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 ($\mu g/m^3$)**	**Slope**	**Intercept ($\mu g/m^3$)**
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**

Parameter Evaluated	Method of Evaluation	Analyte	MARPD	
			MARGA 1	**MARGA 2**
Accuracy	Calculation of MARPD between MARGA results and reference method results	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%**

Parameter Evaluated	Method of Evaluation	Analyte	1-Hour MARPD
Precision	Comparison of results from duplicate monitoring systems	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 SO_2 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 NH_3 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 NO_3^- and HNO_3 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 typically captures the majority of NH_4NO_3. In addition, there are two back-up filters to capture volatized NH_4NO_3 from the Teflon filter, a nylon filter to collect NO_3^- as HNO_3 and a citric acid filter to collect NH_4^+ as NH_3. For the ETV report, NO_3^- concentrations were calculated as the sum of concentrations on the Teflon and nylon filters and NH_4^+ concentrations as the sum of concentrations on the Teflon and citric acid filters. For the manuscript, a quality assurance (QA) assessment of volatilized NH_4NO_3 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 Figure S1).

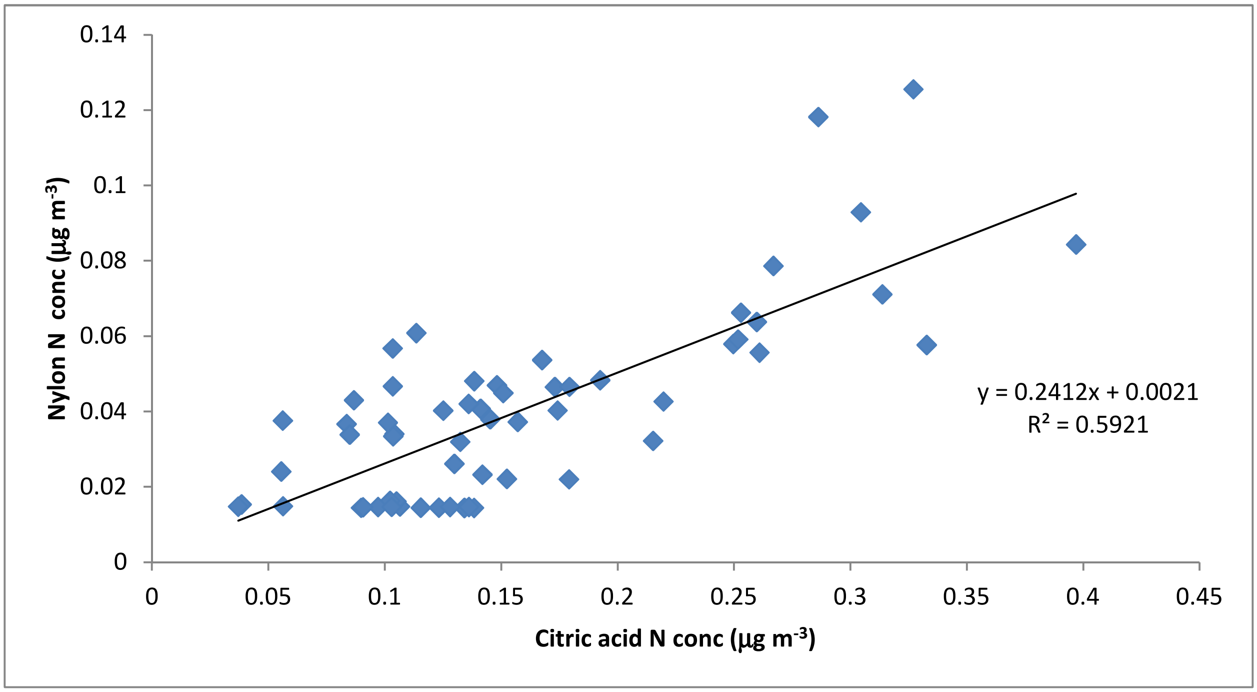

Figure S1. The relationship between the nitrogen (N) concentrations on the nylon and citric acid filters.

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 Figure S1 and the filter pack blank results indicates 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 µg-N to µg-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 µg-N for NH_3, NH_4^+, HNO_3, and NO_3^- and µg-SO_4 for SO_2 and SO_4^{2-}. However, these blank errors had a negligible impact on the results of the ETV report.

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, ≈98% (8319) of them contained valid data. For ≈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 ≈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 SO_2 PFA, ≈29% (1 hour) or 20% (12 hour) of data was below the DL of 0.26 $\mu g\ m^{-3}$ (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 SO_2 concentrations to other instruments.

