

Supplement for “Parameterizations of US wildfire and prescribed fire emission ratios and emission factors based on FIREX-AQ aircraft measurements”

S1 Instrumentation and emission ratios

The PTR-ToF-MS sampled air at 5 Hz through a heated (50°C), 1-m long Teflon inlet with flow rates between 0.5-2.5 L min⁻¹, corresponding to ~1 s residence time. The drift tube was operated at 2.4 mbar to maintain a drift field (E/N ratio) of 120 Td. Ambient air was periodically passed through a platinum catalyst heated to 350°C to determine the instrument background. Data were processed using the Tofware package in Igor Pro (WaveMetrics) following the recommendations by Stark et al. (2015). Each molecular formula measured by the PTR-ToF-MS represents the sum of NMOG isomers. In order to compare molecular-level emission ratios and emission factors to previous studies, we assume that isomer distributions are equivalent to those reported by Koss et al. (2018). We note that the PTR-ToF-MS used during FIREX-AQ is the same as the instrument used to quantify PTR-ToF-MS signals in Koss et al. (2018) with a longer, cooler (40°C) inlet, but similar residence times, with updated calibration factors based on calibrations performed during the campaign.

The NOAA iWAS system was operated to target high concentration fire plume samples, collected through a 1-m inlet and pressurized into electropolished stainless steel canisters. Each canister was pressurized linearly to 4.1 bar within 5-10 seconds. Within 48 hours of each flight, canisters were analysed by a two-channel GC-MS to speciate C₂-C₁₂ hydrocarbons and select oxygen-, halogen-, and nitrogen-containing NMOGs. GC retention times and quadrupole mass spectra were analysed in Igor Pro (WaveMetrics) using the TAG ExploreR and Integrator (TERN) software package in Igor Pro (Isaacman-VanWertz et al., 2017).

For the UCI Whole Air Sampling (WAS) system a total of 797 plume samples and 341 background samples were used for analysis of the 9 western wildfires and 1 prescribed burn. The background samples were taken at a comparable time and altitude as the smoke plume samples. The analysis was based on the WAS data merge, which integrates higher frequency data such as CO (1 Hz) over the WAS sampling time. The average WAS canister fill time was 26 ± 3 s for plume samples and 27 ± 4 s for background samples.

The WAS emission ratios (ERs) were calculated using the method described in Simpson et al. (2011). For each plume sample, the average background mixing ratio for a given VOC was subtracted from the plume value, and a linear fit of the excess mixing ratios was forced through zero, with CO as the reference gas (Yokelson et al., 1999). This ER calculation method was also applied during the ARCTAS and SEAC4RS missions (Liu et al., 2016, 2017; Simpson et al., 2011; Yates et al., 2016). For long-lived VOCs (lifetime > 1 d), ERs were calculated using all smoke samples. For reactive VOCs (lifetime < 1 d), ERs were calculated using samples with an estimated smoke age of less than 60 mins (smoke age calculations are described in Warneke et al., 2022). The fire-averaged ERs calculated using all smoke samples were within 0-13% of those collected based on t < 60 min, except 1,3,5-trimethylbenzene and 2-butyne which were 18% higher and 23% lower, respectively, for t < 60 min. For most plumes, the excess VOC and CO mixing ratios were well correlated (R² > 0.9). The ER for a given plume was not used when R² < 0.5, and R² values between 0.5 and 0.9 were individually inspected for reasonableness. Additional WAS results will be presented in Simpson et al. (2022). ERs for the iWAS and TOGA GC systems were calculated using a similar method. VOCs measured by PTR-ToF-MS were time synchronized to CO and a linear fit was applied using the unweighted Levenberg-Marquardt least-squares method. The slope of the fit of each VOC to CO was used to derive the ERs. In most plumes VOCs were well correlated to CO with R² > 0.9 as shown in Figure S4.

