

# Hydrocarbons and halogenated hydrocarbons over the Southern California Air Basin and the California Central Valley during the CalNex-2010 mission

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## Introduction

The CalNex 2010 mission was designed to examine emissions, chemical transformations, climate processes, transport, and meteorology in California. Objectives included improving emission inventories of greenhouse gases, traditional air pollutants and ozone and aerosol precursors. The NOAA P-3 aircraft was one of the platforms used during the study, which took place during May and June, 2010. Flights covered the Southern California Air Basin, the California Central Valley, and the nearshore ocean atmosphere. This poster presents measurements from a whole air sampler, which was part of the P3 instrument payload. The sampler collected approximately 72 samples per flight. Gases measured from these samples include a wide range of natural and anthropogenic hydrocarbons, halogenated hydrocarbons, organic nitrates, and selected sulfur species. These measurements provide information on emission sources and intensity, on chemical transformations in the atmosphere, and help trace air mass transport and processing.

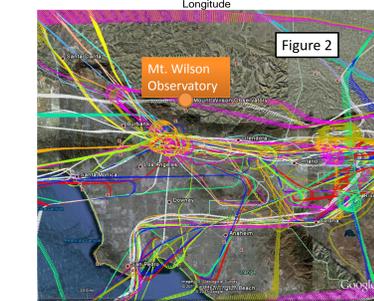
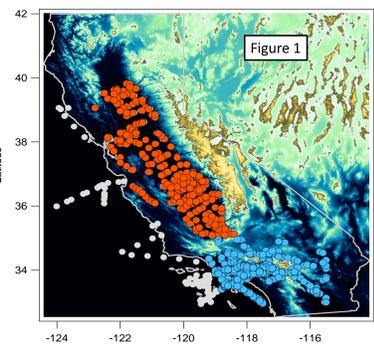
In this poster, we focus primarily on emissions of halocarbon or hydrocarbon gases. For most gases measured here, emissions are strongest in the Southern California region and around Los Angeles. We compare the statistics of trace gas concentrations in a broad regional perspective, i.e., Southern California vs. the rest of California. Then we examine the correlation of carbon monoxide with halocarbon gases as a first step toward calculating emissions from the Southern California Air Basin. A companion poster (Barletta et al.) evaluates emissions of major hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) from the same data set. This poster examines other halocarbon emissions that are relevant to evaluating global budgets of restricted compounds (e.g. methyl chloroform) or which provide a source of reactive organic halogens to the atmosphere (e.g., chloroform, tetrachloroethylene, bromoform). We compare the measurements from the P3 with similar measurements obtained at the Mt. Wilson ground site and with other measurements around the Southern California area and with other urban emission in the US and abroad.

## Statistics and Comparisons

For a broad comparison of trace gas mixing ratios in different regions of California, Table 1 summarizes the statistics for selected samples in the Southern California region (nearshore+land, < 35N, < 2000 m altitude), in the Northern California region (land > 35N, < 2000 m altitude), and an estimate of the background based on offshore samples collected during CALNEX. Though not shown here, the background estimates for CALNEX are in good agreement with measurements from the AGAGE station at Trinidad Head and from measurements of the HIPPO - 3 mission (April/May, 2010) from the central Pacific. Similarly, median and average trace gas mixing ratios from the NoCAL samples are close to the background values. Occasional high concentrations are associated with local emissions (e.g. methyl bromide, perchlorethylene, HCFCs, HFCs), but these emissions have little effect on the average.

A comparison of average trace gas concentrations between SoCAL, where emissions are strongest, and NoCAL is summarized in Figure 4. In this comparison, mean concentration ratios greater than about 1.10 typically indicate significant emissions from the SoCAL region. As shown the probability distributions in Figure 5, concentrations in approximately 30 - 40% of the samples are equivalent between NoCAL and SoCAL. The remaining higher mixing ratios in SoCAL appear to represent a different population of samples. Due to this distribution, the impact on the mean (or median) concentration is relatively small, even when significant emissions are encountered. Thus, for halocarbons, large enhancements are measured for chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, and (somewhat surprisingly) bromodichloromethane, dibromochloromethane, and bromoform. These latter three gases are commonly found from marine emissions, but here they are present in different ratios compared to normal marine ratios (Figure 6). Emissions from treated waters containing bromide ion and dissolved organic matter is a possible source.

