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Discussions

An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds

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Abstract

Ambient air monitoring as part of the US Environmental Protection Agency's (US EPA's) Clean Air Status and Trends Network (CASTNet) currently uses filter packs to measure weekly integrated concentrations. The US EPA is interested in supplementing CASTNet with semi-continuous monitoring systems at select sites to characterize atmospheric chemistry and deposition of nitrogen and sulfur compounds at higher time resolution than the filter pack. The Monitor for AeRosols and GAses in ambient air (MARGA) measures water-soluble gases and aerosols at hourly temporal resolution. The performance of the MARGA was assessed under the US EPA Environmental Technology Verification (ETV) program. The assessment was conducted in Research Triangle Park, North Carolina from 8 September–8 October 2010 and focused on gaseous SO_2, HNO_3 and NH_3 and aerosol SO_4^-, NO_3^- and NH_4^+. Precision of the MARGA was evaluated by calculating the median absolute relative percent difference (MARPD) between paired hourly results from duplicate MARGA units (MUs), with a performance goal of <25 %. The accuracy of the MARGA was evaluated by calculating the median absolute relative percent difference (MARPD) for each MU relative to the average of the duplicate denuder/filter pack concentrations, with a performance goal of ≤ 40 %. Accuracy was also evaluated by using linear regression, where MU concentrations were plotted against the average of the duplicate denuder/filter pack concentrations. From this, a linear least squares line of best fit was applied. The goal was for the slope of the line of best fit to be between 0.8 and 1.2. The MARGA performed well in comparison to the denuder/filter pack for SO_2, SO_4^{2-} and NH_4^+, with all three compounds passing the accuracy and precision goals by a significant margin. The performance of the MARGA in measuring NO_3^- could not be evaluated due to the different sampling efficiency of coarse NO_3^- by the MUs and the filter pack. Estimates of "fine" NO_3^- were calculated for the MUs and the filter pack. Using this and results from a previous study, it is concluded that if the MUs and the filter pack were sampling the same particle size, the MUs would have good agreement in terms of precision and accuracy.

The MARGA performed moderately well in measuring HNO_3 and NH_3, though neither met the linear regression slope goals. However, recommendations for improving the measurement of HNO_3 and NH_3 are discussed. It is concluded that SO_4^{2-}, SO_2, NO_3^-, HNO_3, NH_4^+ and NH_3 concentrations can be measured with acceptable accuracy and precision when the MARGA is operated in conjunction with the recommendations outlined in the manuscript.

1 Introduction

The inorganic aerosol system comprising ammonium sulfate [$(NH_4)_2SO_4$], ammonium bisulfate (NH_4HSO_4), and ammonium nitrate (NH_4NO_3), along with its gas phase precursors, sulfur dioxide (SO_2), ammonia (NH_3), and nitric acid (HNO_3), is of wide-ranging interest to the atmospheric and ecological research communities. This suite of compounds plays a role in particle and cloud formation, influences the optical properties of the atmosphere, and contributes a large fraction of the total atmospheric mass of $PM_{2.5}$ (Adams et al., 1999). Additionally, this system is an important contributor to wet and dry atmospheric deposition of acidity and nutrients, thereby playing an important role in the acidification and eutrophication of terrestrial and aquatic ecosystems (Galloway et al., 2003; Galloway, 1995).

In 1991, the Clean Air Status and Trends Network (CASTNet) began monitoring to quantify temporal and spatial trends in atmospheric concentrations and dry deposition of nitrogen (N) and sulfur (S) compounds. The network currently consists of more than 80 sites within the contiguous US , Canada, and Alaska, which are located in areas where urban influences are minimal. Air concentrations of SO_2, HNO_3, NH_4^+, NO_3^-, and SO_4^{2-} are measured at a weekly integrated time-scale using a 3-stage filter pack (Sickles et al., 1999). The US Environmental Protection Agency (US EPA) is interested in supplementing CASTNet with semi-continuous monitoring systems at select sites to characterize atmospheric chemistry and deposition of N and S compounds at higher time resolution than is provided by the filter pack.

The Monitor for AeRosols and GAses in ambient air (MARGA; Metrohm Applikon B.V., the Netherlands) is an on-line ion chromatography based system that measures water-soluble gases and aerosols at hourly temporal resolution. It is one member of a class of similar instruments that separate gases and aerosols into a liquid sample stream for online analysis, including the particle into liquid sampler (PILS, Weber et al., 2001), the ambient ion monitor (AIM; URG Corporation, USA; Nie et al., 2010), and the gas-particle ion chromatography system (GPIC; Dionex Corporation, USA; Godri et al., 2009). The MARGA (ten Brink et al., 2007), and earlier versions of the system (Wolff et al., 2010; Thomas et al., 2009; Trebs et al., 2004), employs a steam jet aerosol collector (SJAC; Slanina et al., 2001; Khlystov et al., 1995) for sampling of soluble aerosols and a wet rotating denuder (Wyers et al., 1993; Keuken et al., 1988) for the collection of water soluble gases. The MARGA has previously been used for rural and urban air quality monitoring in Europe (Schaap et al., 2011; Makkonen et al., 2012) and Asia (Li et al., 2010). With respect to validation of the commercial MARGA instrument, Makkonen et al. (2012) present a linear regression of collocated MARGA and filter pack aerosol measurements. In addition, this study also presents a linear regression of collocated MARGA and TEI 43iTL SO_2 measurements. However, a comprehensive field-based evaluation of the accuracy and precision of the MARGA, for both gas and aerosol compounds, has not yet been published. While the MARGA technology meets the objectives of EPA's CASTNet program with respect to the suite of compounds measured and temporal resolution, the performance of the instrument must be fully evaluated and documented prior to use within the network.

The objective of the present study was to evaluate rigorously the performance characteristics of duplicate MARGA 1S instruments with respect to agreement between each other and to a reference system consisting of duplicate denuders and filter packs. This evaluation was conducted under the US EPA's Environmental Technology Verification (ETV) program, which verifies the performance of innovative technologies that have the potential to improve the protection of human health and the environment. This paper describes the MARGA and reference denuder/filter pack sampling systems, the methods for quantifying the precision and accuracy of the MARGA, the results of the comparison, and recommendations for controlling the accuracy of the MARGA for routine monitoring applications. A second objective of this paper is to investigate potential reasons for the agreement or disagreement between the MARGA and reference measurement system observed during the ETV test (US EPA, 2011), which is outside the scope of the ETV program. This includes an analysis of potential relationships between instrument performance and meteorology, an expanded assessment and application of data quality control measures and, in some instances, alternative data reduction procedures. To provide a clear linkage between this paper and the ETV report (US EPA, 2011), a summary of the ETV results and an explanation of the differences in the reduction and analysis of the data between the two documents are included in the Supplement.

2 Methods and materials

2.1 Sampling site and scheme

The ETV was conducted at the ambient air innovation research site (AIRS) located on the EPA campus in Research Triangle Park, North Carolina (35.89° N, 78.87° W). Duplicate MARGA units (MUs) were housed in a temperature controlled trailer, which was over 200 m away from the closest building. The MU's inlets were positioned just above the roof of the trailer (≈ 3 m high). Duplicate denuder/filter packs were positioned on the roof of the trailer at the same height as the MU inlets. The horizontal distance between the MU inlets and the denuder/filter packs was less than 2 m. In addition, a continuous Model 43S pulsed fluorescence analyzer (PFA) (Thermo Environmental Instruments (TEI), Mountain View, CA) was used to measure SO_2. The SO_2 PFA was located in a different trailer, ≈ 30 m from the trailer where the MUs and denuder/filter pack systems were located. Information on SO_2 PFA measurements and comparison to the MUs is provided in the Supplement. The ETV test was conducted over a period of 30 days of continuous operation from 8 September 2010 to 8 October 2010.

2.2 Sampling systems

2.2.1 MARGA

Description of MARGA system

The MARGA is an on-line analyzer that semi-continuously measures water soluble gases and aerosols at an hourly temporal resolution using ion chromatography. For the ETV test, a custom inertial separator inlet with an aerodynamic particle size cutoff of ≈ 26 µm was used with the MARGA. After passing through the inlet, the air sample flows through ≈ 4 m of polyethylene tubing (1.25 cm outer diameter) to the sampling box. The sampling box contains a wet rotating denuder (WRD), which consists of two concentric glass cylinders. The glass walls of the WRD are coated with absorption solution, which causes the gases to diffuse into the aqueous film (Keuken et al., 1988; Wyers et al., 1993). The absorption solution consists of 18.2 MΩ.cm double de-ionized water (DDI) water with 10 ppm of H_2O_2 added as a biocide. Particles pass through the WRD and enter the steam jet aerosol collector (SJAC) (Khlystov et al., 1995; Slanina et al., 2001). The SJAC injects steam into the sample flow, which creates a supersaturated environment. This results in the growth of particles by deliquescence after which they are collected by inertial separation. The same absorption solution is also used for the SJAC. Air is drawn through the inlet tubing, the WRD and the SJAC at ≈16.7 L min^{-1} using a vacuum pump (KNF Model PM24214-838, KNF Neuberger, Inc., Trenton, NJ) and mass flow controller (Model DMFM: D-6340DR, M+W Instruments, Leonhardsbuch, Germany).

Each hour, the liquid sample streams from the WRD and SJAC are drawn into syringes with a volume of 25 mL. The syringe collection system is in a tandem configuration, meaning that as a sample is being collected, the previous sample is being injected.

In the syringe pump module, there is another set of syringes (volume = 2.5 mL) for an internal standard. The internal standard containing Li^+ and Br^- is injected simultaneously with the sample and is subsequently mixed with the sample (see the Supplement for additional information on the preparation of this chemical and all other chemicals used for the MARGA). The samples are analyzed using cation and anion ion conductivity detectors (IC, Metrohm USA, Inc., Riverview, FL). For the cation chromatography, the MARGA uses a 500 µL injection loop and a Metrosep C4 150 mm column (Metrohm USA, Inc.) in conjunction with a HNO_3 cation eluent. For the anion chromatography, a 130 µL injection loop and a Metrosep A Supp-10 75 mm column (Metrohm USA, Inc.) are used in conjunction with an anion eluent made up of a mixture of sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). The signal-to-noise ratio for anion chromatography is improved by suppressing the eluent background conductivity. Three ion exchange units housed within a suppressor module are rotated during each cycle, ensuring that each analysis is conducted with a regenerated ion-exchange unit. Phosphoric acid (H_3PO_4) is used to regenerate the ion exchange units.

Quality Assurance/ Quality Control (QA/QC)

During the ETV test, the MUs air flow rates were verified weekly by measuring the flow rate at the atmospheric inlet using a NIST traceable primary standard (DryCal DC-LITE flowmeter, Bios International Corporation, Butler, NJ). Additionally, the MUs inlets and air sampling tubing were cleaned weekly with DDI water and dried with zero grade air. After the completion of the ETV test, a liquid blank was analyzed by running the MUs with the air pumps disconnected and denuder inlets sealed, thus meaning that the MUs were only sampling the absorption solution. Also with the air pumps disconnected and denuder inlets sealed, an external standard test was conducted by replacing the absorption solution with a known liquid standard containing SO_4^{2-}, NH_4^+, and NO_3^- (additional information on the preparation of the external standard is provided in the Supplement). This was done to verify the analytical accuracy as controlled by the internal LiBr standard.