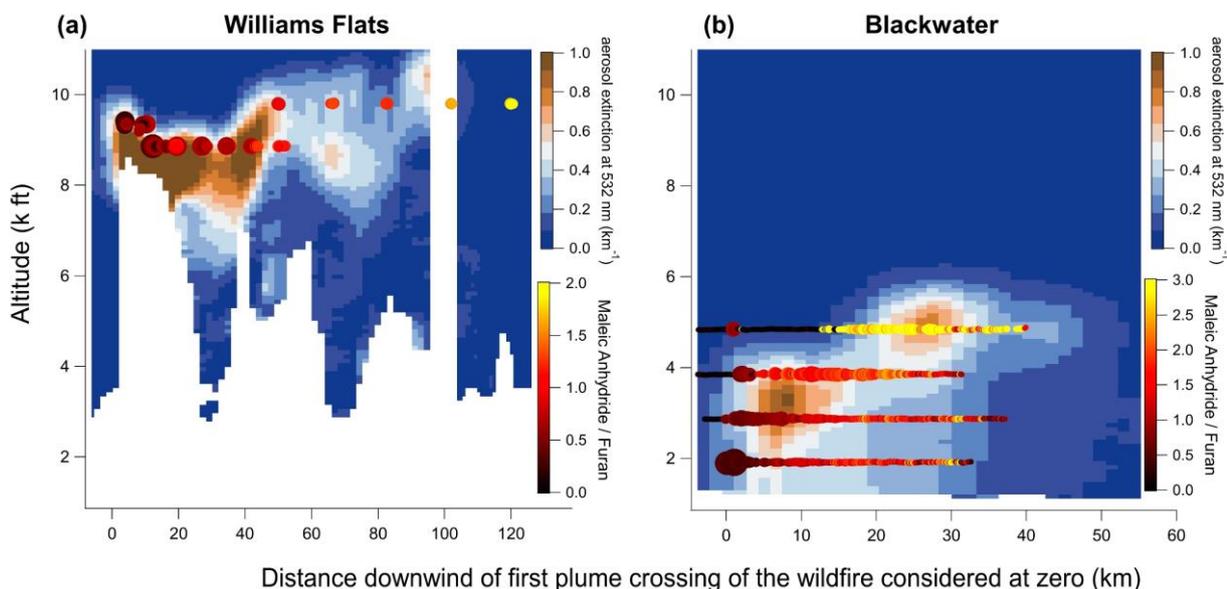


Figure S1: Plots of aerosol extinction obtained by the NASA Langley airborne Differential Absorption Lidar (DIAL) system together with the NASA DC-8 transects colored by the maleic anhydride to furan ratio and sized by CO concentration for the (a) the Williams Flats Fire on 8 August 2019 where we performed raster patterns downwind of the plume and (b) the Blackwater River Fire on 30 August 2019 where we continuously followed the plume downwind at lower altitude compared to Williams Flats where plumes often dilute faster and accelerate photochemistry.

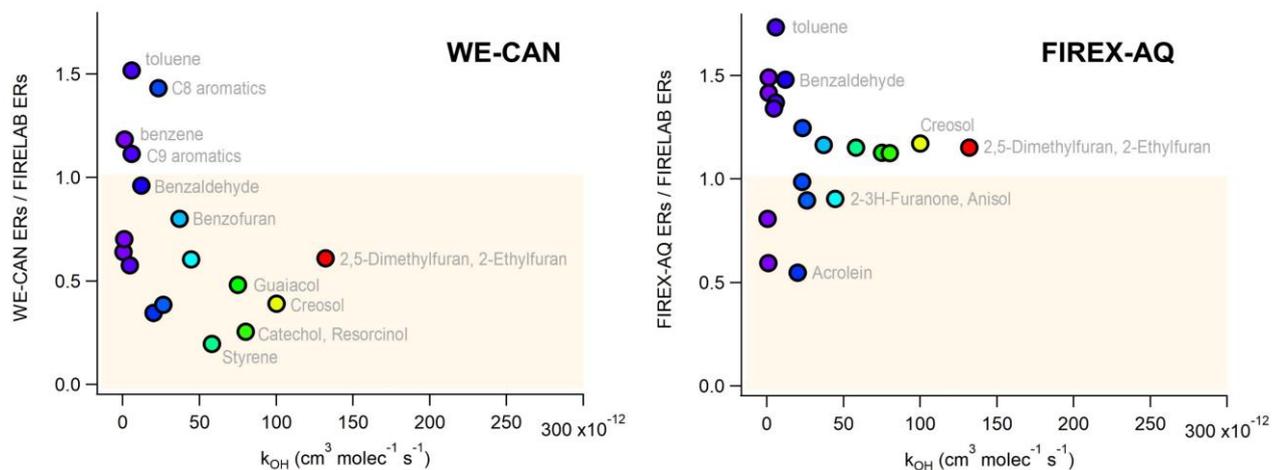


Figure S2: Ratios of campaign average ERs calculated for overlapping compounds from the WE-CAN (left panel) and FIREX-AQ (right panel) field campaign observations to ERs determined from the FireLab study color scaled by their OH reactivity. More reactive compounds had lower ERs for WE-CAN, suggesting the fire plumes studied were more aged than those studied during FIREX-AQ.

