Evidence of continuing methylchloroform emissions from the United States

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[1] We present measurements from three sites during 2001–2002 showing that methylchloroform emissions have continued in the U.S., despite the 1996 production ban under the Montreal Protocol. Available data from urban regions, if representative, suggest that 1997–2002 U.S. emissions declined exponentially from 18.5 to 3.0 Gg/yr. F-11 also showed evidence of ongoing emissions, whereas F-113 emissions have effectively ceased. Continuous in-situ measurements in urban regions provide an effective means of detecting ongoing emissions of banned compounds. Neglecting continuing emissions causes underestimates in tropospheric OH abundance derived from methylchloroform concentrations. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Millet, D. B., and A. H. Goldstein (2004), Evidence of continuing methylchloroform emissions from the United States, *Geophys. Res. Lett.*, *31*, L17101, doi:10.1029/2004GL020166.

1. Introduction

[2] Methylchloroform (CH_3CCl_3, hereafter referred to as MCF) was widely used as an industrial solvent during the second half of the 20th century. Major uses, including vapor degreasing, cold solvent cleaning, aerosol cleaners and adhesives, resulted in virtually all the MCF used eventually being emitted to the atmosphere [*McCulloch and Midgley*, 2001]. The primary atmospheric sink for MCF is reaction with hydroxyl radical (OH), resulting in an atmospheric lifetime of 5–6 years. A significant fraction of emitted MCF enters the stratosphere, where it is photolyzed, releasing chlorine atoms which catalytically destroy ozone. The Montreal Protocol and subsequent amendments banned production and consumption of a variety of ozone depleting gases, including MCF, in developed countries as of January 1, 1996. The protocol also called for a freeze in production and consumption of MCF in developing countries as of January 1, 2003, with complete cessation of use by 2015 [*United Nations Environmental Programme*, 1999].

[3] Based upon government and industry reports, consumption of MCF in the U.S. is estimated to have fallen to zero in 1997 [*McCulloch and Midgley*, 2001]. However, following the production and consumption ban in 1996, sales and production figures are no longer reliable proxies of emissions, since stockpiled and recycled material, and any illicit trade, are not represented. In situ atmospheric measurements in probable emission regions provide a reasonable means of both detecting non-compliance and estimating actual emissions.

2. Experimental

[4] We present MCF measurements from four deployments at three U.S. sites between July 2001 and August 2002: Granite Bay, CA (GBY), on the eastern edge of the Sacramento metropolitan area (July 27–September 17, 2001); Pittsburgh, PA (Pittsburgh Air Quality Study, PAQS) (January 9–February 12 and July 9–August 10, 2002); and Trinidad Head (Intercontinental Transport and Chemical Transformation study, ITCT), a coastal site in northern California (April 19–May 22, 2002). All sites are at approximately the same latitude (38°45′N–41°03′N). Volatile organic compounds were measured hourly with an in situ GC/MS/FID system that is described in detail elsewhere [*Millet et al.*, 2004]. CO was measured by gas filter correlation infrared absorption at ITCT and PAQS, but not GBY (TEI 48C at ITCT; Teledyne 300 at PAQS). Concentration timelines from these studies are shown in Figure 1, along with data representing more remote sites, from the NOAA/CMDL in situ GC network (National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory, 2002, available at http://www.cmdl.noaa.gov/info/ftpdata.html; hereinafter referred to as NOAA, 2002).

3. Results and Discussion

[5] Atmospheric levels of MCF have been declining since their peak in 1992 [*Prinn et al.*, 2001] owing to decreased production and use in response to reductions mandated under the Montreal Protocol, culminating in the 1996 ban. There has also been a decrease in the variability observed at background measurement stations, indicative of reduced emissions [*Krol et al.*, 2003]. Background concentrations measured during the campaigns (Figure 1) were consistent with NOAA network observations, showing a continuing decline.

