JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. D6, 4185, doi:10.1029/2001JD001116, 2003

Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998: 1. Providing independent verification of CO and PCE emissions inventories

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 12 June 2002; published 26 March 2003.

[1] Atmospheric mixing ratios of carbon monoxide (CO) and perchloroethylene (PCE, C_2Cl_4) were measured above the canopy at Harvard forest, MA every half-hour for 3 years starting in January 1996. Pollution enhancements are strongly correlated with winds from the southwest, the direction of the New York City–Washington, D. C., corridor, as compared to background levels observed during northwest winds traveling from Canada. We establish the ratio of CO to PCE pollution enhancements by wind direction, by season, and by year and use these results to test the quality of county-level and national source emission inventories for these two gases. The EPA carbon monoxide emission county-level inventories and the McCulloch and Midgley sales-based national-level PCE release estimates are found to be in accord with our independent observations of urban/industrial releases. For the New York City–Washington, D. C., corridor the inventory-based CO_I/PCE_I emissions ratio of 584 (kg/kg) for 1996 falls well within the range of observationally-based $\Delta CO/\Delta PCE$ pollution plume ratios of 388 to 706 (kg/kg) and is only 11% higher than the observed mean of 521 ± 90 (kg/kg). On the basis of this agreement, PCE emission estimates for 1997 and 1998 are derived from the CO inventory emissions values and the observed $\Delta CO/\Delta PCE$ ratios in pollution plumes for those years; despite the call for voluntary cutbacks, urban/industrial emissions of PCE appear to be on the rise. *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:* pollution, carbon monoxide, perchloroethylene, emissions, New York City

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: 1. Providing independent verification of CO and PCE emissions inventories, *J. Geophys. Res.*, *108*(D6), 4185, doi:10.1029/2001JD001116, 2003.

1. Introduction

[2] Much of today's current atmospheric research, including ozone layer depletion, greenhouse warming, and urban smog, is concerned with the rate and type of species released from ground sources. Methods for estimating these releases have centered on emissions inventories, which in turn have been based on factory self-reports about their emissions, audited sales of chemical manufacturers, and measurements at a local level (automobile exhaust, smoke stack, forest) that have been scaled up to the county, state, or national level. In the case of chlorine-containing compounds, modelers seeking to characterize the industrial emissions for the U.S. have relied upon county and state emission reports to the U.S. Environmental Protection Agency (EPA), which in turn are based on factory inventories, or upon the audited sales of the major producers (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].

[3] 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 in remote (far from polluting sources) locations have monitored global background levels of various species since the 1970s. By contrast, few long-term high-frequency studies with sampling sites downwind of emitting sources have sought to establish release rates at the regional scale. Exceptions

0148-0227/03/2001JD001116

include measurements taken at the Mace Head, Ireland station of the GAGE/AGAGE (Global Atmospheric Gas Experiment/Advanced Global Atmospheric Gas Experiment) sampling network. These observations have been combined with both a simple climatological long-range transport model and a sophisticated Lagrangian dispersion model to derive fluxes of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2F-$CClF_2$), 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]. In the continental U.S., emissions 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 NOAA/CMDL observations made in the largely 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].

[4] To date, no air measurements made in close proximity to the urban/industrial emitting sources of the Northeast corridor have yet been made available. Nor has the quality of the factory- and sales-based inventories for this region been independently verified. It is the purpose of this paper to provide an independent test, based on atmospheric observations, of the quality of available emissions inventories for two species: carbon monoxide, found principally in motor exhaust; and PCE (perchloroethylene, tetrachloroethene), a dry cleaning and industrial degreasing agent. These two gases are subject to regulations (CO) or voluntary cutbacks (PCE) in emissions, and their concentrations are known to be in decline in the rural U.S. and in Europe [*Environmental Protection Agency* (*EPA*), 1994; *Hurst et al.*, 1998; *Derwent et al.*, 1998b].

[5] In this study, atmospheric measurements of CO and PCE concentrations were taken every 24 minutes over the 3 years of 1996–1998 off a tower at Harvard forest, Massachusetts, downwind of the Northeast urban-industrial corridor, including the greater metropolitan region of New York City. We compare enhancements in concentrations observed at Harvard forest to emission rates from the ground as provided by the well-documented EPA carbon monoxide emissions, which are reported on a per county basis, and a composite PCE inventory, derived by combining the EPA/TRI (Toxic Release Inventory) records and the McCulloch and Midgley sales-based country-level tallies.

[6] In addition to CO and PCE, nine other compounds (H_2, CH_4, methyl chloroform (CH_3CCl_3), chloroform ($CHCl_3$), CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 ($C_2Cl_3F_3$), halon-1211 ($CBrClF_2$), and sulfur hexafluoride (SF_6)), many of them ozone-depleting and/or greenhouse gases, were measured simultaneously at Harvard forest for the years 1996 through 1998, the first 3 years after the full implementation of the Montreal Protocol for many of the above species in developed countries. Having once verified the quality of the CO and PCE emissions inventories for the New York City–Washington, D. C., region, we use CO and PCE as reference gases to determine the urban/industrial source strengths of the other nine compounds. The experiment and results for all the gases are documented in full by *Barnes* [2000]. The source strength results of those gases subject to the Montreal Protocol and the comparison of these results to existing U.S. emission inventories are the focus of the companion paper [*Barnes et al.*, 2003a]. The urban/industrial signature of molecular hydrogen is examined separately by *Barnes et al.* [2003b].

2. FACTS CO and PCE Pollution Enhancements

[7] The relationship between the atmospheric concentrations of the two long-lived (relative to transport time) trace species of CO and PCE may be used to quantify their relative source strengths. By applying a correlation analysis to the pollution enhancements, ΔCO and ΔPCE (where Δ is the height of the pollution signal above the background), as measured by the Forest and Atmosphere Chromatographs for Trace Species (FACTS) instrument at Harvard forest, we deduce the relative regional pollution sources of CO and PCE, $\Delta CO/\Delta PCE$. Since the two species are measured simultaneously, most variability in dilution by clean air (e.g. variation in the planetary boundary layer height) is canceled out in the ratio. Having established the $\Delta CO/\Delta PCE$ correlation based on direct observations, we will derive the ratio of the known absolute sources of CO and PCE based on available inventories (I) for the region, CO_I/PCE_I. If the two ratios, $\Delta CO/\Delta PCE$ and CO_I/PCE_I, are in agreement, we will have provided an independent check of the CO and PCE inventories, relative to each other. Barring the possibility that $\Delta CO/\Delta PCE$ and CO_I/PCE_I are both offset by the same amount, we may use the relationship as a basis from which to derive emission rates for the other gases measured by FACTS. *Barnes et al.* [2003a, 2003b] calculate annual source strengths of six pollutants using CO and, separately, PCE as reference compounds.

[8] Harvard forest is located in Petersham, Massachusetts (42.48°N, 72.18°W, 340 m) and receives "clean" background air from the northwest (Canada) about 39% of the time and "dirty" polluted air from the southwest (New York City–Washington, D. C., corridor, including western and central Connecticut) 34% of the time. Wind direction and speed are monitored simultaneously on top of the tower by a three-axis sonic anemometer at 8 Hz [*Goulden et al.*, 1996]. For 3 years, starting in January 1996, FACTS, a fully automated, in situ, four-channel gas chromatographic instrument with electron capture detectors, began simultaneous measurements of eleven atmospheric gases above the forest canopy (29 m) every 24 min around the clock, including CO and PCE. Carbon monoxide was measured using a unibeads 1s precolumn (2 m in length), a molecular sieve 5A main column (4 m), and an ECD doped with nitrous oxide (10–20 ppm) [*Elkins et al.*, 1996], for an overall precision of 1.21% (2.31 ppb). Here, field precisions were calculated as 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 from a two-point running mean, and the precision is equated to the coefficient of variation (standard deviation/mean) of the residuals. Perchloroethylene was measured using an OV-101 20% precolumn and main column (2 m and 4 m, respectively), for a precision of 2.63% (0.23 ppt). Calibration gases were provided by NOAA/CMDL. A full description of the FACTS instrument, calibration, and

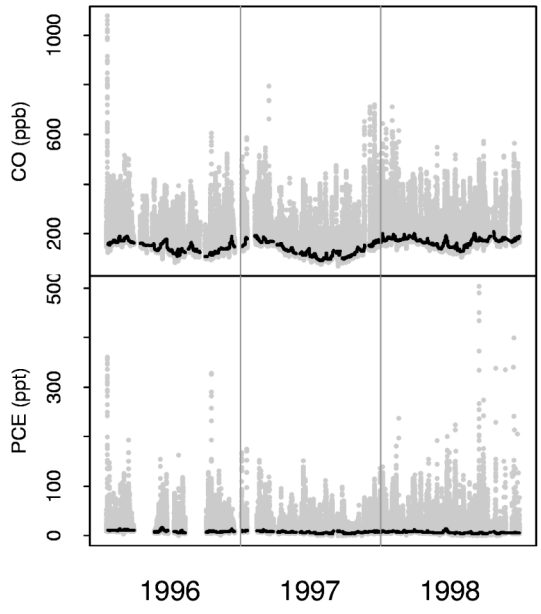


Figure 1. Time series of CO and PCE measured by FACTS spanning 1 January 1996 to 31 December 1998. Background signals (black line) are based on a running quantile of 0.2 and an interval size of 10 days. Pollution plumes are clearly evident above the background.

estimates of the analytical precision for the suite of gases is provided by *Barnes* [2000].