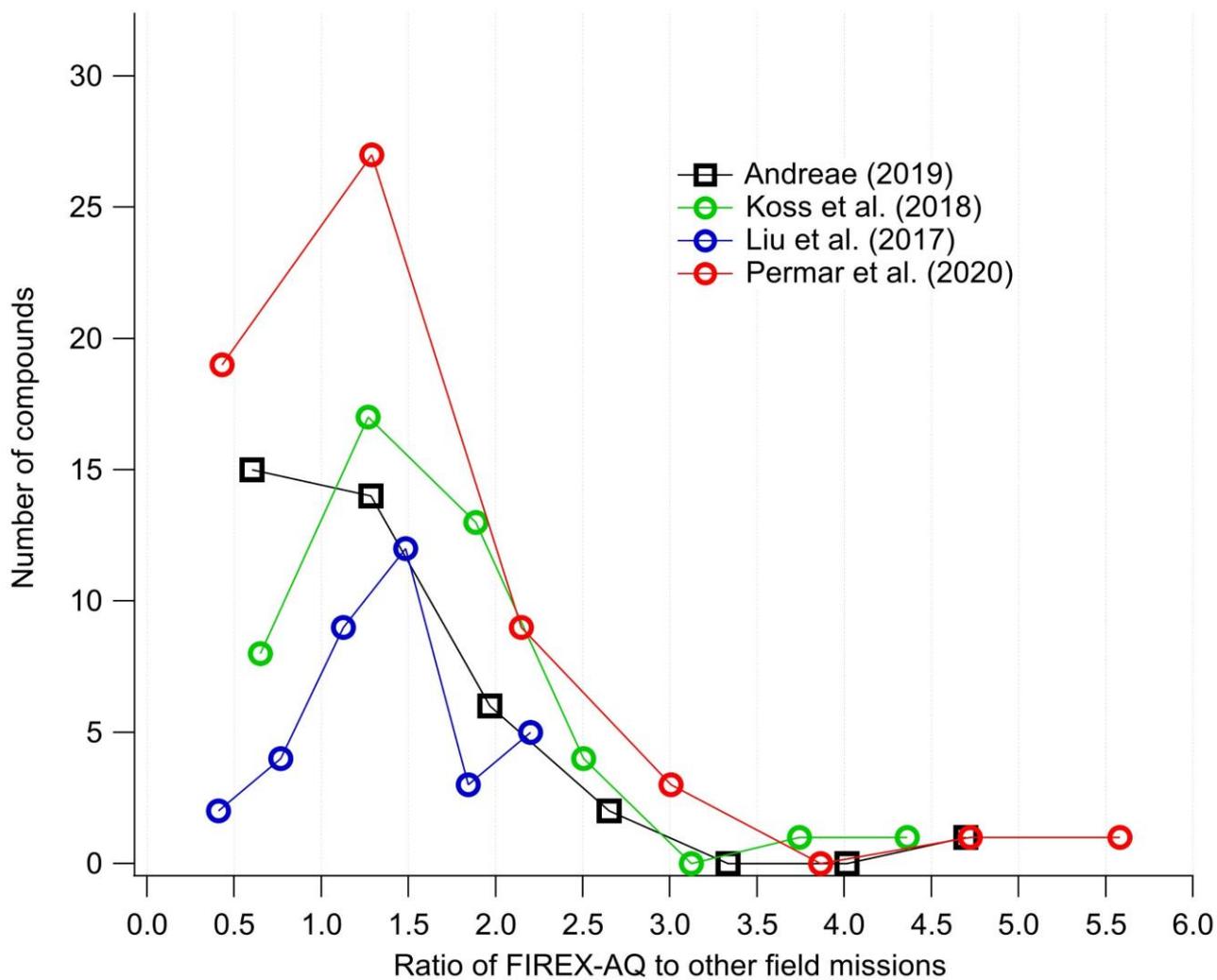


Figure S3: Histograms of the FIREX-AQ EFs ratio to other field missions.

