Supporting Information for:

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

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Contents

Solutions used in MARGA ion chromatography system

The MARGA system requires the following chemicals: absorbance solution, internal standard solution, ion chromatography (IC) eluents, and suppressor regenerant. All chemicals are prepared with 18.2 MΩ.cm double deionized (DDI) water.

The absorbance solution serves as the medium for gases to diffuse into in the WRD and to supersaturate the SJAC to allow particles to grow and thus produce a condensate of water soluble aerosol. It is also used as a carrier liquid to allow the sample to flow through the MARGA system. Absorption solution is made in batches of 20 L using DDI water. Additionally, to prevent the growth of bacteria in the MARGA system, 10 ppm hydrogen peroxide (0.7 mL of 30% H_2O_2) is added to the absorbance solution. During continuous operation, the MARGA requires 5 L of absorption solution per day. The absorption solution is replenished (~ 35 L) weekly.

As the WRD and SJAC samples are injected from the syringes to the detector box, the sample is automatically mixed with an internal standard that contains a known concentration of lithium bromide (LiBr). The making of the lithium bromide solution requires two steps. First, a stock solution is prepared by dissolving 4000 mg of LiBr (6.94% Li, 79.90% Br) in a 1 L volumetric flask, yielding concentrations of 320 mg L^{-1} Li and 3680 mg L^{-1} Br. This stock is stable for at least 12 months, if stored away from light and refrigerated. Internal standard stock solution (5.6 mL) is then injected into a 5 L container using a pipette. The container is then filled up with DDI water to a weight of 5600 g. This gives final concentrations of 320 μg L^{-1} for Li and 3680 μg L^{-1} for Br. The Li and Br internal standard concentrations were verified by an independent IC system. Stocks are prepared from NIST-traceable LiBr standards (Fisher Scientific, Pittsburgh, PA). The internal standard is replenished bimonthly.

Separate eluents are needed for both the cation and anion ICs. The cation eluent is prepared by injecting 2.08 mL of pure methanesulfonic acid (MSA) into a 10 L container, which is filled with 10 kg of DDI water. This yields a final MSA concentration of 3.2 mmol L^{-1}. The anion eluent is prepared by adding 8.68 g of sodium carbonate monohydrate and 6.72 g of anhydrous sodium bicarbonate to 10 kg DDI water, which yields a final concentration of 7.0 mmol for sodium carbonate and 8 mmol of sodium bicarbonate. Eluents are prepared from certified chemicals (Fisher Scientific, Pittsburgh, PA). Eluents are replenished biweekly.

To further improve the sensitivity of the anion IC, a suppressor regenerant is used. This chemical improves sensitivity by suppressing eluent background conductivity. An ion-exchange unit is regenerated before each analysis with phosphoric acid. The phosphoric acid in the ion-exchange unit is then rinsed by anion eluent. The suppressor regenerant is made by combining 5 kg of DDI water and 125 mL of 85% phosphoric acid (H_3PO_4) in a 5-L container, giving a final concentration of 0.35 mol L^{-1} of H_3PO_4. The regenerant is made from a certified phosphoric acid stock (Fisher Scientific, Pittsburgh, PA). Regenerant is replenished bimonthly.

Additional information on external standard liquid solutions

External standard liquid solutions were made by dissolving chemicals using 18.2 MΩ.cm double deionized (DDI) water. The chemicals used were ammonium nitrate (NH_4NO_3) (Fisher Scientific, Pittsburgh, PA), ammonium sulfate ($(NH4)_2SO_4$) (Fisher Scientific, Pittsburgh, PA), potassium chloride (KCl) (Fisher Scientific, Pittsburgh, PA), sodium nitrate ($NaNO_3$) (Fluka, St. Louis, MO), and magnesium sulfate heptahydrate ($MgSO_4$ $7H_2O$) (Fluka, St. Louis, MO). All chemicals were ACS (American Chemical Society) grade. Each external standard solution was diluted to the desired concentration using 18.2 MΩ.cm double deionized (DDI) water.

Additional information on methodology used to determine detection limit

The traditional approach used to determine the detection limit involves combining data from all analytical channels (in this study, there are four different channels including denuder and SJAC samples from both sample boxes) into a single data set. From this single data set, the standard deviation and number of analyses are used to determine the detection limit. The advantage of this approach is that, for an experiment of given duration, a larger number of observation (i.e., degrees of freedom) are available to calculate the detection limit. However, with this approach it is unknown whether the detection limit is strictly a function of the analytical core of the system or is a combination of the analytical and sampling components of the system. In other words, the standard deviation may reflect a combination of random error plus systematic error between channels. To investigate this possibility, the traditional detection limit approach was conducted in conjunction with the Dunn’s test (Dunn, 1964) and the Brown-Forsythe test (Brown and Forsythe, 1974) to compare channels. The Dunn’s test and the Brown-Forsythe test are non-parametric tests that can be used to determine if there are significant differences in the median concentrations (Dunn’s test) and variance (Brown-Forsythe test) across channels. In further detail, the Dunn’s test (Dunn, 1964) is a non-parametric statistical test of the difference in medians among multiple groups. It is a rank-sum type test in which the null hypothesis is that the probability of observing a randomly selected value from the one group that is larger than a randomly selected value from another group equals one half. Dunn’s test is appropriate for comparing multiple groups consisting of continuous data. In this case, Dunn’s test is used to assess whether the differences in analytical detection limits calculated for individual MARGA channels (Denuder1, Denuder2, SJAC1, SJAC2) are at least partially the result of systematic differences (bias) among the channels.The Brown–Forsythe test (Brown and Forsythe, 1974) is a non-parametric statistical test for the equality of variances among multiple groups. For each observation, a transformation (z) is calculated as its deviation from the corresponding group median. A one-way analysis of variance (ANOVA) is performed on z, in which the F statistic represents the Brown-Forsythe test statistic. In this case, the Brown-Forsythe test is used to assess whether the differences in analytical detection limits calculated for individual MARGA channels (Denuder1, Denuder2, SJAC1, SJAC2) are at least partially the result of differences in precision (variance) among the channels.

