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Supplement of

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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Supplementary Material for:

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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Summary of the results of the ETV report

Table S1. Summary of the accuracy and precision results of the MARGA Environmental Technology Verification (ETV) program report (Table from U.S. EPA, 2011).

Parameter Evaluated	Method of Evaluation	Results				
		Analyte	MARGA 1		MARGA 2	
	Slope		Intercept ($\mu\text{g}/\text{m}^3$)	Slope	Intercept ($\mu\text{g}/\text{m}^3$)	
Accuracy	Regression analysis comparison to reference samples	SO ₂	1.16^a	0.16	1.08	0.13
		HNO ₃	0.780	0.35	0.596	0.28
		NH ₃	0.930	-0.14	0.987	-0.08
		SO ₄ ²⁻	1.02	0.30	0.986	0.22
		NO ₃ ⁻	2.48	-0.15	1.73	-0.05
		NH ₄ ⁺	1.02	-0.23	0.993	-0.25
		SO ₂ ^b	0.962	0.50	0.890	0.44
Accuracy	Calculation of MARPD between MARGA results and reference method results	Analyte		MARPD		
				MARGA 1	MARGA 2	
		SO ₂		31.2%	18.9%	
		HNO ₃		34.1%	25.8%	
		NH ₃		33.1%	18.2%	
		SO ₄ ²⁻		17.3%	9.1%	
		NO ₃ ⁻		86.9%	58.7%	
NH ₄ ⁺		19.2%	25.3%			
SO ₂ ^b		19.8%	14.1%			
Precision	Comparison of results from duplicate monitoring systems	Analyte		1-Hour MARPD		
		SO ₂		10.4%		
		HNO ₃		24.8%		
		NH ₃		22.4%		
		SO ₄ ²⁻		6.5%		
		NO ₃ ⁻		27.3%		
		NH ₄ ⁺		6.3%		

^a Bolded numbers indicate that the performance goal was met. The performance goals are provided in the manuscript.

^b Comparison to SO₂ pulsed fluorescence analyzer (1 hr data), all other comparisons relative to 12-hr denuder/filter pack.

Differences in the reduction and analysis of the data between this manuscript and the ETV report

A description of the data reduction and analysis used in this manuscript is provided in Sections 3.1 (raw data adjustments) and 3.2 (data collection and detection limits). For the data used in the ETV report, none of the raw data adjustments described in this manuscript (section 3.1) were applied, with the exception of subtracting an NH₃ denuder blank (blanks were not subtracted from other compounds). Treatment of data in regards to detection limits was also different between the ETV report and this manuscript. In the ETV report, both MARGA and denuder/filter pack 12-hour concentrations less than twice the MARGA detection limit (2DL) were excluded from comparison. For the manuscript, measured concentrations were assessed in comparison to their respective measurement system detection limit. As described in the manuscript, there was a significant amount of NO₃⁻ and HNO₃ concentrations below 2DL (see Table 1 in manuscript). Therefore for the manuscript, 12-hour concentrations <2DL were included for both the MARGA and the denuder/filter pack. In the ETV report, 1-hour MARGA data and 12-hour denuder/ filter pack below the detection limit were assigned a ½ DL value. For the manuscript, concentration values below the DL were kept as measured.

In the filter pack system, the Teflon filter is the first filter in a series that captures NH₄NO₃. In addition, there are two back-up filters to capture volatilized NH₄NO₃ from the Teflon filter, a nylon filter to collect NO₃⁻ as HNO₃ and a citric acid filter to collect NH₄⁺ as NH₃. The amount of volatilization is dependent on temperature. For the ETV report, NO₃⁻ concentrations were calculated as the sum of concentrations on the Teflon and nylon filters and NH₄⁺ concentrations as the sum of concentrations on the Teflon and citric acid filters. For the manuscript, a quality assurance (QA) assessment of volatilized NH₄NO₃ on the nylon and citric acid filters was conducted based on the theory that the molar equivalent nitrogen (N)

concentrations on the filters should be the same. Analysis of the molar N concentrations from the two filters was conducted using linear regression (see Fig. S1).

