

Atmospheric variability and emissions of halogenated trace gases near New York City

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ABSTRACT

Elevated mixing ratios of chlorofluorocarbons (CFC-11 and CFC-12), and sulfur hexafluoride (SF₆) have been observed at Lamont-Doherty Earth Observatory (LDEO), located approximately 25 km north of New York City (NYC). Emissions and transport of these gases are of interest because of their global warming potential, the role of CFCs in depletion of stratospheric ozone and information they provide on the transport of atmospheric pollutants. Comparison of trace gas time series with meteorological data indicates that both NYC and the region to the southwest (New Jersey and the Philadelphia–Washington DC area) are significant sources of CFCs, and confirms that NYC is an unusually large source of SF₆. From 1996 to 2005 the elevation of CFC-12 mixing ratio above that of the remote (well mixed) atmosphere has decreased on average by 5.2 ± 0.6 ppt y⁻¹, whereas that of CFC-11 has not changed significantly (0.0 ± 2.0 ppt y⁻¹). From 1998 to 2006, the elevation of SF₆ mixing ratios above that of the remote atmosphere declined by 0.4 ± 0.1 ppt y⁻¹. Time series of the same gases measured at Harvard Forest, 205 km northeast of LDEO, demonstrate transport of air masses with elevated levels of these gases from their source region to central Massachusetts. Emissions in the local area around LDEO were quantified through analysis of diurnal cycles. Local CFC-12 emissions decreased ca. 95% between 1996 and 2005 while CFC-11 emission decreased ca. 51% during the same period. Local SF₆ emissions decreased by 47% between 1998 and 2005.

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1. Introduction

The chlorofluorocarbons, CFC-11 and CFC-12, are man-made gases that have been used in large quantities as refrigerants, foam blowing agents and propellants. Production and use of CFCs were controlled under the Montreal Protocol (adopted in 1987) and subsequent amendments, due to their contributions to stratospheric ozone destruction. As a result, global emissions of CFC-11

are estimated to have decreased by 98% between 1987 and 2000 and CFC-12 emissions by 94% (AFEAS, 2008). Current CFC-12 emissions result largely from its use as a refrigerant gas, whereas CFC-11 emissions are mainly from releases from previously manufactured closed cell foam (AFEAS, 2008). Due to decreasing global emissions, remote atmospheric mixing ratios of all CFCs were decreasing by 2002 (NOAA/CMDL, 2004). Sulfur hexafluoride (SF₆), like CFCs, is a compound of predominantly anthropogenic origin. Its primary use is as an electrical insulator in high voltage switchgear. It has not been significantly regulated, although voluntarily emission reductions have been reported (e.g. EPA, 2010), and its mixing ratio is rising in the remote atmosphere by 0.2 to 0.3 ppt per year (e.g. Harnisch and Hohne, 2002; Levin et al., 2010).

Atmospheric time series provide useful information on concentrations and emissions strength of gases of environmental concern, and can also provide useful data for calibration and

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validation of atmospheric models (e.g. Prather et al., 1987; Peters et al., 2004). Independent emission estimates based on time series analysis can serve as a useful check of emission estimates based on reported production and records of use on a variety of geographical scales. For CFCs, observation of atmospheric mixing ratios is the only direct way to determine emissions as new production approaches zero. For SF₆, emission estimates can be made from records of use and production for some geographic areas (e.g. Smythe, 2004; EIA, 2008) and estimates based on atmospheric observations can supplement and provide a cross check for these records (e.g. Levin et al., 2010). Many studies of SF₆ and CFCs have used time series collected at remote locations to investigate the budget of these gases in the global troposphere (e.g. Elkins et al., 1993; Cunnold et al., 1997; Geller et al., 1997; Maiss and Brenninkmeijer, 1998). More recently, time series from locations that are intermittently influenced by pollution from urban areas have been used to investigate regional emissions (e.g., Bakwin et al., 1997; Biraud et al., 2000; Barnes et al., 2003; Li et al., 2005) while others have used measurements from aircrafts to derive emission estimates for these and other gases (e.g. Hurst et al., 2006; Millet et al., 2009).

Atmospheric measurements within or near a metropolitan area provide insights on local emissions and transport, and such time series have been reported for CFCs and SF₆. Ho et al. (1998) and Ho and Schlosser (2000) describe elevated CFC-11, CFC-12 and SF₆ mixing ratios near New York City (NYC). Time series data have also been used to characterize elevated levels of CFCs and other halocarbons in and around urban areas including a Taiwanese industrial park (Chang et al., 2001), Krakow, Poland (Lasa and Sliwka, 2003) and Bristol, UK (Khan et al., 2009). Buchmann et al. (2003) observed elevated levels of CFCs and other halocarbons at a site outside Zurich, Switzerland and used them to estimate emissions. Flask samples have also been used to document elevated levels of CFCs and other halocarbons. For example, Barletta et al. (2006) reported observations from 45 cities in China. These studies show the promise of using atmospheric samples to understand and estimate emissions and atmospheric transport in urban areas.

