

Seasonal Variability in Anthropogenic Halocarbon Emissions

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Ambient concentrations of eight predominantly anthropogenic halocarbons were measured via in situ gas chromatography in California's South Coast air basin for both summer and fall during the 2005 Study of Organic Aerosols at Riverside (SOAR). Ongoing emissions of the banned halocarbons methylchloroform and CFC-11 were observed in the South Coast air basin, whereas CFC-113 emissions have effectively ceased. We estimate anthropogenic emissions in the South Coast air basin for methylchloroform, CFC-11, HCFC-141b, chloroform, tetrachloroethene (PCE), trichloroethylene (TCE), and dichloromethane based on regressions of halocarbon to carbon monoxide mixing ratios and carbon monoxide emission inventories. We estimate per capita methylchloroform and chloroform emissions in the South Coast air basin for the year 2005 to be 6.6 ± 0.4 g/(person·year) and 19 ± 1 g/(person·year), respectively. We compare our results to national emission estimates calculated from previous work; for several compounds, emissions in the South Coast air basin are significantly lower than national per capita emissions. We observed strong seasonal differences in anthropogenic emissions of methylchloroform and chloroform; emissions were 4.5 and 2.5 times greater in summer than in fall, respectively. Possible seasonal sources include landfills and water chlorination. We conclude that seasonal variability in methylchloroform emissions has not been included in previous inventories and may cause errors in methylchloroform emission estimates after the year 2000 and seasonally resolved inversion calculations of hydroxyl radical abundance.

1. Introduction

Emissions of many halocarbons are regulated due to their stratospheric ozone depleting potential and as hazards to human health, they are also of concern due to their positive radiative forcing in Earth's atmosphere (1–3). Some of the historical and current applications of halocarbons include commercial and industrial solvents, degreasing agents, refrigerants, and aerosol propellants (4, 5). Production of methylchloroform (MCF), CCl₃F (CFC-11), and Cl₂FCFCl₂

(CFC-113) has been banned by the Montreal Protocol with a minimal number of exceptions for critical purposes in a few developing countries (2). Cl₂FCCH₃ (HCFC-141b) is scheduled to be phased out by 2030 and is becoming of greater regulatory interest in the United States (2). Many halocarbons have relatively long atmospheric lifetimes due to slow removal processes by atmospheric oxidants, which is partly responsible for their high stratospheric ozone depletion potential and global warming potential (GWP) (1). CFC-11 and methylchloroform are particularly potent as greenhouse gases because they have GWPs much greater than that of carbon dioxide, 4750 and 146 over 100 years, respectively (1).

Accurate estimates of methylchloroform emissions are crucial since the atmospheric mass budget is used to estimate ambient concentrations, trends, and distributions of hydroxyl radicals (OH); and underestimates in methylchloroform emissions may lead to larger uncertainties in calculations of global OH abundance (6–8). Previous studies conclude, despite regulatory efforts, that emissions of several banned halocarbons continue due to stockpiling, leaks in old/disposed equipment, and possibly illicit trade (8–12). For example, studies measuring halocarbons in off-gas from municipal solid waste (MSW) landfills report considerable emissions owing to degrading waste that contains halocarbons (3, 13–15). There is a significant potential storage bank of methylchloroform in landfills owing to its pervasive use as a solvent and vapor pressure depressant in paints, aerosols, adhesives, and other household products that were widely available during much of the latter half of the 20th century (16).

While biogenic emissions of chloroform comprise the majority of global emissions, anthropogenic emissions are significant. Currently, anthropogenic chloroform is mainly formed as a byproduct of water chlorination since paper manufacturing is no longer an important source owing to the phase out of chlorine in the paper processing industry (17).

In light of the ozone depletion, climate change, and human health implications, the objectives of this study are to determine the state of emissions for banned anthropogenic halocarbons in Southern California; examine seasonality of anthropogenic halocarbon emissions; and estimate halocarbon emissions for the South Coast air basin.

2. Materials and Methods

Ambient mixing ratios of halocarbons and carbon monoxide (CO) were measured in situ during the 2005 Study of Organic Aerosols at Riverside (SOAR) campaign in Riverside, CA and reported with hourly resolution. The observation site (33°N 58', 117°W 19') was located on the University of California, Riverside campus in the South Coast air basin, typically downwind of the major metropolitan areas of Los Angeles and Orange County. Mixing ratios of eight halocarbons with predominant anthropogenic sources were measured using a gas chromatograph equipped with a mass selective detector and a flame ionization detector (GC/MS-FID). Additional details on the GC/MS-FID instrument, carbon monoxide and meteorological measurements have been published previously (18).