[9] The resulting three-year time series for CO and PCE, presented in Figure 1, clearly demonstrate frequent pollution enhancements (ΔCO and ΔPCE) above their respective background signals (CO_o and PCE_o). In order to determine the ratio of pollution enhancements, ΔCO/ΔPCE, needed for this analysis, the background signals with their seasonal cycles and interannual trends must first be removed from the original CO and PCE mixing ratio time series (CO and PCE) (where $\Delta CO = CO - CO_o$ and $\Delta PCE = PCE - PCE_o$). To separate out the background signals from the overall time series, a running quantile with an interval size of 10 days and a quantile probability of 0.2 is used over the three years of data. It has been shown that the running quantile probability of 0.2 captures the regional background level for several gases at Harvard forest without the interference of any low concentration stratospheric inputs [*Goldstein et al.*, 1995]. A sensitivity test on the window size, from $\frac{1}{2}$ to 30 days, indicated that the 10-day window yields nearly the same result as the 30-day window. The high degree of agreement between the FACTS background results and the measurements of the NOAA flasks networks reflects their common tie to the NOAA calibration scales and further indicates that no bias was introduced by the FACTS instrument (Figure 2).

[10] Because ΔCO and ΔPCE are independent variables with independent errors and noise, it is necessary to determine a correlation slope (ΔCO/ΔPCE) with an orthogonal distance regression (ODR), in which residuals orthogonal to the regression line are minimized [*Press et al.*, 1986, p. 662]. In this calculation, the two variables ΔCO and ΔPCE are first trimmed of outliers (the lower 1st percentile and the upper 99th percentile are removed) and then scaled by their standard deviations to render them dimensionless and therefore commensurate for comparison.

[11] It is not appropriate to apply standard statistical techniques when determining the uncertainty in the slope of the orthogonal distance regression. Because the time series of CO and PCE are serially correlated, the data are not purely heterogeneous and the true number of degrees of freedom is much smaller than the number of data points; that is, the ratio of concentrations over a given pollution plume are not independent of each other. Further, since the time-consuming calculation of the actual number of degrees of freedom would add little or nothing to the method or the conclusions, it is economical to employ a merit function. Variances in ΔCO and ΔPCE observations are due both to instrument error and to atmospheric variation that brings sample air from different source regions. Here, we use the standard deviations (σ_x and σ_y) of ΔCO (x direction) and ΔPCE (y direction) to reflect the physical parameter of the atmospheric variance of each gas, in contrast to *Bakwin et al.* [1997] who used two times the measurement precision. To estimate the goodness of fit of the ODR of the line $y(x) = mx + b$, we use the merit function, χ^2, for a straight-line model that varies in both the x and y directions:

$$\chi^2(m,b) = \sum \left[(y_i - b - mx_i)^2 / \left(\sigma_{yi}^2 + m^2 \sigma_{xi}^2 \right) \right]$$

[*Press et al.*, 1986, p. 660]. The uncertainty, δm, of the slope of the ODR, m_o, is defined as the range of slope values, m_j, surrounding m_o for which $\chi^2(m_j, b_j) - \chi^2(m_o, b_o) (= \Delta\chi^2)$ is less than 6.17, for a 95.4% confidence interval [*Press et al.*, 1986, p. 692]. Normally, to find this $\Delta\chi^2$, we would minimize it with respect to m, but with the occurrence of m in the denominator of χ^2, $\partial\Delta\chi^2/\partial m = 0$ is nonlinear. To avoid this difficulty, we use a multivariate Monte Carlo simulation approach whereby we randomly vary the intercept and slope to define the shape of the merit function, $\Delta\chi^2$, over intercept-slope space. With $\Delta\chi^2$ thus established, we find the range of slopes values, m_j, for the 95.4% confidence interval as required. Finally, since those pollution data points with extreme CO and PCE values carry more weight in determining the slope of the fitted line, the error inherent in the slope analysis will be smaller when the ΔCO and ΔPCE enhancements are large.

3. Observed ΔCO/ΔPCE Orthogonal Distance Regressions

[12] The Harvard forest site receives on average four to five significant pollution plumes per month. Given this, for statistical robustness, the ΔCO and ΔPCE time series are binned into 3-month seasons (where winter = December, January, and February) for a total of 12 seasons over the 3 years. This seasonal method provides an additional benefit in the case of PCE for which there are a number of gaps in the 1996 data set. For that year, all seasons are represented, but several are comprised of only 2 months of data. To confirm that there are enough data points in each season, the percentage of "pollution points," where the measured atmospheric concentration rose above the background, was determined for CO and PCE for the two cases of "all

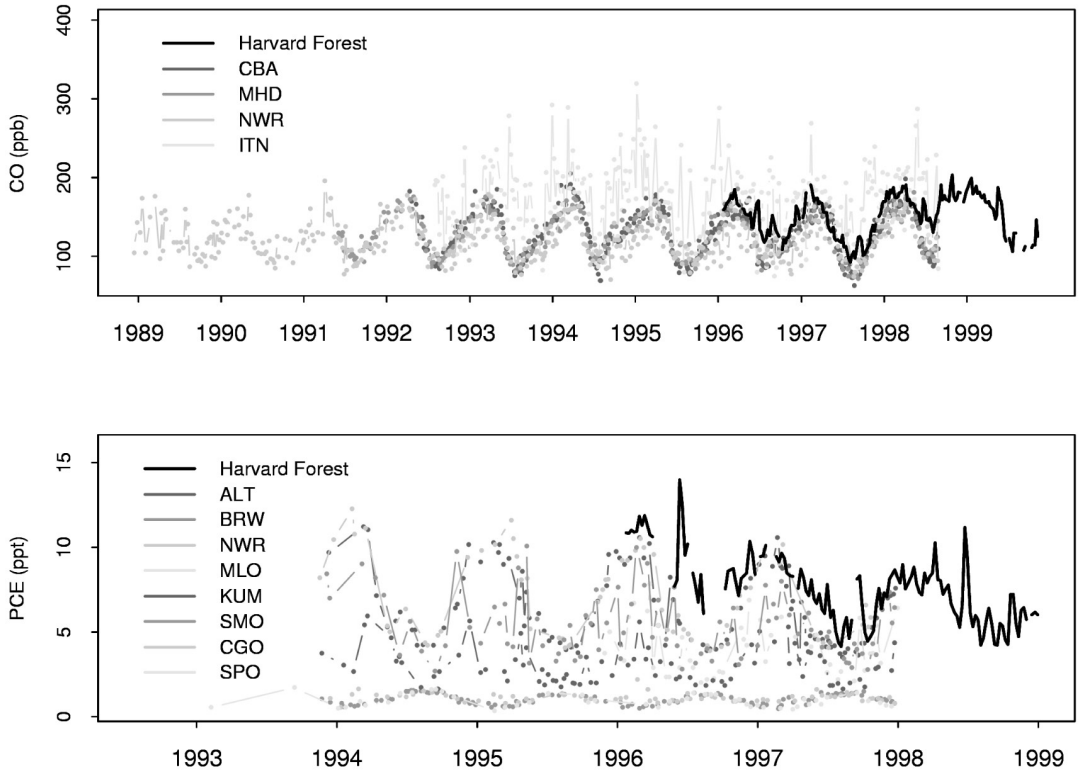


Figure 2. Comparison of Harvard forest background signals as measured by FACTS (green line) to those measured at the remote stations of *National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory* (*NOAA/CMDL*) [1998]. All data were retrieved from the NOAA/CMDL web site (ftp://ftp.cmdl.noaa.gov). CO flask measurements were taken at the Northern Hemisphere sites of Cold Bay, Alaska (CBA); Grifton, North Carolina (ITN); Mace Head, Ireland (MHD); Niwot Ridge, Colorado (NWR); and Wisconsin (LEF). PCE flask measurements were sampled at Alert, North West Territories, Canada (ALT); Barrow, Alaska (BRW); Niwot Ridge, Colorado (NWR); Mauna Loa, Hawaii (MLO); Cape Kumahkahi, Hawaii (KUM); Tutuila, American Samoa (SMO); Cape Grim, Tasmania (CGO); and South Pole, Antarctica (SPO). See color version of this figure at back of this issue.

the data'' and ''southwest winds only.'' In all cases and seasons, the number of data points is substantial (between 172 and 4148) and more than adequate for this study.