Results and analysis of Dunn’s test and Brown-Forsythe’s test

The results of the Dunn’s test and Brown-Forsythe test for each analyte are presented in Table S1.

Table S1. Results of the Dunn’s test (DU) and Brown-Forsythe test (BF) for individual MARGA channels. Top row indicates channels being compared: S1 = SJAC Sample Box 1, D1 = Denuder Sample Box 1, etc. For the Brown-Forsythe test, p values are reported with bold indicating statistical significance at the 10% level. For Dunn’s test, N and D indicated not significantly different versus significantly different, respectively.

		S1-S2	S1-D1	S1-D2	S2-D1	S2-D2	D1-D2
NO_3^-	DU	N	N	N	N	N	N
	BF	**0.09**	0.86	0.45	**0.08**	**0.04**	0.60
SO_4^{2-a}	DU	N	**D**	**D**	**D**	**D**	N
	BF	0.80	0.18	0.24	0.29	0.38	0.88
SO_4^{2-}	DU	N	**D**	**D**	**D**	**D**	N
	BF	0.80	0.18	0.24	0.29	0.38	0.88
NH_4^+	DU	N	N	**D**	N	**D**	**D**
	BF	0.71	**0.04**	**0.01**	**0.10**	**0.02**	0.35
Na^+	DU	N	**D**	**D**	**D**	N	N
	BF	0.86	0.48	0.84	0.65	0.97	0.70
Na^+	DU	N	N	N	N	N	N
	BF	0.28	0.15	0.22	**0.02**	**0.05**	0.89
K^+	DU	N	N	N	N	N	N
	BF	0.19	0.85	0.72	0.26	0.35	0.87

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

The results of Dunn’s test and Brown-Forsythe test (Table S1) indicate that the sampling components of the MARGA are influencing the detection limit of all the compounds except K^+. The influence of the sampling components of the MARGA on the detection limit varies from compound to compound. In both SO_4^{2-} detection limit analyses there were multiple channels that had significant differences in median concentrations. For NO_3^-, the detection limit was not influenced by differences in channel medians, but was influenced by differences in the channel variance with three of the six channel to channel comparisons having a Brown-Forsythe p-value less than 0.10. It is not known what is causing the significant differences in channel variance, but it is hypothesized that inconsistency in peak integration may be an issue. Differences in channel median concentrations and/or concentration variance also influenced the determined detection limit for Na^+ and NH_4^+. It can therefore be concluded that analytical detection limits calculated by combining channels is function of variability related to random error in individual channels, systematic differences across channels, and differences in variance across channels.

Additional analysis of the detection limits in comparison to previous studies

Thomas et al. (2009) and Wolff et al. (2010) determined detection limits in field conditions using the GRAEGOR system, which is quasi-similar to the MARGA system. However, they used different methodologies to determine their detection limit. Therefore, in order to make an equivalent comparison, the detection limits were also calculated for this study using the Thomas et al. (2009) and Wolff et al. (2010) detection limit methodologies. Thomas et al. (2009) calculated average blanks using average blank values plus three standard deviations of the blank value, whereas Wolff et al. (2010) used three standard deviations of the blank value. The results are shown in Table S2.

Table S2. Calculate detection limits from this study using different methodologies

	Detection limit calculation for data in this study using different methodologies (μg m^{-3})			Previous studies detection limits (μg m^{-3})			
	This study	Thomas et al. (2009)	Wolff et al. (2010)	Thomas et al. (2009)		Wolff et al. (2010)	
				MPIC	CEH	NEU	EGER
NO_3^-	0.056	0.066	0.065	0.077	0.150	0.093	0.130
HNO_3	0.057	0.066	0.066	0.079	0.191	0.094	0.132
SO_4^{2-a}	0.048	0.093	0.056	0.201	0.116	-	-
SO_2	0.032	0.073	0.037	0.123	0.254	-	-
SO_4^{2-}	0.064	0.112	0.075	-	-	-	-
SO_2	0.043	0.086	0.050	-	-	-	-
NH_4^+	0.021	0.025	0.025	0.117	0.180	0.074	0.022
NH_3	0.020	0.024	0.023	0.111	0.161	0.055	0.021
Na^+	0.029	0.030	0.030	-	-	-	-
Na^+	0.026	0.033	0.033	-	-	-	-
K^+	0.038	0.038	0.045	-	-	-	-

In summary, regardless of the detection limit methodology, the detection limits determined in this study are lower than those determined by Thomas et al. (2009) and Wolff et al. (2010) for all nitrogen and sulfur compounds with the exception of NH_3. NH_3 detection limits determined in this study are lower than those reported by Thomas et al. (2009) and Wolff et al. (2010) at the grassland NEU site, but similar to those reported by Wolff et al. (2010) at the forest (EGER) site.

