresponding hourly observation. The v_{tr} precision experiment was conducted adjacent to the MARGA measurement location and comprises 110 hourly observations.

The uncertainty of the gradient concentration is also quantified during co-location tests. Again, the concentrations from the two sample boxes are regressed against each using a slope and intercept from orthogonal least squares regression. The residuals of the regression represent the random error of the concentration difference between the two boxes. The standard deviation of the residuals provides a measure of the precision of the denuder and SJAC measurements for

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

individual analytes, which also represents the precision of the concentration gradient ($\sigma_{\Delta c}$), which can also be defined as the gradient detection limit following Wolff et al. (2010). The relationship between precision and concentration is quantified by regressing $\sigma_{\Delta c}$ on the average concentration (C) between the two boxes. Precision is expected to be a function of concentration. Therefore concentration gradient precision was calculated at three different co-location events (June, July and October 2012) during the sampling periods in order to have a wide range of concentrations.

Air-surface exchange fluxes and their associated concentration gradient uncertainty and flux uncertainty were determined over 3-week representative period (23 September – 14 October, 2012) at the sampling site.

2.5. Ancillary measurements

A variety of meteorological parameters and surface characteristics were measured during sampling. The influence of these factors on air-surface exchange flux will be examined in the companion paper. In this paper, the meteorological parameters, wind speed, air temperature and global radiation will be presented to provide basic information on meteorological conditions during the 3-week representative period. Wind speed and air temperature were measured using the sonic anemometer (R.M. Young Model 81000V, Traverse City, MI) at a height of 2.6 m. Global radiation was measured using the Reb Q7.1. Net Radiometer (Campbell Scientific, Logan, UT). Other surface characteristics reported in this paper include canopy height, which was measured manually and leaf area index. Single-sided leaf area index (LAI) was measured by destructive (prior to canopy closure) and optical methods (LICOR Model LAI-2000, LICOR Biosciences, Lincoln, NE)

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

3. Results and Discussion

3.1. Analytical Experiments

3.1.1. Accuracy

In the following analysis, results from liquid standard tests are expressed as equivalent air concentration unless otherwise noted. Also, though liquid standards obviously only contain dissolved ionic forms (i.e., NO_3^-, NH_4^+, SO_4^{2-}), results are reported for both SJAC and denuder samples, adjusting for molecular weight to express denuder results in equivalent gas phase concentration (i.e., HNO_3, NH_3, SO_2). The results of the liquid blank are provided in the Supporting Information. Only SO_4^{2-} had a significant blank (value > 0.001 µg m^{-3}). Further analysis by an independent IC system has confirmed that both the absorption solution and the MARGA system components contribute to the SO_4^{2-} blank. The relationship between the expected and observed (response) concentrations of the external liquid standards was investigated by regression analysis (See Figure in Supporting Information). For NH_4^+, NH_3 and K^+ there is good agreement between expected and observed concentrations, with the linear regression slopes for all compounds between 1.00 and 1.04, and offsets close to zero (< 0.006). For Na^+, the external standard response was not as accurate, producing slope values of 0.90 for both SB1 and SB2 and offsets of 0.013 and 0.011 for SB1 and SB2, respectively. This appears to be related to peak integration characteristics but is currently under investigation.

For the sulfur compounds (SO_4^{2-} and SO_2) associated with anion IC detection, excellent regression slopes were also observed (1.00), however, offsets (intercepts) can be observed using linear regression, which are not reflected in the blank. These offsets range from 0.09-0.13 µg m^{-3} for SO_2 and SO_4^{2-}. Linear regression analysis of NO_3^- and HNO_3 produced good regression slopes, ranging from 1.06-1.07 and similarly offsets that are not reflected in the blank, ranging