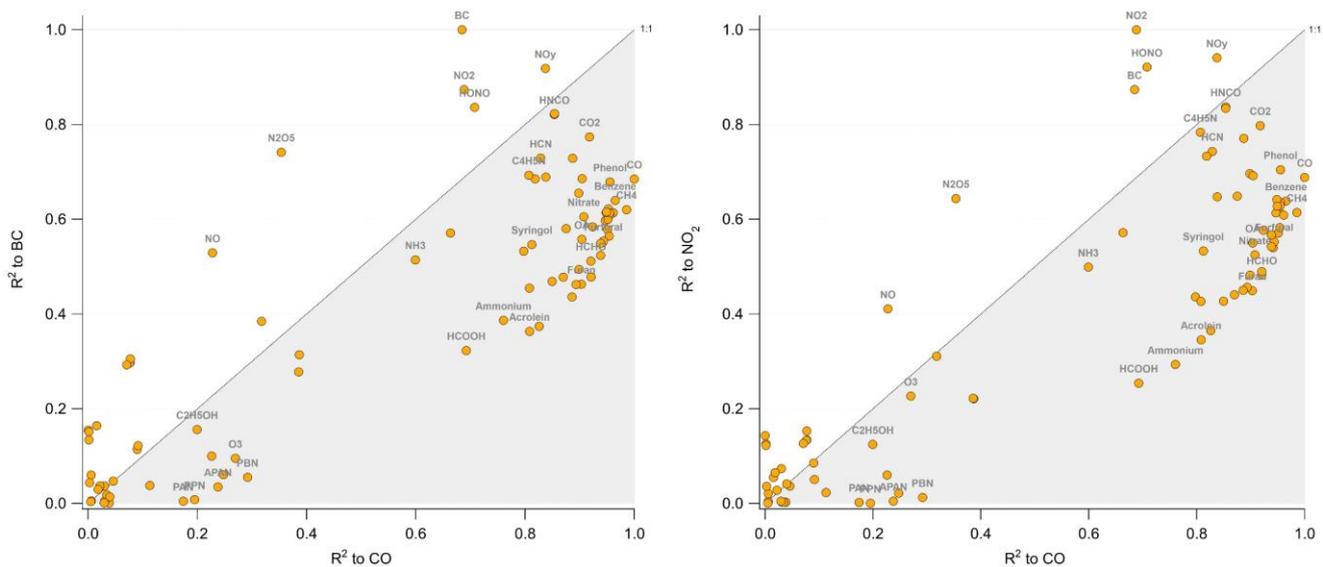


Figure S4: Relationship of the squares of correlation coefficients of gas- and particle-phase compounds/species to BC (left panel) and NO_2 (right panel) against the squares of their correlation coefficients to CO (bottom axis).

