

Supplementary information:

In-situ measurements of NH₃: instrument performance and applicability

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Figure S1 summaries the reported concentrations from the instruments during the intercomparison study, with summary statistics presented on Table S1 for the same period. During the campaign to investigate the homogeneity of the reported concentration, both windspeed (figure 1) and atmospheric stability (figure S1) were considered. It is clear from the atmospheric stability that there were periods of stable conditions that resulted in a build-up of NH₃ and non-uniform concentrations across the field site.

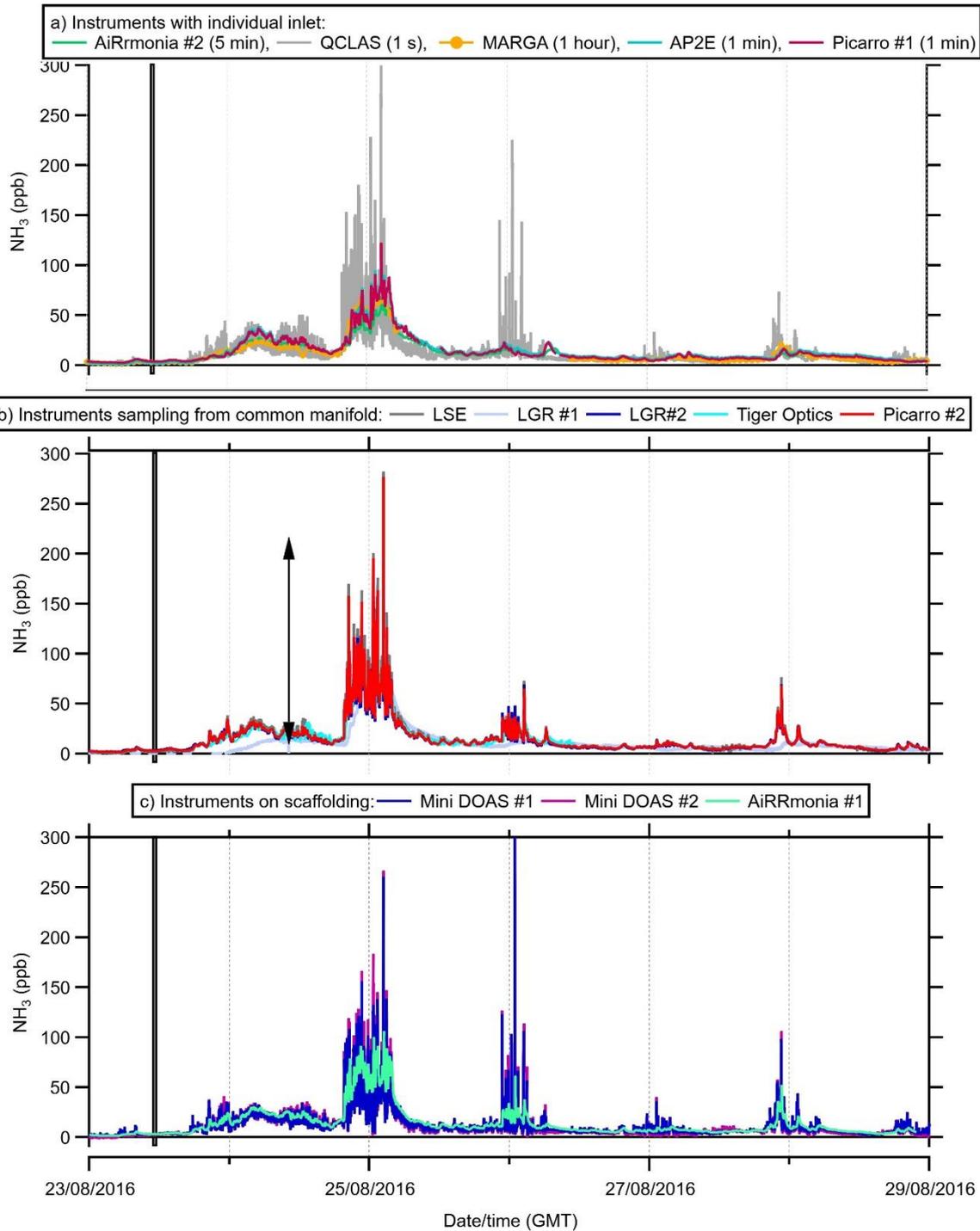


Figure S1. a) Summary of the raw concentrations from the instruments on a linear scale for the whole range for i) instruments with individual inlet set-up 2) instruments subsampling from the manifold and 3) instruments on scaffolding. Number in brackets is the reporting time resolution of each instrument. The thick black line is the fertilisation of both fields and the black arrow indicates the point at which the laser position was changed on the LGR #1.

