Observations of Volatile Organic Compounds in Biomass Burning Plumes During POLARCAT/ARCTAS

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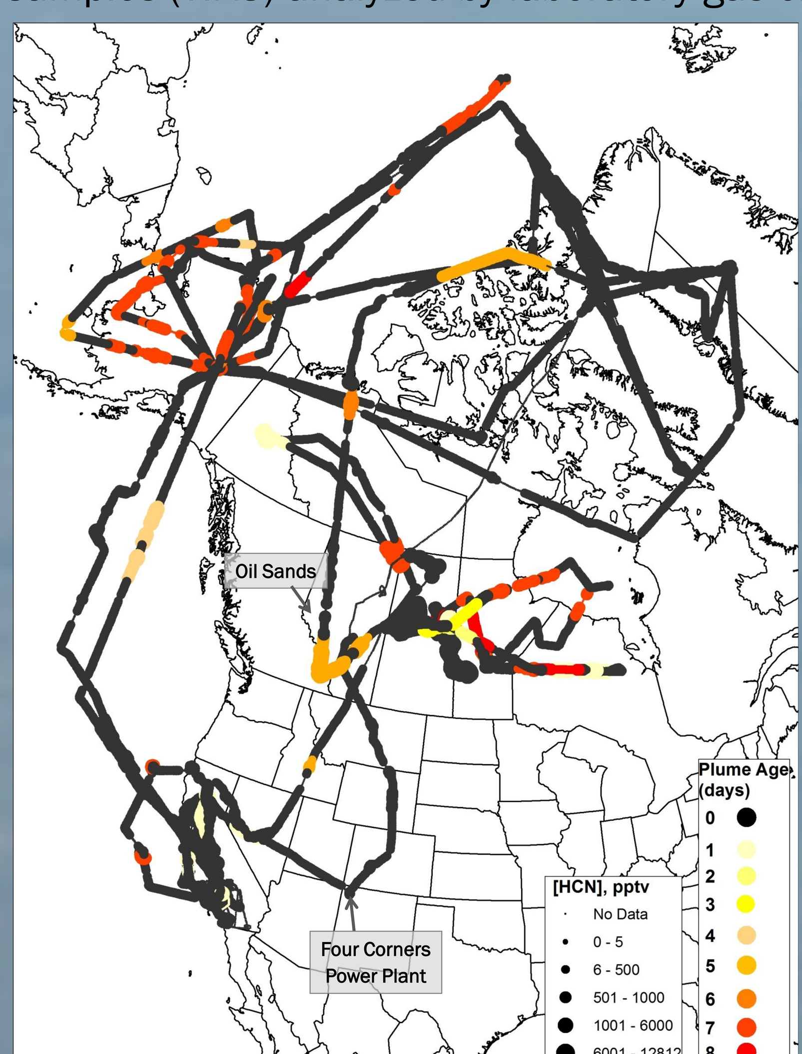
Biomass Burning Plumes

During the POLARCAT/ARCTAS study in 2008, the NASA DC-8 sampled biomass burning plumes of varying ages and origins over Alaska, the Canadian Arctic, California, and the Boreal Region of Central Canada.

Several instruments on the DC-8 made observations of volatile organic compounds (VOCs), including the Trace Organic Gas Analyzer (TOGA), a Proton-transfer mass spectrometer (PTR-MS), Chemical ionization mass spectrometers (CIMS), and whole-air samples (WAS) analyzed by laboratory gas chromatography (GC).



Biomass burning plumes were identified by elevated HCN (CIMS), acetonitrile (CH_3CN; TOGA, PTR-MS), and CO mixing ratios. Ages and origins were estimated using back trajectories and sampling location.

Figure 1. All ARCTAS flight tracks, with identified biomass burning plume encounters colored by estimated age.

VOC Intercomparisons

In general, there is very good agreement between the observations of VOCs measured by more than one instrument, as shown in these comparison plots.