Supplementary Tables and Figures

Table S3. MARGA blank concentrations expressed as equivalent air concentration for each sample box (SB).

	Blank concentration (µg m^{-3})							
	NO_3^-	HNO_3	SO_4^{2-}	SO_2	NH_4^+	NH_3	Na^+	K^+
SB1	0.001[a]	0	0.040	0.037	0	0	0	0
	0.006[b]	0.003	0.013	0.012	0	0	0	0
	33[c]	37	33	37	33	37	33	37
SB2	0.001	0	0.034	0.035	0	0.001	0	0
	0.003	0.001	0.015	0.011	0	0.005	0	0
	37	35	37	35	37	35	37	35

[a] Mean concentration

[b] ± 1 standard deviation

[c] Number of observations

Table S4. Orthogonal least squares regression coefficients comparing SB1 (x) to SB2 (y). Results are reported for individual colocation experiments during June-July (Period 1), August (Period 2), and October, 2012 (Period 3). Number of hourly observations for each period are approximately 87, 138, and 73, respectively.

Period	1	2	3	1	2	3
	--------	Slope	-------	-------	Intercept	-------
NH_3	0.94	1.03	0.95	-0.10	-0.01	-0.08
NH_4^+	1.06	1.01	1.02	-0.03	-0.01	-0.01
HNO_3	0.86	1.02	1.00	0.05	-0.02	-0.01
NO_3^-	0.87	1.06	1.03	0.02	-0.02	0.01
SO_2	0.97	1.04	1.03	-0.02	-0.01	-0.05
SO_4^{2-}	1.02	0.99	1.01	0.09	0.05	0.01

Table S5. HNO_3 and NO_3^- external standard runs and the difference between expected and observed concentration.

	SB1 concentrations (µg m^{-3})			SB2 concentrations (µg m^{-3})		
	Exp[a]	Obs[b]	Difference[c] (offset)	Exp	Obs	Difference (offset)
HNO_3	0	0	0	0	0	0
	0.133	0.192	0.060	0.128	0.181	0.053
	0.380	0.528	0.149	0.366	0.502	0.136
	1.345	1.523	0.178	1.303	1.479	0.176
	2.302	2.483	0.181	2.219	2.404	0.186
NO_3^-	0	0.001	0.001	0	0.001	0.001
	0.131	0.186	0.05	0.126	0.183	0.057
	0.374	0.518	0.144	0.360	0.488	0.128
	1.324	1.487	0.163	1.283	1.435	0.153
	2.266	2.438	0.172	2.184	2.369	0.185

[a] Expected concentration.

[b] Observed concentration.

[c] Difference between expected and observed concentration (i.e. observed concentration minus expected concentration).

Table S6. Detection limit results for individual MARGA channels.

		Exp conc[b] (µg L^{-1})	Median Obs[c] (µg L^{-1})	St Dev[d] (µg L^{-1})	N[e]	T-stat	Liq Conc DL (µg L^{-1})	Air Conc DL (µg m^{-3})
NO_3^-	D1	5.34	7.64	0.76	19	1.33	2.02	0.050
	D2		8.05	0.65	14	1.35	1.76	0.044
	S1		7.60	0.75	19	1.33	2.00	0.050
	S2		7.89	1.14	20	1.33	3.03	0.076
	Average NO_3^-/HNO_3						**2.20**	**0.055/0.056**
SO_4^{2-}[a]	D1	0.00	2.15	0.74	37	1.31	1.93	0.048
	D2		2.05	0.70	35	1.31	1.83	0.046
	S1		1.65	0.54	33	1.31	1.41	0.035
	S2		1.49	0.62	37	1.31	1.62	0.040
	Average SO_4^{2-}/SO_2						**1.70**	**0.042/0.028**
SO_4^{2-}	D1	19.47	26.40	0.63	19	1.33	1.68	0.042
	D2		27.06	0.98	14	1.35	2.65	0.066
	S1		27.39	1.08	19	1.33	2.87	0.072
	S2		25.92	0.63	20	1.33	1.67	0.042
	Average SO_4^{2-}/SO_2						**2.21**	**0.055/0.037**
NH_4^+	D1	4.91	5.11	0.26	19	1.33	0.69	0.017
	D2		5.51	0.33	14	1.35	0.89	0.022
	S1		4.93	0.17	20	1.33	0.45	0.011
	S2		4.91	0.19	20	1.33	0.50	0.013
	Average NH_4^+/NH_3						**0.63**	**0.016/0.015**
Na^+	D1	1.75	1.63	0.49	19	1.33	1.30	0.033
	D2		1.53	0.45	14	1.35	1.22	0.030
	S1		1.39	0.35	20	1.33	0.93	0.023
	S2		1.42	0.45	20	1.33	1.19	0.030
	Average						**1.16**	**0.029**
Na^+	D1	5.00	7.25	0.28	20	1.33	0.74	0.019
	D2		7.16	0.20	21	1.33	0.53	0.013
	S1		7.03	0.44	18	1.33	1.17	0.029
	S2		7.01	0.54	21	1.33	1.43	0.036
	Average						**0.97**	**0.024**
K^+	D1	4.91	5.14	0.64	20	1.33	1.70	0.042
	D2		5.68	0.58	21	1.33	1.54	0.038
	S1		5.03	0.67	18	1.33	1.79	0.045
	S2		5.31	0.53	21	1.33	1.40	0.033
	Average						**1.61**	**0.040**

[a] Detection limits for SO_4^{2-} and Na^+ were determined using two liquid standard with different concentrations.
[b] Expected concentration.
[c] Median observed concentration.
[d] ± 1 standard deviation.
[e] Number of observations.