[13] For each of the twelve seasons for which the ODR of $\Delta CO/\Delta PCE$ is calculated, seven different cases are considered (Figure 3): 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* = $\sqrt{(-1 \times \text{momentum flux})}$, a measure of turbulent exchange with the overlying atmosphere). The two cases of ''northwest winds only'' and ''southwest winds only'' are chosen because the Harvard forest station receives most of its airflow from these directions, with the most polluted air from the southwest and the fastest winds and least polluted (background) air from the northwest (Figure 4). A spatial study of back trajectories (using the HYSPLIT model [*Draxler and Hess*, 1998]) further confirms that air parcels traveling over the Northeast urban/industrial corridor (SW) are highly polluted as compared to those arriving from Canada (NW) (Figure 5). In this spatial study, the pollution episode of mid-June 1997 is examined and related to concurrent synoptic conditions. Initially, winds originating in the northwest transport air to Harvard forest with background concentrations of CO and PCE. These concentrations rapidly increase as the wind flow pattern shifts south and they reach maximum values in air parcels traveling from the southwest over the urban/industrial corridor. Immediately as the winds shift back to the north, the CO and PCE concentrations begin to drop and they return to their background levels as soon as the transport trajectory originates in the northwest again. An extensive back trajectory study of CO and O_3 in air arriving at Harvard forest by *Moody et al.* [1998] suggests that winds may be grouped into seven flow patterns. The two patterns of ''southwest flow'' with fresh pollutants and ''west flow'' with the most aged air from the Midwest both approach the tower from the southwest. Because most of the gases studied here have lifetimes substantially longer (months) than the travel times from the Midwest (days), our analysis of southwest winds (SW) for the entire southwest

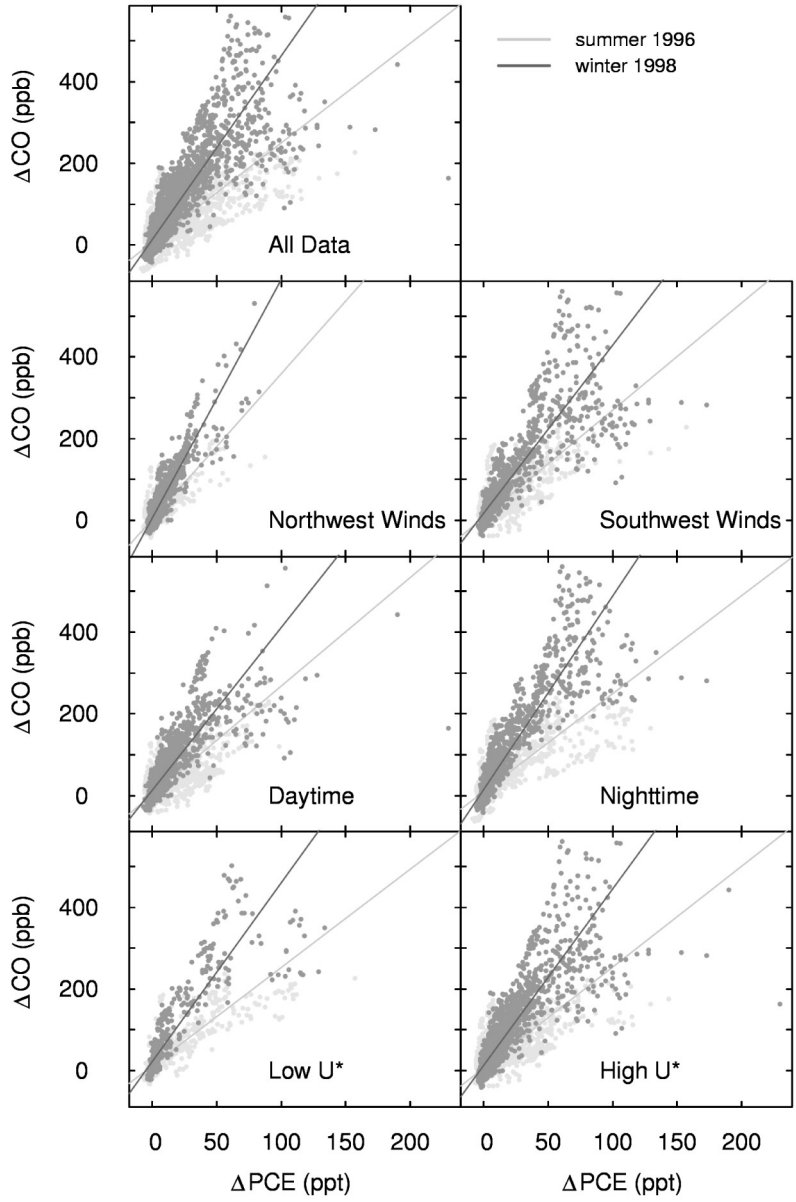


Figure 3. CO enhancements (ΔCO) versus PCE enhancements (ΔPCE) for the two seasons of summer 1996 (light shading) and winter 1998 (dark shading). The orthogonal distance regressions are drawn through the data of each season. Seven cases are displayed: all data; northwest winds only; southwest winds only; daytime only (6 am to 6 pm); nighttime only (6 pm to 6 am); high U* (>0.2 m/s); and low U* (<0.2 m/s). The slopes for all seasons and all cases are displayed in Figure 6 and tabulated in Table 1.

quadrant makes no distinction between the two Moody et al. flow patterns, but further study might prove interesting.

[14] The resulting ΔCO/ΔPCE orthogonal distance regressions, converted from ppb/ppt to kg/kg by virtue of their molecular weights ($\Delta CO/\Delta PCE\ (kg_{CO}/kg_{PCE}) = \Delta CO/\Delta PCE$ (ppb/ppt) * 1000 ppt/ppb * 28.010 g_{CO}/mole / 165.834 g_{PCE}/mole), are depicted in Figure 6. All seven cases track each other well, with high NW slopes and low SW slopes bracketing the other values and with the "all data" case appropriately representing the mean. That there is 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. The winter values of the NW are 2 to 3 times those of the SW and portray a seasonality not found in the SW direction. This may be attributed to the use of wood stoves in the winter for home heating in the rural NW. The high CO/PCE ratio during the stagnant (low U*)

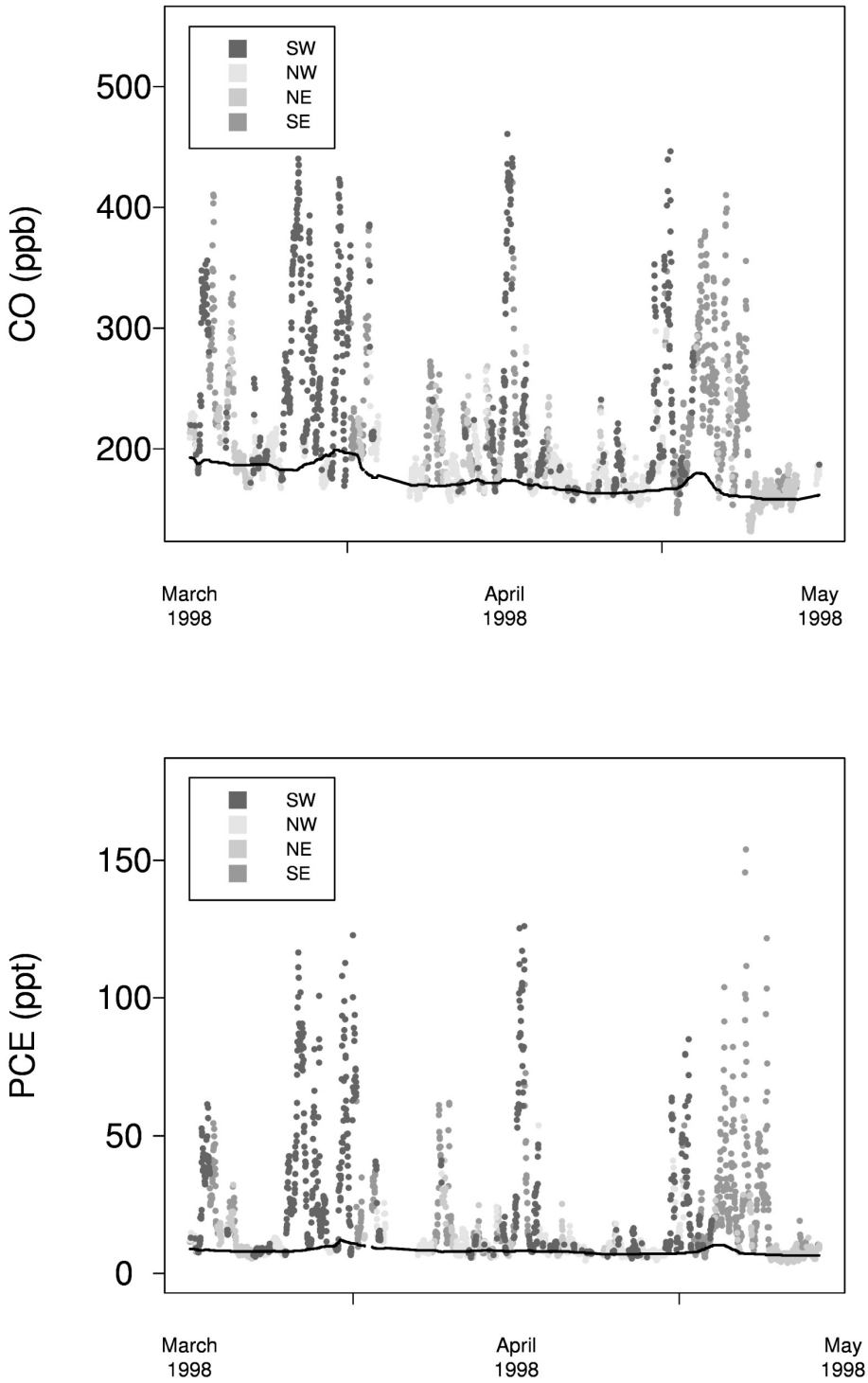
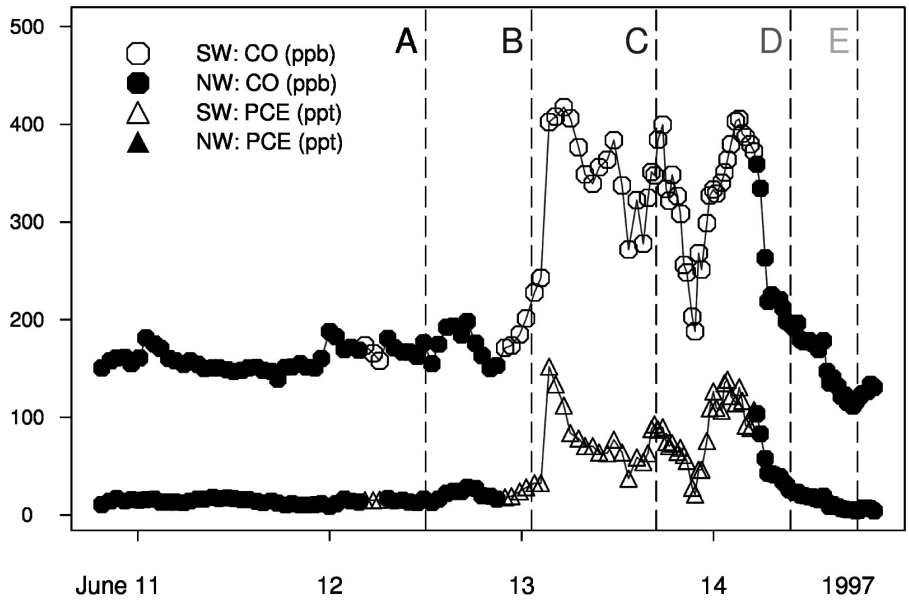


Figure 4. Time series of CO (ppb) and PCE (ppt) in spring 1998. Background signals (black line) are defined by a running quantile of 0.2 with a 10 day window. Strong pollution enhancements above the background signal correlate most strongly with winds arriving to the Harvard forest tower from the southwest (black dots).

winter events of 1997 likewise is explained by the build up of CO from wood burning in the vicinity of the tower itself.