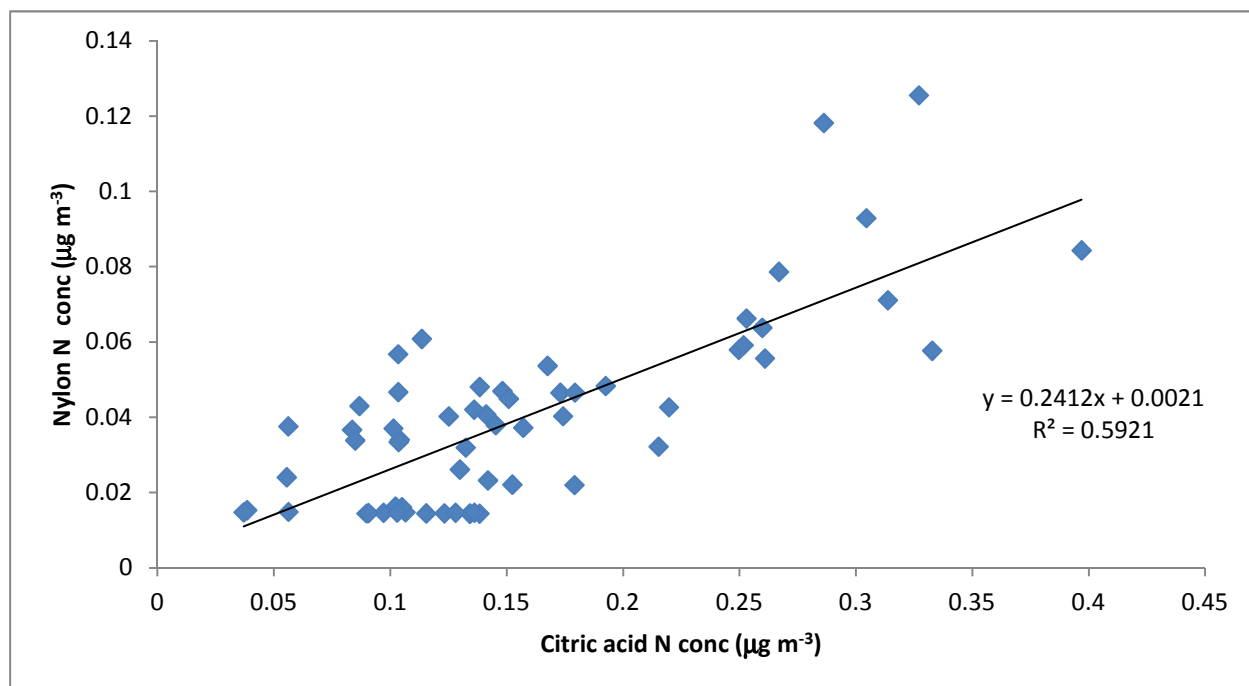


Fig. S1. The relationship between the nitrogen (N) concentrations on the nylon and citric acid filters.

The line of best fit shows that the citric acid filter has N concentrations ≈ 4 times higher than that of the nylon filter. Analysis of Fig. S1 and the filter pack blank results indicate that a significant but variable blank associated with the citric acid filter is likely contributing to this result.

Therefore, for the manuscript, the sum of concentrations on the Teflon and nylon filters is used to calculate both NH_4^+ and NO_3^- concentrations. NO_3^- volatilized from the Teflon filter was corrected by adding the amount of NO_3^- collected on the backup nylon filter to the NO_3^- remaining on the Teflon filter. Similarly, NH_4^+ lost from the Teflon filter was estimated and corrected by assuming that the NO_3^- collected on the backup nylon filter was associated entirely with NH_4NO_3 volatilized from the Teflon filter.

In the manuscript, there are corrections from the ETV report. As stated earlier in this section, in the ETV report a NH_3 denuder blank was subtracted from the measured concentrations. However, during this calculation the units were not converted from $\mu\text{g-N}$ to $\mu\text{g-NH}_3$. Therefore, the NH_3 denuder concentrations reported and analyzed in the ETV report are systematically 17.65% lower than they should have been. Small errors associated with the denuder/filter pack blank results in the ETV report should be noted. Specifically, five blank values were reported in that report, instead of the correct number of six and also it was not stated that the units presented for blank results are $\mu\text{g-N}$ for NH_3 , NH_4^+ , HNO_3 , and NO_3^- and $\mu\text{g-SO}_4$ for SO_2 and SO_4^{2-} . However, these blank errors had a negligible impact on the results of the ETV report.