[6] MCF concentrations and variability at the Trinidad Head site were comparable to those observed at the NOAA background stations. The lack of excursions above background levels indicates that this site was not coherently impacted by MCF emissions, either from local sources or via long range transport from Asia. During the other three measurement campaigns, however, enhanced concentrations of MCF were frequently observed, indicative of ongoing U.S. urban/industrial emissions. Pollution enhancements
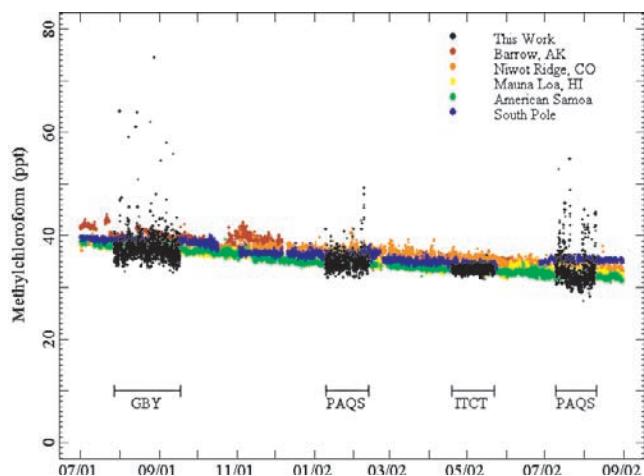
Figure 1. MCF concentrations measured at Granite Bay (GBY), Pittsburgh (PAQS) in summer and winter, Trinidad Head (ITCT), and at the NOAA/CMDL CATS network stations.

(Δx for species x) were calculated by subtracting the background concentrations, represented by a 10 day running 0.1 quantile, from the original time series. MCF enhancements were most strongly correlated with enhancements of C_5 and C_6 alkanes and aromatic species such as toluene and xylenes, compounds which, like MCF, are extensively used as solvents. Figure 2 shows ΔMCF plotted against Δisopentane (C_5H_{12}) for the 4 deployments, with regression parameters given in Table 1. Enhancement ratios (ΔMCF/ΔC_5H_{12}) did not show a statistically significant dependence on wind direction, indicating that the measurements were not biased by nearby non-representative sources.

[7] To enable comparison of these results with earlier studies and estimate MCF emissions, we calculated pollution enhancements relative to CO (Table 1). The measured ΔMCF/ΔCO ratio was 2.6 times higher in summer than winter in Pittsburgh, while the summer and winter ΔMCF/ΔC_5H_{12} enhancement ratios were roughly equal. This difference is likely due in part to increased evaporative emissions in summer, which are an important source of both MCF and isopentane but not of CO. CO emissions may vary seasonally as well. The ΔMCF/ΔCO enhancement ratio inferred for Granite Bay (0.144 g/kg) was slightly higher than that in Pittsburgh in summer (0.083 g/kg).

[8] F-11 (CCl_3F) also showed evidence of summertime emission. The ΔF-11/ΔCO enhancement ratio observed in Pittsburgh during the summer of 2002 (0.39 g/kg) was comparable to that of east coast emissions during 1998 (0.36–0.43 g/kg) [*Barnes et al.*, 2003]. Emissions were not detectable in Pittsburgh during winter. The Granite Bay ΔF-11/ΔCO enhancement ratio (0.64 g/kg) was higher than Pittsburgh in summer; however, the correlation coefficient, while significant at the 95% confidence level, was too low to attach much meaning to the associated enhancement ratio. The Trinidad Head data showed no significant enhancements of F-11 above background.

[9] In contrast to MCF and F-11, elevated concentrations of F-113 (CCl_2FCClF_2) were not observed during any of the field deployments, and ΔF-113/ΔCO correlation coefficients were not significantly different than zero

(Table 1). This suggests an effective cessation of F-113 emissions, at least in the regions where observations were made. Approximately 99% of cumulative F-113 production has been for applications resulting in short-term (<1 year) release to the atmosphere (Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), available at http://www.afeas.org), while F-11 was more frequently used in applications (e.g., closed shell foam and air conditioners) which result in slower release. The observed ongoing F-11 emissions are therefore likely due at least in part to slow leakage from and disposal of these longer-term products.

