JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. D6, 4186, doi:10.1029/2001JD001117, 2003

Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998:
2. A study of the efficacy of the Montreal Protocol and other regulatory measures

Diana H. Barnes, Steven C. Wofsy, Brian P. Fehlau, and Elaine W. Gottlieb
Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

James W. Elkins, Geoffrey S. Dutton, and Stephen A. Montzka
Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, USA

Received 11 July 2001; revised 6 May 2002; accepted 14 June 2002; published 26 March 2003.

[1] Background concentrations, emission rates, and trends in emission rates for five trace gases are inferred for the northeastern United States from continuous atmospheric observations at Harvard Forest in central New England for 1996–1998. Mixing ratios of gases regulated by the Montreal Protocol (CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2F-$CClF_2$), CH_3CCl_3, and halon-1211 ($CBrClF_2$)) are referenced to CO and PCE (perchloroethylene, tetrachloroethene, C_2Cl_4) to determine their urban/industrial source strengths and to test existing estimates of U.S. emissions. Despite the full imposition by 1996 of the Montreal Protocol ban on production by developed countries, our data show that significant releases to the atmosphere continue and that only emissions of CFC-12 and CH_3CCl_3 declined in the region during this period. A broader historical and geographical study of emissions reveals that from 1986 to 1996 the international treaty has reduced U.S. emissions of CFC-11, CFC-12, CFC-113, and CH_3CCl_3 by 87%, 70%, 93%, and 87%, respectively, but current trends suggest persistent emissions for many years following. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* Montreal Protocol, pollution, CFCs, methyl chloroform, halon-1211, perchloroethylene

Citation: Barnes, D. H., S. C. Wofsy, B. P. Fehlau, E. W. Gottlieb, J. W. Elkins, G. S. Dutton, and S. A. Montzka, Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998: 2. A study of the efficacy of the Montreal Protocol and other regulatory measures, *J. Geophys. Res.*, *108*(D6), 4186, doi:10.1029/2001JD001117, 2003.

1. Introduction

[2] The release of gases believed to damage the ozone layer was addressed internationally by the Montreal Protocol to Reduce Substances that Deplete the Ozone Layer in 1987 [*United Nations Environmental Programme* (*UNEP*), 1987] and the London [*UNEP*, 1990] and Copenhagen [*UNEP*, 1992] amendments. The majority of the targeted substances, including CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2F-$CClF_2$), methyl chloroform (CH_3CCl_3), and halon-1211 ($CBrClF_2$), (hereinafter referred to as the "banned" or "regulated" substances) were scheduled for 100 percent reductions in production and consumption of freshly manufactured product by 1 January 1996 (1 January 1994 for halon-1211) in developed countries (hereafter referred to as the 1996 Montreal Protocol "full ban," although allotments still allowed for sales to developing countries) [*UNEP*, 1997]. Global background measurements taken in remote (far from the pollution sources) locations over the last decade have indicated a deceleration in the associated atmospheric growth rates, followed by a decline in atmospheric concentrations for many of these species, as production and use of these chemicals waned in anticipation of the coming ban [*Elkins et al.*, 1993; *Derwent et al.*, 1998a, 1998b; *Montzka et al.*, 1999]. Of the above mentioned species restricted under the Montreal Protocol, only concentrations of CFC-12 and halon-1211 are still increasing in the atmosphere.

[3] Residual emissions rates are of particular concern to atmospheric modelers whose studies of stratospheric ozone depletion and global warming may be rendered incorrect by inaccurate estimates of emissions. For example, the global distribution of the atmosphere's primary scavenger, the hydroxyl radical (OH), is too variable in space and time to be studied directly [*Spivakovsky et al.*, 1990] and, instead, must be inferred from measurements of those gases whose principle loss mechanism is destruction by OH. The purely man-made methyl chloroform has been particularly

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useful in this regard [*Prinn et al.*, 1995; *Montzka et al.*, 2000]. Given accurate estimates of the industrial emissions and measurements of the atmospheric concentrations of CH_3CCl_3, the rate of its destruction and its lifetime in the troposphere may be established. By then weighting the frequency of reaction of CH_3CCl_3 with OH, the global mean concentration and trend of OH may be determined [*Prinn et al.*, 2001]. The derived value of OH is used in turn to calculate the atmospheric lifetimes, ozone depleting potentials, and global warming potentials of many environmentally important gases.

[4] To characterize the industrial emissions in the United States, modelers have relied upon county and state emission reports to the EPA (U.S. Environmental Protection Agency), which in turn are based on factory inventories, or upon the audited sales of the major producers (see http://www.epa.gov) [*McCulloch et al.*, 1994, 1999; A. McCulloch et al., personal communication, 2001; *McCulloch and Midgley*, 1996; *Midgley*, 1989, 1992; *Midgley and McCulloch*, 1995; P. M. Midgley, personal communication, 2001]. With the passing of the 1996 Montreal Protocol full ban deadline for developed countries (1994 for H-1211), self reports by factories and audited sales are no longer useful proxies of emissions in developed countries. Further, the announcement of the Protocol may have led to changes in behavior, such as stock hoarding and price increases, making emissions harder to predict than before. Beyond 1996, emission estimates of the banned gases have been calculated on the global scale [*McCulloch et al.*, 2001; *McCulloch and Midgley*, 2001] (available at http://www.afeas.org., incorporating both continued production and sales in developing countries and emission functions for short-, medium-, and long-term reservoirs for developing and developed countries; emission estimates specific to the United States have not been reported.

[5] In addition to the factory- and sales-based inventories, observations by long-term global air sampling networks with flask sites or in situ stations located downwind of emitting sources have sought to establish release rates over the years. Measurements from the Mace Head, Ireland station of the GAGE/AGAGE (Global Atmospheric Gas Experiment/Advanced Global Atmospheric Gas Experiment) sampling network were combined with a simple climatological long-range transport model or with a sophisticated Lagrangian dispersion model to derive fluxes of CFC-11, CFC-12, CFC-113, CH_3CCl_3, CCl_4, CO, CH_4, N_2O, CO_2, and O_3 advected from the European continent for the years 1987 through 1996 [*Fraser et al.*, 1996; *Simmonds et al.*, 1996; *Cunnold et al.*, 1997; *Derwent et al.*, 1998a, 1998b]. *Biraud et al.* [2000] have inferred 1996–1997 European flux estimates of CFCs, N_2O, CH_4, and CO_2 by scaling their emissions to the reference tracer ^{222}Rn. The NOAA/CMDL (National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory) sampling network data, with its combination of station gas chromatograph measurements (for CFC-11, CFC-12, CH_3CCl_3, and CCl_4 at Barrow, Alaska; Niwot Ridge, Colorado; Mauna Loa, Hawaii; American Samoa; and the South Pole) and flask air samples (for CFC-113 and halon-1211 at 12 stations worldwide), have been used to quantify global emissions for 1992 through 1998 [*Montzka et al.*, 1999]. Finally, continental U.S. emissions and source trends of CFC-11, CFC-12, CFC-113, CH_3CCl_3, CCl_4, CO, CH_4, $CHCl_3$, N_2O, and SF_6 were derived from observations made in the rural, agricultural and/or forested lands of North Carolina (November 1994 through October 1997) and Wisconsin (June 1996 through October 1997) [*Bakwin et al.*, 1997; *Hurst et al.*, 1998].

[6] To date, no long-term record of U.S. pollution emissions of the banned species measured by a station in close proximity to the major emitting sources of the Northeast urban/industrial corridor has been made available, either before or after the Montreal Protocol ban of 1 January 1996. This study provides an independent measure of emissions of several radiatively-active and ozone-depleting gases from this region for the years 1996 through 1998, the first 3 years after the full implementation of the Montreal Protocol, using continuous measurements at a strategically-placed site in central New England. The Harvard Forest research site lies downwind of the Northeast urban/industrial corridor, including the greater metropolitan region of New York City, and is subject to emissions from nearby highways, landfills, sewage treatment plants, agriculture, and wood burning. Background signals, annual trends, and seasonal cycles determined from the data are in excellent agreement with values observed at remote sites in nearly all cases [*Barnes*, 2000]. Unlike remote sampling sites, Harvard Forest receives pollution plumes 3 to 5 times per month with concentrations well in excess of the background signal extracted from the data. A study of the pollution plumes themselves, their content and the history of their change over seasons and years, gives excellent data on the sources of important regulated gases and provides insight to the efficacy of policies aimed at mitigating those emissions.

[7] We have related enhancements in observed concentrations of CO and PCE (perchloroethylene, tetrachloroethene, C_2Cl_4) made at Harvard Forest to emission rates from the ground [*Barnes et al.*, 2003], based on the well-documented EPA emissions of CO, which are reported on a per county basis, and a composite PCE inventory, derived from the EPA/TRI (Toxic Release Inventory) records and the McCulloch and Midgley sales-based country-level tallies. In this paper we use both CO and PCE independently as reference gases to estimate the seasonal character and the inter-annual trend of urban/industrial emissions of the regulated gases CFC-11, CFC-12, CFC-113, CH_3CCl_3, and halon-1211 on a per capita basis. These regulated gases are all man-made substances used by industry and consumers, have no natural sources, and have primary sinks in the stratosphere (except CH_3CCl_3 which is mostly destroyed in the troposphere by OH) where they participate in ozone depletion (Table 1). Of this group, CFC-11, CFC-12, and CFC-113 are also potent greenhouse gases. The results of this study are used to establish the recent urban pollution history of those gases regulated by the Montreal Protocol; to test the existing inventories for the New York City–Washington, D. C., corridor and for the continental United States; to compare these results with those of Europe and the world; and to assess the regional compliance with mitigation policies.

2. Urban/Industrial Pollution for the New York City–Washington, D. C., Corridor

[8] The relative source strengths of correlated trace species may be used to quantify emission rates if the source of

Table 1. Main Sources and Sinks[a]

		Sources and Uses		Sinks		Greenhouse Gas?	Ozone Depleting Gas?
Species	Regulated?	Anthropogenic	Naturally Occurring	OH?	Other		
CO	yes	combustion of fossil fuels, biomass burning	oxidation of CH_4 oxidation of NMHCs	yes	soils (10%)	no	no
PCE	yes[b]	dry-cleaning solvent, degreasing agent	oceans (5%)	yes	negligible	no	no
CFC-11	yes	aerosol propellant, refrigerant, air-conditioning agent, cleaning solvent, blowing agent for plastic foams	none	no	stratosphere	yes	yes
CFC-12	yes	aerosol propellant, blowing agent for plastic foams, refrigerant air-conditioning agent	none	no	stratosphere	yes	yes
CFC-113	yes	refrigerant, cleaning solvent, blowing agent for plastic foams	none	no	stratosphere	yes	yes
CH_3CCl_3	yes	degreasing agent, cleaning solvent, aerosol propellant	none	yes	stratosphere, ocean	yes	yes
H-1211	yes	fire extinguishers	none	no	photolysis	no	yes

[a] CO from *Novelli et al.* [1998] and *Khalil and Rasmussen* [1990]. PCE, CH_3CCl_3, and $CHCl_3$ from *Keene et al.* [1999]. Additional CH_3CCl_3 information from *Midgley and McCulloch* [1995]. CFC-11, CFC-12, and CFC-113 from *Freemantle* [1990]. H-1211 from *Fraser et al.* [1999]. H_2 from *Novelli et al.* [1999]. CH_4 from *Lelieveld et al.* [1998]. SF_6 from *Geller et al.* [1997].

[b] PCE is subject to voluntary cut-backs only.

any reference compound is known. In our case, we use both CO and PCE as reference gases from which to derive emission rates for the banned substances. Although the sources of these reference gases are different (CO is found principally in motor exhaust and PCE is a dry cleaning and industrial degreasing agent), emissions are co-located in densely populated areas [*Barnes et al.*, 2003]. An EPA CO emissions inventory of anthropogenic sources is available for all 3 years (1996–1998) (http://www.epa.gov/air/data/nettier.html); secondary CO production from hydrocarbons in the summer months are not included in the survey. Inventories of PCE emissions are available for 1996 only (http://www.epa.gov/enviro/tris) [*McCulloch and Midgley*, 1996; P. M. Midgley, personal communication, 2001]; 1997 and 1998 PCE emission estimates are derived from the 1997 and 1998 CO inventory values and the ratio of CO/PCE in pollution plumes observed during this study [*Barnes et al.*, 2003, Table 4]. Over the years of this experiment, urban/industrial CO emissions declined slightly, by ~2.7% per year, while PCE emissions exhibited no uniform trend.