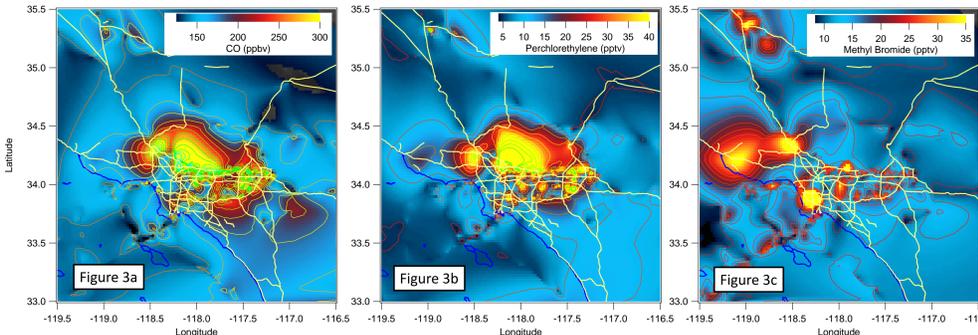
As expected all hydrocarbons (except isoprene), are significantly enhanced in the SoCAL samples. This leads to similar enhancements in alkyl nitrates, which are photochemical products of hydrocarbon oxidation. Enhancements in hydrocarbons and alkyl nitrates are found to be related to atmospheric reactivity and source emission pattern. In general, the NoCAL samples represent more photochemically aged air masses.



## Sample Locations/Distributions

Samples for this analysis were selected by altitude and region. All samples collected below 2000m were selected. Excluding most offshore samples, the region was divided at 35N latitude into 2 groups ("SoCAL" =<35N (=604 samples), and "NoCAL" =>35N (=318 samples)). These are shown as red circles (=NoCAL) and blue circles (=SoCAL) on Figure 1 (left). Data are also shown from samples (N=120) collected at the Mount Wilson Observatory. Figure 2 shows the location of the site with an overlay of flight tracks of the P3B aircraft. Upslope flow reaching the site typically represents a mixture of Los Angeles urban emissions.

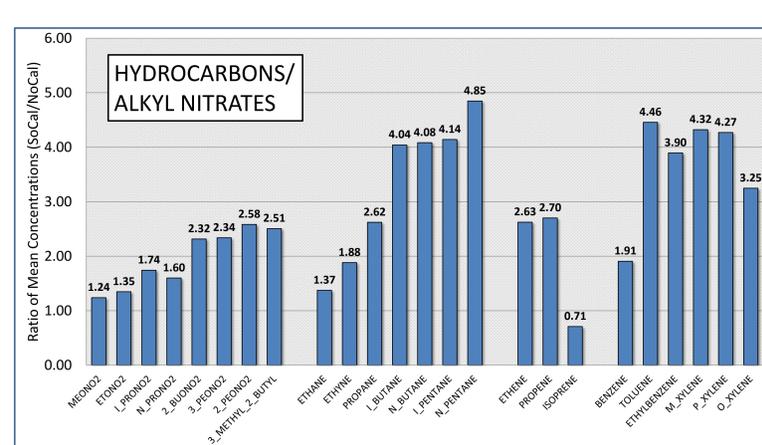
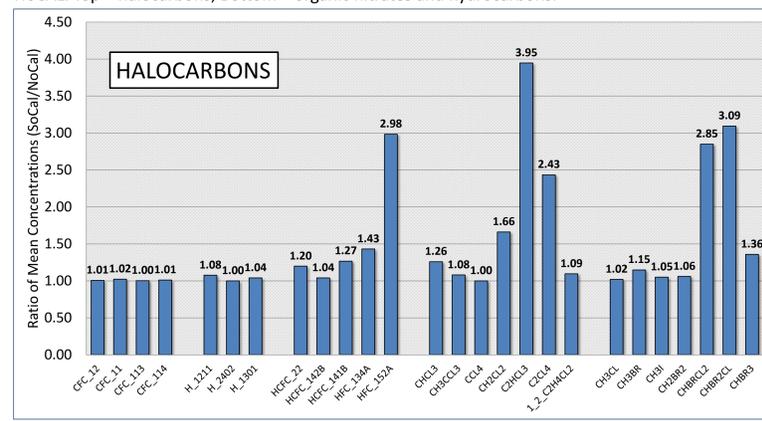
Tracer correlation analysis is commonly used to estimate emissions of one gas/aerosol from its correlation with a second gas whose emission rate is well defined. For gases with primarily urban emissions, carbon monoxide is most often the "reference gas", and that is what we do here. The technique is most straightforward when relating emissions from a common source process (e.g., biomass burning, automobile exhaust, etc.). However, the technique has also been applied to estimate emissions for different source processes from a common region. Multiple point sources are mixed with more area-wide sources to produce a general correlation between chemical emissions, though unmixed single point sources can be sampled from the aircraft. Treatment of these point sources in the tracer correlation analysis adds some uncertainty to the results. For most of the gases discussed here, there is a good spatial correlation with the distribution of the reference gas (e.g. compare Fig 3A and 3B). Some other gases show a stronger influence of point sources unrelated to the urban "background", and tracer correlation analysis is more complex in these cases. See for example the comparison between methyl bromide (Fig. 3c) versus CO (Fig. 3a).



