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# HFC-152a and HFC-134a emission estimates and characterization of CFCs, CFC replacements, and other halogenated solvents measured during the 2008 ARCTAS campaign (CARB phase) over the South Coast Air Basin of California

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## Abstract

This work presents results from the NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) study. Whole air samples were obtained on board research flights that flew over California during June 2008 and analyzed for selected volatile organic compounds, including several halogenated species. Samples collected over the South Coast Air Basin of California (SoCAB), which includes much of Los Angeles (LA) County, were compared with samples from inflow air masses over the Pacific Ocean. The levels of many halocarbon species were enhanced significantly over the SoCAB, including compounds regulated by the Montreal Protocol and subsequent amendments (e.g., enhancements of 13 pptv and 11 pptv for CFC-11 and CFC-12, respectively). Emissions estimates of HFC-152a ( $0.98 \pm 0.05$  Gg) and HFC-134a ( $1.40 \pm 0.11$  Gg) in LA County for 2008 were obtained using the observed HFC:CO enhancement ratio. The emission rates were extrapolated to the SoCAB ( $1.48 \pm 0.07$  Gg for HFC-152a and  $2.12 \pm 0.17$  Gg for HFC-134a) and US ( $30.1 \pm 1.5$  Gg for HFC-152a and  $43.0 \pm 3.4$  Gg for HFC-134a) using population data. In addition, emission rates of the two HFCs in LA County and SoCAB also were calculated by a second method that utilizes air quality modeling. Estimates obtained using both methods agree well.

## 1 Introduction

Chlorofluorocarbon (CFC) compounds are used in a variety of applications including refrigeration, air conditioning, foam blowing, and as aerosol propellants (McCulloch et al., 2003; Sturrock et al., 2002). The harmful impact of CFCs on stratospheric ozone has led to their phase out governed by the regulations in the Montreal Protocol and subsequent amendments (WMO, 2007; UNEP, 2003). A total phase out for the production and consumption of CFCs, methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ), halons, and carbon tetrachloride ( $\text{CCl}_4$ ) was imposed in developed countries in 1996, and a global ban is scheduled

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for 2010 (2015 for CH<sub>3</sub>CCl<sub>3</sub>; UNEP, 2003). Methyl chloroform is used as an industrial cleaner and degreaser (McCulloch, 2001), halons are used in fire-fighting (Butler et al., 1998), and CCl<sub>4</sub> is a solvent and chemical intermediate for CFC production (Altshuler, 1976; Sturrock et al., 2002). Other halogenated compounds discussed in this study are used in the industrial sector, mainly as solvents and degreasers (methylene chloride, CH<sub>2</sub>Cl<sub>2</sub>; chloroform, CHCl<sub>3</sub>; trichloroethane, C<sub>2</sub>HCl<sub>3</sub>; and tetrachloroethene, C<sub>2</sub>Cl<sub>4</sub>).

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were introduced as substitutes for CFC compounds. HCFCs are used in air conditioning, refrigeration, and foam plastic applications (McCulloch et al., 2003). They still contribute to the destruction of stratospheric ozone and are considered a transitional species; HCFC consumption and production were frozen in developed countries in 1996 and 2004, respectively (2013 for developing countries), and a 100% global phase-out is mandated by 2040 (EC, 2008). HFCs are being introduced as replacement compounds for both CFCs and HCFCs since they do not harm stratospheric ozone. However, HFCs typically have high global warming potentials (GWP) because of their ability to absorb infrared radiation and relatively long lifetimes (~years) (Forster et al., 2007). The GWPs for the two HFCs investigated in this study, HFC-134a and HFC-152a, are 1300 and 140, respectively (Forster et al., 2007). The high GWP for HFC-134a has led to the European Union phasing out HFC-134a in new vehicles in 2011 with a total ban in 2017 (EP, 2006). HFC-134a is the main refrigerant used in car air conditioners (McCulloch et al., 2003) and is the most abundant HFC in the atmosphere with an estimated background concentration of 43±0.2 pptv in 2008 (based on the average of the lowest quartile of the inflow samples from this study, discussed in Sect. 3.1). HFC-152a mainly is used as a foam-blowing agent and in aerosol spray applications, and is a possible alternative to HFC-134a in car cooling systems due to its lower GWP. While background levels of HFC-152a are relatively low, 6±0.4 pptv in 2008 (based on the average of the lowest quartile of the inflow samples from this study, discussed in Section 3.1), atmospheric levels of this compound are increasing exponentially primarily because of emissions in North America (Stohl et al., 2009, and references therein).

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Emissions estimates of halogenated compounds often are obtained through “bottom-up” methods based on production and consumption/usage data. However, the uncertainties of government and industry reports can affect the source estimates significantly. Additionally, production data are lacking for species produced by a limited number of manufacturers. This study uses a different approach (i.e. “top-down” methods) to determine emissions estimates using atmospheric measurements.

The NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) study was conducted in two deployments (ARCTAS-A during April 2008 and ARCTAS-B during June-July 2008) involving DC-8, P-3, and B-200 aircrafts. Before the second deployment, four research flights on board the NASA DC-8 aircraft were sponsored by California Air Resources Board (CARB) and performed over California in June 2008. These four flights focused on the characterization of the atmosphere over California and conducted many low altitude passes over significant pollution source regions, including the San Joaquin Valley and South Coast Air Basin (SoCAB). The main objectives of the California deployment (ARCTAS-CARB) were the improvement of state emission inventories for greenhouse gases and aerosols, the characterization of offshore pollutants from shipping and natural sources, and the characterization of upwind boundary conditions for modeling local surface ozone and PM<sub>2.5</sub>. A general overview of the mission design and scientific themes of the ARCTAS and CARB flights are given in Jacob et al. (2010).

Among the different measurements, whole air samples were collected on board the DC-8 and analyzed for selected volatile organic compounds (VOCs). This study focuses on selected halocarbon species collected over the SoCAB, with special attention to the area around Los Angeles (LA). The SoCAB contains the largest urban area in the western United States with a population of over 15 million living in an area that is approximately 160 km long and 100 km wide (SCAQMD, 2008). It includes all of Orange County and the western, urbanized portions of Los Angeles, Riverside, and San Bernardino Counties. The basin forms a low plain flanked by the Pacific Ocean to the west and surrounded on other sides by mountains which channel and confine air

masses.

Although previous studies report emissions of HFCs from European sites (Maione et al., 2008; Reimann et al., 2002; 2004; Buchmann et al., 2003) and emissions of regulated CFCs and other halogenated compounds in North America (Hurst et al., 2006; Millet et al., 2009; Barletta et al., 2009) this study is the first time that halocarbons from the SoCAB have been examined. This work makes an important contribution to the validation and improvement of California emission inventories by providing a characterization and quantification of several halogenated species, including selected greenhouse gases that are used extensively in California such as the CFC replacement compounds. Additionally, estimates of the HFC-152a and HFC-134a emission rate from LA County are obtained using two methods: (1) In the “chemical ratio” method, atmospheric measurements of the HFC:CO ratio are combined with the reported CO emission rate from LA County for 2008. The 2008 HFC-152a and HFC-134a emission rate estimates calculated for LA County then are extrapolated to the entire SoCAB and US; (2) In the “AQM” method, an air quality model of the SoCAB is employed to calculate the emission rate needed to reproduce field measurements obtained during the ARCTAS-CARB campaign. The emission rates used in the model are adjusted incrementally until the levels from the simulations match the field measurement data. Emission rate estimates are obtained for both LA County and the SoCAB using this method.