[9] In a method parallel to that employed by *Barnes et al.* [2003], correlation analysis is applied to the enhancements observed in pollution plumes from the Northeast urban/industrial corridor of the regulated gases and each of the references gases, CO and PCE. From this we determine both the seasonal character of the trace gas emissions, relative to CO and PCE, and the annual urban/industrial emissions for the 3 years of 1996, 1997, and 1998. Our conclusions here are necessarily bound by the limitations of the correlation between the available inventories and our observations. The 11% difference between the 1996 inventory (584 kg_{CO}/kg_{PCE}) and observed (521 kg_{CO}/kg_{PCE}) CO/PCE ratios [*Barnes et al.*, 2003] will be taken as our figure of merit for the CFCs, methyl chloroform, and halon-1211 emissions determined below. The annual emissions obtained here are then compared to all other available source estimates, both locally and abroad.

2.1. Methods

[10] Harvard Forest is located in Petersham, Massachusetts (42.48°N, 72.18 W, 340 m) and receives "clean" background air from the northwest (Canada) and "dirty" polluted air from the southwest (New York City–Washington, D. C., corridor, including western and central Connecticut). Starting in January 1996, FACTS (Forest and Atmosphere Chromatographs for Trace Species), a fully automated, in situ four-channel gas chromatographic instrument, began measurements of eleven atmospheric gases above the forest canopy (29 m) once every 24 min. CFC-11, CFC-12, CFC-113, and halon-1211 were simultaneously measured using a unibeads 2s precolumn and main column (1.5 m and 2.5 m long, respectively) for respective precisions of 0.21% (0.56 ppt), 0.22% (1.15 ppt), 0.79% (0.68 ppt), and 1.39% (0.06 ppt). Here, field precisions were based on the average of 72 monthly precisions (36 months for the years 1996–1998 and two calibration tanks). Each monthly precision was based on one tank, run in sequence with the other tank and two airs, for a frequency of 1 in every 48 min. Measurements of standards are detrended by subtraction of a two-point running mean, and the precision is equated to the coefficient of variation (standard deviation/mean) of the residuals. Methyl chloroform was measured on the same channel as PCE with an OV-101 20% precolumn and main column (2 m and 5 m long, respectively) for a precision of 0.79% (1.01 ppt). Calibration gases were provided by NOAA/CMDL. A full description of the FACTS instrument, calibration procedures, and estimates of the analytical precision for the suite of gases is provided by *Barnes* [2000].

[11] Time series for the five gases (Figure 1) over the 3 years demonstrate that both the background trace gas mixing ratios and the pollution enhancements vary on inter-annual, seasonal, and diurnal timescales. The background signal ($\mathbf{z_o}$) is determined by applying a 0.2 running quantile on a window size of ten days to the original time series (z) [*Barnes et al.*, 2003] (Table 2). The background levels and seasonal cycles are consistent with those measured by the NOAA/CMDL stations and flasks (http://www.cmdl.noaa.gov) [*National Oceanic and Atmospheric Administration/CMDL*, 1998] (Figure 2). Slightly higher Harvard Forest baselines for CFC-12, CH_3CCl_3, and H-1211 may be attributed to an overall diffuse enhancement of these gases in the Northeast urban/industrial source region. Only CFC-11 in 1996 and CFC-113 in 1998 exhibit

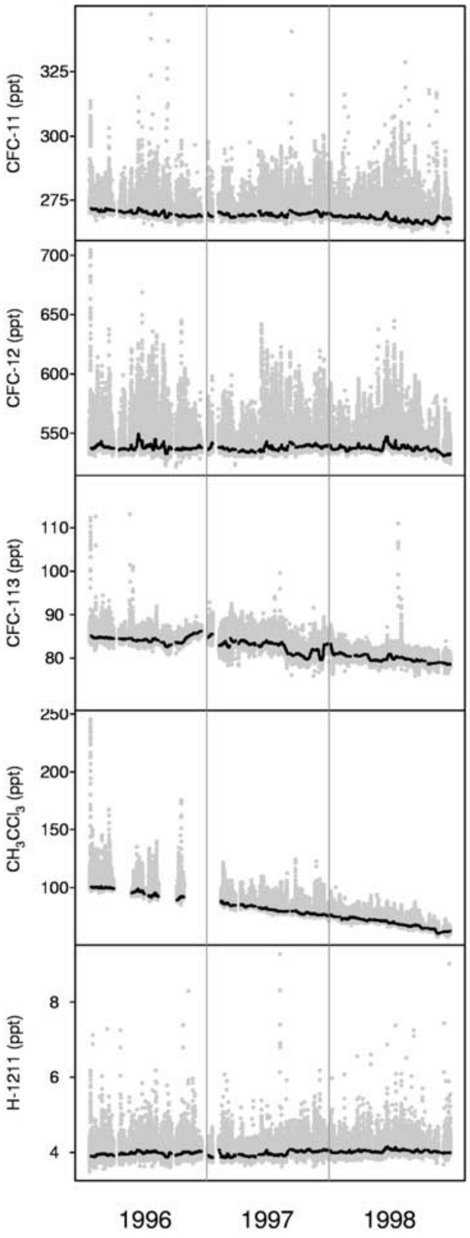

Figure 1. Time series of five species measured by FACTS spanning 1 January 1996 to 31 December 1998. Background signals (black line) are based on a running quantile of 0.2 and an interval size of 10 days. Pollution plumes are clearly evident above the background. Methyl chloroform (CH_3CCl_3) exhibits a notable decline in background concentrations along with a dampening in the pollution variation.

unexpectedly low values compared to the other stations. Since the conclusions reached below depend on the height of the pollution plumes above the background signal and not the absolute concentrations, the small differences found between the NOAA/CMDL and FACTS background levels, which may reflect small calibration errors, are not of concern here.

[12] To characterize the urban/industrial emissions, their seasonality, and inter-annual variation of the gases measured by FACTS, a similar ratio and error method to that described in *Barnes et al.* [2003] is employed. The pollution enhancements, $\Delta \mathbf{z}$, are found by subtracting the background signal, $\mathbf{z_o}$, from the original time series, z: $\Delta z = (z - \mathbf{z_o})$. The correlations between each species with CO and PCE are determined as the ratios of their enhancements, $\Delta z/\Delta \mathbf{CO}$ and $\Delta z/\Delta \mathbf{PCE}$, as obtained from the slope of the orthogonal distance regression (ODR) [*Press et al.*, 1986, p. 660] of z versus CO and z versus PCE. As shown by *Barnes et al.* [2003], the uncertainty in the ODR slopes is defined as the range of slope values surrounding the ODR for which the difference in the merit function, χ^2 (where $\chi^2\ (m, b) = \sum\ [(y_i - b - mx_i)^2\ /\ (\sigma_{yi}^2 + m^2\ \sigma_{xi}^2)]$), between the ODR and surrounding slopes is less than 6.17 (the level of the 95.4% confidence interval [*Press et al.*, 1986, p. 692]).

[13] The ODR slopes are calculated for each of the twelve three-month seasons in 1996, 1997, and 1998 (with winter = December, January, and February) and for seven subsets of the data: all data; northwest winds only (NW); southwest winds only (SW); day (6 am to 6 pm); night (6 pm to 6 am); high U* (>0.2 m/s); and low U* (<0.2 m/s) (where U* = $\sqrt{(-1 * \text{momentum flux})}$, a measure of turbulent exchange with the overlying atmosphere). In all cases and seasons, the slopes are statistically significant with t values well above 2.617, the 0.995 confidence interval for greater than 120 degrees of freedom. The slopes are converted from ppt/ppt to kg/kg based on the ratio of their molecular weights. The degree of correlation between the pollution enhancements of the species, z, and the reference gases CO and PCE for southwest winds during summer 1997 is illustrated in Figure 3. Numerical values for the SW case are provided in full in Table 3, including the ODR slopes and slope errors of $\Delta z/\Delta \mathbf{CO}$ (g/kg) and $\Delta z/\Delta \mathbf{PCE}$ (kg/kg) for each species, z. The pollution-driven correlations are strong for all but CFC-113, for which emissions are small. The negative correlations for CFC-113 in fall 1996, winter and spring 1997, and fall 1998 reflect either instrument error, sources that are not correlated either spatially or temporally with emissions of CO and PCE, or emissions that too small for this analysis to distinguish above the noise. As discussed by *Barnes et al.* [2003], the southwest direction is emphasized because Harvard Forest receives most of its polluted airflow from that region (Figure 4). Sector SW4 (as defined by *Barnes et al.* [2003] is again used to represent the urban/industrial source region of the New York City–Washington, D. C., corridor, including western and central Connecticut. Cross-correlation studies between each species and PCE and CO again indicate that these species co-vary out to time lags of about 2 days (Figure 5), well within Sector SW4. The only exception is again for CFC-113, suggesting either that the sources of this gas are not co-located with CO and PCE or that CFC-113 has diffuse rather than individual disperse sources.

2.2. Seasonal Cycles in Emissions

[14] The seasonal character of the urban/industrial emissions for the New York–Washington, D. C., corridor may be determined by examining the time series of emission ratios, $\Delta z/\Delta \boldsymbol{x}$ (kg/kg), (where $\boldsymbol{x}$ is either CO or PCE), as shown in Figure 6. Emission ratios computed from the seven subsets of the data track each other well. That there is

Table 2. Background Mixing Ratios, Lifetimes, Seasonal Amplitudes, and Annual Trends

Species	Ambient Mixing Ratio (1996–1998)	Atmospheric Lifetime, years[a]	Mean Seasonal Amplitude, ppb or ppt	Harvard Forest Annual Trend, ppb or ppt per year (1996–1998)	Literature Annual Trends,[b] ppb or ppt per year
CO	151.3 ppb	0.17	27.4	+10.198 (±2.855)	−2.3 (± 0.2) for 1990–1995
PCE	7.5 ppt	0.45	2.5	−1.345 (±0.150)	NA
CFC-11	269.2 ppt	45	0.8	−1.183 (±0.134)	−0.8 (±0.2) for 1995–1996
CFC-12	537.6 ppt	87	1.7	−0.164 (±0.399)[c]	+3–6 for 1995–1996
CFC-113	82.3 ppt	100	0.8	−2.234 (±0.141)	−1.1 for 1994
CH_3CCl_3	96.5 ppt[d]	4.8	0.7	−12.771 (±0.126)	−18 (±2) for 1995–1996
H-1211	3.99 ppt	24	0.03	+0.031 (±0.008)	+0.16 (±0.016) for 1995–1996

[a] Steady state lifetimes for CFC-12, H-1211, CFC-11, and CFC-113 from [*Volk et al.*, 1997]. CH_3CCl_3 lifetime from *Montzka et al.* [1999]. CO lifetime from *Novelli et al.* [1998]. PCE lifetime from [*Wang et al.*, 1995]. H_2 lifetime from *Novelli et al.* [1999]. CH_4 lifetime from *Lelieveld et al.* [1998]. $CHCl_3$ lifetime from *Khalil and Rasmussen* [1999]. SF_6 lifetime from *Ravishankara et al.* [1993].

[b] Annual trends for CFC-12, CFC-11, and CH_3CCl_3 from *Derwent et al.* [1998a]; CH_4 from *Derwent et al.* [1998b]; CFC-113 from *Simmonds et al.* [1996]; CO from *Novelli et al.* [1998]; H_2 from *Novelli et al.* [1999]; H-1211 from *Butler et al.* [1998]; $CHCl_3$ from *Khalil and Rasmussen* [1999]; and SF_6 from *Geller et al.* [1997].

[c] The last 2 months, November and December 1998, were aberrantly low and not included in this calculation.

[d] For the year 1996.

little to distinguish between the day and night or the high and low U* cases strongly suggests that build up of local emissions during slow winds and heightened concentrations during nighttime low boundary layer conditions are negligible compared to the influence of regional emissions and seasonal and wind direction effects. Only the NW case with its small enhancements and therefore greater uncertainty shows a tendency for nonconformity, particularly for H-1211. The effect of small plumes on the analysis is likewise evident for CFC-113, for which the emission ratios are often negative, an unreasonable result given the urban/industrial uses of this gas.