Background mixing ratios for the eight halocarbons measured during the campaign were obtained from similar latitude remote field monitoring stations from the Advanced Global Atmospheric Gases Experiment (AGAGE) network (data available at <http://agage.eas.gatech.edu/>) and the National Oceanic and Atmospheric Administration's (NOAA)

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monitoring stations in the Earth System Research Laboratory (ESRL) (data available online at http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_conc.html) at Trinidad Head, California (41°N, 124°W, 120 m elevation) and Niwot Ridge, Colorado (40°N, 106°W, 3018 m elevation), respectively. Background concentrations were also confirmed from clean inflow conditions during a easterly wind event (November 16–22) when the wind shifted to come consistently from the Santa Ana Mountains delivering air that had not been exposed to the heavily polluted conditions in the predominant westerly direction.

To detect whether emissions have continued in the South Coast air basin for 4 of the halocarbons banned or restricted by the Montreal Protocol (MCF, CFC-11, CFC-113 and HCFC-141b) we compared SOAR measurements to mean background mixing ratios and their variances. Compounds that had consistent exceedances above one standard deviation from the mean background mixing ratios were determined to have emissions in the South Coast air basin.

Correlations and regressions between ambient halocarbon mixing ratios and simultaneous CO measurements at the Riverside site were done using statistical packages in IGOR Pro 6.12. We simultaneously tested for linear correlation, and performed regressions using a traditional Levenberg–Marquardt least-squares method and a trust-region Levenberg–Marquardt least orthogonal distance method to account for uncertainties in both the halocarbon and CO measurements. Owing to the relatively minor errors in CO measurements, both regression methods yielded similar results. CO is an effective tracer of anthropogenic emissions in the South Coast air basin when averaged over the 30 min GC/MS-FID sample. All regressions of halocarbons to CO are performed using both the summer and fall SOAR measurements except in examinations of seasonality and in the cases of CFC-11 and HCFC-141b, which are limited to fall data. Seasonal differences in halocarbon emissions were examined by comparing regressions to CO from each season. Since methylchloroform background mixing ratios significantly decreased over the period of our campaign, it is reported in the regressions as the mixing ratio enhancement above the mean background mixing ratio during either segment of the campaign (ΔMCF).

We report ratios ($\Delta z/\Delta\text{CO}$) for each of the halocarbons as the increase in halocarbon mixing ratio (Δz) per increase in CO mixing ratio (ΔCO), which is determined using the slope of the regression. Halocarbon emission estimates for the South Coast air basin are calculated using the halocarbon:CO ratios and CO emission estimates obtained from the California Air Resources Board for 2005 (19). We estimate per capita emissions for the South Coast air basin using a population estimate of 17.2 million (20) and normalize national estimates by Millet et al. (12) for comparison using a U.S. population estimate of 296 million (21). In some cases it is not appropriate to use CO as a tracer and scaling factor for anthropogenic emissions due to potential biogenic contributions and seasonal differences. It is justifiable for our analyses since there are no statistically significant seasonal differences in anthropogenic CO emissions in the South Coast air basin and there were no forest fires in the region during either portion of the campaign, which would have been the only significant contributor to biogenic CO emissions since biogenic volatile organic compound emissions in this region are low compared to anthropogenic CO sources (19, 22). Many emission inventories of CO are inaccurate due to significant underestimates in mobile emissions with the exception of California (23). The CO emission inventories we use from the California Air Resources Board are based largely on their Mobile Vehicle Emission Model (MVEI) since ~80% of CO emissions are from on-road sources (18). These CO inventories are acceptable to

use for scaling halocarbon emissions since the most recent version of the MVEI model is consistent with other fuel-based inventories (23).