Table S7. Summary statistics for select meteorological variables, air concentrations, and fluxes during the period 23 September – 14 October, 2012.

	Meteorology			Concentration ($\mu g\ m^{-3}$)						Flux ($ng\ m^{-2}\ s^{-1}$)					
	W.S.[c] ($m\ s^{-1}$)	u_* ($m\ s^{-1}$)	Air Temp. (^oC)	NH_3	NH_4^+	HNO_3	NO_3^-	SO_2	SO_4^{2-}	NH_3	NH_4^+	HNO_3	NO_3^-	SO_2	SO_4^{2-}
Mean	0.8	0.1	15.9	0.4	0.7	0.3	0.4	0.5	1.9	9.1	-1.0	-4.3	-3.1	-5.5	-4.0
Median	0.7	0.1	15.5	0.3	0.7	0.2	0.3	0.1	1.8	3.9	-0.4	-1.8	-1.6	-1.9	-2.4
S.D.[a]	0.5	0.1	5.8	0.3	0.3	0.3	0.3	1.1	0.8	11.7	2.1	6.4	4.3	16.8	5.1
Max.	2.4	0.5	28.7	1.6	1.5	1.8	1.2	8.8	4.3	82.8	6.6	6.6	18.1	46.7	17.7
Min.	0.0	0.0	4.4	0.0	0.2	0.0	0.0	0.0	0.5	-1.4	-14.6	-38	-35.4	-245	-28.9
N[b]	474	474	474	449	376	451	384	451	384	406	358	407	366	407	366

