Determining correction factors for seasonal and regional variability in the tracer ratio method:

The seasonal variability in the ΔCFC-12:ΔCO and ΔCFC-11:ΔCO enhancement ratios, observed during a three year period (1996-1998) in the Northeastern US (Barnes et al., 2003), was used as a starting point to calculate correction factors for HFC-134a (the main CFC-12 replacement) and HFC-152a emissions estimates (CFC-11 also was used as a blowing agent), respectively. The summer ΔX:ΔCO enhancement ratio observed by Barnes et al. (2003) was about 40% (for X = CFC-12) and 30% (for X = CFC-11) higher than the average annual enhancement ratio. However, the seasonality in the SoCAB is expected to be weaker compared to the seasonality observed in the Northeastern US because of the lower temperature difference between summer and winter in the SoCAB.

In a study by Papasavva et al. (2009) regular leakage rates were estimated for the individual States in the US for the refrigerant HFC-1234yf (2,3,3,3-tetrafluoropropene), which is potential alternative for HFC-134a in mobile air conditioning (MAC) systems. Regular leaks (i.e. permeation of the refrigerant from hoses, connections, and compressors) increase with temperature and higher emissions of refrigerants are expected during the summer months and in warmer climates. The authors used the temperature-dependent equation reported in Eq. 1 of Papasavva et al. (2009) to calculate how regular leak rates (g-vehicle yr^{-1}) vary with temperature. The summer to winter ratio for regular leaks obtained using temperatures characteristic of the Northeastern US (ratio of ~ 4) was about two times higher than the ratio obtained using the 2008 summer and winter average temperature reported for downtown Los Angeles (ratio of ~ 2).

In light of the data from Barnes et al. (2003) and Papasavva et al. (2009), the seasonal variability correction factors for HFC-134a and HFC-152a are 1.2 and 1.1, respectively. It should be noted that the temperature-dependent equation used to adjust the correction factors from Barnes et al. (2003) is designed to predict how leaks of refrigerants from MAC systems change with temperature and does not describe the behavior of foam blowing agents. Uncertainties associated with the correction factors (10% for both HFCs) are determined by examining the spread in the ratio between the summer and the annual average $\Delta X:\Delta CO$ enhancement ratio observed in Barnes et al. (2003) during the three year period.

Regional effects (warmer climates having greater leakage rates than colder climates due to higher temperatures and more frequent MAC usage) also may need to be considered, but are difficult to estimate. Papasavva et al. (2009) predicts that the leakage rate (gram per vehicle) of MAC refrigerants from cars in California will be about 4% higher than the national average in 2017. This result suggests that regional effects may not affect estimates of US HFC-134a emissions significantly.

References for this section

Barnes, D. H., Wofsy, S. C., Fehlau, B. P., Gottlieb, E. W., Elkins, J. W., Dutton, G. S., Montzka, S. A.: Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998: 2. A study of the efficacy of the Montreal Protocol and other regulatory measures, J Geophys Res, 108, 4186, 2003.

Papasavva, S., Luecken, D. J., Waterland, R. L., Taddonio, K. N., Andersen, S. O.: Estimated 2017 refrigerant emissions of 2,3,3,3-tetrafluoropropene (HFC-1234yf) in the United States resulting from automobile air conditioning, Environ Sci Tech, 43, 9252-9259, 2009.

Formulas used to calculate average concentrations in the AQM method:

In the simulations, the average hourly concentration of each species was calculated at each cell and vertical layer – for both HFCs, the concentration at 80 × 30 × 5 locations was calculated every hour. In order to find the average mixing ratio of species *i* in a cell *k* at hour *hr* ($\bar{c}_{hr,i,k}$) the weighted average of all five vertical layers was calculated, accounting for differences in air pressure and layer thickness. The equation for $\bar{c}_{hr,i,k}$ is,

$$\bar{c}_{hr,i,k} = \frac{n_{hr,i,k}}{n_{hr,air,k}} = \frac{\sum_{j=1}^{N_L} P_{hr,i,j,k} V_j / RT_{hr,k}}{\sum_{j=1}^{N_L} P_{hr,air,j,k} V_j / RT_{hr,k}} = \frac{\sum_{j=1}^{N_L} c_{hr,i,j,k} P_{hr,air,j,k} d_j}{\sum_{j=1}^{N_L} P_{hr,air,j,k} d_j}, \qquad (1)$$

where $n_{hr,i,k}$ and $n_{hr,air,k}$ are the total number of moles of species *i* and air, respectively, in cell *k* at hour *hr*. $P_{hr,i,j,k}$ and $P_{hr,air,j,k}$ are the average partial pressures of species *i* and air, respectively, in layer *j* of cell *k* at hour *hr*. The concentration of species *i* in layer *j* of cell *k* at hour *hr*, $c_{hr,i,j,k}$, was determined from simulations. V_j is the volume of layer *j*, $T_{hr,k}$ is the temperature of cell *k* at hour *hr* (the model assumes that the temperature is not a function of height), *R* is the ideal gas constant, and N_L is the number of vertical layers (N_L = 5). The volume of each cell layer (V_j) is the area of each cell (25 km^2) times the layer height (d_j).

