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Variability in Atmospheric Chlorofluorocarbons (CCl_3F and CCl_2F_2) near a Large Urban Area: Implications for Groundwater Dating

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Chlorofluorocarbons (CFCs) are frequently used as tracers for age dating of young groundwaters. However, in urban environments with many CFC point sources, uncertainties in the delivery of CFCs to groundwater (input function) complicate quantitative interpretation of observed CFC distributions. To assess the potential impact of elevated atmospheric CFC mixing ratios on CFC-based groundwater ages near a large coastal urban center, we measured atmospheric mixing ratios of CFCs in Palisades, NY, 25 km north of New York City. We present and discuss a 16-month record of atmospheric CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) obtained from gas chromatographic analyses taken at intervals of approximately 10 min. Nearly all measured values are in excess of remote Northern Hemisphere (NH) atmospheric mixing ratios. The mean mixing ratios of CFC-11 and CFC-12 are 6 and 13% higher, respectively, than those measured at a remote NH location during the same time period. The temporal trends of CFC-11 and CFC-12 differ from those of the remote atmosphere. Diurnal, weekly, and seasonal patterns are evident in the measured CFC distributions, in addition to variations resulting from regional meteorological conditions. These observations indicate that, to effectively use CFCs as groundwater dating tools near local or regional sources, their local atmospheric input functions must be explicitly defined.

Introduction

Young groundwaters (recharged within the past 50 years) generally contain dissolved chlorofluorocarbons (CFCs) (1), which in principle are valuable tools for quantification of groundwater recharge rates, flow velocities, and flow directions. However, since CFCs enter most natural waters by gas exchange with the atmosphere, knowledge of the CFC delivery history from the atmosphere to the groundwater (input function) in a given region is a necessary precondition for its use as a dating tool. In many previous studies (e.g., refs 2–5), it has been assumed that local atmospheric mixing ratios were approximately equal to those measured at remote atmospheric monitoring sites. (Because the density of air in

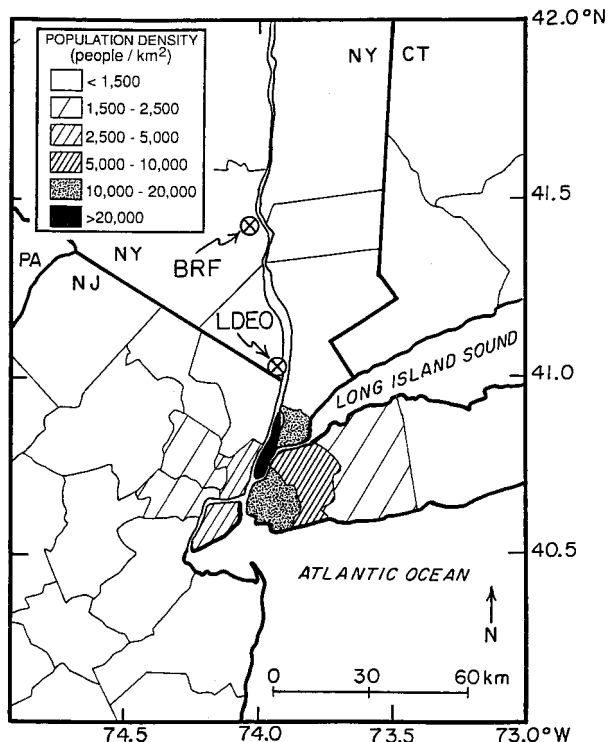


FIGURE 1. Map of the New York (NY) metropolitan area, showing the 31 counties that comprise the NY Consolidated Metropolitan Statistical Area (CMSA). Also shown are locations of Lamont-Doherty Earth Observatory (LDEO), where CFC and meteorological measurements were made, and Black Rock Forest (BRF), where additional meteorological measurements were made. Population densities of counties to the south of LDEO near the core of the NY CMSA are generally much greater than those to the north.

the atmosphere varies with altitude, CFC data are reported as mole fractions: the relative number of CFC molecules in an air sample. In atmospheric chemistry, mole fractions are often called “mixing ratios”). In these studies, CFC ages were obtained by converting measured CFC concentrations in groundwater to equivalent atmospheric mixing ratios using known solubility relationships (6) and recharge temperature. These calculated mixing ratios are then compared with the remote atmospheric mixing ratios to obtain apparent CFC ages.