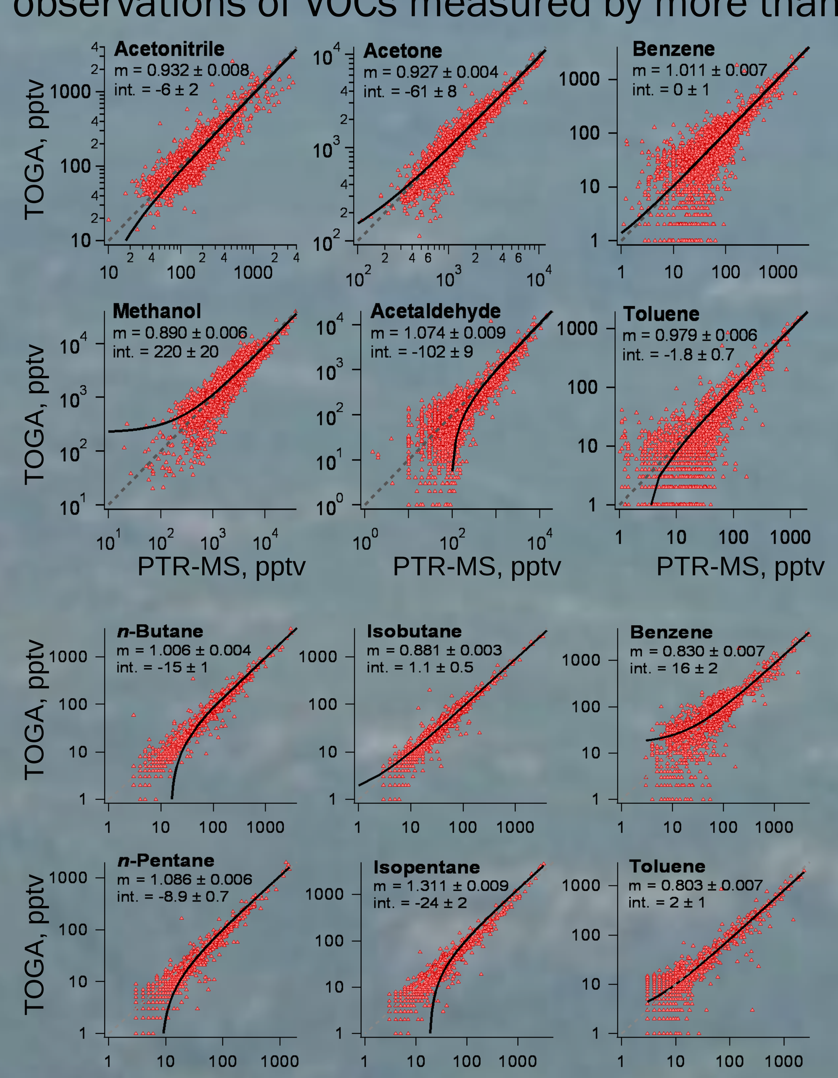


Figure 2. Plots of TOGA v. PTR-MS observations of selected VOCs (top six plots), and plots of TOGA v. WAS observations of selected VOCs (lower six plots). The solid black best-fit lines were determined using orthogonal distance regression. The dotted grey lines show $y = x$.

Ratio of Butane Isomers

The ratio [*i*-butane]/[*n*-butane] in North America is believed to be between 0.4 and 0.6 in the troposphere due to similar k_{OH} (Parrish, 1998). This implies consistent emission ratios across sources. However, emission ratios of butane isomers can vary significantly with source type. Thus, the history of an air mass should be considered when assessing the quality of observed butane mixing ratios.