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

406 from 0.05-0.06 µg m^{-3} (see Figure in Supporting Information). Further investigation of the
407 difference between expected and observed concentrations for NO_3^- and HNO_3 at individual
408 external standard levels show that the difference (observed concentration minus expected
409 concentration) at the lowest concentration external standard (equivalent expected air
410 concentrations are 0.131 µg m^{-3} and 0.133 µg m^{-3} for NO_3^- and HNO_3, respectively) is
411 considerably smaller than for the other higher external standard concentrations (see Table in
412 Supporting Information).Therefore, a nonlinear (quadratic) standard curve was fitted which
413 produced slightly higher r^2 values and lower offset values and in comparison to the linear fit (see
414 Figure in Supporting Information). Thus it is hypothesized that a nonlinearity response occurs at
415 low NO_3^- concentrations. It is proposed that a similar nonlinear behavior at low concentrations
416 may also exist for SO_4^{2-} and SO_2. However, in this experiment, the lowest SO_4^{2-} and SO_2
417 external standard concentrations (expected equivalent air concentrations are 0.476 µg m^{-3} and
418 0.318 µg m^{-3} for SO_4^{2-} and SO_2, respectively) may have been too large to observe this
419 nonlinearity as use of a quadratic standard curve on the SO_4^{2-} and SO_2 data (see Figure in
420 Supporting Information) did not reduce the intercept relative to linear regression. More recent
421 results (not shown), however, support the presence of non-linearity in SO_4^{2-} and SO_2 responses at
422 low concentrations. These results suggest that the response is non-linear below a SO_4^{2-}
423 concentration of 0.27 µg m^{-3} (equivalent to a SO_2 concentration of 0.18 µg m^{-3}). Therefore, it
424 was concluded that it was more appropriate to not adjust concentrations for the linear regression
425 slope and offset below these concentration values and to only subtract the experimentally
426 determined blank. For HNO_3 and NO_3^-, quadratic standard curves are used for external standard
427 adjustments and linear functions are used for the other remaining compounds.
428

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

429 *3.1.2. Analytical Detection Limit*

430 A summary of the detection limit analysis for each analyte is provided in Table 1.
431 Detection limits in Table 1 were determined by incorporating data from all four channels for
432 each analyte. Calculated detection limits were low for all compounds ranging from (in equivalent
433 air concentration) 0.020 µg m^{-3} for NH_3 to 0.064 µg m^{-3} for SO_4^{2-}. In summary, the results of
434 Dunn's test and Brown-Forsythe test indicate that the sampling components of the MARGA are
435 influencing the detection limit of all the compounds except K^+ (for full results and analysis of the
436 Dunn's test and Brown-Forsythe test, see the appropriate section in the Supporting Information).
437 Therefore, the influence of systematic difference among channels was examined by calculating
438 the detection limit for individual channels using Equation (1), then averaging the four detection
439 limits. Using this methodology, detection limits were lower for all the compounds that had been
440 identified as having a significant difference in median channel concentration or channel
441 concentration variance (all compounds except K^+) with the exception of the 1.75 µg L^{-1} Na^+
442 standard, which was approximately the same. The largest decrease in detection limit was for the
443 19.47 µg L^{-1} SO_4^{2-} standard, which decreased by 0.009 µg m^{-3}. The average decrease in
444 detection limit for the compounds was 0.004 µg m^{-3}. For K^+, the only compound that was
445 determined to have no significant difference in median channel concentration or channel
446 concentration variance, the detection limit was slightly higher than for the previous method
447 (0.038 µg m^{-3}) with a value of 0.040 µg m^{-3}. The NH_4^+, NO_3^-, HNO_3, SO_2 and SO_4^{2-} detection
448 limits from this study (using detection limits from Table 1 for this study) are lower than those
449 determined under field conditions in the Thomas et al. (2009) and Wolff et al. (2010) studies,
450 which used the GRAEGOR system (see Table in Supporting Information). NH_3 detection limits
451 determined in this study are lower than those reported by Thomas et al. (2009) and Wolff et al.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

(2010) at a grassland site, but are similar to Wolff et al. (2010) at the a forest site. This aforementioned comparison takes into account differences in the methodology used for determining detection limits. The lower detection limits observed in this study may be attributed to differences in temperature related detector stability, stability of liquid flow rates or other factors. The detection limit values as well as additional information on adjusting detection limits for different methodologies is provided in the Supporting Information.