[a] S.D.= ± 1 standard deviation

[b] N = number of observations

[c] W.S. = Wind Speed

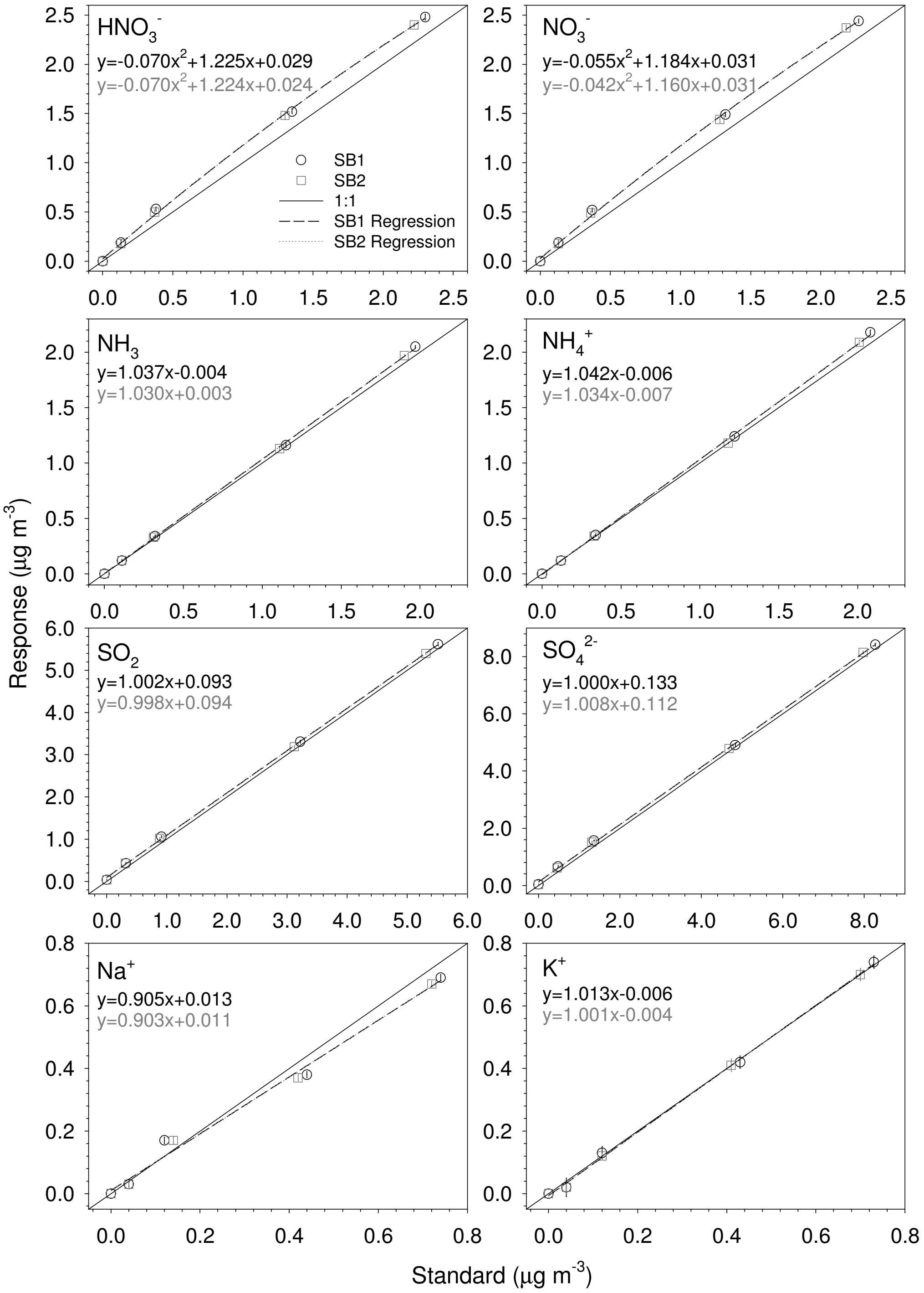

Figure S1. Results of external standard tests. Response is given in equivalent air concentration (μg m^{-3}).

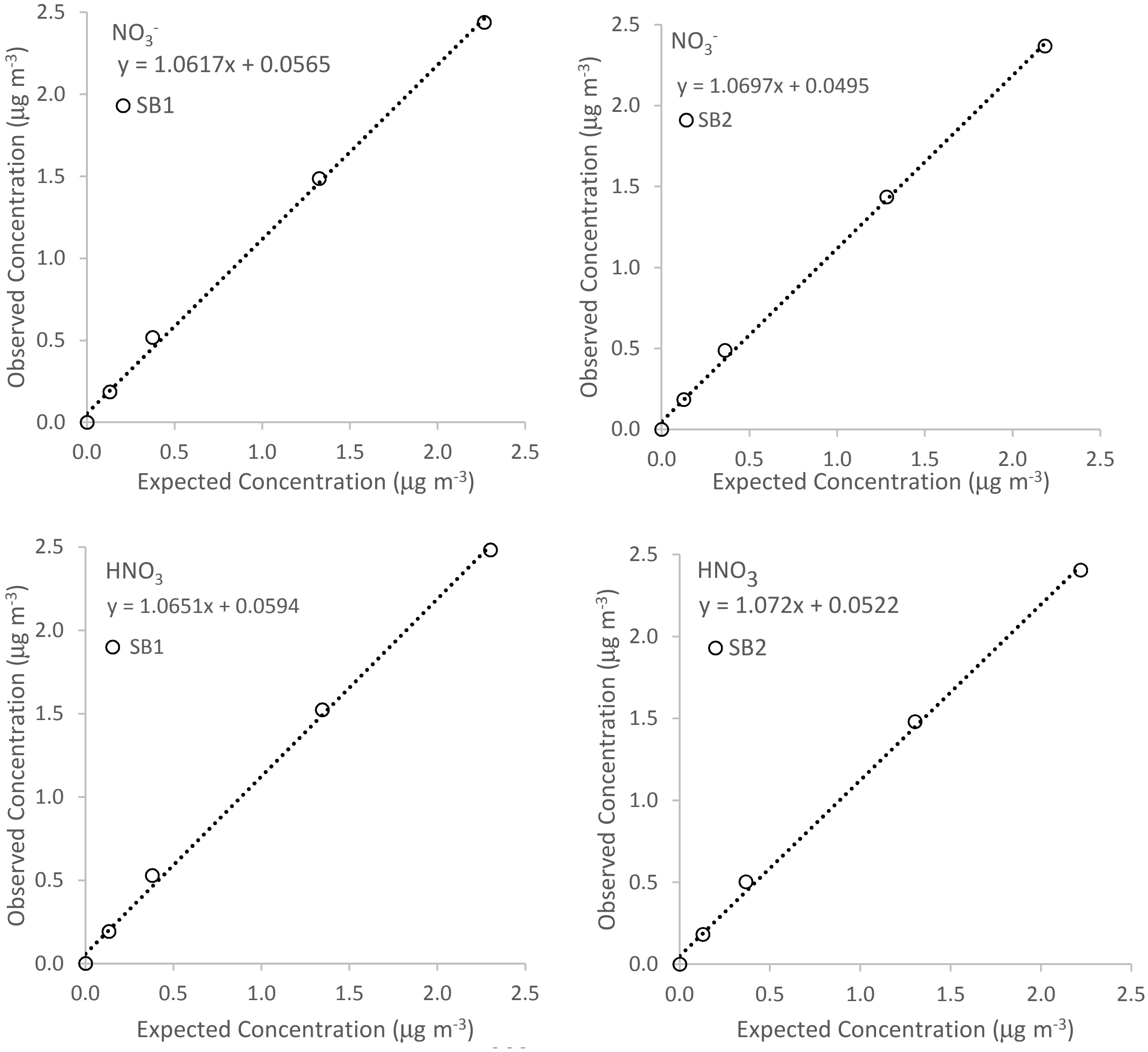

Figure S2. NO_3^- linear regression analysis for external standard tests.