Here, we present 8–9 years of CFC-11, CFC-12 and SF₆ mixing ratios from Lamont-Doherty Earth Observatory (LDEO) located ~

25 km north of NYC (Fig. 1). These time series are extensions of those presented by Ho et al. (1998) and Ho and Schlosser (2000), and we examine them for the time periods between June 1996 and June 2005 for CFCs and August 1998 to May 2006 for SF₆. CFC data from July 2005 on were compromised by a failure in the analytical system and are not included in this analysis. Monitoring of both CFCs and SF₆ ceased at LDEO in May 2006. Temporal variability in each time series is explored and interpreted in the context of emissions and transport of these gases within the NYC area and the larger northeastern US region.

2. Methods

Atmospheric CFC-11, CFC-12 and SF₆ mixing ratios were measured at LDEO at approximately 15-min intervals. Samples were pumped into the laboratory from an inlet located approximately 100 m from buildings at the site and 10 m above ground level, and measured by an automated gas chromatograph with two electron capture detectors (GC-ECD). For details on sample collection and analysis, see Ho et al. (1998) and Ho and Schlosser (2000). Analytical precision for CFC-11, CFC-12 and SF₆ were usually better than 1%. Trace gas data from Harvard Forest (HF) in Petersham, MA, approximately 205 km northeast of NYC, are also analyzed. Barnes (2000) and Barnes et al. (2003) provide details of sample collection and analysis for this site. CFC mixing ratios from both sites are reported in this work on the SIO 98 scale (Prinn et al., 2000) whereas SF₆ measurements for both sites are reported on the NOAA 2000 scale (NOAA/CMDL, 2004). Daily wind speed and direction data from Central Park within NYC are also used in the analysis of trace gas data (NOAA/NCDC). Wind data from this location was chosen because NYC is expected to be a significant source of these gases. Wind direction at Central Park and Black Rock Forest (~ 80 km north of NYC) are generally in good agreement (Ho et al., 1998) indicating that winds from Central Park describe transport in the lower Hudson region encompassing LDEO reasonably well.

Emissions were estimated from the diurnal cycles at LDEO using a method derived from Buchmann et al. (2003). Buchmann et al. (2003) observed the slope of increasing mixing ratios due to the

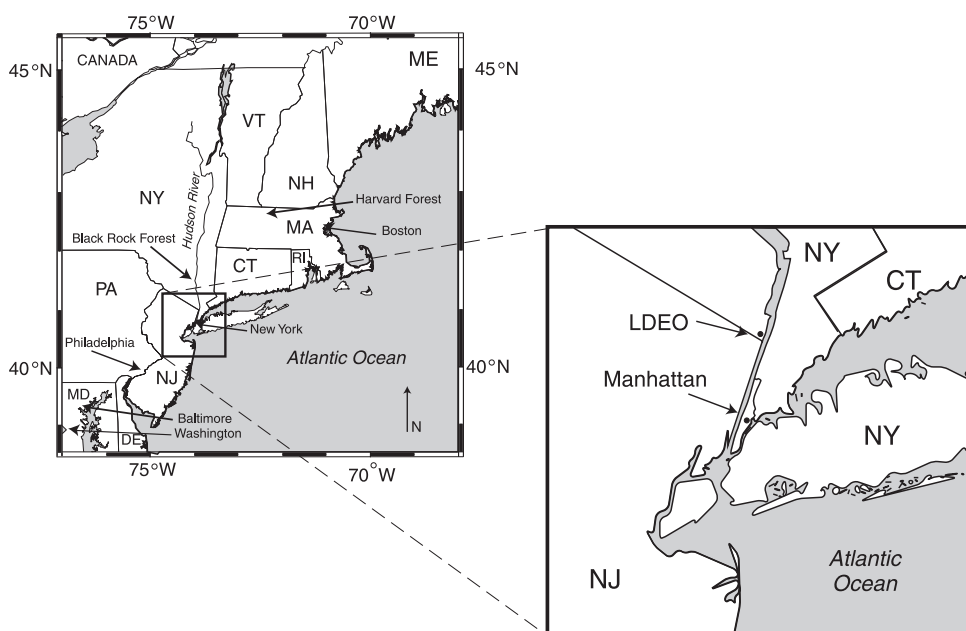


Fig. 1. Map of the northeastern United States, showing the locations of LDEO, Black Rock Forest, and HF.

flux of gases into the stable nocturnal boundary layer. This slope, observed over a selection of individual days, was used to estimate emission rates. Our method first removes the highest 1% of mixing ratio observations for each year. Mixing ratios at LDEO follow a nonstandard highly skewed distribution. This step produces distribution functions for mixing ratio which are roughly log normal and serves to remove random variability in average diurnal cycles induced by the occasional occurrence of extremely high mixing ratios. Next, each year of data is divided into four sets, representing the northwest, northeast, southwest and southeast, based on daily average wind direction. Data were separated by wind direction because SF₆ and CFC mixing ratios, and hence diurnal cycle strength, are strongly dependent on wind direction at LDEO. Finally, data were averaged by hour of day to produce four average diurnal cycles for each year. Averaged diurnal cycles were utilized because smooth and repeated individual diurnal cycles in trace gas mixing ratios are rarely discernible in the LDEO time series due to short term variability in mixing ratios, particularly for SF₆. This methodology was chosen over the original method of Buchmann et al. (2003) because although both methods produced similar estimates of trace gas flux when applied to the LDEO time series, this method produced an estimate with smaller uncertainties.