3.2. Gradient flux experiments

3.2.1. Concentration Gradient Precision (Gradient Detection Limit)

As previously described, the concentration gradient precision, which can also be defined as the gradient detection limit is the standard deviation of the residuals of the orthogonal least squares regression of SB1 (y) versus SB2 (x) following Wolff et al. (2010). Scatterplots of SB1 versus SB2 concentrations measured during three colocation experiments in June, August, and October, 2012 are included in the Supplemental Information. The three colocation experiments consist of approximately 89, 138, and 73 hourly observations, respectively.

Results of the orthogonal least squares analysis by colocation period are summarized in a Table provided in the Supporting Information. Slopes are within ± 0.06 of unity with the exception of NO_3^- and HNO_3 during the first period, in which SB1 was lower than SB2 by ≈ 15%. The reason for this underestimate is not obvious. A low bias of SB1 relative to SB2 for both NH_3 and HNO_3 may indicate an effect of inlet tubing condition. Routine visual observation of the SB inlet tubing indicates that SB1, which is positioned closed to the ground, tends to accumulate dust more rapidly than SB2. As the colocation experiments are meant to serve as a QC measure for fluxes measured during the period prior to colocation, inlets are replaced after,

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

475 rather than before, colocation experiments. Thus, the bias observed during colocation period 1
476 may reflect a dirtier inlet on SB1. This would not, however, explain the bias for NO_3^- aerosol
477 unless the loss of NH_3 and HNO_3 in the inlet promoted NH_4NO_3 dissociation.
478 Results of the combined colocation experiments are summarized in Table 2. In general,
479 concentrations during the three experiments were low, < 0.65 µg m^{-3}, with the exception of SO_4^{2-}
480 The gradient detection limit, defined as the standard deviation of the residuals of the orthogonal
481 least squares regression of SB1 versus SB2 concentrations ($\sigma_{\Delta C}$) ranges from 0.02 µg m^{-3} for
482 NO_3^- to 0.049 µg m^{-3} for SO_2. The residual standard deviations determined in this study, which
483 assume a Gaussian distribution, are considerably lower than the Gaussian standard deviations
484 (i.e., gradient detection limits) determined by Wolff et al. (2010) for NH_3, NH_4^+, HNO_3, and
485 NO_3^-, which range from 0.093 µg m^{-3} for HNO_3 at a forest site to 0.44 µg m^{-3} for NO_3^- at a
486 grassland site. Expressed as a percentage of the average concentration during co-location, the
487 gradient detection limit ($\sigma_{\Delta C}/C_{ave}$) ranges from 2.1% for SO_4^{2-} to 9.0% for NH_3. Unfortunately, a
488 direct comparison of $\sigma_{\Delta C}$ expressed as a percentage of average concentration between this study
489 and Wolff et al. (2010) study cannot be made as the average concentration during the co-location
490 experiments is not reported by Wolff et al. (2010).
491 When comparing gradient detection limits, it is important to consider the relationship
492 between concentration gradient precision and concentration. As discussed by Wolff et al.
493 (2010), for some species the standard deviation of the orthogonal least squares residuals tends to
494 increase with air concentration. Thus, the gradient detection limit varies with air concentration.
495 The relationship between gradient detection limit and air concentration observed during our
496 experiments is provided in a Figure in the Supporting Information. For this analysis, orthogonal
497 least squares residuals were combined for the three colocation experiments and sorted into 7 bins

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

defined by air concentration. Within each bin, which individually contained ≈ 42 observations, the standard deviation of the residuals and corresponding bin average concentration were calculated. With the exception of NO_3^-, all species show an increase in gradient precision with increasing concentration. In most cases, it appears that that relationship between gradient precision and concentration weakens as concentrations increase. Consistent with Wolff et al. (2010), our results suggest that for some compounds, and most likely including NO_3^-, the relationship between precision and air concentration should be considered when calculating gradient and flux detection limits at the hourly time scale. The lack of relationship observed for NO_3^- may be due to a relatively narrow range of low concentration observed during the colocation experiments. It is likely that this precision/concentration relationship is a general feature of the measurement system and would likely be present over a larger range of NO_3^- concentrations. Similar to Wolff et al. (2010), empirical functions relating gradient precision and concentration were used in this study. These were derived using the plot between bin residual standard deviation and concentration (see Figure in Supporting Information) to predict a gradient detection limit for each hourly observation based on corresponding air concentration. The relationship between gradient precision and concentration were determined using regression and are presented in the Supporting Information. In this study, median relative gradient detection limit uncertainty ($\sigma_{\Delta C}/\Delta C$) was 19.6% for NH_3, 90.4% for NH_4^+, 29.6% for HNO_3, 29.2% for NO_3^-. These are all lower than the equivalent median relative gradient detection limit uncertainty values ($\sigma_{\Delta C}/\Delta C$) reported by Wolff et al. (2010) at a grassland site, which were 36.3%, 129.6%, 40.1% and 49.4% for NH_3, NH_4^+, HNO_3 and NO_3, respectively. Thomas et al. (2009) used a different methodology to determine concentration gradient precision that is not comparable to the methodology used in this study.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