[15] Ideally, when assessing the seasonal character of emissions of a given gas against those of a reference gas, the emissions of the reference gas should be known to be constant throughout the year. This is not the case for CO emissions, for which secondary production in summertime introduces its own seasonality. In a previous study, *Prather* [1985] and *Prather et al.* [1987] followed a similar procedure with CFC-11 as the reference gas to estimate the seasonal emissions from Europe for several halocarbons. By assuming that the emission rates for CFC-11 were steady throughout the year, Prather et al. defined seasonal variations for the other gases. More recently, *McCulloch and Midgley* [1996] concluded that releases of PCE due to industrial activities are uniform with season. It is evident from our CFC-11/PCE (kg/kg) results that CFC-11 and PCE emissions cannot both be uniform (Figure 6). With the exception of *Prather*'s [1985] and *Prather et al.*'s [1987] conclusions based on CFC-11 in the 1980s, little attempt has be made to establish the seasonal nature of those sources releasing Montreal Protocol banned substances. In this discussion of seasonal cycles, we consider only those features that are present in both the CO and PCE ratios.

[16] The FACTS data point to some seasonality in the emissions of CFC-11, CFC-12, and CH_3CCl_3, with highest values consistently found in the summer and lowest in the winter, despite the lack of seasonal patterns in the background signals of these gases. The high degree of similarity between the ratios of CFC-11 and CFC-12 to both CO and PCE at Harvard Forest strongly suggests that these gases were emitted by colocated sources. In the case of CFC-12, which is used primarily as a coolant in car air conditioners most in demand in the hotter weather, the summertime maximum may be the result of leakage either from the refilling process, even though shops are supposed to recover the gas, or from the air conditioners themselves when they are on and pressurized, despite being tightly sealed systems. Moreover, the decline in peak summer values of CFC-12 over the 3-year period may be consonant with its replacement by HCF-134a (CF_3CFH_2) in newer cars. Methyl chloroform emissions also exhibit seasonality with a decreasing amplitude over the 3 years, in keeping with the Montreal Protocol ban. The releases of CH_3CCl_3 observed at Harvard Forest are higher in the summer and fall and lower in the winter and spring, a cycle that is opposite to that reported by *Prather* [1985] and *Prather et al.* [1987] for European air. For halon-1211, the seasonal variation found in H-1211/CO is not corroborated by H-1211/PCE, suggesting that the observed seasonality is due to that of CO and not to the emissions of H-1211 itself.

2.3. Annual Rates and Interannual Trends in Urban/Industrial Emissions

[17] The unique siting of Harvard Forest downwind of a huge source region in conjunction with the availability of CO and PCE inventories for Sector SW4 [*Barnes et al.*, 2003] allows for an estimation of the annual urban/industrial emissions, $\boldsymbol{z}_{\mathbf{E}}$, of the banned gases, z, over the years 1996 through 1998. A similar study of the non-urban/industrial NW case is not provided here, due to the weak pollution signals received from that direction.

[18] We have shown that for 1996 the ratio of the CO and PCE pollution enhancements, $\mathbf{\Delta CO/\Delta PCE}$, agrees with the ratio of their emissions inventories, $\mathbf{CO_I/PCE_I}$, to within 11%, and we have calculated PCE inventory results ($\mathbf{PCE_I}$) for 1997 and 1998 on the basis of the available 1997 and 1998 CO inventory values ($\mathbf{CO_I}$) [*Barnes et al.*, 2003]. Here, to determine the annual urban/industrial emissions, $\boldsymbol{z}_{\mathbf{E}}$, for all 3 years, we equate the ratio of the pollution enhancements of the regulated gas, Δz, versus the reference gas, $\Delta \boldsymbol{x}$ (either CO or PCE), with the ratio of their emissions, $\boldsymbol{z}_{\mathbf{E}}/\boldsymbol{x}_{\mathbf{I}}$, $\Delta z/\Delta \boldsymbol{x}$ (ppt/ppt) = $\boldsymbol{z}_{\mathbf{E}}/\boldsymbol{x}_{\mathbf{I}}$ (kg/kg). That is, the urban/industrial emissions for each year may be calculated as $\boldsymbol{z}_{\mathbf{E}}$ (kg/person/year) = ($\Delta z/\Delta \boldsymbol{x}$) * $\boldsymbol{x}_{\mathbf{I}}$, where $\boldsymbol{x}_{\mathbf{I}}$ is the emission rate for the reference gas in kg/person/year for

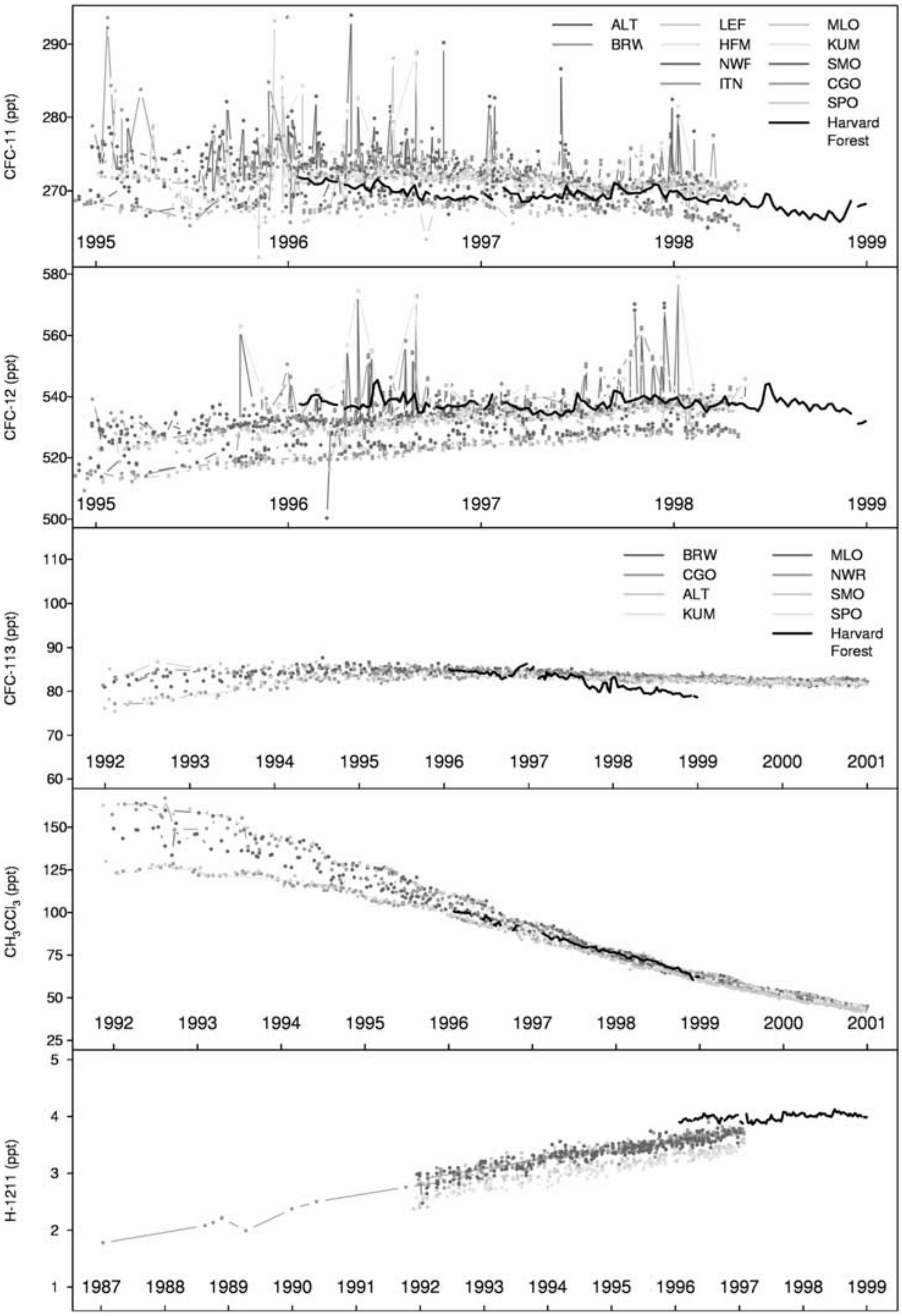

Figure 2. Comparison of Harvard Forest background signals as measured by FACTS (green line) to those measured at the remote stations of NOAA/CMDL [*NOAA/CMDL*, 1998]. All data were retrieved from the NOAA/CMDL web site: ftp://ftp.cmdl.noaa.gov. The flask data for H-1211 were sampled at: Alert, North West Territories, Canada (ALT); Barrow, Alaska (BRW); Niwot Ridge, Colorado (NWR); Mauna Loa, Hawaii (MLO); Tutuila, American Samoa (SMO); and South Pole, Antarctica (SPO). Flasks measurements of CFC-11, CFC-12, CFC-113, and CH_3CCl_3 were sampled at the same sites as for H-1211, as well as Wisconsin (LEF); Harvard Forest, Massachusetts (HFM); Grifton, North Carolina (ITN); Cape Kumahkahi, Hawaii (KUM); and Cape Grim, Tasmania (CGO). See color version of this figure at back of this issue.

Sector SW4 [*Barnes et al.*, 2003, Table 4]. We can obtain total annual emissions for the SW4 region using its population of 34,400,000, as estimated by the U.S. Census Bureau (http://www.census.gov) for the year 1998.

[19] When taking the average of the southwest slopes of $\Delta z/\Delta \mathbf{CO}$ and $\Delta z/\Delta \mathbf{PCE}$ over each year to determine the annual $\Delta z/\Delta x$ ratio, it is not always advisable to simply include all four seasons. This is especially true for emission

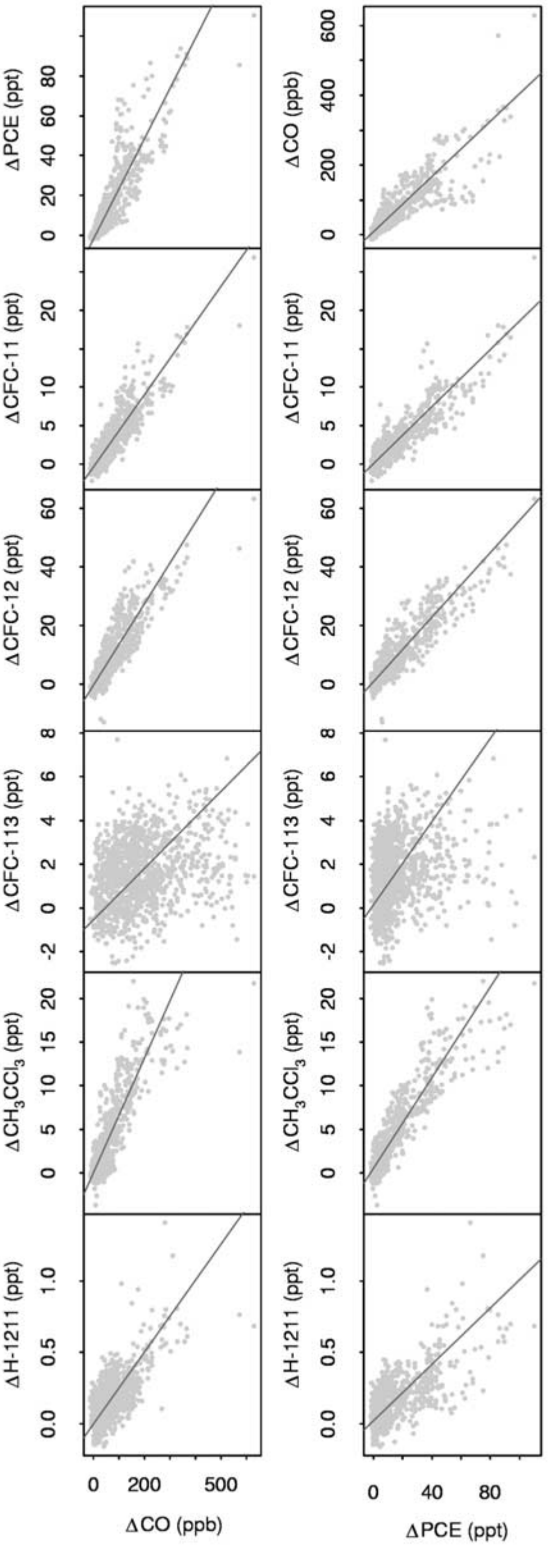

Figure 3. Data points and orthogonal-distance regression lines for $\Delta z/\Delta \mathbf{CO}$ (left column) and $\Delta z/\Delta \mathbf{PCE}$ (right column) where z represents each gas during summer 1997. The pollution-driven correlations are strong for all but CFC-113, for which emissions are small. Full seasonal results are presented in Figure 6.

ratios versus CO, for which urban emissions are elevated by secondary CO production from hydrocarbons in summer, an additional source not covered by the inventories. Furthermore, in the summertime, weaker winds and higher planetary boundary layer depths make for longer and more frequent stagnation events, during which local emissions near the site may build up, offsetting the regional signal. In wintertime the system is more flushed out. To address these concerns, both the PCE and CO ratios are used to assess the annual average ratio of emissions, $\Delta z/\Delta x$, and, in addition to using the whole year (all four seasons), we examined data for the winter season alone and for winter and spring combined. The whole year case is retained in order to capture any seasonal variations in the emissions of the banned gases themselves.