$P_{hr,air,j,k}$ was determined by calculating the average air pressure in layer *j*. $P_{hr,i,j,k}$ is expressed in terms of the known quantity $c_{hr,i,j,k}$ using the ideal gas law,

$$c_{hr,i,j,k} = \frac{n_{hr,i,j,k}}{n_{air,i,j,k}} = \frac{P_{hr,i,j,k}}{P_{air,j,k}} \Rightarrow c_{hr,i,j,k} P_{hr,air,j,k} = P_{hr,i,j,k}. \qquad (2)$$

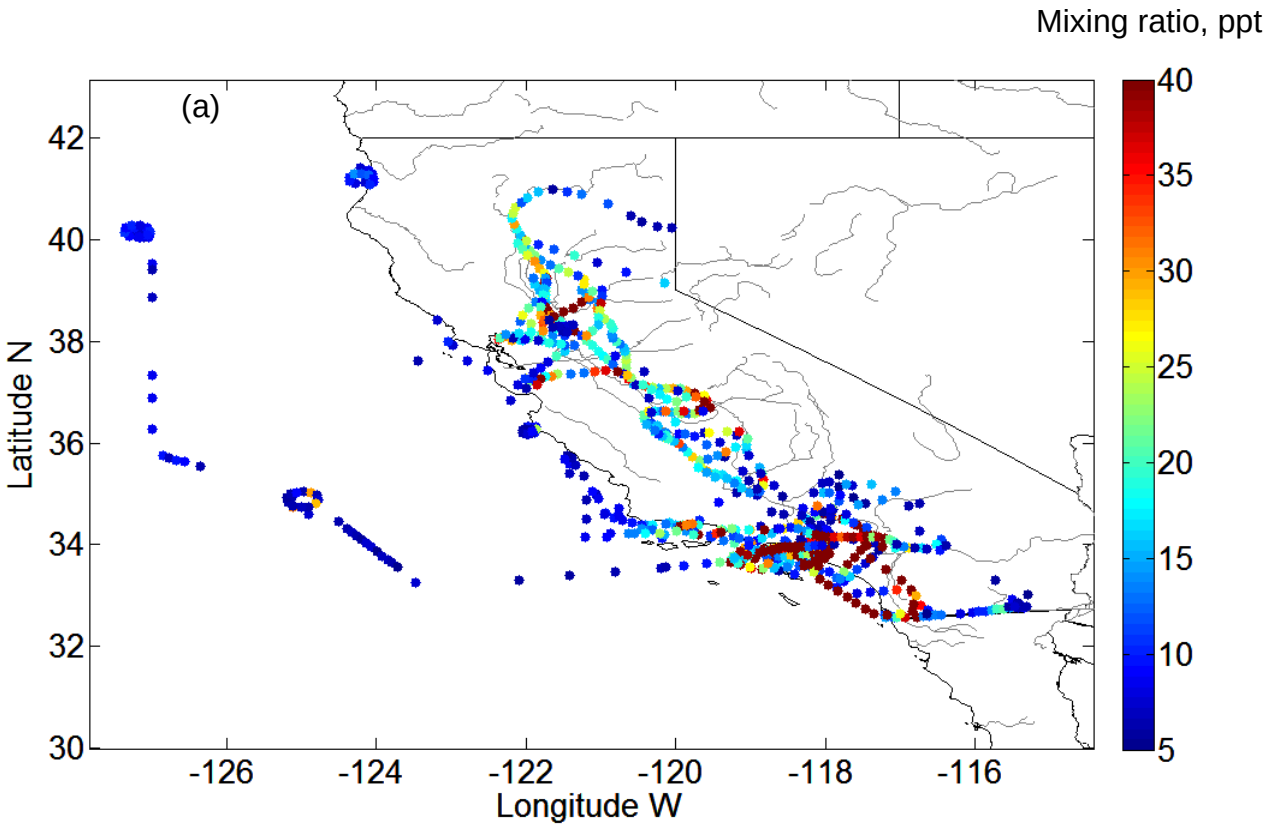
The average concentration of species *i* across the LA area or SoCAB at a given hour is calculated by averaging $\bar{c}_{hr,i,k}$ over all cells in the area of interest,