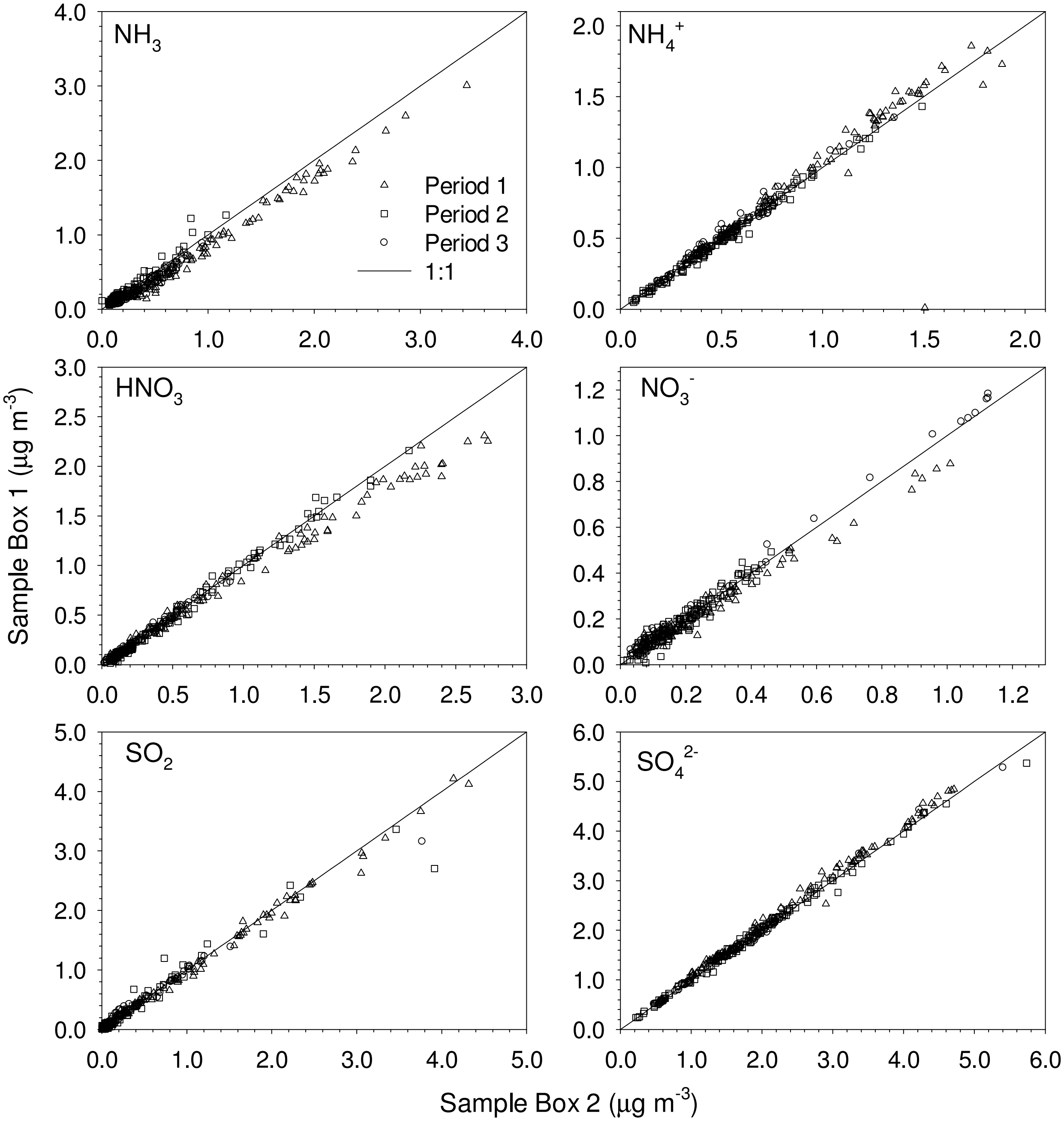

Figure S3. Scatterplots of concentrations measured by MARGA sample boxes 1 and 2 during three colocation experiments represented by different symbols (Period 1= June-July 2012; Period 2 =August 2012; Period 3= October 2012)