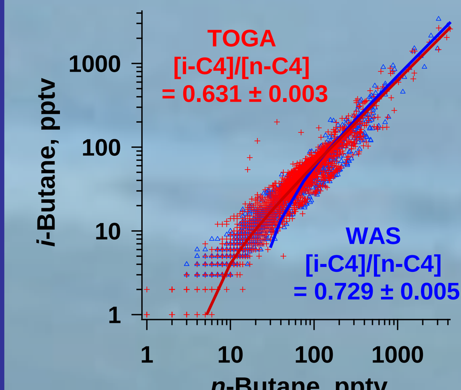
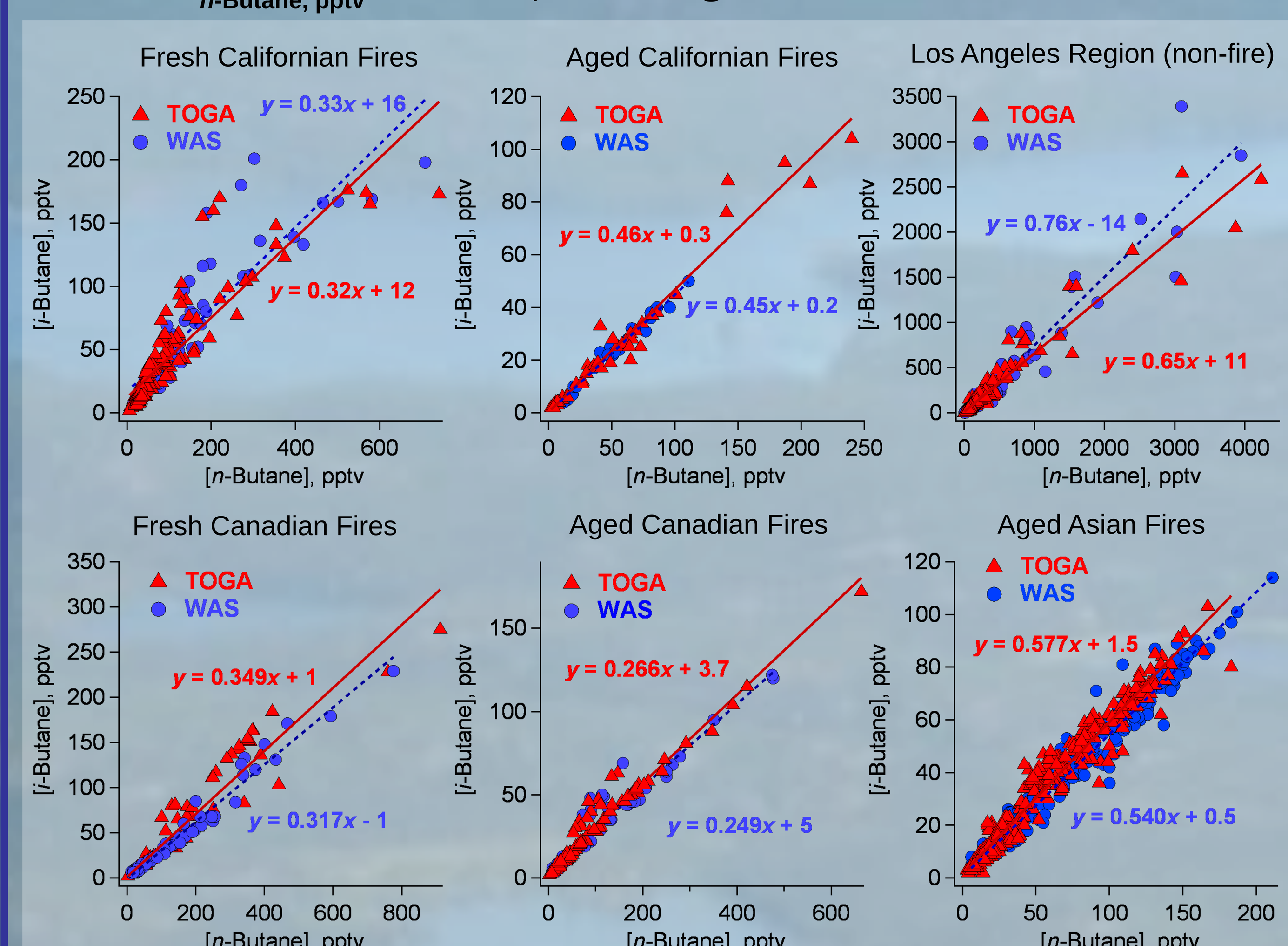


Figure 3. (left) Log-log correlation plot of butane isomers as measured by TOGA and WAS during entire ARCTAS mission.