A weighted linear regression was applied to the averaged diurnal cycle. The most linear six hour period between 18:00 and 1:00 was used for the regression with each point weighted by mean standard error. For each wind direction, annually averaged rates of increase (ppt h⁻¹) of each gas were converted to fluxes (kg km⁻² y⁻¹) assuming an annual average nocturnal boundary layer height of 750 m (Holzworth, 1967). Uncertainty in annual average boundary layer height as reported by Holzworth (1967) was approximately 17%. The uncertainty in slope fit and boundary layer height were propagated in order to estimate uncertainty in emissions. These estimates were assumed to be representative of the region within approximately 75 km of LDEO based on average wind speed during the 6 h period over which the slopes were determined.

3. Results and discussion

3.1. Pollution events at LDEO

Daily averaged mixing ratios for the years with complete SF₆ and CFC data (1999 to 2004) were sorted by daily wind direction, averaged, and expressed as percent excess above remote atmosphere (Fig. 2). Highest CFC mixing ratios are found to the south/southwest, confirming the observations of Ho et al. (1998). CFC-12 mixing ratios were higher in proportion to CFC-11 when winds were from the southeast, the direction of NYC. SF₆ mixing ratios were elevated with winds from all directions as reported by Ho and Schlosser (2000) but analysis of a longer time series indicates that levels are highest with winds from the south/southeast, the direction of NYC (Fig. 2). A similar pattern of mixing ratios with wind direction is observed in all years with an exception in 2001 when a number of unusually high SF₆ mixing ratio events occurred while winds were primarily from the northeast, probably the result of small transient sources very close to LDEO. High CFC mixing ratios were more likely to occur during periods of low wind speeds (<2 m s⁻¹), due to longer residence times of air masses in the region, while at high wind speeds (>4 m s⁻¹) CFC mixing ratios were close to remote atmosphere values. High SF₆ mixing ratios were observed during both low and high wind speeds as result of strong local emissions of SF₆. Higher wind speeds were also generally observed when winds were from the northeast and northwest, which may contribute to lower mixing ratios at these times.

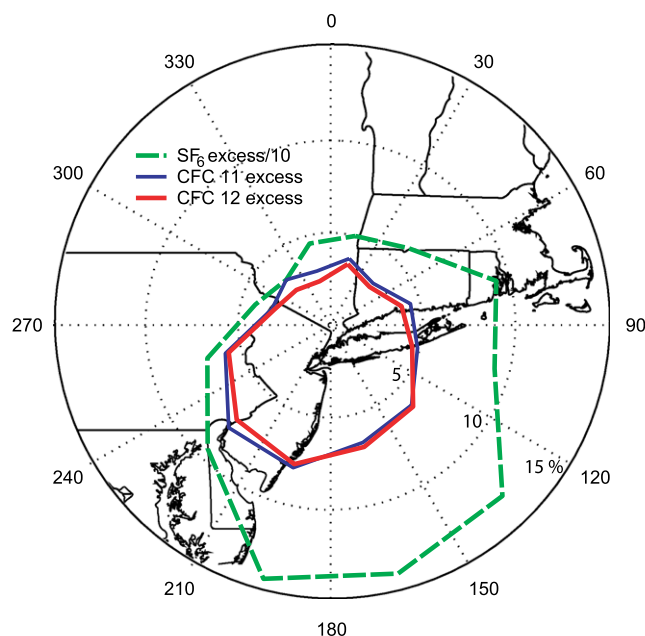


Fig. 2. Trace gas levels expressed as percent excess above remote atmosphere with wind direction averaged from 1999–2004. Much larger elevations of SF₆ are observed in all directions compared to both CFCs.

3.2. Time series trends

Seasonal cycles, discussed below, and decreasing mixing ratios dominate the monthly-averaged CFC time series (Fig. 3a,b). CFC-11 mixing ratios at LDEO decreased steadily, by approximately 12.4 ppt (4%) between the second half of 1996 and the first half of 2005, similar to the 15.4 ppt (6%) decrease observed in the remote atmosphere at a similar latitude (Niwot Ridge, CO; NOAA/ESRL). CFC-12 mixing ratios at LDEO decreased rapidly between 1996 and 1998 and more slowly in subsequent years, with an overall decrease of 56.9 ppt (9%) between 1996 and 2005. Over the same period, remote atmosphere levels rose slightly (1.3 ppt, <1%). SF₆ mixing ratios at LDEO were variable but decreased approximately 1.4 ppt (18%) between the end of 1998 and beginning of 2006 whereas remote atmosphere mixing ratios increased by 1.3 ppt (29%) over the same period (Fig. 3c). As a result, the monthly CFC-11 excess above remote atmosphere mixing ratios did not decrease significantly (0.0 ± 2.0 ppt y⁻¹) over this period, whereas the CFC-12 excess decreased by 5.2 ± 0.6 ppt y⁻¹ and the SF₆ excess decreased by approximately 0.4 ± 0.1 ppt y⁻¹. Monthly standard deviations of both CFCs and SF₆, which provide a measure of the strength of local and regional emissions (e.g., Hurst et al., 1998), varied over time in a similar fashion as mixing ratios.