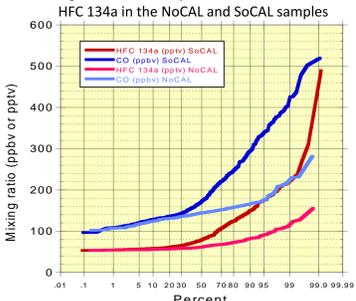
**Table 1.** Statistical summary of halocarbons, hydrocarbons and alkyl nitrates by region for samples < 2 Km altitude. Background is derived from offshore samples.

Compound	Southern California <35N					Northern California >35N					Background/CALNEX					
	N	Min	Max	Median	Std.Dev.	N	Min	Max	Median	Std.Dev.	Median	Mean	Std.Dev.			
CFC-12	604	526	589	536	539	318	525	546	535	535	534	535	6			
CFC-11	604	239	468	248	252	318	239	260	246	246	245	245	3			
CFC-113	604	75.3	86.3	77.8	78.0	318	75.5	81.3	77.8	77.8	77.8	77.8	1.0			
CFC-114	604	15.9	17.6	16.3	16.4	318	15.9	17	16.2	16.2	16.2	16.3	0.3			
H-1211	604	4.13	16.15	4.51	4.68	0.83	318	4.12	5.33	4.33	4.35	4.35	0.13			
H-2402	604	0.46	0.48	0.47	0.47	0.00	318	0.46	0.477	0.47	0.5	0.5	0.0			
H-1301	604	3.15	7.59	3.28	3.38	0.42	318	3.11	3.50	3.24	3.25	3.25	0.06			
HCFC-22	604	213	1068	256	285	82	318	212	602	230	238	31	223	224	9	
HCFC-142B	604	19.6	37.7	22.1	22.4	1.8	318	19.9	25.7	21.3	21.5	21.0	0.9	20.9	21.0	0.9
HCFC-141B	604	18.7	216.2	24.6	28.0	15.4	318	18.5	37.4	21.5	22.1	2.6	20.7	21.2	1.8	
HFC-134A	604	53	489	79	94	43	318	54	155	62	66	13	58	59	5	
HFC-152A	604	7	317	44	68	61	318	7	129	18	23	15	13	14	7	
CH2CL2	604	6.6	86.5	13.9	15.6	6.4	312	7.1	21.6	11.8	12.4	2.2	11.1	12.0	15.5	
CH2CL3	604	7.9	14.9	9.1	9.3	0.9	318	7.9	10.8	8.6	8.7	0.4	8.8	8.9	0.4	
CCL4	604	88.4	95.8	91.3	91.4	1.3	318	88.3	96.1	91.3	91.5	1.5	91.1	91.3	1.4	
CH2CL4	604	29	1130	55	73	60	311	29	144	40	44	12	36	41	13	
C2H2CL2	604	0.1	85.9	1.2	2.4	4.9	318	0.0	4.4	0.4	0.6	0.6	0.3	0.4	1.4	
C2CL4	604	2.46	150.6	10.7	17.4	18.2	318	3.35	88.87	5.97	7.16	6.60	5.52	5.27	1.45	
1,2-C2H2CL2	604	6.9	26.7	15.0	15.3	2.5	318	8.1	18.3	14.2	13.9	1.9	13.9	14.2	2.8	
CH3CL	604	526	1015	577	579	34	318	535	1024	564	568.3	37.3	568	569	18	
CH3BR	604	8.1	249.8	12.9	15.0	12.2	318	8.3	147.2	10.1	13.1	12.6	9.5	11.5	5.3	
CH3I	604	0.08	3.14	0.52	0.54	0.28	318	0.12	6.99	0.38	0.51	0.59	0.40	0.44	0.32	
CH2BR2	604	0.61	1.68	1.01	1.04	0.19	318	0.76	1.32	0.97	0.98	0.09	1.00	1.03	0.22	