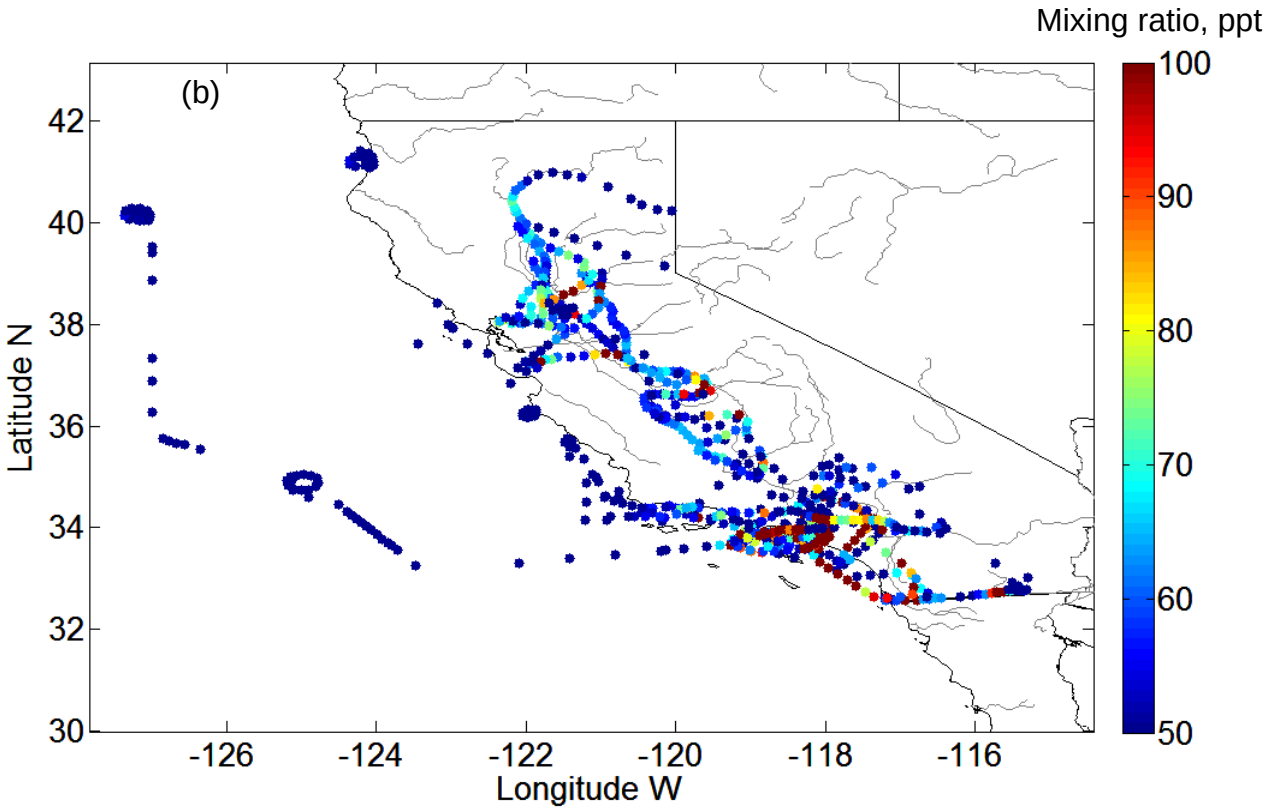
$$\bar{c}_{hr,i,area} = \frac{1}{N_C}\sum_{k=1}^{N_C}\bar{c}_{hr,i,k}\ , \qquad (3)$$

where N_c is the total number of cells comprising the region of interest and the subscript *area* is either *LAA* or *SoCAB*.

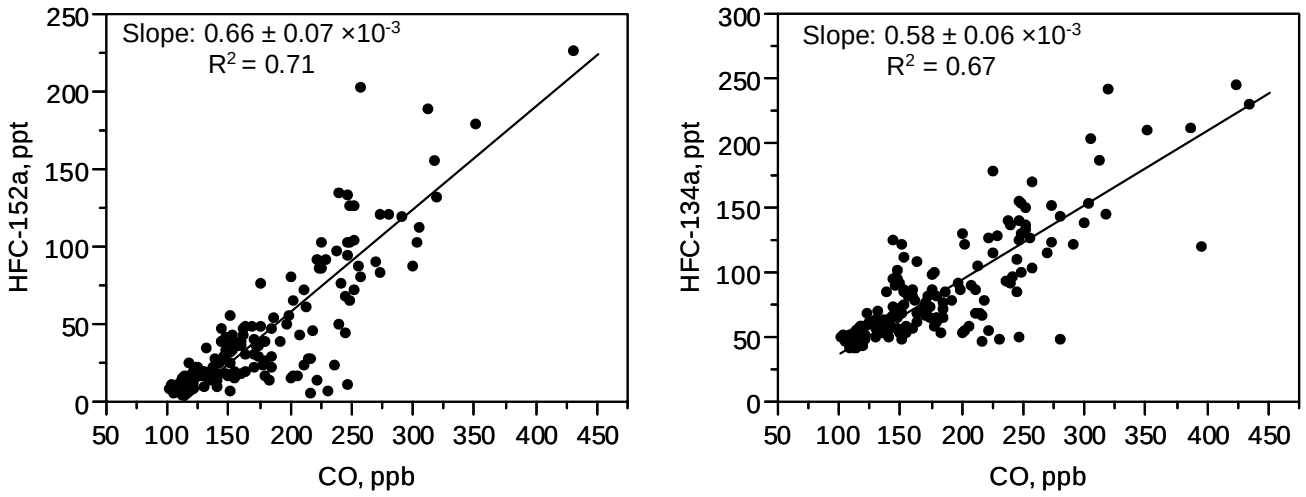
In the simulations, the diurnal profile of HFC-152a and HFC-134a varies with elevation. For each hour the average concentration of species *i* across the LA area or SoCAB at a vertical layer *j* is,