2.2.2 Denuder/filter pack

Description of denuder/filter pack system

The reference methodology was based on compendium method IO-4.2 (U S EPA, 1999). Ambient air was sampled by drawing in air at a flow rate of 10 L min^{-1} through an inlet cyclone with a particle size cutoff of 2.5 µm, and then through a series of denuders and filters. Samples were collected every 12 h. Two denuders were used in series, the first one coated with Na_2CO_3 to collect acid gases (i.e. SO_2 and HNO_3), and the second coated with phosphorus acid (H_3PO_3) to collect basic gases (i.e. NH_3). This was followed by a Teflon filter for the collection of particles. Behind the Teflon filter was a nylon filter, which collects volatilized HNO_3^- from the disassociation of NH_4NO_3. Total NO_3^- filter pack concentrations were the sum of the equivalent NO_3^- collected on the Teflon and nylon filters. NO_3^- collected on the nylon filter was also used to calculate total NH_4^+ filter pack concentrations. This was done by adding the NH_4^+ molar equivalent of the NO_3^- concentration on the nylon filter to the Teflon filter NH_4^+ concentration. The temperature of the denuder/filter pack system was partly regulated by a fan. NH_3 and NH_4^+ denuder/filter pack samples were analyzed by automated colorimetry based on EPA method 350.1 (US EPA, 1993a). For HNO_3, NO_3^-, SO_2 and SO_4^{2-}, the denuder/filter pack samples were analyzed by ion chromatography based on EPA method 300.0 (US EPA, 1993b).

Quality Assurance/Quality Control (QA/QC)

During every week of sampling, one set of denuders and filterpacks (i.e. one sample) were reserved as trip blanks. The trip blanks were kept in their shipping containers (i.e. they were not handled in the field). However, they were extracted and analyzed like other denuder/ filter pack samples.

The denuder/filter pack flow rates were verified periodically by a NIST-traceable flow transfer standard (DryCal DC-LITE flowmeter, Bios International Corporation, Butler, NJ) and a dry gas meter.

Analytical methods were evaluated by using NIST-traceable standard solutions. The solutions were prepared to contain concentrations within the range observed during the ETV test. In addition, a set of duplicate samples and calibration check standards were analyzed for every batch of samples analyzed in the laboratory.

2.3 Methodology used for evaluation of the MARGA

In this assessment, measurement of the following gases and aerosols by the MARGA was evaluated: SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^-, and $NH4^+$. The MUs were evaluated for precision and accuracy. Precision was evaluated by calculating the median absolute relative percent difference (MARPD) between paired hourly results from the duplicate MUs. Thus the ARPD was calculated as:

$$\text{ARPD} = \frac{|C(\text{MU1})_i - C(\text{MU2})_i|}{[C(\text{MU1})_i + C(\text{MU2})_i]/2} \cdot 100 \tag{1}$$

where $C(\text{MU1})_i$ and $C(\text{MU2})_i$ are air concentrations measured by each of the MUs for the ith sampling period. From this, the median value of the ARPD values (MARPD) was used. The precision goal for each compound was to have a MARPD less than 25 %.

The accuracy of the MUs was evaluated in comparison to the denuder/filter pack system. As stated, the MARGA measures at an hourly temporal resolution. Therefore, 1 h MU data were averaged to 12 h for comparison to the denuder/filter pack. The accuracy of the MUs was evaluated by calculating the median absolute relative percent difference (MARPD) to the average of the duplicate denuder/filter pack concentrations. The ARPD was calculated as:

$$\text{ARPD} = \left|\frac{C_i - \overline{C(d/f)_i}}{\overline{C(d/f)_i}}\right| \cdot 100 \qquad (2)$$

where C_i is the 12-h averaged concentration measured by a MU and $C(d/f)_i$ is the mean concentration of the duplicate denuder/filter pack samples for the ith sampling period. In addition, accuracy was evaluated by linear regression, i.e., the 12 h averaged concentrations of each MU were plotted against the average of the corresponding duplicate denuder/filter pack concentrations. From this, a linear least squares line of best fit was applied. The goal was for the slope of the line of best fit to be between 0.8 and 1.2.

3 Results and discussion

3.1 Raw data adjustments

Raw MU air concentration data was adjusted based on differences between the measured and recorded air flow rates, liquid blanks and biases in calibration standard checks. The average measured flow rates were 16.48 L min^{-1} for MARGA unit 1 (MU1) and 15.98 L min^{-1} for MARGA unit 2 (MU2). The MARGA calculates concentrations using a flow rate of 16.7 L min^{-1}, therefore the raw data concentrations were adjusted upward by 1.4 % for MU1 and by 4.5 % for MU2. The results of the liquid blanks, external standards and the analytical bias are presented in the Supplement. Liquid blanks for all the species (SO_2, SO_4^{2-}, HNO_3, NO_3^-, NH_3, and NH_4^+) ranged from 0 to 0.15 µ g m^{-3} for both MU1 and MU2. The analytical bias (after subtracting the liquid blank concentration) for SO_2, SO_4^{2-}, HNO_3, and NO_3^- was acceptable ranging from +4.5 % to +11.2 % for MU1 and +3.5 % to +10.7 % for MU2. The analytical bias for NH_3 and NH_4^+

was not as good, with values ranging from –22.7 % to –14.5 % for MU1 and –24.4 % to –21.1 % for MU2. Blanks were subtracted from the measured concentrations, and the SO_2, SO_4^{2-}, HNO_3 and NO_3^- measurements were adjusted for their respective analytical biases. However, the bias adjustment of NH_3 and NH_4^+ was not as straightforward. Consequently, details of the bias correction for these compounds are presented in the discussion of the NH_4^+ and NH_3 results (Sects. 3.4.5 and 3.4.6, respectively).

Denuder/filter pack concentrations were adjusted by subtracting the average concentration of six trip blanks (Table of results is provided in the Supplement). Blank values were zero or small for all the compounds apart from NH_3, which had a high and variable blank, with an average value of 1.38 ± 0.43 µg. In addition, it should be noted that the laboratory QA/QC results showed very good performance of the analytical instruments. More information on the results of the laboratory QA/QC procedures can be found in the corresponding ETV report (US EPA, 2011).

3.2 Data collection and detection limits

A summary of the data collection over the 30 day ETV period for the MUs and the denuder/filter pack is presented in Table 1. With respect to data completeness, the MUs performed extremely well over the ETV period, collecting valid 1-h data ≈ 98 % of the time. For MU1, the only loss of data occurred when the inlet was cleaned and the air flow rate checked. MU2 had an occasionally reoccurring hardware and software problem, which was responsible for almost all of the additional invalid data. As mentioned, to compare the MARGA data to the denuder/filter pack, the MARGA 1-h data were averaged into 12 h averages. None of the data loss events were longer than 5 h , therefore all 12 h averages were based on a minimum of 7 full h of data and were included in the data analysis. All 120 samples collected from the denuder/filter pack systems were successfully collected and analyzed.

The number of sample results greater than the detection limit (DL) and greater than twice the detection limit (2DL) for each target analyte are also provided in Table 1. MARGA detection limits were determined by using four times the noise of anion and cation IC detector signal. For the MUs, all NH_3 and NH_4^+ averages were greater than 2DL. No 12 h and ≈0.2 % of 1 h SO_4^{2-} average concentrations were below the DL. Approximately 2 % of both 1 h and 12 h MU SO_4^{2-} concentrations were below 2DL. SO_2 and HNO_3 concentrations were closer to their detection limits with ≈6 % (1 h) or 2 % (12 h) of collected MU SO_2 data below the DL and ≈13 % (1 h) or 4 % (12 h) below 2DL. HNO_3 had ≈6 % (1 h) or 2 % (12 h) of MU concentration data below the DL. Approximately 18 % (1 h) or 9 % (12 h) of MU HNO_3 concentrations were below 2DL. Out of the compounds measured by the MARGA for this study, NO_3^- concentrations were closest to their DL, with ≈9 % (1 h) or 4 % (12 h) below the DL and 27 % (1 h) or 22 % (12 h) of MU concentrations below 2DL.

For the denuder/filter pack, very few (from zero to 7 %) of the SO_2, SO_4^{2-}, NH_3 and NH_4^+ concentrations were below either the DL or 2DL (Table 1). For HNO_3, ≈3 % of concentrations were below the DL, and 15 % were below 2DL. For the filter pack, NO_3^- had by far the most concentrations below the DL and 2DL. For the Teflon filter, ≈57 % of NO_3^- concentrations were below the DL and 88 % were below 2DL. The nylon filter had ≈ 3 % of concentrations below the DL and ≈81 % below 2DL. For the data analysis, the measured concentration values were used. The high percentage of NO_3^- filter pack concentrations around or below the DL should be taken into consideration when evaluating the performance of the MARGA for NO_3^-.

3.3 Meteorological conditions during the ETV period

The meteorological conditions during the ETV period varied significantly. Figures 1a and1b present precipitation and air temperature, respectively, at Raleigh-Durham (RDU) airport (approximately 8 km from the sampling site). From 9/8 to 9/25 the meteorological conditions are characterized as hot and dry, with daily maximum hourly temperatures generally above 30 °C and no precipitation apart from small amounts on 9/11 and 9/12. From 9/26 to 9/30, the conditions were cool and wet with ≈16.5 cm of total precipitation during the period, and hourly temperatures varying from 17 to 26 °C.

Following the rain event, conditions were again dry, but temperatures were cooler with maximum hourly temperatures between 18 to 26 °C.

3.4 Evaluation of measured MARGA aerosol and gas concentrations

3.4.1 SO_4^{2-}

The SO_4^{2-} concentration trends for the MUs and the filter pack are presented in Fig. 2. Both the MUs and the filter pack measured similar SO_4^{2-} concentrations during the ETV period. SO_4^{2-} concentrations were generally higher before the rain event of 9/26 to 9/30, with the period from 9/22 to 9/24 having the highest concentrations. During the rain event, concentrations decreased and then stayed low. Subsequently, concentrations generally increased to the end of the ETV period. The mean filter pack SO_4^{2-} concentration was 2.40 $\mu g\ m^{-3} \pm 1.41$(1 standard deviation). The MU mean SO_4^{2-} concentrations were slightly higher, at 2.63 $\mu g\,m^{-3} \pm 1.38$ and 2.57 $\mu g\,m^{-3} \pm 1.38$ for MU1 and MU2 respectively.

The MARGA also performed well for SO_4^{2-}, passing all precision and accuracy goals. The precision between the MU's was excellent for SO_4^{2-} with a MARPD of 3.2 % . The accuracy of SO_4^{2-} was also excellent, with slope values for the regression analysis of 0.97 and 0.98 for MU1 and MU2 (Fig. 3). The accuracy was also very good with values of 12.7 % MARPD for MU1 and 7.3 % MARPD for MU2. The good performance of the MUs in measuring SO_4^{2-} is supported by the study by Makkonen et al. (2012), which also compared measured MARGA concentrations to those from a Teflon filter using linear regression and reported a slope value of 0.85 for SO_4^{2-}.

3.4.2 SO_2

The measured SO_2 concentration trends during the ETV period are presented in Fig. 4. Both the denuder and the MUs measured similar SO_2 concentrations during the ETV period. Generally, SO_2 concentrations were higher before the rain event on 9/26, with the highest measured concentration occurring on 9/16. After the beginning of the rain event, concentrations decreased rapidly and stayed low until almost the end of the ETV period (10/7), when concentrations started to increase. The average SO_2 concentration measured during the ETV by the denuder system was 2.08 µg m^{-3} ± 2.64. MU concentrations were slightly higher, with MU1 having an average SO_2 concentration of 2.38 µg m^{-3} ± 2.94 and MU2 having an average concentration of 2.20 µg m^{-3} ± 2.79.