The SO_2 concentration trend for the PFA, as well as the concentration trends for the MUs and the denuder are shown in Figure S2. The average SO_2 concentration measured during the ETV by the PFA was 2.07 $\mu g\ m^{-3}$ ± 2.86. The SO_2 concentration measured by the denuder was extremely similar (2.08 $\mu g\ m^{-3}$ ± 2.64). MU concentrations were slightly higher than both the PFA and the denuder with MU1 measuring an average SO_2 concentration of 2.38 $\mu g\ m^{-3}$ ± 2.94 and MU2 measuring an average concentration of 2.20 $\mu g\ m^{-3}$ ± 2.79. The MARGA also performed well in comparison to the SO_2 PFA. The slope values for the MARGA concentrations against the 12-hour PFA concentrations were 1.02 for MU1 and 0.96 for MU2 (Figure S3a), 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 (Figure S3b), the slope values were as expected similar to the 12-hour averaged values (1.00 for MU, 0.94 for MU2).

The MARPD values for SO_2 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. Figure S4 presents the SO_2 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 H_2O_2 was used to provide a H_2O_2 concentration of 10 ppm for the absorption solution. Anion eluent (7.0 mmol/8.0 mmol Na_2CO_3/ $NaHCO_3$) was prepared from pure material (>99.5%, ACROS Organics, Fisher Scientific, Pittsburgh, PA, USA). 2M HNO_3 (Sigma-Aldrich) was used to prepare the cation eluent (3.2 mmol). For the regenerant, 85% phosphoric acid was used. Pure NH_4NO_3 (99.9%, certified ACS, Fisher Scientific) and $(NH_4)_2SO_4$ (99.0% certified ACS, Fisher Scientific) were used to prepare additional liquid standards of NH_4^+, NO_3^-, and SO_4^{2-}.

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]	0.153	0.077	0.024	0.004	0	0.147	0.147	0.026	0.038	0	0
	(0.039)[d]	(0.039)	(0.066)	(0.011)	(0.010)		(0.026)	(0.019)	(0.027)	(0.027)		
	n =36[e]	n =26	n =36	n =37	n =37	n =37	n =36	n =32	n =37	n =35	n =37	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	1.131	1.902	1.903	0.810	0.780	1.700	1.657	1.926	1.887	0.949	0.862
	(0.025)	(0.095)	(0.033)	(0.040)	(0.029)	(0.038)	(0.027)	(0.020)	(0.035)	(0.047)	(0.023)	(0.026)
	n =19	n = 20	n =18	n =20	n =19	n = 18	n =20	n =20	n =20	n =19	n =19	n =19
% analytical bias	+4.5	+5.9	+8.1	+9.9	-22.7	-24.4	+4.5	+3.5	+1.3	+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_2CO_3 denuder	SO_2	0.24[a] (0.32)[b]
	HNO_3	0
H_3PO_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

