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Supplement of

**Isotopic characterization of nitrogen oxides (NO_x), nitrous acid (HONO),
and nitrate ($p\text{NO}_3^-$) from laboratory biomass burning during FIREX**

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Description of NO_x online concentration measurement

NO and NO_x concentrations were measured with a Thermo Scientific Model 42i chemiluminescence NO/NO_x analyzer, with ± 0.4 ppbv precision and 0.2 ppbv zero noise at 1 minute time resolution. In the NO channel, O₃ generated by an ozonator titrates NO to excited state NO₂ which subsequently produces luminescence that is proportional to NO concentration. In the NO_x channel, the sample gas stream first flows through a heated molybdenum catalyst (325 °C) that converts NO₂ to NO before entering the NO+O₃ reaction chamber. The auto cycle mode (NO/NO_x) switches the mode solenoid valve automatically on a 10 second cycle so that NO, NO₂, and NO_x concentrations are determined. It is known that some NO_y species including HONO, HNO₃, organic nitrate and PAN can be partially converted to NO in the hot molybdenum catalyst, causing positive artifacts in measured NO_x (Reed et al., 2016). In this study, only the HONO interference was corrected for. This was done by subtracting the ADS measured HONO concentration (mean value across each whole fire) from Thermo analyzer measured NO_x concentration averaged across the whole fire; this provided the approximate lower limit of the NO_x concentration by assuming HONO is 100% converted to NO on the Molybdenum catalyst (e.g. (Dunlea et al., 2007; Febo et al., 1995). Contributions from HNO₃, PAN and gaseous organic nitrate are not of major concern because no photo-oxidation is involved in indoor fires (Koss et al., 2018; Selimovic et al., 2018; Stockwell et al., 2014). In addition, we do not expect that other reactive nitrogen species such as NH₃ and hydrogen cyanide (HCN) interfere with NO₂ measurement. A particulate matter filter (Millipore, 1 μ m PTFE) was always placed before the inlet of the NO_x analyzer. The NO channel was calibrated before and after the entire Fire Lab experiments with standard NO (10 ppmv in N₂) diluted with zero air (Thermo Fisher Scientific, Model 111) via a gas dilution calibrator (Thermo Fisher Scientific, Model 146i) and NO₂ response of the NO_x channel using O₃ titration is within $\pm 5\%$ accuracy. The NO_x measurement verified the concentration of the NO_x collected for isotopic analysis, and the original NO_x data is available in the NOAA FIREX archive (FIREX, 2016).

Table S1 Information of fuels measured for $\delta^{15}\text{N}$ -biomass. Acronyms: ponderosa pine (PIPO), lodgepole pine (PICO), Engelmann spruce (PIEN), Douglas-fir (PSME) and subalpine fir (ABLA). Each fuel is a mixture of one or multiple compositions (different parts from the vegetation) including duff, litter, canopy, rotten, shrub. $\delta^{15}\text{N}$ of each composition (5th column) was measured in replicates using the method described in section 2.2.3. Composition mass weighted $\delta^{15}\text{N}$ in 6th column are calculated by mass weighting $\delta^{15}\text{N}$ of each composition (5th column) with nitrogen content (=sample weight $\times\%$ N). Mixture mass weighted $\delta^{15}\text{N}$ (8th column) is calculated by mass weighting $\delta^{15}\text{N}$ (6th column) with fraction in mixture (7th column).

Sample	Fuel Compo.	Sample Weight (mg)	%N	$\delta^{15}\text{N}$ (‰)	Compo. Mass Weighted $\delta^{15}\text{N}$ ‰	Fraction in Mixture	Mixture Mass Weighted $\delta^{15}\text{N}$ (‰)
PIPO	Duff	4.87	1.1	0.32	0.39	0.16	0.1
PIPO	Duff	5.00	1.1	0.31			
PIPO	Duff	5.36	1.2	0.51			
PIPO	Litter	4.75	0.5	1.27	0.94	0.29	
PIPO	Litter	7.60	0.5	0.59			
PIPO	Canopy	4.76	0.9	-0.11	-0.10	0.31	
PIPO	Canopy	5.16	0.9	-0.10			
PIPO	Rotten	7.06	0.1	1.15	-1.33	0.18	
PIPO	Rotten	10.14	0.1	-2.29			
PIPO	Rotten	10.30	0.1	-1.55			
PIPO	Rotten	10.37	0.1	-2.82			
PICO	Duff	4.69	0.5	-2.95	-2.53	0.20	-3.5
PICO	Duff	16.31	0.4	-1.83			
PICO	Duff	10.58	0.6	-2.63			
PICO	Litter	4.45	0.8	-2.73	-3.09	0.11	
PICO	Litter	4.75	0.9	-3.38			