Overall, the MARGA performed well for SO_2, passing all precision and accuracy goals. The precision between the MUs was 11.5 % MARPD for 1-h averages, which is well within the MARPD goal of 25 % . The MUs performed well in comparison to denuder and PFA measurement techniques. For details on the performance of the MUs in comparison to the SO_2 PFA, the reader is referred to the Supplement. Against 12-h denuder concentrations (Fig. 5), the slope values were 1.11 for MU1 and 1.05 for MU2, which are well within the accuracy goal of 0.8 to 1.2. The MARPD between the MARGA SO_2 concentrations and denuder concentrations was 20.3 % for MU1, and 10.9 % for MU2, which is well within the accuracy goal of 40 % . Measured MARGA SO_2 concentrations were compared to those measured by a TEI 43iTL SO_2 monitor in a study by Makkonen et al. (2012). Similarly to this study, the MARGA compared well with a linear regression slope of 0.90.

3.4.3 NO_3^-

The NO_3^- concentration trends during the ETV period are presented in Fig. 6. The MUs and the filter pack showed a similar concentration pattern. However, there was a large difference in the NO_3^- concentrations measured by the MUs and the filter pack and also between the MUs. The concentrations measured by MU1 were higher than MU2 for almost the entire ETV period. Likewise, MU2 concentrations were almost always higher than the filter pack over the ETV period. The largest difference in measured concentrations occurred when there were peaks in concentration. In the period from

9/8 until 9/20 the NO_3^- concentrations for all the instruments fluctuated, with the highest peaks occurring on 9/11. On 9/21, there was a rapid increase in NO_3^- for both MUs, and MU NO_3^- concentrations were then consistently high until 9/25. The increase on 9/21 is much smaller for the filter pack, however the pattern is very similar. After the beginning of the rain event on 9/26, there was a rapid decrease in NO_3^- concentrations, and concentrations then stayed low until almost the end of the ETV period (10/6). During the 9/26 to 10/6 period, the MUs and the filter pack concentrations were the most similar. On 10/7 there was a large NO_3^- peak for MU1, and as with the other NO_3^- peaks this peak was smaller for MU2 and smaller still for the filter pack. The average NO_3^- concentration during the ETV for MU1 was 0.53 $\mu g\,m^{-3}$ ± 0.38, which was higher than for MU2 with a value of 0.41 $\mu g\,m^{-3}$ ± 0.28. Both MU average concentrations were higher than the filter pack, which had an average concentration of 0.32 $\mu g\,m^{-3}$ ± 0.14.

In an initial comparison to the filter pack, the MUs apparently performed poorly for NO_3^-, passing only one of the accuracy goals and not the precision goal. The linear regression analysis for NO_3^- (Fig. 7) shows both slopes to be well above the slope goal of 1.2, with values of 2.36 and 1.73 for MU1 and MU2, respectively. In comparison to the filter pack, the MARPD for MU1 is 43.1 % , which is just above the MARPD accuracy goal. The MARPD for MU2 however, is within the accuracy goal with a value of 30.7 % . The MU's precision MARPD is 30.8 % , which is marginally above the precision goal.

After further investigation, the poor agreement between the MUs and the filter pack for NO_3^- was found to be the result of the different sampling efficiency of coarse NO_3^- by the MUs and the filter pack. As mentioned in Sect. 2.2, the filter pack had a particle size cut-off of 2.5 µm aerodynamic diameter, whereas the MARGA customized inlet had a cut-off of ≈6 µm. The explanation for the difference between the MUs is related to the performance of the inlets. As mentioned, the inlet cut-off is determined by inertial separation (a schematic of the inlet is provided in the Supplement). It is hypothesized that the fans controlling the bypass flow rate through the inlets on MU1 and MU2 were operating at different speeds and thus creating different particle size cut-points for the MUs. The evidence for the different sampling efficiency of coarse NO_3^- can be observed through the examination of NO_3^- and the cation species expected to be associated with coarse particle NO_3^-. Figure 8 shows the concentration trend of NO_3^- during the ETV period, with the concentration trend of three compounds that are often components of coarse NO_3^- aerosols, sodium (Na), magnesium (Mg), and calcium (Ca). Sodium nitrate ($NaNO_3$) and magnesium nitrate ($Mg(NO_3)_2$) can form through the reaction of nitric acid with sodium and magnesium in sea-salt particles (Gibson et al., 2006).

$$NaCl_{(a)} + HNO_{3(g)} \rightarrow NaNO_{3\,(a)} + HCl_{(g)} \tag{R1}$$

$$MgCl_{2\,(a)} + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2HCl_{(g)} \tag{R2}$$

Calcium and magnesium are components of mineral dust such as calcium carbonate ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) and can also react with nitric acid to form calcium nitrate ($Ca(NO_3)_2$) and $Mg(NO_3)_2$ (Gibson et al., 2006).

$$CaCO_{3(a)} + 2HNO_{3(g)} \rightarrow Ca(NO_3)_{2(a)} + H_2O + CO_{2(g)} \tag{R3}$$

$$CaMg(CO_3)_{2(a)} + 4HNO_{3(g)} \rightarrow Ca(NO_3)_{2(a)} + Mg(NO_3)_{2(a)} + 2H_2O + 2CO_{2(g)} \tag{R4}$$

The influence of coarse NO_3^- on total NO_3^- measured by the MUs can be observed by comparing the coarse cation component concentrations to the corresponding measured NO_3^- concentrations, in particular where there are concentrations peaks (Fig. 8). For example, for Na^+, the largest peaks occur on 9/15, 9/17, 9/21 and 9/25. For all these peaks, there is a large difference in measured Na^+ concentrations between the instruments, with MU1 measuring higher concentrations than MU2 and MU2 measuring higher concentrations than the filter pack. During the same time periods there are also similar differences in measured concentrations for Mg^{2+}. However, the Mg^{2+} concentrations are much smaller than those of Na^+. For Mg^{2+}, there is also a large difference in measured concentrations between the instruments for a peak on 10/7. The same trend can also be observed on 10/7 for Ca^{2+}, however the measured Ca^{2+} peaks are much larger in magnitude than for Mg^{2+}. Again, during the corresponding time period for NO_3^-, a similar pattern in measured concentrations between the instruments can be observed.

To further examine the influence of coarse NO_3^- sampling efficiency on the difference in measured NO_3^- concentrations, the estimated contribution of coarse NO_3^- was subtracted from both the MUs and the filter pack. However, this was only done using Na^+, because of observed anomalies in the Ca^{2+} and Mg^{2+} data. This is evidenced by elevated MU2 Ca^{2+} concentrations during the rain event period from ≈9/27 to 9/30 (Fig. 8). During this period, almost all other compound concentrations are at zero or near zero. There also appears to be some inaccuracy associated with Mg^{2+} filter pack measurements. An examination of this concentration trend shows that there are no zero measurements during the ETV period, even during the rain event, when the concentrations of many other aerosol compounds are zero. This suggests that the Mg^{2+} filter pack blank values were not accurate. As a result of the possible error associated with Ca^{2+} and Mg^{2+} concentrations, these compounds were not considered for further analysis. It should be stated that the objectives of the ETV test were to assess the performance of the MARGA in measuring HNO_3, NO_3^-, NH_3, NH_4^+, SO_2 and SO_4^{2-}. Therefore it was not a priority of the ETV test to ensure that other compounds such as Ca^{2+} and Mg^{2+} were measured accurately.

To evaluate the potential impact of different sampling of coarse NO_3^- by the instruments, $NaNO_3$ concentrations were subtracted from total NO_3^- concentrations, yielding an estimate of NO_3^- that is assumed to represent the “fine” fraction sampled by the filter pack. This was done by assuming that all Na^+ observed was in the form of $NaNO_3$. The results of this adjustment are shown in Figure 9, which presents the concentration trend, and Fig. 10, which presents the regression analysis. As can be observed in

Fig. 9, the concentration trends for NO_3^- now agree more closely, both in the comparison of MUs to the filter pack and between the MUs. The periods of largest disagreement are from 9/22 to 9/26 and the peak on 10/7, which are the times when there were large Mg^{2+} and Ca^{2+} peaks. The linear regression analysis for NO_3^- (Fig. 10) produces slopes that are much closer to 1, 1.28 and 0.82 for MU1 and MU2, respectively. Representative accuracy and precision MARPD could not be calculated with the adjusted NO_3^- data due to the large number of negative and near zero concentration values. However, it was concluded that if the MUs and the filter pack were sampling the same particle size, the MUs would have good agreement for NO_3^- in terms of precision and accuracy. This is supported by the results from Makkonen et al. (2012), in which NO_3^- measurements were made simultaneously by the MARGA and a Teflon filter, with both measurement systems having the same particle size cut-off of 10 µm. Linear regression between the measurement systems produced a slope of 0.9.

3.4.4 HNO_3

The HNO_3 concentration trends for the MUs and the filter pack are presented in Fig. 11. The HNO_3 diurnal variation can be observed clearly in this data, with HNO_3 concentrations higher during the day as expected. The daytime peaks occur due to the production of the hydroxyl radical (OH) and its subsequent reaction with nitrogen dioxide (NO_2). A noticeable difference can be observed between the denuder and MARGA concentration trends, with typically the MUs measuring lower concentrations than the denuder during the day, and higher concentrations than the denuder at night. These concentration differences are probably a result of the nature of HNO_3, which is a “sticky” gas. It is hypothesized that HNO_3 adsorbs onto active sites on the MUs inlet and tubing. Factors that may affect adsorption include HNO_3 concentration, the temperature of the inlet and tubing, and the moisture content of the sample air stream. All of these factors can vary on a diurnal cycle. Pre- rain event, the daily concentration of HNO_3 is fairly consistent, apart from a large peak during the daytime on 9/15. During the rain event, concentrations decreased and remained low. After the rain event, there is a general increase in concentrations until the end of the ETV period. It can be observed that the difference between MARGA and denuder concentrations is less in the post-rain period. The mean denuder concentration was 0.91 µg m^{-3} ± 0.79. The MU1 mean concentration during the ETV period was similar with a value of 0.90 µg m^{-3} ± 0.62. MU2 concentrations were slightly lower with a mean concentration of 0.74 µg m^{-3} ± 0.48.

The MARGA performed moderately for HNO_3. The MARPD between the MUs was 22.8 %, which met by a small margin the precision goal of 25 % . However, the MUs did not meet the accuracy slope goal, with MU1 having a slope of 0.73 and MU2 having a slope of 0.57 (Fig. 12). However, both MUs did meet the accuracy MARPD goal, with values of 21.2 % for MU1 and 29.0 % for MU2. As previously mentioned, it was hypothesized that HNO_3 was adsorbed onto active sites in the tubing and inlet, and that factors that vary diurnally influenced this, thus causing the diurnal cycle of under and over measurement in comparison to the denuder. To investigate this phenomenon further, the denuder and MARGA concentrations were averaged over 24 h. Fig. 13 presents the 24 h averaged concentrations measured by the instruments during the ETV. By averaging over 24 h, the effect of the diurnal cycle and thus the adsorption is partly accounted for. This results in an improvement in the similarity of the concentration trends for the MUs and the denuder. Using 24 h averages, the slope values for the MUs against the denuder also improved. The slope for MU1 improved to 0.90 (Fig. 14), passing the slope accuracy goal of 0.8. However, the slope for MU2 (0.69) did not improve enough to pass the accuracy goal (Fig. 14). In addition, the accuracy MARPD also improved, with values of 11.2 % and 17.1 % for MU1 and MU2, respectively. The precision MARPD also improved slightly to 18.7 %.