$$\bar{c}_{hr,i,j} = \frac{1}{N_C}\sum_{k=1}^{N_C}c_{hr,i,j,k}\ . \qquad (4)$$

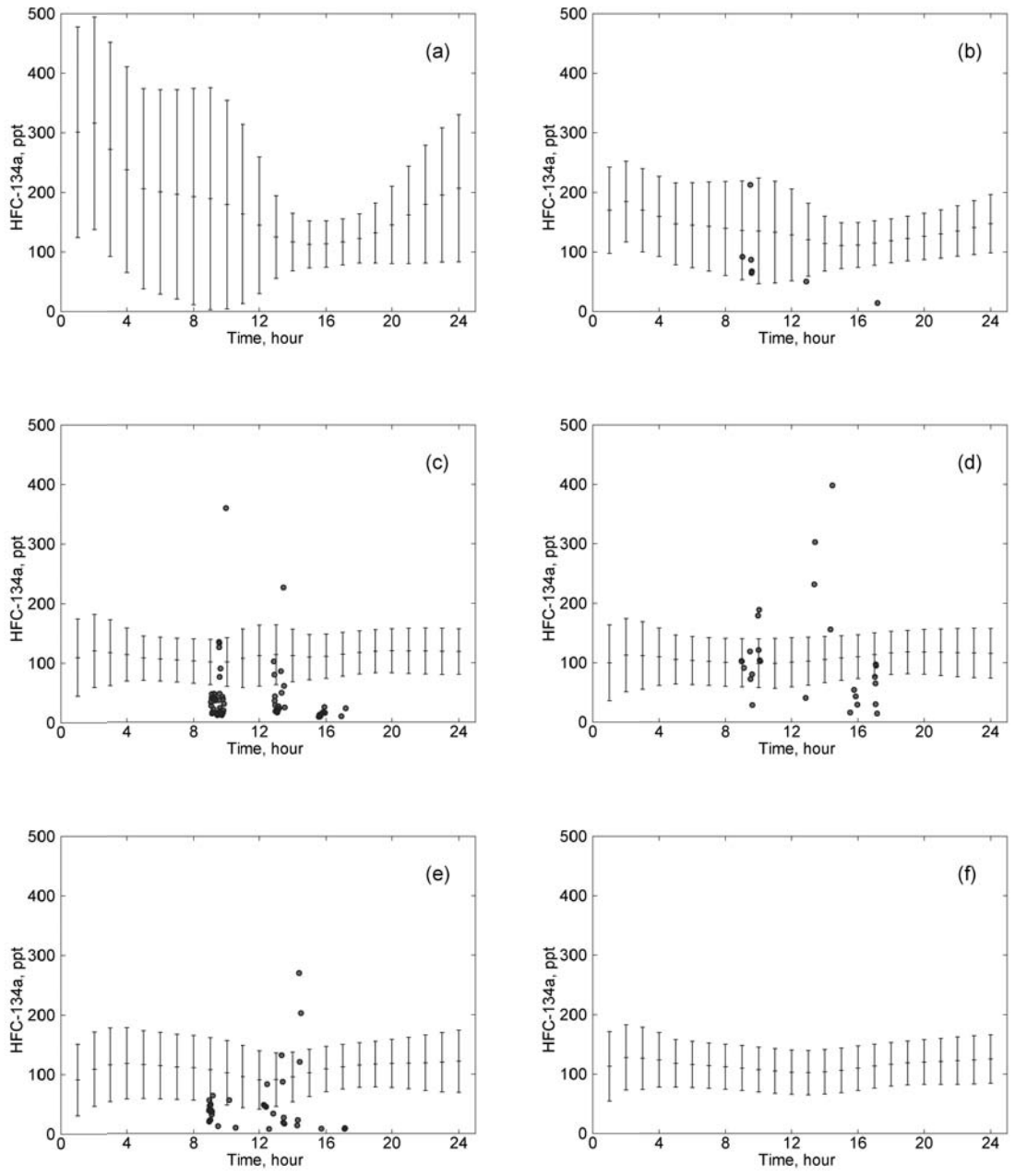

Mixing ratio, ppt
(a)
Latitude N
Longitude W
42
40
38
36
34
32
30
-126
-124
-122
-120
-118
-116
40
35
30
25
20
15
10
5


Mixing ratio, ppt
(b)
Latitude N
Longitude W
42
40
38
36
34
32
30
-126
-124
-122
-120
-118
-116
100
90
80
70
60
50

Supplementary Figure 1. Mixing ratios (in ppt) of (a) HFC-152a and (b) HFC-134a measured during ARCTAS-CARB study.