[20] Graphs of the annual urban pollution emissions for each species, z, as derived from southwest CO and PCE ratios averaged over the whole year, the winter season only, and winter and spring combined, are provided in Figure 7. Statistical confidence intervals of 1-σ are marked by black vertical lines. Even though the 1997 and 1998 PCE inventory values were derived from the 1997 and 1998 CO inventory results rather than obtained from independent PCE surveys, the annual urban emission results derived here from PCE may be considered more reliable than those from CO; the FACTS measurements of PCE have a better figure of merit (89.8) than those of CO (27.6), where the figure of merit is defined as the ratio of observed atmospheric variance of a given species over its instrumental precision [*Barnes*, 2000]. Moreover PCE has no known seasonal variation for emissions, as opposed to CO with its secondary production in summer. Again, the negative values found for CFC-113 are not considered valid for the reasons given above. In Figure 7, the CFC-11 and H-1211 emissions over the years of this experiment do not exhibit the noticeable decline evident in the CFC-12 and CH_3CCl_3 emissions results.

[21] We can characterize the region's urban/industrial emission history quantitatively by averaging the six cases of the annual urban pollution emissions for each species over the 3 years (Table 4). Interannual trends are provided only for those species that show monotonic increases or decreases over the 3 years. Of the regulated gases, emissions of CFC-12, CH_3CCl_3, and CO are decreasing, as expected given their restrictions, but significant emissions still remain. Such a dramatic decline in the CH_3CCl_3 emission rates was evident in the diminishing heights of the pollution plumes themselves over the years of this experiment, as seen in the original CH_3CCl_3 atmospheric concentration time series (Figure 1). Regional emissions of CFC-11 are rising, surprisingly, despite the decline in its global atmospheric growth rate, witnessed as early as 1989 [*Elkins et al.*, 1993]. The emissions of H-1211 do not exhibit any distinguishable trend pattern. For CFC-113 in 1997, the negative 1997 result prevents any reliable conclusions with regards to its interannual trend. PCE emissions do not exhibit a decline, despite the calls for voluntary cutbacks of its use.

3. Discussion: Available Inventories and Long-Term Observational Records

[22] These annual emissions estimates of the Montreal Protocol banned gases for the New York City–Washington,

Table 3. Δz/CO and $\Delta z/\Delta$PCE ODR slopes for all species (z) for Southwest Winds[a]

z	Year	Season	$\Delta z/\Delta$CO Slope, g/kg	$\Delta z/\Delta$CO Slope Error, g/kg	$\Delta z/\Delta$PCE Slope, kg/kg	$\Delta z/\Delta$PCE Slope Error, kg/kg
CFC-11	1996	winter	0.245	0.037	0.117	0.021
		spring	0.286	0.032	0.133	0.025
		summer	0.361	0.036	0.182	0.024
		fall	0.271	0.037	0.121	0.028
	1997	winter	0.243	0.040	0.126	0.020
		spring	0.233	0.030	0.148	0.020
		summer	0.377	0.042	0.229	0.027
		fall	0.298	0.035	0.171	0.022
	1998	winter	0.249	0.032	0.184	0.023
		spring	0.281	0.035	0.138	0.017
		summer	0.430	0.040	0.187	0.018
		fall	0.341	0.038	0.129	0.015
CFC-12	1996	winter	1.046	0.157	0.475	0.092
		spring	1.023	0.114	0.433	0.081
		summer	1.454	0.140	0.690	0.088
		fall	0.928	0.116	0.445	0.065
	1997	winter	0.608	0.097	0.310	0.050
		spring	0.636	0.082	0.410	0.057
		summer	1.257	0.141	0.739	0.085
		fall	0.878	0.101	0.507	0.064
	1998	winter	0.521	0.065	0.384	0.047
		spring	0.701	0.087	0.344	0.042
		summer	1.138	0.103	0.497	0.046
		fall	0.798	0.085	0.301	0.034
CFC-113	1996	winter	0.125	0.022	0.056	0.012
		spring	0.122	0.018	0.063	0.014
		summer	0.107	0.017	0.052	0.010
		fall	−0.077	0.080	0.031	0.029
	1997	winter	−0.144	0.075	−0.074	0.030
		spring	−0.196	0.420	0.113	0.053
		summer	0.136	0.029	0.080	0.018
		fall	0.133	0.062	0.090	0.063
	1998	winter	0.085	0.018	0.060	0.016
		spring	0.087	0.056	0.043	0.022
		summer	0.096	0.029	0.042	0.020
		fall	−0.081	0.036	−0.030	0.008
CH_3CCl_3	1996	winter	0.735	0.125	0.352	0.059
		spring	0.749	0.133	0.343	0.060
		summer	0.705	0.097	0.327	0.042
		fall	0.691	0.191	0.266	0.062
	1997	winter	0.436	0.109	0.207	0.049
		spring	0.342	0.052	0.219	0.033
		summer	0.386	0.044	0.231	0.026
		fall	0.437	0.053	0.260	0.033
	1998	winter	0.238	0.030	0.174	0.022
		spring	0.251	0.031	0.125	0.016
		summer	0.270	0.026	0.122	0.012
		fall	0.244	0.027	0.096	0.011
H-1211	1996	winter	0.0162	0.0030	0.0078	0.0017
		spring	0.0199	0.0026	0.0104	0.0023
		summer	0.0220	0.0025	0.0105	0.0017
		fall	0.0208	0.0031	0.0088	0.0015
	1997	winter	0.0172	0.0033	0.0086	0.0016
		spring	0.0150	0.0022	0.0094	0.0016
		summer	0.0174	0.0021	0.0100	0.0013
		fall	0.0176	0.0023	0.0103	0.0016
	1998	winter	0.0104	0.0016	0.0077	0.0011
		spring	0.0163	0.0023	0.0081	0.0011
		summer	0.0162	0.0017	0.0070	0.0008
		fall	0.0128	0.0016	0.0051	0.0006

[a] The slope errors defining the 95.4% confidence intervals were determined using a multivariate Monte Carlo simulation approach described in full by *Barnes* [2000].

D. C., corridor are the first of their kind. No other measurements or inventories for the same region are available for comparison. Inventories that do exist for these gases, however, include the factory-based, county-level tallies of the U.S. EPA for the northeastern United States, and the United States as a whole (http://www.epa.gov), and the sales-based country- or regional-level emissions estimates of McCulloch and Midgley for the United States, North America,

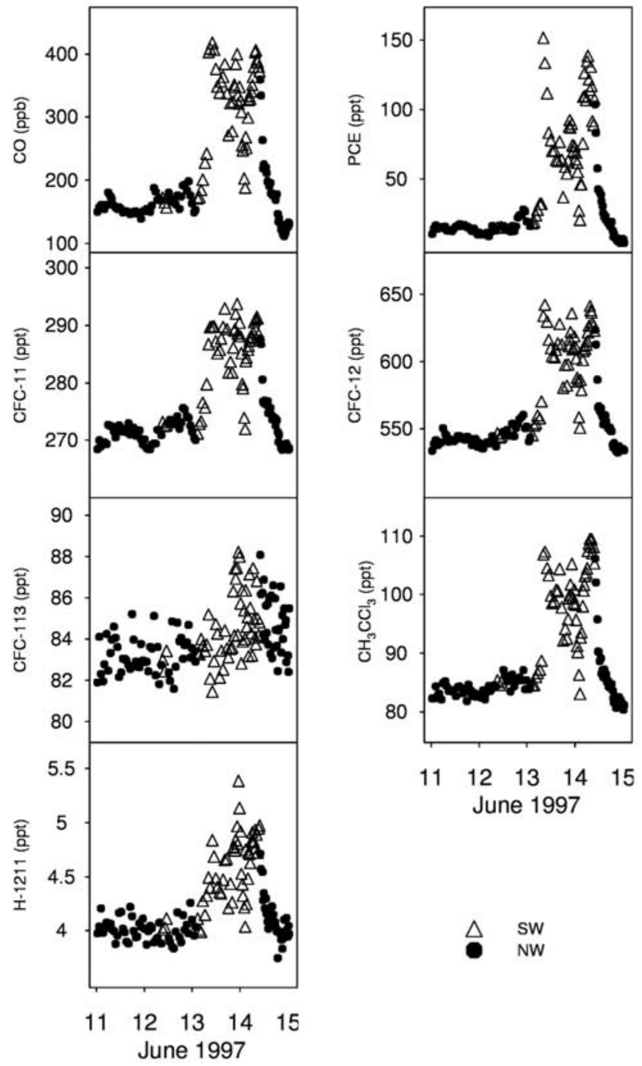

Figure 4. The pollution plume of 12 to 15 June 1997 is presented for all species. A high degree of correlation in the enhancement, with low atmospheric concentrations associated with northwest winds (solid circles) and high mixing ratios with southwest winds (open triangles). This is to be expected since most of these gases are known to be anthropogenic in origin with sources located in urban/industrial locales.

Europe, and the world [*McCulloch et al.*, 1994; *McCulloch and Midgley*, 1996; *Midgley*, 1989, 1992; *Midgley and McCulloch*, 1995; P. M. Midgley, personal communication, 2001]. Both the EPA/CEIS and the EPA/OAR provide CO emissions estimates. The EPA Toxic Release Inventory covers the gases CFC-11, CFC-12, CFC-113, and H-1211, as well as PCE. This inventory does not represent all fifty states or all counties in its tally, and as with PCE, it considers only those facilities whose releases total more than 10,000 tons per annum and that employ 10 people or more, a policy that often results in severe underreporting [*Barnes et al.*, 2003]. The McCulloch and Midgley inventories cover the gases CFC-11, CFC-12, CFC-113, CH_3CCl_3, and PCE, in some cases beginning as early as 1970 and ending with the phase-out in 1995. Based on the audited reports of the annual sales of producers, this inventory takes into consideration the short-, medium-, and long-term uses of the gases when predicting annual emissions from the sales data.

[23] Complementing the New York City–Washington, D. C., corridor measurements made by FACTS are a handful of long-term observations by global air sampling networks with flask sites or in situ stations located downwind of emitting sources that have sought to establish release rates over the years for various locales. Continental U.S. emissions of CFC-11, CFC-12, CFC-113, and CH_3CCl_3 (as well as CO, CH_4, $CHCl_3$, and SF_6) were derived for a single year (June 1996 through October 1997) based on observations made in the rural agricultural and/or forested lands of North Carolina and Wisconsin [*Bakwin et al.*, 1997; *Hurst et al.*, 1998]. European air measurements, monitored by GAGE/AGAGE at the Mace Head sampling station, have been combined with both a simple climatological long-range transport model and a sophisticated Lagrangian dispersion model to derive fluxes of CFC-11, CFC-12, CFC-113, CH_3CCl_3, and CO (as well as CCl_4, CH_4, CO_2, N_2O, and O_3) advected from the European continent for the years 1987 through 1996 [*Fraser et al.*, 1996; *Simmonds et al.*, 1996; *Cunnold et al.*, 1997; *Derwent et al.*, 1998a, 1998b]. In addition, *Biraud et al.* [2000] have inferred 1996–1997 European flux estimates of CFCs, N_2O, CH_4, and CO_2 by scaling their emissions to the reference tracer ^{222}Rn. Global emission estimates of CFC-11, CFC-12, CFC-113, CH_3CCl_3, and H-1211 have been derived for 1992–1997 by the NOAA/CMDL sampling network [*Montzka et al.*, 1999] and global H-1211 releases based on observations in the Southern Hemisphere and production figures since as far back as 1963 are provided by *Fraser et al.* [1999].

[24] By compiling all the above inventory- and observational-based emissions estimates, we gain insight into the geographical distribution of the emitting sources, the historical trends in those emissions before, during, and after the 1996 Montreal Protocol full-ban deadline for developed countries, the quality of the various assessments, and the efficacy of the Montreal Protocol for each species.