3.4.5 NH_4^+

As mentioned in Sect. 3.1, the adjustment of NH_4^+ for the external standard analytical bias was more complicated than for other compounds and therefore warrants a detailed discussion. Presented in Figure 15 are the NH_4^+ concentration trends during the ETV period after applying the analytical bias adjustment for the external standard results, similar to the other compounds. NH_4^+ concentrations were generally at their highest from 9/8 to 9/26 (pre-rain event). When the rain event started on 9/26, there was then a rapid decrease in concentrations. During the rain event concentrations remained low, before slowly increasing towards the end of the ETV period. From 9/8 until ≈9/25, the MUs measured higher concentrations in comparison to the filter pack (≈24 % for MU1 and ≈31 % for MU2). From ≈9/25 until 10/8, the filter pack and MU concentrations were more similar, with filter pack concentrations generally slightly higher than those of the MUs. Fig. 16a presents the NH_4^+ concentration trend unadjusted for the external standard and Fig. 16b shows the corresponding concentration difference (Filter pack minus MUs) between the filter pack and the MUs. The unadjusted data in Fig. 16a show that before ≈9/25, the MU and filter pack concentrations were very similar, and that after that date filter pack concentrations were consistently higher than MU concentrations. This pattern is shown more clearly by examination of the concentration difference between the filter pack and the MUs (Fig. 16b). It can be observed that before 19:00 on 9/25, the concentration difference fluctuates between positive and negative, with there being no discernible pattern. From 19:00 on 9/25 until the end of the ETV period, a different pattern emerges with the filter pack concentrations consistently higher than the MU concentrations.

A possible explanation for this change in pattern is related to the presence of bacteria in the MARGA system. Bacteria are aerosolized from almost all surfaces including soil, plants and water surfaces (Burrows et al., 2009a) and are therefore ubiquitous in the atmosphere (Despres et al., 2012; Burrows et al., 2009b; Jaenicke, 2005), and therefore it can be assumed that the MARGA is routinely sampling bacteria.

The SJAC and WRD both represent pathways by which bacteria may be introduced to the liquid flow path of the MARGA. Though the SJAC steamer operates at ≈150 °C, the temperature of the liquid sample in the bottom of the SJAC (≈35 °C) and the sample air stream near the steamer outlet (≈40 °C) are sufficiently cool for bacteria to survive.

Deposition of large particles in the WRD is another potential source of bacteria. Thomas et al. (2009) characterized the performance of the GRAEGOR, which employs the same sampling collection system as the MARGA. They found that while sampling PM_{10}, there was a 3.3 % loss of the Na^+ aerosol to the WRD due to the gravitational settling of particles. Because of the larger particle cut-off (≈26 µg) used in the present study, the potential losses to the WRD are even greater.

Liquid samples from the WRD and the SJAC flow through a 1 mum pore size Teflon filter prior to analysis by the IC system. Many bacteria are smaller than 1 mum, and may pass through the filter and accumulate on filters associated with the IC system. It can be concluded that contamination in the WRD sample stream or the SJAC sample stream would only affect that sample type. However, contamination in the IC system would affect both the SJAC and WRD samples. Therefore, contamination in both the SJAC and denuder sample streams or contamination in the IC system could explain potential NH_4^+ losses which would negatively bias NH_4^+ and NH_3 air concentrations.

Microbiological processing of NH_4^+, which has been put forth as an explanation for NH_4^+ loss in precipitation samples (Ramundo and Seastedt, 1990; Krupa, 2002), is a possible explanation for NH_4^+ underestimation. However, NH_4^+ consumption by nitrifying bacteria would also have the effect of an increase in NO_3^-, which was not observed. Thus our hypothesis is that the NH_4^+ is being incorporated into biomass (i.e., immobilized).

High concentrations of particulate Na^+ (Fig. 8) were observed between 9/21 to 9/25, with the highest peaks occurring on 9/21 and 9/25. As described in Sect. 3.4.3, the MUs measured higher concentrations of Na^+ due to the sampling of coarse aerosol. It is hypothesized that these coarse aerosols contained bacteria and were introduced to the MARGA systems, contributing to the observed NH_4^+ loss from 9/25 onwards. Our ongoing MARGA field sampling supports this explanation as similar NH_4^+ loss events, hereafter referred to as “bacterial consumption events” have continued to be observed. These “bacterial consumption events” are associated with marine air masses, which are indicated by the presence of the Na^+ aerosol, which is emitted by sea spray. Sea spray is also a source of bacteria (Blanchard and Syzdek, 1982). Bacteria and other microorganisms can have an atmospheric residence time on the order of days and weeks (Burrows et al., 2009a). This is because many microorganisms have defense mechanisms allowing them to survive the environmental stress of air transport such as UV radiation and varying pH and moisture levels (Burrows et al., 2009a). Therefore a possible explanation is that the "bacterial consumption events" are caused by transported marine bacteria associated with coarse aerosols. It is not known whether the coarseness or the source of the aerosol (i.e. marine) or a combination of both are factors in the "bacterial consumption events". However, it should be considered that marine bacteria may be more adept at colonizing in the aqueous environment of the MARGA sampling system. Further evidence for associating the NH_4^+ losses with bacterial consumption is from our ongoing field sampling where the MARGA system has been rinsed using 0.1 % peracetic acid as a disinfectant after a "bacterial consumption event" has occurred. This practice has to been found to stop the bacterial consumption of NH_4^+. This has been confirmed by running external standards with known a NH_4^+ concentration before and after the rinse. Due to the uncertainty associated with the cause of the "bacterial consumption events", the geographic areas that could be affected by "bacterial consumption events" are unknown.

A previous study by Wolff et al. (2010), which made deposition measurements using the GRAEGOR, supports the hypothesis of bacterial consumption of NH_4^+. They concluded that low NH_4^+ concentrations measured by one of their sample boxes was the result of bacterial consumption of NH_4^+. Wolff et al. (2010) hypothesized that the bacteria survived on the walls of the SJAC. However, it should be noted that unlike this study, the absorption solution used in the Wolff et al. (2010) study did not contain hydrogen peroxide.

As previously discussed, an external standard was run after the ETV period. Results showed the analytical bias for NH_4^+ to be −14.5 % for MU1 and −21.1 % for MU2. It is assumed that the negative bias is related to microbiological processes, therefore a correction method is needed to compensate for this. Complex factors regarding microbial populations make this a difficult task. For instance, the dynamics of the microbial population regulate the amount of NH_4^+ that can be consumed. In this case, we assume for simplicity that the population size is limited by carbon or phosphorous, rather than nitrogen, and that the loss of NH_4^+ is therefore not proportional to the NH_4^+ concentration. Given this, we assume that it is more appropriate to correct for the external standard by applying an offset (difference between observed and expected concentration, see Table 1) instead of a percentage. This gives offset values of 0.16 µg m^{-3} and 0.23 mug m^{-3} for MU1 and MU2, respectively. The concentration difference between the MU's and filter pack (Fig. 16b) suggests that the data from 19:00 on 9/25 onwards is affected by the bacterial consumption, therefore the offset adjustment was applied to this portion of the data. Furthermore, in ongoing field sampling, two external standards have been run after a "bacterial consumption event" and have confirmed that an offset correction for NH_4^+ is appropriate.

To support the offset adjustment of this data, ammonium sulfate ratios (NH_4^+/SO_4^{2-}) were investigated. The molar ratio NH_4^+/SO_4^{2-} in North Carolina is typically between 1.25 to 2.0 (Walker et al., 2006; Baek and Aneja, 2004; McCulloch et al., 1998) with a value of 2.0 indicating the complete neutralization of SO_4^{2-}. Using this range as a guide, the molar ratio of NH_4^+/SO_4^{-2} can be used to assess if an offset adjustment is appropriate for the post 9/25 period. To calculate this ratio, the amount of NH_4^+ associated with SO_4^{2-} has to be determined. This involves estimating the amount of NH_4NO_3. For NH_4Cl, it was assumed that concentrations were negligible. This is supported by the filter pack results (cutoff = 2.5 µm) for the ETV period, in which all of the Cl^- concentrations collected by a Teflon filter were below the detection limit of ≈0.074 µg m^{-3}. To estimate NH_4NO_3, the NO_3^- molar equivalent of the measured Na^+ was subtracted from the total NO_3^-. This calculation assumes that the cation component of the NO_3^- aerosol is either NH_4^+ or Na^+. From examination of the cation component of the NO_3^- concentrations in Fig. 8, it can be determined that there is only a small amount of error in this assumption. The NO_3^- (adjusted for Na^+ concentrations) was then subtracted from NH_4^+ leaving the NH_4^+ associated with SO_4^{2-}. The molar ratio NH_4^+/SO_4^{2-} was calculated for both the MUs and the filter pack. For the MUs, the molar ratio NH_4^+/SO_4^{2-} was calculated with NH_4^+ data being adjusted and unadjusted for the offset. The molar ratios NH_4^+/SO_4^{2-} for the ETV period are shown in Fig. 17. From 9/8 until 9/24, the filter pack NH_4^+/SO_4^{2-} ratio is almost completely between 1.5 and 2.0. Similarly, during this period, the corresponding NH_4^+/SO_4^{2-} ratio for the unadjusted NH_4^+ data is also almost completely between 1.5 and 2.0 and follows quite closely the trend of the filter pack. Therefore both ratios are in the normal range of 1.25 to 2.0. However, the NH_4^+/SO_4^{2-} ratio, for the NH_4^+ data that has been offset adjusted for the external standard is often above 2.0 during the 9/8 to 9/24 period. On 9/25 and 9/26 there is a decrease in the ratios for both the adjusted and unadjusted NH_4^+/SO_4^{2-} ratios. However, both ratios are in the typical range of 1.25 to 2.0, therefore there is no clear evidence for which one is more accurate. In the period from 9/27 to 9/30, the ratios are not presented as these values were invalid and uninterpretable due to the near zero aerosol concentrations during this period. From 10/1 to 10/8, the filter pack NH_4^+/SO_4^{2-} ratio was lower than before the precipitation event, with ratios varying from ≈1.25 to 1.85. Adjusted MU ratios are similar to those of the filter pack, ranging from ≈1.0 to 1.9. It can be observed that the adjusted MU1 ratio is higher than adjusted MU2 ratio. Unadjusted MU ratios are much lower than both the filter pack and the adjusted MU ratios, with the majority of the ratio during this period below 1.0, and thus outside the normal range of 1.25 to 2.0. Overall, it can be concluded that the NH_4^+/SO_4^{2-} ratio supports not adjusting the data before 9/24. In the 9/25 to 9/26 period, there is no clear evidence to support either the adjusted or the unadjusted ratios, and the data in the 9/27 to 9/30 period are uninterpretable due to near zero aerosol concentrations. However, the NH_4^+/SO_4^{2-} ratios do support an offset adjustment of the data from 10/1 onwards.

As a result of the analysis of the concentration difference between the filter pack and the MUs and the NH_4^+/SO_4^{2-} ratios, the NH_4^+ concentrations were adjusted as an offset from 9/25 19:00. This time was selected as the start of the “bacterial consumption event” because it is the beginning of the change in concentration difference between the filter pack and the MUs (Fig. 16b). It is acknowledged that there are some uncertainties associated with this adjustment. Firstly, by the use of the offset, it is assumed that the bacterial consumption of NH_4^+ is constant. Additionally, this approach assumes negligible analytical bias.