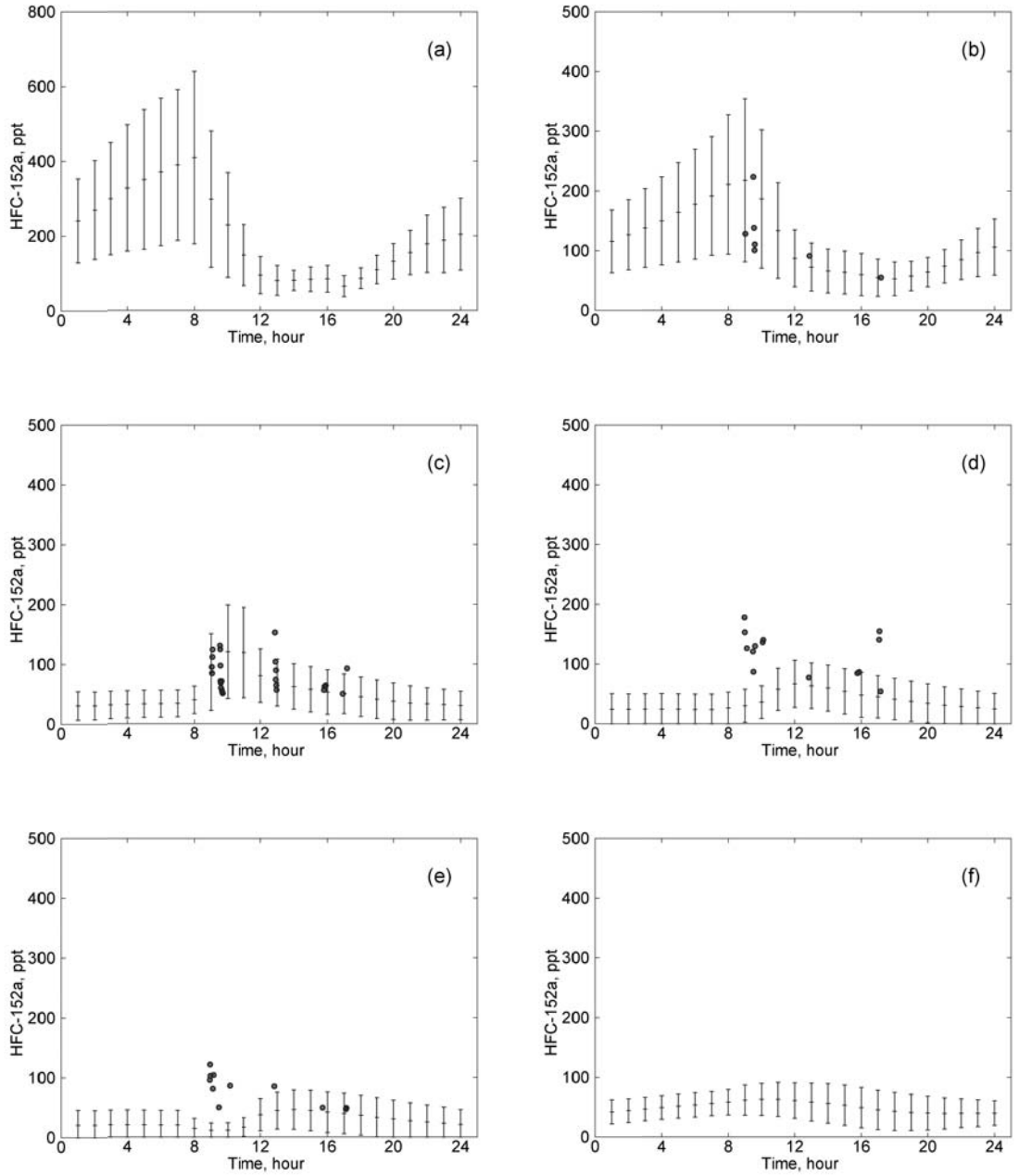


Supplementary Figure 2. Mixing ratios of HFC-152a and HFC-134a versus CO for the samples collected over the SoCAB.



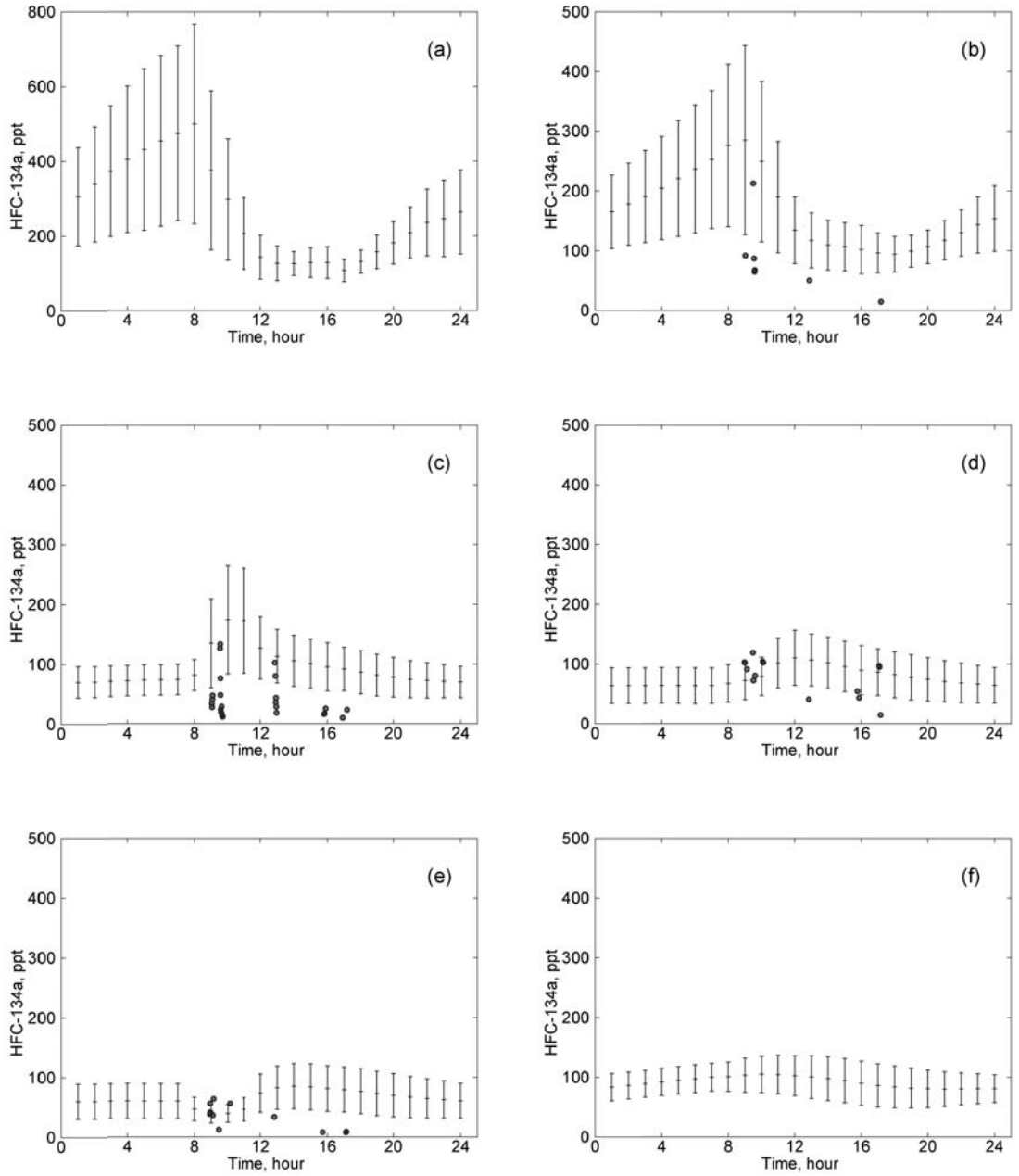
Supplementary Figure 3: The mean concentration and 1-σ values of HFC-134a at different vertical layers in the cells comprising the SoCAB, as calculated by the UCI-CIT model using the September 9, 1993 meteorological data set and landuse data from the USGS. The mean concentration in the (a) lowest layer, (b) second layer, (c) third layer, (d) fourth layer, and (e) highest layer are calculated using Eq. (4) in the Supplementary Material. The average