By using CFCs along with tracers that are not usually affected by local sources (tritium, tritium/ ^3He), several investigators (e.g., refs 2–4 and 7) have demonstrated that in some areas atmospheric CFC mixing ratios appear to be similar to those measured in the remote atmosphere, indicating that the global atmospheric background mixing ratios are reasonable approximations of the actual input function in those regions. However, since CFCs have no natural sources and densely populated regions use and release these compounds in large quantities, remote atmospheric background mixing ratios might not be appropriate input functions near urban areas. This problem was pointed out in an examination of the potential use of CFCs as age dating tools at a continental site in an industrial region of central Europe (8). In the following, we present and discuss a 16-month record (July 1996–October 1997) of atmospheric CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) from a coastal location in the northeastern United States (near New York City) and examine potential systematic biases in CFC-derived ground-

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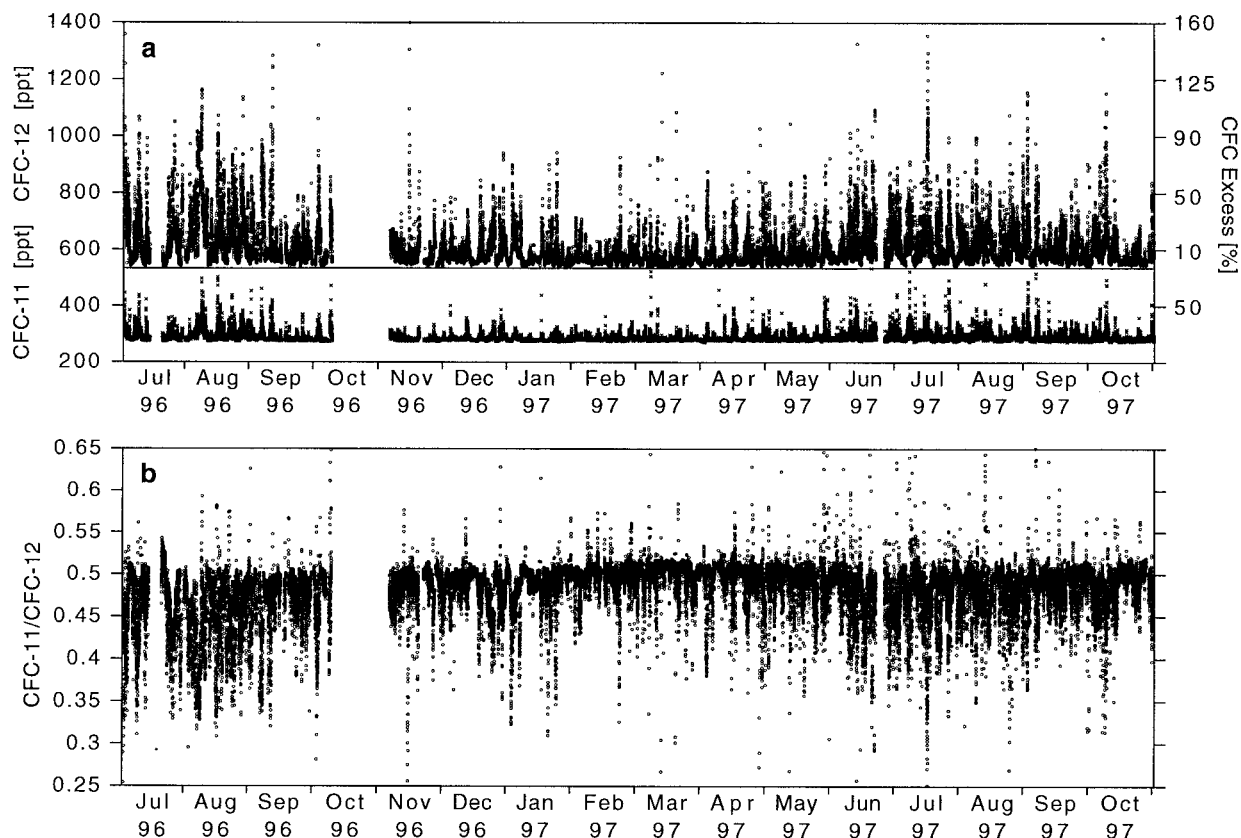


FIGURE 2. (a) Time series of CFC-11 (crosses) and CFC-12 (open circles) mixing ratios at LDEO from July 1996 through October 1997. Gaps in the LDEO data are due to instrument problems. CFC excess is calculated as $(C_{LDEO} - C_{NWR})/C_{NWR}$, where C_{LDEO} and C_{NWR} are mixing ratios at LDEO and Niwot Ridge, CO, respectively. (b) Time series of CFC-11/CFC-12 ratio at LDEO from July 1996 through October 1997. The ratio is generally lower in the summer months, indicating greater input of CFC-12 relative to CFC-11 during that period.

water ages that can be caused by elevated atmospheric CFC mixing ratios near an urban area.