The MU concentration trends after being adjusted for an offset from 19:00 on 9/25 onwards are provided in Fig. 18. Observation of the post 9/25 period shows that the offset adjustment results in the MU concentrations being very similar to the filter pack. Noticeably, the last 12-h average shows very small differences in concentrations, 0.58 for MU1 and 0.63 for MU2, in comparison to 0.62 for the filter pack. This supports the validity of applying the offset adjustment. The overall average concentrations for the MUs are very similar, $0.89\,\mu g\,m^{-3} \pm 0.50$ and $0.90\,\mu g\,m^{-3} \pm 0.48$ for MU1 and MU2, respectively. The filter pack concentrations are slightly lower with a value of $0.83\,\mu g\,m^{-3} \pm 0.48$.

The MARGA met all accuracy and precision goals for NH_4^+. The precision between the MUs was excellent with a MARPD of 5.3 %. The accuracy for NH_4^+ was also excellent, as the accuracy MARPD values for MU1 and MU2 were 6.7 % and 8.6 %, respectively. The slope values from the linear regression analysis were 1.02 for MU1 and 0.97 for MU2 (Fig. 19). The excellent performance of the MARGA in measuring NH_4^+ is supported by the study by Makkonen et al. (2012) in which measured MARGA NH_4^+ concentrations were compared to NH_4^+ concentrations from a Teflon filter using linear regression, resulting in a slope value of 0.91 for NH_4^+.

3.4.6 NH_3

The NH_3 concentration trends during the ETV test are presented in Fig. 20a. Similarly, to other compounds, concentrations were generally highest before the rain event on 9/26. Pre-rain event, the NH_3 concentrations fluctuated with concentrations generally higher during the day and lower at night. These daytime peaks may be due the temperature dependence of the NH_3 compensation point of the vegetation and soil surrounding the site (Massad et al., 2010). During the rain event, concentrations decreased. After the rain event, there were a couple of concentration peaks (on 9/30 and 10/7), but generally concentrations stayed low. It should be noted that the concentrations presented in Fig. 20a are unadjusted for the external standard analytical bias, due to the potential for bacterial consumption, which will be discussed in the following paragraph.

As discussed in Sect. 3.4.5, the MARGA is susceptible to the deposition of coarse aerosols and thus bacterial cells, leading to the potential development of bacterial colonies in the MARGA, resulting in the possible loss of NH_3 as well as NH_4^+. Therefore, before adjusting the concentration data for the external standard analytical bias, the unadjusted MU and filter pack concentration trends were examined (Fig. 20a) in combination with the concentration difference between the filter pack and the MUs (Fig. 20b) to identify any unexpected concentration trends, which would indicate that NH_3 was affected by bacterial consumption.

The evidence of bacterial consumption for NH_3 is not as clear as it is for NH_4^+. However, it can be observed that there is a change in the concentration difference values around 9/23 (see Fig. 20b). Before 9/23, the denuder concentration was generally slightly higher than the MUs concentrations. However, there were variations in the concentration difference, with MU2 occasionally having a larger concentration than the denuder. Starting on 9/23, the concentration difference increased. This increased concentration difference was fairly constant for a few days, but after ≈9/26 the concentration difference decreased. Thereafter the concentration difference fluctuated with large concentration difference peaks on 9/30 and 10/7, however, the denuder concentration was never greater than the MUs concentration, unlike in the pre-9/23 period.

It is proposed that the "bacterial consumption event" for NH_3 started at 19:00 on 9/23. As discussed, ongoing research experience indicates that "bacterial consumption events" are triggered by marine air masses, which often contain coarse Na^+ aerosols. As discussed, there were high Na^+ concentrations on 9/21 and 9/22 (Fig. 8). The offset adjustments for NH_3

($0.23\,\mu g\,m^{-3}$ for MU1 and $0.25\,\mu g\,m^{-3}$ for MU2) are larger than the NH_4^+ offsets ($0.16\,\mu g\,m^{-3}$ for MU1 and $0.23\,\mu g\,m^{-3}$ for MU2). These differences and the occurrence of denuder NH_4^+ losses before the SJAC NH_4^+ losses (9/25) may indicate that the denuder is more susceptible to bacterial contamination than the SJAC.

It is acknowledged that the effects of the "bacterial consumption event" are not as clear for NH_3 as they are for NH_4^+. Factors that may be hindering the observation of the "bacterial consumption event" include possible tubing and inlet adsorption of NH_3 and a high variable NH_3 denuder blank (see Sect. 3.1).

The MU concentration trends after adjusting the response to the external standard as an offset from 19:00 on 9/23 are presented in Fig. 21. Observation of the post-9/23 period indicates that the denuder and the MUs concentration trends are now closer. Overall though, the denuder still generally has higher concentrations in this period. The largest concentration difference between the denuder and MUs is for the 9/30 and 10/7 peaks. Noticeably, the last 12-h average shows a small difference in concentrations, 0.48 for MU1, and 0.53 for MU2, in comparison to 0.46 for the filter pack. This supports the validity of applying an offset adjustment.

The MARGA performed moderately well for NH_3. The precision between the MUs was 22.8 %, which met the precision goal of 25 %. The accuracy results were mixed. The accuracy MARPD values were good, with a MARPD of 27.0 % for MU1 and 22 % for MU2. However, the NH_3 slope values for the linear regression were not as good, with values of 0.65 for MU1 and 0.72 for MU2 (Fig. 22), which are below the minimum slope goal of 0.8. Similarly to HNO_3, NH_3 is a "sticky" gas, therefore it is thought that the difference in measured concentrations is likely the result of the adsorption of NH_3 onto active sites on the MUs inlet and tubing. In addition, there was a variable NH_3 denuder blank, which may have influenced the agreement between the denuder and the MUs. It is also possible that there was some inaccuracy associated with the external standard offset adjustment, as the adjustment does not take into account any analytical bias.

3.5 Summary of MARGA evaluation

A summary table of the performance of the MARGA in regards to the precision and accuracy goals is presented in Table 2. It should be noted that NO_3^- is not included in the summary table. This is the due to the different sampling efficiency of coarse NO_3^- by the instruments. Results from the adjustment of the data for the coarse NO_3^- fraction show that the MARGA would have had good agreement with the filter pack, if they were sampling the same particle size. However, uncertainty in the correction for coarse NO_3^- precludes a quantitative assessment of MARGA accuracy and precision. The ability of the MARGA to measure NO_3^- accurately is supported by the findings of the Makkonen et al. (2012) study.

The MARGA performed extremely well in comparison to the denuder/filter pack for SO_2, SO_4^{2-} and NH_4^+ with all three compounds passing all their accuracy and precision goals by a significant margin.

The MARGA performed moderately well in comparison to the denuder/filter pack for HNO_3. HNO_3 passed the precision goal and the accuracy MARPD goal. However, both slope values were below the goal of 0.8. The performance of the MARGA in measuring HNO_3 was likely influenced by the adsorption of HNO_3 onto the sampling tubing and inlet. The effect of adsorption on measured MARGA concentrations was partly quantified by averaging the data over 24 h. By averaging over 24 h, the performance of the MARGA for HNO_3 improved in all the precision and accuracy tests. This resulted in MU1 passing the slope accuracy goal. However, the slope value for MU2 (0.69) did not pass the goal.

The MARGA also performed moderately for NH_3. Both MU1 and MU2 passed the precision and accuracy MARPD goals, however they did not pass the slope accuracy goal, with slope values of 0.65 for MU1 and 0.72 for MU2. Similarly to HNO_3, it is thought that adsorption by the sample tubing and inlet may have influenced the measured NH_3 concentrations. Other factors that may have influenced the agreement between denuder and MU measured concentrations include a variable NH_3 denuder blank and the accuracy of the external standard offset adjustment.

4 Conclusions and recommendations

In comparison to the denuder/filter pack, the MARGA performed very well in measuring concentrations of SO_2, SO_4^{2-} and NH_4^+, with all three species passing their precision and accuracy goals by a large margin. The performance of the MARGA in measuring NO_3^- could not be evaluated as the MARGA and filter pack had different particle cutoffs, which influenced the sampling of coarse NO_3^-. The MARGA performed moderately well in measuring HNO_3 and NH_3 in comparison to the denuder. In this study, the sample air stream was drawn through a ≈4 m length of 0.5” O.D. Polyethylene tubing. To improve the performance of the MARGA in measuring HNO_3 and NH_3, it is recommended that a more inert tubing material, such as perfluoroalkoxy (PFA) Teflon, be used (Neuman et al., 1999), and that the length of tubing be as short as possible. Ideally, the length of sample tubing could be minimized by locating the sample box at the point of atmospheric sampling. To improve the performance of the inlet for HNO_3 and NH_3, it is recommended that the inlet be Teflon coated.

To improve the accuracy of MARGA NH_3 and NH_4^+ measurements, it is recommended that when a “bacterial consumption event” occurs (identified by a sudden change in the NH_4^+/SO_4^{2-} ratio), that at least two external standards be analyzed with different concentrations to quantify the slope and offset of NH_3 and NH_4^+ adjustments. After running the external standards, it is recommended that the bacterial contamination be eliminated by “disinfecting” the system with peracetic acid, which has been observed to successfully clean the liquid flow path during subsequent field experiments.

It can be concluded that SO_4^{2-}, SO_2, NO_3^-, HNO_3, NH_4^+ and NH_3 concentrations can be measured with acceptable accuracy and precision when the MARGA is operated in conjunction with the recommendations outlined above. Ongoing MARGA projects are investigating the periodic loss of NH_4^+ in more detail and the feasibility of gradient flux measurements as a potential application for the MARGA.

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Table 1. Summary of data collection and detection limits for each compound and for each measurement system.

			1-h data			12-h data		
		Detection Limit	Number of data points[a]	>DL	>2DL	Number of data points[b]	>DL	>2DL
SO_2	MU 1	0.05 µg m^{-3}	716	671	619	60	59	58
	MU 2		694	653	612	60	59	57
	Denuder	0.079 µg m^{-3c}	–	–	–	120	120	117
SO_4^{2-}	MU 1	0.08 µg m^{-3}	716	716	705	60	60	59
	MU 2		692	689	676	60	60	59
	Teflon filter	0.147 µg m^{-3}	–	–	–	120	118	114
HNO_3	MU 1	0.10 µg m^{-3}	716	665	599	60	59	55
	MU 2		694	654	564	60	59	54
	Denuder	0.106 mug m^{-3}	–	–	–	120	117	102
NO_3^-	MU 1	0.10 µg m^{-3}	716	649	545	60	59	48
	MU 2		692	634	492	60	57	45
	Teflon filter	0.13 µg m^{-3}	–	–	–	120	52	14
	Nylon filter	0.13 µg m^{-3}	–	–	–	120	81	23
NH_3	MU 1	0.05 µg m^{-3}	716	716	716	60	60	60
	MU 2		694	694	694	60	60	60
	Denuder	0.072 µg m^{-3}	–	–	–	120	119	117
NH_4^+	MU 1	0.05 µg m^{-3}	716	716	716	60	60	60
	MU 2		693	693	693	60	60	60
	Teflon filter	0.095 µg m^{-3}	–	–	–	120	114	112

[a] Maximum number of hourly data points that could be collected was 720.

[b] Maximum number of 12-h data points that could be collected was 60 for each MU, 120 for the duplicate filter denuder systems combined.

[c] Estimated denuder/filter pack concentration detection limits calculated using the mass detection limit and the average denuder/filter pack flow rate during the ETV test.

Table 2. Summary of the performance of the MARGA in achieving accuracy and precision goals.