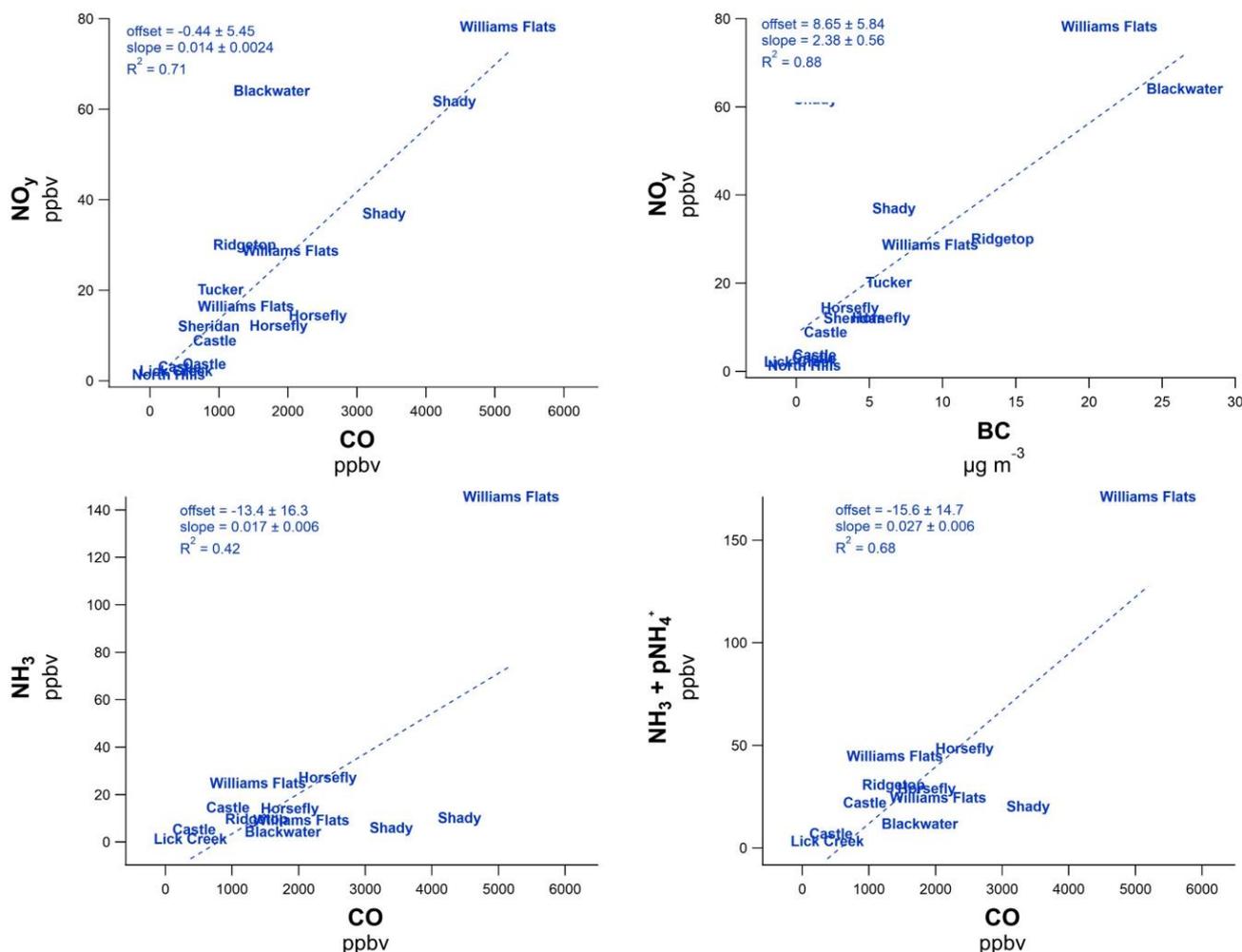


Figure S5: Correlation plots of the N-containing species to CO and black carbon. The dashed line indicates the linear fit and the name of each FIREX-AQ fire is centered on the data points.

References

- Liu, X, Y Zhang, LG Huey, RJ Yokelson, Y Wang, et al. (2016). Agricultural fires in the southeastern U.S. during SEAC4RS: Emissions of trace gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol, *J Geophys Res Atmos* 121, 7383–7414, doi:10.1002/2016JD025040
- Liu, X, LG Huey, RJ Yokelson, V Selimovic, IJ Simpson, et al. (2017). Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications. *J Geophys Res Atmos* 122, 6108-6129, doi:10.1002/2016JD026315
- Simpson, IJ, SK Akagi, B Barletta, NJ Blake, Y Choi, et al. (2011). Boreal forest fire emissions in fresh Canadian smoke plumes: C1-C10 volatile organic compounds (VOCs), CO₂, CO NO₂, NO, HCN and CH₃CN, *Atmos Chem Phys* 11, 6445-6463, doi :10.5194/acp-11-6445-2011
- Simpson, IJ, S Meinardi, B Barletta, NJ Blake, B Biggs, et al. (2022). Volatile organic compound (VOC) distributions and emissions during FIREX-AQ using Whole Air Sampling (WAS), in preparation
- Yates, EL, LT Iraci, HB Singh, T Tanaka, MC Roby, et al. (2016). Airborne measurements and emission estimates of greenhouse gases and other trace constituents from the 2013 California Yosemite Rim wildfire, *Atmos Environ* 127, 293-302, <http://dx.doi.org/10.1016/j.atmosenv.2015.12.038>

Yokelson, RJ, JG Goode, DE Ward, RA Susott, RE Babbitt, et al. (1999). Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy, *Journal of Geophysical Research: Atmospheres*, 104(D23), 30109, doi:10.1029/1999JD900817

Warneke, C., Schwarz, J. P., Dibb, J., Kalashnikova, O., et al. (2023). Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ), *Journal of Geophysical Research: Atmospheres*, 128, e2022JD037758, doi:10.1029/2022JD037758