Figure 4. (below) Plots of [*i*-C4]/[*n*-C4] from selected regions and biomass burning sources sampled during ARCTAS.



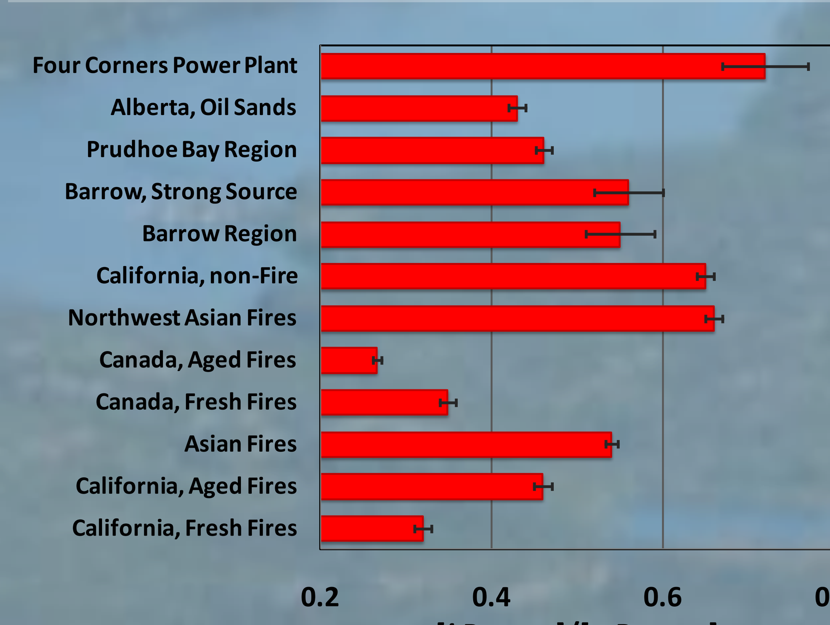


Figure 5. Ratios of butane isomers in selected regions and from various biomass burning source regions as measured by TOGA. Error bars are the standard errors in the slopes of the data (see Figure 4 plots above).

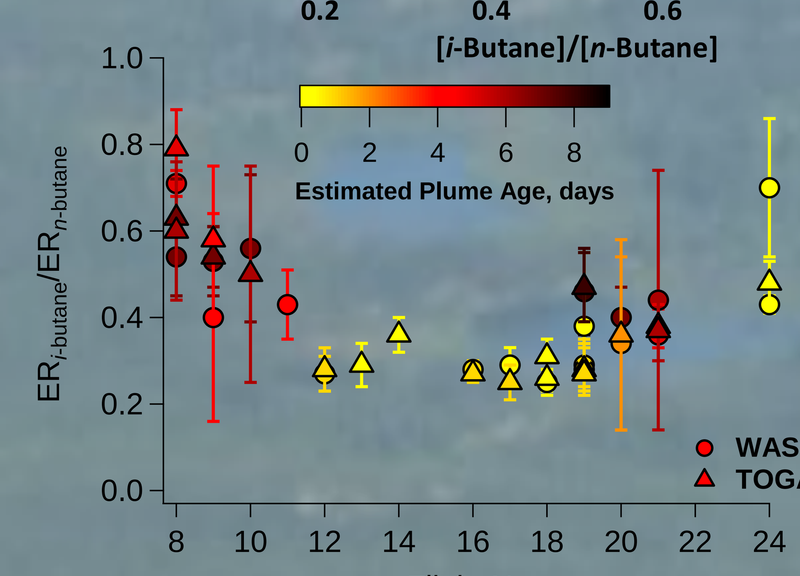


Figure 6. Ratios of butane isomers *Enhancement Ratios* (ERs) from biomass burning plume encounters, colored by the estimated age of the biomass burning plume.

D. D. Parrish *et al.*, J. Geophys. Res. 103, 1998.

Enhancement Ratios

Using data from the biomass burning plume encounters, we determined enhancement ratios, ER (ΔVOC/ΔCO), for selected VOCs in individual fire plumes. Although ERs of some VOCs vary significantly between plumes of different ages or origins, there is generally good agreement between the measurement instruments for plume-specific ERs.