## 2 Analysis and distribution of volatile organic compounds

### 2.1 Collection and analysis of air samples

During the four flights of ARCTAS-CARB a total of 617 whole air samples were collected in 2-L electropolished stainless steel canisters equipped with a Swagelok metal bellows valve on board four flights in a DC-8 aircraft. The canisters were flushed with ultra-high purity (UHP) helium and then evacuated to  $10^{-2}$  Torr in a laboratory at the

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University of California, Irvine (UC Irvine) prior to shipment to the field. Seventeen Torr of degassed ultrapure Milli-Q water was added to the canisters in order to passivate the surface of the internal walls, minimizing the absorbance of selected compounds inside the canisters. During each sampling, which takes approximately one minute, the canisters were pressurized to 40 psi using a metal double bellows pump. Canisters were filled at 1–3 min intervals during ascents and descents, and every 2–8 min during horizontal flight legs. A maximum of 168 canisters were filled for each flight on the DC-8. After each flight, the canisters were shipped back to the laboratory at UC Irvine and the contents analyzed within seven days of sample collection for more than 75 gases, including non-methane hydrocarbons, halocarbons, alkyl nitrates, sulfur compounds, and oxygenated compounds.

A detailed description of the analytical system used in this study is described in Colman et al. (2001). Briefly,  $2440 \pm 3 \text{ cm}^3$  (STP) of an air sample is preconcentrated in a stainless steel loop filled with glass beads and submerged in liquid nitrogen. The sample is heated to approximately  $80^\circ\text{C}$ , and split into six different column/detector combinations using UHP helium as the carrier gas: (1) DB-1 column (J&W; 60 m, 0.32 mm I.D., 1  $\mu\text{m}$  film thickness) output to a flame ionization detector (FID); (2) DB-5 column (J&W; 30 m, 0.25 mm I.D., 1  $\mu\text{m}$  film thickness) connected in series to a RESTEK 1701 column (5 m, 0.25 mm I.D., 0.5  $\mu\text{m}$  film thickness) and output to an electron capture detector (ECD); (3) RESTEK 1701 column (60 m, 0.25 mm I.D., 0.50  $\mu\text{m}$  film thickness) output to an ECD; (4) PLOT column (J&W GS-Alumina; 30 m, 0.53 mm I.D.) connected in series to a DB-1 column (J&W; 5 m, 0.53 mm I.D., 1.5  $\mu\text{m}$  film thickness) and output to an FID; (5) DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5  $\mu\text{m}$  film thickness) output to a nitrogen phosphorus detector (NPD); (6) DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5  $\mu\text{m}$  film thickness) output to a quadrupole mass spectrometer detector (MSD, HP 5973). The MSD is set to operate in selected ion monitoring (SIM) mode with one ion chosen to quantify each compound in order to achieve the maximum selectivity and to avoid potential interferences. All gas chromatographs and detectors used in this study are manufactured by Hewlett Packard.

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The precision of the measurements varies by compound and by mixing ratio: 1% for the CFCs and  $\text{CCl}_4$ ; 2% for the HCFCs; 5% for HFC-134a and  $\text{CH}_2\text{Cl}_2$ ; 2% for Halon-1211, methyl halides,  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{CHBr}_3$ . The measurement accuracy also varies by compound: 2% for CFCs (except 5% for CFC-114); 10% for the HCFCs,  $\text{C}_2\text{Cl}_4$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$ ; 5% for halons, HFC-134a,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_3\text{Br}$ .

The original standard for the calibration of the NMHCs is gravimetrically prepared from National Bureau of Standards and Scott Specialty Gases standards (accuracy  $\pm 5\%$ ). These standards are used for the calibration of the highly pressurized whole air standards (2000 psi) contained within aluminum cylinders. After the initial addition of 17 Torr of degassed ultrapure Milli-Q water the air sample is transferred from the cylinder to an electropolished stainless steel pontoon (34 L) equipped with a Swagelok metal bellows valve. A higher degree of stability inside the pontoon has been determined for higher molecular weight hydrocarbons, alkyl nitrate, sulfur species and some of the halocarbons. During the analysis a working standard is analyzed every eight samples, and once a day a series of different standards, including primary standards, is analyzed.

Carbon monoxide levels were measured *in situ* on the DC-8 by a differential absorption CO measurement (DACOM) instrument (Sachse et al., 1987). The HFC:CO ratio, along with CO emissions data, is used to determine the HFC-152a and HFC-134a emission rate in the LA area and SoCAB (see Sect. 3.2.1).

## 2.2 Distribution of ARCTAS-CARB air samples

The 617 air samples obtained on board four DC-8 flights during the ARCTAS-CARB campaign were collected both over California and off the California coast. An additional 139 air samples were collected over California on board two transit flights from California to Cold Lake, Canada (Flights 16 and 24), where the DC-8 was stationed for the second phase of ARCTAS. The majority of the samples were collected at low altitude during the daytime as illustrated in Fig. 1 and Table 1. Figure 1 shows the



geographic distribution of the samples color-coded by the airplane's altitude during the sampling. Air samples were collected over two main source regions: the San Joaquin Valley (SJV) and South Coast Air Basin (SoCAB). Low level passes around the San Diego area and along the border between the United States and Mexico occurred during Flights 12 and 15, respectively. This work examines only the field measurements obtained over the SoCAB and in the inflow air masses over the Pacific Ocean.

Among the 756 canisters collected over California, 196 were obtained over the SoCAB (outlined by a gray line in Fig. 2). A subset (90 samples) of the SoCAB samples was obtained over the LA area (included in the red dashed line in Fig. 2). All of these canisters were filled during low altitude passes capturing freshly emitted air masses. The LA area samples were collected at an average altitude of  $1.1 \pm 1.3$  km, with more than 80% of the canisters (75 out of 90) filled below 2 km and only 11 samples (~10%) above 3 km. The average sampling altitude over the SoCAB was  $1.0 \pm 1.4$  km.

A polluted air mass can be transported far from its origin making the source identification difficult. The use of backward trajectories is a useful and common tool for investigating the movement of air masses. For instance, kinematic back trajectories, in conjunction with a detailed characterization of the composition of pollution plumes, were used in documenting the impact of Asian outflow on North America (i.e. Liu et al, 2003, Barletta et al., 2009). However, the influence of sources located far away from the collection site can be neglected if air masses are sampled within the planetary boundary layer or at altitudes low enough to suggest minimum mixing of freshly emitted pollution plumes with free tropospheric air affected by transported air pollution (Millet et al., 2009). Therefore, the authors assume that measured pollutant concentrations were due primarily to local sources, not transported air masses.

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### 3 Discussion

#### 3.1 General trend in halocarbons in the LA area and SoCAB

In order to establish the contribution from local sources to halocarbon levels measured over the LA area and SoCAB, the inflow concentration of halocarbon species was determined from a set of 60 air samples collected far offshore during Flight 14 along a south to north leg over the Pacific Ocean (Fig. 1). These samples contained air moving toward California with minimal North American influence, but do not represent the regional background as they could be affected by polluted air masses intercepted over the Pacific Ocean. Instead, the ocean air samples characterize the inflow towards California before being impacted by fresh pollution plumes generated within North America.