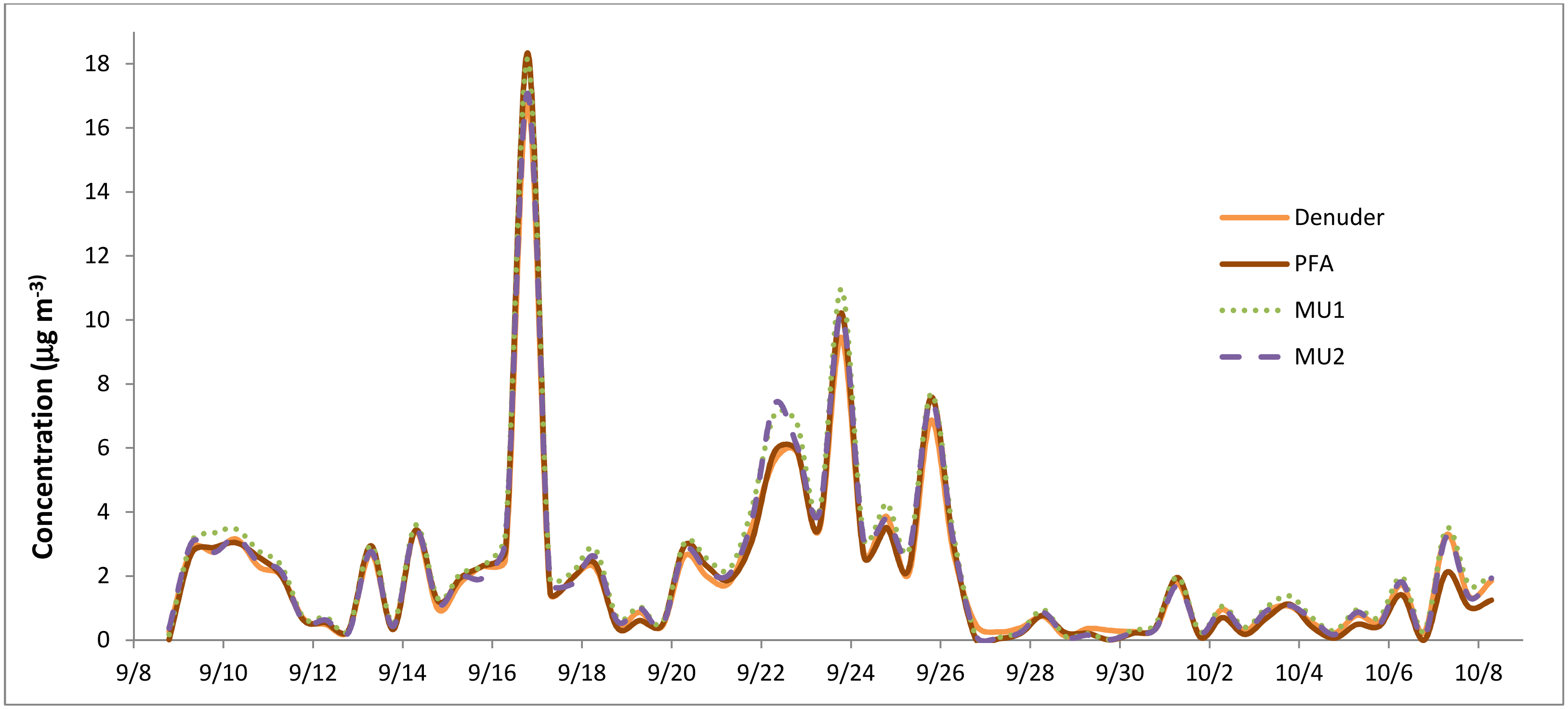

Figure S2. PFA, Denuder and MUs measured SO_2 concentrations during the ETV period (September 8th, 2010-October 8th, 2010).