Experimental Section

Sampling Location. CFCs were measured at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University in Palisades, NY (Figure 1; 41.00 °N, 73.91 °W; resident population 996 in 1990), located on the west bank of the Hudson River, 25 km north of New York City (NYC; estimated population 7.3 million in 1995). The 31 counties of the New York (NY) Consolidated Metropolitan Statistical Areas (CMSA), which include northern New Jersey, Long Island, southeastern Connecticut, and one county in Pennsylvania, had an estimated population of 20.1 million in 1995. The combined population of four counties to the northwest of LDEO is only about 4% of the total population of the NY CMSA.

CFC Analysis. Atmospheric air from a wooded area, 100 m from the nearest building at LDEO, is drawn continuously through 150 m of 1 cm i.d. multilaminate tubing (Dekoron) to the laboratory with a diaphragm pump at a rate of 7 L min⁻¹. Downstream of the pump, air is vented into the laboratory after passing through a quartz microfiber coalescing filter (Balston), where most of the moisture and particulates are removed. At designated times, air is diverted at a flow rate of 100 mL min⁻¹ to fill a 2 mL sample loop after passing through a chemical ($Mg(ClO_4)_2$) and a physical (Nafion) dryer. Subsequently, the sample is injected into a gas chromatograph (GC; Shimadzu 8A) equipped with an electron capture detector (ECD) by ultrahigh-purity (99.999%) N₂ carrier gas. Two cylinders of N₂ are connected to a gas distribution manifold to supply an uninterrupted flow of carrier gas. The N₂ is passed through a molecular sieve 13×

trap to remove impurities. CFC-11 and CFC-12 are separated from other gases by first passing through a 1.5 m precolumn and then a 2.5 m analytical column, both packed with Unibeads 2S. The columns are kept in an oven at 120 °C, and the detector is set isothermally at 300 °C. In this configuration, CFC-12 elutes at ~2.3 min, and CFC-11 elutes at ~4.6 min. Measurement precisions (1σ) for CFC-11 and CFC-12 are ±1 and ±2 parts per trillion (ppt), respectively.

The analogue output of the GC-ECD is converted to a digital signal with a 20-bit analog-to-digital (A/D) converter board (SS420, Scientific Software) and analyzed by a commercially available chromatography data system (EZ Chrom). The results are stored on a personal computer. Sample selection between air, working standard, or N₂ (blank) is made by a four-port stream selection valve (Valco). The sample injection system consists of an eight-port multi-port valve (Valco), a 10-port two-position valve (Valco), and two solenoid valves (Skinner). The valves are regulated by two eight-port input-output (I/O) boards controlled by an integrator (Shimadzu CR 501). Analogue signals from a thermistor and barometer are converted into digital signals with the built-in A/D converter in the integrator and the signals transferred to a personal computer via a RS-232 board.

The BASIC program controlling the injection system determines the stability of the baseline before each analysis. When the baseline is stable (±10 μV over 10 s), another air sampling sequence is initiated. This leads to an interval of approximately 10 min between samples. A set of three standards is analyzed after 20 discrete air samples. First, N₂ (blank) from the carrier gas stream is analyzed via the same route as the air samples to ensure that no contamination has occurred. Then, successive analyses of 1, 2, and 5 mL of the working standard are performed. During data reduction,

