Emissions from Western Wildfires and Southeastern Agricultural Fires: An analysis of VOC measurements from the NASA DC-8 during FIREX-AQ

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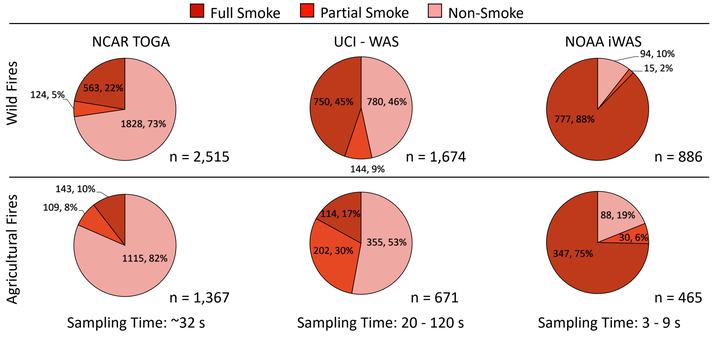
1. FIREX-AQ: Investigating regional and global impacts of biomass burning

- Fire Influence on Regional to Global Environments and Air Quality (FIREX-AQ) research project
- Investigated emissions from western wild fires and southeastern agricultural fires
- NASA DC-8 Airborne Laboratory Sampled nearly 100 unique fires in 20 US states over 2 months
- Measured VOCs with several discrete and continuous sampling instruments
  - NOAA integrated whole air sample GC-MS (NOAA iWAS/GC-MS)
  - NOAA Proton Transfer Reaction Mass Spectrometer (NOAA PTR-MS)
  - NCAR Trace Organic Gas Analyzer GC-MS (NCAR TOGA/GC-MS)
  - University of California Irvine whole air sampler GC-FID/ECD/MS (UCI WAS/GC-FID/ECD/MS)
  - CU Boulder Compact Atmospheric Multi-Species Spectrometer (CAMS)

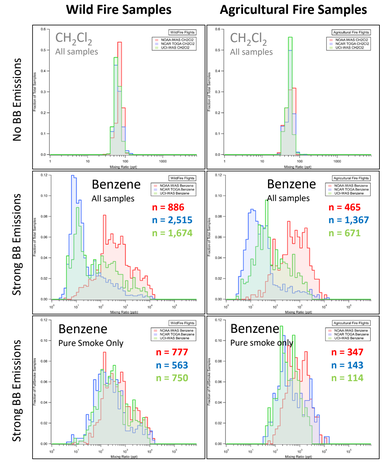
Instrument/ Parameter	NOAA iWAS/GC-MS	UCI WAS/GC-MS	NCAR TOGA GC-TOF-MS	NOAA PTR-TOF-MS	CAMS Ethane
Type of sampling	Fast-fill grab samples Electronically controlled	Grab samples Manually opened	In-situ (w/ preconc.) every 105 seconds	In-situ (no preconc.) Continuous	In-situ Continuous
Sample Acquisition	**4 to 9 (± 1) seconds** depending on altitude	**20 to 120 second** canister fill times	**~ 32 seconds**	1-10 Hz sample rate	1 Hz
Sampling Statistics	**Avg. = 69 per flt.** Max. = 72 per flt. **Total = 1510**	**Avg. = 119 per flt.** Max. = 168 per flt. **Total = 2609**	**Avg. = 250 per flt.** Max depends on flt. **Total = 4257**	Continuous	Continuous
Analysis System	Automated 2-channel GC w/ quadrupole MSD	5-channel GC w/ FID, ECD, Quad MS	1-channel GC w/ HR-TOF-MS	$H3O^+$ HR-TOF-MS *can have multiple isomers on each mass	Laser absorption spectroscopy

2. NOAA iWAS targeted plume sampling captured more full smoke samples critical for characterizing emissions and plume chemistry

- Sampling frequency and duration varied considerably instrument to instrument
- Binary smoke flags were used to determine how much of each discrete sample contained smoke as compared below in the pie charts

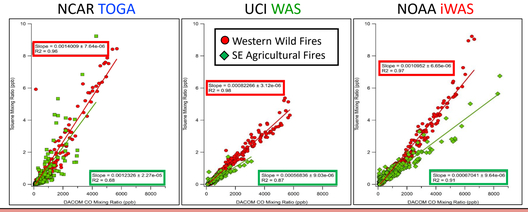


NOAA iWAS targeted plume sampling and rapid-fill canisters captured more full smoke samples than any other discrete VOC instrument even with far fewer total samples.

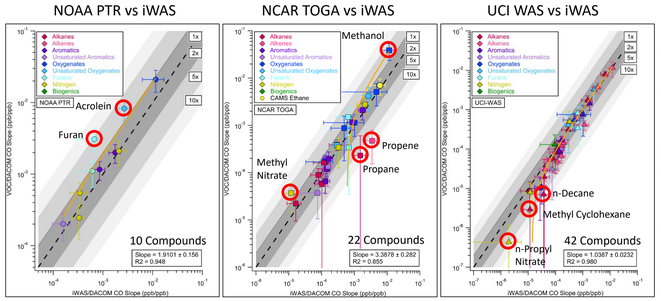


Comparison of mixing ratio distributions for WF vs. AG fires

- **TOP LEFT**: Narrow distribution (good agreement) for long-lived VOC that are not emitted from biomass burning (BB)
- **MIDDLE LEFT**: For VOCs with strong BB emissions such as benzene, the distribution spits into two modes representing the "full smoke" samples at high mixing ratios and "non-smoke" regional background values at lower mixing ratios
- **BOTTOM LEFT**: Comparing "full smoke" only samples narrows the distributions indicating an overall agreement between the various measurement techniques
- **BOTTOM**: The fast-fill, targeted iWAS samples were better able to characterize VOC composition of narrow agricultural plumes