3.3. Cross-and auto-correlation of time series

The auto correlation function of each trace gas time series reflects the average duration of pollution events and, with a known wind speed, illustrates the spatial extent of the source region of the gases (e.g., Prather et al., 1987; Bakwin et al., 1997). Auto correlation functions of LDEO time series for each year are very similar, with correlation of CFC-11 and CFC-12 generally dropping in an exponential fashion to 0.2 after about 1 day. CFC-11 auto correlation was slightly higher than that of CFC-12, corresponding to a difference in lag time of approximately 0.1 day. The SF₆ autocorrelation generally drops more quickly than that of CFCs, reaching a 0.2 level after only 6 h. Average surface wind speeds at Central Park and Black Rock

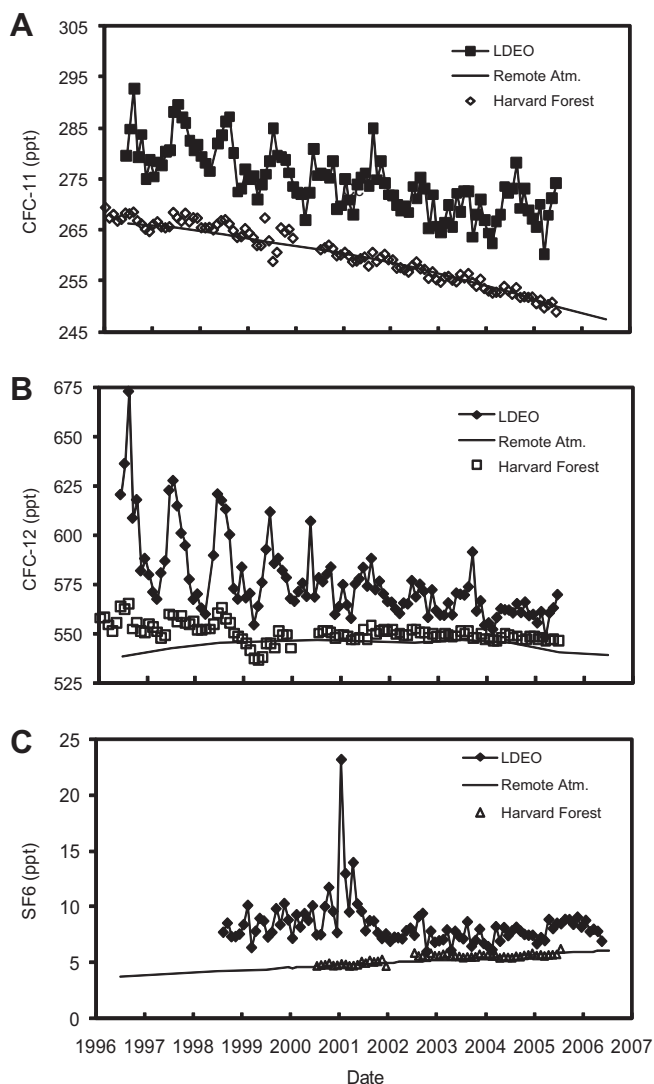


Fig. 3. Monthly average mixing ratios of trace gases at LDEO compared to averages from Harvard Forest and remote atmosphere levels at Niwot Ridge CO.

Forest are approximately 2 m s^{-1} , and based on this value an average wind speed of 3.4 m s^{-1} is expected for the atmospheric mixed layer (Wark et al., 1998). At this wind speed, a lag time of 1 day equivalent to a radius of around 300 km indicating that CFC mixing ratios are influenced by sources from across the 300 km long NYC/Washington D.C. corridor. The 6 h lag of the SF_6 time series corresponds to a smaller 75 km radius. This smaller source region reflects the fact that based on reported emissions from electrical utilities, over 40% of SF_6 emissions in the NYC-DC corridor come from NYC (EIA, 2008).

Cross correlations of CFCs and SF_6 demonstrate the level of similarity between all three time series. The cross correlation between CFC-11 and CFC-12 drops off in a fashion very similar to the auto correlation functions of these gases, indicating that source distributions of the two gases are similar. Correlation of CFC-11 with SF_6 is quite low, less than 0.2 at a 0 lag, while CFC-12 is somewhat more correlated with SF_6 (0.35 at 0 lag). This indicates that the source distribution of SF_6 is more similar to that of CFC-12 than CFC-11 perhaps due to stronger emissions from NYC. Cross correlation was generally consistent from year to year but in 2001, when SF_6 mixing ratios were unusually variable, the correlation functions of SF_6 with both CFCs were unusually low suggesting, as

noted above, that an atypical source close to LDEO was responsible for these high SF_6 mixing ratios.

3.4. Annual, weekly and diurnal cycles

Whereas both CFC-11 and CFC-12 have seasonal cycles at LDEO with lower mixing ratios in winter and higher in summer, no equivalent seasonal cycle was observed for SF_6 (Fig. 3), in accordance with Ho et al. (1998) and Ho and Schlosser (2000). The majority of the observed seasonal variation in CFC mixing ratios is believed to be due to variation in emission strength, although seasonal changes in atmospheric transport may also have an impact, as suggested by Ho et al. (1998). Lack of a seasonal cycle in SF_6 mixing ratios indicates constant level of emissions throughout the year. Between 1996 and 2004, the first and last years with a full seasonal cycle, the amplitude of the cycle has decreased by approximately 88% for CFC-12 and by 38% for CFC-11. The larger decrease in the seasonal cycle of CFC-12 compared to CFC-11 probably reflects the phase out of CFC-12 as a refrigerant gas, a use that is seasonally variable, while much of the remaining stock of CFC-11 is contained in foams and released at a steady rate throughout the year.

