Supplementary material

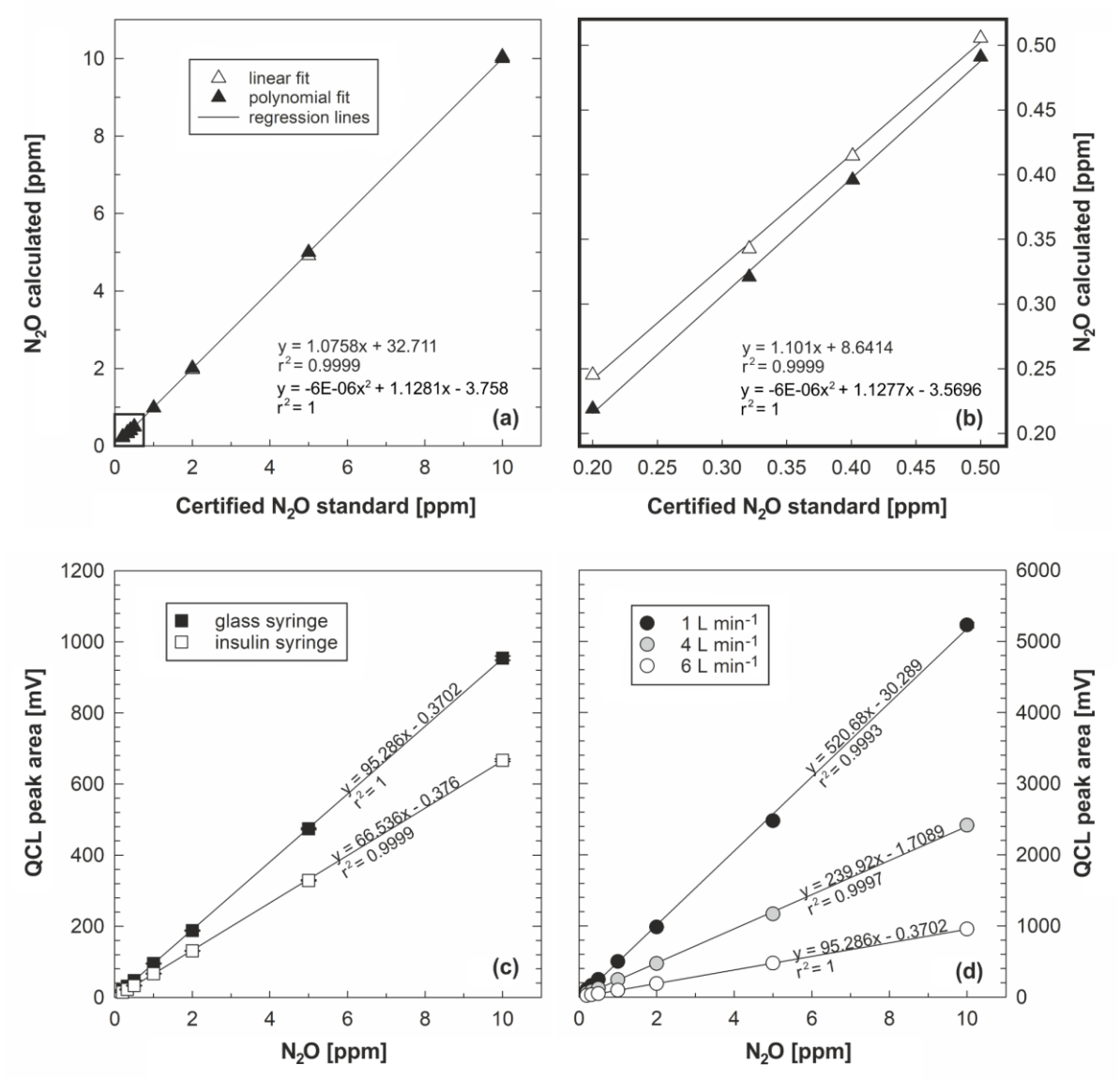

Figure S1: Tests conducted prior to the main study showing the calculated normal linear relationship between output peak area and N_2O concentration for different scenarios and for different ranges of N_2O standards injected (a) from 0.200 to 100 ppm and (b) from 0.200 to 5 ppm; regression lines in (c) illustrate the effect of using different syringe types on output peak area of the QCL; (d) demonstrates the effect of flow rate in L min^{-1} on the slope of associated regression lines and output peak area.

