Supplement of

Versatile soil gas concentration and isotope monitoring: optimization and integration of novel soil gas probes with online trace gas detection

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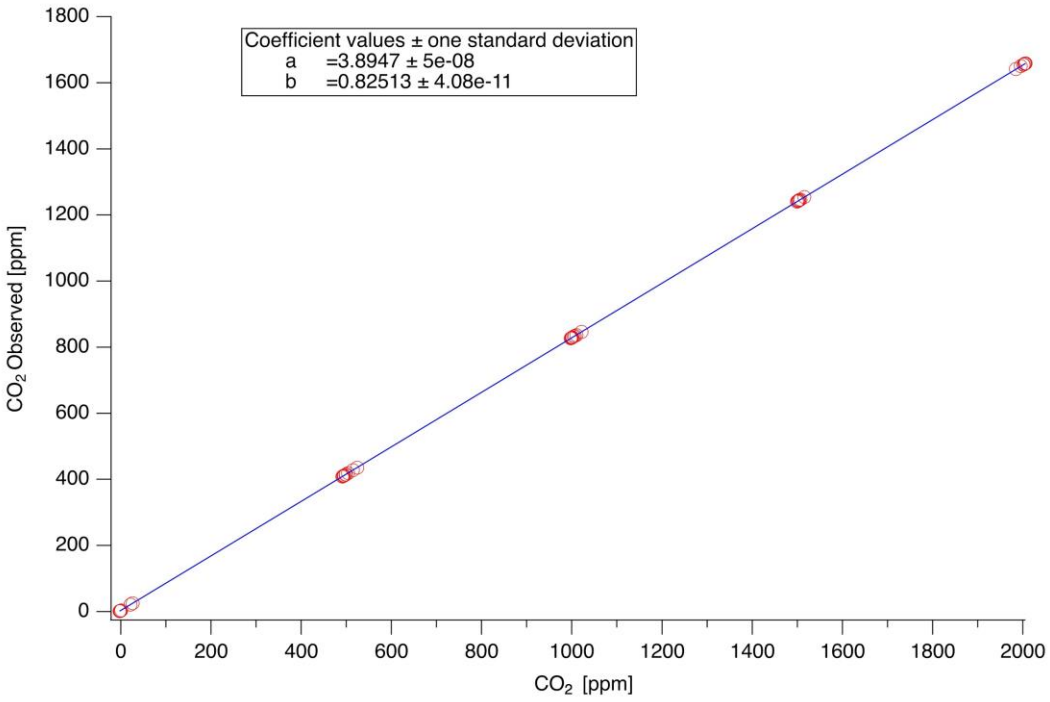

Figure S1. Calibration of absolute concentration of CO_2 in silica matrix (System 1 Dual) between observed and controlled dilution mixtures using linear regression relationship