A weekly cycle, attributed to variable emission rates, with lowest mixing ratios observed Sunday had also been observed for CFCs but not SF_6 (Ho et al., 1998; Ho and Schlosser, 2000). The weekly cycles in CFC mixing ratio observed by Ho et al. (1998) with data from July 1996 to June 1997 indicated highest mixing ratios during Monday through Wednesday. Analysis of LDEO data from 1997 on indicated a temporal pattern similar to that observed by Oster et al. (1996) with higher mixing ratios Tuesday through Friday (Fig. 4a). High mixing ratios earlier in the week observed by Ho et al. (1998) were related to a small number of very high mixing ratio events in 1996 which may have originated from an atypical source. Higher mixing ratios of CFCs during the work week were attributed by Oster et al. (1996) to variation in industrial and commercial activity utilizing CFCs. The magnitude of the weekly cycle of CFCs decreased from 1996 to 2004 in a manner similar to the seasonal cycle, again indicating decreasing emissions.

Diurnal cycles, caused by the buildup of emissions in the stable nocturnal boundary layer, were observed for all trace gases, as reported by Ho et al. (1998) and Ho and Schlosser (2000). The average diurnal cycle for SF_6 was larger compared to that of the CFCs reflecting strong local emissions. The shape of these diurnal cycles was consistent in all years and generally similar to the diurnal patterns of SF_6 observed by Hurst et al. (1998) as well as the diurnal patterns for radon, which is emitted at a more or less steady rate from the soil, observed by Oster et al. (1996) and DiCarlo et al. (2009). Diurnal pattern of CFC mixing ratios at LDEO differed from those observed by Oster et al. (1996), which were influenced by strong variation in emission rates by time of day. At LDEO CFC-11 mixing ratios increased less rapidly from 16:00 to 22:00 compared to CFC-12 and SF_6 . The increase in CFC-12 and SF_6 mixing ratios is a close inverse to average temperature, reflecting greater vertical atmospheric mixing at higher temperatures (Fig. 4b). Hence, the slower increase in CFC-11 mixing ratio may reflect a more distant geographic source compared to the other two gases, consistent with the interpretation by Ho et al. (1998). This interpretation is also consistent with other lines of evidence for proportionally stronger CFC-12 and SF_6 emissions from NYC.

3.5. Comparison to Harvard Forest data

Harvard Forest (HF) is located in central Massachusetts, approximately 205 km northeast of NYC (Fig. 1). An automated GC-ECD system there has recorded the mixing ratios of many trace

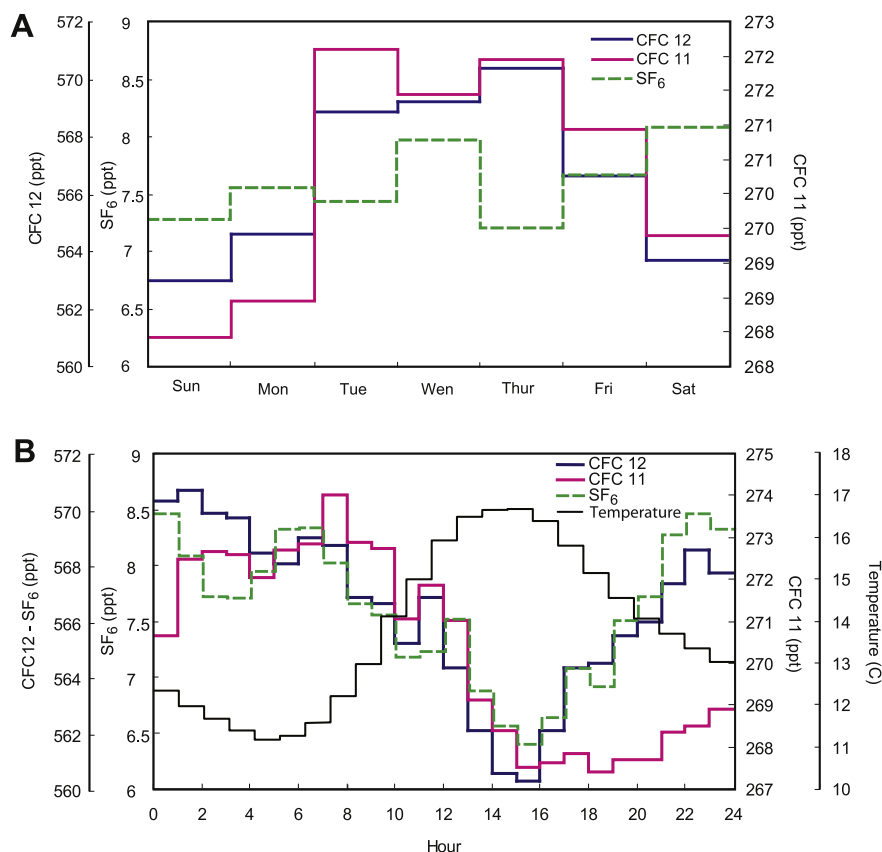


Fig. 4. A representative example (2002) of annually averaged weekly (A) and diurnal (B) cycles in trace gases at LDEO.

