

Seasonal Variability and Long Term Trends of Chlorofluorocarbon Mixing Ratios in the Unsaturated Zone

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To investigate processes that might affect chlorofluorocarbon (CFC) mixing ratios at the water table, a time series was obtained of unsaturated zone soil gas CFCs to depths of ca. 4 m at a site near New York City (NYC). Observed CFC 11, 12, and 113 mixing ratios were lower in winter than expected from either a local, high-resolution time series or remote atmospheric mixing ratios. A diffusion model, which includes seasonal changes in soil temperature, moisture, and CFC solubility, reproduces to first order the observed soil gas mixing ratios for CFC 11 and 12. Underestimation by the model of the seasonal cycle of CFC 11 points to changing levels of sorption to soils due to seasonal changes in temperature as an additional cause of the cycle seen in CFC 11 mixing ratios in soil air. In the case of spring recharge, low CFC mixing ratios in soil air caused by increased solubility may result in low CFC 11 concentrations in groundwater and, when dating groundwater recharged before the 1990s with CFCs, older apparent ages by up to 4 years. Attempts to observe average atmospheric CFC levels from soil gas are also significantly hindered by these seasonal fluctuations. Our results indicate the importance of considering seasonal changes in soil temperature when making precise observations of even very moderately soluble gases in the unsaturated zone and shallow groundwater.

Introduction

CFCs (e.g., CFC 11 (CCl_3F), CFC 12 (CCl_2F_2), CFC 113 ($\text{C}_2\text{Cl}_3\text{F}_3$)) are anthropogenic gases, manufactured primarily as refrigerants, foam blowing agents, solvents, and propellants, which have been widely applied as transient tracers for dating of ocean water (e.g., refs 1, 2, 3, 4) and groundwater (e.g., refs 5, 6, 7, 8, 9, 10). Production and use of CFCs were controlled under the Montreal Protocol and Amendments, due to their

contribution to stratospheric ozone destruction. As a result, remote atmospheric mixing ratios for CFC 11, 12, and 113 have not increased since 1993, 2000, and 1993, respectively (11, 12), making application of CFCs as transient tracers for very recently recharged water almost impossible. However, CFCs continue to be used to date groundwater recharged before the 1990s due to their known performance and relative ease of measurement.

There are a number of additional factors that could potentially complicate the use of CFCs as transient tracers in groundwater studies. In areas with deep unsaturated soil zones, diffusive transport time from the surface to the water table may create significant bias in apparent groundwater ages (13). Degradation of CFCs has been observed in anoxic environments (e.g., refs 6, 14, 15). Elevated concentrations of CFCs in the atmosphere close to urban areas can cause bias in derived tracer ages (e.g., refs 6, 16). Absorption of CFC 11 and 12 to soils has been demonstrated in unsaturated soils with high levels of organic matter (17), which may affect CFC concentrations in groundwater. Variations in solubility of CFCs near shallow water tables due to soil temperature fluctuation may also potentially effect tracer ages (18). Contamination of waters by CFCs delivered to the environment from sources including landfills or septic tanks may also limit use of CFCs as tracers (e.g., refs 7, 10).

Oster et al. (6) performed extensive sampling of soil air CFCs over a time period of approximately one year and Engesgaard et al. (19) investigated some of the processes mentioned above through observation of deep soil profiles and modeling. However, no studies published to date have included both long-term monitoring of CFCs in soil air and of local atmospheric CFC mixing ratios. To investigate potential influences of processes occurring in the unsaturated soil zone on CFC mixing ratios above the water table, we collected a long (4.2 year) CFC time series in the unsaturated soil zone. A high-resolution atmospheric record of CFCs 11 and 12 collected nearby allows a simple diffusive transport model to be used to compare soil gas mixing ratios to those expected from various known processes. These results are interpreted with respect to environmental processes applicable to a variety of gases and the impact these processes may have on CFC ages determined for groundwater recharged before the 1990s.

Materials and Methods

Sampling Locations. Atmospheric time series for CFC 11 and 12 were collected at Lamont-Doherty Earth Observatory (LDEO) in Palisades, NY, approximately 25 km north of New York City on the west bank of the Hudson River. The majority of soil air CFC samples were collected in Sparkill, NY (41.03 ° N, 73.92 ° W), approximately 3 km to the northwest of Palisades. An additional 20 soil profiles were collected at 10 other sites in the region surrounding New York City. The Sparkill site is a wooded area approximately 1000 m² in size located adjacent to suburban developments. Soil at the site consists of fine-grained sand and silt with some clay-rich layers. Soil organic content is moderate and amounts to ca. 2 wt % near the surface and drops to ca. 0.3% below 1 m depth. Soil pH was approximately 6 at the surface increasing to 8 below 1 m depth.

Sample Collection and Analytical Methods. Soil air CFC samples were collected at 25 cm depth intervals using a commercial soil gas vapor probe (AMS Inc., American Falls, ID) with a stainless steel sampling tube driven to the desired depth. Single time point atmospheric samples were also collected during each sampling event. Samples analyzed for