[10] Observed ΔMCF/ΔCO enhancement ratios for the two Pittsburgh deployments and the Granite Bay deployment, along with enhancement ratios for the northeastern U.S. observed during 1996–1998 [*Barnes et al.*, 2003], provide insight into the recent decline in MCF emissions, relative to CO (Figure 3). Emission inventory data (Environmental Protection Agency (EPA), National Emission Inventory, 1999, available at http://www.epa.gov/ttn/chief/net/index.html, hereinafter referred to as EPA, 1999) indicate that annual U.S. anthropogenic CO emissions have remained stable in recent years ($9.2^{+1.5}_{-0.7} \times 10^{10}$ kg/year from 1990–1999), and thus we attribute the decreasing ΔMCF/ΔCO values solely to reductions in MCF production and use brought about by the Montreal Protocol. Clearly the Montreal Protocol has been very effective, but it has not been completely successful in eliminating U.S. MCF emissions.
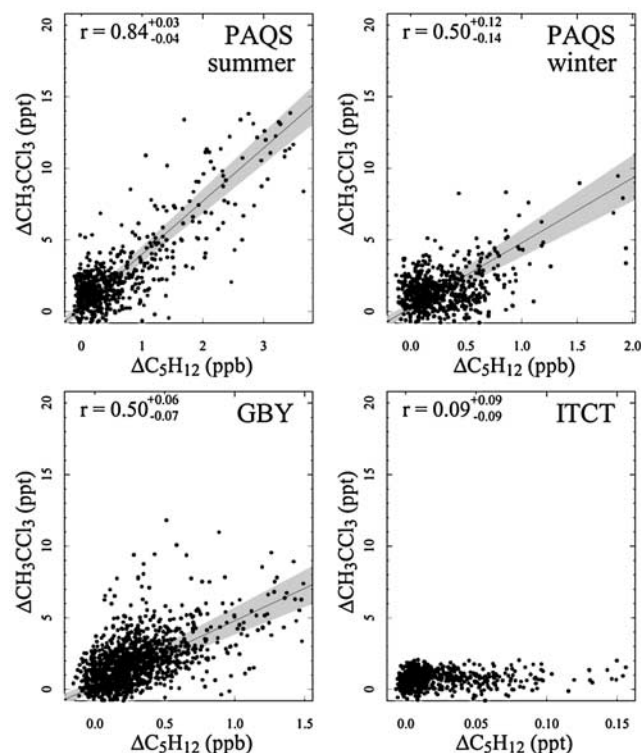

Figure 2. MCF and C_5H_{12} enhancements over background. Reduced major axis regression and 95% confidence intervals are indicated by the lines and shaded regions and were corrected for serial correlation. Statistical outliers (≥ 0.99 quantile) were removed prior to performing the regressions.

Table 1. Halocarbon Enhancement Ratios[a]

x	Study	$\Delta x/\Delta CO$ (g/kg)	Corr. Coef.	$\Delta x/\Delta C_5H_{12}$ (g/g)	Corr. Coef.
MCF	PAQS (sum)	0.083 ± 0.010	$0.72^{+0.07}_{-0.10}$	0.0068 ± 0.0005	$0.84^{+0.03}_{-0.04}$
	PAQS (win)	0.032 ± 0.004	$0.42^{+0.11}_{-0.12}$	0.008 ± 0.001	$0.50^{+0.12}_{-0.14}$
	GBY[b]	0.144 ± 0.011	$0.49^{+0.06}_{-0.07}$	0.012 ± 0.001	$0.50^{+0.06}_{-0.07}$
F-11	PAQS (sum)	0.394 ± 0.063	$0.50^{+0.12}_{-0.15}$	0.033 ± 0.004	$0.61^{+0.09}_{-0.11}$
	PAQS (win)	0.248 ± 0.046	$0.12^{+0.18}_{-0.19}$	0.070 ± 0.014	$0.17^{+0.20}_{-0.21}$
	GBY[b]	0.640 ± 0.053	$0.18^{+0.08}_{-0.08}$	0.052 ± 0.004	$0.18^{+0.08}_{-0.08}$
F-113	PAQS (sum)	0.064 ± 0.015	$-0.19^{+0.24}_{-0.22}$	0.005 ± 0.001	$-0.30^{+0.25}_{-0.21}$
	PAQS (win)	0.057 ± 0.015	$-0.15^{+0.28}_{-0.25}$	0.017 ± 0.006	$-0.23^{+0.35}_{-0.30}$
	GBY[b]	0.267 ± 0.025	$-0.02^{+0.09}_{-0.09}$	0.022 ± 0.002	$-0.02^{+0.09}_{-0.09}$

[a]Regression parameters calculated by reduced major axis regression. Quoted uncertainties are 95% confidence limits and have been corrected for serial correlation.
[b]CO was not measured at Granite Bay. The enhancement ratio was estimated by scaling the $\Delta MCF/\Delta C_5H_{12}$ enhancement ratio by the $\Delta C_5H_{12}/\Delta CO$ enhancement ratio observed in Pittsburgh during the summer (12 g/kg). The measured $\Delta C_5H_{12}/\Delta CO$ enhancement ratio in Sacramento ($\sim$20 km upwind of GBY) during the study period was 19 g/kg (California Air Resources Board, available at http://www.arb.ca.gov/aqd/aqdcd/aqdcddld.htm); thus the Granite Bay enhancement ratio we use is a conservative estimate.