Volatilization of NH_4NO_3 from the Teflon filter

The extent of the volatilization of NH_4NO_3 from the Teflon filters to the back-up filters is expected to be dependent on temperature. During the sampling period (9/8–10/8) the Teflon and nylon filters contributed 42% and 58%, respectively to total NO_3^- concentration. The influence of temperature on volatilization was examined by comparing the % relative contribution of each filter to total NO_3^- concentration during two periods with different average air temperatures. During the sampling period before the rain event (9/8 18:00- 9/26 06:00), which had an average hourly air temperature of 25.2°C , the relative contribution of the individual filters to total NO_3^- concentration was 35% for Teflon and 65% for nylon. For the sampling period after the beginning of the rain event (9/26 06:00-10/8 18:00), which had an average hourly air temperature of 18.1°C , the relative contribution of the filters was 51% and 49% for Teflon and

nylon, respectively. These results support that NH_4NO_3 volatilization from filters is influenced by temperature.

Performance of the MARGA in comparison to the SO_2 pulsed fluorescence analyzer (PFA)

As discussed in the manuscript, the performance of the MARGA in measuring SO_2 was also evaluated in comparison to a 43S SO_2 PFA (Thermo Environmental Instruments (TEI), Mountain View, CA), which measures SO_2 continuously. SO_2 PFA concentrations were collected as five minute averages. The SO_2 PFA was zeroed and spanned daily and concentrations were adjusted based on the results of the zero and span. The accuracy of the MARGA in comparison to the SO_2 PFA was evaluated using the same methodology as for the denuder/filter pack. Therefore, the accuracy of the MUs was evaluated by calculating the median absolute relative percent difference (MARPD) relative to SO_2 PFA concentrations and by determining the slope value using linear regression analysis. However, as the SO_2 PFA makes five minute average measurements, the accuracy evaluation was conducted for both 1-hour and 12-hour averaged concentrations.

For the SO_2 PFA, data was excluded during the daily zero and span and also due to occasional instrument malfunction. As mentioned, SO_2 data was measured using 5-minute averages. Of a possible 8640 five minute data averages during the ETV period, $\approx 98\%$ (8319) of them contained valid data. For $\approx 75\%$ of the ETV period, daily zero and span events were 45 min in length and were during one individual hour. This resulted in there being only 25% of 5 minute averages valid during an individual hour, and thus these hours were excluded. Accordingly during the ETV, the SO_2 PFA had a data collection of $\approx 96\%$ for 1 hour averages. There were

always 11 valid hours of data for each 12 hour average, therefore no 12 hour average data period was excluded.

For the SO₂ PFA, ≈29% (1 hour) or ≈20% (12 hour) of data was below the DL of 0.26 μg m⁻³ (converted from 0.1 ppb, assuming standard atmospheric pressure (1 atm) and standard temperature (298 K), and ≈37% (1 hour) or ≈33% (12 hour) of data was below 2DL. The amount of data either close to or below the DL should be taken into consideration when comparing the pulsed fluorescence analyzer SO₂ concentrations to other instruments.

The SO₂ concentration trend for the PFA, as well as the concentration trends for the MUs and the denuder are shown in Fig. S4. The average SO₂ concentration measured during the ETV by the PFA was 2.07 μg m⁻³ ± 2.86 (1 standard deviation). The SO₂ concentration measured by the denuder was extremely similar (2.08 μg m⁻³ ± 2.64). MU concentrations were slightly higher than both the PFA and the denuder with MU1 measuring an average SO₂ concentration of 2.38 μg m⁻³ ± 2.94 and MU2 measuring an average concentration of 2.20 μg m⁻³ ± 2.79. The MARGA also performed well in comparison to the SO₂ PFA. The slope values for the MARGA concentrations against the 12-hour PFA concentrations were 1.02 for MU1 and 0.96 for MU2 (Fig. S5a), which is lower than the slope values for the MARGA against the denuder (1.11 for MU1, 1.05 for MU2). Against 1-hour averaged PFA concentrations (Fig. S5b), the slope values were as expected similar to the 12-hour averaged values (1.00 for MU, 0.95 for MU2).

The MARPD values for SO₂ between the MARGA and 12-hour averaged PFA concentrations were 20.8% for MU1 and 14.6% for MU2, which was similar to the MARPD between the MUs and the denuder (20.3% for MU1, 10.9% for MU2). Against 1-hour averaged PFA concentrations, MARPD values were higher than those for 12-hour PFA, 28.8% for MU1

and 22.1% for MU2, respectively. These higher values are partly due to the low 1-hour concentrations used in these calculations.

The denuder was also compared to the 12 hour averaged PFA concentrations. Fig. S6 presents the SO₂ regression analysis between the two measurement techniques. The slope was 0.91, which is lower than either of the MU's slope value against the PFA. The accuracy MARPD was 12.5%, which is similar to the MARPD between the MUs and the 12 hour PFA values.