[15] Numeric values corresponding to Figure 6 for the SW and NW cases are provided in Table 1, along with slope errors derived in the manner described above and number of observations for each season. For the SW case, the mean, trimmed mean, median, and confidence interval for the mean are 521, 516, 493, and 90, respectively. For the NW, the same values are 826, 817, 793, and 177. With each of the 12 seasons containing only 12 to 15 pollution plumes, it is



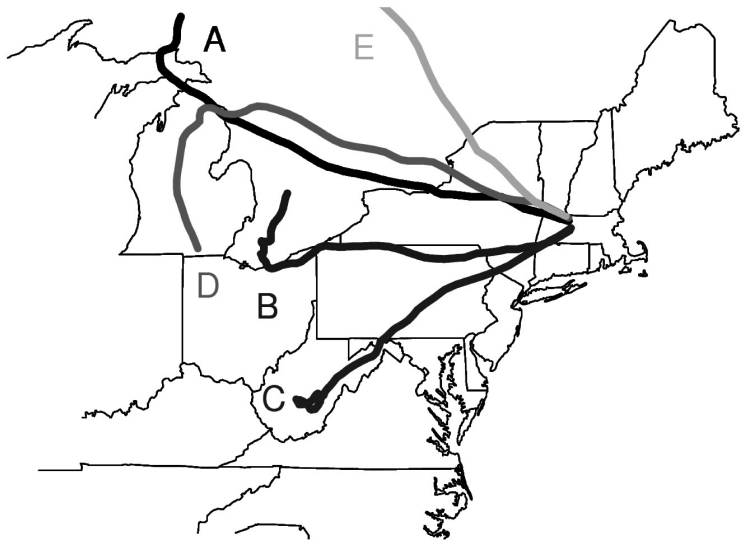


Figure 5. Back trajectories for the pollution plume of 12 through 14 June 1997. The trajectories were begun at 200 m, 3 days back, and used wind data from NGM meteorology (Nested Grid Model, part of NCEP's Regional Analysis and Forecast System [*Hoke et al.*, 1989]). CO (ppb) and PCE (ppt) weak and strong enhancements coincide with winds arriving at the Harvard forest tower (green triangle) from the northwest and southwest respectively, as measured by a sonic anemometer. Five vertical lines, labeled A through E, indicate those times for which back trajectory plots are provided. The back trajectories demonstrate that northwest winds are clean, southwest winds are polluted, and winds shifting between the two are partly polluted. See color version of this figure at back of this issue.

possible for one anomalous pollution event to skew a given season's resulting ratio; the tight agreements between the mean and the trimmed mean in both cases reduce this concern. That the coefficients of variation (95.4% confidence interval/slope for each season) are similar regardless of wind direction is noteworthy, suggesting that the air from the SW is not influenced by some huge point source downwind. These SW and NW values, ranging from 388 to 1151, are the ones that will be used to test the inventories.

4. Inventories for CO and PCE

[16] The two inventories under consideration here are derived from the EPA's CO emissions survey for the U.S.

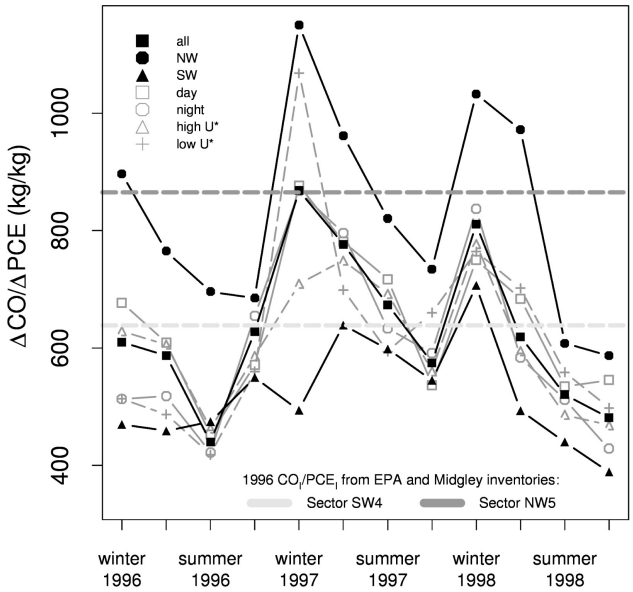


Figure 6. ΔCO/ΔPCE (kg/kg) orthogonal distance regressions for each season and for seven cases of: all data; northwest winds only (NW); southwest winds only (SW); day (6 am to 6 pm); night (6 pm to 6 am); high U* (>0.2 m/s); and low U* (<0.2 m/s). All seven cases track each other well, with high NW slopes (solid circles) and low SW slopes (solid triangles) bracketing the other values and with the "all data" case appropriately representing the mean. There is little to distinguish between the day and night or the high and low U* cases. The winter values of the NW are two to three times those of the SW and portray a seasonality not found in the SW direction. SW and NW values for all seasons are listed in Table 1, along with their slope error and number of observations. Inventory-based results for Sectors NW5 (dark shaded line) and SW4 (light shaded line) in 1996 are compared to the FACTS orthogonal distance regressions of ΔCO/ΔPCE (kg/kg) for the twelve seasons in 1996, 1997, and 1998. The agreement for both the north and the south cases is remarkable.

by county and a combination of the EPA's Toxic Release Inventory (EPA/TRI) for PCE by county and the McCulloch and Midgley PCE sales study for North America (Canada, the U.S., and Puerto Rico inclusive).

[17] The EPA CO data are generated by State and Local Air Monitoring Stations (SLAMS) as part of the Aerometric Information Retrieval System (AIRS) [*EPA*, 1997] (http://www.epa.gov/air/data/nettier.html). The monitoring stations are operated by state and local environmental agencies and are not distributed uniformly across the land. Each state is responsible for submitting annual emissions for the state as a whole (but not for each county) to the EPA, which then summarizes the results into National Air Quality and Emissions Trends Reports [*EPA*, 1997] for the Center for Environmental Information and Statistics (CEIS) (http://www.epa.gov/ceis). The EPA does not provide error estimates of the emission values. The EPA CO emissions values by county for the northeastern U.S. in 1996, the only year of overlap between this experiment and all the inventories, are mapped in Figure 7a. Given that the largest sources of CO are road transportation and combustion [*EPA*, 1997], it is not surprising that those counties which contain or neighbor large cities, e.g., Baltimore, Boston, New York, Philadelphia, Pittsburgh, and Washington, D. C., are responsible for the bulk of CO emissions. The largely rural counties in Virginia and West Virginia have the lowest absolute CO emissions. This urban/rural contrast does not hold true, however, when the CO emissions are considered on a per capita basis. Using county level 1998 population counts, as estimated by the U.S. Census Bureau (http://www.census.gov) to produce a per capita CO emissions map (Figure 7b), a distinct pattern emerges. New York City and environs have the lowest per capita emission rates and are surrounded by wide bands of counties whose values increase slowly with distance from New York City. The counties with the greatest per capita emissions are at the furthest distances from New York City, predominantly in Virginia and West Virginia. That such a pattern should emerge between CO and population is not unexpected given that cars are a major source of CO emissions. The low per capita CO emissions for New York City in particular may be explained by the overwhelmingly high population density and the greater reliance on public transportation in that area.

