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A novel injection technique: using a field-based quantum cascade laser for the analysis of gas samples derived from static chambers

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Supplementary material

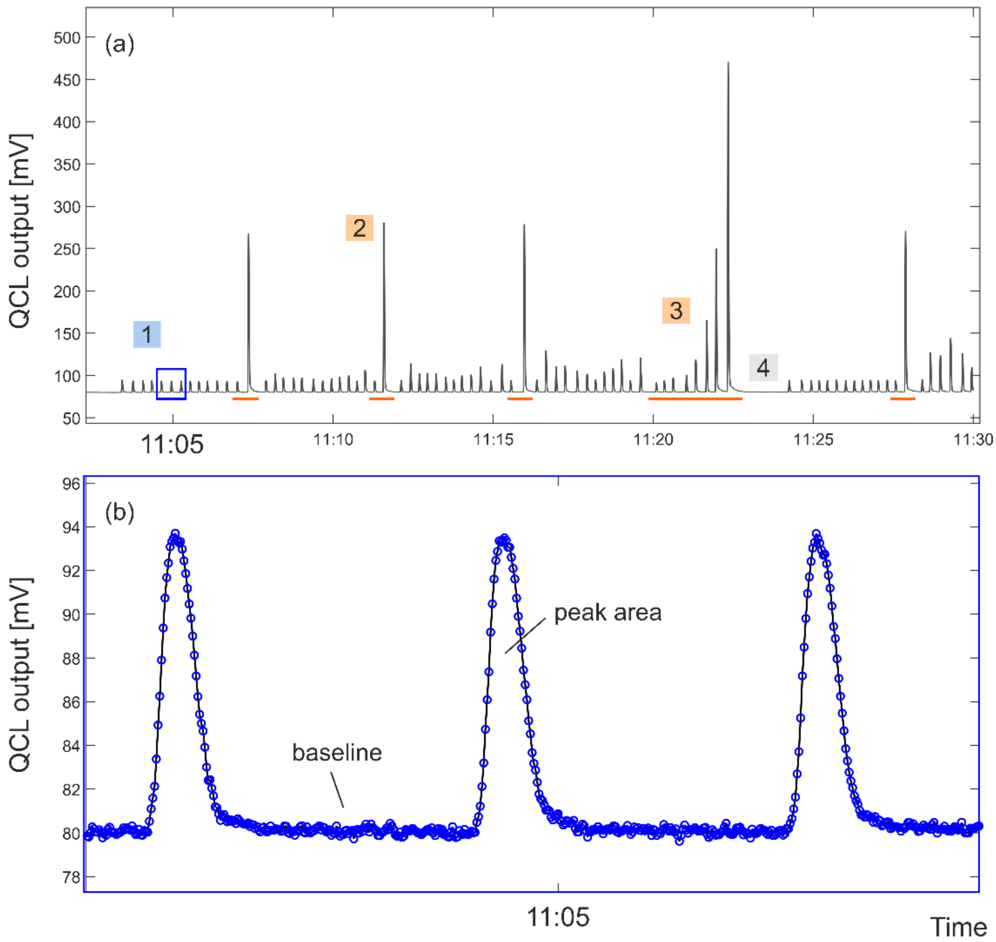

Figure S1: Example of QCL output data depicting how a one half-hourly peak progression sequence looked like. Panel (a) shows the full sequence for injected N_2O samples and standards in a given half-hour from 11-11:30 AM, 17 September 2020. Panel (b) captures three individual peaks from within this period (1) (blue rectangle). Single measurement points are depicted by blue dots with the black line showing an interpolated curvature. Orange bars underneath individual peaks in panel (a) distinguish injected N_2O standards from N_2O samples. (2) identifies 1 ppm and 5 ppm standards injected after every 12 samples, here serving as a running control; (3) shows an example of an injected standard line of known N_2O concentration (range: 0.2–10 ppm); and (4) the lag time that was required to ensure sufficient flushing of the QCL sample cell after injecting a sample or standard (here 10 ppm) of higher N_2O concentration.

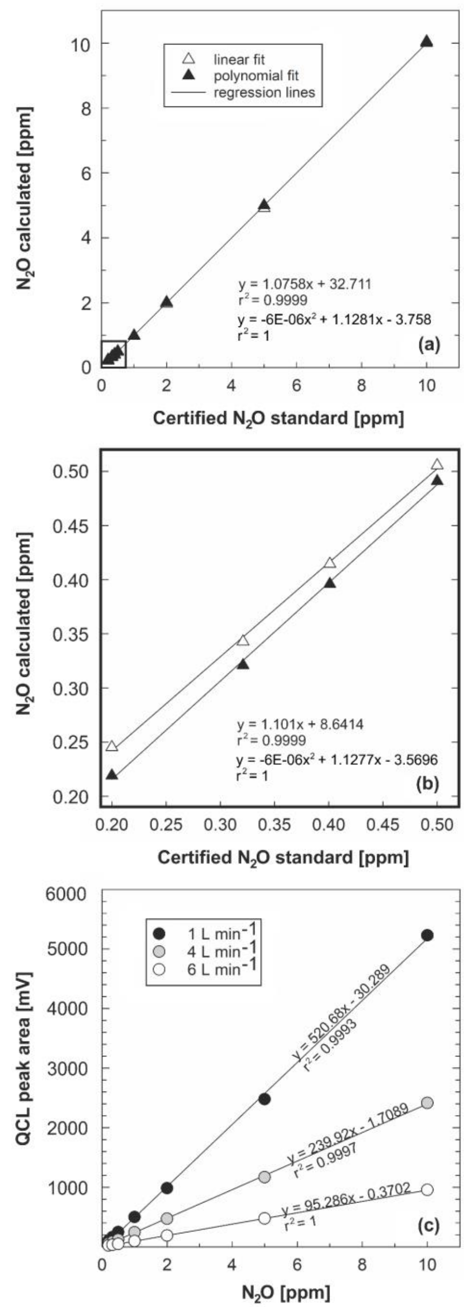

Figure S2: Tests conducted prior to the main study showing the calculated normal linear relationship between output peak area and N_2O concentration (C_{N2O}) for different scenarios and ranges of N_2O standards injected: (a) from 0.2 to 10 ppm, and (b) from 0.2 to 0.5 ppm. (c) demonstrates the effect of flow rate in L min^{-1} on the slope of the associated regression lines, output peak area and measured N_2O concentration in ppm.

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
17-Sep-19	Sample injection into QCL

Table S2: Certified N_2O standards used in this study and associated uncertainty levels. Standards printed in bolt fond were used in quadratic curve models to calculate final N_2O concentration of the samples taken from static chambers.

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}). 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 the 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 [No.]	**Treatment** [kg N ha^{-1}]	**GC (A)** F_{N2O_GC}	**QCL (B)** F_{N2O_QCL}	**Mean** (A+B)/2	**Difference** (A-B)	**Difference (%)** ((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