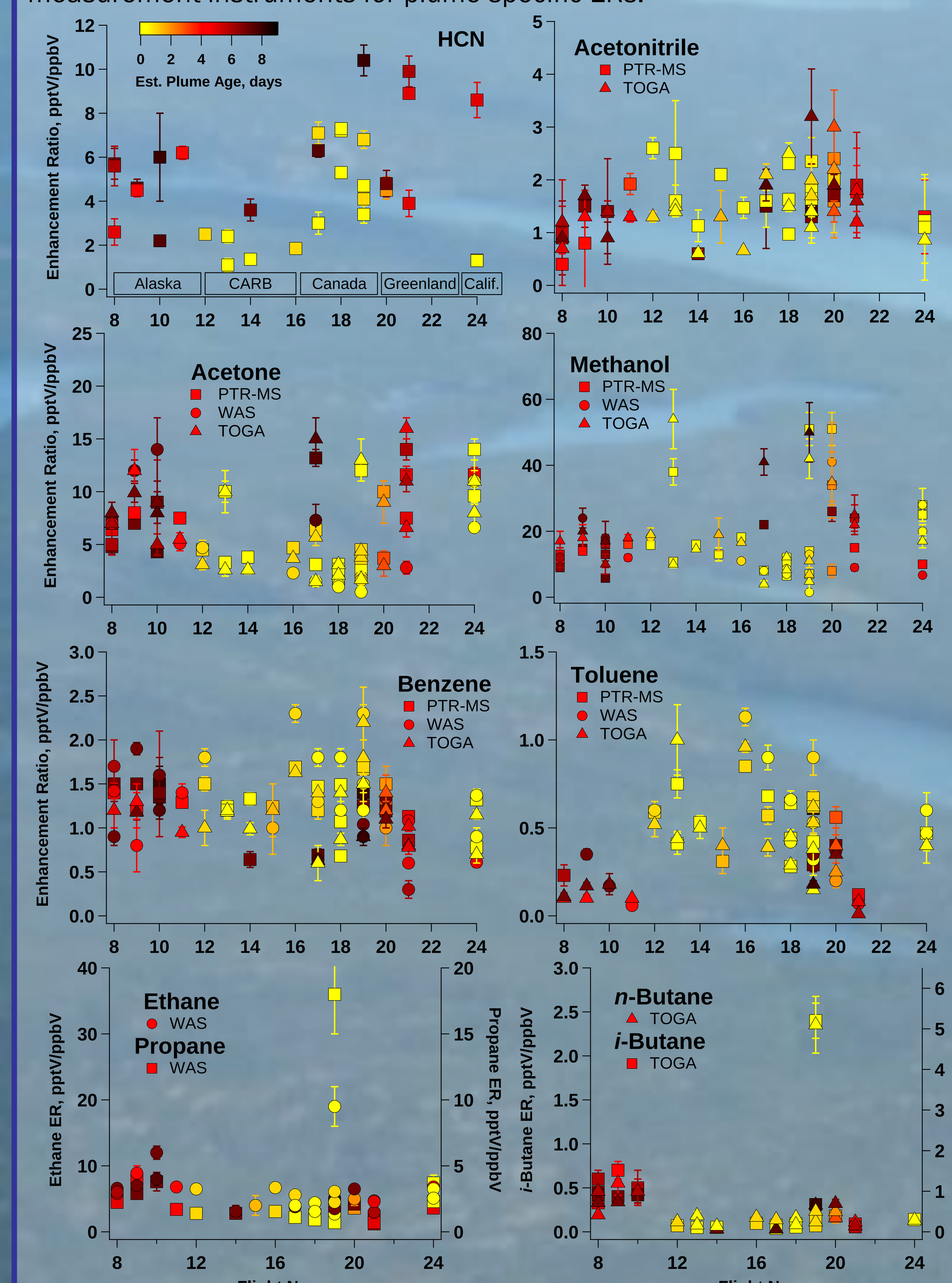


Figure 7. Observed VOC enhancement ratios versus CO for individual plume groups by flight and colored by estimated plume age.