concentration over all vertical layers in the SoCAB (f) is calculated using Eq. (3) in the Supplementary Material. Measurements from the ARCTAS-CARB flights are shown as solid black dots. No measurements were collected in the lowest layer.



Supplementary Figure 4: The mean concentration and 1-σ values of HFC-152a at different vertical layers in the cells comprising the LA area, as calculated by the UCI-CIT model using the September 9, 1993 meteorological data set and landuse data from the USGS. The mean concentration in the (a) lowest layer, (b) second layer, (c) third layer, (d) fourth layer, and (e) highest layer are calculated using Eq. (4) in the Supplementary Material. The average

concentration over all vertical layers in the LA area (f) is calculated using Eq. (3) in the Supplementary Material. Measurements from the ARCTAS-CARB flights are shown as solid black dots. No measurements were collected in the lowest layer.



Supplementary Figure 5: The mean concentration and 1-σ values of HFC-134a at different vertical layers in the cells comprising the LA area, as calculated by the UCI-CIT model using the September 9, 1993 meteorological data set and landuse data from the USGS. The mean concentration in the (a) lowest layer, (b) second layer, (c) third layer, (d) fourth layer, and (e) highest layer are calculated using Eq. (4) in the Supplementary Material. The average

concentration over all vertical layers in the LA area (f) is calculated using Eq. (3) in the Supplementary Material. Measurements from the ARCTAS-CARB flights are shown as solid blank dots. No measurements were collected in the lowest layer.

Supplementary Table 1a: Wind speed and direction in Long Beach, CA during the four ARCTAS-CARB flights in June 2008 and the six simulation days. The June 2008 data is taken from the official National Weather Service Daily Summary, available online at <http://www.wrh.noaa.gov/lox/main.php?suite=fire_weather&page=historical>.

	06/16/08		06/18/08		06/20/08		06/22/08			08/27/87		08/28/87		09/08/93		09/09/93		10/18/95		10/19/95	
Time	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Simulation hour	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction
11:53 PM	0		0		0		3	ESE	12 AM	1	SSW	2	SSW	1	SW	3	S	2	ESE	3	WSW
10:53 PM	3	Var.	3	S	6	ESE	0		11 PM	0	W	1	S	0	SSW	3	SSE	2	ESE	2	WNW
9:53 PM	3	NW	8	SE	5	ESE	6	ESE	10 PM	1	NNW	0	E	1	SW	3	S	4	SW	1	WSW
8:53 PM	3	NW	8	SSE	3	NW	0		9 PM	1	NW	1	SSW	1	W	3	S	1	WSW	5	NW
7:53 PM	8	NW	6	S	5	WNW	6	NW	8 PM	2	W	2	SSW	3	W	2	W	1	SW	5	WNW
6:53 PM	9	WNW	12	SSE	3	W	12	WNW	7 PM	3	W	2	WSW	4	W	4	W	1	SW	6	W
5:53 PM	9	NW	13	S	7	WNW	12	WNW	6 PM	5	W	3	W	4	W	4	W	3	S	7	WNW
4:53 PM	8	WNW	6	WNW	0		7	SSE	5 PM	7	W	5	W	6	W	5	W	7	S	9	WNW
3:53 PM	6	Var.*	12	WNW	7	NW	8	SSW	4 PM	7	W	5	W	7	W	7	W	9	S	10	NW
2:53 PM	7	S	12	WNW	7	SSW	10	SSW	3 PM	7	W	6	WSW	6	W	6	W	6	NNW	6	WNW
1:53 PM	8	S	10	W	6	S	9	SSW	2 PM	7	W	4	SW	5	WSW	5	WSW	8	NNW	5	NW
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11:53 AM	7	SSE	7	S	8	S	9	S	12 PM	5	W	4	SW	4	SW	5	WSW	6	SSW	7	NNW
10:53 AM	3	Var.	6	S	0		7	S	11 AM	4	W	2	W	2	SW	3	W	3	SSW	5	NNW