TABLE 1. Monthly Mean and Variability in CFC Mixing Ratios at LDEO

	CFC-11				CFC-12			
	mean ^a	σ^a	σ^b (%)	N ^c	mean	σ	σ (%)	N
Jul 1996	291.9	19.7	6.7	2543	639.6	97.7	15.3	2539
Aug 1996	300.0	27.1	9.0	3359	676.5	106.6	15.8	3359
Sep 1996	286.3	17.4	6.1	2748	611.8	79.0	12.9	2748
Oct 1996	290.8	21.6	7.4	709	621.2	87.8	14.1	709
Nov 1996	281.9	7.3	2.6	2640	585.0	73.6	12.6	2641
Dec 1996	285.7	11.4	4.0	3376	591.2	46.9	7.9	3377
Jan 1997	282.3	8.5	3.0	3398	582.9	49.7	8.5	3400
Feb 1997	285.3	8.2	2.9	2849	574.1	33.4	5.8	2849
Mar 1997	284.6	13.4	4.7	3370	570.4	38.9	6.8	3385
Apr 1997	287.4	15.1	5.2	3024	583.8	52.8	9.0	3024
May 1997	287.7	14.6	5.1	3203	589.9	49.5	8.4	3202
Jun 1997	295.3	21.6	7.3	2910	626.0	78.2	12.5	2910
Jul 1997	296.9	26.0	8.8	3377	631.0	93.8	14.9	3376
Aug 1997	294.3	17.5	5.9	3290	618.1	63.1	10.2	3290
Sep 1997	293.1	21.5	7.3	3279	604.2	62.7	10.4	3279
Oct 1997	289.5	16.4	5.7	3244	597.9	64.7	10.8	3244

^a Monthly mean and standard deviation (σ) of CFC mixing ratios given in ppt. ^b Standard deviation relative to mean monthly mixing ratios. ^c Number of samples; instrument problems in October 1996.

standards from two consecutive runs are used to bracket the intervening 20 air samples.

Meteorological parameters measured at LDEO's weather station (including wind speed, wind direction, temperature, precipitation, and barometric pressure) are logged by the instruments. Every hour, the data are transferred automatically to a UNIX workstation where they are archived until data reduction. Good agreement between wind direction data from LDEO and Black Rock Forest (BRF; 41.41 °N, 74.03 °W), located 70 km north of NYC in the Hudson Highlands on the west bank of the Hudson River, indicates that wind direction data from the LDEO weather station are representative of regional winds.

Standard Preparation. The working standard was prepared by filling an Acuflex-treated aluminum cylinder (Scott Specialty Gases) with atmospheric air at LDEO. Atmospheric air was pumped with a three-stage compressor (Rix Industries) through a series of coalescing filters, backpressure regulator, check valve, and chemical dryer (Aquasorb) into the gas cylinder over a period of 2 h. The working standard was then compared with a primary standard filled at Niwot Ridge, CO, and calibrated by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL). The results in this paper are reported on the NOAA/CMDL CFC scale (9, 10). The working standard was recalibrated to ensure that CFC mixing ratios in the tank had not changed.

Results and Discussion

CFCs have been measured at LDEO since July 1996 (Figure 2a). Both CFC-11 and CFC-12 mixing ratios are nearly always in excess of remote Northern Hemisphere (NH) atmosphere mixing ratios for the same time period (Niwot Ridge, CO; 40.1 °N, 105.5 °W; J. Butler, personal communication, 1997). However, some background values of CFC-11 and CFC-12 from LDEO, determined as the mean value of the lowest 5% bin of the monthly data, were on average only 2.2 and 1.6% higher than Niwot Ridge background values for the same months. During these periods with stable "background" CFC mixing ratios at LDEO, the wind directions at both LDEO and BRF are usually from the northwest, and back trajectory maps indicate that most of the air masses were derived from Canada and the Arctic.

Temporal trends in the background data from LDEO, calculated as the slopes of linear least-squares fits to the lowest 1–5% of the data from each month, indicate that