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522 *3.2.2. Flux Uncertainty*

523 Of 504 possible hourly observations (during period of 3 weeks), there were ≈ 445/380
524 gradient measurements and ≈ 410/360 flux measurements for gas/aerosol compounds,
525 respectively. During this period, canopy height was approximately 1 m with a single-sided leaf
526 area index of about 3.5 m^2 m^{-2}. Example time series of meteorology, air concentrations, and
527 fluxes are given in the Supporting Information. Summary statistics for select meteorological
528 variables, air concentrations, and fluxes are provided in a Table in the Supporting Information.
529 Hourly air concentrations of nitrogen compounds ranged from near zero to ≈ 2.0 µg m^{-3}, with
530 mean concentrations ranging from 0.3 µg m^{-3} for HNO_3 to 0.7 µg m^{-3} for NH_4^+. While HNO_3,
531 NH_3, and NO_3^- showed distinct diurnal patterns with mid-day peaks, NH_4^+ did not. Relative to
532 nitrogen compounds, SO_2 and SO_4^{2-} exhibited a wider range of hourly concentrations from near
533 zero up to 8.8 and 4.3 µg m^{-3}, respectively. SO_2 displayed a distinct recurring diurnal pattern of
534 peak concentration during the day while SO_4^{2-} temporally correlated with NH_4^+. Average
535 concentrations of SO_2 and SO_4^{2-} were 0.5 and 1.9 µg m^{-3}, respectively.

536 Over the period of fluxes analyzed, air temperatures generally ranged from 5 to 10 ºC at
537 night to a maximum near 25 ºC during the day. Wind speed and u_* ranged from near zero at
538 night to daytime maxima of ≈ 1.5 to 2.0 and 0.25 to 0.3 m s^{-1}, respectively. Fluxes of all
539 compounds followed the diurnal profile of friction velocity, with peak fluxes during the daytime
540 and fluxes near zero at night. With the exception of NH_3, all fluxes on average were directed
541 toward the grass canopy. NH_3 showed a distinct diurnal profile of emissions during the day and
542 fluxes near zero or slightly negative overnight. As previously mentioned, a companion paper

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

focusing on the air-surface exchange processes of individual compounds over a longer sampling period is forthcoming.

Individually, percentages of hourly chemical concentration gradients larger than the corresponding gradient detection limit were 86%, 42%, 82%, 72%, 74%, and 69% for NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, and SO_4^{2-}, respectively. As expected, percentages were lowest for aerosol species, owing to their relatively low deposition velocities and correspondingly smaller gradients relative to gas phase species. The majority of concentration gradients exceeded the gradient detection limit. As the hourly flux detection limit is calculated by replacing ΔC with $\sigma_{\Delta c}$ in Equation (3), the percentage of gradients larger than the gradient detection limit also represents the percentage of fluxes greater than the flux detection limit.