As expected, the average mixing ratios for all halogenated compounds in the inflow air were lower than the average levels measured over the LA area and SoCAB. Additionally, the variation in the halocarbon levels was much lower in the inflow samples compared to samples obtained over the mainland (Table 2), which is consistent with the presence of significant land-based emission sources. The fraction of samples collected in the LA area and SoCAB that contained halocarbon mixing ratios higher than the inflow samples was determined by calculating the number of samples with levels exceeding the average inflow mixing ratio plus two standard deviations ( $2\sigma$ ). This high reference level (average inflow plus  $2\sigma$ ) was set to avoid overestimating the halocarbon enhancement in the LA area and SoCAB.

For the CFCs and their replacements, with the exception of CFC-113 and CFC-114, concentrations exceeding the reference level were observed in a majority (60–80%) of air samples obtained over the LA area and SoCAB (Table 2 and Fig. 3). The CFC-114 mixing ratios measured in these regions were similar to the inflow air masses, with ~30% of the samples showing enhanced levels. Reduced enhancements also were observed for CFC-113 over the SoCAB (37% of samples with enhanced mixing ratios) but not over the LA area (60% of samples with enhanced mixing ratios). A relatively small fraction of samples with enhanced mixing ratios were observed for halon-2402

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(14% and <1% in the LA area and the SoCAB, respectively), halon-1301 (27% in both regions; Fig. 4a), and  $\text{CCl}_4$  (14% and 17% in the LA area and SoCAB, respectively). However, halon-1211 and  $\text{CH}_3\text{CCl}_3$  levels were enhanced in a majority of the collected samples (~55%; Fig. 4b and c).

5 Although previous studies reported ongoing emissions of regulated CFCs and other halogenated compounds in North America (Hurst et al., 2006; Millet et al., 2009; Barletta et al., 2009), the consistently enhanced levels measured during the ARCTAS-CARB flights allow a closer identification of one possible source region (i.e. California) and show the presence of such sources during the summer of 2008. Among the 196  
10 air samples obtained over the SoCAB during the ARCTAS-CARB study a small fraction collected during Flight 12 contained exceptionally high levels of halocarbons (Fig. 5). Three consecutive samples collected during 13:22-13:26 (local time) at an altitude of 0.3 km over the northern area of the Orange County (near +33.8 latitude, -118.0 longitude) and five consecutive samples collected during 14:20-14:29 (local time) at an altitude of 0.6-1.0 km over a south-west to north-east leg across the SoCAB contained  
15 the highest levels of many halogenated compounds observed during the study. For example,  $\text{C}_2\text{Cl}_4$  mixing ratios were 75-90 pptv in the first set of three samples and 35-156 pptv in the second set of five samples compared to  $2.9 \pm 1.0$  pptv in the inflow (Fig. 5). The sources responsible for these high emissions are not known, but the locations of these exceptionally high halocarbon enhancements are presented here as they may be important sites for future studies.

### 3.2 Regional emission rate estimates for HFC-152a and HFC-134a

Figure 6 shows the mixing ratios of HFC-152a and HFC-134a measured in the SoCAB during the ARCTAS-CARB study. Measured concentrations of both HFC-152a and HFC-134a over the mainland were significantly higher than in the inflow air mass. A  
25 factor of five enhancement over the mainland compared to the inflow was observed for HFC-152a, with  $48 \pm 61$  pptv and  $43 \pm 40$  pptv in the LA area and SoCAB, respectively, versus  $9 \pm 5$  pptv in the inflow (Table 2). The HFC-152a inflow level calculated in our

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study is in excellent agreement with the AGAGE (Advanced Global Atmospheric Gases Experiment) measurements at Trinidad Head, California ( $8.7 \pm 0.5$  pptv measured by the GC-MS Medusa instrument in June 2008; AGAGE, 2010). About 12% of the samples collected over the LA area and the remaining SoCAB had a mixing ratio higher than 100 pptv (representing about 10 times the levels in the inflow air masses). The highest measured mixing ratios were 213, 133, and 127 pptv over LA, versus 370, 279, and 303 pptv over the remaining SoCAB. For HFC-134a, the average mixing ratio enhancement in the LA area ( $89 \pm 77$  pptv) and SoCAB ( $88 \pm 67$  pptv) was approximately twice the average mixing ratio measured in the inflow ( $46 \pm 2$  pptv), with a lower absolute enhancement compared to HFC-152a. The number of samples with a mixing ratio higher than 100 pptv (representing about double the levels in the inflow) over LA and the remaining SoCAB was 29% and 23%, respectively. These relatively large enhancements indicate the presence of significant emission sources of HFC-152a and HFC-134a in the LA area and SoCAB.

There was considerable spatial variability in both HFC and HCFC concentrations in the LA area and SoCAB, suggesting that these species are released mostly from localized point sources rather than released evenly across the regions. Although the nature of these specific sources is unknown, a study by Scheutz et al. (2007) on the release of halogenated species from insulation foam in home appliances during shredding operations supports this hypothesis. Many CFC replacements, such as HCFC-141b, HCFC-142b, HCFC-22, and HFC-134a, often are used as blowing agents in appliances. The release of these HCFCs and HFCs into the atmosphere during the life of an appliance is negligible (Kjeldsen et al., 2003). However, those species can be released when the discarded appliances are shredded and while the shredded material is stockpiled waiting to be shipped for final disposal. Scheutz et al. (2007) found that on average 24% of the initial blowing agents content is released during the shredding process from three US shredder facilities. Such facilities in the SoCAB may be responsible for the spikes in CFC replacements observed during the ARCTAS-CARB flights.

Vehicle air-conditioning units also may contribute significantly to HFC-134a emissions. HFC-134a can be emitted slowly during normal driving or in large amounts during accidents, servicing, and dismantlement at the end of a vehicle's drivable life. Wimberger (2010) took HFC-134a samples from vehicles on dismantler lots in California and found that on average only 27% of the initial HFC-134a remained in the air-conditioning system before dismantlement.

### 3.2.1 Emission rate estimates from the “chemical ratio” method

The first method of obtaining emission rate estimates of HFC-152a and HFC-134a uses the HFC:CO concentration ratio obtained from field measurements in the LA area (the red area in Fig. 2). The measured volume ratios were converted into mass ratios and multiplied by the 2008 CO emission rate in LA County, providing an estimate of HFC-152a and HFC-134a emissions in LA County for 2008. The ARCTAS-CARB flights flew over part of LA County and it is assumed that the HFC:CO slope for the LA area (land area  $\sim 3700 \text{ km}^2$ ) is the same as the HFC:CO slope that would be observed over the entire LA County ( $\sim 10518 \text{ km}^2$ ).