	Precision	Accuracy			
		MU1		MU2	
	MARPD (%)[a]	MARPD[b] (%)	Slope[c]	MARPD (%)	Slope
SO_2	**11.5**[d]	**20.3**	**1.11**	**10.9**	**1.05**
SO_4^{2-}	**3.2**	**12.1**	**0.97**	**8.3**	**0.98**
HNO_3-12-h	**22.7**	**21.2**	0.73	**29.0**	0.57
HNO_3-24-h	**18.7**	**11.0**	**0.90**	**17.1**	0.69
NH_4^+	**5.3**	**6.7**	**1.02**	**8.6**	**0.97**
NH_3	**22.8**	**27.0**	0.65	**22.0**	0.72

[a] The precision goal for the MARPD was to be <25 %.

[b] The accuracy goal for the MARPD was to be <40 %.

[c] The accuracy goal for the slope was to be between 0.8–1.2.

[d] Bolded values indicate the goal was passed.

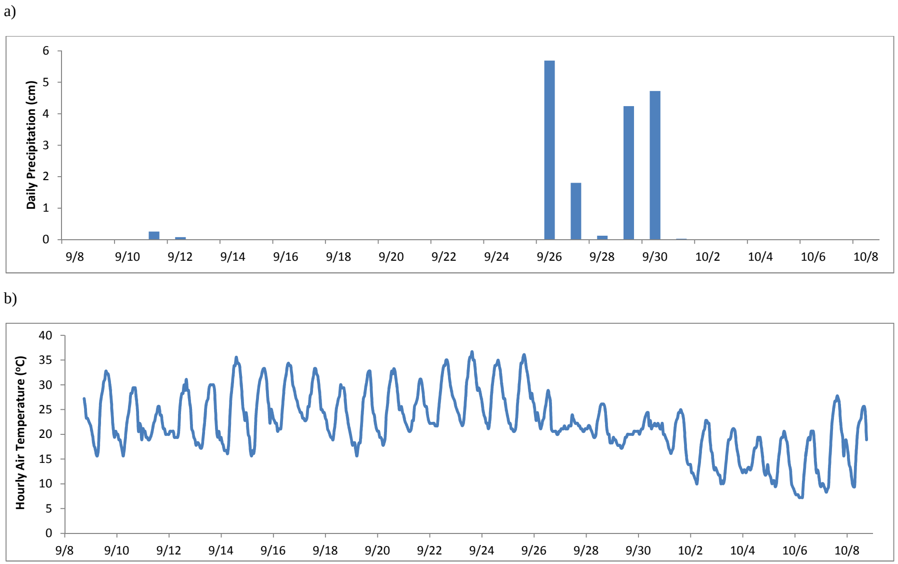

Fig. 1. (a) Daily precipitation and **(b)** hourly air temperature at RDU airport (≈ 8km from sampling site) during the ETV period (September 8 2010–8 October 2010).

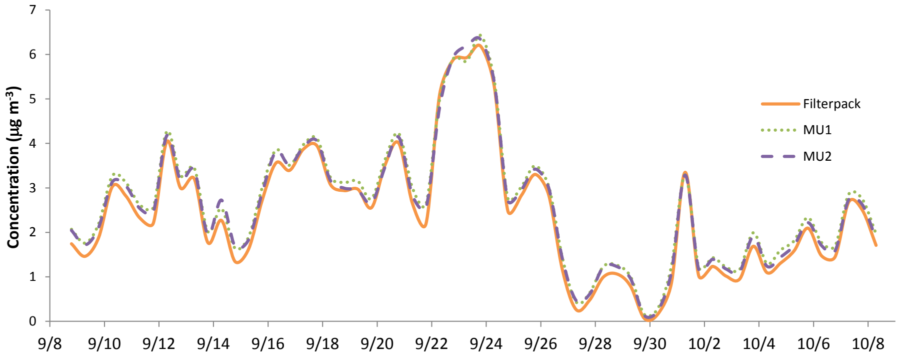

Fig. 2. Filter pack and MUs measured SO_4^{2-} concentrations during the ETV period.

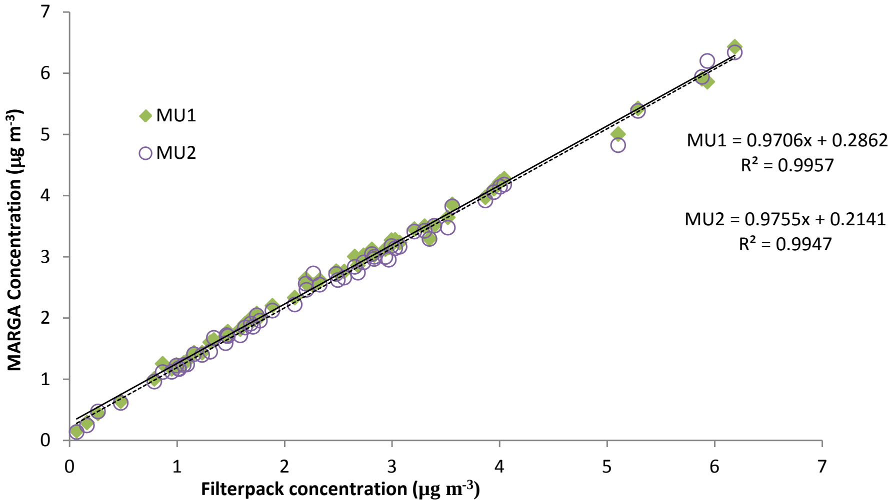

Fig. 3. Regression analysis of MARGA SO_4^{2-} concentrations against filter pack SO_4^{2-} concentrations.

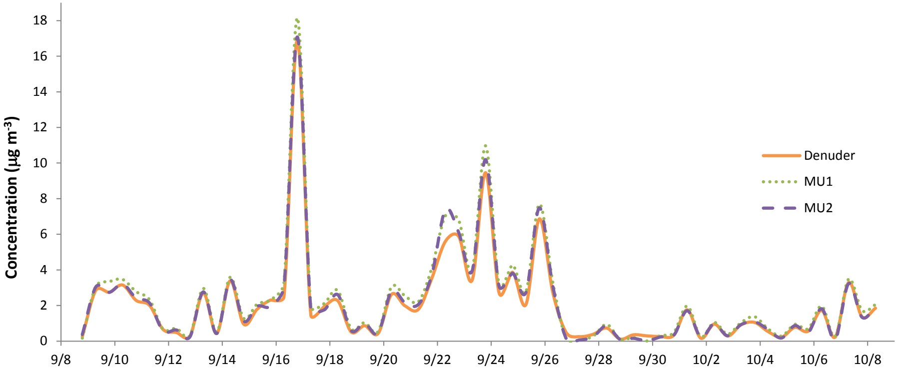

Fig. 4. Denuder and MUs measured SO_2 concentrations during the ETV period.

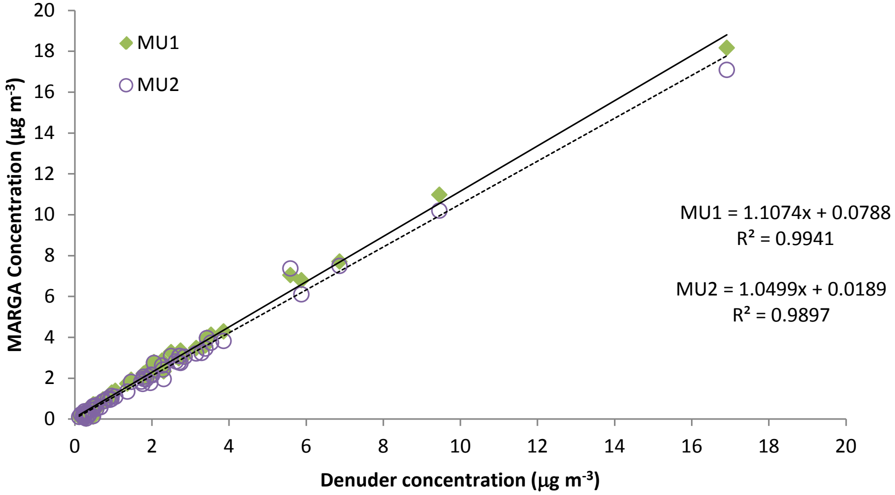

Fig. 5. Regression analysis of MARGA SO_2 concentrations against denuder SO_2 concentrations.

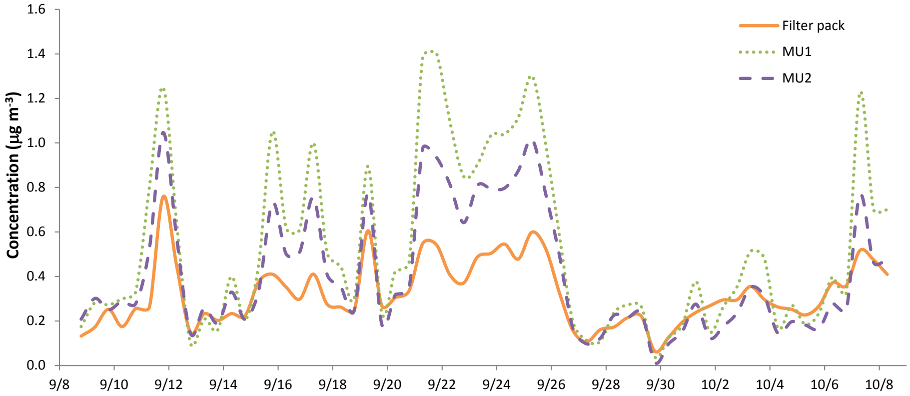

Fig. 6. Filter pack and MUs measured NO_3^- concentrations during the ETV period.

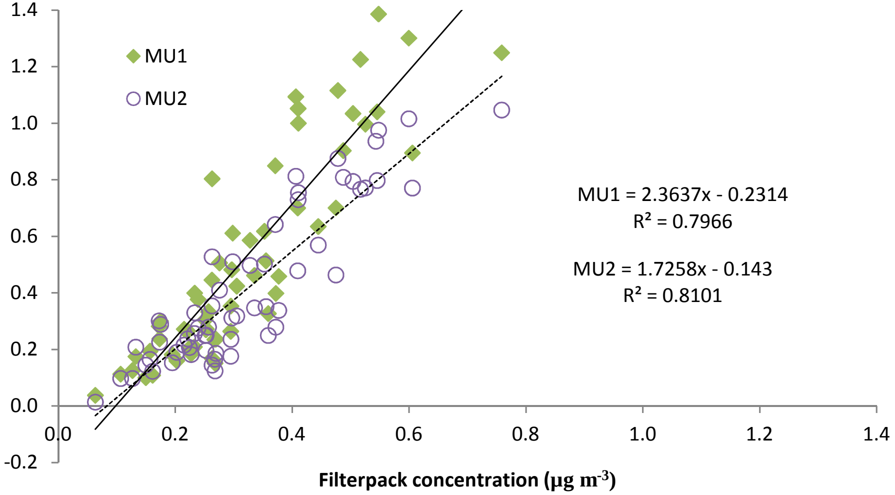

Fig. 7. Regression analysis of MARGA NO_3^- concentrations against filter pack NO_3^- concentrations.