gases since 1996. Trace gas levels at HF are highly dependent on wind direction, with pollution events usually corresponding to winds from the southwest, and have been interpreted as representing emissions from the NYC-DC corridor (Barnes, 2000; Barnes et al., 2003). CFC-11 mixing ratios at LDEO are higher than at HF (Fig. 3a), the mixing ratios excess above remote atmosphere values at LDEO average almost six times higher than at HF, due to its closer proximity to emission sources. CFC-12 mixing ratios were much higher at LDEO than at HF (Fig. 3b). CFC-12 mixing ratios excess above remote atmosphere levels averaged seven times higher than those at HF. Since SF₆ mixing ratios at LDEO have also been much higher than at HF, excess above the remote atmosphere at LDEO is 21 times higher than that at HF. Higher levels of SF₆ at LDEO are attributed to closer proximity to NYC sources and the same appears to apply, to a much lesser extent, to CFC-12.

High mixing ratio events at HF typically occur soon after events at LDEO when winds are from the south (Fig. 5), reflecting a common source. Cross correlation between the time series at LDEO and HF provides insight into the transport between sites. Overall correlation is low because pollution events observed at LDEO are observed at HF only under favorable wind conditions. However, looking at data from 2002 as an example, correlation is somewhat elevated (0.30 to 0.35) out to a lag of 0.7 and 0.6 days for CFCs and SF₆, respectively. At an average wind speed for the mixed layer of 3.4 m s^{-1} , this lag corresponds closely to the 205 km distance between LDEO and HF. Maximum mixing ratios observed at HF averaged 25, 30 and 13% of the maxima observed at LDEO for CFC-11, CFC-12, and SF₆, respectively. The travel times and dispersion of the sharp SF₆ peaks between LDEO and HF agree well with expectations from atmospheric dispersion modeling. For example, trajectories calculated with the NOAA HYSPLIT model (Draxler and

Hess, 1997) for 28 July 2002, when pollution events were observed at both sites, indicates air mass at LDEO passing over HF after 0.7 days. A 1-h long tracer release modeled for the same time period predicts, similar to observations, a dilution of 90% between LDEO and HF due to dispersion.

When plotting trace gas mixing ratios against each other, the slope of a linear regression represents the relative emission strengths of these gases (e.g. Bakwin et al., 1997; Barnes et al., 2003). Taking data from 2002 as an example, this method is used to compare the strength of emissions as observed at LDEO and HF. At LDEO, a much lower CFCs:SF₆ ratio is observed (slopes of 1.1 for CFC-11:SF₆, 2.2 for CFC-12:SF₆) compared to that at HF (slopes of 4.1 for CFC-11:SF₆, 5.8 for CFC-12:SF₆). This reflects the greater influence of strong SF₆ sources from NYC on the LDEO time series. However, emission ratios of CFC:SF₆ for the entire US in 2003, calculated from estimates by Hurst et al. (2006) for CFCs and EPA (2010) for SF₆, were much higher than observed at either LDEO or HF, with values of 9.4 for CFC-11:SF₆ and 18.8 for CFC-12:SF₆. This indicates either unusually strong emissions of SF₆, or unusually weak emissions of CFCs, influenced the mixing ratios observed at both sites. In contrast, the ratio of CFC-11:CFC-12 in 2002 was similar at LDEO (0.5) and HF (0.6), as well as similar to that for the whole US in 2003 (0.5) (Hurst et al., 2006) indicating that no disproportionate source of either CFC affected these sites at that time.

3.6. Local emission estimates

Using a variation of the methods of Buchmann et al. (2003) as described above, the strength of local CFC and SF₆ sources were estimated from their diurnal cycles. Emission estimates and their uncertainties (standard deviation) are provided in Table 1. Local CFC