This method has been used extensively to estimate emissions of several species (Reimann et al., 2005; Greally et al., 2007; Millet et al., 2009). The validity of the chemical ratio method relies on three main assumptions: (1) the two species are correlated strongly, (2) the emission rate of one of the two species is well-known (CO in this case), and (3) the chemical compounds have a lifetime longer than the typical transport time, which is true for CO (lifetime  $\sim 2$  months), HFC-152a ( $\sim 1.5$  yr), and HFC-134a ( $\sim 14$  yr) (Forster et al., 2007). Figures 7 and 8 show the strong correlation of HFC-152a and HFC-134a with CO for the samples collected in the LA area. Data points with a CO mixing ratio below 100 ppbv were excluded as they likely are from air masses not affected by anthropogenic emissions. Although different emission sources likely are responsible for the emission of CO and the two HFCs, the co-location of CO and HFC sources within the LA area results in the good correlation observed between these species (coefficient of determination  $R^2 = 0.85$  for HFC-152a vs CO and

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$R^2 = 0.67$  for HFC-134a vs. CO). The slope of the linear regression line through the data points represents the HFC:CO molar ratio. A ratio of  $0.57 \pm 0.03 \text{ mmol mol}^{-1}$  and  $0.53 \pm 0.04 \text{ mmol mol}^{-1}$  were observed for HFC-152a:CO, and HFC-134a:CO, respectively. These volume ratios were multiplied by molecular weights to convert them into mass ratios, and then multiplied by the 2008 CO emission rate in LA County (1,958 tons per day, or  $\sim 2 \times 10^9$  grams per day; CARB, 2010). Using this method the 2008 emissions estimates of HFC-152a and HFC-134a in LA County were  $0.98 \pm 0.05 \text{ Gg}$  and  $1.40 \pm 0.11 \text{ Gg}$ , respectively. The high correlation observed between HFC-152a and CO ( $R^2 = 0.85$ ) results in a smaller uncertainty in the calculated final emissions ( $\sim 5\%$ ) compared to the uncertainty in the emission rate of HFC-134a ( $\sim 8\%$ ).

Emissions estimates for the SoCAB and United States were obtained by assuming emissions are directly proportional to population density, an approach used in previous studies (Li et al., 2005; Stohl et al., 2009). Stohl et al. (2009) stated that global emissions estimates calculated using population data likely overpredict emissions from developing countries, but this error is less significant when the use of the population data is confined to a single nation. Using this extrapolation method, the 2008 emissions of HFC-152a and HFC-134a in the SoCAB were  $1.48 \pm 0.07 \text{ Gg}$  and  $2.12 \pm 0.17 \text{ Gg}$ , respectively, and  $30.1 \pm 1.5 \text{ Gg}$  and  $43.0 \pm 3.4 \text{ Gg}$  in the United States.

Greally et al. (2007) estimated that HFC-152a global emissions for the 1994–2004 period increased at an average rate of  $\sim 14\%$  per year (with a slight acceleration in 2000–2004) reaching  $28 \text{ Gg}$  in 2004. Assuming the same rate of increase through 2008, a global estimate of  $47 \text{ Gg}$  in 2008 was extrapolated from their work. This emissions estimate for 2008 agrees well with the global emission estimate of  $37 \text{ Gg yr}^{-1}$  obtained by Stohl et al (2009) for the years 2005–2006. The estimate calculated for the US in 2008 using the ARCTAS-CARB data ( $30 \text{ Gg}$ ), if accurate, would make the US the primary emitter of HFC-152a in the world. Other studies estimate lower HFC-152a emissions in the US. Stohl et al. (2009) estimated that US emissions of HFC-152a in 2005 and 2006 are  $10.1 \text{ Gg}$  and  $12.5 \text{ Gg}$ , respectively ( $\sim 24\%$  increase between the two years). If the US maintained this high annual increase through 2008, Stohl et

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al.'s (2009) estimate yields 19 Gg in 2008, significantly below the estimate in this study. Even lower estimates from the US are reported by Millet et al. (2009) with 5.7–9.7 Gg in 2006, representing less than one-quarter of the 2006 global estimates given by Stohl et al. (2009) and Greally et al. (2007). The discrepancy between the HFC-152a emissions estimates for the US from previous studies and the current study is not known, but it is possible that specific source regions investigated in those studies were not representative of the overall emissions in the US. In Millet et al. (2009), emissions were derived from the TEXAQS-II study over Southern Texas during September–October 2006. Stohl et al. (2009) used field measurements from nine locations across the world in deriving their estimate. It should be noted that the United States generally is regarded as the biggest emitter of HFC-152a (Ashford et al., 2004) and the US emission rate estimates from Stohl et al. (2009) and Millet et al. (2009) are less than 50% of the total global emissions predicted by Greally et al. (2007) and Stohl et al. (2009).

The total mass of HFC-134a emissions in the US for 2008 calculated using the ARCTAS-CARB data is  $43.0 \pm 3.4$  Gg, which agrees very well with the estimates of 43 Gg (22–60 Gg range, for 2006) calculated by Manning and Weiss (2007). In that work, the HFC-134a emissions were first estimated for the western US using ground-based observations at the AGAGE measurement station at Trinidad Head on the Northern California coast, and then extrapolated to the US using population data. The US emission rate estimate of HFC-134a in our study is greater than values reported in Stohl et al. (2009) (33 Gg in 2005 and 29 Gg in 2006) but close to the upper limit reported by Millet et al. (2009) ( $12\text{--}39$  Gg yr<sup>-1</sup> during 2004–2006).

### 3.2.2 Emission rate estimates from the “AQM” method

This study utilizes a second method to obtain emissions estimates of HFC-152a and HFC-134a in LA County and the SoCAB during 2008 using an air quality model to reproduce field measurements obtained during ARCTAS-CARB flights. In the model it is assumed that HFC-152a and HFC-134a are emitted at a constant rate from urban areas across the SoCAB. The emission rates are incrementally adjusted until the

average mixing ratio from the simulations matches the average mixing ratio from field measurements.

Air quality simulations were performed using 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 of California (Griffin et al., 2002a, b). The UCI-CIT model uses a horizontal 80×30 rectangular grid with five vertical layers, the highest layer extending to 1100 m. Each grid cell corresponds to a 5 km×5 km region.

The predicted concentration of HFC-152a and HFC-134a was determined primarily by the emission rates and meteorology. Although these two HFC species react with OH, loss due to chemical reaction and deposition is insignificant compared to loss from transport (Forster et al., 2007). Since a complete meteorological data set was not available for the June 2008 field campaign, multiple simulations were conducted using meteorological data sets from field campaigns that occurred in the SoCAB during 27–28 August 1987 (Meng et al., 1998), 8–9 September 1993 (Griffin et al., 2002b), and 18–19 October 1995 (Knipping and Dabdub, 2002). The wind patterns during the August 1987, September 1993, October 1995, and June 2008 field campaigns are similar – relatively calm winds during the night and early morning and steady on-shore winds midday. A comparison of wind speed and direction at three locations in the SoCAB is provided in Supplement Table 1. Conducting simulations using six different meteorological data sets created a range of predicted HFC-152a and HFC-134a mixing ratios that were compared to field measurements. The emission rate in the model was incrementally adjusted until the average mixing ratios from the six simulations matched the average mixing ratio measured during the ARCTAS-CARB flights in the LA area and SoCAB.

The UCI-CIT model spins up for five simulation days allowing the system to reach a steady diurnal cycle. The data presented here are from the last simulation day. In the simulations, HFC-152a and HFC-134a were emitted from urban cells at a constant rate every hour. Separate sets of simulations were conducted to determine the urban

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emission rates in the LA area and SoCAB. As in the chemical ratio method, simulation results from the LA area were extrapolated to LA County. The inflow concentration for HFC-152a (9 pptv) and HFC-134a (46 pptv) were obtained from field measurements over the Pacific Ocean.