Table S1: Chronology of experimental activities.

Date	Activity
15-Aug-19	Trial site fenced off
	Preliminary injection into QCL: testing different syringe types
20-Aug-19	Installation of chamber collars
30-Aug-19	Preliminary injections into QCL: testing different flow rates
10-Sep-19	Treatment application to chamber and soil plots
	Gas and soil sampling – run 1
11-Sep-19	Gas and soil sampling – run 2
12-Sep-19	Gas and soil sampling – run 3 & 4
13-Sep-19	Gas and soil sampling – run 5
14-Sep-19	Gas and soil sampling – run 6
15-Sep-19	Gas and soil sampling – run 7 & 8
16-Sep-19	Gas and soil sampling – run 9

Table S2: Certified N_2O standards used in this study and associated uncertainty levels. Certified N_2O standard concentrations printed in bolt fond were used in quadratic curve models to calculate final sample N_2O concentration.

N_2O [µL L^{-1}] [ppmv]	**Uncertainty** [alpha/beta] [%]	**Background** (gas)	**Company** (name)
0.200	± 0.01	Nitrogen	BOC Ltd.
0.321	± 0.1–0.9%	Cryogenic UltraPure Air	Praxair, Inc.
0.3252	± 0.01	Air	NIWA
0.401	± 0.1–0.9%	Cryogenic UltraPure Air	Praxair, Inc.
0.500	± 0.01	Nitrogen	BOC Ltd.
1.00	± 0.01	Nitrogen	BOC Ltd.
2.00	± 0.02	Nitrogen	BOC Ltd.
5.00	± 0.1	Nitrogen	BOC Ltd.
10.00	± 0.2	Nitrogen	BOC Ltd.
20.00	± 0.2	Nitrogen	BOC Ltd.
50.00	± 1.0	Nitrogen	BOC Ltd.
100.00	± 1.0	Nitrogen	BOC Ltd.

Table S3: This table presents the measured values of nitrous oxide fluxes (F_{N2O}) analysed by GC and QCL, soil water-filled pore space (WFPS), soil ammonium (NH_4^+) and nitrate (NO_3^-) content of the control (AN_0) and across the different treatments of ammonium-nitrate (AN_{300}, AN_{600}, AN_{900}) applied The associated standard error of the mean (SEM) is provided at the right hand side of each control/treatment column.