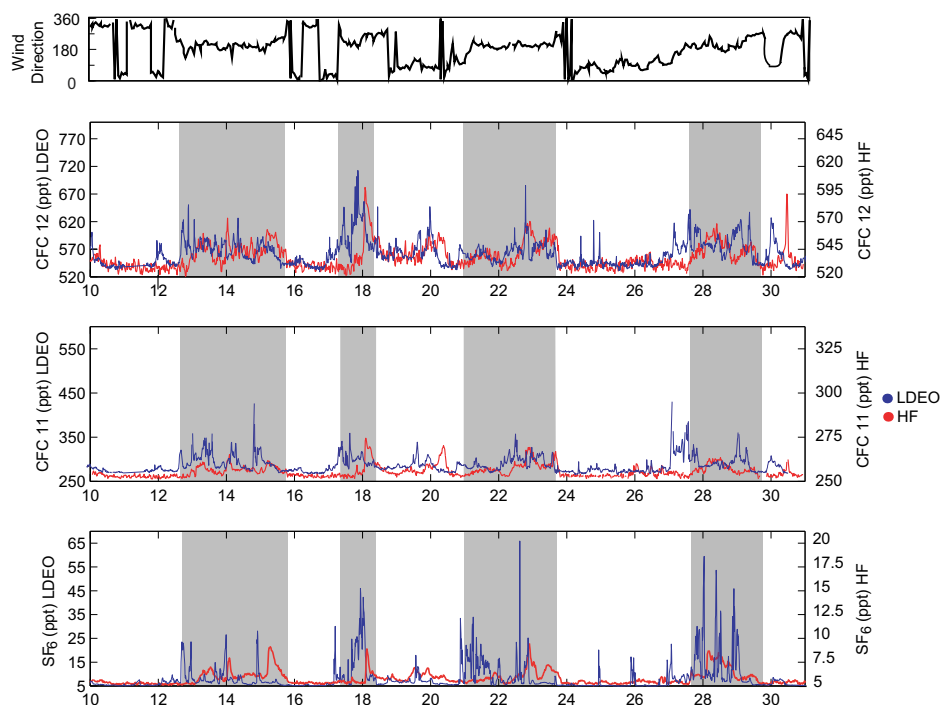


Fig. 5. Pollution events observed at LDEO and at Harvard Forest in July 2002 and hourly wind direction at Harvard forest. Gray highlights periods of wind from the southwest.

emissions from the south were generally lower than those from the north. In contrast local SF_6 emission estimates from the SE were highest in all years. Emissions from the SW were the second highest in 1999 and 2000 after which emissions from the SW, NW and NE were similar. As noted previously in discussing mixing ratios, an exception occurred in 2001 when a number of unusual large pollution events during winds from the north were observed, resulting in much higher estimated emissions rates for the NW. Emissions of CFC-11 and CFC-12 in the region around LDEO appear to have fallen by 51% and 95%, respectively, between 1997 and 2004. SF_6 emissions averaged across all directions dropped by 47% between 1999 and 2005.

One study of regional CFC and SF_6 emissions for the NYC–Washington DC corridor is available for comparison to emissions at LDEO. This study described by Barnes (2000) and Barnes et al. (2003) is based on the time series data collected at HF. CFC emissions, in kg person^{-1} , as estimated by Barnes et al. (2003) were generally consistent, given some decrease in emissions over time, with rates for the entire US as estimated by Bakwin et al. (1997), Hurst et al. (2006) and Millet et al. (2009) for the years 1995, 2003 and 2005, respectively. SF_6 emission rates determined by Barnes (2000) were much higher than estimates by Bakwin et al. (1997) and Hurst et al. (2006) or than would be expected from US inventory based estimates (EPA, 2010). The observation of high SF_6 mixing ratios air masses at both LDEO and HF as described above suggests that the high SF_6 emission rates estimated by Barnes (2000) are the result of a strong influence of SF_6 emissions from NYC on the HF time series.

Using the area of $94,000 \text{ km}^2$ and population of 34,416,906, considered by Barnes et al. (2003), emissions for the NYC–Washington DC corridor, originally reported in kg person^{-1} , can be compared to emission estimates from LDEO in kg km^{-2} . Barnes et al. (2003) estimated emissions of 55 kg km^{-2} in 1997 and 46 kg km^{-2} in 1998, somewhat less than most emission estimates from LDEO in the same years. CFC-11 emissions estimates by Barnes et al. (2003) were 16.5 kg km^{-2} in 1997 and 19.5 kg km^{-2} in 1998

within the range observed at LDEO for the same years. SF_6 emission rates by Barnes (2000) were 12.1 kg km^{-2} in 1997 and 9.5 kg km^{-2} in 1998. These values were slightly higher or comparable to estimates from LDEO when winds were from the NW or NE as well as the SW, with the exception of the years 1999 and 2000, but lower than estimates when winds were from the SE. These comparisons suggest that the local CFC-12 emission rate around LDEO, during the period from 1997–1998, exceeded regional emission rates and

Table 1

Estimated LDEO emission rates in $\text{kg km}^{-2} \text{ y}^{-1}$ of CFC-11, CFC-12, and SF_6 based on their diurnal cycles.