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  $h$  ( $\bar{c}_{h,i,k}$ ) the weighted average of all five vertical layers was calculated, accounting for differences in air pressure and layer thickness. The equation for  $\bar{c}_{h,i,k}$  is,

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

where  $n_{h,i,k}$  and  $n_{h,air,k}$  are the total number of moles of species  $i$  and air, respectively, in cell  $k$  at hour  $h$ .  $P_{h,i,j,k}$  and  $P_{h,air,j,k}$  are the average partial pressures of species  $i$  and air, respectively, in layer  $j$  of cell  $k$  at hour  $h$ . The concentration of species  $i$  in layer  $j$  of cell  $k$  at hour  $h$ ,  $c_{h,i,j,k}$ , was determined from simulations.  $V_j$  is the volume of layer  $j$ ,  $T_{h,k}$  is the temperature of cell  $k$  at hour  $h$  (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<sup>2</sup>) times the layer height ( $d_j$ ).

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

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

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

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

where  $N_C$  is the total number of cells comprising the region of interest and the subscript area was either *LA* or *SoCAB*.

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

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

Figure 9 shows the average concentration and 1- $\sigma$  values of HFC-152a in the cells comprising the SoCAB for each layer (Fig. 9a–e) and the weighted average of all five layers (Fig. 9f) using the 9 September 1993 meteorology data set (see Supplementary Fig. 1 for similar plots of HFC-134a in the SoCAB, and Supplementary Figs. 2 and 3 for similar plots of HFC-152a and HFC-134a in the LA area). Similar results were obtained using the other five meteorological data sets. Model predictions were compared to field measurements from the ARCTAS-CARB flights, which are shown as black dots in Fig. 9.

At the lowest layer in the UCI-CIT model (0–38.5 m) the average concentration in the LA area and SoCAB was relatively high in the morning but decreased during the day as onshore winds increase and relatively clean ocean air blows into the region, pushing HFC-152a and HFC-134a eastward out of the SoCAB. In the late afternoon and evening the wind speed decreases, resulting in an accumulation of the HFCs. A similar trend was seen in the second layer (38.5–154 m). In the upper three layers of the model (layer 3 = 154–308 m; layer 4 = 308–671 m; layer 5 = 671–1100 m), vertical

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mixing transports the HFCs upward from the lower layers as the winds increase midday, resulting in elevated mixing ratios in the upper layers at that time. It should be noted that although the mixing ratio was highest at the ground layer and generally decreased with altitude, the overall diurnal pattern in a cell (averaging over all five layers) was determined primarily by the mixing ratio in the upper layers since those layers are significantly taller than the lower layers.

Figure 9 demonstrates that the UCI-CIT model was able to reproduce measurements from the ARCTAS-CARB flights well qualitatively – most measurements fall within a factor of two of the mean predictions. In order to compare the results from the UCI-CIT model to field measurements quantitatively, the average predicted concentration in the LA area and SoCAB during 8AM-6PM was determined by averaging the values of  $\bar{c}_{h,i,LA}$  from  $h=8$  to  $h=17$ , the time range in which the field measurements were collected,

$$\hat{c}_{i,area} = \frac{1}{10h} \sum_{h=8}^{17} \bar{c}_{h,i,LA}. \quad (5)$$

The average measured mixing ratios in the LA area and SoCAB were determined in a similar manner as  $\hat{c}_{i,area}$  in Eq. (5). Air samples collected at altitudes between 0 m and 1100 m during the ARCTAS-CARB flights were sorted by elevation into five bins that are the same height as the layers in the UCI-CIT model. The average concentration in each bin was calculated and the total mixing ratio from 0 m to 1100 m was determined by taking a weighted average of all five layers, accounting for differences in air pressure and layer size.

Table 3 lists the average measured and predicted mixing ratios of HFC-152a and HFC-134a in the LA area and SoCAB during 8 a.m.–6 p.m. Six different meteorological data sets were used in the UCI-CIT model. Although the value of  $\hat{c}_{i,area}$  is dependent upon meteorology, Table 3 shows that model predictions of the average concentration of HFC-152a and HFC-134a in the LA area and SoCAB for all six meteorological data sets vary less than 35% from the mean value.

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The emission rate estimates were determined by incrementally adjusting the emission rate from urban cells in the model until the average  $\hat{c}_{i,area}$  from all six simulations was the same as the average mixing ratio in the LA area and SoCAB determined from field measurements. The urban emission rates for these two regions,  $E_{urban,LAA}$  and  $E_{urban,SoCAB}$ , were multiplied by the fraction of urban cells in those regions to obtain the average emission rate in the LA area and SoCAB,  $E_{avg,LAA}$  and  $E_{avg,SoCAB}$ . The average emission rate in LA County,  $E_{avg,LAC}$ , was calculated by multiplying  $E_{avg,LAA}$  by the ratio of land area in LA County to the land area in the LA area ( $10518 \text{ km}^2/3700 \text{ km}^2$ ). The UCI-CIT model uses landuse data collected during the 1970s by the United States Geological Survey (USGS). Based on this data, the fraction of urban cells in the LA area and SoCAB is 76% and 49%, respectively. However, there has been considerable urban sprawl in the SoCAB since the 1970s. An alternate scenario was examined in which 100% of the cells in the SoCAB are classified as urban (all cells in the SoCAB emit at the same rate). The actual fraction of urban cells in the LA area and SoCAB is between 100% and the fraction provided by the USGS.

Emission rates for LA County and the SoCAB from the AQM method agree well with estimates from the chemical ratio method described in the previous section (Table 4). Using land use data from the 1970s to determine which cells are classified as urban, the UCI-CIT model predicts LA County 2008 emissions of 0.72 Gg and 1.04 Gg for HFC-152a and HFC-134a, respectively. For the SoCAB, the model predicts emissions of 0.91 Gg and 1.29 Gg for HFC-152a and HFC-134a, respectively. For the scenario where all cells are classified as urban, the UCI-CIT model predicts LA County emissions of 0.65 Gg and 1.12 Gg for HFC-152a and HFC-134a, respectively. For the SoCAB, the model predicts emissions of 1.08 Gg and 1.55 Gg for HFC-152a and HFC-134a, respectively. Therefore, the emissions estimates obtained using the AQM method were within a factor of 1.5 of estimates obtained using the chemical ratio method.

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There are some limitations in using the AQM method to obtain estimates of HFC emission rates: (1) Although field measurements were obtained over a large area at many different elevations, it is possible that a disproportionate number of measurements were gathered over locations that have relatively low or high mixing ratios. Non-representative sampling could lead to incorrect predicted emission rates since the emission rates in the model were adjusted until mixing ratios from simulations match measured mixing ratios. However, non-representative sampling would affect all other methods as well; (2) In the simulations, it was assumed that the HFC emission rates were constant for all urban cells at all times. The true emission rates are not constant in time and may vary significantly among urban cells. This constant emission rate assumption was made to compare emissions determined from the AQM method to emissions determined by the chemical ratio method, which uses the 24-h average CO emission rate in LA County. Both methods assume a constant emission rate during all hours of the day; (3) Actual wind fields during the June 2008 field campaign were similar, but not exactly the same, as the wind fields during the August 1987, September 1993, and October 1995 field campaigns, which were used in the simulations. The wind speed during the June 2008 field campaign tends to be higher than during the other three field campaigns, which has the effect of lowering predicted emission rates. If the wind is calmer, pollutants are removed from the SoCAB at a slower rate which lowers the emission rate needed to reproduce measured concentrations. However, although the June 2008 wind velocity is known for several locations in the SoCAB, the wind velocity at most locations is not known and would have to be estimated for most of the SoCAB, creating additional uncertainties in the predictions.