9:53 AM	5	SSW	0		0		7	SSE		10 AM	4	W	1	S	1	ESE	2	W	3	WSW	3	SW
8:53 AM	0		0		0		5	S		9 AM	3	W	0	SW	0	W	1	WNW	2	W	2	SSW
7:53 AM	0		0		0		7	SSE		8 AM	2	WNW	1	NW	1	WNW	1	WSW	2	SSW	1	WSW
6:53 AM	0		0		0		3	SSE		7 AM	1	WNW	2	W	1	W	1	NNW	4	SE	1	SSW
5:53 AM	0		0		0		0			6 AM	1	WNW	2	SW	2	WNW	1	WNW	3	ESE	2	W
4:53 AM	0		0		0		3	S		5 AM	1	NW	2	W	1	WNW	1	WSW	4	ESE	2	WSW
3:53 AM	3	NNW	0		0		3	ESE		4 AM	2	WNW	1	WSW	1	W	1	WSW	3	SE	3	SW
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1:53 AM	5	NNW	5	SSE	3	S	0			2 AM	2	WNW	1	SSW	1	WSW	1	W	3	SSE	1	S
12:53 AM	3	NNW	5	SSE	0		5	SSE		1 AM	2	NW	1	SSW	1	WSW	1	W	2	ESE	0	E

* Var. = Variable wind speed

Supplementary Table 1b: Wind speed and direction in Hawthorne, CA during the four ARCTAS-CARB flights in June 2008 and the six simulation days. The June 2008 data is taken from the official National Weather Service Daily Summary, available online at <http://www.wrh.noaa.gov/lox/main.php?suite=fire_weather&page=historical>.

	06/16/08		06/18/08		06/20/08		06/22/08			08/27/87		08/28/87		09/08/93		09/09/93		10/18/95		10/19/95	
Time	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction		Simulation hour	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction
11:53 PM	0		0		3	SSW	6	WSW		12 AM	0		3	WSW	2	WSW	2	S	3	SSW	3	NW
10:53 PM	5	WSW	7	ESE	0		6	Var.*		11 PM	1	NW	1	W	1	SSW	2	SSE	3	SSW	3	NW
9:53 PM	7	WSW	6	SE	9	W	5	SW		10 PM	1	NW	1	WNW	1	SSW	2	S	4	SSW	3	NW
8:53 PM	5	SW	0		7	W	5	WSW		9 PM	1	W	2	W	3	SW	2	S	5	SSW	3	WNW
7:53 PM	7	WSW	5	WSW	5	W	7	W		8 PM	4	WSW	5	W	4	WSW	3	WSW	4	SSW	3	WNW
6:53 PM	7	W	7	WSW	7	WNW	12	WSW		7 PM	5	WSW	6	WSW	5	WSW	5	WSW	4	SSW	4	WNW
5:53 PM	12	W	9	WSW	7	W	12	WSW		6 PM	8	W	7	WSW	6	W	7	WSW	4	SSW	7	WNW
4:53 PM	8	W	10	WSW	8	W	8	W		5 PM	11	W	8	W	7	W	7	W	6	SSW	9	W
3:53 PM	12	WSW	8	WSW	12	W	10	WSW		4 PM	12	W	9	W	9	WSW	10	W	6	SSW	8	W
2:53 PM	9	W	8	W	13	WSW	10	WSW		3 PM	11	W	10	WSW	8	WSW	10	WSW	7	SSW	9	W
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12:53 PM	9	W	9	WSW	9	WSW	6	W		1 PM	9	W	7	W	8	WSW	7	W	8	SW	6	WSW
11:53 AM	6	W	9	W	12	WSW	8	W		12 PM	8	W	6	W	6	WSW	6	WSW	6	SW	5	SW
10:53 AM	8	W	5	WSW	3	ESE	5	S		11 AM	7	W	5	WSW	4	WSW	5	W	4	SW	3	W

9:53 AM	0		3	3	Var.	0		10 AM	7	W	4	W	1	SSW	2	WSW	2	WNW	2	WSW
8:53 AM	0		0	0		3	SSE	9 AM	5	WSW	3	W	1	WSW	2	WSW	3	N	1	SW
7:53 AM	3	W	0	0		3	SE	8 AM	2	WNW	4	W	0		2	WSW	3	N	2	SSW
6:53 AM	3	WSW	0	0		3	E	7 AM	1	WNW	4	WSW	1	SW	0		3	N	3	SSW
5:53 AM	0		0	0		0		6 AM	1	W	3	WNW	2	WSW	1	WSW	3	N	4	SSW
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3:53 AM	0		0	0		5	E	4 AM	3	WNW	1	WNW	2	WSW	1	WSW	4	NW	4	SSW
2:53 AM	0		0	0		0		3 AM	4	WNW	2	W	2	WSW	1	WSW	3	NNW	1	WSW
1:53 AM	6	WSW	0	3	SW	5	SE	2 AM	3	WNW	2	WNW	2	SW	2	WSW	3	SSW	2	WSW
12:53 AM	6	WSW	0	5	SE	5	ESE	1 AM	3	WNW	2	W	1	WSW	2	WSW	2	SW	1	SE

* Var. = Variable wind speed

Supplementary Table 1c: Wind speed and direction in Santa Ana, CA during the four ARCTAS-CARB flights in June 2008 and the six simulation days. The June 2008 data is taken from the official National Weather Service Daily Summary, available online at <http://www.wrh.noaa.gov/lox/main.php?suite=fire_weather&page=historical>.