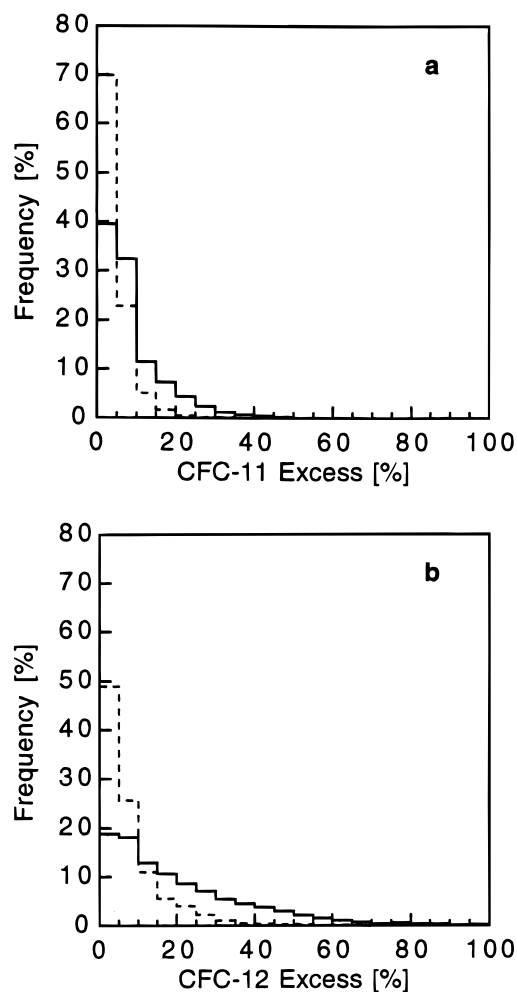


FIGURE 3. Frequency distribution of (a) CFC-11 and (b) CFC-12 excess (5% bins) at LDEO from summer months (JJA) and winter months (DJF). Dotted line is the winter; solid line is the summer. For both CFC-11 and CFC-12, excesses relative to the Northern Hemisphere remote atmosphere occur more frequently during summer as compared to winter.

CFC-11 and CFC-12 increased at $+2.4 \pm 0.1$ and $+2.6 \pm 0.3$ ppt yr⁻¹, respectively, over 16 months beginning in July 1996. These temporal trends differ from the NH remote station trends as well as recent trends (November 1994–January 1996) from a continental site in the southeastern United States. For the NH remote atmosphere in 1995, CFC-11 decreased at -1.2 ± 0.6 ppt yr⁻¹ and CFC-12 increased at $+4.9 \pm 0.6$ ppt yr⁻¹ (10). In a recent study of atmospheric trace gases at a rural site in eastern North Carolina, measured CFC mixing ratios were aggregated into 5–15 and 15–25% bins as representative of regional background values (11). Temporal trends from these two bins were -0.8 and -0.9 ± 0.1 ppt yr⁻¹ (CFC-11) and $+5.4$ and $+5.9 \pm 0.3$ ppt yr⁻¹ (CFC-12), consistent with the pattern for remote atmosphere values. We did not calculate temporal trends using the same data bins because CFC mixing ratios at LDEO are generally elevated relative to background values, and 5–25% bins usually do not represent regional background values.

At LDEO, during periods of strong northwesterly winds, both CFC-11 and CFC-12 were nearly constant and close to remote NH background values. Such conditions occurred more frequently during winter months (December, January, February), when mean and maximum wind velocities (2.5 and 30 m s⁻¹ at LDEO; 3.2 and 15.9 m s⁻¹ at BRF) were generally higher than in summer (June, July, August) (1.7 and 20 m s⁻¹ at LDEO; 1.4 and 9.6 m s⁻¹ at BRF). Usually,