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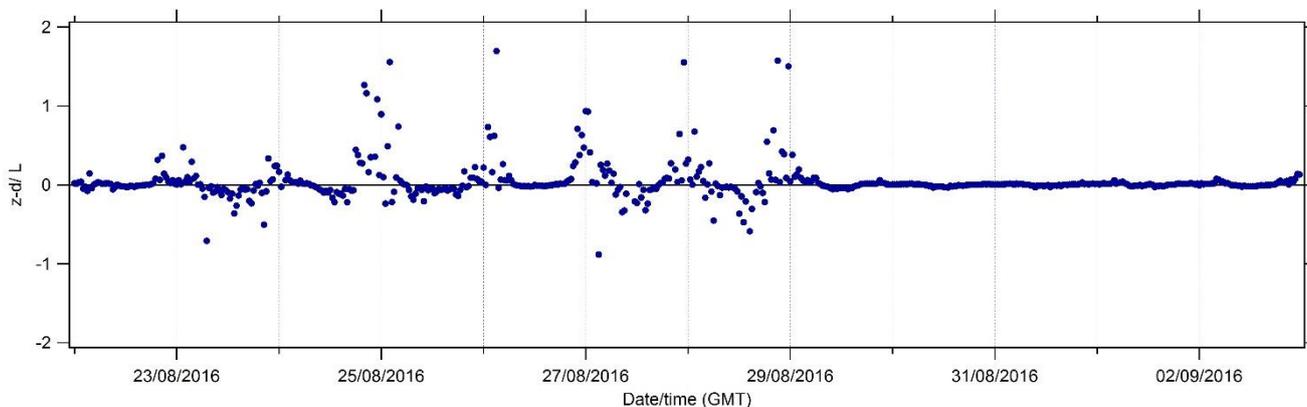


Figure S2. Atmospheric stability during the campaign at Easter bush from the 22/08/2016 to 03/08/2016.

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Table S1. Summary of statistics of NH₃ measurements by instruments for the period of 23/08/2016 00:00 to 29/08/2016 00:00 based on 1 hour averages. NOTE: Data is not paired.

Instrument	μ_A (ppb)	μ_M (ppb)	χ_{\min} (ppb)	χ_{\max} (ppb)	Data Capture (%)
miniDOAS #1	12.37	8.23	1.98	65.14	100
miniDOAS #2	12.21	7.21	-0.23	73.04	100
AiRRmonia #1	13.75	8.96	1.72	74.94	98
AiRRmonia #2	11.77	8.34	2.43	57.21	100
QCLAS	12.12	7.73	1.25	68.26	100
AP ₂ E	14.68	10.33	1.12	81.94	100
Picarro #1	13.77	9.17	2.69	77.71	99
Picarro #2	14.40	9.02	1.98	82.07	100
LGR #1*	12.58	7.91	3.67	67.20	77
LGR #2	13.82	9.08	2.14	76.77	100
Tiger Optics*	23.03	17.65	8.57	75.25	42
LSE	15.51	9.25	0.67	92.93	100
MARGA	11.61	6.20	1.50	63.91	80
OGS	14.14	9.02	1.63	81.45	99
Average [§]	13.5				

Data capture was lower for *LGR #1 only includes data from the 24/08/16 10:00 (GMT) and #Tiger Optics data only for the period of the 23/08/16 22:00 to 26/08/16 11:00. [§]Only instruments with at least 98% data coverage.