PICO	Litter	7.06	0.8 5	-3.15			
PICO	Canopy	4.45	0.9 3	-4.17	-4.16	0.40	
PICO	Canopy	5.24	0.8 8	-4.14			
PICO	Shrub	4.48	0.9 0	-3.51	-3.36	0.09	
PICO	Shrub	6.60	0.8 8	-3.21			
PSME	Duff	4.90	0.7 4	-0.08	0.39	0.15	-0.8
PSME	Duff	9.95	0.8 7	0.79			
PSME	Litter	4.53	0.7 2	-2.41	-2.30	0.11	
PSME	Litter	6.69	0.7 2	-2.19			
PSME	Canopy	4.66	0.8 7	-2.59	-2.33	0.46	
PSME	Canopy	5.99	0.8 6	-2.08			
PSME	Rotten	7.76	0.3 1	2.02	1.67	0.28	
PSME	Rotten	7.08	0.3 1	1.74			
PSME	Rotten	10.09	0.3 0	1.23			
Chamise	Canopy	5.27	1.1 4	-3.03	-2.84		
Chamise	Canopy	5.42	1.1 4	-2.66			
PIEN	Duff	4.68	1.3 2	-1.38	-1.41	0.17	-2.8
PIEN	Duff	5.03	1.4 0	-1.43			
PIEN	Canopy	4.59	0.9 5	-3.95	-3.50	0.31	
PIEN	Canopy	6.19	0.9 5	-2.70			
PIEN	Canopy	5.48	0.9 8	-3.84			
ABLA	Duff	5.25	1.1 7	-1.57	-1.40		
ABLA	Duff	6.47	1.2 0	-1.25			

ABLA	Litter	4.38	1.0 0	-4.02	-3.85
ABLA	Litter	6.24	0.9 1	-3.66	

Table S2 Comparisons between [HONO]_{ADS} with mean values of various high resolution methods including MC/IC, FTIR, CES and PTR-ToF. Missing data points are results of instrumental issues.

Fire no.	ADS(ppb)	MCIC(ppb)	CES(ppb)	FTIR(ppb)	PTR-ToF (ppb)
8	25.7	25.7	22.4	29.5	29.5
9	21.3	24.9	19.7	--	--
10	42.2	44.2	46.6	--	--
11	112.3	69.8	103.3	--	--
14	25.3	24.5	35.6	25.7	41.3
15	51.0	76.2	58.9	37.9	50.2
16	70.0	56.4	70.1	56.4	--
17	47.1	53.3	39.4	35.1	--
18	45.3	38.3	50.0	41.3	50.0
19	23.8	41.5	28.4	24.3	30.9
20	52.5	42.9	56.8	41.9	--
21	9.9	6.0	--	7.0	16.2
22	40.0	32.0	--	14.5	42.1

Table S3 Data for NO_x concentration measured by NO_x analyzer and NO_x collection system.

Fire #	NO _x _analyzer (ppb)	NO _x _collected (ppb)
2	113.5	147.9
3	151.3	124.7
5	182.7	123.8
6	60.2	94.7
7	313.0	398.3
8	100.5	91.7
9	80.5	73.6
10	156.2	229.7

11	498.9	571.8
12	33.9	36.2
14	39.5	70.0
15	38.9	43.5
16	338.3	443.3
19	84.3	73.3