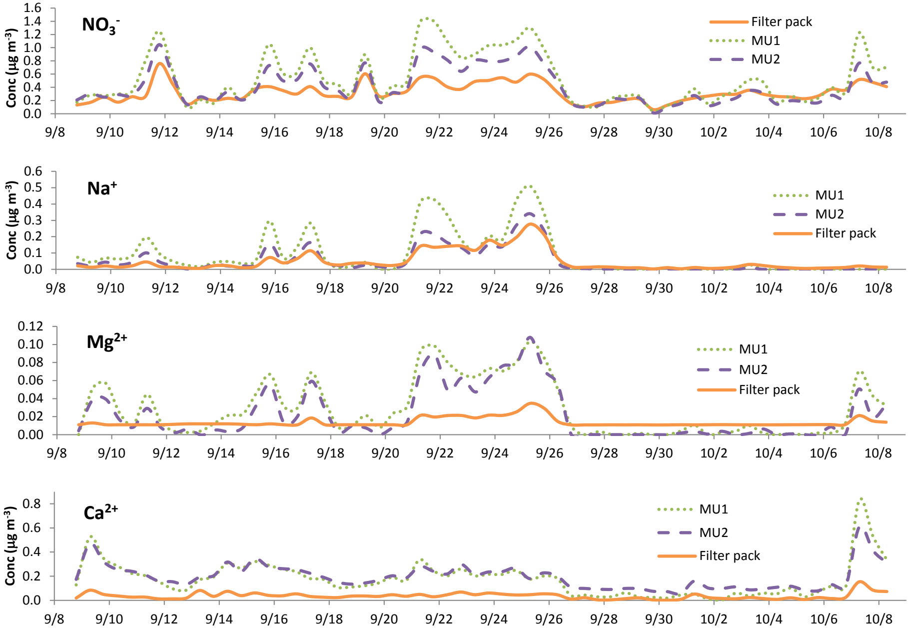

Fig. 8. Concentration trends of NO_3^- and 3 compounds (Na^+, Mg^{2+}, Ca^{2+}) that are often components of the coarse NO_3^- aerosol.

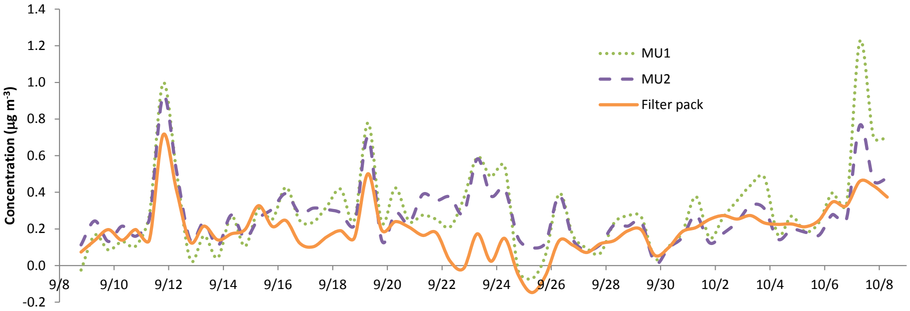

Fig. 9. Concentration trends of estimated "fine" NO_3^- (total NO_3^- minus $NaNO_3$) for the MUs and filter pack during the ETV period.

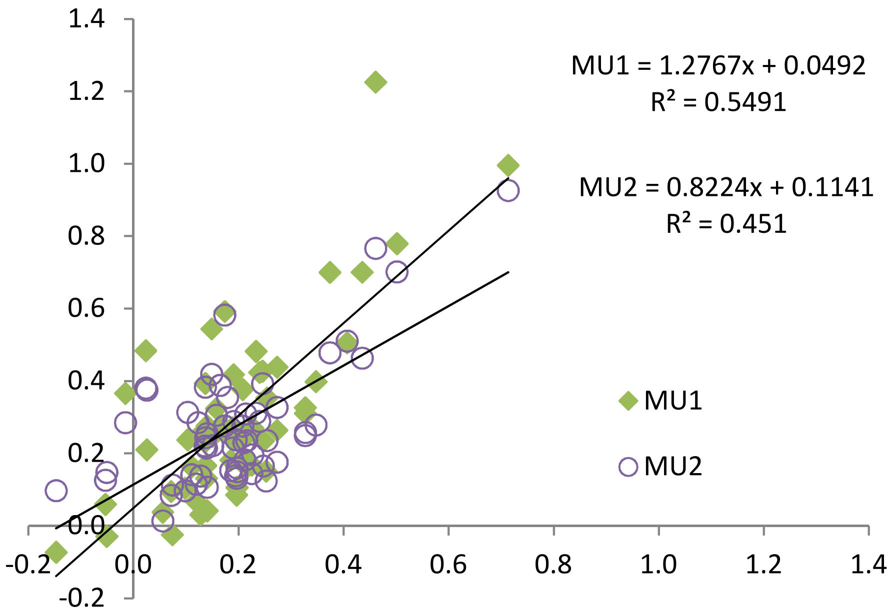

Fig. 10. Regression analysis of estimated MARGA "fine" NO_3^- (total NO_3^- minus $NaNO_3$) concentrations against filter pack "fine" NO_3^- (total NO_3^- minus $NaNO_3$) concentrations.

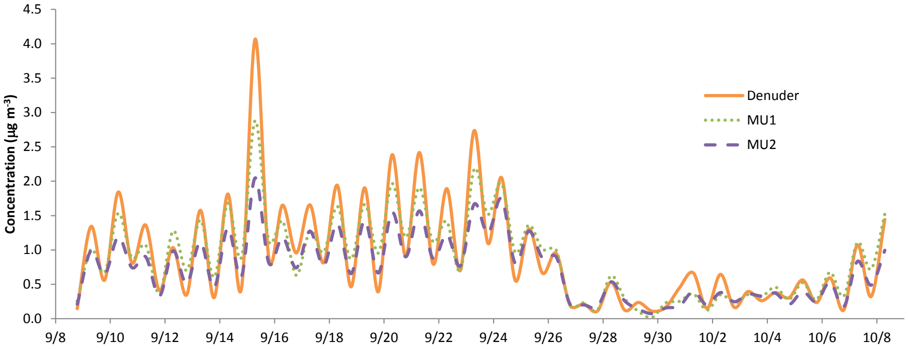

Fig. 11. Denuder and MUs measured HNO_3 concentrations during the ETV period.

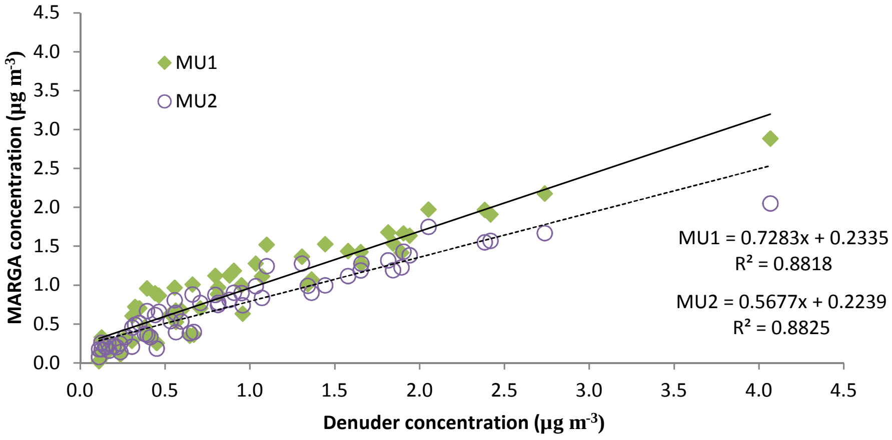

Fig. 12. Regression analysis of MARGA HNO_3 concentrations against denuder HNO_3 concentrations.

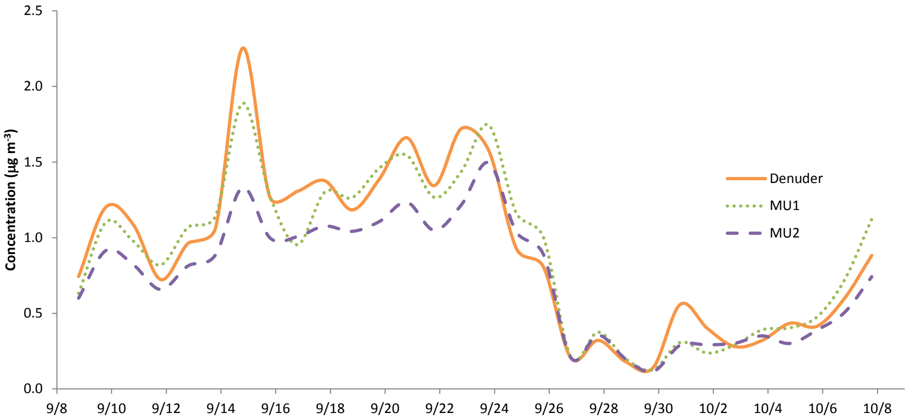

Fig. 13. Denuder and MUs measured 24 h average HNO_3 concentrations during the ETV period.

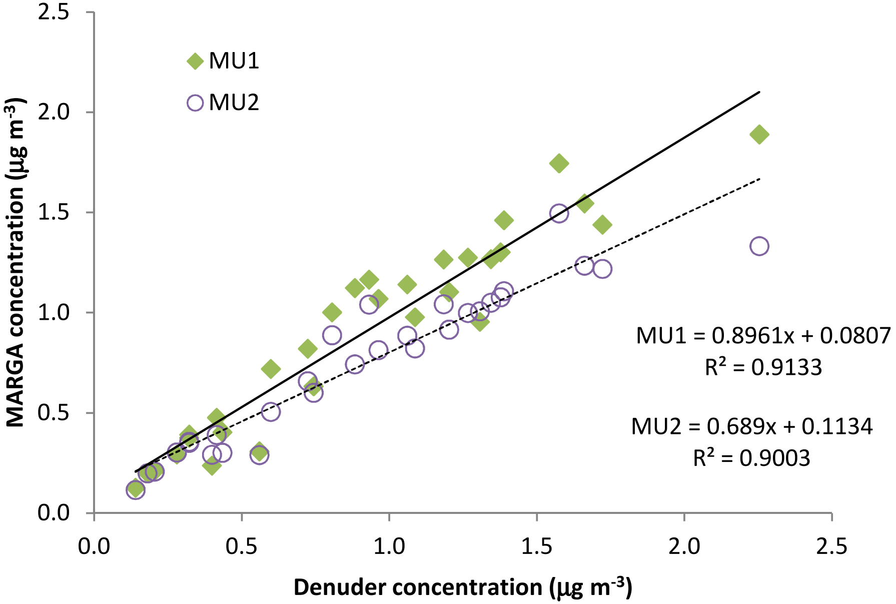

Fig. 14. Regression analysis of 24 h average MARGA HNO_3 concentrations against denuder HNO_3 concentrations.

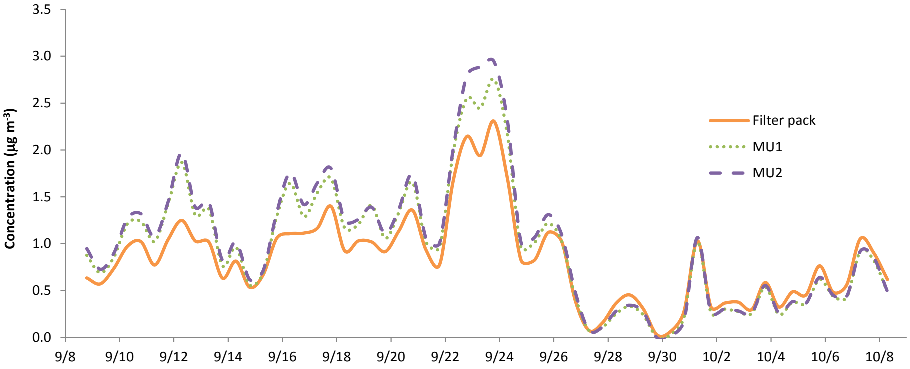

Fig. 15. Filter pack and MUs measured NH_4^+ concentrations (after adjusting for the external standard as a percentage) during the ETV period.