[11] OH is the atmosphere's primary oxidant and determines the atmospheric residence times of pollutants such as methane and HCFCs as well as gas-phase components of smog. Because of its short lifetime ($\sim$1 second), OH concentrations are highly variable in space and time. Long-term atmospheric measurements of MCF have provided the standard means of inferring the spatial and temporal distribution of OH [*Krol et al.*, 1998; *Krol and Lelieveld*, 2003; *Montzka et al.*, 2000; *Prinn et al.*, 2001; *Prinn et al.*, 1995]. Using emission estimates and known oxidation rate constants, atmospheric measurements of MCF have been inverted to estimate OH concentrations, distribution, and trends. *Prinn et al.* [2001] estimated that OH levels increased in the 1980s, and decreased in the 1990s with a 10% overall decrease from 1979–2000, a finding with important implications for the atmospheric lifetimes, and thus the potential impacts, of a large number of pollutants. However, the reliability of such conclusions depends upon the accuracy of MCF emission estimates. *Prinn et al.* [2001] calculated the additional MCF emissions necessary during 1996–2000 for a zero trend in OH, but dismissed this possibility because they considered the large magnitude of required additional emissions to be unrealistic. Here we use observations of continuing U.S. MCF emissions to test the null hypothesis that there has in fact been no change in OH.

[12] We employ two methods to scale pollution enhancement ratios to absolute emissions. Both are subject to the assumption that the observed ratios are representative of U.S. urban/industrial emissions. The first uses a U.S. MCF emission estimate for 1995 (49.9 Gg) [*Bakwin et al.*, 1997], under the assumption that pre-1996 sales and production data accurately reflect emissions. Scaling was performed by extrapolating an exponential fit to the observed $\Delta MCF/\Delta CO$ enhancement ratios (dot-dashed line, Figure 3) back to 1995. With the second method, per capita MCF emissions estimated for the northeastern U.S. in 1996 (0.122 kg/person; [*Barnes et al.*, 2003]) are scaled to the national level by multiplying by the 1996 U.S. resident population (269,394,284; U.S. Census Bureau, 1996, available at http://www.census.gov/). These two approaches result in excellent agreement, with 1996 emissions of 31.6 and 32.9 Gg respectively. Adopting the second method, we estimate that U.S. emissions were 5.1 Gg in 2001 and 3.7 Gg in 2002, approximately 27–38% of U.S. emissions in 1998 and 11–

16% of 1996 emissions. By contrast, according to industry sales and production data, North American consumption of MCF has been zero since 1997 [*McCulloch and Midgley*, 2001].

[13] Global MCF emissions are currently estimated at 39.5, 24.2, 21.4, and 19.7 Gg for the years 1997–2000, with zero emissions from North America [*McCulloch and Midgley*, 2001]. However, our analysis indicates that U.S. MCF emissions were in fact significant during that period: 18.8, 13.6, 9.8, and 7.1 Gg, for 1997–2000 respectively (from an exponential fit to the post-1996 data; solid line in Figure 3). Underestimates of emissions are not limited to the United States, as shown by *Krol et al.* [2003] and
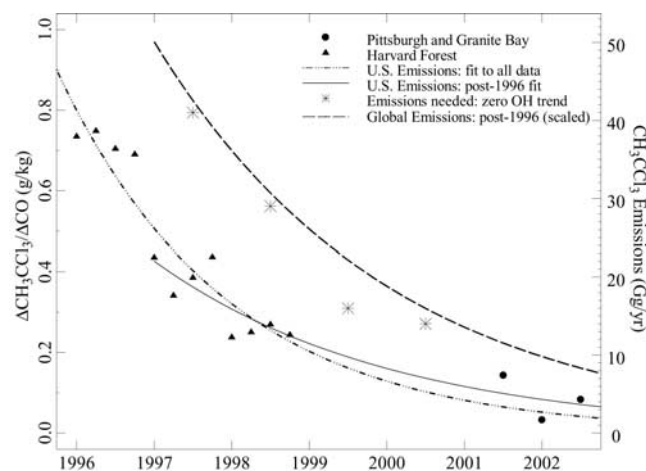

Figure 3. $\Delta MCF/\Delta CO$ pollution enhancements observed in Granite Bay and Pittsburgh during 2001 and 2002. Also shown are 1996–1998 enhancement ratios for the northeastern U.S. as measured at Harvard Forest [*Barnes et al.*, 2003]. Absolute emissions were estimated by scaling the enhancement ratios to 1996 emission estimates (see text). Three fit lines are shown: U.S. emissions based on an exponential fit to all data (dot-dashed line); U.S. emissions based on an exponential fit to the post-1996 data (solid line); and global unreported emissions estimated by scaling the post-1996 U.S. emission function (dashed line; see text). Asterisks indicate the unreported global emissions required for a zero trend in OH [*Prinn et al.*, 2001].