CH2BRCL2	604	0.10	3.67	0.54	0.69	0.51	318	0.15	0.67	0.22	0.24	0.07	0.21	0.26	0.43	
CH2BR2CL	604	0.09	2.90	0.43	0.54	0.43	318	0.10	0.54	0.17	0.17	0.04	0.18	0.21	0.31	
CH2BR3	604	0.19	4.02	1.26	1.39	0.72	318	0.37	2.52	1.01	1.03	0.26	1.02	1.21	0.75	
MEONO2	604	3.7	24.0	10.5	10.8	3.2	318	4.5	16.7	8.7	8.7	1.5	9.2	9.3	3.2	
ETONO2	604	1.9	19.8	7.2	7.8	3.1	318	2.6	11.6	5.6	5.8	1.5	5.7	5.7	2.1	
1-PRONO2	604	2.3	55.6	13.2	15.7	9.0	318	2.8	27.3	8.6	9.0	3.9	7.2	7.9	3.9	
2-PRONO2	604	0.6	5.3	1.4	1.7	1.0	318	0.3	3.2	1.0	1.1	0.5	0.9	0.9	0.5	
3-PRONO2	604	1.2	59.4	9.9	13.9	9.9	318	1.1	28.7	5.0	5.7	3.6	4.2	4.9	3.4	
2-PEONO2	604	0.4	18.1	2.9	3.9	3.0	318	0.3	9.1	1.4	1.7	1.2	1.0	1.2	0.9	
3-PEONO2	604	0.2	31.7	4.2	5.8	4.9	318	0.3	14.9	1.7	2.3	1.9	1.0	1.5	1.3	
3-ME-2-BUTYL	604	0.4	57.6	9.8	13.0	11.0	318	0.4	28.2	4.3	5.2	4.1	1.8	2.7	2.6	
ETHANE	604	547	9244	1625	1894	954	318	839	3144	1326	1379	376	1284	1251	323	
ETHYNE	604	62	2579	303	434	353	318	64	2033	209	231	167	168	160	56	
PROPANE	604	30	6811	706	1077	1039	318	62	2034	336	411	304	192	234	172	
I-BUTANE	603	5	2680	109	211	270	318	3	419	33	52	55	18	29	30	
N-BUTANE	604	5	3506	179	332	391	318	5	512	53	81	83	28	45	50	
I-PENTANE	599	3	3352	177	384	472	313	5	894	58	93	115	15	26	32	
N-PENTANE	595	3	1458	84	192	229	312	3	336	24	40	49	9	16	18	
ETHENE	601	10	2279	158	317	373	318	11	4513	73	121	337	32	41	26	
PROPENE	593	3	5097	36	82	238	307	3	706	19	30	58	16	20	15	
ISOPRENE	296	3	444	29	53	68	224	3	1614	13	75	217	4	7	7	
BENZENE	604	6	437	58	81	67	318	8	442	38	43	36	29	27	11	
TOLUENE	581	3	1145	70	155	298	306	3	437	22	35	44	7	10	10	
ETHYLBENZENE	597	3	178	19	30	30	314	3	63	5	8	7	4	5	2	
M-XYLENE	412	3	558	28	62	79	103	3	163	7	14	21	6	7	5	
P-XYLENE	412	3	406	22	46	57	112	3	106	6	11	14	5	6	4	
O-XYLENE	361	3	156	15	26	27	72	3	55	6	8	8	6	6	6	

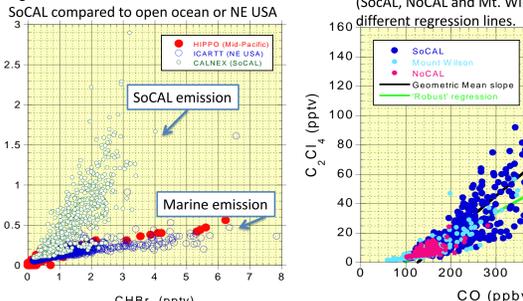
**Figure 4.** Ratio of average trace gas concentrations in the selected samples from SoCAL to those in NoCAL. Top = halocarbons; Bottom = organic nitrates and hydrocarbons.