Patterns of flux uncertainty are summarized in Figures 1 and 2. Overall uncertainty in the transfer velocity (σ_{vtr}) was estimated as 0.0041 m s^{-1} (n = 660), which is applied as σ_{vtr}/v_{tr} to estimate the hourly fractional or percentage uncertainty in v_{tr}. Figure 1 shows diurnal patterns of uncertainty in v_{tr} and chemical gradients for each compound. The graphs generally show that total flux uncertainty (Equation 4) is dominated by uncertainty in the chemical gradients during the day but that uncertainty in the chemical gradients and v_{tr} are of the same order at night. Because the chemical gradients are influenced by air concentration and the impact of the air surface exchange process itself on the magnitude of the gradient, both of which are changing in time, diurnal patterns in uncertainty of the chemical gradient are less distinct than that of v_{tr}, which ranges from > 50% at night to ~ 5% during the day. However, $\sigma_{\Delta c}/\Delta C$ generally peaks during the day when concentration gradients are smallest due to turbulent mixing. It should be noted that the largest flux uncertainty occurs at night when fluxes are near zero. Because the

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

majority (> 90%) of the cumulative flux occurs during the day, these very large uncertainties characterize only a minor fraction of the overall flux to the ecosystem.

Total flux uncertainty is summarized in Figure 2. When both day and night periods are considered, median total flux uncertainties are 31%, 121%, 42%, 43%, 67%, and 56% for NH_3, NH_4^+, HNO_3, NO_3^-, SO_2, and SO_4^{2-}. Considering only concentration gradients above the gradient detection limit, reduces the median uncertainties to 28%, 69%, 37%, 41%, 56%, and 50%, respectively. Flux uncertainties for nitrogen compounds are generally similar to those reported by Wolff et al. (2010). However, when comparing flux uncertainties between studies it should be acknowledged that the transfer velocity uncertainty will vary from site to site depending on meteorological conditions. Furthermore, the methodology for determining the transfer velocity uncertainty could be different, as it is between this study and the Wolff et al. (2010) study. When only daytime concentration gradients above the detection limit are considered, the uncertainties further reduce to 26%, 67%, 34%, 36%, 53%, and 47%.

4. Conclusions

This paper presents for the first time an assessment of the performance of a MARGA 2S instrument as applied for the measurement of air-surface exchange of nitrogen and sulfur compounds. Analytical detection limits were low for all compounds from 0.02 µg m^{-3} for NH_3 to 0.064 µg m^{-3} for SO_4^{2-}. The NH_4^+, NO_3^-, HNO_3, SO_2 and SO_4^{2-} detection limits reported in this study are lower than those determined under field conditions in the Thomas et al. (2009) and Wolff et al. (2010) studies, both of which used the GRAEGOR system. Three colocation experiments were conducted to determine concentration gradient precision. Concentration gradient precision ranged from 0.02 µg m^{-3} for NO_3^- to 0.049 µg m^{-3} for SO_2. Chemical

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

588 concentration gradients determined in this study compares favorably to those determined by
589 Wolff et al. (2010). Over a period of three weeks in early fall, 2012, we find that the majority of
590 chemical gradients exceed the corresponding detection limit and are therefore distinct from zero.
591 Over the range of meteorological conditions observed, median flux uncertainty ranges from ≈
592 31% for NH_3 to ≈ 121% for NH_4^+. Flux uncertainties reported here for nitrogen compounds are
593 similar to those of the GRAEGOR as reported by Wolff et al. (2010).

594 While the characteristics of the analytical system reported here should be generally
595 applicable to the MARGA 2S, the assessment of gradient precision and flux uncertainty will vary
596 to some extent for different meteorological and atmospheric chemical conditions, though not
597 dramatically. Overall, we find that the flux uncertainties are similar to other wet chemical
598 methods and that the instrument is sufficiently precise for flux gradient applications. It is
599 recommended that colocation experiments be conducted regularly for long-term deployments
600 (e.g., monthly) or for each short term intensive deployment to properly account not only for any
601 short term systematic bias that may develop between the two sample boxes but also to assess the
602 relationship between concentration gradient precision and concentration. A companion paper
603 focusing on the air-surface exchange processes of individual compounds over a longer period of
604 study at our site is forthcoming.

605

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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

611 instrument. This manuscript has been reviewed by EPA and approved for publication. Mention
612 of trade names does not constitute endorsement or recommendation of a commercial product by
613 U.S. EPA.

614

615 **Description of Supporting Information**

616 Solutions used in the MARGA ion chromatography system; additional information for the
617 methodology used to determine the detection limit; Additional information on external standard
618 liquid solutions; results and analysis of the Dunn's and Brown-Forsythe tests; additional results
619 of the detection limits in comparison to previous studies; additional tables, figures and
620 references.