[18] To create a comparable per capita distribution for PCE releases is more difficult. It is the policy of the EPA/TRI (http://www.epa.gov/enviro/tris), which is commissioned to report on PCE emissions, to consider only those facilities that both employ ten or more full-time employees and exceed an established threshold of 10,000 lbs/year (the reporting units of the EPA) of chemical used. Further, the EPA Toxic Release Inventory does not represent all 50 states or all counties in its tally. In the case of PCE emissions, these EPA/TRI criteria result in severe underreporting, as

Table 1. ΔCO/ΔPCE Orthogonal Distance Regressions for Southwest and Northwest Winds

Year	Season	ΔCO/ΔPCE Slope, kg/kg	95.4% confidence interval, kg/kg	N
		Southwest Direction		
1996	winter	469.85	83.56	474
	spring	458.88	82.67	427
	summer	474.31	66.61	842
	fall	549.61	90.14	542
1997	winter	493.70	79.96	542
	spring	638.89	90.21	733
	summer	598.31	70.83	1044
	fall	544.92	70.24	839
1998	winter	706.40	95.40	844
	spring	493.40	60.18	950
	summer	439.66	41.69	1613
	fall	388.48	43.30	1300
		Northwest Direction		
1996	winter	896.61	132.34	628
	spring	765.17	117.06	581
	summer	696.01	130.02	591
	fall	684.92	88.81	874
1997	winter	1150.53	167.76	743
	spring	961.75	93.41	1526
	summer	820.97	88.46	1289
	fall	734.18	79.39	1335
1998	winter	1032.69	114.19	1139
	spring	971.89	100.99	1295
	summer	607.97	62.55	1453
	fall	587.00	67.46	1256

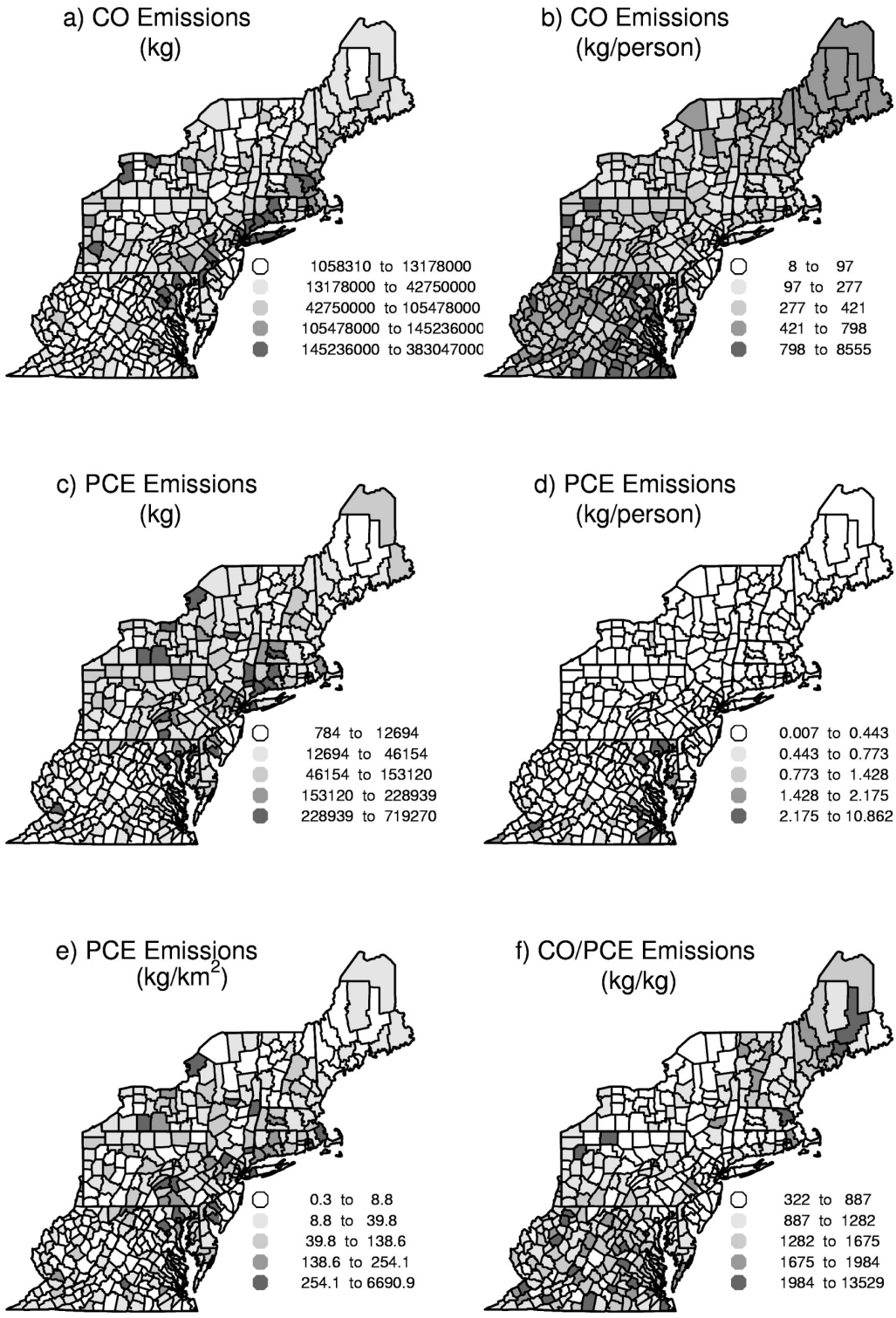


Figure 7. County-level maps of the Northeast for (a) CO emissions (kg); (b) per capita CO emissions (kg/person); (c) PCE emissions (kg); (d) per capita PCE emissions (kg/person); (e) the PCE spatial distribution (kg/km^2); and (f) the ratio of CO and PCE emissions (kg/kg). These values for the year 1996 are based on inventories by the EPA for CO and PCE and by McCulloch and Midgley for PCE. County population and land area statistics are provided by the U.S. Census Bureau for the year 1998.

Table 2. Comparison of EPA/TRI and McCulloch and Midgley (M&M) PCE Emissions (kg)

PCE, kg	1991	1992	1993	1994	1995	1996
USA (EPA/TRI)	7,678,976	5,731,827	5,109,562	4,854,743	4,338,380	3,520,160
North America (M&M)	133,833,000	103,244,000	85,638,000	79,922,000	88,721,000	100,120,000
M&M/EPA	17.4	18.0	16.8	16.5	20.5	28.4

becomes evident when the national total is compared to that given by an independent survey produced by McCulloch and Midgley [*McCulloch and Midgley*, 1996; P. M. Midgley, personal communication, 2001]. In an effort to characterize global PCE emissions, McCulloch and Midgley audited the sales of PCE by major PCE producers to different world regions. Accepting McCulloch and Midgley's assertion that PCE sales in a given year may be considered equivalent to PCE releases to the atmosphere (±5%), the values for North America (Canada, the U.S., and Puerto Rico) for the years 1991 through 1996 outstrip those reported by the EPA/TRI by, on average, an astonishing factor of 19.6 (Table 2). This differential cannot be explained away by the inclusion of Canada, despite it having twice the landmass and one third the population of the United States. A reasonable explanation lies instead with the history of PCE and its uses. PCE provided a replacement for carbon tetrachloride (CCl_4), a known carcinogen, in commercial, coin-operated, industrial, and garment rental dry cleaning operations. Such dry cleaning comprises the majority of PCE use (50%), along with CFC-113 manufacturing in Louisiana, New Jersey, Texas, and Michigan (25%), organic solvent cleaning (15%), and other solvents and miscellany (10%) [*EPA*, 1989]. With numerous neighborhood dry cleaning facilities employing less than ten people or emitting below 10,000 pounds per annum, a substantial component of PCE emission sources are not included in the EPA/TRI inventory.

[19] For the purposes of creating a county-level 1996 PCE emissions map in kilograms for the Northeast, both the EPA/TRI county-level information with its large PCE emitters (EPA_{county}) and the McCulloch and Midgley North America regional total for the same year ($M\&M_{NA}$) are employed. The difference between the two, that is, the North America annual sales-estimated PCE not accounted for by the U.S. national sum of the EPA/TRI's larger emitters (EPA_{US}), is distributed across all counties by population. Population is chosen as the preferred distribution parameter (as opposed to energy use, for example) because it is more closely affiliated with the spatial variability of dry cleaning facilities. Each county's PCE emissions, then, is a sum of the large EPA emitters and the remaining population-distributed sales data:

$$PCE_{county} = (M\&M_{NA} - EPA_{US}) * (POP_{county}/POP_{NA}) + EPA_{county}$$

where POP_{county} and POP_{NA} are the populations of each county and of North America, respectively.

[20] The results of this inventory algebra are presented in Figure 7c in kilograms of PCE emitted by county. No clear pattern emerges from this distribution, with the exception that nearly all low values lie in Virginia and West Virginia. Counties with high values do not systematically correspond with major urban/industrial centers. Exactly where the EPA large emitters are located becomes apparent when the reconstructed per capita spatial spread of PCE is considered (Figure 7d). A pattern does emerge when the land distribution of PCE emissions is considered (PCE in kg/km^2), with higher values found concentrated in the middle sector of counties in the Northeast and lower values in western Pennsylvania, West Virginia, and Virginia, and in Vermont, New Hampshire, and Maine (Figure 7e).

[21] With spatial inventories for CO and PCE derived from their various studies once established, a map depicting the ratios of CO/PCE emissions by county for 1996 may now be constructed (Figure 7f). From the vantage point of Harvard forest, the distribution of CO/PCE appears to display little spatial variability. The highest values of this map lie far from Harvard forest in Virginia and West Virginia, reflecting the weakness of both PCE and CO emissions there. It is from this map that CO_I/PCE_I will be determined and compared to the FACTS $\Delta CO/\Delta PCE$ results.

5. Concentration Enhancements and Inventories Compared

[22] If, as is suggested by the CO/PCE map above, the emissions surrounding Harvard forest are indeed uniform, the direction of the wind, the exact area traveled over by an air parcel, and the emitting sources encountered on the air parcel's path are not critically important. The results of this study would then be regional in scale, characterizing emissions for the entire Northeast. To check if this is indeed the case, the inventory-based CO/PCE (kg/kg) map is divided into 14 sectors, seven in the southwest and seven in the northwest, that radiate out from Harvard forest at increasing angles and distances, with Sector NW7 being the northernmost (Figure 8). For each sector, the total CO emissions (defined as ΣCO_i over $counties_i$), per capita CO emissions ($\Sigma CO_i/\Sigma pop_i$), total PCE emissions (ΣPCE_i), per capita PCE emissions ($\Sigma PCE_i/\Sigma pop_i$), and PCE emissions per area ($\Sigma PCE_i/\Sigma area_i$) are calculated (Table 3). As expected, Sectors SW3 and SW4, which encompass the larger urban centers of the mid-Atlantic seaboard, contain the bulk of the CO and PCE emissions.