Calibration for our halocarbon measurements on the GC/MS-FID was performed by dynamic dilutions of ppm level standards from gas cylinders to near ambient concentrations in clean air (Aadco Zero Air Generator). Accuracies are better than 10% based on accuracy of the gas standards (5%, Apel-Riemer) and two mass flow control devices (1% of full scale, MKS) used in dilution (24). We also compare our local background levels during the Easterly wind event to background mixing ratios from remote sites to check the accuracy of our reported mixing ratios. Using measured background mixing ratios for compounds that showed no emission influences during the Easterly wind event (i.e., MCF, CFC-11, CFC-113) we calculated precision values of better than or equal to $\pm 4\%$. Additionally, the small 95% confidence intervals and strong correlation coefficients in the halocarbon:CO regressions are indicative of reasonable precision in our measurements. The largest uncertainty in our emission estimates and their seasonality is due to uncertainties in the CO emission inventory we used for scaling emissions.

3. Results and Discussion

3.1. Continued Emissions of Regulated Halocarbons. We observe continued emissions of three halocarbons regulated by the Montreal Protocol in the South Coast air basin. Figure 1a shows elevated ambient mixing ratios of methylchloroform in the South Coast air basin during both seasons of the SOAR campaign superimposed on decreasing background mixing ratios, indicative of continued emissions in the region. Similar to methylchloroform, we observe enhancements above background mixing ratios in the fall for CFC-11 and HCFC-141b (Figure 1b,c). During the easterly wind episode in the fall, methylchloroform mixing ratios at the site dropped to background levels consistent with remote measurements at Niwot Ridge, Colorado.

Mixing ratios of CFC-11 were significantly above background when air arrived at the site from the rest of the air basin in the westerly direction. Despite significant variability in baseline measurements at the site during the easterly wind event (average: 252 ± 10 ppt) CFC-11 mixing ratios were similar to the remote background mixing ratios at Niwot Ridge (average: 252 ± 1 ppt). We conclude that CFC-11 emissions continue since 50% of the fall measurements during normal westerly wind patterns have statistically significant exceedances (>262 ppt) of calculated mean background mixing ratios. Ongoing emissions of CFC-11 and methylchloroform in the South Coast air basin are in agreement with previous studies in other regions over the past decade (8, 10–12). Continued emissions of HCFC-141b are expected as it is still in production and use until the full phase-out planned for 2030, but we are unable to assess the effectiveness of the current emissions reductions.

We observed enhancements above background mixing ratios during westerly flows and returns to background levels during the easterly wind event for all of the compounds except for CFC-113. In addition to the absence of a correlation to ambient CO mixing ratios, this lack of observable differences between CFC-113 mixing ratios during the easterly wind event and normal westerly flows indicates that CFC-113 emissions have effectively ceased, which is in agreement with previous results for other locations (8, 12).

3.2. Seasonal Variability in Emissions and Possible Sources. For the majority of the halocarbons measured, we observed strong correlations to CO mixing ratios in both summer and fall. Several of the regressions can be seen in Figure 2. The strong correlations to CO are evidence for anthropogenic emissions since in our study CO is a justifiable