	06/16/08		06/18/08		06/20/08		06/22/08			08/27/87		08/28/87		09/08/93		09/09/93		10/18/95		10/19/95	
Time	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction		Simulation hour	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction	Wind speed (mph)	Wind direction
11:53 PM	3	SSW	0		0		6	WSW		12 AM	0		1	SSW	1	SSW	3	SSE	1	SSE	1	W
10:53 PM	5	SSW	0		0		5	SSW		11 PM	1	SSW	0		2	SSW	4	SSE	2	S	0	
9:53 PM	6	SSW	0		7	SSW	7	SW		10 PM	1	SSW	0		2	S	4	S	1	SSE	1	WSW
8:53 PM	9	SSW	9	SW	10	SSW	5	Var.		9 PM	2	S	1	S	3	SSW	3	S	3	S	2	WNW
7:53 PM	9	SSW	7	WSW	7	SSW	6	SSW		8 PM	2	S	3	S	3	SSW	4	SSW	3	SSW	3	W
6:53 PM	10	S	8	SW	6	SSW	8	S		7 PM	2	SW	4	SSW	3	SW	3	SSW	3	SSW	5	W
5:53 PM	9	SW	9	SSW	0		9	S		6 PM	4	WSW	3	SSW	3	SW	4	SW	3	SSE	5	W
4:53 PM	8	SW	14	SW	8	SW	10	SSW		5 PM	4	WSW	4	SSW	4	WSW	4	SW	3	SW	6	W
3:53 PM	6	Var.*	9	SW	6	Var.	12	SSW		4 PM	4	W	3	SW	5	WSW	5	WSW	3	SW	7	W
2:53 PM	8	SW	10	SW	8	SSW	14	SSW		3 PM	5	W	4	WSW	5	SW	5	SW	4	SW	8	W
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12:53 PM	13	SW	9	SSW	8	SW	13	SW		1 PM	4	WSW	3	WSW	5	WSW	6	WSW	3	SW	5	W
11:53 AM	6	Var.	7	WSW	10	SSW	12	SW		12 PM	3	WSW	3	WSW	4	WSW	4	WSW	2	SSW	5	W
10:53 AM	6	SW	0		5	SW	12	SW		11 AM	3	W	2	WSW	2	WSW	2	WSW	2	SSE	2	NW

9:53 AM	3	WSW	5	W	3	SSW	8	SSW		10 AM	3	W	1	SW	1	SSW	1	WSW	2	SSE	1	WSW
8:53 AM	6	SSW	0		5	Var.	0			9 AM	2	WSW	1	S	0		1	WSW	1	SSW	0	
7:53 AM	7	SSW	0		3	S	0			8 AM	1	WNW	1	SW	0		1	SE	1	S	1	W
6:53 AM	5	SSW	3	NNW	0		0			7 AM	1	WNW	1	SW	0		0		2	SSW	1	NNW
5:53 AM	0		0		0		0			6 AM	0		1	SW	1	W	0		1	WSW	1	NNW
4:53 AM	3	SE	3	N	3	NNE	0			5 AM	0		1	WSW	0		0		2	ESE	1	WNW
3:53 AM	0		0		0		0			4 AM	1	WNW	1	WSW	0		0		2	SSE	1	SSW
2:53 AM	0		0		0		0			3 AM	1	WNW	0		1	WNW	0		2	ESE	1	SSE
1:53 AM	0		3	SW	3	SW	3	SW		2 AM	1	NW	0		0		1	SW	3	SE	1	SSW
12:53 AM	3	WSW	5	WSW	3	SSW	0			1 AM	1	WNW	0		0		1	SW	4	SSE	2	SSW

* Var. = Variable wind speed

Supplementary Table 2a: Emissions estimates (Gg) of HFC-152a and HFC-134a in LA County for 2008 using the AQM method.

	USGS Data Scenario*		100% Urban Scenario†	
Meteorology	HFC-152a	HFC-134a	HFC-152a	HFC-134a
Aug. 27, 1987	0.54	1.00	0.49	0.90
Aug. 28, 1987	0.63	1.17	0.46	0.93
Sept. 8, 1993	0.82	1.40	0.74	1.26
Sept. 9, 1993	0.73	1.25	0.64	1.09
Oct. 18, 1995	0.67	1.15	0.50	0.91
Oct. 19, 1995	0.93	1.57	1.04	1.63
Average	0.72	1.26	0.65	1.12
Standard deviation	0.14	0.20	0.22	0.29

(*) This scenario uses 1970s land-use data from the United States Geological Survey. The fraction of urban cells in the LA area, from which LA County emissions estimates are extrapolated, is 76%; (†) This scenario assumes 100% of the cells in the SoCAB are urban.

Supplementary Table 2b: Emissions estimates (Gg) of HFC-152a and HFC-134a in the SoCAB for 2008 using the AQM method.

	USGS Data Scenario*		100% Urban Scenario†	
Meteorology	HFC-152a	HFC-134a	HFC-152a	HFC-134a
Aug. 27, 1987	0.83	1.15	0.96	1.34
Aug. 28, 1987	0.75	1.11	0.90	1.33
Sept. 8, 1993	1.20	1.51	1.42	1.78
Sept. 9, 1993	1.10	1.39	1.24	1.58
Oct. 18, 1995	0.84	1.52	0.97	1.78
Oct. 19, 1995	0.72	1.06	1.01	1.39
Average	0.91	1.29	1.08	1.53
Standard deviation	0.20	0.21	0.20	0.21

(*) This scenario uses 1970s land-use data from the United States Geological Survey. The fraction of urban cells in the SoCAB is 49%; (†) This scenario assumes 100% of the cells in the SoCAB are urban.