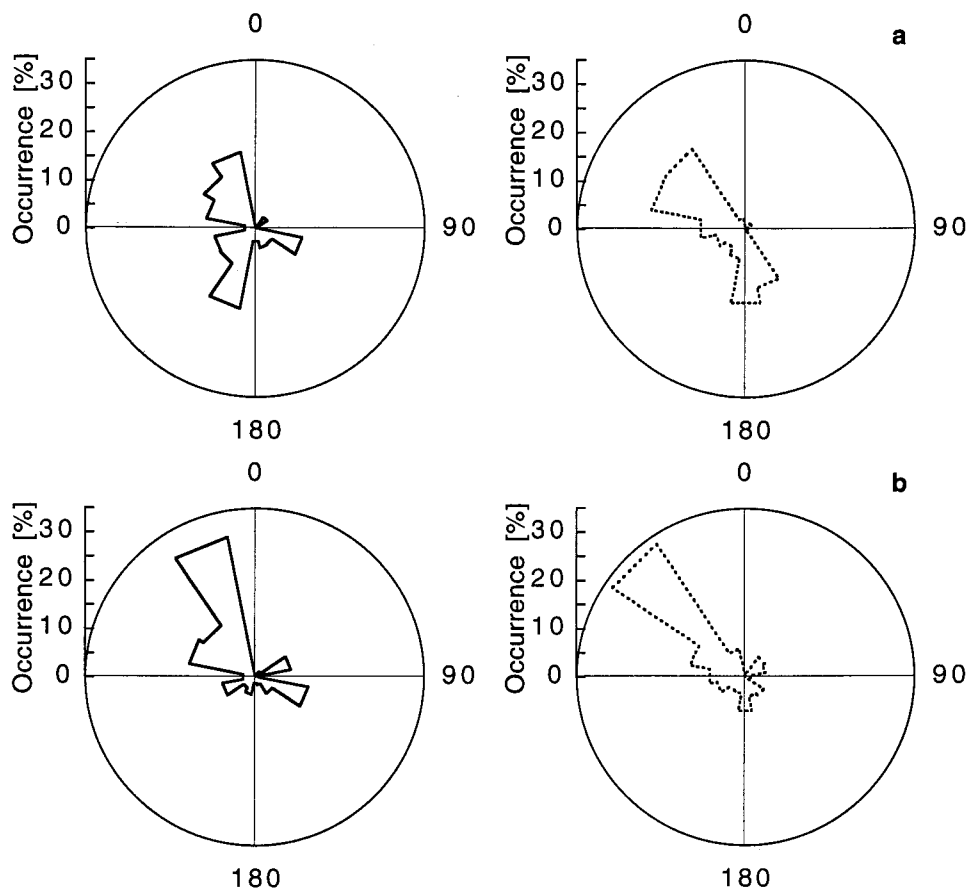


FIGURE 4. Wind roses at LDEO and BRF for (a) summer (JJA) and (b) winter (DJF). Solid line is LDEO; dotted line is BRF. Prevailing winds during the winter are from the northwest, with little contribution from the south–southwest. During the summer, the frequency of south–southwesterly winds is much greater. Directions associated with wind speeds $<1 \text{ m s}^{-1}$ ($\sim 10\%$ of data) have been omitted.

CFC mixing ratios were highest (spikes in Figure 2) when winds were from the south–southwest. The mixing ratios for CFC-11 and CFC-12 at LDEO are more variable during summer months (Table 1), as are the frequency of occurrence and magnitude of CFC mixing ratios in excess of NH remote station values (Figure 3a,b). This contrast between summer and winter may be due to both seasonal emission variations and atmospheric transport patterns. The latter probably plays a larger role as the prevalent wind direction is from the northwest during winter months (Figure 4a,b). Temporal trends of CFC excess (1989–1992) from a rural site along with CFC excesses from an urban region of central Europe in 1989 (8) were extrapolated here to estimate the excess in an urban region of central Europe in 1996–1997. Mean CFC excesses measured at LDEO above NH background (6% for CFC-11; 13% for CFC-12) differed from those estimated for central Europe (10% for CFC-11; 6% for CFC-12). The difference in observed CFC-12 mixing ratios between the two regions could be due to the greater number of air conditioners used in the northeastern United States.

In addition to seasonal differences in the LDEO data, daily and weekly variations are also evident. Relatively high values were observed at night, followed by a decline in the morning hours, toward a minimum in the late afternoon (Figure 5a). Diurnal variations in mixing ratios of CFCs are influenced on this short time scale by both temporal variability in source strength and radiatively driven vertical mixing of the atmosphere following breakup of the nocturnal stable boundary layer. These observations at LDEO are consistent with diurnal patterns observed by others (8, 11). Weekly patterns were evident for data averaged over 1 year (Figure 5b). Both CFC-11 and CFC-12 increased rapidly from Sunday to Monday. Maximum mixing ratios were observed from Monday through

Wednesday. They begin to decrease on Thursday and reached minimum values on Sunday. The amplitude of the weekly cycle between the lowest and highest mixing ratios was approximately 2% (6 ppt) for CFC-11 and 4% (23 ppt) for CFC-12. Similar quasi-periodic weekly variations were also found in central Europe (8), but a maximum was observed on Thursday/Friday, and amplitudes were 20% (CFC-11) and 12% (CFC-12) between the highest and lowest mixing ratios. The lower amplitude at LDEO as compared to the central European site could be primarily due to temporal rather than spatial differences. Since the weekly cycle in the averaged CFC data is probably not due to weekly variation in atmospheric transport, it is more likely due to variations in industrial and commercial activities in the NY metropolitan area. Individual weekly trends based on daily mean values sometimes do not show the same quasi-periodic variations due to changing meteorological conditions. For the analyses of seasonal, weekly, and daily patterns, only 12 months of data from July 1996 through June 1997 were used.