Literature Enhancement Ratios (ΔVOC/ΔCO, ppt/ppb)

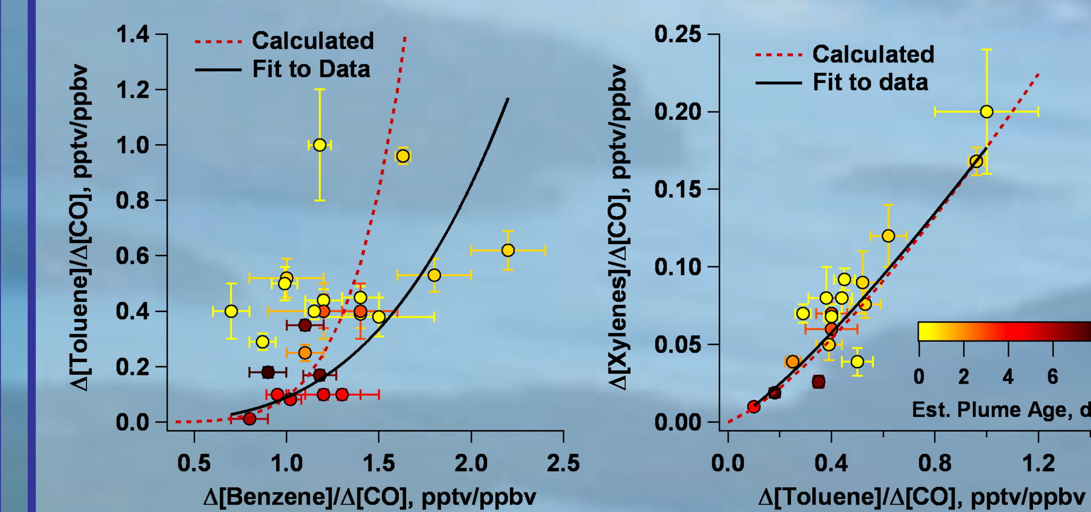
Compound	Ethane	Propane	n-Butane	i-Butane	Benzene	Toluene	HCN	CH_3CN	Methanol	Acetone
Friedli	4.3	0.825	0.19	0.055	1.15	0.55				
Christian							0.5-5.3			
de Gouw					0.80-1.41	0.06-0.44		1.2-3.2	2-21	2.9-22.8
Duck								1.51		
Jost	3.0-4.4	0.6-0.8	0.17-0.2	0.06-0.07	0.72-1.2	0.73-0.82		3.7-4.1		3.6-5.1
Yokelson					3.4		3.2-15.2	4.3	25.4	6.6

T. J. Christian *et al.*, J. Geophys. Res. 112, **2007**. J. A. de Gouw *et al.*, J. Geophys. Res. 111, **2006**. T. J. Duck *et al.*, J. Geophys. Res. 112, **2007**. H. R. Friedli *et al.*, Glob. Biogeochem. Cyc. 15, **2001**. C. Jost *et al.*, J. Geophys. Res. 108, **2003**. R. J. Yokelson *et al.*, Atmos. Chem. Phys. 9, **2009**.

Processing v. Emission Profiles

It has been shown previously that the extent of photochemical processing a biomass burning plume has undergone can be inferred from plots of VOC ERs as a function of ERs of a reference VOC (de Gouw, 2006), based on

$$\left(\frac{\Delta VOC}{\Delta CO}\right) = \text{constant} \times \left(\frac{\Delta ref}{\Delta CO}\right)^{\frac{k_{VOC}-k_{CO}}{k_{ref}-k_{CO}}}.$$



$(k_{toluene} - k_{CO})/(k_{benzene} - k_{CO})$		$(k_{ethylbenzene} - k_{CO})/(k_{toluene} - k_{CO})$	
Calculated (298 K)	From Fit	Calculated (298 K)	From Fit
5.50	3.26 ± 0.08	1.30	1.22 ± 0.05

Figure 8. Observed VOC ERs versus CO, plotted as a function of a reference VOC's observed ERs.