date	AN_0	SEM	AN_{300}	SEM	AN_{600}	SEM	AN_{900}	SEM
	GC nitrous oxide flux [F_{N2O_GC} in nmol N_2O m^{-2} s^{-1}]							
10-Sep-2019	0.04	0.05	3.56	1.20	1.95	0.19	2.49	0.52
11-Sep-2019	0.13	0.04	9.93	1.97	9.63	3.44	14.88	3.55
12-Sep-2019*	0.06	0.05	8.67	1.73	8.02	2.92	15.87	3.96
12-Sep-2019*	0.06	0.01	8.42	2.62	8.19	3.23	14.87	3.15
13-Sep-2019	-0.05	0.03	6.43	3.00	11.57	3.68	15.16	3.76
14-Sep-2019	0.03	0.01	7.46	2.19	10.71	3.43	16.71	2.46
15-Sep-2019*	0.02	0.03	5.03	0.80	10.21	2.84	14.85	3.58
15-Sep-2019*	0.03	0.03	6.92	1.57	9.98	2.96	13.88	2.75
16-Sep-2019	0.02	0.04	3.06	1.33	6.37	2.45	10.29	1.67
	QCL nitrous oxide flux [F_{N2O_QCL} in nmol N_2O m^{-2} s^{-1}]							
10-Sep-2019	0.00	0.03	3.65	1.18	2.17	0.19	2.74	0.60
11-Sep-2019	0.21	0.05	9.40	1.83	8.88	3.14	13.57	3.04
12-Sep-2019*	0.14	0.07	8.19	1.60	7.94	2.92	15.17	3.71
12-Sep-2019*	0.06	0.02	8.02	2.47	8.04	3.11	15.46	3.57
13-Sep-2019	0.09	0.08	6.25	2.77	10.91	3.33	15.09	4.05
14-Sep-2019	0.03	0.02	7.30	2.10	10.66	3.24	17.22	2.71
15-Sep-2019*	0.17	0.01	5.30	0.86	9.46	2.42	14.81	3.65
15-Sep-2019*	0.18	0.03	6.95	1.33	10.27	2.89	14.36	2.69
16-Sep-2019	0.06	0.01	3.28	1.63	6.63	2.51	10.97	1.99
	Water filled pore space of the soil [%]							
10-Sep-2019	79.43	0.48	78.66	1.82	78.06	1.40	82.30	2.35
11-Sep-2019	81.64	0.59	84.97	1.68	80.16	0.53	82.13	1.79
12-Sep-2019	82.18	1.12	80.63	1.23	79.35	1.05	79.20	1.00
13-Sep-2019	79.62	0.95	79.72	1.87	76.62	2.08	78.13	1.76
14-Sep-2019	79.43	0.56	80.60	2.00	78.37	1.74	77.78	1.19
15-Sep-2019	79.79	0.50	81.70	2.65	77.17	1.49	76.81	0.37
16-Sep-2019	77.92	1.06	81.05	1.98	73.93	1.60	77.41	1.80
	Soil ammonium [kg NH_4^+ ha^{-1}]							
10-Sep-2019	1.82	0.50	81.73	5.20	89.36	2.72	264.63	17.19
11-Sep-2019	0.81	0.11	52.26	7.18	141.51	11.08	233.63	33.62
12-Sep-2019	2.15	0.57	44.61	6.52	109.37	6.77	213.76	3.41
13-Sep-2019	2.21	0.33	36.88	6.75	124.48	9.36	194.76	18.88
14-Sep-2019	3.71	0.09	20.31	5.07	59.88	6.05	188.70	18.05
15-Sep-2019	1.84	0.64	9.58	0.99	78.98	12.30	155.84	18.49
16-Sep-2019	1.80	0.29	13.21	3.23	38.50	4.59	124.38	7.64

	Soil nitrate [kg NO_3^- ha^{-1}]							
10-Sep-2019	2.99	0.37	83.67	3.87	104.95	1.33	267.77	15.17
11-Sep-2019	2.46	0.18	69.08	6.54	149.95	8.62	248.89	33.69
12-Sep-2019	2.29	0.07	79.41	6.57	142.52	8.61	230.94	7.36
13-Sep-2019	1.64	0.20	82.21	7.92	149.85	6.25	232.40	13.77
14-Sep-2019	1.84	0.35	73.37	12.71	114.20	8.41	237.77	8.96
15-Sep-2019	2.47	0.31	78.91	1.51	162.60	8.72	231.51	16.94
16-Sep-2019	1.85	0.22	92.49	16.22	134.38	7.60	211.88	18.92

* flux measurements conducted twice daily at 10 AM and 12 PM
SEM = standard error of the mean

Table S4: Results from the linear functional relationship analysis (orthogonal regression). Columns labelled C_{N2O} show results of the regression analysis when using standardised N_2O concentrations. Columns labelled F_{N2O} provide results based on standardised N_2O fluxes. Part of the regression analysis was to characterise both data streams by treatment and control, i.e. first including all data (AN_0, AN_{300}, AN_{600}, AN_{900}) in the analysis and then, separately, only the control (AN_0).