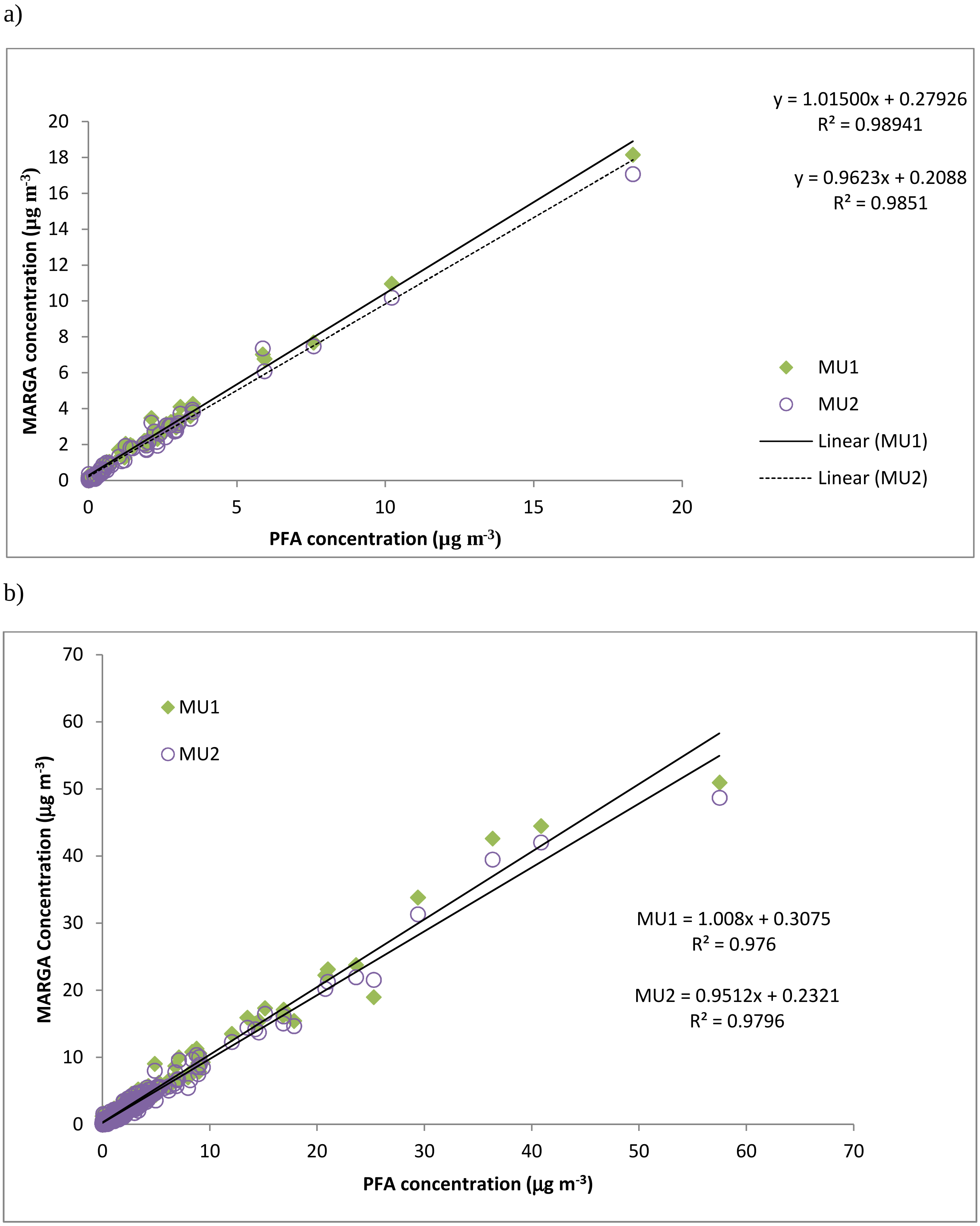

Figure S3. Regression analysis of MARGA SO_2 concentrations against a) 12-hour PFA SO_2 concentrations b) 1-hour PFA SO_2 concentrations.

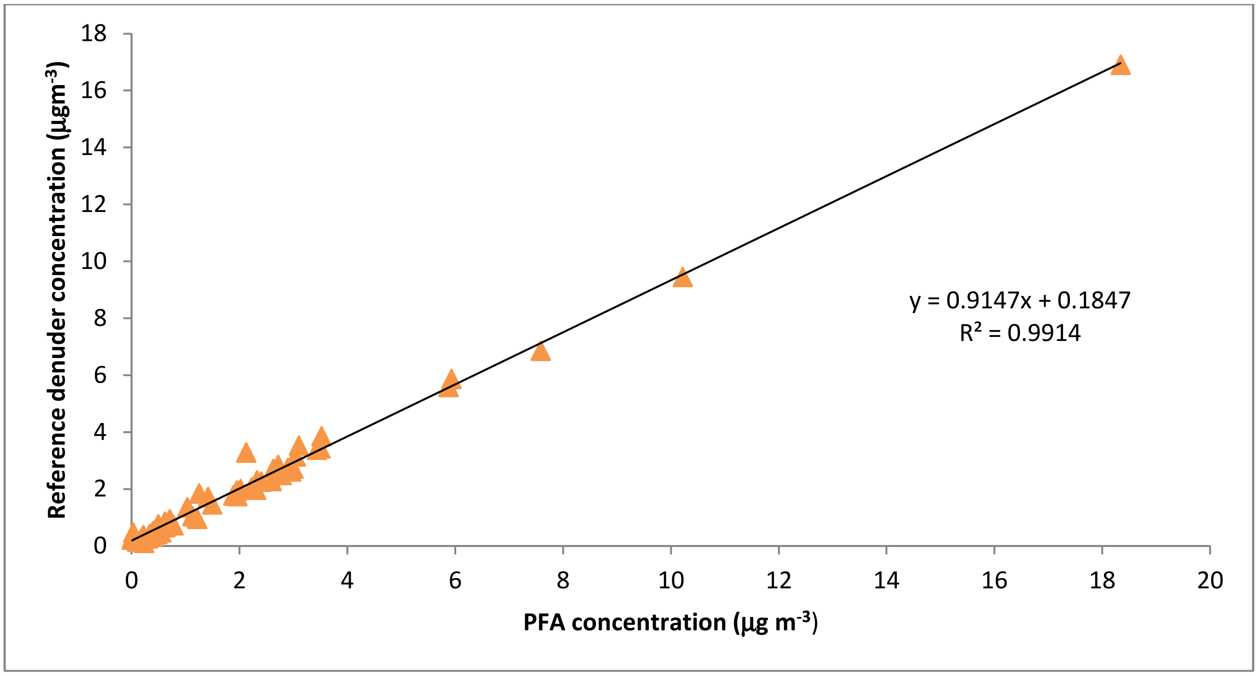

Figure S4. Regression analysis of denuder SO_2 concentrations against 12-hour PFA concentrations.