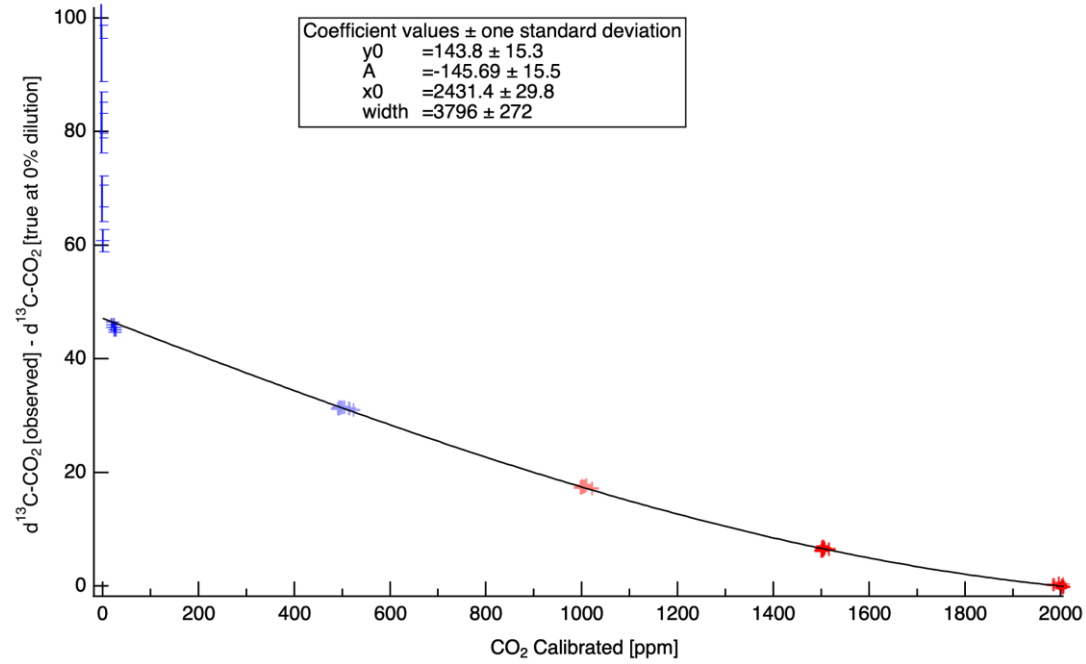

Figure S2. $\Delta\ ^{13}C\text{-}CO_2$ calibration from the concentration dependent relationship of dual $\delta^{13}C\text{-}CO_2$ vs observed $[CO_2]$. The Gaussian equation was used to fit the relationship between ($\delta^{13}C\text{-}CO_2$ observed - $\delta^{13}C\text{-}CO_2$ true and CO_2 concentration. $\delta^{13}C\text{-}CO_2$ calibration offset calibration curve was used to correct observations.