	C_{N2O} all AN	**C_{N2O}** AN_0 only	**F_{N2O}** all AN	**F_{N2O}** AN_0 only
Number of observations	432	108	108	27
Response mean	-0.003164	0.3272	-0.004008	0.3776
Explanatory mean	0.003164	-0.3272	0.004008	-0.3776
Response variance	0.9811	1.238	0.9860	1.139
Explanatory variance	1.021	0.5551	1.023	0.6029
r^2 value	0.9928	0.1753	0.9922	0.0939
r value	0.9964	0.4187	0.9961	0.3064
Angle between Y on X and X on Y	0.2068	42.32	0.2229	54.59
Major eigenvalue	1.999	1.384	2.005	1.241
Minor eigenvalue	0.003606	0.4096	0.003901	0.5017
Bootstrap resampling	200	200	200	200
Ordinary least squares:				
Constant	-0.006253	0.532	-0.007926	0.537
Standard error	0.003914	0.1038	0.007861	0.26
Lower	-0.01331	0.3101	-0.02204	-0.02
Upper	0.001710	0.734	0.006998	1.030
Slope	0.9766	0.625	0.9778	0.421
Inverse least squares:				
Constant	-0.006276	1.49	-0.007957	2.072
Standard error	0.003902	0.6585	0.007902	82.46
Lower	-0.01369	0.9211	-0.02246	-44.95
Upper	0.001786	3.478	0.007118	18.732
Slope	0.9837	3.567	0.9854	4.486
Major axis:				
Constant	-0.006264	1.108	-0.007941	1.326
Standard error	0.003904	0.44	0.007872	40.17
Lower	-0.01349	0.7105	-0.02217	-19.84
Upper	0.001610	2.484	0.006920	9.937
Slope	0.9801	2.387	0.9815	2.511

Table S5: Bland-Altman analysis for F_{N2O_GC} and F_{N2O_QCL} distinguished by treatment in units nmol m^{-2} s^{-1}, if not specified otherwise. This table provides a summary based on mean F_{N2O_GC} and F_{N2O_QCL} across replicates of the same treatment. Fig. 4, instead, illustrates the results of individual F_{N2O_GC} and F_{N2O_QCL} (not depicted in the below table) for each replicate and each treatment as the percentage mean difference between the two methods, i.e. GC (A) and QCL (B).

Sampling	**Treatment**	**GC (A)**	**QCL (B)**	**Mean**	**Difference**	**Difference (%)**
[No.]	[kg N ha^{-1}]	F_{N2O_GC}	F_{N2O_QCL}	(A+B)/2	(A-B)	((A-B)/mean)*100
1	0	0.04	0.00	0.02	0.04	182.48
1	300	3.56	3.65	3.61	-0.09	-2.59
1	600	1.95	2.17	2.06	-0.23	-11.11
1	900	2.49	2.74	2.61	-0.24	-9.24
2	0	0.13	0.21	0.17	-0.08	-44.70
2	300	9.93	9.40	9.67	0.53	5.51
2	600	9.63	8.88	9.26	0.75	8.11
2	900	14.88	13.57	14.22	1.31	9.20
3	0	0.06	0.14	0.10	-0.08	-78.52
3	300	8.67	8.19	8.43	0.48	5.69
3	600	8.02	7.94	7.98	0.08	0.98
3	900	15.87	15.17	15.52	0.70	4.51
4	0	0.06	0.06	0.06	0.00	1.93
4	300	8.42	8.02	8.22	0.39	4.79
4	600	8.19	8.04	8.11	0.15	1.82
4	900	14.87	15.46	15.16	-0.59	-3.89
5	0	-0.05	0.09	0.02	-0.14	-595.36
5	300	6.43	6.25	6.34	0.18	2.88
5	600	11.57	10.91	11.24	0.66	5.88
5	900	15.16	15.09	15.13	0.07	0.49
6	0	0.03	0.03	0.03	0.00	4.14
6	300	7.46	7.30	7.38	0.16	2.19
6	600	10.71	10.66	10.68	0.05	0.47
6	900	16.71	17.22	16.96	-0.51	-3.02
7	0	0.02	0.17	0.09	-0.15	-157.04
7	300	5.03	5.30	5.17	-0.27	-5.22
7	600	10.21	9.46	9.84	0.75	7.67
7	900	14.85	14.81	14.83	0.03	0.22
8	0	0.03	0.18	0.10	-0.15	-149.70
8	300	6.92	6.95	6.94	-0.02	-0.34
8	600	9.98	10.27	10.13	-0.29	-2.86
8	900	13.88	14.36	14.12	-0.48	-3.39

9	0	0.02	0.06	0.04	-0.04	-105.26
9	300	3.06	3.28	3.17	-0.22	-6.86
9	600	6.37	6.63	6.50	-0.26	-4.02
9	900	10.29	10.97	10.63	-0.68	-6.39