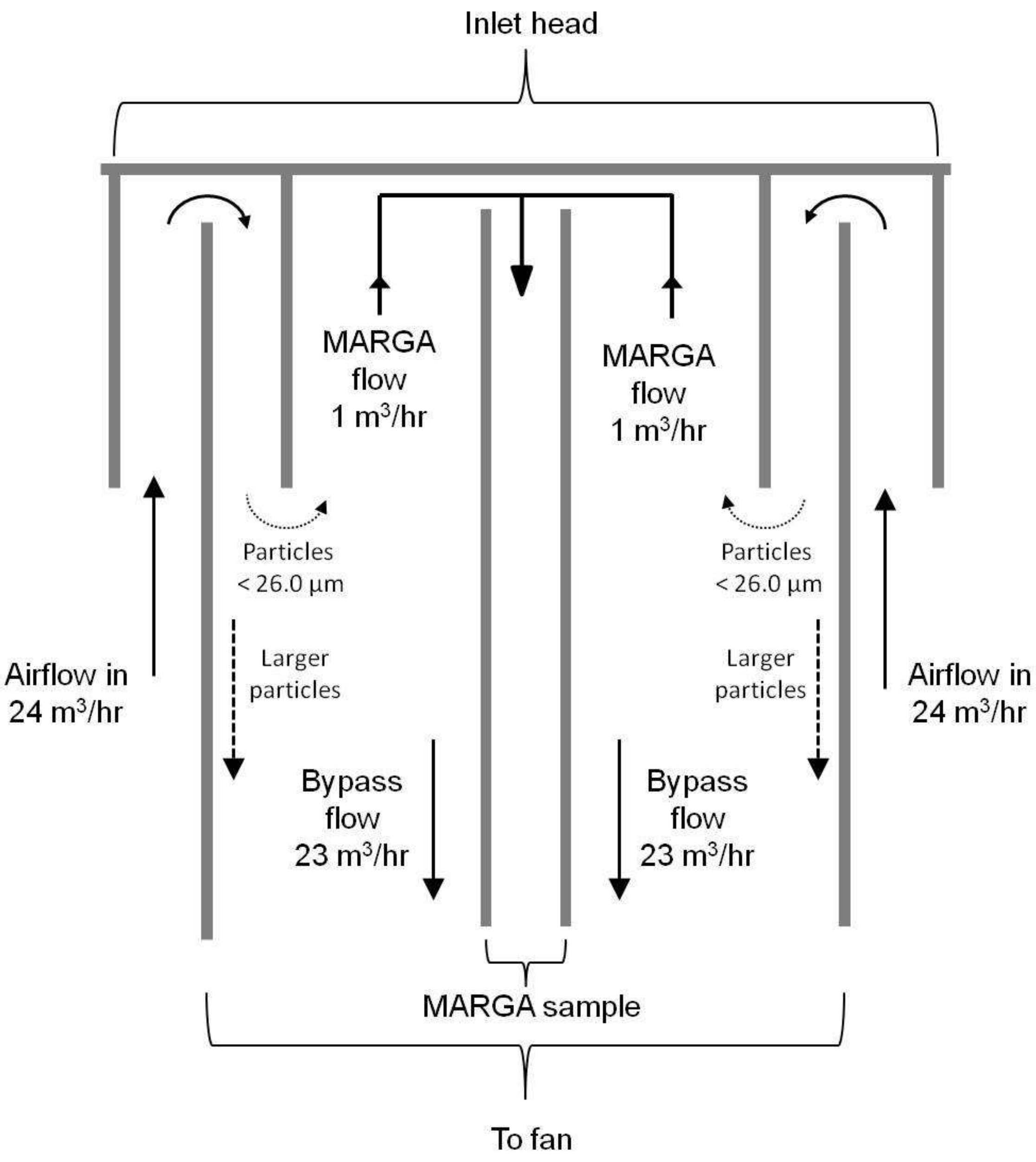

Figure S5. Schematic of MARGA inlet.