[23] When CO/PCE is integrated over every sector (ΣCO_i over $counties_i$ / ΣPCE_i over $counties_i$), a surprising result emerges. There is a marked North-South gradient in CO/PCE with the highest values in Sectors NW4 through NW7 and the lowest values in Sectors SW1 through SW5 (Table 3). The reason for this gradient is found in the opposite trend of PCE emissions (kg/km^2), with highest values in the south and lowest in the north, traceable to large emitters of PCE. This North-South distinction corroborates the $\Delta CO/\Delta PCE$ results of FACTS with a higher

NW average of 826 ± 177 kg_{CO}/kg_{PCE} and a lower SW average of 521 ± 90 kg_{CO}/kg_{PCE} (Figure 6; Table 1). The remarkable agreement in both the SW and NW values indicates that the high NW results are not merely due to bigger errors in the slope analysis but indeed reflect a difference in emission sources between the rural northwest and the urban/industrial southwest. The average rural northwest value of 826 ± 177 kg_{CO}/kg_{PCE} is further corroborated by the CO/PCE ratio of 748 kg_{CO}/kg_{PCE} in pollution enhancements observed in the predominantly rural/agricultural region of eastern North Carolina from December 1994 to August 1996 [*Bakwin et al.*, 1997]. Given the rural NW to urban SW distinction, it would be inappropriate to generalize the FACTS results for the Northeast region as whole; instead, this experiment, with its suite of gases that are primarily anthropogenic in origin, focuses principally on the southwest and is urban/industrial in scope [*Barnes et al.*, 2003a].

[24] A cross-correlation study between PCE and CO, using time domain analysis in the manner of *Prather* [1985] and *Prather et al.* [1987], reveals that these species covary significantly out to time lags of about 2 days (Figure 9). Thus we infer that PCE and CO sources are generally co-located and that their pollution enhancements are caused primarily by sources within 2 days transport upwind of Harvard forest [*Bakwin et al.*, 1997]. At typical wind speeds of 2–3 m/s, this translates to 350–500 km away. Given that the range of the southwest sector results is narrow (526 to 806), that Sector SW4 (with a fetch of 600 km) has a CO/PCE value of 584 kg/kg that lies well in the middle of the other seven southwest sector values, and that this sector contains the greater metropolitan New York City area, Philadelphia, Baltimore, and Washington, D. C., Sector SW4 is chosen here to provide the definitive test of inventory-based urban/industrial ratio of CO_I/PCE_I. Although many highly populated and industrial districts of Connecticut, including Hartford, are contained in Sector SW4, we choose to refer to this region as the New York City–Washington, D. C., corridor in deference to the omission of Boston. Northeast winds carrying pollution from Boston are not only rare but contain an additional ocean signature and are most often associated with storm conditions. The lack of reliable observations notwithstanding, we feel confident that Boston emissions are similar in character to those of the rest of the eastern urban/industrial seaboard.

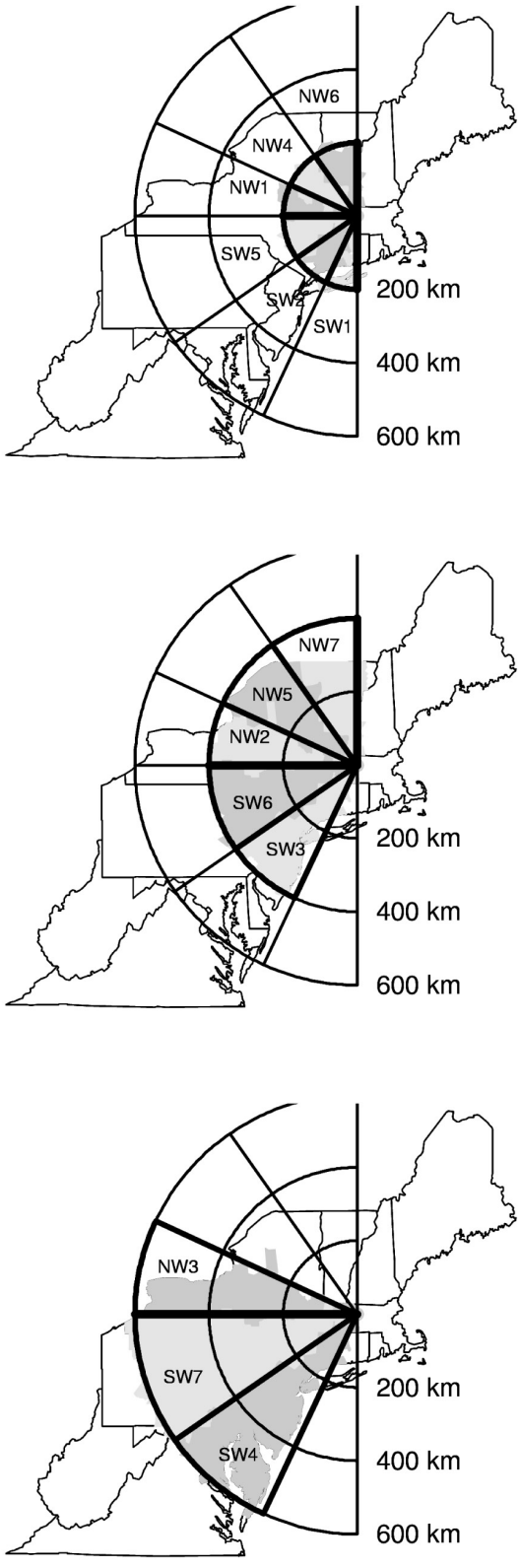


Figure 8. (opposite) The Northeast map is divided into 14 sectors, seven in the southwest and seven in the northwest. The sectors radiate out from Harvard forest at increasing angles and distances, with Sector NW7 being the northernmost. The counties of Sector SW2 are also contained in Sector SW3; likewise, Sector SW4 contains those counties found in SW3, etc. Sector SW4 encompasses all the larger urban/industrial centers of the mid-Atlantic seaboard: New York City; Philadelphia; Baltimore; and Washington, D.C.

6. Urban/Industrial Releases of CO and PCE for the 1990s

[25] Inventory values for Sector SW4 are available for all 3 years (1996, 1997, and 1998) for CO (Table 4), but only for 1996 for PCE. Given the strength of the agreement between $\Delta CO/\Delta PCE$ and CO_I/PCE_I established for 1996, we use $1/(\Delta CO/\Delta PCE) \times CO_I$ to determine PCE (kg) for

Table 3. Defining the New York City Metro Area: Comparing SW and NW Sectors 1 Through 7 for 1996

Sector	CO, kg	CO/Pop,[a] kg/Person	PCE, kg	PCE/Pop, kg/Person	PCE/Area, kg/km^2	CO/PCE, kg/kg
			Southwest			
1	288,123,998	174.3	524,285	0.317146	119.7	549.6
2	751,855,608	236.9	1,202,032	0.378675	124.2	625.5
3	4,310,930,938	171.8	8,195,676	0.326675	221.8	526.0
4	6,365,994,768	185.0	10,897,577	0.316634	138.8	584.2
5	169,820,582	205.8	285,311	0.345782	23.6	595.2
6	673,447,219	234.6	947,161	0.330018	20.3	711.0
7	1,465,673,472	260.0	1,819,151	0.322731	15.9	805.7
			Northwest			
1	196,265,462	246.1	305,309	0.382829	32.7	642.8
2	491,322,283	243.4	688,522	0.341082	22.1	713.6
3	1,076,286,988	249.1	1,458,520	0.337518	31.3	737.9
4	104,052,211	261.5	99,599	0.250270	9.7	1044.7
5	184,584,355	248.9	182,631	0.246293	4.9	1010.7
6	96,010,790	327.8	92,897	0.317146	7.8	1033.5
7	253,383,682	363.3	221,213	0.317146	9.1	1145.4

[a]Populations for the different sectors are based on 1998 estimates by the U.S. Census Bureau (http://www.census.gov).

1997 and 1998. To extract annual emission rates of $\Delta CO/\Delta PCE$ from the seasonal values available, we averaged the southwest slopes over each year. It is not advisable to simply include all four seasons in this average since, for CO, urban emissions are known to be elevated by secondary production from hydrocarbons in summer, an additional source not covered by the inventories. Furthermore, in the wintertime, stronger winds and lower planetary boundary layer depths make for fewer and shorter stagnation events, during which local emissions build up. For these reasons, in addition to using the mean of all four seasons for the annual $\Delta CO/\Delta PCE$ emission rate, we also use $\Delta CO/\Delta PCE$ for the winter season alone and for winter and spring combined to assess the annual emissions of PCE in kg. The average of these three results for 1997 and 1998 are listed in Table 4.

[26] Over the years of this experiment, urban/industrial CO emissions declined monotonically at ~2.7% per year, while PCE exhibited no uniform trend. A longer historical overview of the inventories for Sector SW4 sector indicates significant changes in CO and PCE emissions over the last decade (Figure 10). The remarkable agreement between the inventories and the measurements of this experiment is again evident in this figure. Increasingly strict regulations concerning CO emissions from cars and cutbacks on the use of PCE in dry cleaning led to rapid declines for both over the 1990s. Because of a lag between the impact of the CO and PCE regulations over these years, the ratio of CO/PCE experiences a sharp rise and fall, with a peak value in 1994 of ~900 kg/kg. By 1996, 1997, and 1998, the CO/PCE ratio returned to its original levels of the early 1990s. 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 on the rise since 1994.