Information on chemicals

All MARGA solutions were prepared in 18.2 MΩ.cm DDI water. 30% pure H₂O₂ was used to provide a H₂O₂ concentration of 10 ppm for the absorption solution. Anion eluent (7.0 mmol/8.0 mmol Na₂CO₃/ NaHCO₃) was prepared from pure material (>99.5%, ACROS Organics, Fisher Scientific, Pittsburgh, PA, USA). 2M HNO₃ (Sigma-Aldrich) was used to prepare the cation eluent (3.2 mmol). For the regenerant, 85% phosphoric acid was used. Pure NH₄NO₃ (99.9%, certified ACS, Fisher Scientific) and (NH₄)₂SO₄ (99.0% certified ACS, Fisher Scientific) were used to prepare additional liquid standards of NH₄⁺, NO₃⁻, and SO₄²⁻.

Supplementary tables and figures

Table S2. Results of blank and external standard run on both MUs after the ETV period.

	SO ₂		HNO ₃		NH ₃		SO ₄ ²⁻		NO ₃ ⁻		NH ₄ ⁺	
	MU1	MU2	MU1	MU2	MU1	MU2	MU1	MU2	MU1	MU2	MU1	MU2
Obs Blank ^a	0.132 ^c (0.039) ^d n = 36 ^e	0.153 (0.039) n = 26	0.077 (0.066) n = 36	0.024 (0.011) n = 37	0.004 (0.010) n = 37	0 n = 37	0.147 (0.026) n = 36	0.147 (0.019) n = 32	0.026 (0.027) n = 37	0.038 (0.027) n = 35	0 n = 37	0 n = 36
Exp Conc ^a	1.085	1.068	1.759	1.732	1.048	1.031	1.626	1.601	1.731	1.704	1.110	1.092
Obs Conc ^{a, b}	1.134 (0.025) n = 19	1.131 (0.095) n = 20	1.902 (0.033) n = 18	1.903 (0.040) n = 20	0.810 (0.029) n = 19	0.780 (0.038) n = 18	1.700 (0.027) n = 20	1.657 (0.020) n = 20	1.926 (0.035) n = 20	1.887 (0.047) n = 19	0.949 (0.023) n = 19	0.862 (0.026) n = 19
% analytical bias	+4.5	+5.9	+8.1	+9.9	-22.7	-24.4	+4.5	+3.5	+11.3	+10.7	-14.5	-21.1

^a Units are µg m⁻³

^b The blank value has been subtracted from the observed concentration.

^c Mean values

^d 1 standard deviation

^e n is the number of hourly values

Table S3. Results of denuder/filter pack trip blanks (n= 6) collected during the ETV period.

		Blank (μg)
Na ₂ CO ₃ denuder	SO ₂	0.24 ^a (0.32) ^b
	HNO ₃	0
H ₃ PO ₃ denuder	NH ₃	1.38 (0.43)
Teflon filter	SO ₄ ²⁻	0.14 (0.34)
	NO ₃ ⁻	0.05 (0.13)
	NH ₄ ⁺	0.31 (0.12)
Nylon filter	NO ₃ ⁻	0