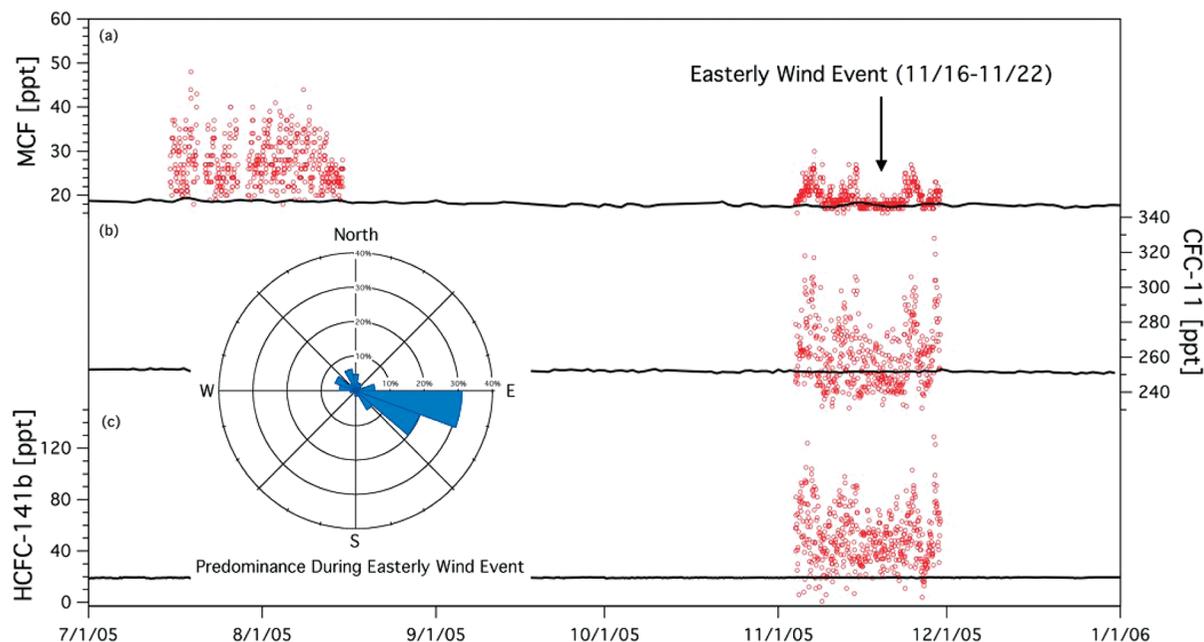


FIGURE 1. (a) Methylchloroform, (b) CFC-11, and (c) HCFC-141b mixing ratios during the SOAR campaign (red \circ) compared to background measurements (black lines) at Niwot Ridge (a,b) and Trinidad Head (c). The wind rose indicates wind direction as predominance during the comparatively clean Easterly inflow (November 16–22).