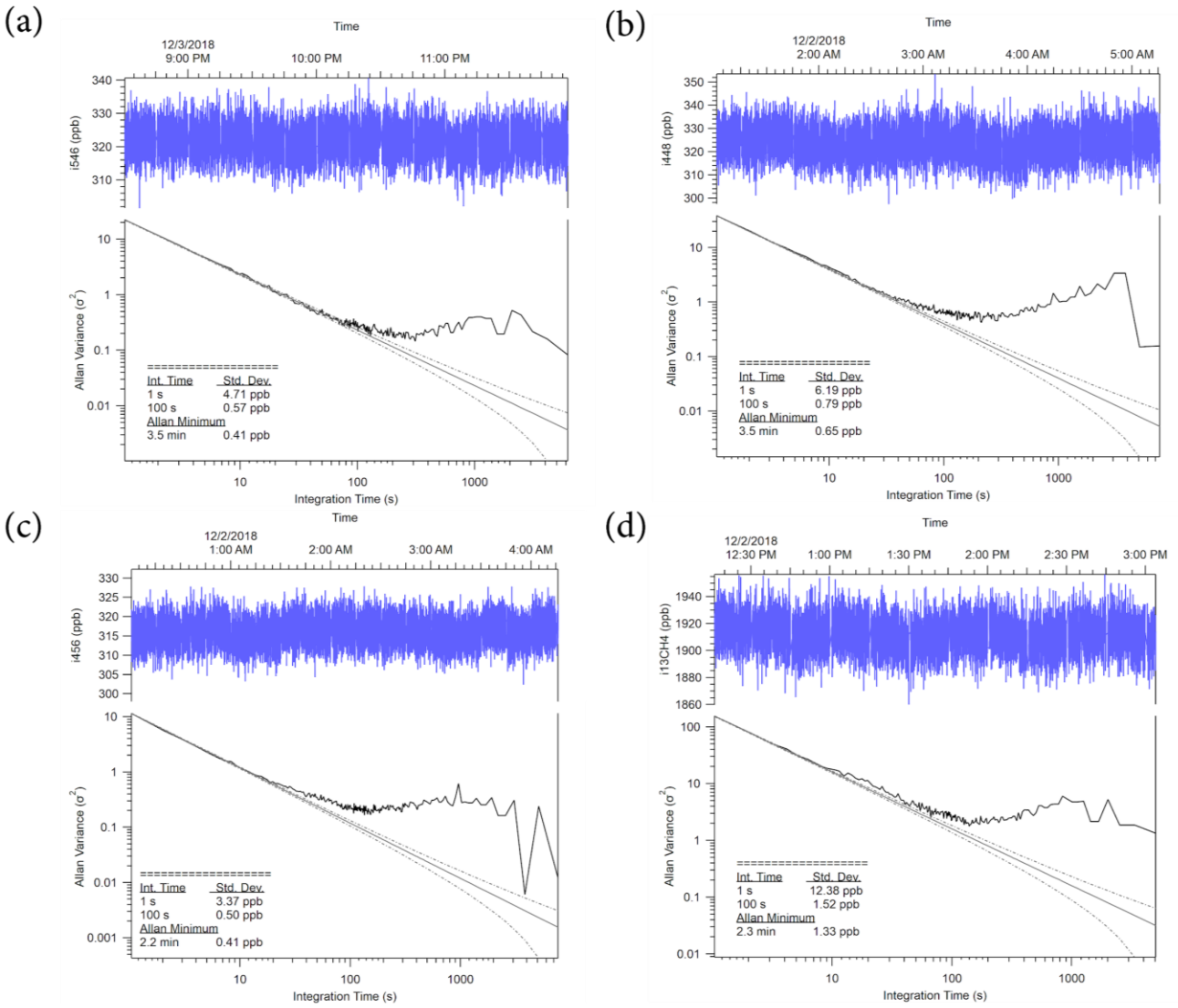

Figure S3. Allan-Werle plots of precision for individual minor isotopes N_2O 456 and 546 (top), 448 and ^{13}C-CH_4 (bottom). Precision for □456 = 1.3 per mil, □456 =1.4permil, □448 = 2.2 per mil, and □^{13}C = 0.7 per mil

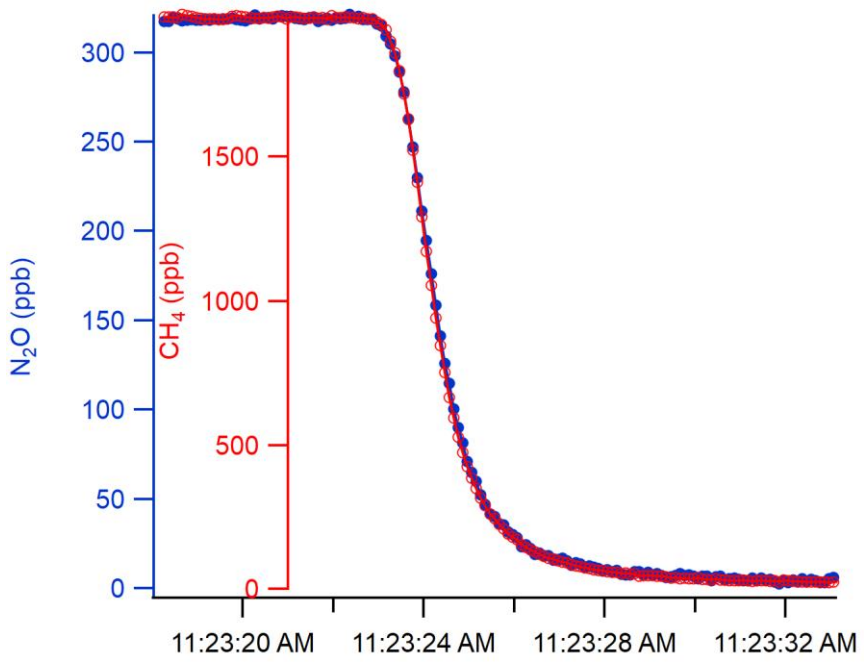

Figure S4. Improvement in the time response with the addition of the insert. Time Response of 76m standard cell with insert. P=30 Torr, flow 1 slpm.

Table S1. Soil matrix description and particle size distribution

Type of Matrix	**Soil ID**	**Vendor**	**Particle size distribution (units)**	**Type of soil**
Granusil 4095[1]	Silica	Covia Corporation	8 (0%), 16 (0.28%), 20 (27.66%), 30 (52.55%), 40 (15.99%), 50 (3.22%), 70 (0.22%), 100 (0.04%), 140 (0.02%), 200 (0.28%)[a]	High purity industrial quartz, Hardness (Mohs) 7.0, Moisture content <0.1%.
Type of Soil	**Soil ID**	**Source Site**	**Sampling Location**	**Properties**
Tropical Rainforest	Soil 1	Biosphere 2 Tropical Rainforest	Shaded Lowland (dieffenbachia, vine)	Sandy, silty loam (40-70% sand 36% silt and 30% clay)[b]; and C:N 8.75; pH 7-8[c]
Tropical Rainforest	Soil 3		South facing terrace (ginger, hibiscus)	

a Mesh units ASTM; [b] (Lin et al., 1999) in (Smith et al., 2020); [c] (Van Haren et al., 2005)

Table S2. Measurement precision of the 76 m dual TILDAS for N_2O/CH_4 isotopes

	Mixing Ratio (ppb)	□ (‰)
δ546 N_2O ($^{15}N^{14}N^{16}O$)	0.46	1.4
δ456 N_2O ($^{14}N^{15}N^{16}O$)	0.42	1.3
δ448 N_2O ($^{14}N^{14}N^{18}O$)	0.72	2.2
^{13}C-CH_4	1.3	0.7

Table S3. References used to estimate the 3D map for N_2O isotopic signatures of bulk $\delta^{15}N$ (x-axis), $\delta^{18}O$ (y-axis), and site preference (z-axis) (Figure 12b).