^a Mean value

^b 1 standard deviation

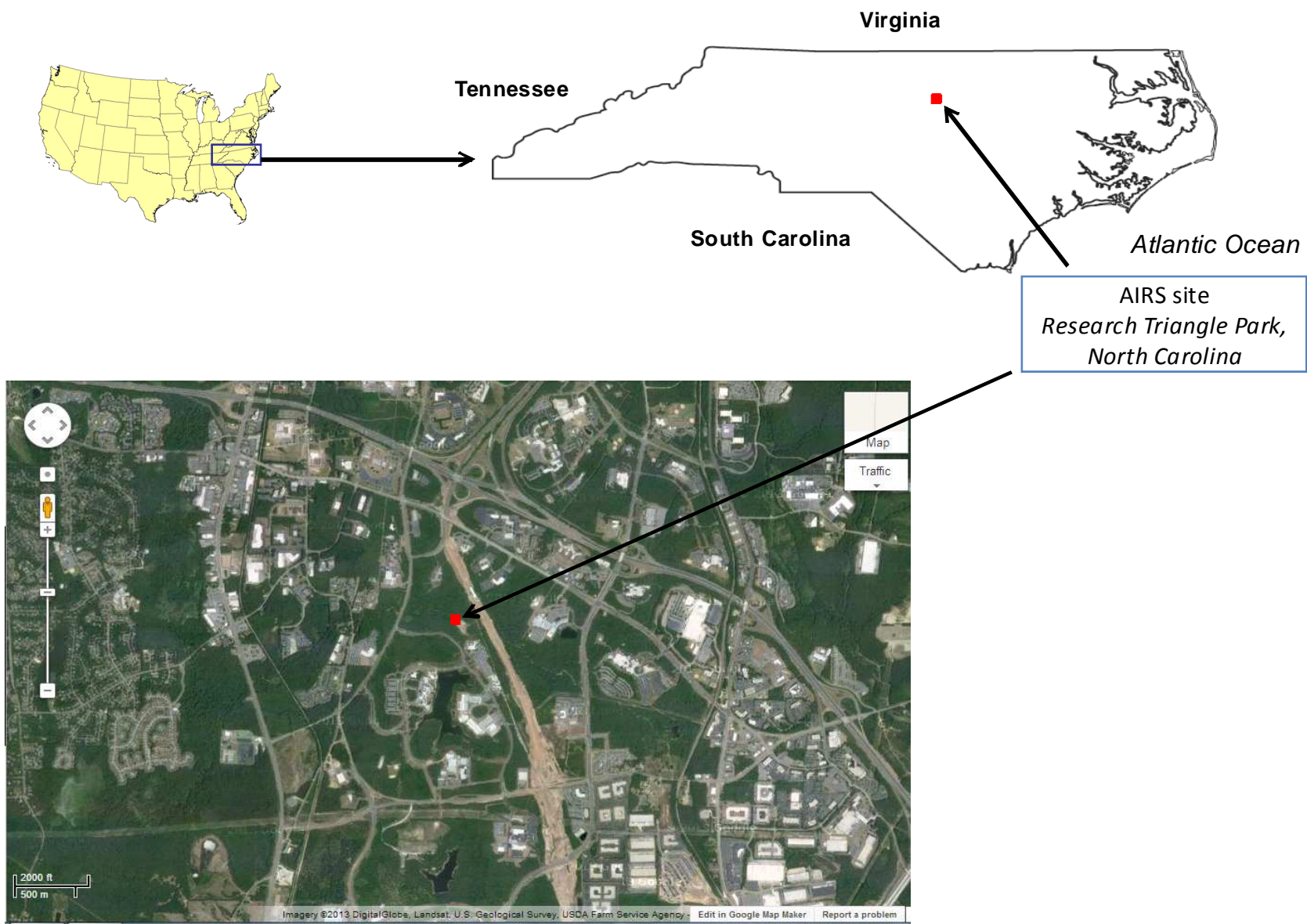


Fig. S2. Location and surrounding area of the ambient air innovation research site (AIRS) sampling site.