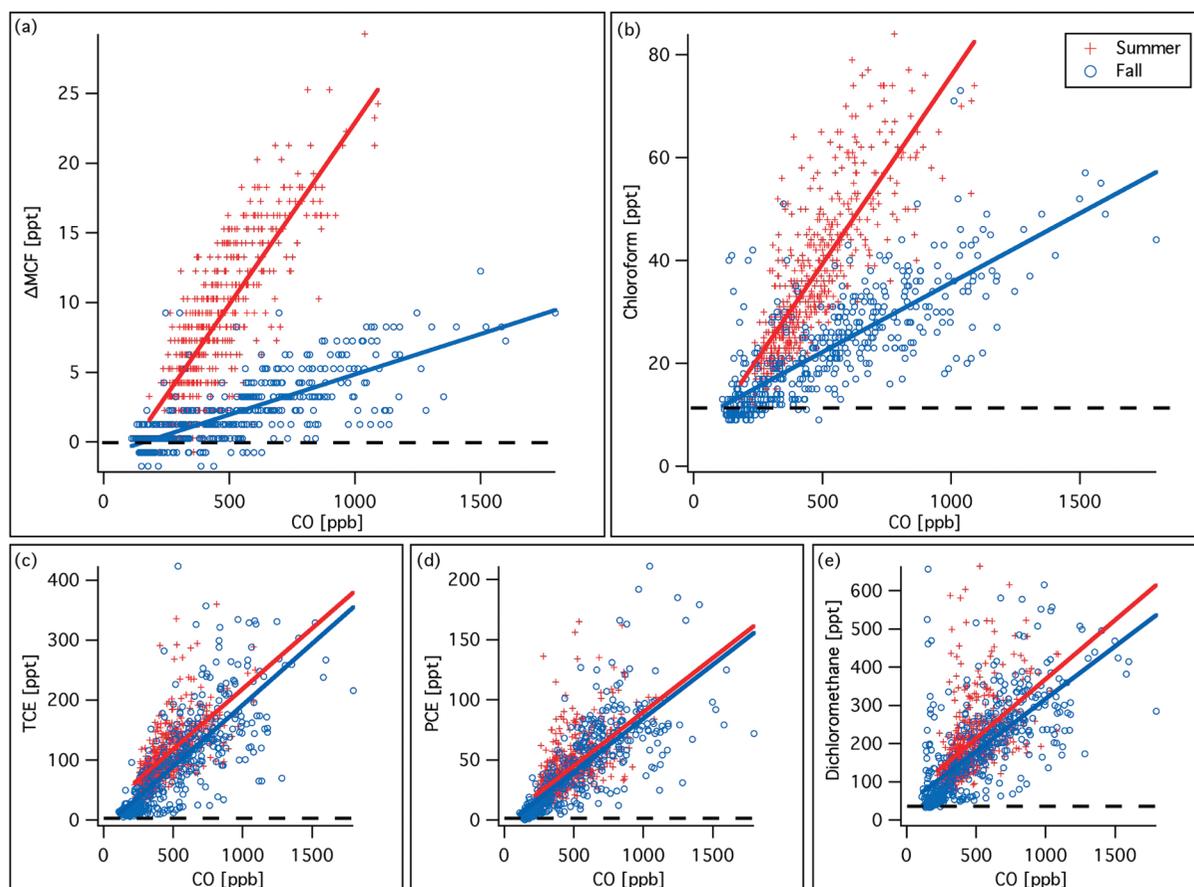


FIGURE 2. Seasonal regressions of (a) methylchloroform (as enhancement above background), (b) chloroform, (c) TCE, (d) PCE, and (e) dichloromethane to ambient carbon monoxide mixing ratios for both summer (red +) and fall (blue \circ). Dashed lines indicate average remote background levels with negligible standard deviations on these scales. Correlation coefficients and slopes are given in Table 1.

tracer for anthropogenic sources. It also allows us to examine seasonal variability since no statistically significant variation was observed in CO mixing ratios between seasons during the SOAR campaign or in modeled CO emissions for the South Coast Air basin (22).

Anthropogenic methylchloroform and chloroform emissions show distinct seasonality in the South Coast air basin (Figure 2a,b). Regressions with CO correlate well for both compounds in summer and fall with greater halocarbon:CO ratios ($\Delta z/\Delta CO$) in the summer. Based on our regressions,

TABLE 1. Halocarbon:CO Ratios and 2005 Emission Estimates for Halocarbons (\pm 95% Confidence Intervals)

Halocarbon (z)	$\Delta z/\Delta CO$ [ppt/ppb]	Correlation Coefficient (r^a)	South Coast Air Basin Emissions [Gg/year]	South Coast Air Basin per capita Emissions [g/(person·year)]	U.S. per capita Emissions [g/(person·year)] ^{a,b}
chloroform (fall)	0.027 \pm 0.002	0.78 (0.75–0.81)	0.17 \pm 0.01	10 \pm 1	44 (34–57)
chloroform (summer)	0.073 \pm 0.005	0.8 (0.77–0.83)	0.47 \pm 0.03	27 \pm 2	
methylchloroform (fall)	0.0058 \pm 0.0004	0.76 (0.72–0.80)	0.041 \pm 0.003	2.4 \pm 0.2	9.5 (6.8–11.8)
methylchloroform (summer)	0.026 \pm 0.002	0.8 (0.77–0.83)	0.19 \pm 0.01	11 \pm 1	
CFC-11 (fall)	0.032 \pm 0.004	0.56 (0.49–0.62)	0.24 \pm 0.03	14 \pm 2	37 (24–47)
HCFC-141b (fall)	0.029 \pm 0.005	0.44 (0.36–0.50)	0.18 \pm 0.03	11 \pm 2	15 (7–23)
dichloromethane	0.31 \pm 0.03	0.62 (0.58–0.66)	1.4 \pm 0.1	82 \pm 8	81 (54–108)
TCE	0.21 \pm 0.02	0.74 (0.71–0.77)	1.5 \pm 0.1	86 \pm 8	26 (16–34)
PCE	0.088 \pm 0.005	0.73 (0.70–0.75)	0.78 \pm 0.04	46 \pm 3	88 (51–135)

^a 95% confidence intervals in parentheses. ^b Annual averages from Millet et al. (12) for 2004–2006.