Despite these caveats, it appears that the emissions estimates from air quality simulations are credible since (1) the predicted emissions of HFC-152a and HFC-134a in LA County and the SoCAB determined from the AQM method are quite similar to estimates determined from the chemical ratio method and (2) most field measurements are within a factor of two of the mean concentration predicted in the LA area and SoCAB.

## 4 Conclusions

For the first time the concentration of important halocarbons were measured in LA County and the SoCAB of California and compared to samples obtained from relatively clean inflow air masses. Elevated concentrations were observed for many species regulated by the Montreal Protocol and subsequent amendments, including CFCs. Accurate knowledge of halocarbon levels in the atmosphere allows policymakers to assess the effectiveness of mitigation strategies. Additionally, it is particularly important to assess accurately the atmospheric levels of  $\text{CH}_3\text{CCl}_3$  because this species is used to estimate global concentrations the hydroxyl radical (OH). Errors in the determination of global OH levels can be significant if emission sources in developed areas are not properly characterized. Millet and Goldstein (2004) calculate that global OH was underestimated by 7.2% for 2000 and 11% for 1997 by neglecting ongoing methyl chloroform emissions by non-Article 5 nations.

Two methods were employed to estimate the emissions of HFC-152a and HFC-134a from LA County and the SoCAB in 2008. The close agreement between the results from the two methods lends credence to the emission estimates presented in this paper. Additionally, 2008 emissions estimates of the two HFCs in the US were derived by extrapolating the results from the chemical ratio method. For HFC-152a, the US emissions calculated in this study were higher than previous estimates, likely due to the location of field measurements used to derive the estimates, while the HFC-134a US emissions calculated in this study agreed better with previous estimates.

Although the samples used to calculate these emissions estimates were collected during a brief period of time and the ARCTAS-CARB sampling campaign captures a brief snapshot of California's lower troposphere, halocarbons rarely are measured over locations containing important sources, such as the SoCAB. The emissions estimates from this study serve as a reference for other studies where emissions are estimated from observations in remote locations (where the atmospheric lifetime of relatively short lived species, less than 2 years, is on the same timescale of global

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**Table 1.** Statistics of air samples collected over California and off the California coast during the four ARCTAS-CARB flights and two transit flights.

Flight Date (Flight #)	Number of samples	Altitude Range (km)	Sampling Time Range*
18/06/2008 (#12)	152	0.08–4.5	08:38–14:34
20/06/2008 (#13)	165	0.29–6.7	10:43–18:12
22/06/2008 (#14)	168	0.08–9.1	08:17–17:19
24/06/2008 (#15)	132	0.15–9.1	09:43–17:17
26/06/2008 (#16)**	51	0.32–5.3	07:31–09:29
13/07/2008 (#24)**	88	0.34–4.0	13:10–15:43
Total	756		

\* Local Time

\*\* Includes only the samples collected over California.

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**Table 2.** Data from air samples obtained in the inflow air mass, over the LA area, and over the SoCAB during the ARCTAS-CARB flights.

	Inflow ( <i>n</i> = 60)			SoCAB ( <i>n</i> = 106)				LA ( <i>n</i> = 90)			
	Range (Min-Max)	Mean	SD	Range (Min-Max)	Mean	SD	% High samples*	Range (Min-Max)	Mean	SD	% High samples*
CFCs											
CFC-12	520–534	528	4	523–654	541	13	73	523–564	539	9	69
CFC-11	240–250	245	2	241–498	259	27	79	242–394	258	21	76
CFC-113	74.4–78.6	76.3	0.8	75.3–82.7	77.9	1.1	37	75.3–80.7	78.1	1.0	60
CFC-114	15.5–16.5	16.1	0.2	15.5–16.8	16.3	0.3	33	15.7–16.8	16.3	0.2	28
HCFCs											
HCFC-22	186–240	201	10	186–926	280	107	66	186.4–926	276	100	62
HCFC-142b	18.4–23.7	20.1	1.1	18–856.5	46.5	95.9	68	18–856.5	59.4	136.9	62
HCFC-141b	18.5–23.5	19.7	1.0	18.1–236.9	30.2	21.3	68	18.1–101.9	29.9	16.0	63
HFCs											
HFC-134a	43.1–54.0	45.9	2.3	41.7–702	87.8	67.3	81	41.7–702.0	89.1	76.6	72
HFC-152a	5.1–31.0	8.9	5.0	4.7–398.3	47.5	61.1	56	4.7–212.8	42.5	40.3	60
Halons											
H-1211	4.15–4.46	4.26	0.06	4.14–6.45	4.52	0.41	55	4.14–5.66	4.50	0.32	58
H-2402	0.50–0.52	0.51	0.01	0.48–0.53	0.51	0.01	< 1	0.48–0.53	0.51	0.01	14
H-1301	3.0–3.6	3.3	0.1	2.9–4.3	3.4	0.2	27	2.9–4.3	3.4	0.2	27
Regulated Solvents											
CH <sub>3</sub> CCl <sub>3</sub>	11.6 – 12.6	12.2	0.2	11.8–17.9	12.9	1.0	58	11.8–16.6	13.0	1.1	56
CCl <sub>4</sub>	90.3 – 93.6	91.9	0.8	90.8–94.8	92.8	0.7	17	91.7–94.8	92.8	0.6	14
Other Solvents											
CHCl <sub>3</sub>	6.0–15.0	9.2	1.9	6–56.0	15.7	8.9	44	6.6–44.3	15.5	8.3	46
CH <sub>2</sub> Cl <sub>2</sub>	22.9–61.9	36.3	8.7	24.5–318.6	64.8	51.4	37	24.5–248.7	62.4	38.4	47
C <sub>2</sub> HCl <sub>3</sub>	0.10–0.61	0.23	0.08	0.08–24.5	2.1	3.1	85	0.2–12.1	1.8	1.9	72
C <sub>2</sub> Cl <sub>4</sub>	1.4–5.1	2.9	1.0	1.36–156.3	13.2	18.6	57	1.51–70.9	11.9	11.6	61

\* number of samples with a mixing ratio  $\geq$  mean of inflow air +  $2\sigma$  (see text for explanation).

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**Table 3.** Average measured and predicted mixing ratios of HFC-152a and HFC-134a in the LA area and SoCAB (0–1100 m in elevation) during 8AM–6PM, in pptv.

