

Distribution of chlorofluorocarbons (CFCs) and their replacements measured over the South Coast Air Basin (SoCAB) and the Central Valley during the CalNex-2010 study.

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Introduction

The CalNex-2010 air quality and climate change field study was conducted by the National Oceanic and Atmospheric Administration (NOAA) and the California Air Resources Board (ARB) during May-June 2010. We present results from the whole air samples collected onboard the NOAA P-3 aircraft. A total of 72 samples were collected during each flight and were analyzed at UCI for volatile organic compounds (VOCs), including several halogenated species.

This study focuses on the characterization and distribution of selected halocarbons (Table 1) measured over two major source regions in California: the Southern California Air Basin (SoCAB) and the California Central Valley (CV) in response to one of the main objectives of CalNex (i.e. provide observations to improve emission inventories for greenhouse gases).

Table 1. Properties of the reported CFCs, HCFCs, and HFCs [1].

	Chemical formula	Lifetime -yr-	Radiative efficiency -W m ⁻² ppbv ⁻¹ -	GWP -100 yr -
CFC-12	CCl ₂ F ₂	100	0.32	10,900
CFC-11	CCl ₃ F	45	0.25	4,750
CFC-113	CCl ₂ FCClF ₂	85	0.3	6,130
CFC-114	CClF ₂ CClF ₂	300	0.31	10,000
HCFC-22	CHClF ₂	12	0.2	1,810
HCFC-142b	CH ₃ CClF ₂	17.9	0.2	2,310
HCFC-141b	CH ₂ CCl ₂ F	9.3	0.14	725
HCFC-124	CHClFCF ₃	5.8	0.22	609
HFC-134a	CH ₂ FCF ₃	14	0.16	1,430
HFC-152a	CH ₂ CHF ₂	1.4	0.09	124

Previous Results: ARCTAS-CARB 2008

In 2008, CARB sponsored four research flights over the SoCAB during the ARCTAS NASA airborne study. Table 2 summarizes the emissions of HFC-152a and HFC-134a for 2008 in LA County, the SoCAB, and in the US [2]. The emissions estimates are derived using both the tracer ratio method (also employed to derive emission estimates with the CalNex data set) and air quality simulations with the UCI-CIT Air Quality Model, a three-dimensional Eulerian urban photochemical model designed to study the dynamics of pollutant transformation and transport in the SoCAB.

Table 2. Emissions in Gg/yr

	LA County	SoCAB	US	Global
HFC-152a				
Tracer Ratio Method [2]	0.82 ± 0.11	1.60 ± 0.22	32 ± 4	
AQM Method [2]	0.72 ± 0.14 ^(a) 0.65 ± 0.22 ^(b)	0.91 ± 0.20 ^(a) 1.08 ± 0.20 ^(b)		
Stohl et al. (2009) [3]			12.5	37
Greally et al. (2007) [4]				28 ± 4
Millet et al. (2009) [5]			7.6 (5.7-9.7) ^(c)	
HFC-134a				
Tracer Ratio Method [2]	1.16 ± 0.22	2.12 ± 0.28	43 ± 6	
AQM Method [2]	1.26 ± 0.20 ^(a) 1.12 ± 0.29 ^(b)	1.29 ± 0.21 ^(a) 1.53 ± 0.21 ^(b)		
Stohl et al. (2009) [3]			28	156
Millet et al. (2009) [5]			27 (12-39) [†]	
Manning and Weiss (2007) [6]			43 (22-60) [†]	

[2] Barletta et al., 2011; (a) Left value from AQM method uses USGS land-use data from the 1970s. Right value assumes all cells are urban; (b) values in parentheses are the minimum and maximum values reported in that study; [3] US Estimates are for 2006. Global estimates are for the 2005-2006 period; [4] Estimates are for 2004; [5] Estimates are for the 2004-2006 period; [6] Estimates are for 2006.