7. Conclusions

[27] Special note needs to be made about the strength of the agreement between the observationally based FACTS southwest $\Delta CO/\Delta PCE$ values, which range from 388 to 706 and have a mean of 521 ± 90 kg_{CO}/kg_{PCE} (Table 1), and the Sector SW4 inventory-based CO_I/PCE_I ratio of 584 kg_{CO}/kg_{PCE} (Table 3). Given the disparity of the sources of information, the manipulation of the inventories required for PCE, and the possibility for error in all inventories and measurements utilized, the closeness of the agreement is striking. By establishing that the ratio of measured enhancements $\Delta CO/\Delta PCE$ does indeed equal the inventory ratio CO_I/PCE_I, the estimates and tallies of the EPA CO, the EPA/TRI PCE for the large emitters, and the McCulloch and Midgley sales-based PCE inventories have been independently checked. This success in source reconciliation demonstrates that long-term atmospheric observations made in close proximity to the emitters are a viable means for establishing release rates. We need not depend solely upon emissions inventories for these values, but can measure them directly.

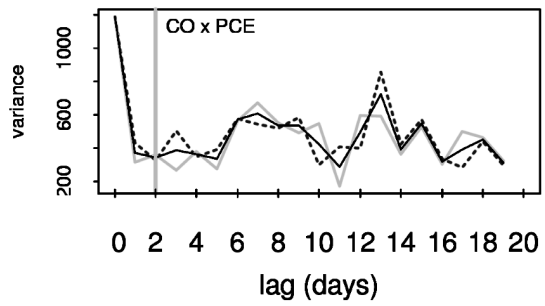


Figure 9. Covariance of CO with PCE for July 1997 through December 1997, southwest winds only, plotted against lag time. Dotted dark shaded (light solid) lines show results for positive (negative) lags; the solid black line represents the mean. The data are based on daily means with the lowermost and uppermost 1% of all values truncated to the first and 99th percentile values, respectively, to remove outliers. These species covary significantly out to time lags of about 2 days, indicating that not only are PCE and CO generally colocated, but their pollution enhancements are caused primarily by sources within 2 days transport upwind of Harvard forest.

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

Species	1996 Pollution, kg/Person	1997 Pollution, kg/Person	1998 Pollution, kg/Person	Annual Trend,[b] kg/Person/yr	Standard Error of Slope
CO[c]	184.97	182.18	175.17	−4.898	1.216
PCE[d]	0.317	0.340	0.304	–	

[a]In 1998, Sector SW4 had a population of 34,416,906, as estimated by the U.S. Census Bureau (http://www.census.gov).
[b]An annual trend is only listed for CO whose emissions decreased monotonically over the 3 years. The trend is calculated as the slope through the 3-yearly values.
[c]CO values are based on the EPA inventory results for the SW4 sector for 1996, 1997, and 1998.
[d]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&spring) for those years.

[28] With the correlation between the CO and PCE inventories and FACTS measurements in place, we may proceed with confidence to derive the urban/industrial emissions for the remaining gases measured by FACTS. The 11% difference between the 1996 inventory results (584 kg_{CO}/kg_{PCE}) and observed CO/PCE (521 kg_{CO}/kg_{PCE}) ratios determined here will be taken as our figure of merit for the CFCs, methyl chloroform, and halon-1211 emissions determined next. We will compare our results with available inventories and comment upon the regional conformity to the Montreal Protocol and other mitigation policies such as may be inferred at this time [*Barnes et al.*, 2003a].

[29] **Acknowledgments.** We gratefully acknowledge the back trajectory model runs contributed by J. Lin (Harvard University) and 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

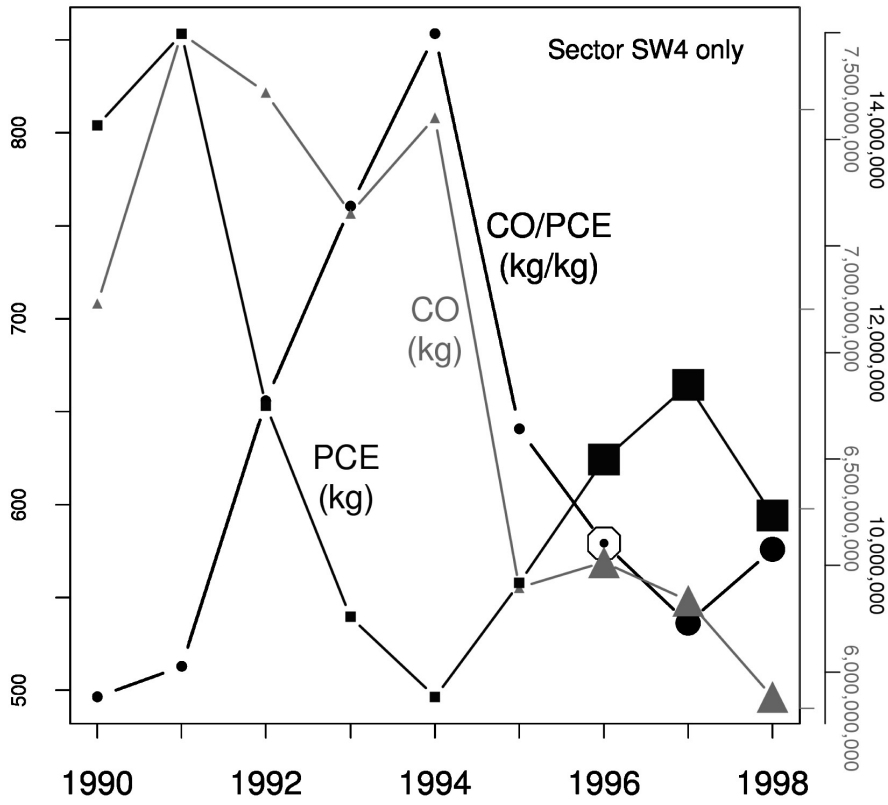


Figure 10. Sector SW4 CO (triangles) and PCE (squares) inventory results for 1990 through 1995. Observationally based results (larger symbols) for 1996, 1997, and 1998 corroborate the inventory results. PCE values for 1997 and 1998 are derived from 1997 and 1998 CO inventory results for the SW4 sector and the mean of the three FACTS CO/PCE emission ratios (CO-all year, CO-winter, CO-winter&spring) for those years. The rapidly changing CO/PCE (dots) ratio over the decade is due to a lag between the CO car emission regulations and the PCE restrictions. By 1996, the year of our inventory-to-observation comparison (large open circle), CO/PCE had nearly returned to its original levels of the early 1990s.

(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 No. 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.

References

Bakwin, P. S., D. F. Hurst, P. P. Tans, and J. W. Elkins, Anthropogenic sources of halocarbons, sulfur hexafluoride, carbon monoxide, and methane in the southeastern United States, *J. Geophys. Res.*, *102*, 15,915–15,925, 1997.

Barnes, D. H., Quantifying urban/industrial emissions of greenhouse and ozone-depleting gases based on atmospheric observations, Ph.D. thesis, Harvard Univ., Cambridge, Mass., 2000.

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.*, doi:10.1029/2001JD001117, in press, 2003a.

Barnes, D. H., S. C. Wofsy, B. P. Fehlau, E. W. Gottlieb, J. W. Elkins, G. S. Dutton, and P. C. Novelli, Hydrogen in the atmosphere: Observations above a forest canopy in a polluted environment, *J. Geophys. Res.*, doi:10.1029/2001JD001199, in press, 2003b.

Biraud, S., P. Ciais, M. Ramonet, P. Simmonds, V. Kazan, P. Monfray, S. O'Doherty, T. G. Spain, and S. G. Jennings, European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland, *J. Geophys. Res.*, *105*, 1351–1366, 2000.

Cunnold, D. M., R. F. Weiss, R. G. Prinn, D. Hartley, P. G. Simmonds, P. J. Fraser, B. Miller, F. N. Alyea, and L. Porter, GAGE/AGAGE measurements indicating reductions in global emissions of CCl_3F and CCl_2F_2 in 1992–1994, *J. Geophys. Res.*, *102*, 1259–1269, 1997.

Derwent, R. G., P. G. Simmonds, S. O'Doherty, and D. B. Ryall, The impact of the Montreal Protocol on concentrations in northern hemisphere baseline and European air masses at Mace Head, Ireland over a ten year period from 1987–1996, *Atmos. Environ.*, *32*, 3689–3702, 1998a.

Derwent, R. G., P. G. Simmonds, S. O'Doherty, and D. B. Ryall, European source strengths and Northern Hemisphere baseline concentrations of radiatively active trace gases at Mace Head, Ireland, *Atmos. Environ.*, *32*, 3703–3715, 1998b.

Draxler, R. R., and G. D. Hess, An overview of the HYSPLIT-4 modeling system for trajectories, dispersion, and deposition, *Aust. Meteorol. Mag.*, *47*, 295–308, 1998.

Elkins, J. W., et al., Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, *23*, 347–350, 1996.

Environmental Protection Agency, Locating and estimating air emissions from sources of perchloroethylene and trichloroethylene, *EPA-454/R-97-003*, Washington, D. C., 1989.

Environmental Protection Agency, Protection of stratospheric ozone, significant new alternatives policy final rule, *Rep. 59*(*53*), 13,044 pp., Washington, D. C., March 18 1994.

Environmental Protection Agency, National air pollutant emission trends, 1900–1996, *EPA-454/R-97-011*,Washington, D. C., 1997.

Fraser, P., D. Cunnold, F. Alyea, R. Weiss, R. Prinn, P. Simmonds, B. Miller, and R. Langenfelds, Lifetime and emission estimates of 1,1,2-trichlorotrifluorethane (CFC-113) from daily global background observations June 1982–June 1994, *J. Geophys. Res.*, *101*, 12,585–12,599, 1996.