To monitor the homogeneity across the field site the path of the miniDOAS instruments had UKCEH ALPHA@s in triplicate placed at 3 positions between the instrument and reflector. Table S2 is a summary of the average concentration of the ALPHA@s for exposure period 1 and the average reported concentrations for the same period from instruments which took part in the field campaign.

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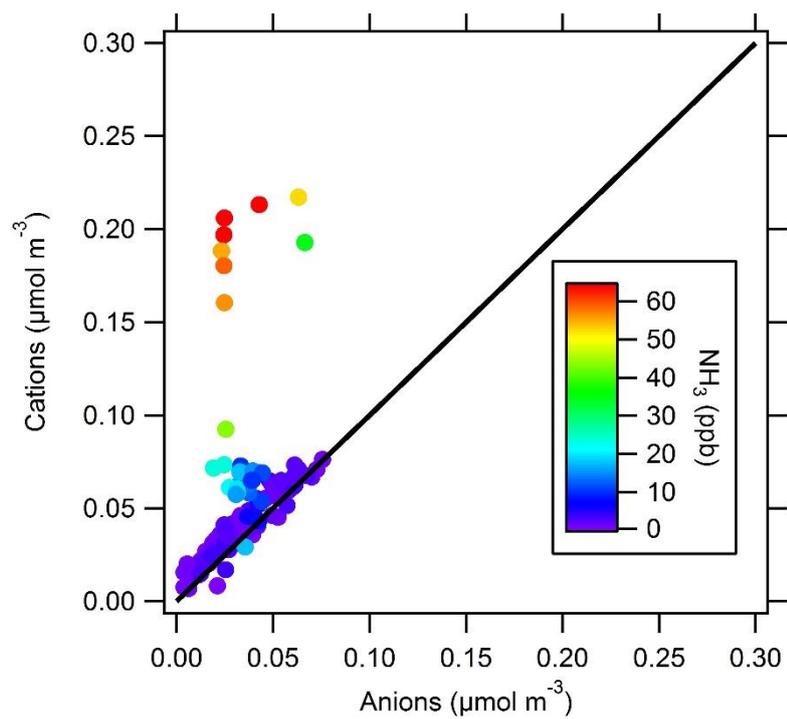
Table S2 Average concentrations from instrumentation ALPHA® exposure periods based on reported instrument concentrations (Refer to table 1 for instrument reporting resolution time). Both LGR #1 and the Tiger Optics are excluded from this comparison.

Instrument	Exposure Period 22/08/2016 16:35 to 29/08/2016 16:29	
	Average	Data Capture
	ppb	%
ALPHA®	10.92	100
miniDOAS #1	11.33	99
miniDOAS #2	10.95	100
AiRRmonia #1	13.37	89
QCLAS	10.97	89
AP ₂ E	13.39	100
AiRRmonia #2	10.73	97
Picarro #1	12.49	97
LGR #2	12.54	100
Picarro #2	13.93	91
LSE	13.93	96
MARGA	10.32	83

5 **Table S3. Summary of instrument response time at ambient concentrations based on Error! Reference source not found. for the period of the 22/08 06:00 to 23/03 06:00. Note: Tiger Optics and LGR#1 instruments time response was not calculated as data not available for the period.**

Instrument	$\tau_{1/e}$
	min
Picarro #1	99.5
Picarro #2	49.5
AiRRmonia #1	32.8
AiRRmonia #2	124
LGR #2	28.1
LSE	19.5
AP ₂ E	99.5
MARGA	208

Figure S3 presents evidence that WRD on the MARGA instrument suffered breakthrough to the SJAC, which reported NH_3 (g) as NH_4^+ aerosol.



