Emissions of volatile organic compounds (VOCs) from wildfires and agricultural burning in the United States during SEAC^{4}RS

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Robert J Yokelson[2], Glenn S Diskin[3], and many other SEAC^{4}RS colleagues

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Introduction

- The NASA SEAC^{4}RS mission was flown in late summer 2013 and focused on the southeast US (**Fig. 1**).
- The UC Irvine group collected 2818 whole air samples aboard the NASA DC-8 aircraft during 21 flights (**Fig. 2**). Each air sample was analyzed at UC Irvine using multi-column gas chromatography for 70 compounds:
  - **Carbon dioxide (CO_2)**
  - **Carbon monoxide (CO)**
  - **Methane (CH_4)**
  - **Carbonyl sulfide (OCS)**
  - **27 Halocarbons**
  - **30 Hydrocarbons (NMHCs)**
  - **8 Organic nitrates**
  - **Dimethyl sulfide (DMS)**
- During the mission the DC-8 purposely sampled 16 agricultural fires and 5 wildfires (**Table 1**). Here we present normalized excess mixing ratios (NEMRs) calculated for the fires. These results are preliminary.

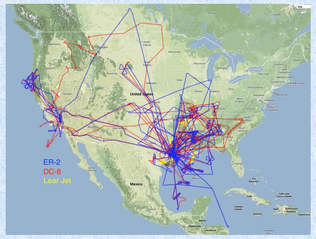


Figure 1. SEAC^{4}RS flight tracks.

Photo credit: Kent Shiffer

Figure 2. Field operations aboard the NASA DC-8 aircraft during the SEAC^{4}RS mission.

Fires sampled during SEAC^{4}RS

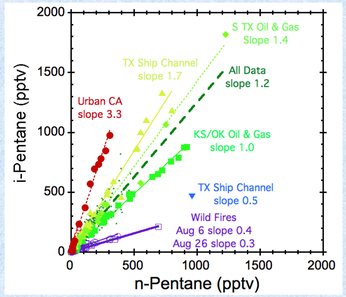
Table 1. Agricultural fires (AG) and wildfires (WF) purposely sampled by the DC-8 during SEAC^{4}RS.

Fire type	Location	Lat (°N)	Lon (°W)	Flt: Date	Peak CO*	Comments
WF-01	OR	41.41	123.63	1: Aug 6	1250 ppb	Forks Complex fire
WF-02	OR	41.87	123.80	1: Aug 6	2436 ppb	Big Windy Complex fire
WF-03	CO	38.21	103.71	5: Aug 16	310 ppb	Colorado fire
WF-04a	ID/WY	44.51	104.43	6: Aug 19	392 ppb	Wyoming fire
WF-04b	KS	37.76	99.11	6: Aug 19	408 ppb	7-10 smoke layers
WF-05	CA	38.15	119.92	9: Aug 26	6031 ppb	Rim fire; well-mixed plume
" "	CA/MT	46.66	113.64	10: Aug 27	968 ppb	Aged Rim fire; ID/MT fires
AG-01	MO	36.83	89.71	14: Sep 6	860 ppb	Single pass (source→ d/wind)
AG-02	LA	32.48	91.86	15: Sep 9	537 ppb	Cross-plume
AG-03	LA	32.35	91.98	15: Sep 9	2210 ppb	Multiple passes
AG-04	AR	36.06	90.90	16: Sep 11	1010 ppb	Long axis (source→ downwind)
AG-05	AR	35.74	90.00	18: Sep 16	485 ppb	Two passes
AG-06	AR	35.66	90.07	18: Sep 16	234 ppb	Possibly aged smoke
AG-07**	AR	35.56	90.18	18: Sep 16	515 ppb	New fire
AG-08**	AR	35.52	90.24	18: Sep 16	435 ppb	Very small fire
AG-09	AR	34.39	90.72	18: Sep 16	265 ppb	New fire
AG-10	MS	33.84	90.84	18: Sep 16	188 ppb	New fire
AG-11	MS	33.78	90.88	18: Sep 16	254 ppb	New fire
AG-12**	MO	36.56	90.21	21: Sep 23	290 ppb	Small fire
AG-13	MO	36.47	90.11	21: Sep 23	857 ppb	Brief but high concentrations
AG-14	AR	36.31	90.58	21: Sep 23	1605 ppb	Multiple passes
AG-15	AR	35.68	91.22	21: Sep 23	239 ppb	Long axis (source→ downwind)
AG-16	AR	36.02	90.85	21: Sep 23	1467 ppb	Multiple passes

* Peak CO values are based on DACOM data from the WAS merge, except Flight 1 which is UCI data from the WAS merge.
** AG fires 7, 8 and 12 were not sampled by WAS. The CO values are based on higher time resolution DACOM peaks.