Goldstein, A. H., C. M. Spivakovsky, and S. C. Wofsy, Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes, *J. Geophys. Res.*, *100*, 21,023–21,033, 1995.

Goulden, M. L., J. W. Munger, S.-M. Fan, B. C. Daube, and S. C. Wofsy, Measurements of carbon sequestration by long-term eddy covariance: methods and a critical evaluation of accuracy, *Global Change Biol.*, *2*, 169–182, 1996.

Hoke, J. E., N. A. Phillips, G. J. DiMego, J. J. Tuccillo, and J. G. Sela, The Regional Analysis and Forecast System of the National Meteorological Center, *Weather and Forecasting*, *4*, 323–334, 1989.

Hurst, D. F., P. S. Bakwin, and J. W. Elkins, Recent trends in the variability of halogenated trace gases over the United States, *J. Geophys. Res.*, *103*, 25,299–25,306, 1998.

McCulloch, A., and P. M. Midgley, The production and global distribution of emissions of trichloroethene, tetrachloroethene and dichloromethane over the period 1988–1992, *Atmos. Environ.*, *30*, 601–608, 1996.

McCulloch, A., P. M. Midgley, and D. A. Fisher, Distribution of emissions of chlorofluorocarbons (CFCs) 11, 12, 113, 114, and 115 among reporting and non-reporting countries in 1986, *Atmos. Environ.*, *28*, 2567–2582, 1994.

McCulloch, A., M. L. Aucott, T. E. Graedel, G. Kleiman, P. M. Midgley, and Y.-F. Li, Industrial emissions of trichloroethene, tetrachloroethene and dichloromethane: Reactive chlorine emissions inventory, *J. Geophys. Res.*, *104*, 8417–8427, 1999.

Midgley, P. M., The production and release to the atmosphere of 1,1,1-trichloroethane (methyl chloroform), *Atmos. Environ.*, *23*, 2663–2665, 1989.

Midgley, P. M., The production and release to the atmosphere of industrial halocarbons, *Ber. Bunsenges. Phys. Chem.*, *96*(3), 293–296, 1992.

Midgley, P. M., and A. McCulloch, The production and global distribution of emissions to the atmosphere of 1,1,1-trichloroethane (methyl chloroform), *Atmos. Environ.*, *29*, 1601–1608, 1995.

Moody, J. L., J. W. Munger, A. H. Goldstein, D. J. Jacob, and S. C. Wofsy, Harvard forest regional-scale air mass composition by patterns in atmospheric transport history (PATH), *J. Geophys. Res.*, *103*, 13,181–13,194, 1998.

National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory, Summary Report, 1996–1997, *Summary Rep. 24*, edited by D. J. Hofmann, J. T. Peterson, and R. M. Rosson, Boulder, Colo., 1998.

Prather, M. J., Continental sources of halocarbons and nitrous oxide, *Nature*, *317*, 221–225, 1985.

Prather, M., M. McElroy, S. Wofsy, G. Russell, and D. Rind, Chemistry of the global troposphere: Fluorocarbons as tracers of air motion, *J. Geophys. Res.*, *92*, 6579–6613, 1987.

Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran: The Art of Scientific Computing*, 2nd ed., Cambridge Univ. Press, New York, 1986.

Simmonds, P. G., R. G. Derwent, A. McCulloch, S. O'Doherty, and A. Gaudry, Long-term trends in concentrations of halocarbons and radiatively active trace gases in Atlantic and European air masses monitored at Mace Head, Ireland from 1987–1994, *Atmos. Environ.*, *30*, 4041–4063, 1996.

D. H. Barnes, B. P. Fehlau, E. W. Gottlieb, and S. C. Wofsy, Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA. (dhb@io.harvard.edu; brian_fehlau@post.harvard.edu; ewg@io.harvard.edu; wofsy@fas.harvard.edu)

G. S. Dutton, J. W. Elkins, and S. A. Montzka, Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, MS-R/E/CG1, Boulder, CO 30305, USA. (Geoff.Dutton@noaa.gov; James.W.Elkins@noaa.gov; Stephen.A.Montzka@noaa.gov)

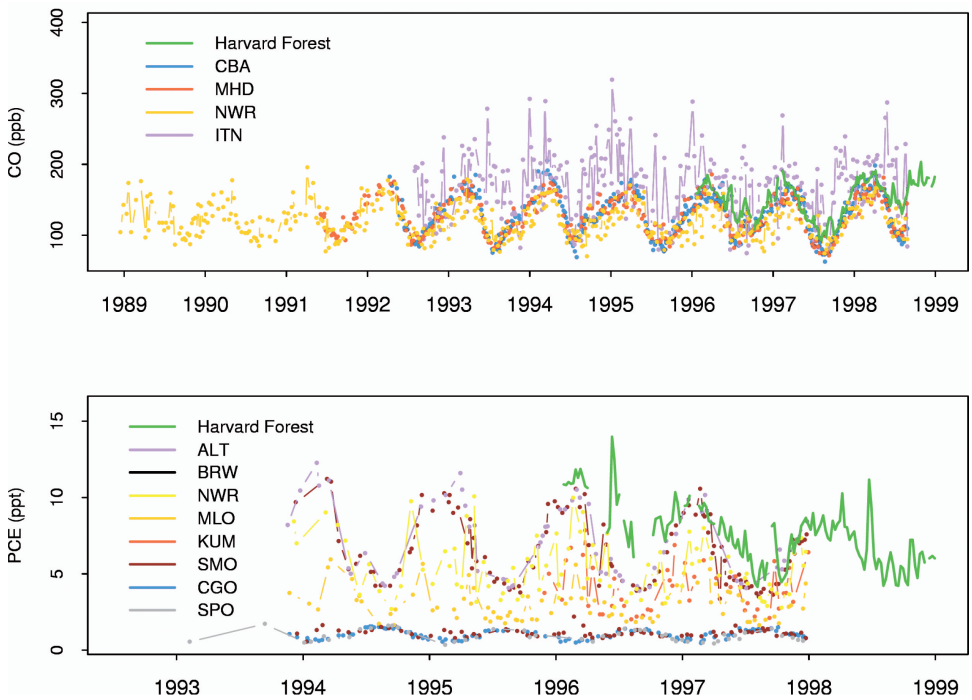


Figure 2. Comparison of Harvard forest background signals as measured by FACTS (green line) to those measured at the remote stations of *National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory* (*NOAA/CMDL*) [1998]. All data were retrieved from the NOAA/CMDL web site (ftp://ftp.cmdl.noaa.gov). CO flask measurements were taken at the Northern Hemisphere sites of Cold Bay, Alaska (CBA); Grifton, North Carolina (ITN); Mace Head, Ireland (MHD); Niwot Ridge, Colorado (NWR); and Wisconsin (LEF). PCE flask measurements were sampled at Alert, North West Territories, Canada (ALT); Barrow, Alaska (BRW); Niwot Ridge, Colorado (NWR); Mauna Loa, Hawaii (MLO); Cape Kumahkahi, Hawaii (KUM); Tutuila, American Samoa (SMO); Cape Grim, Tasmania (CGO); and South Pole, Antarctica (SPO).

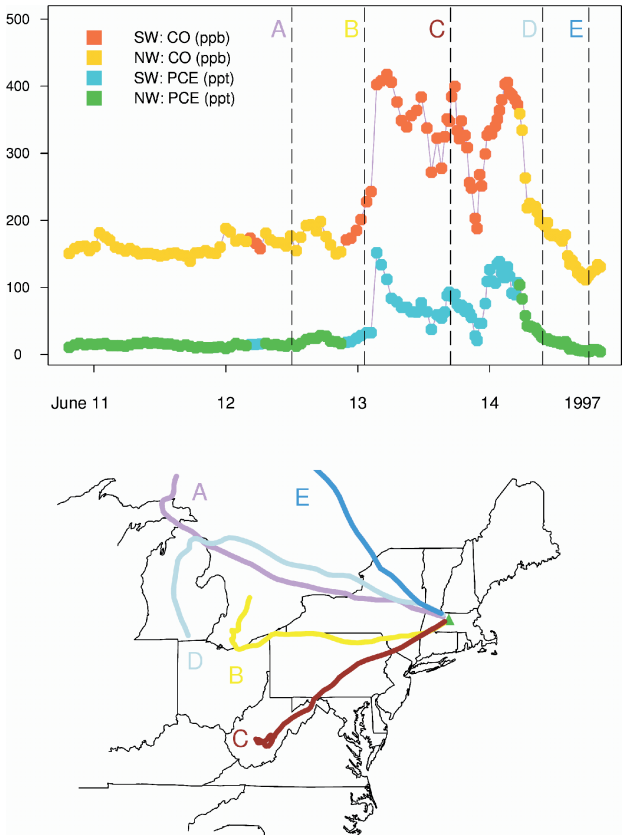


Figure 5. Back trajectories for the pollution plume of 12 through 14 June 1997. The trajectories were begun at 200 m, 3 days back, and used wind data from NGM meteorology (Nested Grid Model, part of NCEP's Regional Analysis and Forecast System [*Hoke et al.*, 1989]). CO (ppb) and PCE (ppt) weak and strong enhancements coincide with winds arriving at the Harvard forest tower (green triangle) from the northwest and southwest respectively, as measured by a sonic anemometer. Five vertical lines, labeled A through E, indicate those times for which back trajectory plots are provided. The back trajectories demonstrate that northwest winds are clean, southwest winds are polluted, and winds shifting between the two are partly polluted.