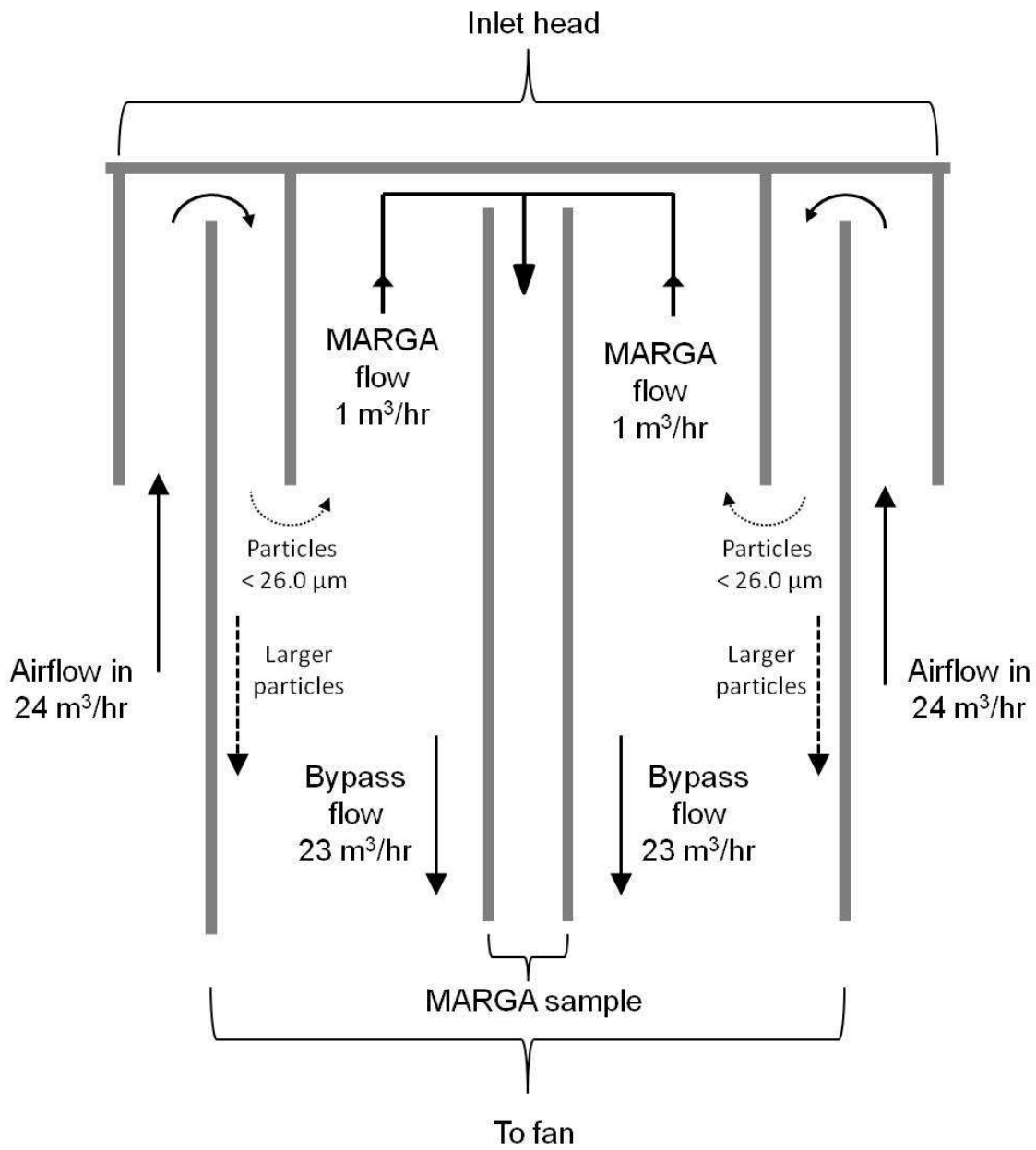


Fig. S3. Schematic of MARGA inlet.