	LA area*		SoCAB*	
	[HFC-152a]	[HFC-134a]	[HFC-152a]	[HFC-134a]
Meteorology				
27 Aug 1987	42	79	68	99
28 Aug 1987	49	92	62	95
8 Sep 1993	64	111	99	130
9 Sept 1993	57	99	91	119
18 Oct 1995	53	91	69	131
19 Oct 1995	73	124	60	91
Average of six simulations	57	100	75	111
Average of field measurements	57	100	75	111

\* Landuse data from the United States Geological Survey. The fraction of urban cells in the LA area and SoCAB is 76% and 49%, respectively.

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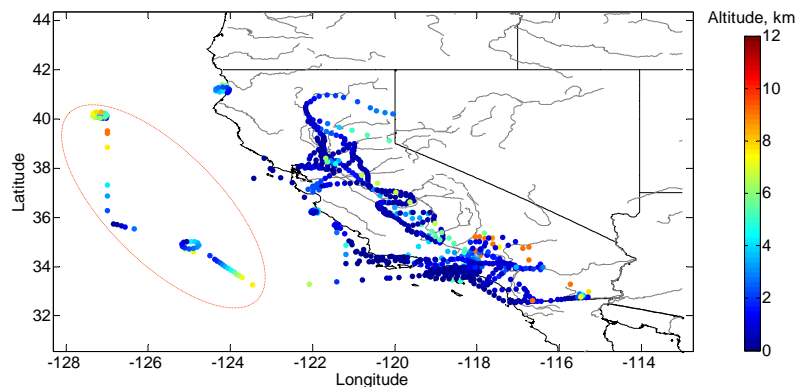


**Table 4.** Summary of emission estimates (in Gg) for HFC-152a and HFC-134a in 2008 for Los Angeles County, the South Coast Air Basin, and the United States.

Region	Chemical Ratio Method		AQM Method	
	HFC-152a	HFC-134a	HFC-152a	HFC-134a
LA County	0.98±0.05	1.40±0.11	0.65–0.72	1.04–1.12
SoCAB	1.48±0.07	2.12±0.17	0.91–1.08	1.29–1.55
US	30.1±1.5	43.0±3.4	N/A	N/A

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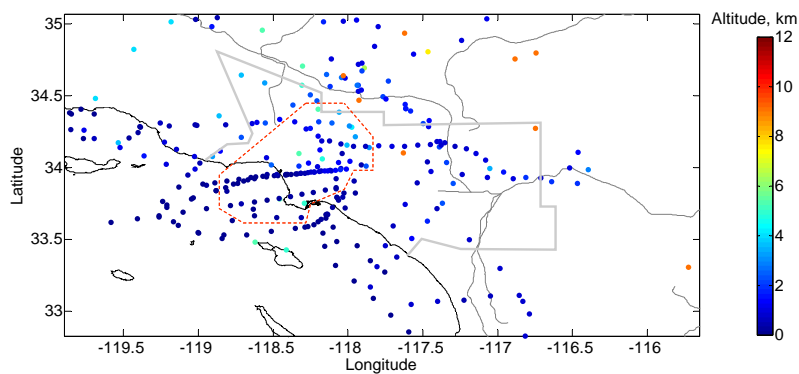
**Fig. 1.** Samples collected over California during the four ARCTAS-CARB flights and two transit flights. The samples are color-coded by altitude. The dotted red oval highlights the samples used to characterize the inflow air (see text for explanation).

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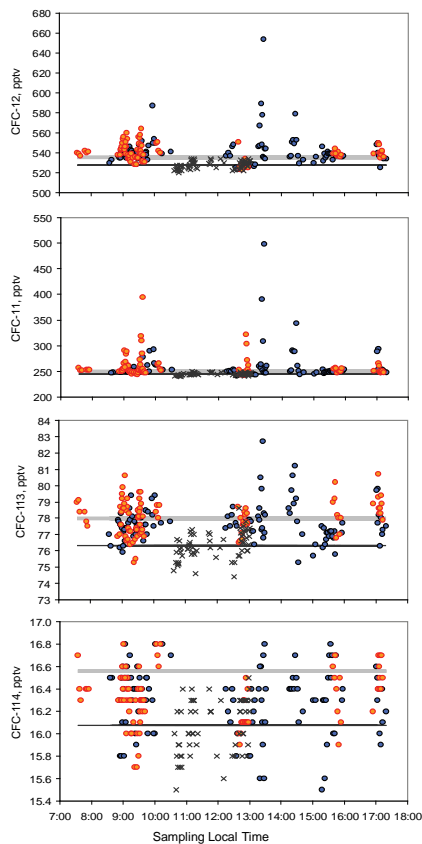
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**Fig. 2.** Location of samples collected in Southern California. The SoCAB is indicated by the solid grey line and samples obtained within the LA area are included within the red dashed line.

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**Fig. 3.** Mixing ratio of CFCs in samples collected over the LA area (orange filled circles), the remaining SoCAB (blue filled circles), and offshore (inflow air masses, black crosses). The black line indicates the average of the inflow, while the grey line represents the average plus 2 standard deviations.

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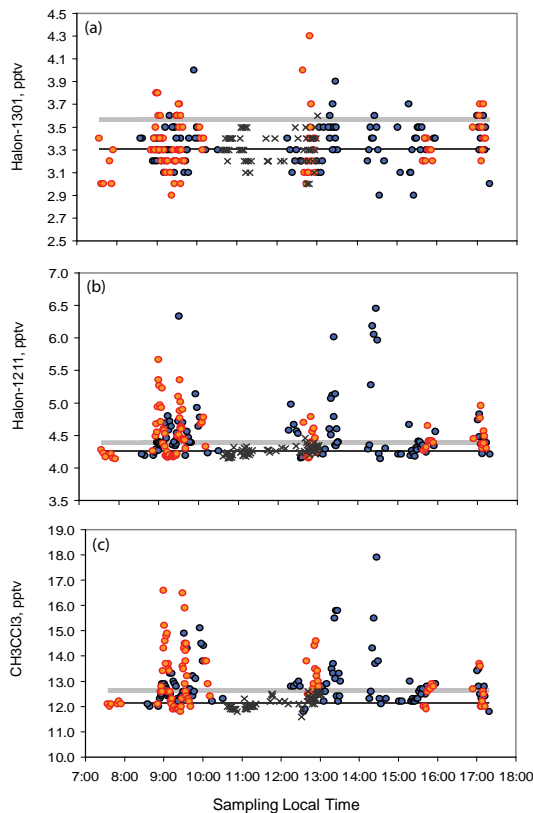
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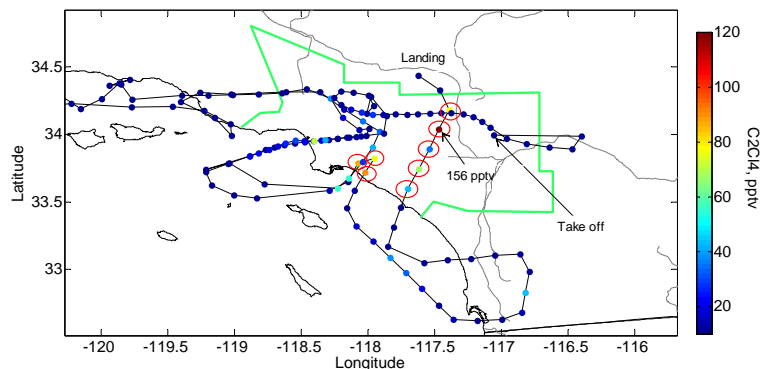




**Fig. 4.** Mixing ratio of **(a)** Halon-1301, **(b)** Halon-1211, **(c)** CH<sub>3</sub>CCl<sub>3</sub> in samples collected over the LA area (orange filled circles), the remaining SoCAB (blue filled circles), and offshore (inflow air masses, black crosses). The black line indicates the average of the inflow, while the grey line represents the average plus 2 standard deviations.