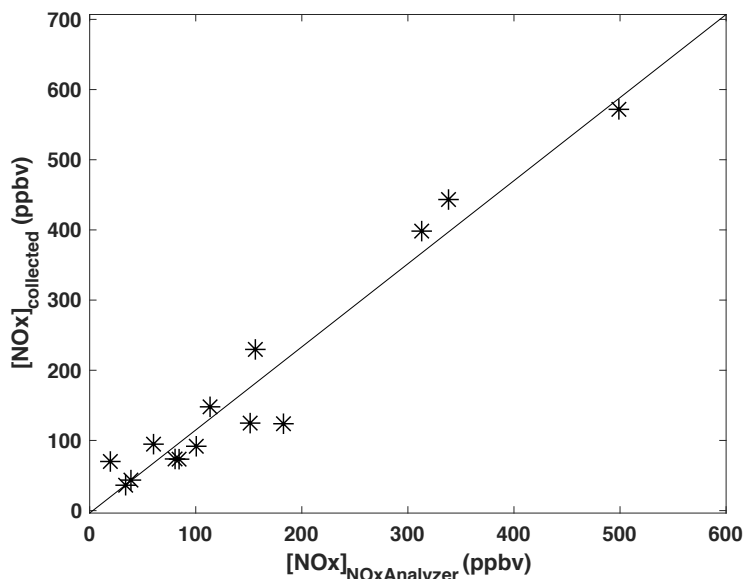


Figure S1 NO_x concentration comparison between NO_x analyzer measurement (mean value over the entire fire) and NO_x collected by the collection system for isotopic analysis. Solid line is linear regression of the dataset: $y = (1.18 \pm 0.08)x + (-3.5 \pm 17.2)$, with $R^2 = 0.94$, $p_{\text{slope}} < 0.001$, $p_{\text{intercept}} = 0.84$, and uncertainty = 1σ .

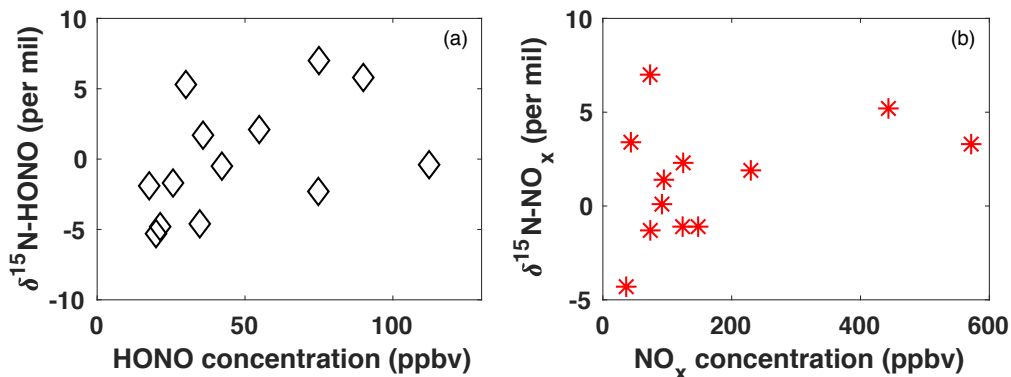


Figure S2. Relationship between $\delta^{15}\text{N}$ value versus concentration for HONO (a) and NO_x (b). p-values for linear correlation are 0.12 (a) and 0.93 (b) respectively.