This principle does not appear to hold for observed ERs of light alkanes (below). This is likely due to the variability of emission ratios of light alkanes versus CO from biomass burning. However, there are strong indications of linear correlations between observed alkane enhancement ratios with CO that are independent of plume age and most likely due to correlated emission profiles from fires.

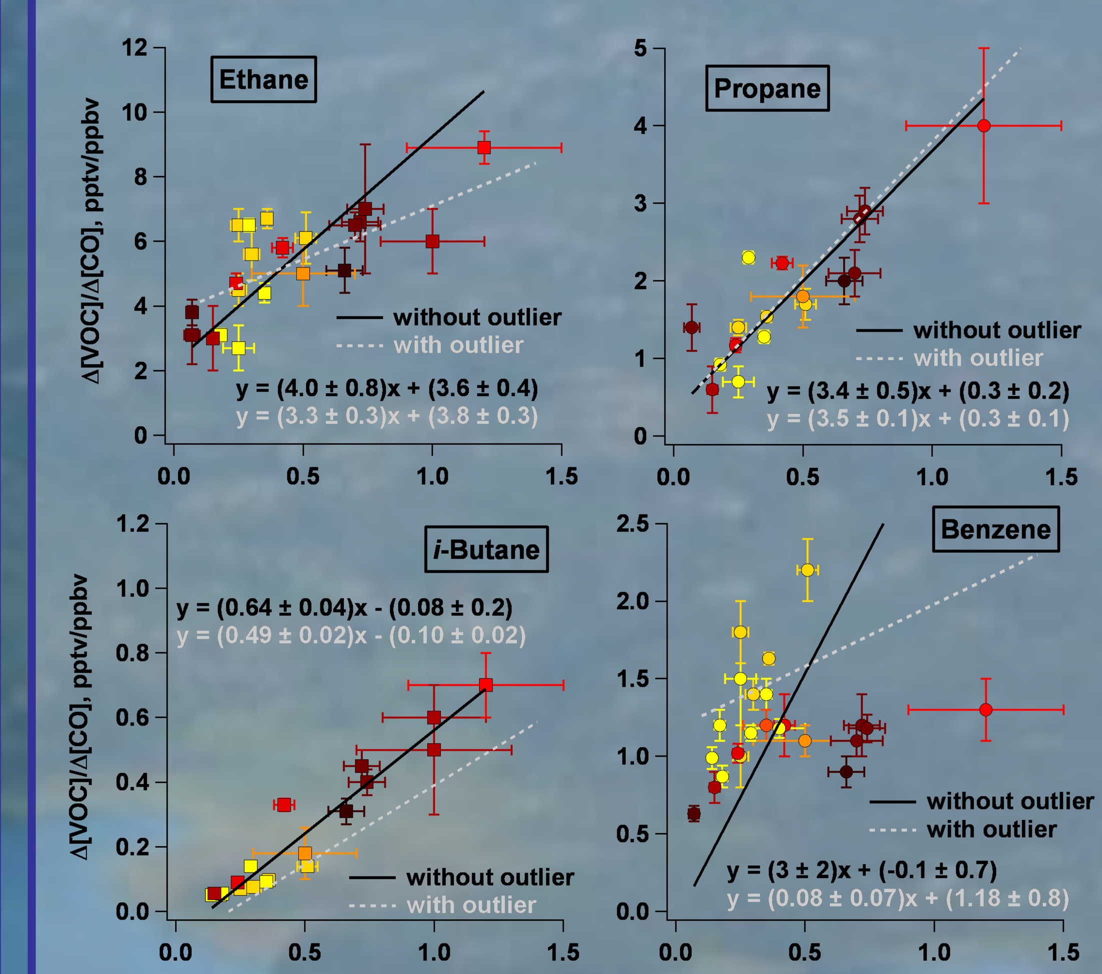


Figure 9. Observed VOC enhancement ratios versus CO, as a function of *n*-butane versus CO. The alkane ER outlier value from Flight 19 is not shown for clarity, although an orthogonal distance regression fit to the data was performed with and without the outlier and both results are included on the plots.