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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
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Published: 22 January 2016

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Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

Tables

Table 1. Detection limit (liquid and air equivalent) results incorporating data from all 4 channels for each analyte.

	Expected Concentration ($\mu g\ L^{-1}$)	Median Observed Concentration ($\mu g\ L^{-1}$)	Observed Standard Deviation[b] ($\mu g\ L^{-1}$)	N	t-value	Liquid Detection Limit ($\mu g\ L^{-1}$)	Air Equivalent Detection Limit ($\mu g\ m^{-3}$)	
							Aerosol	Gas
NO_3^-	5.34	7.75	0.87	72	1.29	2.25	0.056	0.057
SO_4^{2-a}	0	1.82	0.75	142	1.29	1.93	0.048	0.032
SO_4^{2-}	19.47	26.5	1.00	72	1.29	2.58	0.064	0.043
NH_4^+	4.91	5.01	0.33	73	1.29	0.86	0.021	0.020
Na^+	1.75	1.47	0.44	73	1.29	1.15	0.029	-
Na^+	5.00	7.06	0.33	80	1.29	1.03	0.026	-
K^+	4.91	5.22	0.60	80	1.29	1.54	0.038	-

[a] Detection limits for SO_4^{2-} and Na^+ were determined using two liquid standards with different concentrations.
[b] ± 1 standard deviation.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-4, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 22 January 2016

Atmospheric Measurement Techniques Discussions

Table 2. Summary of colocation results.

	N[a]	C_{ave} ($\mu g\ m^{-3}$)[b]	$\sigma_{\Delta C}$ ($\mu g\ m^{-3}$)[c]	σ_C ($\mu g\ m^{-3}$)[d]	C_{max} ($\mu g\ m^{-3}$)[e]	C_{min} ($\mu g\ m^{-3}$)[f]	$\sigma_{\Delta C}/C_{ave}$ (%)[g]
NH_3	300	0.48	0.043	0.51	3.22	0.05	9.0
NH_4^+	299	0.62	0.028	0.38	1.81	0.05	4.5
HNO_3	282	0.61	0.035	0.60	2.52	0.03	5.8
NO_3^-	300	0.24	0.020	0.21	1.18	0.00	8.3
SO_2	285	0.61	0.049	0.82	4.29	0.01	8.0
SO_4^{2-}	297	2.04	0.042	1.06	5.65	0.33	2.1

[a] N is number of observations for all three colocation experiments.
[b] C_{ave} is average air concentration during co-location.
[c] $\sigma_{\Delta C}$ is the standard deviation of the orthogonal least squares residuals (i.e., gradient detection limit).
[d] σ_C is the standard deviation of the air concentration.
[e] C_{max} is the the maximum air concentration
[f] C_{min} is the minimum air concentration.
[g] $\sigma_{\Delta C}/C$ (%) is the gradient detection limit expressed as a percentage of the average air concentration.