3.1. Geographical Variations in Emissions

[25] A comparison of all the available observational and inventory data for each gas is given in kg/person in Figure 8 (CH_3CCl_3 is depicted in Figure 10). Population data for the United States, Canada, Europe, and the world for 1970 through 1998 are provided by the U.S. Census Bureau (http://www.census.gov). The use of population here as a distributor reflects the method by which the emissions were determined (i.e., as functions of CO and PCE in kg/person) and is not a statement on the assumed distribution pattern of these predominantly industrial materials. Gross national product (GNP) for national and regional scales and energy consumption for regional and local scales may be the more appropriate parameters to use for some species [*Prather et al.*, 1987; *Spivakovsky et al.*, 1990; *McCulloch et al.*, 1994].

[26] The closest observational data we have to compare with the FACTS results are the single year measurements for the continental United States provided by *Bakwin et al.* [1997] and *Hurst et al.* [1998]. For CFC-11, CFC-12, CFC-113, and CH_3CCl_3, the agreement is excellent. McCulloch and Midgley inventory results for the United States and

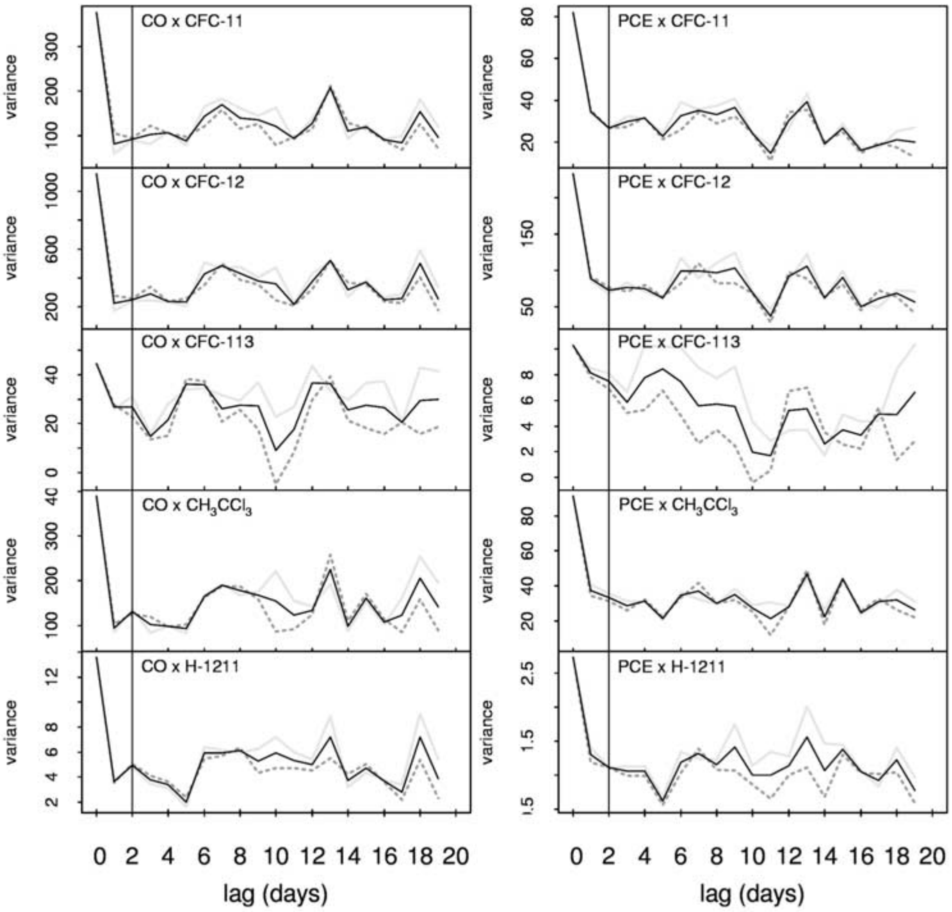

Figure 5. Covariance of each species with PCE and CO for July 1997 through December 1997, southwest winds only, plotted against lag time. Dotted dark shaded (solid light) lines show results for positive (negative) lags; the solid black lines represent the mean. The data are based on daily means with the lowermost and uppermost 1% of all values truncated to the first and ninety-ninth percentile values, respectively, to remove outliers. Most of the species co-vary significantly out to time lags of about 2 days, which is to be expected since most of the gases studied here are known to be anthropogenic in origin with sources located in urban/industrial locales. The only exception is for CFC-113, suggesting either that the sources of this gas are not co-located with CO and PCE or that CFC-113 has diffuse rather than individual disperse sources.

North America for PCE (1988 through1996) and CH_3CCl_3 (1980 through 1996) are also in agreement with the New York City–Washington, D. C., corridor emissions. EPA/TRI inventory results, by contrast, for both the northeastern United Sates and the United States as a whole are substantially lower than either of the United States-based observations for CFC-11, CFC-12, and H-1211, and, as already discussed, for PCE. Only for CFC-113 are the EPA/TRI values in agreement for the years 1996–1998, which is more a reflection of either the decline in these emissions to nearly zero or of the poor correlation of this gas to CO and PCE plumes, than a statement on the quality of the EPA/TRI itself. The EPA CO emission values in kg/person for the New York City–Washington, D. C., corridor are lower than those for the Northeast as a whole or for the Southeast [*Bakwin et al.*, 1997]. These in turn are lower than the EPA/CEIS and EPA/OAR estimates for the United States The main source of CO is transportation, and the lower New York City–Washington, D. C., corridor values most likely reflect the high numbers of urban dwellers, especially in New York City, who use public transportation rather than their own vehicles.

[27] For European air, the AGAGE observational data and the McCulloch and Midgley inventory results are in strong agreement for all their mutual gases of CFC-11, CFC-12, CFC-113, and CH_3CCl_3. Of the gases reported by *Biraud et al.* [2000], the ^{222}Radon-based emissions estimates of CFC-11 and CFC-12 are slightly higher than the other Mace Head results. A comparison of New York City–Washington, D. C., corridor/U.S. pollution to that of Europe reveals that for CFC-11, CFC-12, CH_3CCl_3, CO, and PCE, the northeastern United States emits more on a per capita basis. For CFC-113, the European emissions are the same (and nearly zero in the case of CFC-113) as that of the northeastern United States. The conclusions drawn here from the literature may be corroborated by directly comparing the pollution enhancements seen at Harvard Forest with those of Mace Head, Ireland (Figure 9). Confirming the

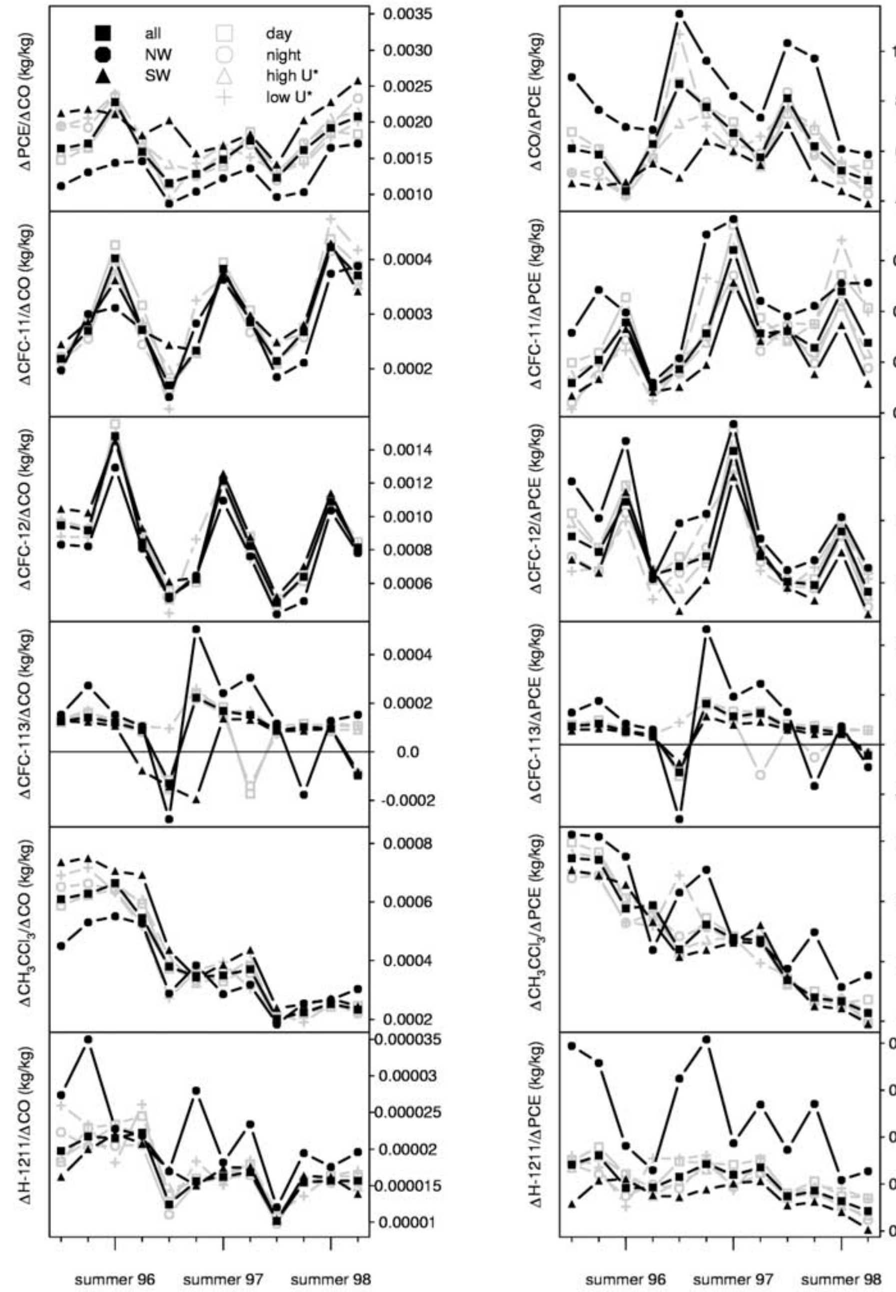

Figure 6. Seasonal study of the urban/industrial emissions for the banned gases. The first column contains $\Delta z/\Delta\mathbf{CO}$ and the second $\Delta z/\Delta\mathbf{PCE}$, both in kg/kg. All seven cases track each other well, with only NW (solid circles) showing a tendency for nonconformity, particularly for H-1211. Seasonal cycles for the ratios are evident for CFC-11, CFC-12, and CH_3CCl_3 with higher values in summertime and lower values in wintertime. Some of the observed seasonal variation may be due in part to the seasonal character of the reference gases, in particular CO whose atmospheric concentrations are elevated by secondary production in the summertime. We consider only those features that are present in both the CO and PCE ratios. The SW slopes (solid triangles) and slope errors for each species are tabulated in Table 3.

above results, for CFC-11, CFC-12, CFC-113, and CH_3CCl_3, the pollution levels witnessed at Harvard Forest are dramatically higher than those seen by European observers; and the emissions trends for CFC-12, CFC-113, and CH_3CCl_3 observed at Harvard Forest agree with those of European releases.