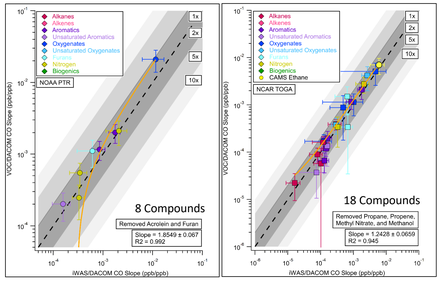


3. VOC measurement techniques agree well for most VOCs



***(Top)** All co-listed compounds compared as VOC/CO slopes for NOAA iWAS and NOAA PTR-MS, NCAR TOGA, CAMS, and UCI-WAS. Outlying compounds are shown circled in red.*

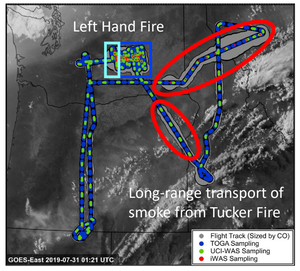
***(Bottom)** Additional comparisons for NOAA PTR-MS and NCAR TOGA with outlying compounds removed.*

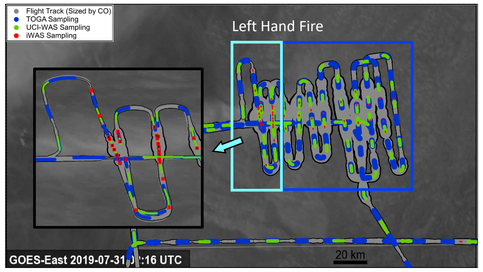


- Here we compare the VOC/CO ratios for full smoke samples only. The different sampling frequencies and durations of the NOAA iWAS, UCI, and TOGA instruments do not allow for a direct comparison
- VOC/CO slopes were compared between NOAA iWAS and NOAA PTR-MS, NCAR TOGA, CAMS, and UCI-WAS for the majority of the VOCs reported.
- There were few notable outliers in this comparison, and most were determined to be caused by known instrument or calibration issues.
- PTR-MS bias may be due to fragments and isomers that are only distinguishable with GC.

Overall there was very good agreement across all VOC/CO ratios for the various instruments

4. Higher frequency sampling improved charaterization of western wild fires and narrow southern agricultural fire plumes



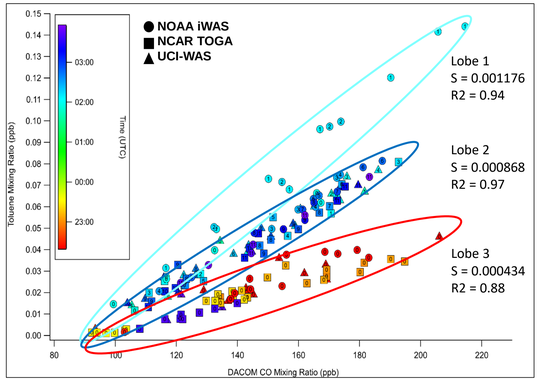


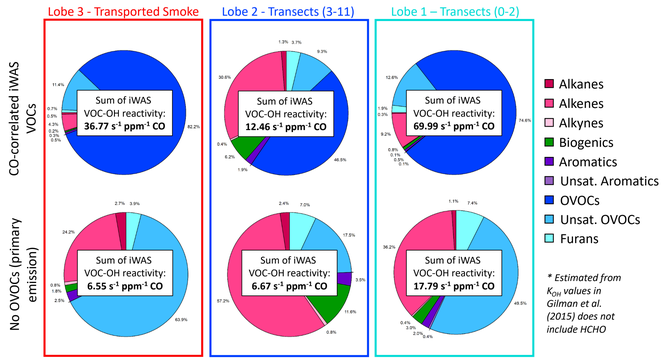
***(Left)** Flight path from 7/30 flight over Tucker and Left Hand wildfires with sampling indicators.*

***(Bottom)** Distribution of Toluene/CO mixing ratios for NOAA iWAS, NCAR TOGA, and UCI-WAS on 7/30 flight.*

***(Right)** Estimated sum of OH reactivity from iWAS VOC measurements on 7/30.*

- The NASA DC-8 sampled the Tucker Fire in Northern CA and the Left Hand Fire in WA on July 30, 2020
- Data from the NOAA PTR-MS and NOAA iWAS showed three discrete Toluene/CO ratios (right) that we attribute to rapid aging of Left Hand Fire (Lobes 1 and 2) and long-range transport of aged plume from Tucker Fire (Lobe 3)
- The freshest smoke from the Left Hand Fire (light blue markers) was not sampled by TOGA or UCI-WAS systems.
- Subsequent calculation of OH reactivity showed that each of discrete region was compositionally unique.
- Comparison of Toluene data from wild fire and agricultural portions of the study showed that NOAA iWAS better captured differences in emissions between fire type.





** Estimated from K_{OH} values in Gilman et al. (2015) does not include HCHO*

Conclusions and Future Work:

- **NOAA iWAS rapid sample collection allowed for more samples in a single plume transect and was easily able to capture full smoke samples in narrow agricultural plumes.**
- **VOC instruments generally agreed well, suggesting accurate quantitation of VOC mixing ratios.**
- **VOC ratios in smoke plumes will be used to investigate photochemical aging of biomass burning emissions.**
- **Emissions from wild fires will be compared to those from agricultural fires to explore differences and determine unique chemical signatures.**
- **Aggregated FIREX-AQ data will be used to update chemical models and emission inventories and improve our collective understanding of biomass burning influence on health and environment.**