Table S6: Bioequivalence analysis for N_2O concentrations (C_{N2O}) and associated fluxes (F_{N2O} in bottom panel of the table). C_{N2O_QCL} and F_{N2O_QCL} were considered bioequivalent when the 90% confidence interval of the difference was completely within the predefined ± 5% bioequivalence range of difference to C_{N2O_GC} and F_{N2O_GC} (corresponding to a test with size 0.05). rep. = replicates, d.f = degrees of freedom, s.e.d = standard error of the difference, LSD = least significant difference

Time/ Treatment	**Mean**		**Standard error of the difference of the mean**			**LSD**	**90% confidence interval**			**Bioequivalence range**			
AN_0	**C_{N2O_GC}** [ppm]	**C_{N2O_QCL}** [ppm]	rep.	d.f	s.e.d	s.e.d	difference (GC-QCL)	lower	upper	GC lower	GC upper	QCL lower	QCL upper
t_0	0.333	0.332	27	26	0.0027	0.0046	0.000	-0.004	0.005	-0.017	0.017	-0.017	0.017
t_{15}	0.333	0.342	27	26	0.0028	0.0048	-0.009	-0.013	-0.004	-0.017	0.017	-0.017	0.017
t_{30}	0.335	0.352	27	26	0.0029	0.0049	-0.016	-0.021	-0.012	-0.017	0.017	-0.018	0.018
t_{45}	0.340	0.354	27	26	0.0027	0.0046	-0.014	-0.019	-0.009	-0.017	0.017	-0.018	0.018
AN_{300}													
t_0	0.333	0.336	27	26	0.0028	0.0048	-0.003	-0.007	0.002	-0.017	0.017	-0.017	0.017
t_{15}	0.822	0.821	27	26	0.1090	0.0186	0.001	-0.017	0.020	-0.041	0.041	-0.041	0.041
t_{30}	1.341	1.327	27	26	0.0168	0.0286	0.014	-0.015	0.042	-0.067	0.067	-0.066	0.066
t_{45}	1.831	1.804	27	26	0.0192	0.0327	0.026	-0.007	0.059	-0.092	0.092	-0.090	0.090
AN_{600}													
t_0	0.336	0.335	27	26	0.0023	0.0042	0.001	-0.003	0.005	-0.017	0.017	-0.017	0.017
t_{15}	0.912	0.912	27	26	0.0160	0.0273	0.000	-0.027	0.027	-0.046	0.046	-0.046	0.046
t_{30}	1.563	1.550	27	26	0.0242	0.0412	0.013	-0.028	0.054	-0.078	0.078	-0.078	0.078
t_{45}	2.143	2.104	27	26	0.0250	0.0427	0.039	-0.004	0.082	-0.107	0.107	-0.105	0.105
AN_{900}													
t_0	0.338	0.337	27	26	0.0028	0.0319	0.001	-0.004	0.005	-0.017	0.017	-0.017	0.017
t_{15}	1.285	1.268	27	26	0.0136	0.1380	0.017	-0.006	0.041	-0.064	0.064	-0.063	0.063
t_{30}	2.338	2.294	27	26	0.0325	0.1959	0.044	-0.012	0.100	-0.117	0.117	-0.115	0.115
t_{45}	3.370	3.379	27	26	0.3900	0.2850	-0.009	-0.076	0.058	-0.169	0.169	-0.169	0.169
Treatment	**F_{N2O_GC}** [nmol N_2O m^{-2} s^{-1}]	**F_{N2O_QCL}**											
AN_0	0.0387	0.1048	27	26	0.0187	0.0319	-0.066	-0.098	-0.034	-0.002	0.002	-0.005	0.005
AN_{300}	6.610	6.483	27	26	0.0809	0.1380	0.127	-0.011	0.265	-0.331	0.331	-0.324	0.324
AN_{600}	8.514	8.329	27	26	0.1149	0.1959	0.185	-0.011	0.381	-0.426	0.426	-0.416	0.416
AN_{900}	13.222	13.265	27	26	0.1671	0.2850	-0.043	-0.328	0.242	-0.661	0.661	-0.663	0.663