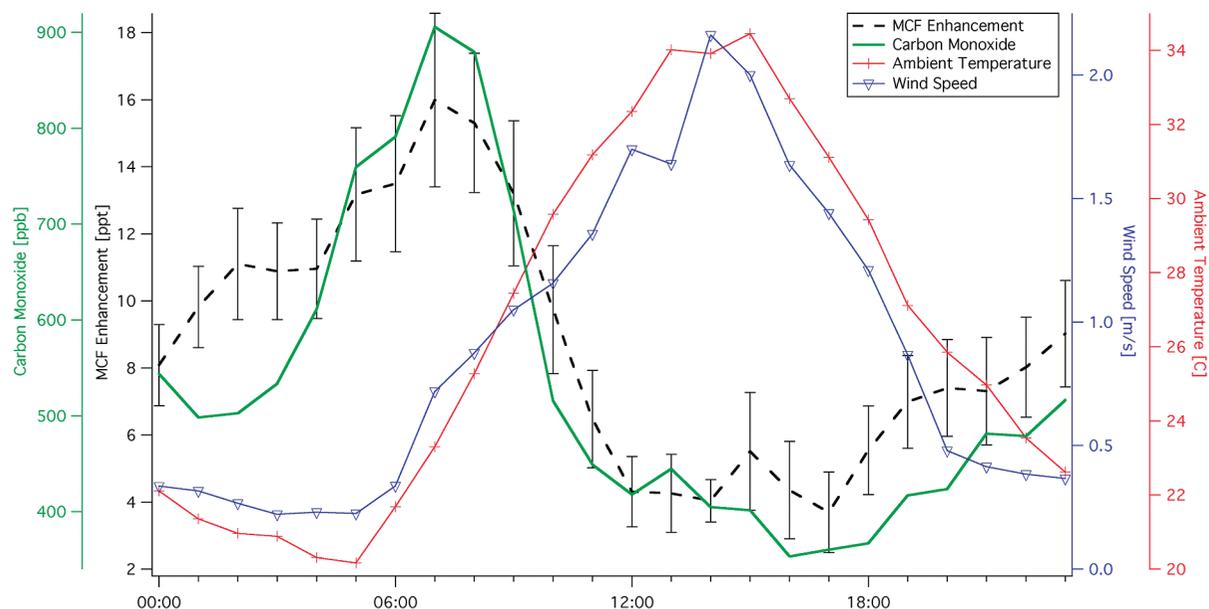


FIGURE 3. Diurnal variation in methylchloroform (plotted as enhancement above background concentration with 95% CIs) shown with carbon monoxide, wind speed, and ambient temperature for summertime data.

anthropogenic emissions of methylchloroform and chloroform are 4.5 and 2.5 times greater in the summer, respectively. Seasonal variability in CO emissions cannot be driving the observed variations due to the reasons stated above nor can it be a dynamic meteorological effect since TCE, PCE, and dichloromethane correlations with CO show no seasonal effects (Figure 2c–e). Biogenic contributions are unlikely since there are strong correlations to CO and previous work by Rhew et al. report no significant biogenic emissions of methylchloroform or chloroform in Southern California ecosystems (25).

The seasonality of methylchloroform emissions has been largely unobserved in the past due to the scale of absolute methylchloroform emissions from aseasonal sources, and the limited number of multi-season measurement campaigns. Multi-season emission estimates in the Eastern United States from 1996 to 1998 do not show any clear seasonal effects due to the sharp decline in total emissions, but 2002 estimates for summer and winter in Pittsburgh, PA show a 2.5 fold increase in MCF emissions (4, 8). Based on these observations, we conclude that there is a seasonally variable source of methylchloroform that has not been included in previous inventories and has become easier to detect as overall emissions decrease.

Seasonal variations in methylchloroform mixing ratios have been reported previously near an urban site in Asia and in a study using AGAGE measurements (11, 26). Both of these studies report a summertime minimum in methylchloroform

mixing ratios, which is driven by increased scavenging by hydroxyl radicals and increased atmospheric dilution in summertime meteorological conditions. In our work, photochemical processes are not significant removal mechanisms for methylchloroform and chloroform during the short transport time across the South Coast air basin owing to their relatively long lifetimes (5.0 years for MCF vs 0.4 years for $CHCl_3$) (1, 17).

Despite the strong seasonal differences there was no significant correlation between methylchloroform or chloroform and ambient temperature ($r = 0.30$ and 0.16), which suggests that the source is not directly dependent on air temperature. Maximum MCF mixing ratios on site in Riverside occur around 7 a.m. due to build-up of emissions in the shallow nighttime boundary layer when dilution is minimized (Figure 3). This diurnal profile and an anticorrelation with horizontal wind speed ($r = -0.44$) suggests there is a local source of methylchloroform in addition to other possible upwind regional sources delivering methylchloroform in the afternoon.

Landfills are a possible candidate for the seasonal source of methylchloroform and chloroform given the considerable concentrations of both in off gas measurements and enhanced gas-phase diffusion with increased temperature and decreased moisture (13, 14, 27). Elevated soil temperatures and dryer soil conditions will accompany higher ambient temperatures in the summer, which will enhance the ability of halocarbons to diffuse through the landfill and its top