To quantify the input function to groundwater for the NY metropolitan area requires knowledge of CFC mixing ratios in the past. However, no continuous atmospheric CFC measurements have been reported for the NY metropolitan area. One approach for estimating past atmospheric CFC mixing ratios would be to search for places, like sand dunes, where these gases might be archived (12). However, for the NY metropolitan area, this method is not feasible because no suitable locations for such measurement exist and because the atmospheric record derived by this method (mean age of 10 years) does not span the entire time interval of interest. Another approach to establish past atmospheric CFC excesses in this region would be to simultaneously measure other age dating tracers in groundwater that are not influenced by local

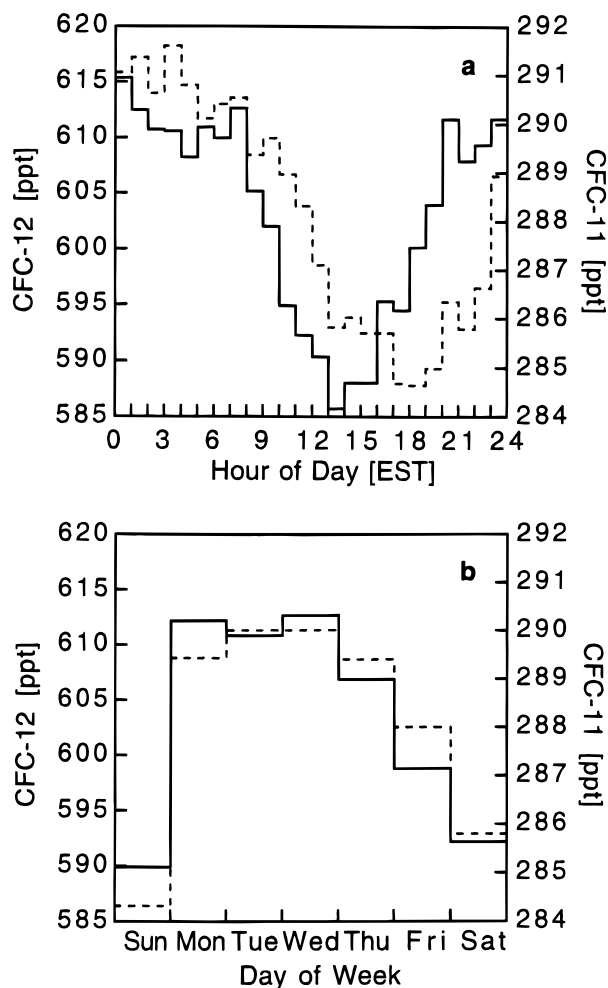


FIGURE 5. Averaged (a) diurnal and (b) weekly cycles of CFC-11 and CFC-12 from July 1996 through June 1997. Dotted line is CFC-11; solid line is CFC-12. Hours are reported in Eastern Standard Time (EST). The diurnal cycle results from break up of the nocturnal stable boundary layer, and the weekly cycle is most likely due to industrial and commercial activities in the NY metropolitan area. In the diurnal cycle, CFC-11 lags behind CFC-12, possibly indicating a more local source for CFC-12 than for CFC-11.

sources (e.g., tritium/ ^3He ; 2, 7). Then CFC excesses could be determined by calculating CFC mixing ratios in the past atmosphere assuming solubility equilibrium with measured groundwater CFC concentrations (6) and comparing them with those of the remote atmosphere. However, in addition to elevated emissions into the local atmosphere, point sources sometimes discharge contaminated water containing CFCs directly into surface and groundwaters. Hence, CFC concentrations measured in groundwater may not represent that achieved through solubility equilibrium with the local atmosphere. Evidence of CFC concentrations much greater than could be achieved by solubility equilibrium with the atmosphere has been found in both groundwaters (W. Aeschbach-Hertig, personal communication, 1996) and surface waters (13) within the NY metropolitan area.