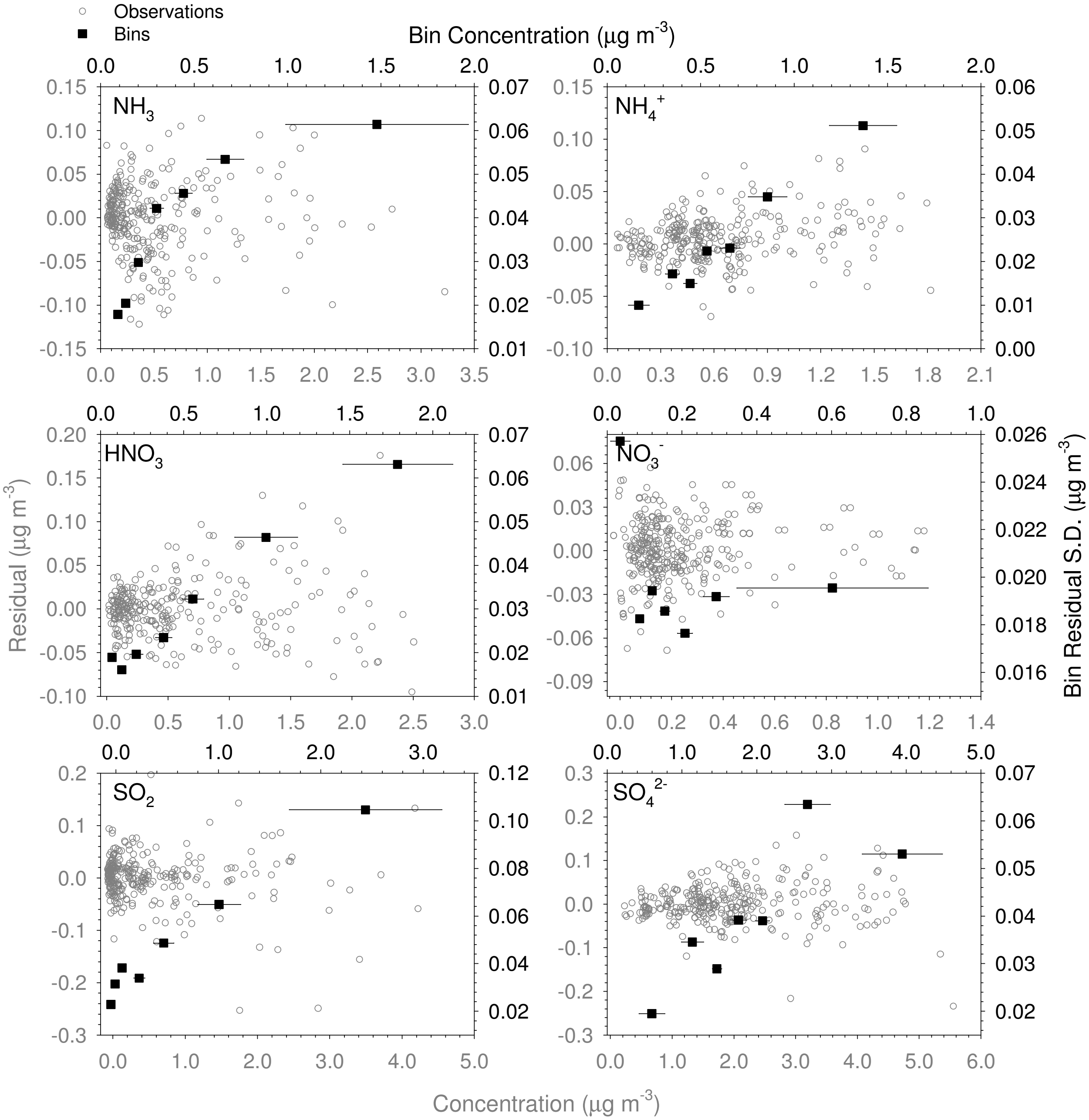

Figure S4. Scatterplots (gray circles) of orthogonal least squares residuals versus average concentration between sample boxes. Data from three colocation experiments are combined. Black squares represent binwise standard deviation of residuals versus concentration. Horizontal bars represent standard deviation of concentration within bin. Individual bins contain ≈ 42 observations.