cover soil (3, 27). Measurements of volatile organic compound (VOC) emissions from a Chinese landfill by Zou et al. showed significant seasonal variation in most of the VOCs including several of the halocarbons; average chloroform concentrations increased by a factor of 3.5 from winter to summer (data was not available for methylchloroform) (15). While recent work by Hodson et al. (13) concluded, based on the seven U.S. landfills in their study, that MCF emissions could only account for 1% of total U.S. MCF emissions, landfills cannot be excluded as our observed seasonal source since site specific data are very important in determining trace gas emissions (3, 14, 15). Halocarbons (including methylchloroform, chloroform, and others described in our work) have been reported over a broad range of concentrations and emissions are very dependent on landfill age, construction, and especially waste inventory (3, 13–15). Landfills that have accepted industrial waste are prone to concentrations of methylchloroform orders of magnitude higher than landfills that contain only municipal solid waste (3). If landfills do contribute to our observed seasonality in methylchloroform and chloroform, then it is reasonable that PCE, TCE, and dichloromethane (Figure 2c–e) show no significant seasonal variation at the Riverside site due to the magnitude of nonlandfill emissions. Unfortunately, due to our lack of summer data, we were unable to examine seasonal differences in CFC-11, which may have shown similar seasonal effects from landfill emissions.

Another possible seasonal source of anthropogenic chloroform is as a byproduct of water chlorination. Chloroform is generated from the reaction of elemental chlorine with humic material in drinking water, wastewater, and swimming pools (5). The produced chloroform partitions into the atmosphere and, in accordance with partitioning theory, more chloroform partitions into the gas phase at higher temperatures (5). High atmospheric concentrations of chloroform have been reported previously near swimming pools (5). While all three types of water mentioned above are likely to have increased temperatures during the summer, we consider swimming pools a likely source due to the increased use and thus chlorination in summer. The suggestion of landfills and water chlorination as potential seasonal sources is not inclusive as other sources may be contributing to both seasonal and aseasonal emissions. Further work is necessary to confirm these sources and determine the extent of these seasonal effects on larger geographic scales. Given the conflicting reports on methylchloroform mixing ratios in landfill off-gas and the inherent variability in landfill composition (3, 13–15), the seasonality of halocarbon emissions from landfills needs to be investigated further before inclusion in emission inventories to avoid potential errors in emissions estimates and calculations of OH abundance.

3.3. Emissions Estimates. Using an emission estimate of 4124 tons anthropogenic CO per day in the South Coast air basin and a population of 17.2 million (19, 20), we calculated emission estimates for all the halocarbons measured (Table 1). Our South Coast air basin estimates are robust because they represent the measurement location, but extrapolation to state and nationwide estimates is highly uncertain. To construct annual estimates of methylchloroform and chloroform emissions, which had significant seasonal variability, we took the mean of the emission estimates from both seasons and compounded the uncertainties. It is important to take into account the seasonal variations in halocarbon emission estimates since annual inventories may be over or underestimated depending on the season of the measurements that the estimates are based on. Our annual per capita emission estimates for methylchloroform and chloroform are 6.6 ± 0.4 g/(person·year) and 19 ± 1 g/(person·year), respectively.

In Table 1, we compare our per capita emission estimates in the South Coast air basin for 2005 with recent national halocarbon emission estimates by Millet et al. (12) using aircraft measurements from 2004–2006. We observe similar emissions in the South Coast air basin to national averages for HCFC-141b and dichloromethane, and fall near the lower end of the national range for methylchloroform and PCE. We estimate significantly greater TCE emissions in the South Coast air basin compared to the previously reported national range. Our chloroform and CFC-11 estimates are slightly lower than Millet et al., which could be due to spatial variability or seasonal dependences in either of our annual estimate calculations. There are significant differences in spatial distribution of sources between the South Coast air basin and larger scales, including both the proposed seasonal sources and aseasonal sources such as industrial operations, which are typically located away from the South Coast air basin due to air quality concerns.

Seasonal variability in anthropogenic chloroform emissions has significant implications for total budgets of chloroform. Several studies have proposed that a larger fraction of the total chloroform budget is anthropogenic than previously estimated; early estimates suggest 10% of the global chloroform budget was anthropogenic while newer studies propose that the anthropogenic contribution is 50% (17, 28). Variability in anthropogenic emissions of chloroform with temperature will be important for total budget estimates, particularly if water chlorination is the major source of anthropogenic emissions and due to the presence of chloroform waste in landfills.

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Note Added after ASAP Publication

The caption of Figure 2 was modified in the version of this paper published ASAP June 10, 2010; the correct version published on June 16, 2010.

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