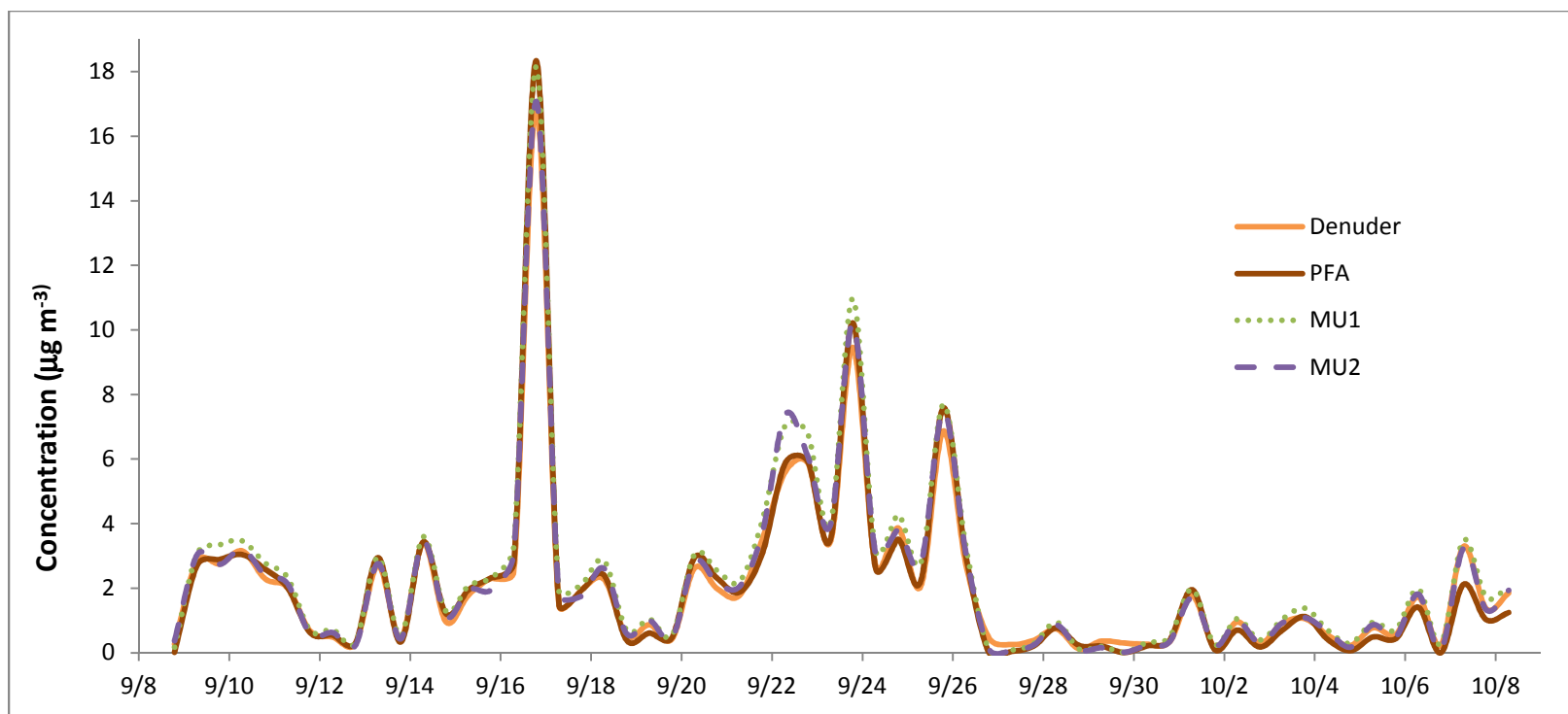
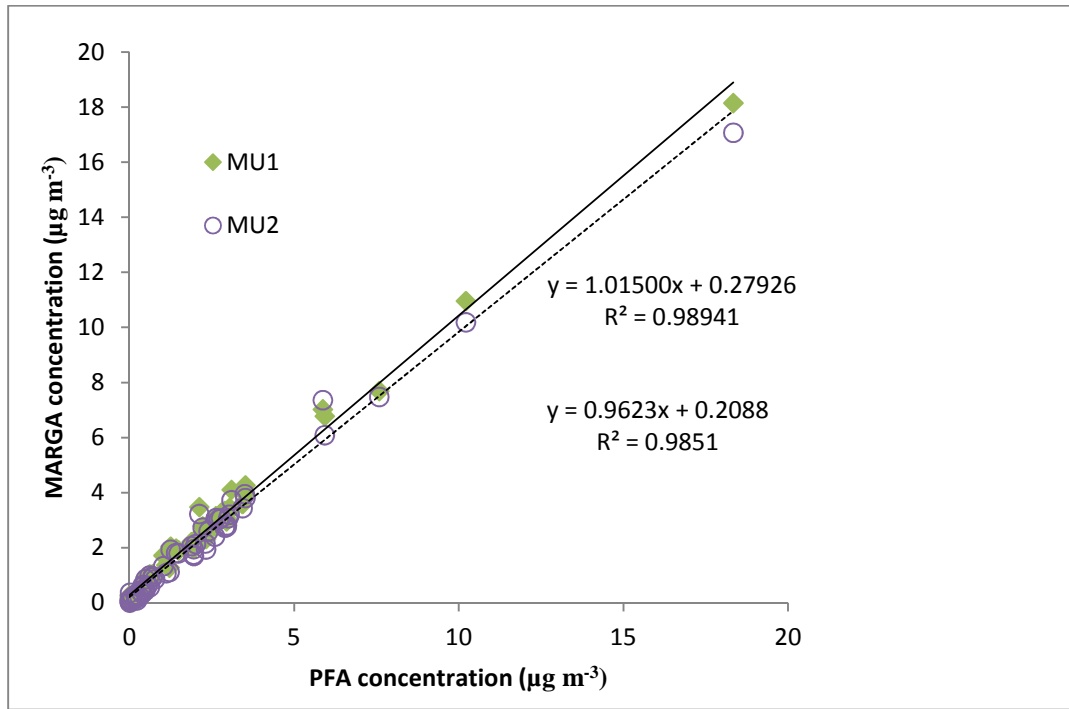


Fig. S4. PFA, Denuder and MUs measured SO₂ concentrations during the ETV period (September 8th, 2010-October 8th, 2010).

a)



b)