[28] Global interannual emissions trends further corroborate those found in Europe and the United States. The per capita global emissions for CFC-11, CFC-12, CFC-113, CH_3CCl_3, and PCE are historically lower than for both the European and United States, a consequence of higher usage of these industrial substances in developed countries. Excep-

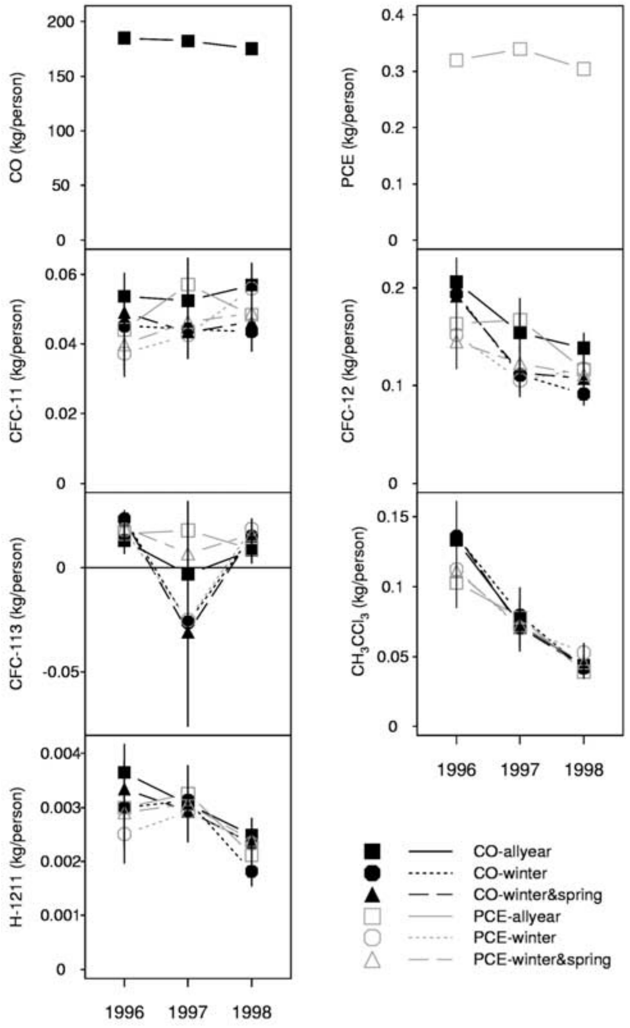

Figure 7. The annual per capita urban pollution emissions, z_E (kg/person). Six cases are considered for each year, with z_E derived from $\Delta z/\Delta\mathbf{CO}$ and $\Delta z/\Delta\mathbf{PCE}$ ratios averaged over the whole year, the winter season only, and winter and spring combined. Statistical confidence intervals of 95.4% are marked by black vertical lines. The negative values found for CFC-113 in 1997 reflect either instrument error, sources that are not correlated either spatially or temporally with emissions of CO and PCE, or emissions that too small for this analysis to distinguish above the noise. The inventory-based results for CO and PCE are provided for comparison.

tions to this pattern arise for H-1211, for reasons explored below. That CFC-113 values for the United States, Europe, and world are now all the same (and nearly zero) suggests that developed countries have almost completely eliminated use of this substance. For CFC-11, CFC-12, CH_3CCl_3, and PCE, emissions for the developed countries are still greater than for the world, suggesting that use of these substances are still continuing, and will for some time to come.

3.2. Continuing Emissions of Regulated Gases in the Post-Montreal Protocol Years

[29] All five regulated compounds, CFC-11, CFC-12, CFC-113, CH_3CCl_3, and H-1211, are purely anthropogenic in origin with industrial uses. The global background concentrations of all five increased rapidly in the atmosphere until the 1996 deadline (1994 for H-1211) of the Montreal Protocol phase-out led to a decline in source strengths, beginning in the late 1980s (Figures 8 and 10). For CFC-11, CFC-113, and CH_3CCl_3, the decline in emissions was followed by a decline in the background concentrations in the early 1990s. A decline in background CFC-12 concentrations is anticipated, given the reduction in emissions, but the turnover has not yet occurred. Halon-1211 emissions have not declined with the same rapidity as the other gases; a turnover in its background concentrations is not expected for many years to come.

3.2.1. Methyl Chloroform

[30] Observations of CH_3CCl_3 have been used repeatedly to infer the global distribution of OH, since the dominant sink is reaction with OH [*Singh*, 1977a, 1977b; *Lovelock*, 1977; *Makide and Rowland*, 1981; *Logan et al.*, 1981; *Chameides and Tan*, 1981; *Prinn et al.*, 1983, 1987; *Khalil and Rasmussen*, 1984; *Fraser et al.*, 1986, *Spivakovsky et al.*, 1990, *Montzka et al.*, 2000]. The abatement of CH_3CCl_3 emissions precipitated by the Montreal Protocol ban has set the stage for a number of unique and never-to-be-repeated atmospheric experiments. Already, with concentrations peaking in late 1991 and declining rapidly since then, CH_3CCl_3 was the first halocarbon restricted by the Montreal Protocol to decrease in the atmosphere [*Prinn et al.*, 1995]. Modelers have anticipated that the cessation of CH_3CCl_3 release will lead to the end of dynamically driven variations in CH_3CCl_3 concentrations in 1 year and reduction of CH_3CCl_3 concentrations to very low levels in 6 years [*Spivakovsky et al.*, 1990]. To test these timescales, and the models that are based on them, the presence of any residual emissions needs to be precisely ascertained.

[31] Up until now, modelers have depended on audited sales of methyl chloroform to characterize its emissions. *Midgley and McCulloch* [1995] developed a country-level distribution of emissions based on industry surveys. They estimated that over 95% of world production was captured by this approach, with over 90% of the emissions being released in the northern midlatitudes [*Midgley*, 1989, 1992]. The bulk of CH_3CCl_3 applications, for example, solvent cleaning, are known to result in rapid emissions, usually within 6 months of sale [*Midgley*, 1989]. Previously, modelers had assumed that 94% of annual sales were released to the atmosphere in the same year [*Prinn et al.*, 1983; *Spivakovsky et al.*, 1990]. By 1997, the second year after the full ban on CH_3CCl_3 production for developed countries, *McCulloch and Midgley* [2001] report zero consumption in North America, marking the end of sales-auditing as a useful indicator of CH_3CCl_3 emissions. National taxes levied on ozone depleting substances increased the cost of the material and the incentive to stockpile, a phenomenon uniquely prevalent in North America [*Midgley*, 1989]. The Northeast urban/industrial pollution history for 1996 to 1998 supports this conclusion, indicating that while CH_3CCl_3 emissions are tailing off, they remain significant.

[32] The 1996 per capita emissions of CH_3CCl_3 of 0.122 kg/person represents an 87% drop in United States per capita emissions since 1986, the year before the Montreal Protocol agenda was announced (Table 4). In the subsequent 3 years, emissions declined by −0.039 ± 0.005 kg/person/year, or by about 36% a year. A linear extrapolation

Table 4. Pollution Releases for the New York City–Washington, D. C., Corridor

Species	1996 Pollution,[a] kg/person	1997 Pollution, kg/person	1998 Pollution, kg/person	Annual Trend,[b] kg/person/year	Standard Error of Slope
CO	184.97	182.18	175.17	−4.898	1.216
PCE	0.317	0.340	0.304	–	
CFC-11	0.045	0.048	0.050	0.003	0.0001
CFC-12	0.175	0.129	0.113	−0.031	0.009
CFC-113	0.019	−0.010	0.014	–	
CH_3CCl_3	0.122	0.074	0.044	−0.039	0.005
H-1211	0.0031	0.0031	0.0022	–	

[a] Each yearly value for the regulated gases is calculated as the mean of the six emissions rates (CO-all year, CO-winter, CO-winter-and-spring, PCE-all year, PCE-winter, and PCE-winter-and-spring). CO values are based on the EPA inventory results for the SW4 sector for 1996, 1997, and 1998. PCE 1996 value based on inventory results for the SW4 sector. PCE 1997 and 1998 values are derived from 1997 and 1998 CO inventory results for the SW4 sector and the mean of the three FACTS CO/PCE emission ratios (CO-all year, CO-winter, CO-winter-and-spring) for those years [*Barnes et al.*, 2003].

[b] Annual trends are listed only for those species whose emissions increased or decreased monotonically over the 3 years. Trends are calculated as the slope through the 3-yearly values.

from the 1994 and 1995 North America sales-derived values along with the 1996, 1997, and 1998 FACTS-based data suggests that CH_3CCl_3 emissions might end completely in early 1999 (Figure 10b: The annual tick marks indicate the midpoints of each year), but an exponential curve through all the points predicts that CH_3CCl_3 emissions will remain significant until as late as the year 2004.

3.2.2. CFCs

[33] From the time of the announcement of the Montreal Protocol in 1987 through to the full ban in 1996, the emissions of CFC-11, CFC-12, and especially CFC-113 declined dramatically. Over the decade 1986 through 1996, U.S. emissions were reduced by 87%, 70%, and 93%, respectively. Nevertheless, emissions to the atmosphere continue to persist at finite values. Indeed, CFC-11 emissions rose over the subsequent 3 years of this study by 0.0026 ± 0.0001 kg/person/year to a 1998 value of 0.050 kg/person (Table 4). *Derwent et al.* [1998a] concluded that the decline in background concentrations of CFC-11 was a mere 1/6 of that expected based on the stratospheric sink, had emissions dropped to zero. CFC-12 declined by -0.030 ± 0.009 kg/person/year in the same period to 0.113 kg/person in 1998, and 0.014 kg/person of CFC-113 was still being emitted by 1998. The predominant reason for these ongoing emissions lies in past uses of the CFCs [*McCulloch and Midgley*, 2001], along with conservation measures such as recycling, possible stockpiling as with CH_3CCl_3, and perhaps illicit trade [*Montzka et al.*, 1996; *Cunnold et al.*, 1997].

[34] A wide range of uses were found for CFCs: aerosol propellants, cleaning solvents, air-conditioning agents, refrigerants, and blowing agents for plastic foams. Only CFCs sold as aerosol sprays, open cell foams, and cleaning solvents were necessarily released soon after manufacture, within 6–12 months [*Gamlen et al.*, 1986; *Fisher and Midgley*, 1994]. In contrast, the CFC-12 tied up in hermetically sealed refrigeration and air-conditioning systems and the CFC-11 in rigid closed cell foams may not be released for over 20 years. The speed of release from these long-term uses is not well known. Once they do leak, CFC-11 and CFC-12 persist in the atmosphere for 45 years and 100 years, respectively (Table 2). For CFC-113, primarily used as a degreasing solvent in the electronics industry, it is estimated that as much as 99% was released within six months of sale [*Fraser et al.*, 1996]. The remaining 1% tied up in refrigeration and closed cell foams is released within 12 years and will remain in the atmosphere for the next 85 years.

3.2.3. Halon-1211

[35] The background concentrations of H-1211 continue to grow in the atmosphere despite its comparatively short lifetime of 17 years [*Fraser et al.*, 1999]. H-1211 is used as a fire-extinguishing agent and since, to date, no suitable substitute has been found for this gas, many extinguishers remain in use. Although H-1211 is not generally tied up in long-term slowly leaking products, such as foam insulation, it may leak slowly from its containers over time. Further, it is possible that consumers may have stockpiled the substance. It is believed that the main reason that H-1211 continues its steady upward trend in the atmosphere is its continued manufacture and consumption by developing countries, for which the Montreal Protocol production ban deadlines have been extended by 10 years [*Butler et al.*, 1998]. The history of official inventories for this gas (Figure 8) indicates that the exponential growth in releases of the 1970s and 1980s halted abruptly by around 1989, presumably reflecting cutbacks by developed countries. As of 1995 Egypt, India, Iran, the Korean Republic, Mexico, Russia, and especially China [*Fraser et al.*, 1999] were still producing this gas; China, Korea, and Russia may continue to do so until the Montreal Protocol ban for developing countries is enacted in 2010 [*UNEP*, 1997]. It comes as a surprise, therefore, that per capita emissions of the New York City–Washington, D. C., corridor are not less than, but slightly higher than, the concurrent global ones for the years 1996–1998. Whether or not this is a feature peculiar to the urban/industrial northeastern United States, or whether production elsewhere is imported and released in the United States, is not known. It is clear, however, that emissions persist in developed countries also and that the accepted view of the global budget may be incorrect.