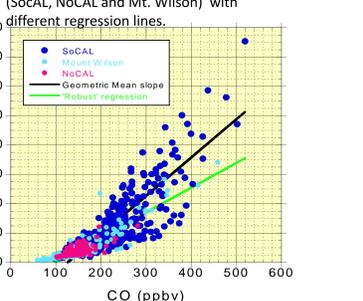
**Figure 5.** Probability distribution of CO and HFC 134a in the NoCAL and SoCAL samples



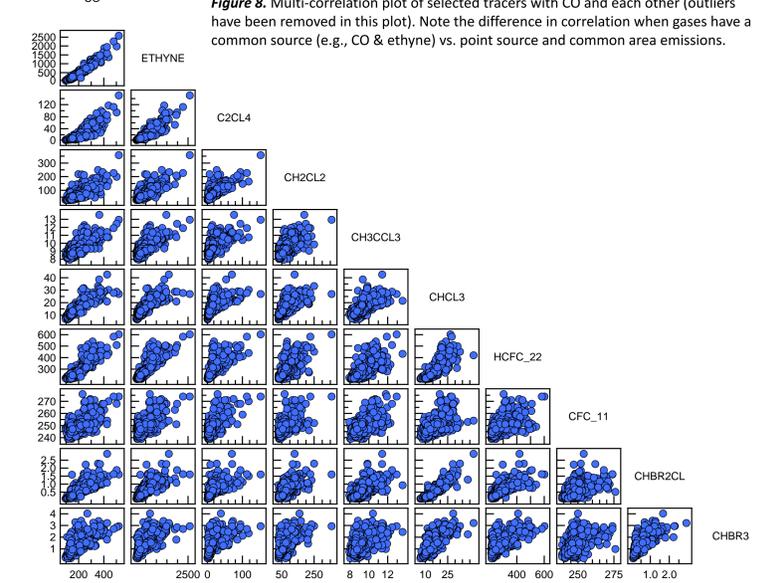
**Figure 6.** Enhanced emission of CHClBr2 in SoCAL compared to open ocean or NE USA



**Figure 7.** Correlation of C2Cl4 with CO (SoCAL, NoCAL and Mt. Wilson) with different regression lines.



**Figure 8.** Multi-correlation plot of selected tracers with CO and each other (outliers have been removed in this plot). Note the difference in correlation when gases have a common source (e.g., CO & ethyne) vs. point source and common area emissions.



**Table 2.** Ratios between CO and various halocarbon gases measured during CALNEX in the LA area, previously in Southern California, estimates reported for USA, and for other major sources outside of the US. Concentration ratios (PPTV of gas X/PPMV CO) were calculated with different statistical techniques. RMA = reduced major axis regression; Rbst = Robust regression (5% trim) (SYSTAT, Ver. 11). See Fig. 7.

Compound	SoCAL, CALNEX (MAY/JUNE 2010)			Mount Wilson, CALNEX (MAY/JUNE 2010)			ITCT-2K2: Los Angeles (APRIL/MAY, 2002)			CARB SoCAL (JUNE, 2008)			USA (Miller et al.) 2002-2005			Riverside (Gentner et al.) 2005			Mexico City (Miller et al.) 2004			Pearl River Delta (Shao et al.) 2004		
	RMA	Robust	Ratio	RMA	Robust	Ratio	RMA	Robust	Ratio	RMA	Robust	Ratio	MA	MA	Ratio	MA	MA	Ratio	MA	MA	Ratio	MA	MA	Ratio
CFCs																								
CFC12	113	9.5	54	8.5	76	7.5	68	7.5	134	22.5	80	21.5	137	13.5	73	14.5	86	76.5	58	86.5	110	19.9	22.2	4.8
CFC11	54	5.5	54	8.5	94	8.5	56	12.5	31	10	27	7.5	236	25	99	31	83	18.5	32	4</				