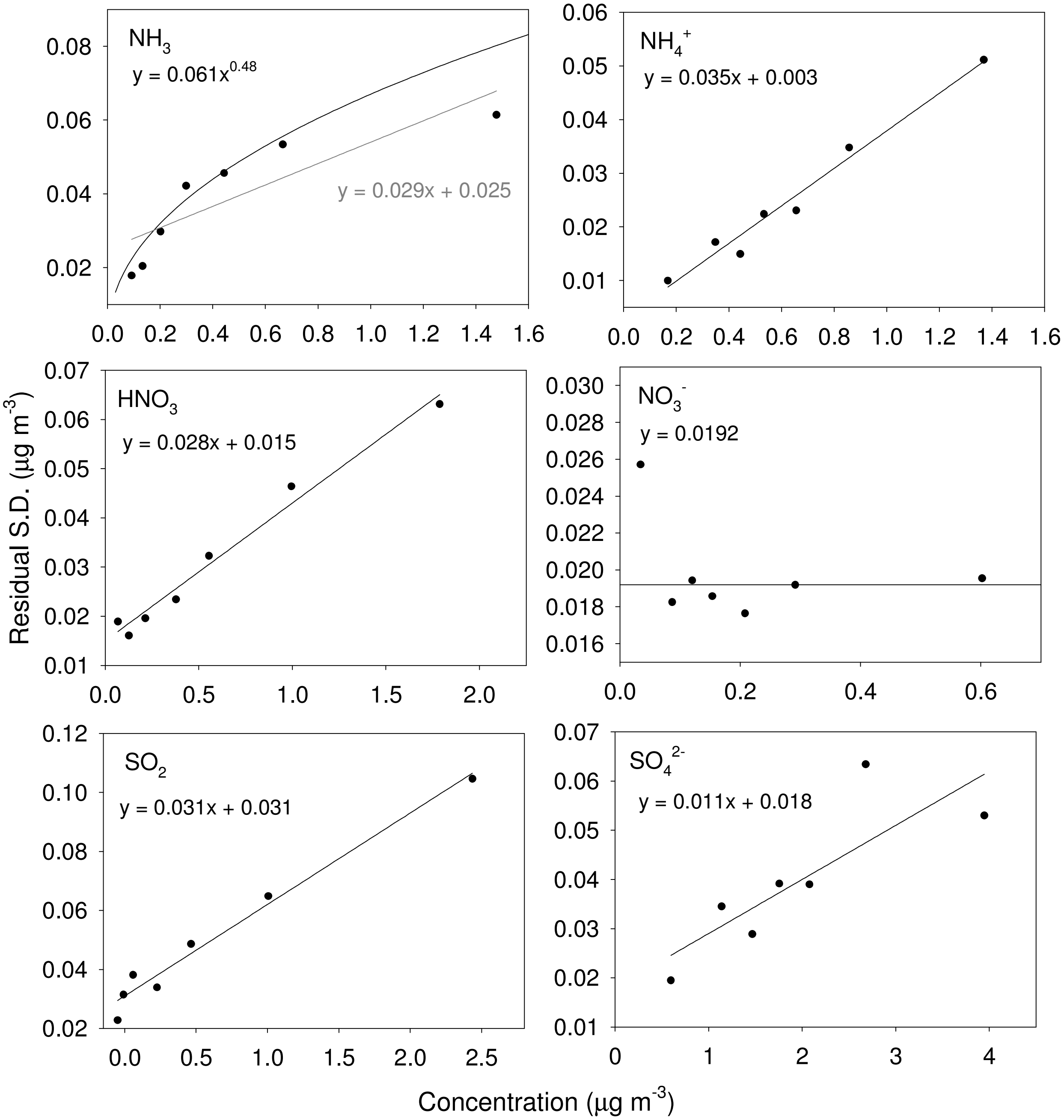

Figure S5. Curves describing relationship between air concentration and the standard deviation of orthogonal least squares fits (gradient precision). Data points represent binwise standard deviation of residual and corresponding average air concentration. Bins comprise ≈ 42 observations.

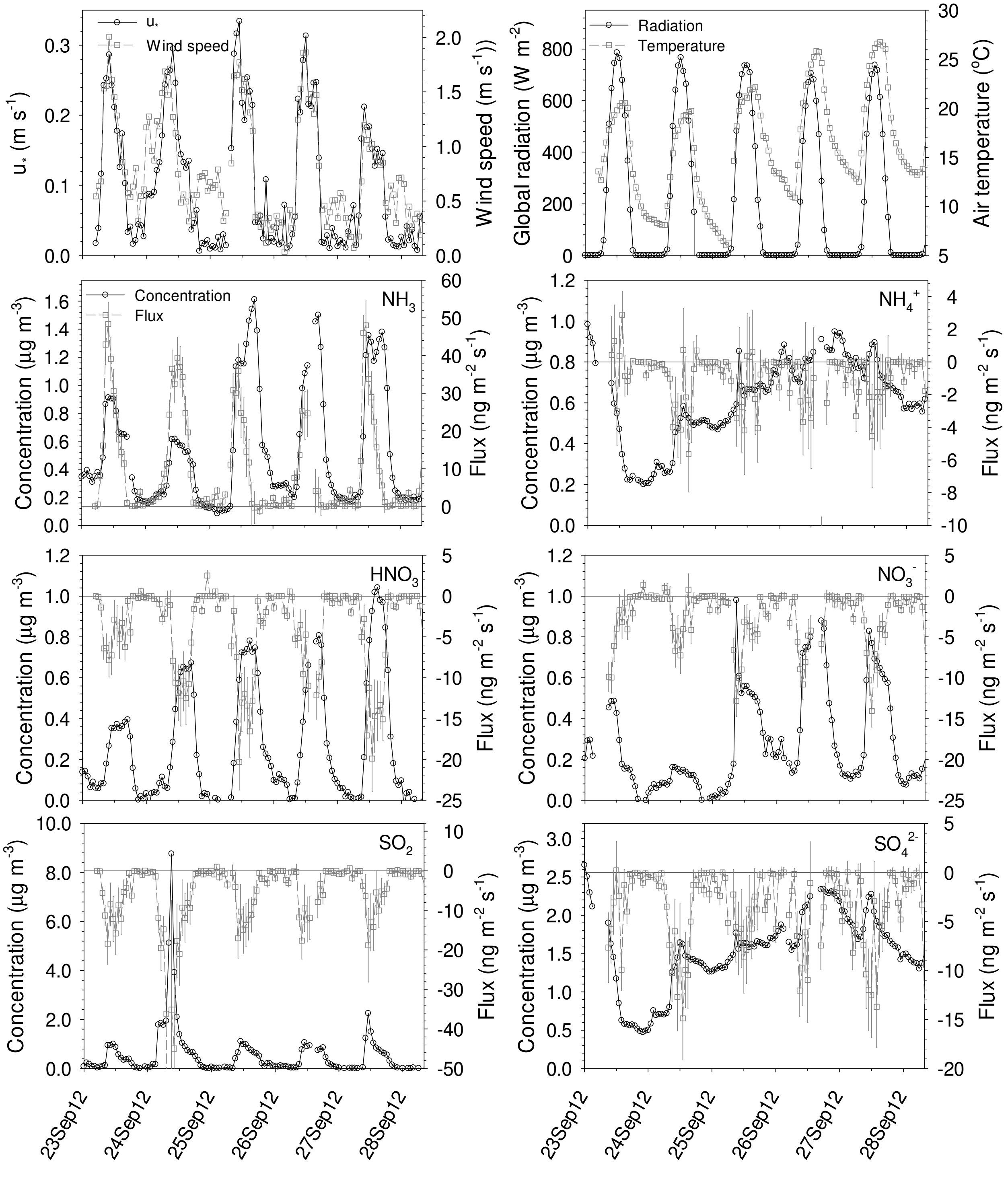

Figure S6. Example time series of meteorological variables, air concentrations, and fluxes. Fluxes also include flux error calculated from equation (4) in the main text. For plots of chemical species, concentrations and fluxes are represented by black circles and gray squares, respectively.

Supporting Information References

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