3.2.4. CO and PCE

[36] Our two reference gases of CO and PCE are subject to restrictions of their own, although not controlled under the Montreal Protocol. Of all the gases considered here, CO alone has natural as well as anthropogenic sources and, as such, is not targeted for a complete phase-out as are the other gases. Notwithstanding, as a toxic substance found in motor vehicle exhaust and a precursor for smog in urban areas, CO has been the focus of air quality discussions for years. In an effort to mitigate emissions, both the United States and Europe in the 1970s and 1980s [*Bakwin et al.*, 1994] legislated the use of exhaust catalytic converter systems on cars. In Europe, the dramatic reductions hoped for by these

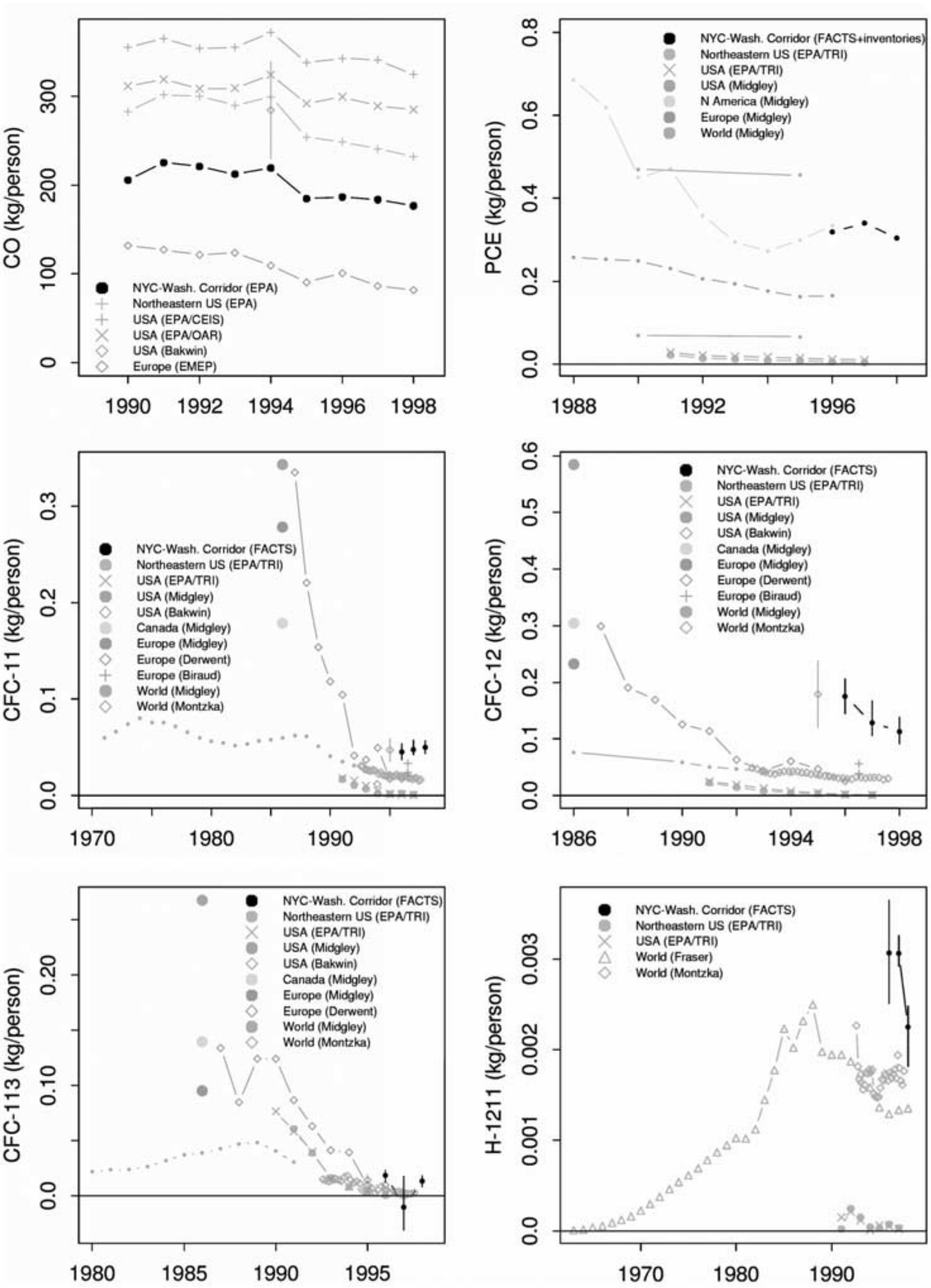

Figure 8. Historical overviews of emissions (kg/person) for all gases, where other independent studies (observations or inventories) are available. NYC–Washington, D. C., corridor (black), northeastern United States (blue), USA (green), Canada or North America (yellow), Europe (red), and world (purple) are compared. Emissions estimates based on experimental studies include: FACTS data for the New York City–Washington, D. C., corridor; *Bakwin et al.* [1997] for the United Stated; *Derwent et al.* [1998a, 1998b] and *Biraud et al.* [2000] for Europe; and *Fraser et al.* [1999] and *Montzka et al.* [1999] for the world. Inventory-based estimates are provided by: EPA/TRI, EPA/CEIS, and EPA/OAR for the northeastern United States (http://www.epa.gov); *McCulloch et al.* [1994], *McCulloch and Midgley* [1996], *Midgley* [1989, 1992], *Midgley and McCulloch* [1995], and P. M. Midgley (personal communication, 2001) for North America (here represented separately as the United States and Canada), Europe, and the world. Population data for the United States, Canada, Europe, and the world for 1970 through 1998 were provided by the U.S. Census Bureau (http://www.census.gov). Vertical lines indicate the range of uncertainty, where known. For the FACTS data, the vertical lines reflect the range of all seasonal results for each year. See color version of this figure at back of this issue.

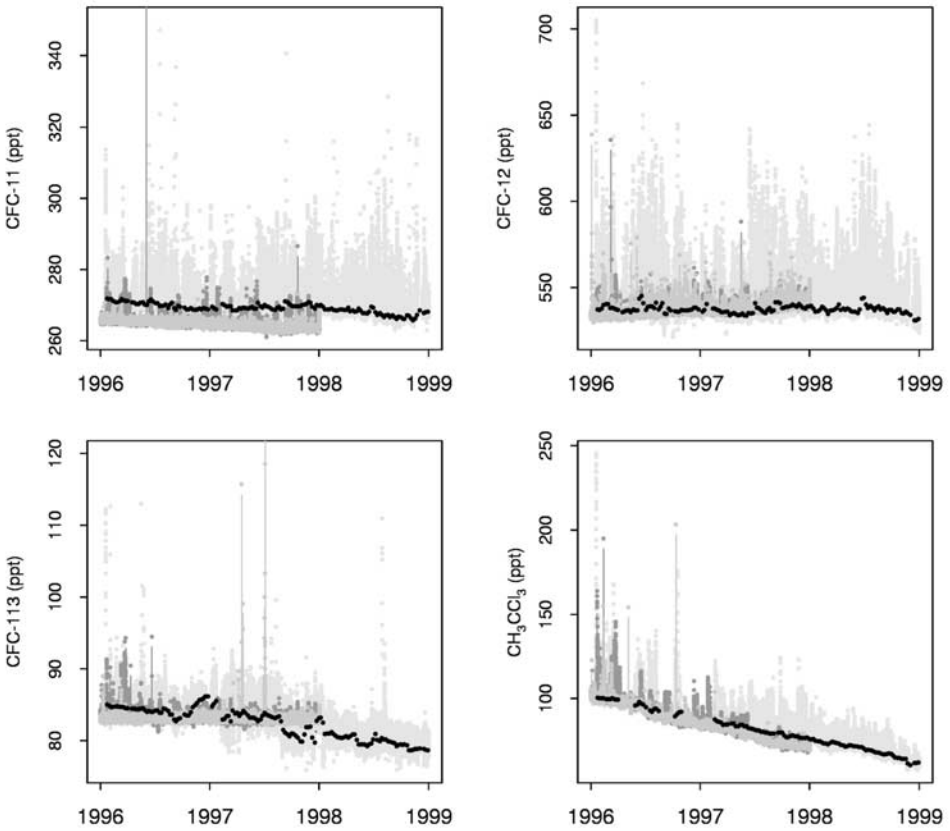

Figure 9. Comparison of Harvard Forest time series (light shading) with its background signal trace (black line) to the Mace Head, Ireland (dark shading) data set from the AGAGE network for the species CFC-11, CFC-12, CFC-113, and CH_3CCl_3. The background levels of the three sites agree, but Harvard Forest pollution levels are dramatically higher than the California and European observations.

measures appears not to have been completely realized; *Eggleston and McInnes* [1987] reported a European CO emission source strength of 100 kg/person that is on par with or lower than that of any year in the 1990s, and as of 1996, CO emissions appear to be on the rise. CO emissions for the northeastern United States, on the other hand, are in decline. Indeed, the motor emissions regulations for this region have been effective throughout the 1990s.

[37] For PCE, the 1996–1998 data we provide here mark the first long-term, observationally based record of emissions for this gas. Our values agree with those inferred from the inventories of McCulloch and Midgley for the United States and North America. On a per capita basis, the northeastern United States levels of PCE are greater than those for North America as a whole, most likely reflecting a convergence of heavy PCE emitters in urban/industrial regions. A downward trend in emissions of PCE for the New York City–Washington, D. C., corridor over the years 1991 through 1994 suggests that some users adhered to the request for voluntary cutbacks [*Barnes et al.*, 2003, Figure 10], by incorporating such practices as turning dry cleaning and extraction processes into closed system operations, regenerating the solvent after use, and incinerating wastes contaminated with chlorinated solvents [*Wiedmann et al.*, 1994]. Whereas the regulatory measures aimed at restricting CO emissions were effective throughout the 1990s, the call for voluntary cutbacks and recycling of PCE appears to have lost its momentum midway through the decade, with PCE emissions generally on the rise since 1994.

4. Conclusions

[38] Long-term high frequency measurements of seven environmentally important species were taken downwind of a major urban/industrial region from 1996 through 1998. Diurnal, seasonal, and interannual variations in the background levels and seasonal and interannual variations in the pollution enhancements were recorded and characterized. The results compared favorably to other known inventories and in situ observations. Background levels for all the gases except CO, CFC-12, and H-1211 were found to be decreasing.

[39] Pollution plumes observed during southwest winds significantly enhance atmospheric concentrations above the background. Per capita emissions from the urban/industrial region of the New York City–Washington, D. C., corridor, derived from the observed pollution signals, 1996–1998 EPA CO inventories, and 1996 PCE inventories, were used to evaluate the quality of existing inventories for the five regulated gases. Previously, our results provided confirmation of the EPA CO emissions surveys [*Barnes et al.*, 2003]; the EPA/TRI tallies, by contrast, are shown here to be by and large worthless as indicators of total annual PCE, CFC-11, CFC-12, and H-1211 releases. Only for CFC-113 are the EPA/TRI values, nearly zero, in agreement with this study's

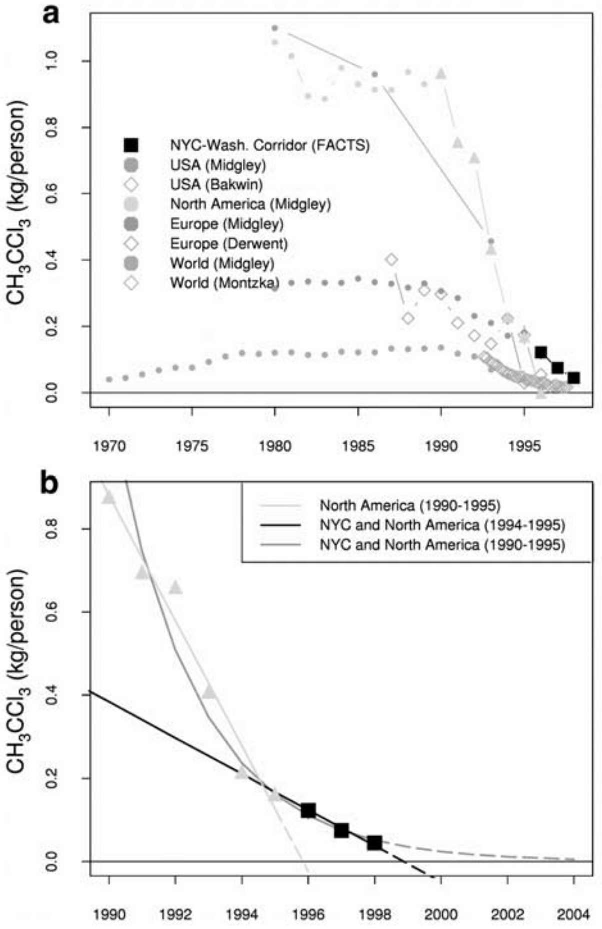

Figure 10. (a) Historical overview of CH_3CCl_3 emissions based on FACTS results for the Northeast urban/industrial corridor and on Midgley sales data for the United States, North America, Europe, and the world [*Midgley*, 1995, personal communication, 2001]. FACTS values (black squares) represent the average of the six CO- and PCE-derived annual per capita emissions, with the error bars depicting the range of all six values for each year. (b) Decline of CH_3CCl_3 from 1990 through 1996, and extrapolation into future. A linear fit through 1990–1995 sales-based emissions suggests that releases ended in 1996. A linear fit through 1994–1995 sales data and 1996, 1997, and 1998 FACTS results suggests an ending date of 1999. An exponential fit through 1990–1995 sales data and the FACTS data indicates that the end of emissions will not occur until 2004. See color version of this figure at back of this issue.

results. The sales-based inventories for PCE and CH_3CCl_3 by McCulloch and Midgley for North America in the 1990s appear highly reliable up until productions and sales of the monitored gases were deemed illegal.