References

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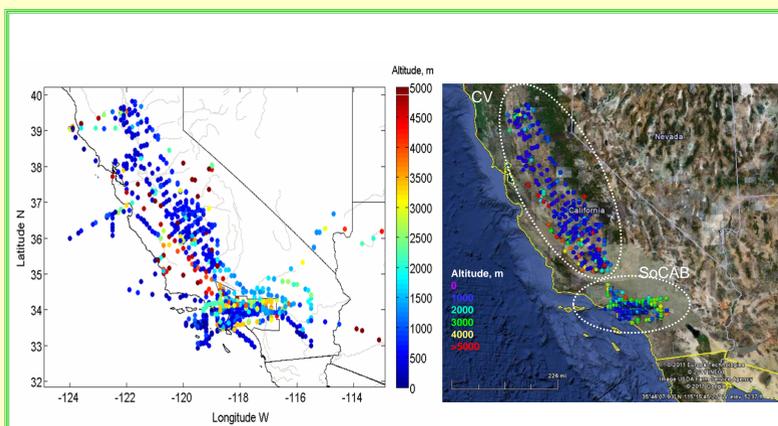


Figure 1. Geographical position of all the samples collected during the study

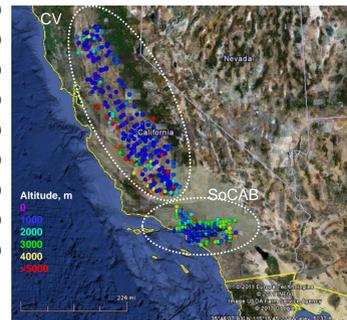


Figure 2. Samples used to characterize the air composition of the CV and SoCAB.

Experimental and Sampling

Whole air samples were collected using 2 L evacuated stainless steel canisters and pressurized to 40 psi. After shipping the samples back to UCI the canisters were analyzed for NMHCs, halocarbons, alkyl nitrates, and selected sulfur compounds. Briefly, after being cryogenically preconcentrated at -196°C in LN₂, the sample is vaporized and split into six different column/detector combinations: three flame ionization detectors, two electron capture detectors, and a mass spectrometer detector.

A total of 1431 samples were collected during the CalNex field study, with extensive sampling carried out over the CV and SoCAB. Samples collected over the ocean were used to characterize the composition of background air entering California before being impacted by sources located over the North American continent.

Results

A summary of the mixing ratios measured during CalNex 2010 for the halocarbons here investigated is given in Table 3.

Considerably higher mixing ratios of HFCs were measured at low altitude in the SoCAB samples (Figure 3). These low altitude enhancements point to the presence of HFCs emission sources in the SoCAB (by contrast, CFC-114 mixing ratios remained overall constant with altitudes in both the SoCAB and the CV).

To estimate emissions from the SoCAB we multiplied the halocarbon/CO mass ratio by the CO annual emission from the SoCAB (3413.5 tons per day [7] – 2008 estimate). To obtain the mass ratio, the halocarbon/CO volume ratio (mmol/mol) was multiplied by the respective molecular weights.

A lack of correlation between the investigated species and CO was observed for the samples collected in the CV. The poor correlation and the considerably lower levels measured over the CV suggest the absence of important sources of HFCs and HCFCs in the CV.

Table 3. Mixing ratios measured over the SoCAB and CV in 2010.

	SoCAB				CV			Background*	
	Min-Max	Average	SD		Min-Max	Average	SD	Average	SD
CFCs									
CFC-12	525 - 589	538	8		525 - 546	535	5	529	2
CFC-11	239 - 468	252	20		239 - 260	246	4	242	1
CFC-113	75.2 - 86.3	78.1	1.5		75.7 - 81.3	77.8	1.1	76.4	0.3
CFC-114	15.9 - 17.6	16.4	0.3		15.9 - 17.0	16.2	0.2	16.0	0.1
HCFCs									
HCFC-22	201 - 1068	288	87		209 - 602	234	27	216	3
HCFC-142b	19.0 - 37.7	22.4	2.0		19.8 - 25.7	21.4	0.9	20.2	0.3
HCFC-141b	18.7 - 216	28.2	16.5		18.5 - 37.4	21.9	2.5	19.6	0.4
HCFC-124	1.54 - 16.9	4.33	2.43		1.52 - 5.08	2.88	0.66	1.95	0.56
HFCs									
HFC-134a	51.3 - 489	96.3	45.6		51.9 - 123	64.2	11.2	54.8	0.9
HFC-152a	5.0 - 317	71.5	64.7		5.1 - 94.1	20.7	13.7	8.5	1.2

* Background calculated as the average of the lowest quartile of the samples collected over the Pacific Ocean