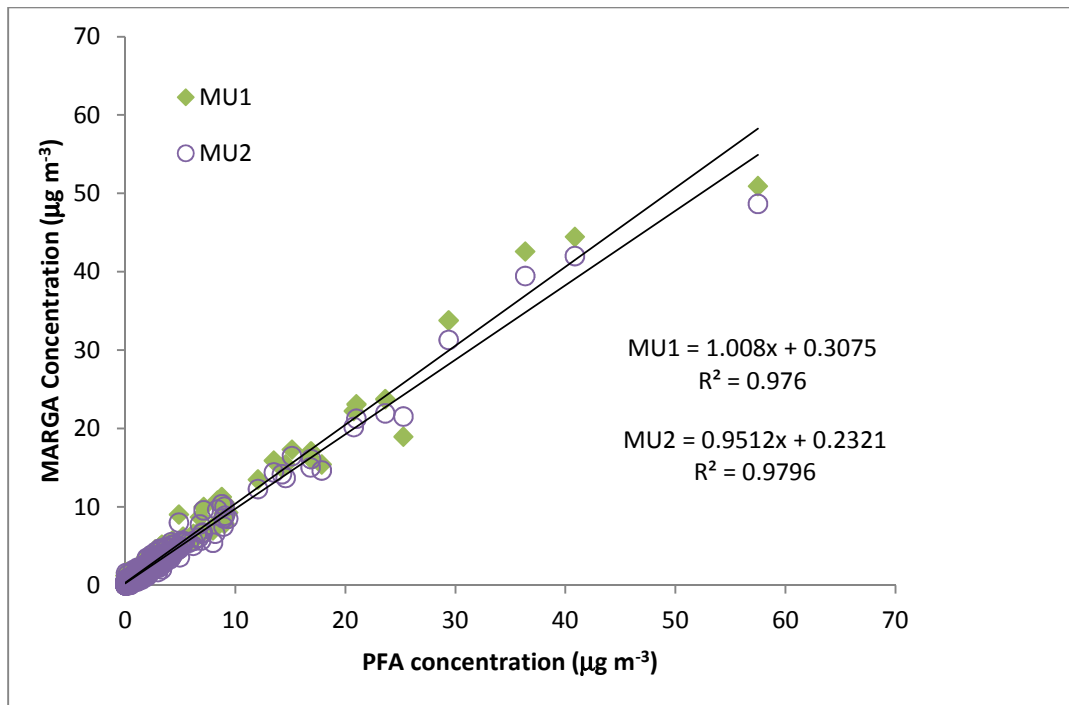


Fig. S5. Regression analysis of MARGA SO₂ concentrations against PFA SO₂ concentrations a) 12-hour MARGA SO₂ concentrations against 12-hour PFA SO₂ concentrations. b) 1-hour MARGA SO₂ concentrations against 1-hour PFA SO₂ concentrations.

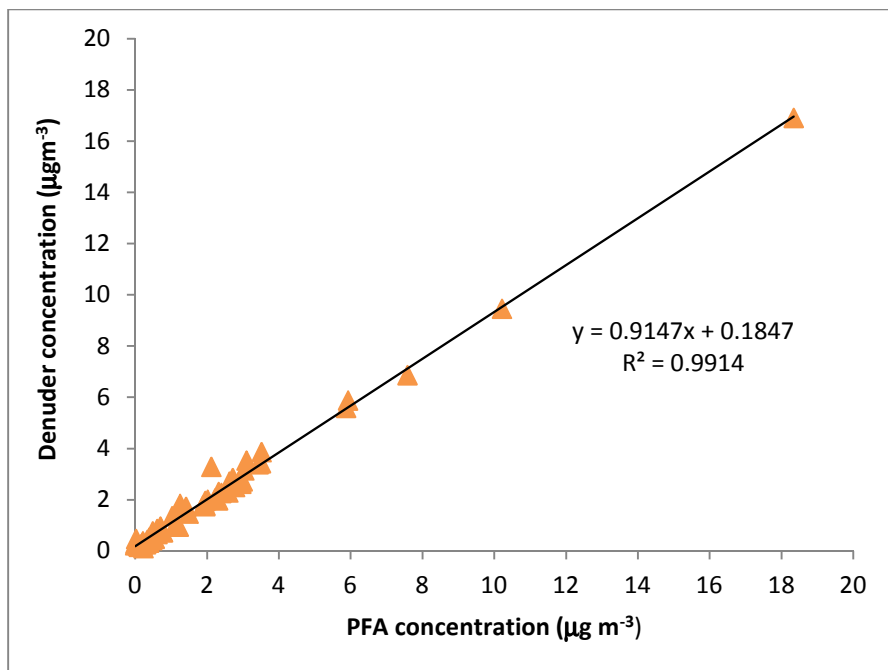


Fig. S6. Regression analysis of denuder SO₂ concentrations against 12-hour PFA concentrations.