[40] This work constitutes the beginning of an observationally based understanding of the urban/industrial pollution history for the northeastern United States in the wake of the Montreal Protocol and other regulatory policies. The Montreal Protocol has been largely successful in curtailing the emissions of ozone depleting substances. In the decade spanning the Protocol's inception to its full deadline for developed countries (1986–1996), U.S. emissions of CFC-11, CFC-12, CFC-113, and CH_3CCl_3 have dropped by 87%, 70%, 93%, and 87%, respectively, and, with the exception of CFC-12 and H-1211, absolute concentrations are now in decline. But while most production has ceased as industries and countries comply with the international treaty, past production stocks are not spent. The emissions for the New York City–Washington, D. C., region, we conclude, are not currently uniformly improving, despite efforts to diminish releases. Pollution levels of CFC-12, CH_3CCl_3, and CO noticeably abated over the 3 years, but CFC-11 releases rose and H-1211 sources held steady. PCE emissions did not diminish, despite the call for voluntary cutbacks in its use. Consumer activities such as recycling and stockpiling, slow leakage from long-term reservoirs, and continuing production and use by developing countries all ensure that, though tapering off, releases to the atmosphere will be consequential for some years to come.

[41] **Acknowledgments.** We gratefully acknowledge the helpful discussions with P. Novelli (NOAA/CMDL), with W. Munger, J. Logan, and C. Spivakovsky (Harvard University), P. Midgley (GSF-National Research Center for Environmental Health) and A. McCulloch (University of Bristol). We thank A. Hayden and D. Hurst (NOAA/CMDL) for assistance in building the instrument, R. Myers, P. Novelli, and B. Hall for standard preparation and analysis, and J. Butler and T. Swanson for field support over the years of this experiment. This work was supported by multiple grants from the Biological and Environmental Research Program (BER), U.S. Department of Energy, through the Northeast Regional Center of the National Institute for Global Environmental Change (NIGEC), project 901214-HAR under the Cooperative Agreement DE-FC03-90ER61010. D.H.B. acknowledges the support of the National Aeronautics and Space Administration, Earth Observing System/Mission to Planet Earth, for the Graduate Student Fellowship in Global Change Research (4137-GC93-0216) during her graduate studies.

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D. H. Barnes, B. P. Fehlau, E. W. Gottlieb, and S. C. Wofsy, Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA. (dhb@io.harvard.edu; brian_fehlau@post.harvard.edu; ewg@io.harvard.edu; wofsy@fas.harvard.edu)

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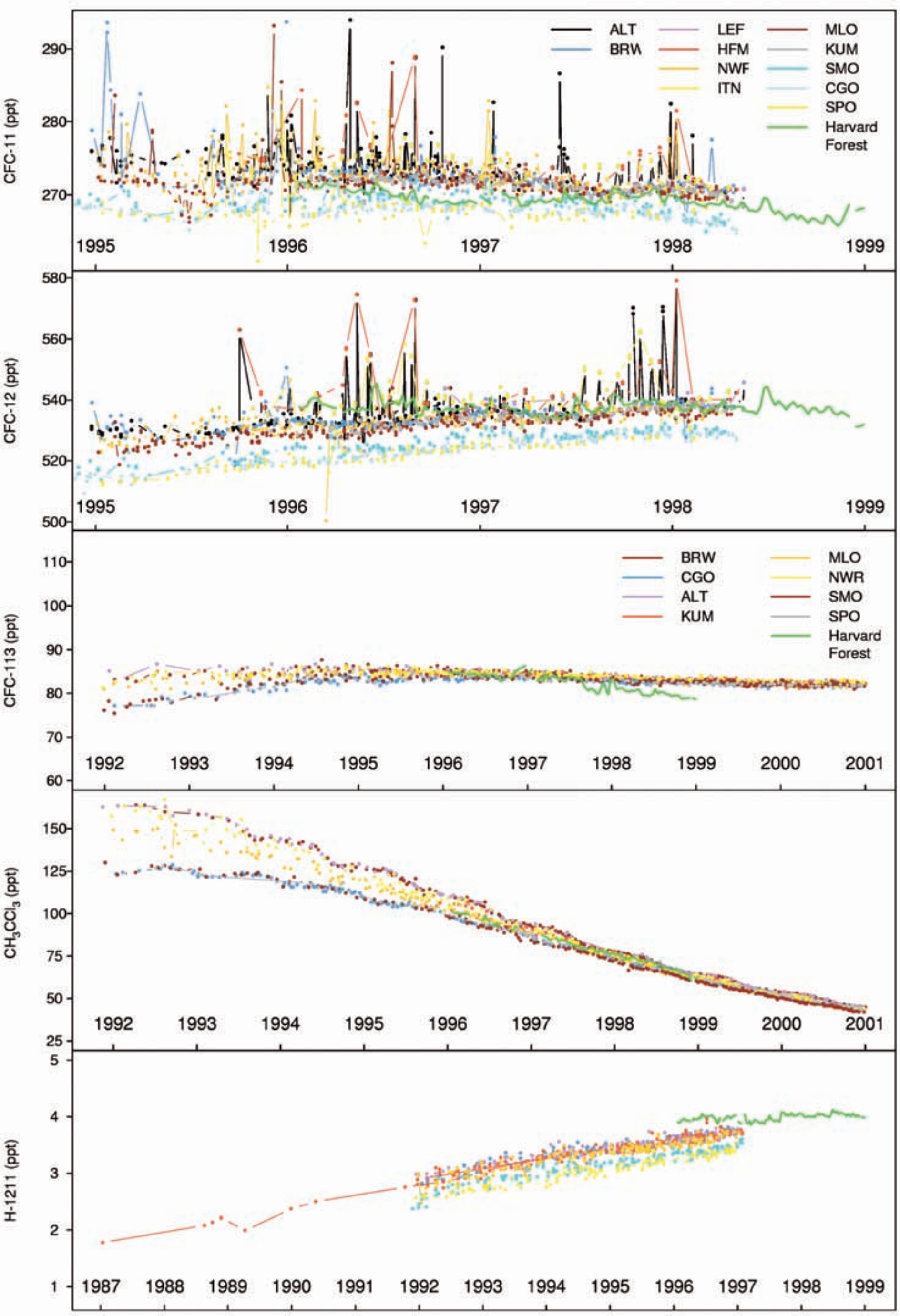
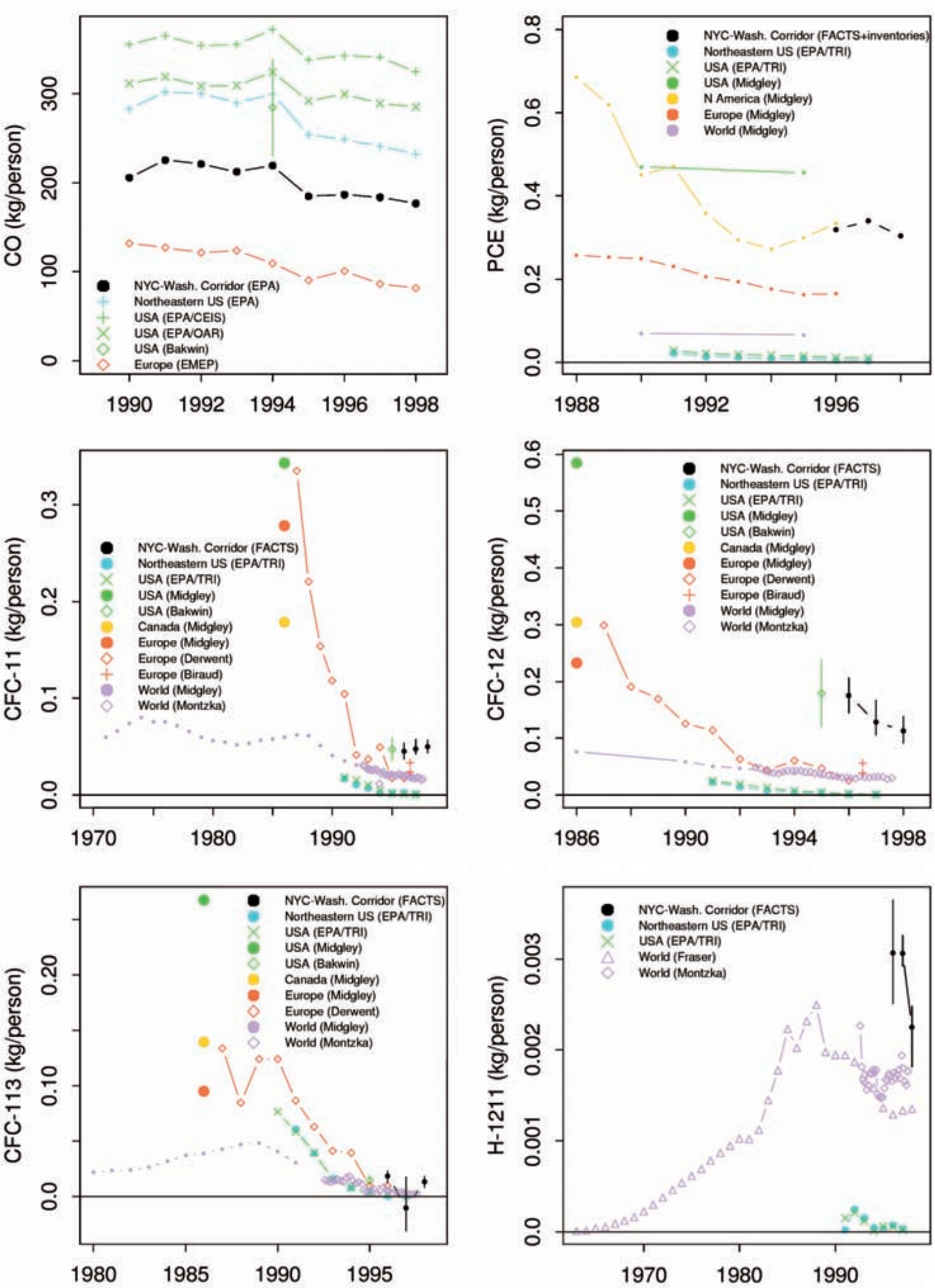


Figure 2. Comparison of Harvard Forest background signals as measured by FACTS (green line) to those measured at the remote stations of NOAA/CMDL [*NOAA/CMDL*, 1998]. All data were retrieved from the NOAA/CMDL web site: ftp://ftp.cmdl.noaa.gov. The flask data for H-1211 were sampled at: Alert, North West Territories, Canada (ALT); Barrow, Alaska (BRW); Niwot Ridge, Colorado (NWR); Mauna Loa, Hawaii (MLO); Tutuila, American Samoa (SMO); and South Pole, Antarctica (SPO). Flasks measurements of CFC-11, CFC-12, CFC-113, and CH_3CCl_3 were sampled at the same sites as for H-1211, as well as Wisconsin (LEF); Harvard Forest, Massachusetts (HFM); Grifton, North Carolina (ITN); Cape Kumahkahi, Hawaii (KUM); and Cape Grim, Tasmania (CGO).



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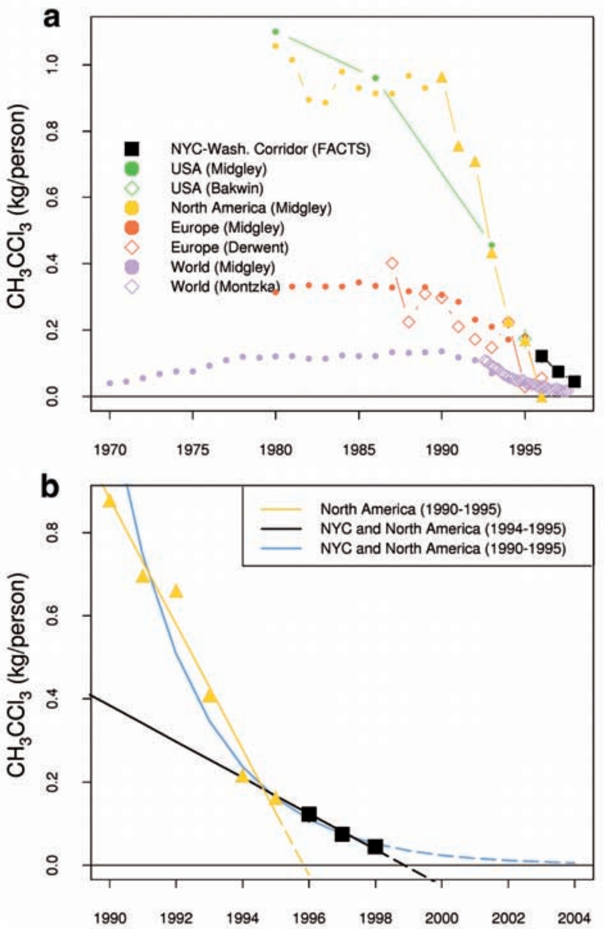

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