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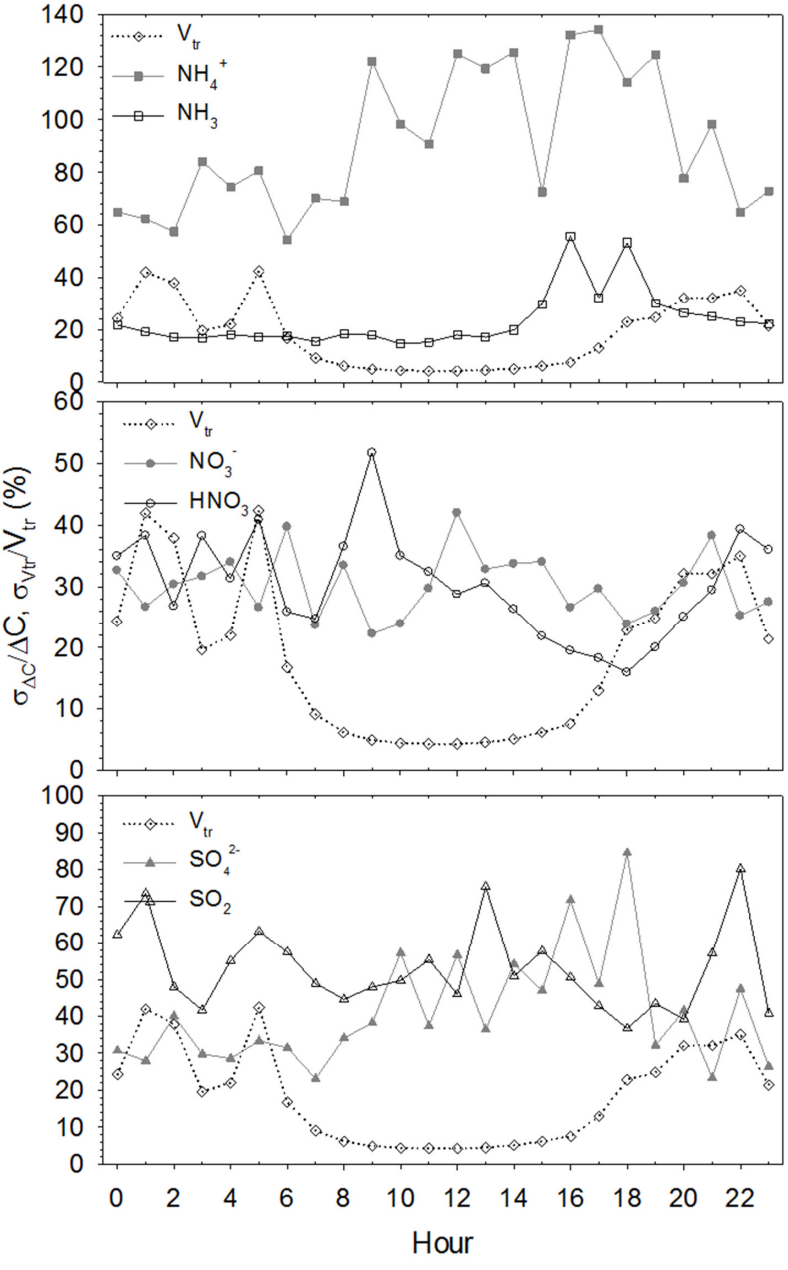
Atmospheric Measurement Techniques Discussions

821 **Figures**



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824 Figure 1. Diurnal profiles of uncertainty in chemical concentration gradients and transfer
825 velocity expressed as a percentage of the corresponding concentration gradient (ΔC) and transfer
826 velocity (v_{tr}). Data points represent median value for the corresponding hour.

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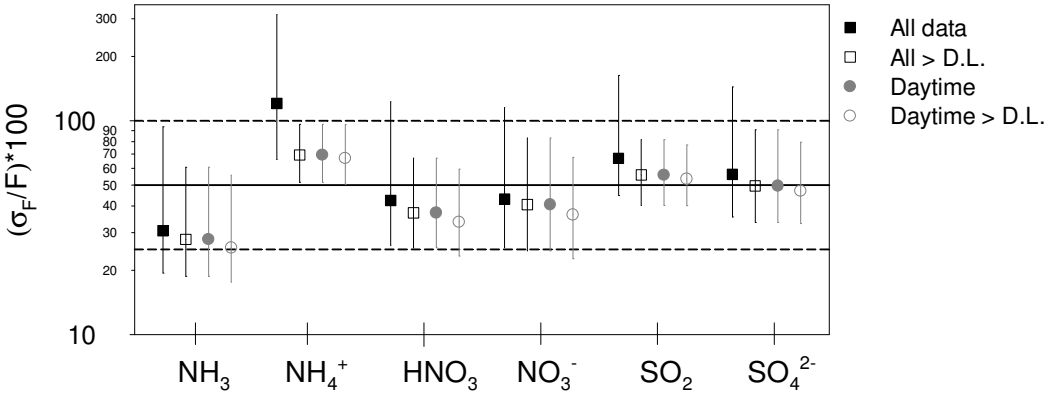

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829 Figure 2. Summary of flux error (Equation (4)) expressed as a median percentage of the flux
830 magnitude. Data are summarized as all data, all fluxes in which the chemical gradient exceeds
831 the gradient detection limit, all daytime data, and daytime data in which the chemical gradient
832 exceeds the gradient detection limit. Error bars represent interquartile range.
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