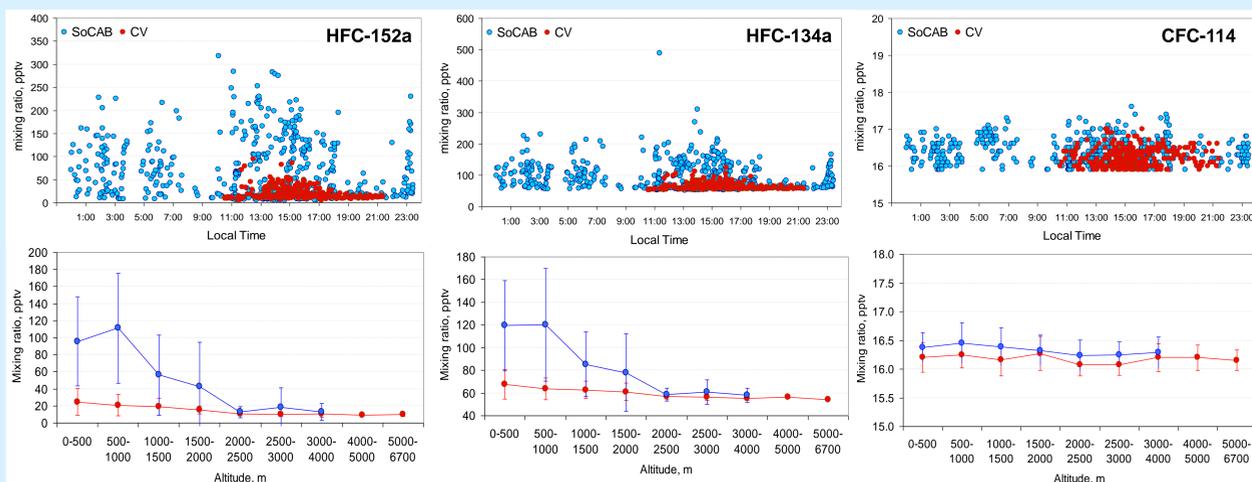


Figure 3. Mixing ratios measured over the SoCAB and CV for HFC-152a, HFC-134a, and CFC-114.

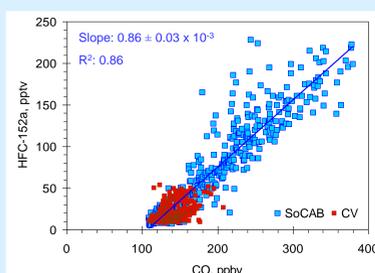
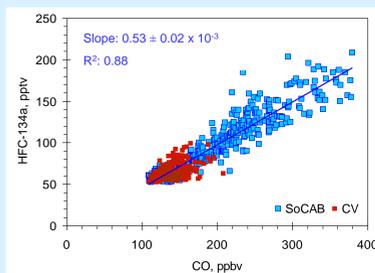


Figure 4. HFC vs CO scatter plot for the SoCAB and CV samples. The orthogonal regression line (and parameters) calculated for the SoCAB points is indicated in blue.

Table 4. Fitting parameters for the HCFC and HFCs here investigated, the calculated emissions for the year 2010, and the corresponding million metric tons of carbon dioxide equivalent (MMTCo₂eq).

	Slope (x10 ⁻³) (Halocarbon:CO)*	R ²	Emissions in SoCAB (Gg/yr)	MMTCo ₂ eq (SoCab)	Emissions in CA† (Gg/yr)	MMTCo ₂ eq (CA)
HCFC-22	0.97 ± 0.04	0.81	3.39	6.14	8.61	15.6
HCFC-142b	0.018 ± 0.001	0.62	0.073	0.17	0.19	0.44
HCFC-141b	0.063 ± 0.006	0.49	0.30	0.22	0.76	0.55
HFC-134a	0.53 ± 0.02	0.88	2.18	3.12	5.54	7.92
HFC-152a	0.86 ± 0.03	0.86	2.29	0.28	5.82	0.72
Total				9.93		25.23
% of GHG in CA				2.1		5.3

* Orthogonal regression
† Emissions extrapolated based on population data

Conclusions

The analysis of the CFC replacements measured during CalNex 2010 highlights the presence of important emission sources within the SoCAB, particularly for HFCs. The average mixing ratio of HFC-152a (71 pptv) was almost 10 times higher than the average background of 8.5 pptv, while a lower enhancement was observed for the samples collected within the CV (average of 20 pptv). HFC-134a also was significantly elevated in the SoCAB with an average level two times higher than the regional background. HCFC enhancements were less significant with respect to background levels measured during this study.

The emission rates of HCFCs and HFCs from the SoCAB in 2010 are estimated from the CalNex data set using the tracer ratio method. The total amount of HCFCs and HFCs released in 2010 by California is derived by extrapolating the SoCAB emission rates using population data and correspond to ~5% of the total 477.7 MMTCo₂eq of green house gases emitted by the state of California [8].