5 **Figure S3. Ion balance of $\text{PM}_{2.5}$ inorganic aerosol from the MARGA instrument and coloured according to NH_3 concentrations.**

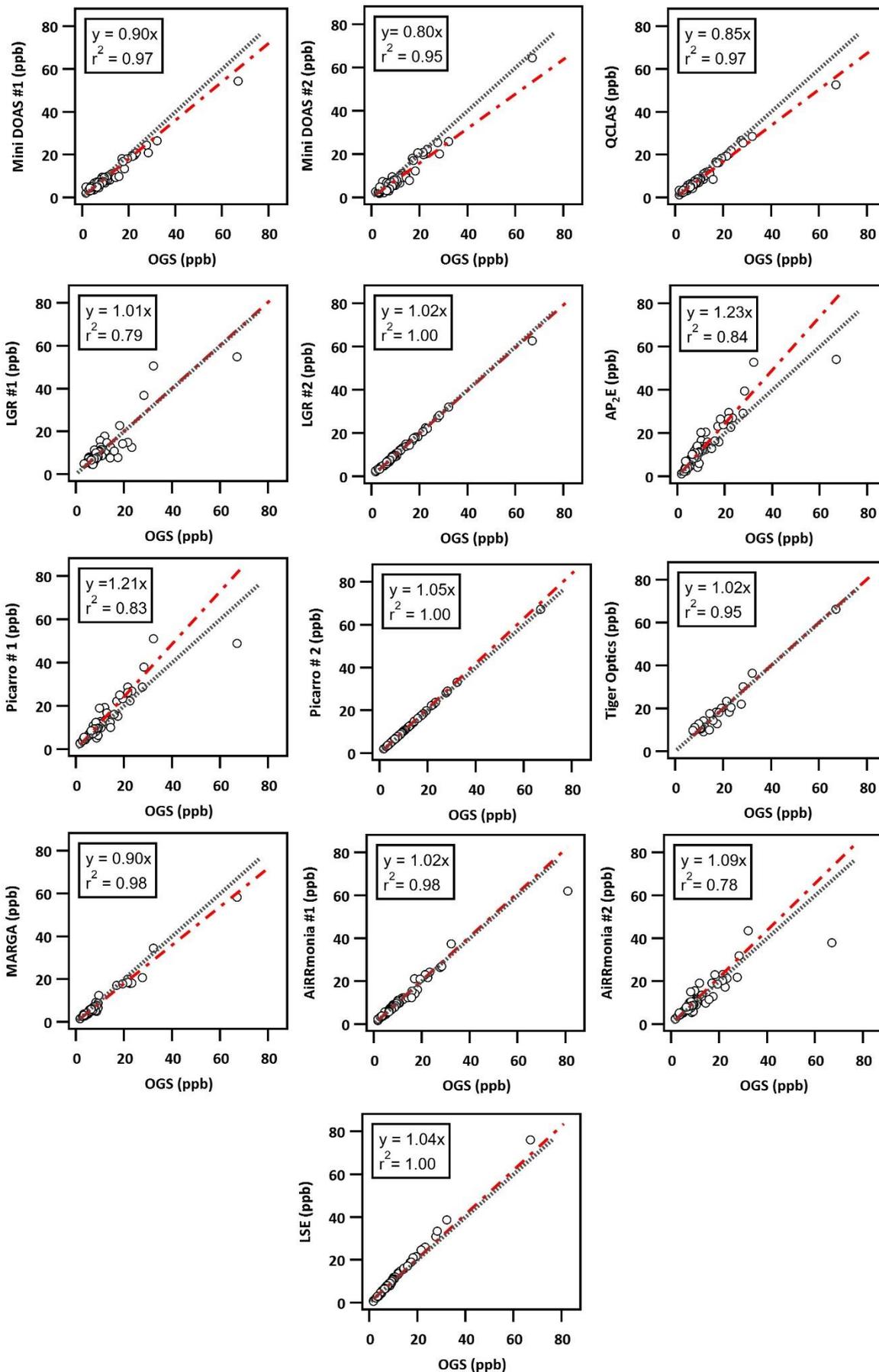


Figure S4. Orthogonal regression (red line, Boggs, 1989) plots of hourly NH_3 concentrations against the OGS for the whole period filtered. Data were filtered for low wind speed and stable/unstable conditions that could have led to inhomogeneity at the site. The dashed black line is the 1:1 line.