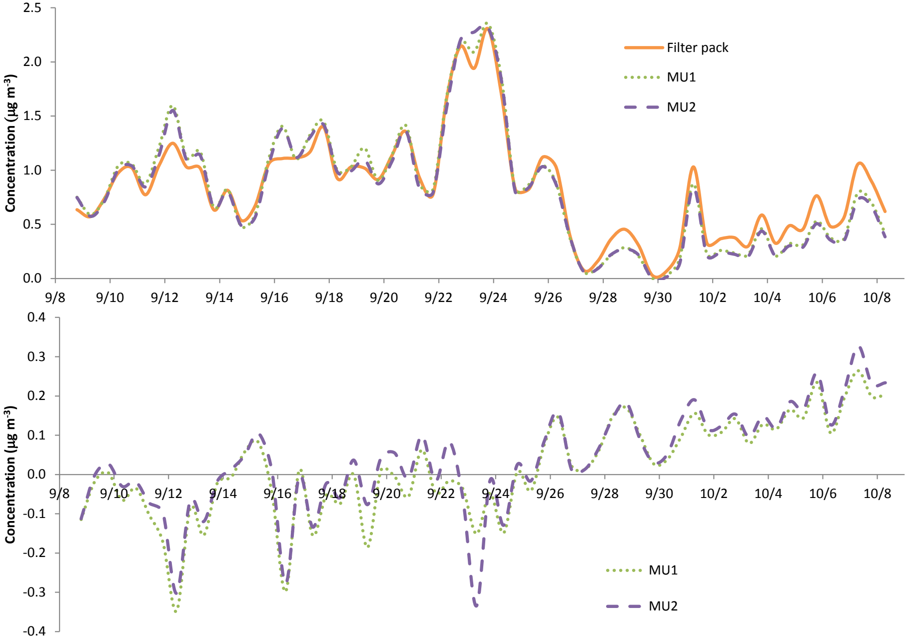

Fig. 16. (a) NH_4^+ concentration trends for the MUs (unadjusted for the external standard) and the filter pack during the ETV period. **(b)** Concentration difference (filter pack minus MUs) between the filter pack and the MUs NH_4^+ concentrations (unadjusted for the external standard).

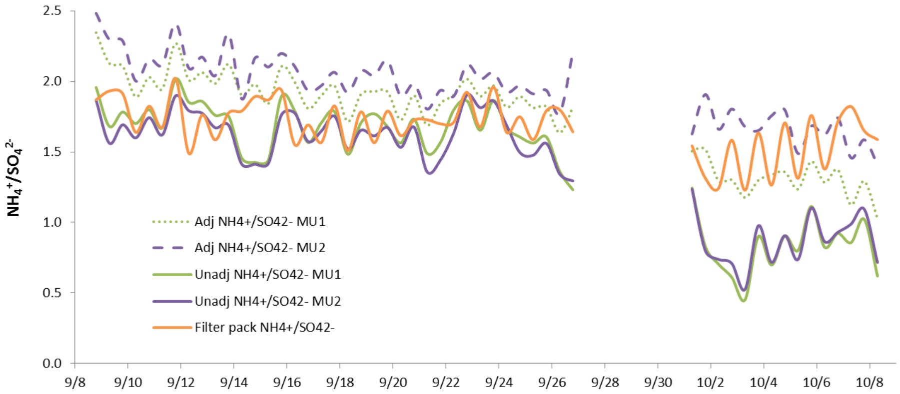

Fig. 17. Ammonium sulfate ratios (NH_4^+/SO_4^{2-}) calculated for the filter pack and the MUs adjusted (Adj) and unadjusted (Unadj) for the offset.

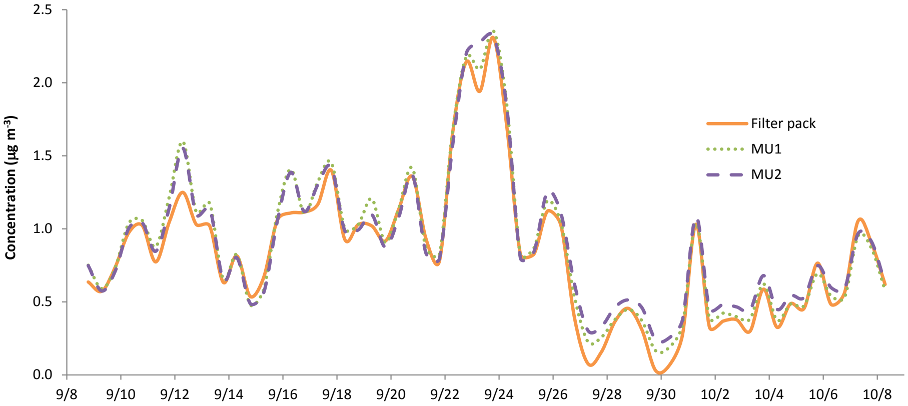

Fig. 18. Filter pack and MUs measured NH_4^+ concentrations (after adjusting for the external standard as an offset after 19:00 on 9/25) during the ETV period.

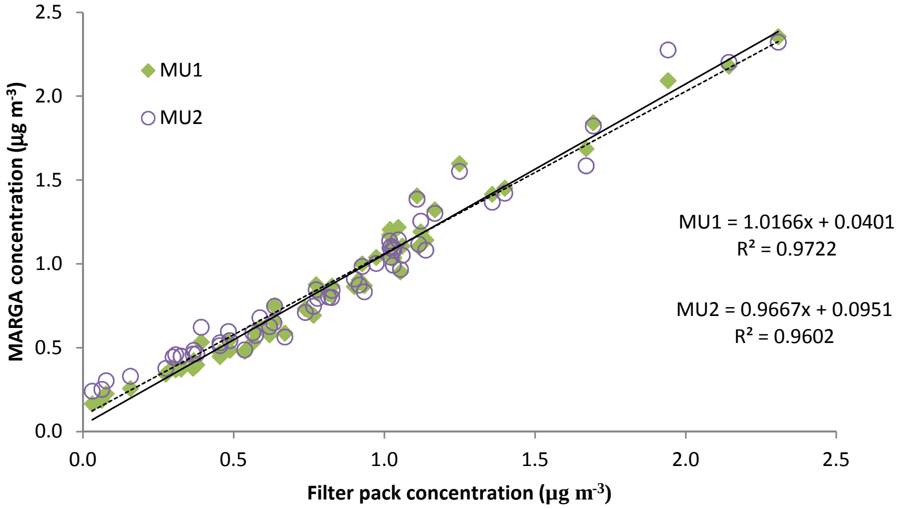

Fig. 19. Regression analysis of MARGA NH_4^+ concentrations against filter pack NH_4^+ concentrations.

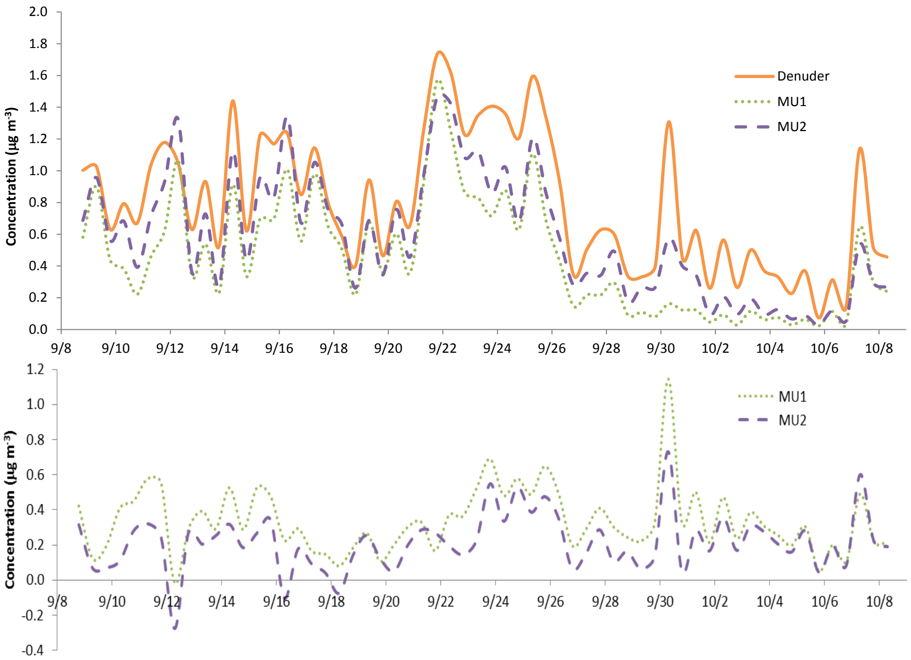

Fig. 20. (a) Denuder and MUs measured NH_3 concentrations (unadjusted for the external standard) during the ETV period. **(b)** Concentration difference (filter pack minus MUs) between the filter pack and MUs NH_3 concentrations (unadjusted for the external standard).

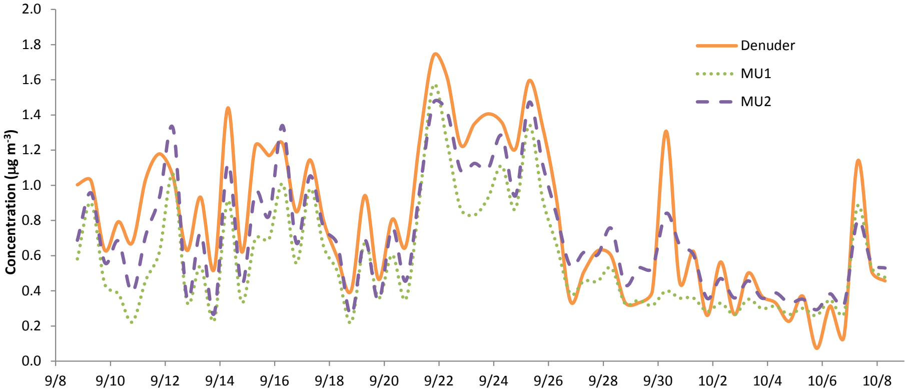

Fig. 21. Filter pack and MUs measured NH_3 concentrations (after adjusting for the external standard as an offset from 19:00 on 9/23) during the ETV period.

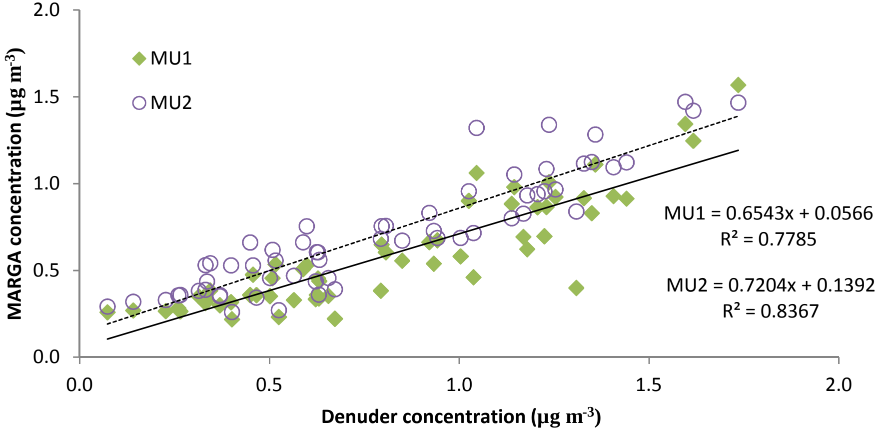

Fig. 22. Regression analysis of MARGA NH_3 concentrations against filter pack NH_3 concentrations.