Microbial activity	Reference
Bacterial Denitrification	(Frame and Casciotti, 2010; Sutka et al., 2006; Toyoda et al., 2005; Zou et al., 2014)
Chemodenitrification	(Jones et al., 2015; Toyoda et al., 2005; Wei et al., 2017)
Bacterial nitrification	(Jung et al., 2014; Sutka et al., 2006; Yoshida, 1988)
AOA	(Hu et al., 2015)
Fungal denitrification	(Sutka et al., 2008)

References

Frame, C. H. and Casciotti, K. L.: Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium, Biogeosciences, 7, 2695–2709, 2010.

Hu, H.-W., Chen, D. and He, J.-Z.: Microbial regulation of terrestrial nitrous oxide formation: understanding the biological pathways for prediction of emission rates, FEMS Microbiol. Rev., 39(5), 729–749, 2015.

Jones, L. C., Peters, B., Lezama Pacheco, J. S., Casciotti, K. L. and Fendorf, S.: Stable isotopes and iron oxide mineral products as markers of chemodenitrification, Environ. Sci. Technol., 49(6), 3444–3452, 2015.

Jung, M.-Y., Well, R., Min, D., Giesemann, A., Park, S.-J., Kim, J.-G., Kim, S.-J. and Rhee, S.-K.: Isotopic signatures of N_2O produced by ammonia-oxidizing archaea from soils, ISME J., 8(5), 1115–1125, 2014.

Lin, G., Adams, J., Farnsworth, B., Wei, Y., Marino, B. D. V. and Berry, J. A.: Ecosystem carbon exchange in two terrestrial ecosystem mesocosms under changing atmospheric CO_2 concentrations, Oecologia, 119(1), 97–108, 1999.

Smith, M. N., Taylor, T. C., van Haren, J., Rosolem, R., Restrepo-Coupe, N., Adams, J., Wu, J., de Oliveira, R. C., da Silva, R., de Araujo, A. C., de Camargo, P. B., Huxman, T. E. and Saleska, S. R.: Empirical evidence for resilience of tropical forest photosynthesis in a warmer world, Nat Plants, 6(10), 1225–1230, 2020.

Sutka, R. L., Ostrom, N. E., Ostrom, P. H., Breznak, J. A., Gandhi, H., Pitt, A. J. and Li, F.: Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances, Appl. Environ. Microbiol., 72(1), 638–644, 2006.

Sutka, R. L., Adams, G. C., Ostrom, N. E. and Ostrom, P. H.: Isotopologue fractionation during N_2O production by fungal denitrification, Rapid Commun. Mass Spectrom., 22(24), 3989–3996, 2008.

Toyoda, S., Mutobe, H., Yamagishi, H., Yoshida, N. and Tanji, Y.: Fractionation of N_2O isotopomers during production by denitrifier, Soil Biol. Biochem., 37(8), 1535–1545, 2005.

Van Haren, J. L. M., Handley, L. L., Biel, K. Y., Kudeyarov, V. N., McLain, J. E. T., Martens, D. A. and Colodner, D. C.: Drought-induced nitrous oxide flux dynamics in an enclosed tropical forest, Glob. Chang. Biol., 11(8), 1247–1257, 2005.

Wei, J., Zhou, M., Vereecken, H. and Brüggemann, N.: Large variability in CO2 and N2O emissions and in 15N site preference of N2O from reactions of nitrite with lignin and its derivatives at different pH, Rapid Commun. Mass Spectrom., 31(16), 1333–1343, 2017.

Yoshida, N.: 15N-depleted N2O as a product of nitrification, Nature, 335(6190), 528–529, 1988.

Zou, Y., Hirono, Y., Yanai, Y., Hattori, S., Toyoda, S. and Yoshida, N.: Isotopomer analysis of nitrous oxide accumulated in soil cultivated with tea (Camellia sinensis) in Shizuoka, central Japan, Soil Biol. Biochem., 77, 276–291, 2014.