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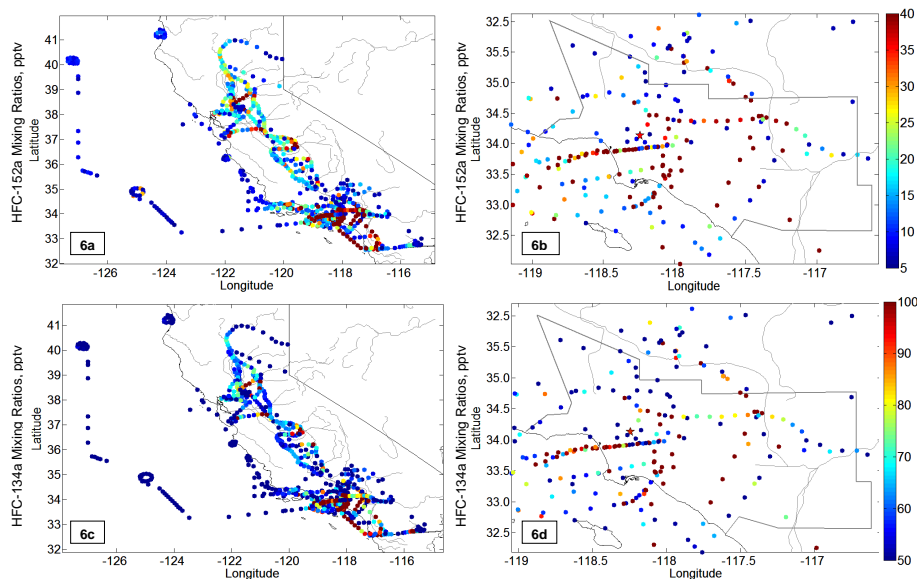


**Fig. 5.** Air samples collected during Flight 12 color-coded by  $C_2Cl_4$  mixing ratios (the line connecting the samples illustrates the flight path). The samples circled in red correspond to canisters showing greatly enhanced halocarbon levels.

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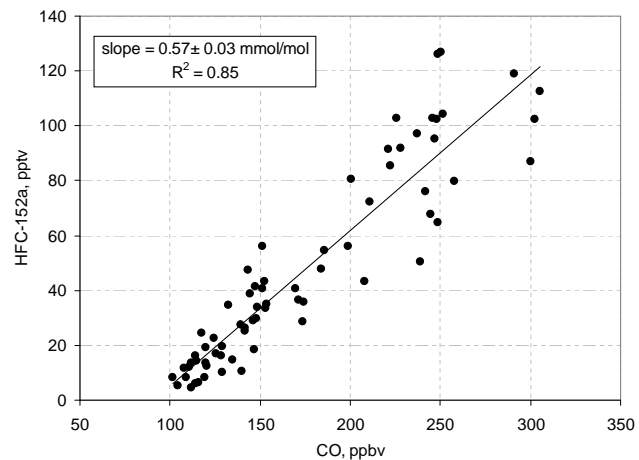


**Fig. 6.** Mixing ratios (in pptv) of **(a–b)** HFC-152a and **(c–d)** HFC-134a measured over the SoCAB. The red star indicates downtown Los Angeles.

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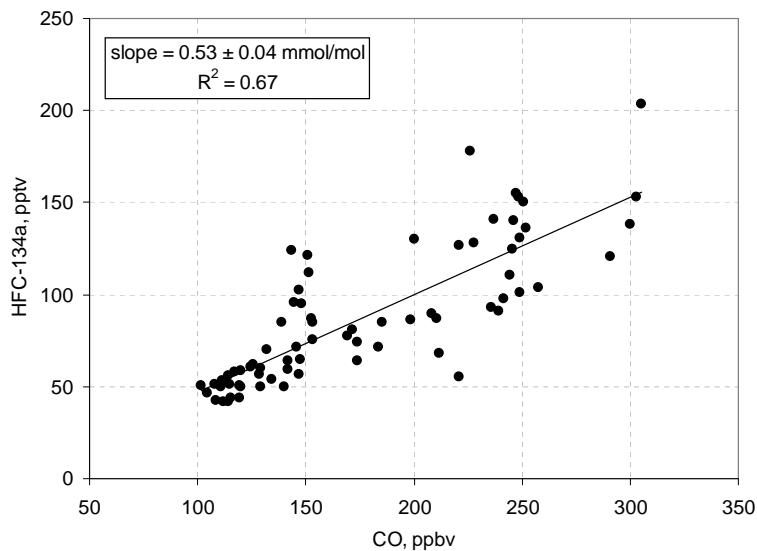
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**Fig. 7.** Mixing ratios of HFC-152a versus CO for the samples collected over the LA area.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Fig. 8.** Mixing ratios of HFC-134a versus CO for the samples collected over the LA area.

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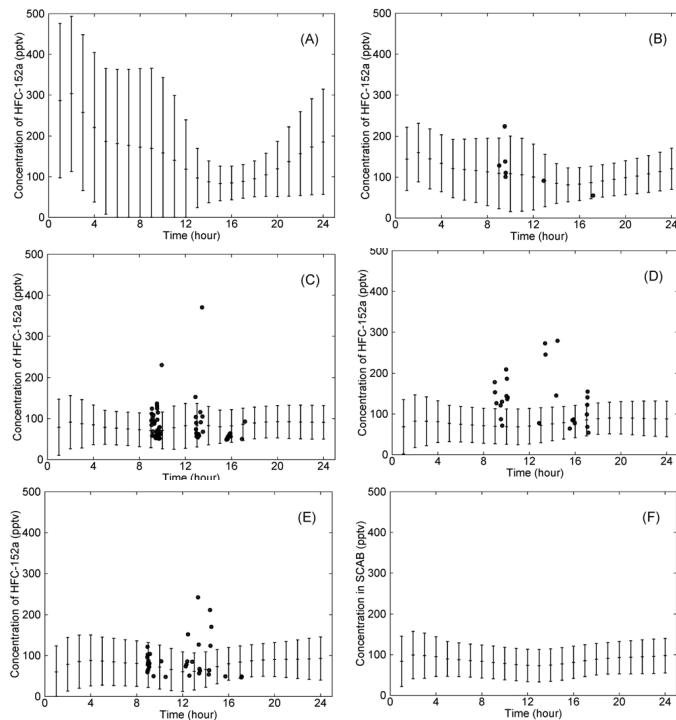
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**Fig. 9.** The mean concentration and  $1\text{-}\sigma$  values of HFC-152a at different vertical layers in the cells comprising the SoCAB, as calculated by the UCI-CIT model using the 9 September 1993 meteorological data set and landuse data from 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). The average concentration over all vertical layers in the SoCAB **(F)** is calculated using Eq. (3). Measurements from the ARCTAS-CARB flights are shown as solid black dots. No measurements were collected in the lowest layer.

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