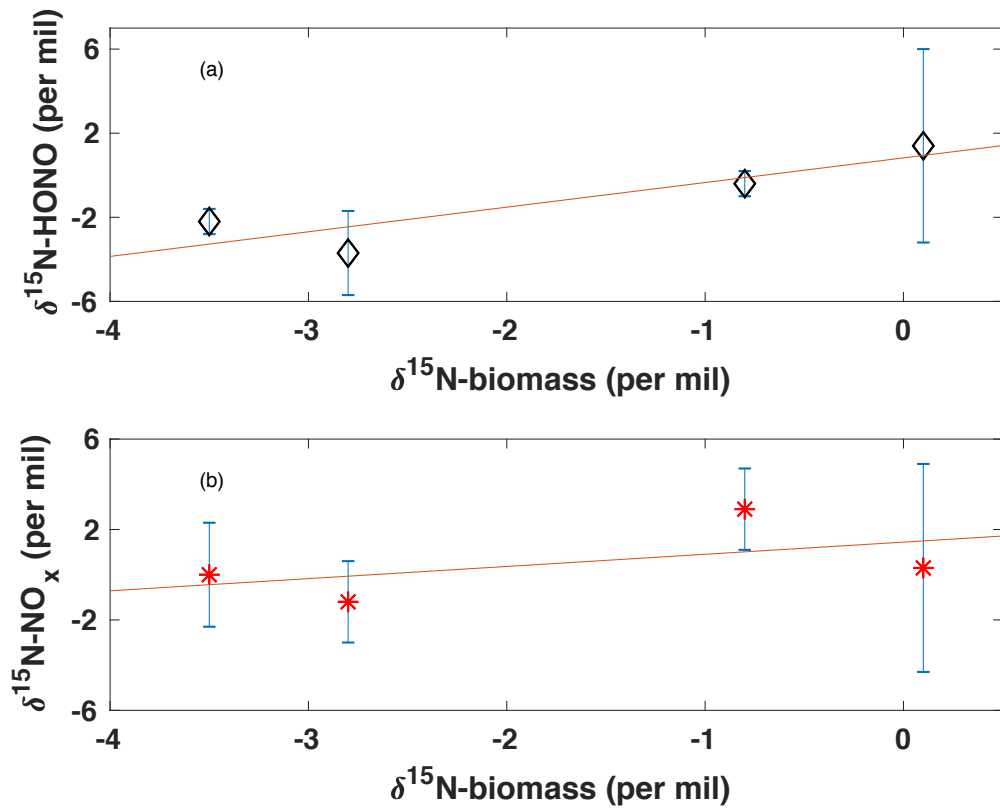


Figure S3. Linear regressions between **(a)** $\delta^{15}\text{N-HONO}$ and $\delta^{15}\text{N-biomass}$, $\delta^{15}\text{N-HONO} = 1.2 \delta^{15}\text{N-biomass} + 0.80$ ($r^2=0.83$, $p_{\text{slope}}=0.1$), and **(b)** $\delta^{15}\text{N-NO}_x$ and $\delta^{15}\text{N-biomass}$ $\delta^{15}\text{N-NO}_x = 0.54\delta^{15}\text{N-biomass} + 1.4$ ($r^2=0.28$, $p_{\text{slope}}=0.5$). The error bars are propagation of replicate uncertainty (1σ) and method uncertainty.

References

Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C. R., Kolb, C. E., Molina, L. T. and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, *Atmospheric Chemistry and Physics*, 7(10), 2691–2704, doi:<https://doi.org/10.5194/acp-7-2691-2007>, 2007.

Febo, Antonio., Perrino, Cinzia., Gherardi, Monica. and Sparapani, Roberto.: Evaluation of a High-Purity and High-Stability Continuous Generation System for Nitrous Acid, *Environ. Sci. Technol.*, 29(9), 2390–2395, doi:10.1021/es00009a035, 1995.

FIREX: FIREX 2016 Fire Lab Data Archive, [online] Available from: <https://esrl.noaa.gov/csd/groups/csd7/measurements/2016firex/FireLab/DataDownload/index.php?page=/csd/groups/csd7/measurements/2016firex/FireLab/DataDownload/> (Accessed 25 March 2019), 2016.

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J. and Gouw, J. de: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, *Atmospheric Chemistry and Physics*, 18(5), 3299–3319, doi:<https://doi.org/10.5194/acp-18-3299-2018>, 2018.

Reed, C., Evans, M. J., Carlo, P. D., Lee, J. D. and Carpenter, L. J.: Interferences in photolytic NO₂ measurements: explanation for an apparent missing oxidant?, *Atmospheric Chemistry and Physics*, 16(7), 4707–4724, doi:<https://doi.org/10.5194/acp-16-4707-2016>, 2016.

Selimovic, V., Yokelson, R. J., Warneke, C., Roberts, J. M., de Gouw, J., Reardon, J. and Griffith, D. W. T.: Aerosol optical properties and trace gas emissions by PAX and OP-FTIR for laboratory-simulated western US wildfires during FIREX, *Atmos. Chem. Phys.*, 18(4), 2929–2948, doi:10.5194/acp-18-2929-2018, 2018.

Stockwell, C. E., Yokelson, R. J., Kreidenweis, S. M., Robinson, A. L., DeMott, P. J., Sullivan, R. C., Reardon, J., Ryan, K. C., Griffith, D. W. T. and Stevens, L.: Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), *Atmos. Chem. Phys.*, 14(18), 9727–9754, doi:10.5194/acp-14-9727-2014, 2014.