Biomass burning source signatures

- **Biomass burning is identified by enhancements of combustion tracers such as CO, HCN, ethene, benzene and *n*-butane (Figs. 5, 6) and by hydrocarbon ratios (Fig. 3).** In principle the ratio of hydrocarbon pairs with similar lifetimes is preserved as the air mass ages.
- *i*-Pentane is a tracer for gasoline evaporation. The *i*-pentane/*n*-pentane ratio is roughly 0.5 for biomass burning[1], 0.9 for natural gas emissions[2], and 3.8 for gasoline evaporation[3] (**Fig. 3**).
  Refs: (1) Simpson et al., ACP, 11, 2010; (2) Gilman et al., ES&T, 47, 2013; (3) *McGaughey et al., AE, 38, 2004.*
- Benzene is a combustion tracer and propane is an oil and gas tracer. During SEAC^{4}RS the benzene/propane ratio was roughly 1.0 for biomass burning and 0.007 for oil and gas sources.



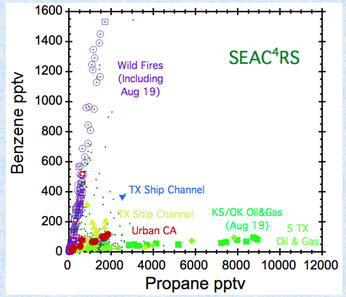


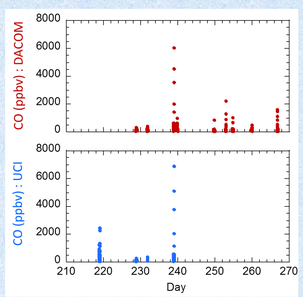
Figure 3. Hydrocarbon ratios encountered for different sources during the SEAC^{4}RS mission.

Definitions: NEMR, EnR, ER, EF

- ***Excess mixing ratio of species X:*** $\Delta X = X_{plume} - X_{bkgd}$ (decreases with plume age due to dilution*)
- ***Normalized excess mixing ratio (NEMR)*** or **enhancement ratio (EnR)**: $\Delta X/\Delta Y$ (Y is a reference species)
- ***Emission ratio (ER):*** The initial value of $\Delta X/\Delta Y$ at the source*
- ***Emission factor (EF):*** g of X released per kg of fuel burned

* *Yokelson et al.* (AMT, 2013) caution that changes in the composition of background air as the plume dilutes can affect the NEMR.

- Here NEMRs were calculated using CO as the reference compound. DACOM CO data were available for all flights considered here except Flight 1. For that flight we use UCI CO data, which agree with DACOM to within 10% (**Fig. 4**). EFs will be calculated in on-going work.
- Excess mixing ratios in the fire plumes were calculated by subtracting off the average background mixing ratio from each plume mixing ratio, as in *Simpson et al.* (ACP, 2011). Linear fits to the excess mixing ratio plots were forced through zero to give the NEMR (**Figs. 5, 6**).



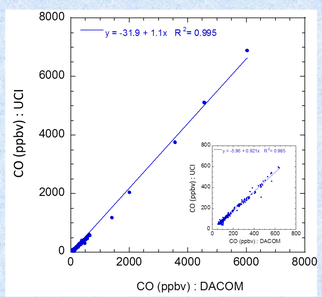


Figure 4. CO mixing ratios measured by **UCI** and **DACOM** during SEAC^{4}RS flights that encountered fires.

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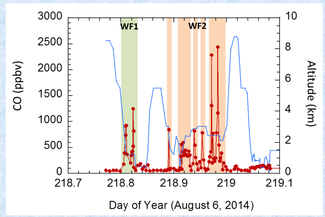
Wildfire NEMRs

- Work to calculate NEMRs and EFs for the compounds measured by UCI is on-going. Here we present selected NEMRs for compounds measured by UCI during Flight 1 (WF 1-2).