Year	Northwest	Northeast	Southwest	Southeast
<i>CFC-11 emissions $\text{kg km}^{-2} \text{ year}^{-1}$</i>				
2004	8.9 ± 4.1	14.6 ± 4.0	3.5 ± 4.9	8.0 ± 6.2
2003	13.0 ± 3.2	15.5 ± 3.6	8.2 ± 10.8	24.5 ± 12.3
2002	16.5 ± 4.2	19.5 ± 4.4	3.9 ± 7.0	16.0 ± 4.7
2001	3.9 ± 5.0	13.7 ± 2.9	12.5 ± 7.3	8.6 ± 6.8
2000	13.2 ± 5.0	12.3 ± 2.9	7.0 ± 5.0	15.0 ± 11.4
1999	15.8 ± 5.7	29.0 ± 8.2	3.5 ± 5.5	6.2 ± 11.3
1998	34.8 ± 6.9	19.5 ± 4.4	15.3 ± 4.8	9.6 ± 5.9
1997	20.3 ± 5.4	19.0 ± 5.5	17.2 ± 12.5	14.8 ± 7.6
<i>CFC-12 emissions $\text{kg km}^{-2} \text{ year}^{-1}$</i>				
2004	10.0 ± 7.3	20.9 ± 5.0	0.0 ± 8.3	0.0 ± 8.7
2003	27.0 ± 7.2	23.6 ± 4.4	0.0 ± 9.2	32.7 ± 7.8
2002	37.2 ± 8.0	28.0 ± 8.0	0.0 ± 15.2	17.1 ± 11.3
2001	46.0 ± 10.1	49.8 ± 10.1	19.3 ± 19.8	38.5 ± 10.6
2000	66.7 ± 15.3	48.8 ± 9.8	19.0 ± 8.9	40.3 ± 13.9
1999	44.9 ± 12.0	64.4 ± 12.9	27.6 ± 18.4	23.5 ± 14.4
1998	105.2 ± 27.3	84.2 ± 20.9	40.5 ± 17.5	41.5 ± 25.8
1997	120.0 ± 25.8	108.1 ± 22.0	77.6 ± 40.3	95.7 ± 31.9
<i>SF₆ emissions $\text{kg km}^{-2} \text{ year}^{-1}$</i>				
2005	8.7 ± 3.3	3.6 ± 1.0	16.9 ± 3.7	5.0 ± 1.6
2004	0.8 ± 1.3	6.9 ± 1.6	13.1 ± 2.7	3.6 ± 2.0
2003	2.9 ± 1.4	5.4 ± 1.0	10.9 ± 3.3	5.7 ± 1.3
2002	8.2 ± 2.4	2.0 ± 1.0	14.3 ± 5.1	6.6 ± 4.3
2001	3.0 ± 1.8	10.9 ± 2.4	28.1 ± 7.0	2.9 ± 3.9
2000	2.7 ± 4.1	5.9 ± 1.5	26.8 ± 6.4	19.7 ± 6.3
1999	8.5 ± 2.9	6.4 ± 1.2	32.2 ± 6.6	16.9 ± 4.7

likewise confirms an unusually strong source of SF₆ emissions to the SE of LDEO.

SF₆ emissions from electrical utilities in NYC located to the SE of LDEO, and northeastern New Jersey, to the SW, are available from the EIA voluntary greenhouse gas reporting database (EIA, 2008). Given the service areas of each utility, these emissions can be expressed as kg km⁻² y⁻¹ for comparison with LDEO estimates. LDEO emission rates from the SE, although high compared to estimates by Barnes (2000), are half to one fifth of the inventory based emissions rate from the major utility in NYC which decreased from 84 kg km⁻² in 1998 to 51 kg km⁻² in 2005. Underestimation compared to inventory based emissions for NYC alone is expected, as the presumed source area sampled at LDEO when winds are from the SE is larger than, and differs from, the NYC utilities service area. The trend in SF₆ emissions from the SE at LDEO and from the NYC utility are similar, LDEO estimates decreased by approximately 3 kg km⁻² y⁻¹ while inventory based estimates decreased by approximately 4 kg km⁻² y⁻¹. LDEO emission rates from the NW and NE quadrants in most years are generally similar to those from the northeastern New Jersey utilities service area, which varied from 3.0 to 5.0 kg km⁻² y⁻¹, as are emissions in the SW from 2001 on. Neither NJ utility emissions, nor those from the NE and NW quadrants, have significant temporal trends.

4. Conclusion

Atmospheric SF₆, CFC-11 and CFC-12 time series from a site 25 km north of NYC provide unique information on the distribution and strength of local emission sources, regional atmospheric transport, and temporal trends. Elevated mixing ratios above the remote atmosphere were observed for all gases, and diurnal periodicity was apparent due to trapping of local emissions in the stable nocturnal boundary layer. Estimates of local emissions near LDEO indicate that CFC-11, CFC-12 and SF₆ releases have decreased. Observed trends in CFC emissions and mixing ratios from the LDEO time series were generally consistent with US and regional emission estimates, and current knowledge about sources of these gases. The decrease in the strength of the unusually large SF₆ emission sources in NYC agreed well with the trend of inventory based emission estimates from NYC, although the NYC inventory emission estimates are larger than the LDEO emission estimates for the SE sector. Under appropriate meteorological conditions, air parcels with high mixing ratios of both SF₆ and CFCs observed at LDEO could later be observed more than 200 km downwind at a trace gas measurement site in central Massachusetts (HF). Comparison of the time series at the two sites demonstrates the impact a distant but strong source can have on mixing ratios, and derived emission estimates, at a relatively remote location.

In the future, similar studies in other urban areas would be valuable for understanding variations in trace gas emissions rates based on local factors. As emissions of CFCs decrease, observation of their mixing ratios are of less interest, and mixing ratios will eventually be too low to reliably mark urban air masses. Hence, measurements of other halogenated gases, such as hydrofluorocarbons (HFCs), which are still released in relatively large amounts, are desirable and have been undertaken in a number of recent studies. Other trace gases from industrial sources, which have low background concentration and are emitted in small quantities, such as SF₅CF₃ or NF₃ may also have potential as tracers for urban air masses. One limitation of this study was the noticeable influence of small nearby sources on the atmospheric time series. A more sophisticated analysis could attempt to identify and eliminate these influences with the use of meteorological data and back trajectory analysis. It is expected that analysis similar to those presented here would be equally useful for understanding the

emissions and transport of a variety of trace gases. In addition to providing temporal trends and emission estimates, this type of time series data could also be useful as a benchmark to diagnose various features of atmospheric models by testing their ability to reproduce time series influenced by pollution events (e.g. Peters et al., 2004).

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