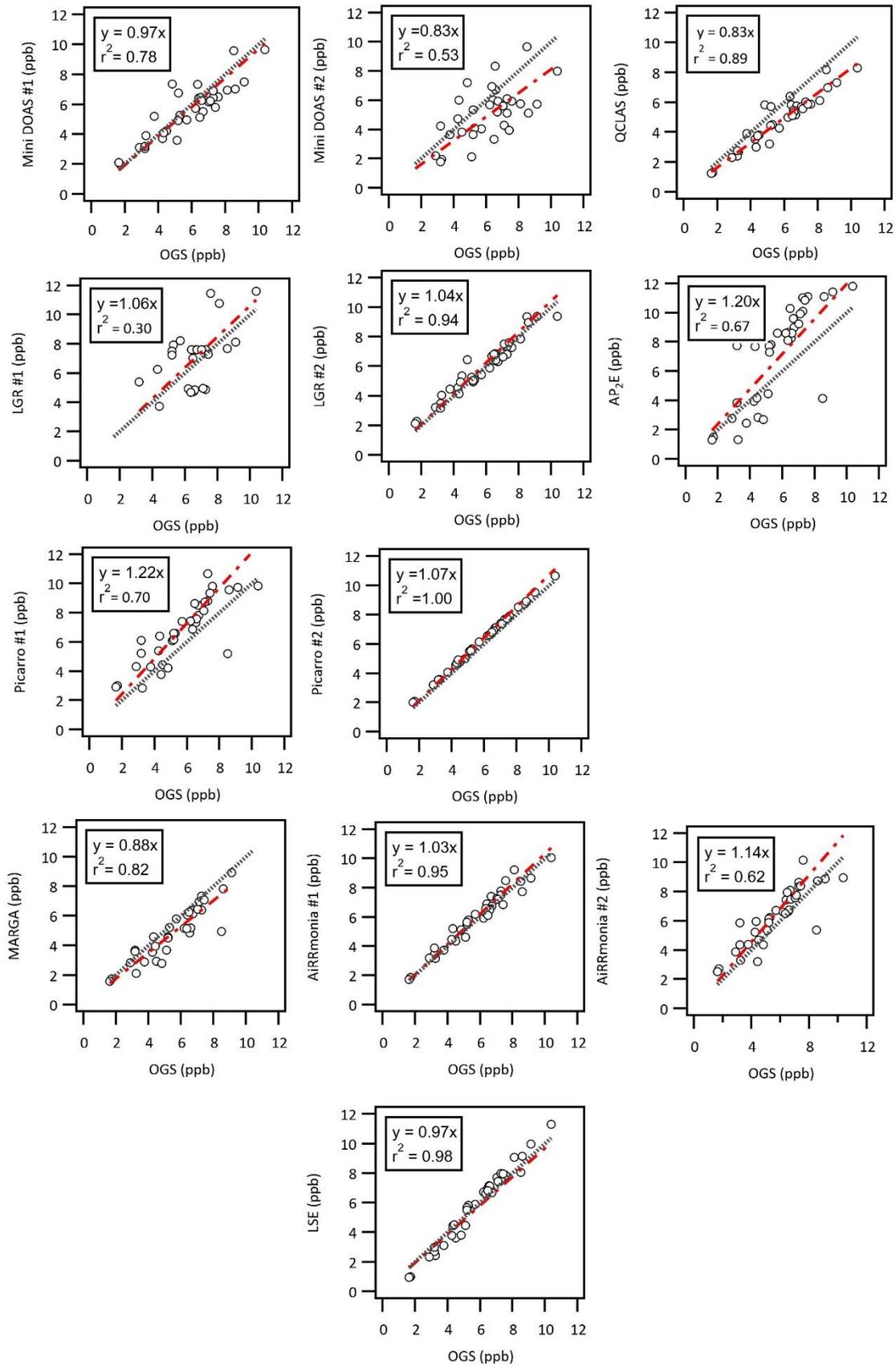
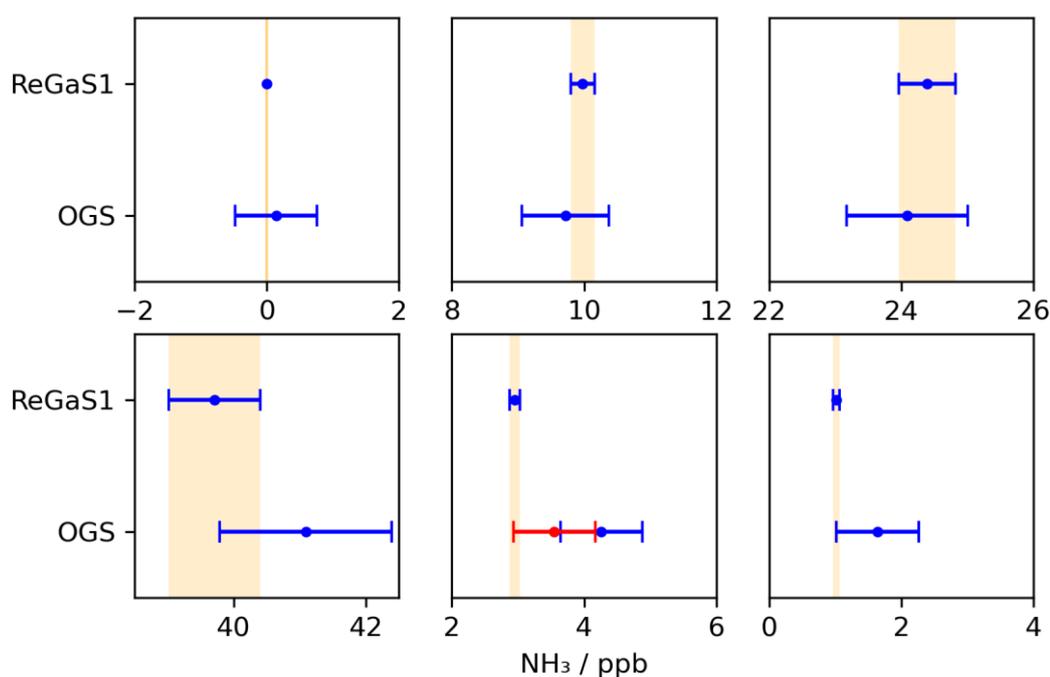