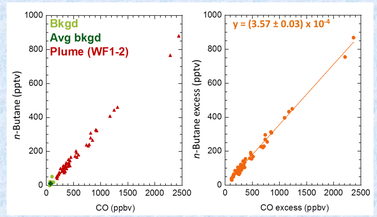
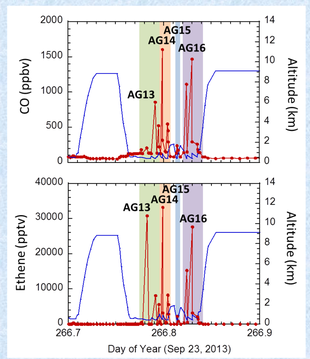


Figure 5. Mixing ratios of CO for Wildfires 1-2, flown on August 6, 2013 (see **Table 1**). The plume and background samples were collected at roughly similar altitudes within the planetary boundary layer (plume: 0.74-3.01 km; bkgd: 0.37-3.10 km). (***Right***) NEMR calculations using *n*-butane as an example.

Agricultural fire NEMRs



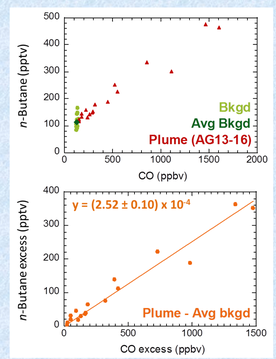


Figure 6. (***Left***) Mixing ratios of CO and ethene for Agricultural Fires 13-16, flown on Sept. 23, 2013 (UCI did not sample AG-12). The smoke and background samples were collected at similar altitudes within the planetary boundary layer (0.38-1.21 km). (***Right***) NEMR calculations using *n*-butane as an example.

Table 2. Wildfire and agricultural fire NEMRs for selected UCI compounds measured during SEAC^{4}RS.

Fire	Compound	Lifetime	Precis. (%)	Bkgd avg. (pptv) ± 1σ	Plume avg. (pptv) ± 1σ	Plume max.	NEMR to CO (ppbv/ppbv) ± 1σ
WF:1-2	Ethane	2-3 mo	1%	494 ± 127	4033 ± 3347	17870	(7.31 ± 0.05) x 10^{-3}
WF:1-2	Ethene	1-2 d	3%	34 ± 29	3668 ± 4470	21610	(8.53 ± 0.19) x 10^{-3}
WF:1-2	Ethyne	2 wk	3%	68 ± 50	1383 ± 1117	5764	(2.58 ± 0.03) x 10^{-3}
WF:1-2	Propene	11 hr	3%	11 ± 13	654 ± 1064	5168	(1.77 ± 0.08) x 10^{-3}
WF:1-2	*n*-Butane	5 d	3%	12 ± 13	184 ± 164	880	(3.57 ± 0.03) x 10^{-4}
WF:1-2	Benzene	1-2 wk	3%	23 ± 16	807 ± 811	4095	(1.69 ± 0.02) x 10^{-3}
WF:1-2	CH_3Cl	1 yr	5%	562 ± 27	644 ± 91	1049	(1.77 ± 0.07) x 10^{-3}
AG:13-16	Ethane	2-3 mo	1%	1174 ± 119	3819 ± 3153	10820	(6.68 ± 0.30) x 10^{-3}
AG:13-16	Ethene	1-2 d	3%	61 ± 19	7086 ± 9620	33210	(1.93 ± 0.09) x 10^{-2}
AG:13-16	Ethyne	2 wk	3%	179 ± 19	2237 ± 2818	10470	(5.57 ± 0.35) x 10^{-3}
AG:13-16	Propene	11 hr	3%	8 ± 5	1821 ± 2465	7963	(4.99 ± 0.17) x 10^{-3}
AG:13-16	*n*-Butane	5 d	3%	113 ± 25	216 ± 114	476	(2.52 ± 0.10) x 10^{-4}
AG:13-16	Benzene	1-2 wk	3%	35 ± 6	560 ± 708	2465	(1.43 ± 0.06) x 10^{-3}
AG:13-16	CH_3Cl	1 yr	5%	457 ± 13	1486 ± 1375	5849	(2.68 ± 0.22) x 10^{-3}
AG:13-16	OCS	2.5 yr	2%	361 ± 17	449 ± 71	614	(1.74 ± 0.17) x 10^{-4}