Palmer et al. [2003], who observed pollution enhancements indicative of continuing emissions in Europe and Japan, respectively. During 1989–1995, U.S. consumption of MCF accounted for on average 44% of the total consumption by all non-Article 5 countries (i.e., industrialized signatories to the Montreal Protocol) [*United Nations Environmental Programme*, 2002]. If residual emissions in other industrialized nations are declining in a similar manner as in the U.S., then our results imply exponentially declining global unreported emissions as indicated by the dashed line in Figure 3. These unreported emissions (43, 31, 22, and 16 Gg for the years 1997–2000) are consistent with the values needed to explain a zero trend in OH (41, 29, 16, and 14 Gg; asterisks in Figure 3) [*Prinn et al.*, 2001]. We conclude that the available data are consistent with the null hypothesis of a zero change in OH, and consequently that calculations of OH trends which rely on post-1996 industry sales data for MCF are highly uncertain.

[14] We note that the MCF emission and trend estimates derived here rely on the accuracy of inventory-based emission estimates for CO, which indicate that total U.S. CO emissions were stable during the 1990s (EPA, 1999). It has been suggested that U.S. vehicular CO emissions may have declined by as much as 5.2% per year during the 1990s [*Parrish et al.*, 2002]. Such a trend, if it continued through 2002, would suggest an approximately 25% decrease in total U.S. CO emissions during 1996–2002 (given that vehicles account for ~80% of anthropogenic U.S. CO emissions (EPA, 1999), and assuming non-vehicle emissions remained relatively constant). In this case, our estimates of MCF emissions for the end of this period would be overestimated by a proportionate amount.

[15] We can estimate the bias introduced into OH concentrations calculated from MCF concentrations which neglect these unreported emissions. From the continuity equation for tropospheric MCF,

$$OH = (kM)^{-1}\left(E - \frac{dM}{dt}\right), \tag{1}$$

where OH and M are the globally averaged OH and MCF abundances, k is the rate constant for reaction between these species, and E is the MCF emission rate. The relative error in calculated OH due to underestimated MCF emissions is then given by

$$\frac{OH_2}{OH_1} = \frac{E_2 - \frac{dM}{dt}}{E_1 - \frac{dM}{dt}} = 1 + \frac{\Delta E}{E_1 - \frac{dM}{dt}}. \tag{2}$$

Here, OH_2 and OH_1 are the OH concentrations calculated using two different emission estimates E_1 and E_2, with $E_2 = E_1 + \Delta E$. For 1997–2000, with MCF concentrations declining exponentially with rate constant 0.182 yr^{-1} [*Montzka et al.*, 2000], from an annual average of 83 ppt in 1997 to 46 ppt in 2000 (NOAA, 2002), we calculate that neglecting ongoing MCF emissions by non-Article 5 nations leads to global OH underestimates of 11% in 1997, decreasing to 7.2% in 2000. In addition, since residual MCF emissions are presumably largest in the Northern

Hemisphere, they are likely to account for some of the north-south asymmetry in OH which is otherwise implied.

[16] There is inevitably some uncertainty involved in extrapolating measurements taken in a limited number of urban areas during discrete sampling intervals to larger spatial and temporal scales. In addition, assessing any seasonality in emissions would require longer-term datasets. Accurate quantification of ongoing emissions in the post Montreal Protocol phase-out era are an important prerequisite to accurately determining OH concentrations, and in particular OH distributions and trends, from MCF measurements. Ultimately, deriving the necessary constraints on these emissions will require analysis of in situ data encompassing the range of globally significant emission regions.

[17] The purpose of this analysis has been to test the likelihood of the null hypothesis of a zero change in OH. We find that the emissions implied from analysis of available data from the U.S., if representative of residual emissions for other nations, are in fact consistent with a zero change in OH. We propose that the time-dependence of residual MCF emissions would be most accurately represented as an exponentially decaying function with rate constant 0.326 yr^{-1}.

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