Figure S5. Orthogonal regression (red line, Boggs, 1989) plots of the instrumentation against the OGS for periods when the ensemble median < 10ppb. The dashed black line is the 1:1 line.

Table S4. Summary of the theoretical NH₃ concentration produced by the ReGaS1 system and the concentrations reported by the instrumentation, where μ_A - arithmetic mean, σ_A - arithmetic standard deviation.

Theoretical concentration from ReGaS1	ReGaS1 expanded uncertainty (k=2)	LSE		LGR#2		OGS		
ppb	ppb	μ_A (ppb)	σ_A (ppb)	μ_A (ppb)	σ_A (ppb)	μ_A (ppb)	σ_A (ppb)	Calculated expanded uncertainty (k=2) (ppb)
0.00	n/a	-0.77	0.44	0.16	0.03	0.14	0.02	0.62
9.98	0.18	8.18	0.53	5.58	0.37	9.72	0.21	0.66
24.39	0.43	22.55	0.65	18.03	0.83	24.09	0.39	0.92
39.71	0.69	41.31	0.66	33.93	0.58	41.09	0.16	1.3
2.95	0.08	5.59	4.56	6.06	4.68	4.26	0.99	0.62
1.02	0.05	1.34	0.55	2.13	0.729	1.64	0.08	0.62



5 Figure S6: Comparison of ReGaS1 reference concentrations and the calculated uncertainty of the OGS instrument. Error bars indicate the expanded uncertainty ($k = 2$, ReGaS1 and OGS). The orange box indicate the regions where measurement results agree to ReGaS1 reference values at the 95% confidence level. The red data point (lower middle plot) is the non-averaged OGS reading after a longer waiting period (at 14:00 o'clock in Figure 13a). ReGaS1 and OGS values, except at about 3 ppb with averaging, are metrologically compatible.