Measurements of soil air indicate that high temporal variability of atmospheric CFC mixing ratios is smoothed by diffusion in the vadose zone (8). Hence, mean values of atmospheric mixing ratios should be representative of concentrations in the vadose zone. However, quantifying initial concentrations in groundwater (and hence the age) depends on knowledge of the thickness of the vadose zone and diffusion constants of CFCs in the soil (14). It is well-known that CFCs in groundwater sometimes deviate from

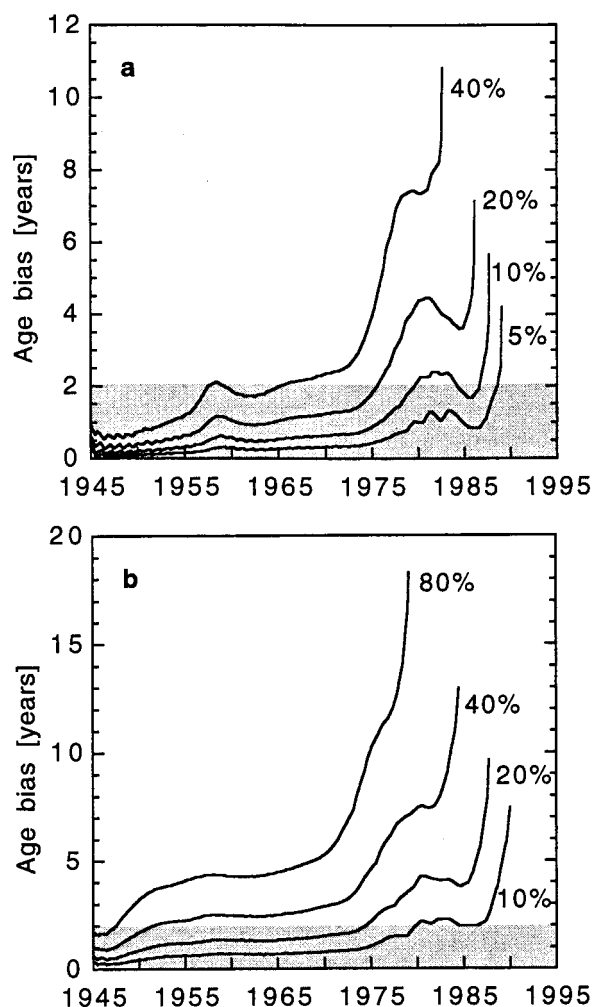


FIGURE 6. Potential age bias caused by excess CFCs if remote atmosphere (a) CFC-11 and (b) CFC-12 mixing ratios are used to calculate groundwater age near emission source regions. Age biases were calculated assuming constant excesses of 5, 10, 20, 40% (CFC-11) and 10, 20, 40, and 80% (CFC-12) above remote NH atmosphere mixing ratios (S. Walker, P. Salameh, and R. Weiss, personal communication, 1996) up to the year 1995.5. The generally assumed uncertainty (2 years) in groundwater dating with CFCs is indicated in gray.

equilibrium with the atmosphere. Elevated concentration in groundwater could be due to contamination associated with other organic contaminants (4) or sorption onto solids in the aquifer (15). Concentrations below the solubility equilibrium with the atmospheric mixing ratios are most likely due to in situ degradation by anaerobic bacteria (8, 16, 17).

Since atmospheric CFC mixing ratios are influenced by strong local emissions and regional-scale atmospheric mixing near large urban regions, the bias in groundwater ages created by assuming remote atmosphere values depends on the magnitude of CFC excesses and the year of groundwater recharge. If atmospheric CFC excesses near the NY metropolitan area in the past were the same as during 1996–1997, then the groundwater age bias is only moderate. However, if CFC-11 or CFC-12 excesses in the past were much greater than in 1996–1997, then apparent groundwater ages derived from CFCs, assuming remote NH atmospheric mixing ratios as the input function, would be considerably younger than actual ages (Figure 6a,b).

Since global production and emissions of CFCs were greater in the two decades preceding the CFC measurement

period presented here, atmospheric excesses in the NY metropolitan area were most likely greater as well. This conclusion is supported by observations in central Europe, where greater CFC excesses, reflecting greater production and emission, were observed for the period 1989–1992 (8). Given this greater local input function in the past and hence uncertainties in groundwater ages derived from CFCs in and near urban areas, the method may only be useful for resolving groundwater ages on decadal time scales in such regions. Under these circumstances, similar to methods based on tritium generated from atmospheric testing of nuclear weapons (“bomb” tritium), the presence of CFCs primarily indicates that groundwater contains significant components recharged within the past 50 years. To fully utilize CFCs for age dating of groundwater in such environments, direct measurements of atmospheric mixing ratios and knowledge of factors that control CFC input from the soil zone into groundwater will be necessary.

Acknowledgments

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