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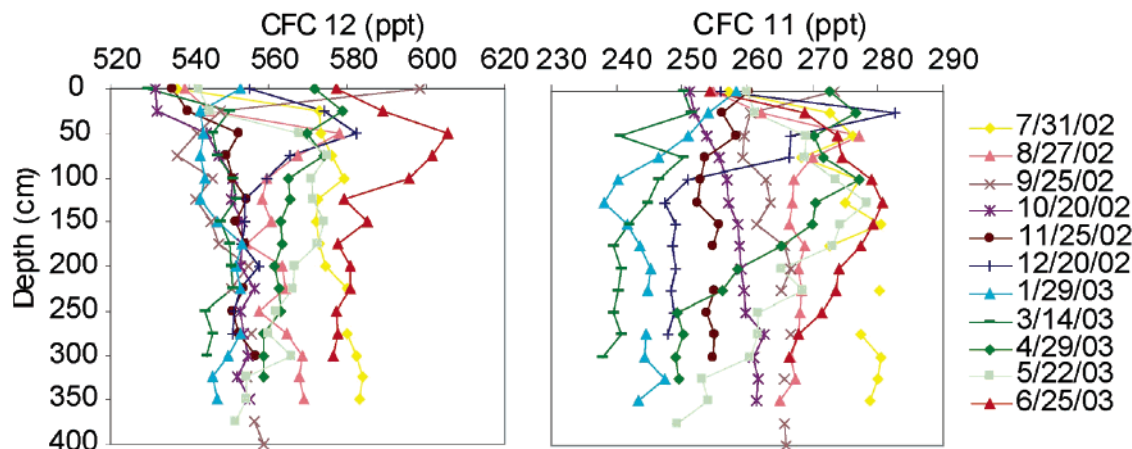


FIGURE 1. Yearlong series of profiles of soil gas mixing ratios of CFC 12 and CFC 11 in Sparkill NY (0 cm represents atmospheric sample).

CFCs were collected in wetted 50 mL ground glass syringes with polycarbonate stopcocks and analyzed within 12 h of collection. No statistically significant deviations were observed when air standards were stored for up to 12 h and analyzed in the same fashion as samples. Typically, reproducibility for duplicate CFC 11 and 12 soil air samples was close to analytical precision (on average within 1%). Averaged reproducibility for CFC 113 was 2%. Occasionally, disagreement between duplicates of up to 10% occurred, particularly when large gradients in mixing ratio with depth were present. This was attributed to mixing of soil air during sampling.

CFC air samples were analyzed with a cryogenic cold trap system and a gas chromatograph (GC) with electron capture detector (ECD) as applied by Smethie et al. (3). Several different analytical columns were used in this system, primarily DBVRX capillary and Krytox and Porisil B/Carbo-graph packed columns. Data for CFC 113 were fragmentary because, when using the DBVRX column, CFC 113 coeluted with dichloromethane, preventing accurate quantification. All CFC mixing ratios are reported on the SIO 98 scale (20).

Results and Discussion

Atmospheric CFC Mixing Ratios at LDEO and Sparkill. At LDEO, monthly average atmospheric CFC mixing ratios are elevated above remote atmosphere values as previously reported (16). From 2000 to 2003, annual average mixing ratios of CFC 11 and 12 at LDEO were approximately 4–5% higher than remote atmosphere levels as measured at Niwot Ridge, CO, (12). An important assumption in interpreting soil air data from Sparkill is that atmospheric mixing ratios are the same for the CFCs at Sparkill and LDEO. To test this assumption, mixing ratios from 45 single time point atmospheric samples collected at Sparkill were compared to mixing ratios obtained from an automated GC system at LDEO (16) at roughly the same time. Average mixing ratios for CFC-11 and CFC-12 at Sparkill were similar (within 2–3%) to those at LDEO. No local continuous atmospheric data are available for CFC 113. Thus, single time point air measurements could only be compared to remote atmosphere values. A number of atmospheric CFC 113 samples from Sparkill appear to have mixing ratios that are substantially (up to 11%) below those of the contemporary remote atmosphere (Supporting Information, Table 1). The reason for this observation is unknown as no analytical problems could be detected, no significant storage effects were observed as described above, and the standard was successfully calibrated annually against a master standard. However the quality of some of the CFC 113 observations may be compromised; hence CFC 113 fluctuations in soil gas are considered relative to atmospheric samples collected on the same day.

Soil Gas Mixing Ratios at Sparkill. For individual soil air profiles at Sparkill, CFC 11 and 12 mixing ratios varied more in the top 1 m compared to values below 2 m depth due to variations in atmospheric mixing ratios (Figure 1). Looking at a full year time series of profiles, below 2 m depth CFC 12 mixing ratios are less variable than at the surface consistent with observations for SF_6 (21) and for prior work on CFCs (6). However, looking at the same time period, soil gas mixing ratios for CFC 11 below 2 m are variable, more so than monthly average atmospheric mixing ratios from LDEO. Specifically, CFC mixing ratios in soil gas appear to have a seasonal cycle with values that are consistently lower than those observed in the atmosphere in winter (Figure 2, 3b). Average CFC 11 mixing ratios in soil air from 2 to 3 m depth over the entire time series were 3% below the average of the atmospheric record from LDEO. Despite the seasonal fluctuation, when averaged over periods of more than one year, CFC mixing ratios in the soil would be expected to be equal to those in the atmosphere. These small differences may be explained at least in part by the asymmetry of the seasonal cycle where mixing ratios are low in winter but only slightly elevated in summer. The trends for CFC 12 in soil air from 2 to 3 m at Sparkill and monthly mean air at LDEO over the period spanned by the time series are similar with values of -4.4 ± 1.7 and $-3.2 \pm 0.8 \text{ ppt year}^{-1}$, (\pm standard error), respectively. For CFC 11, trends in soil air mixing ratio were not significant ($0.6 \pm 1.8 \text{ ppt year}^{-1}$) while the atmosphere decreased by $-1.4 \pm 0.5 \text{ ppt year}^{-1}$ (\pm standard error). Over this same period, remote atmosphere trends for CFC 12 and CFC 11 were -0.2 ± 0.2 and $-2.1 \pm 0.1 \text{ ppt year}^{-1}$, respectively (12). The local atmospheric trend in CFC 12 is larger than that of the remote atmosphere while for CFC 11 both trends are similar indicating that despite the cessation of active use of CFC 12, significant local emissions continue, resulting in mixing ratios that differ from those in the remote atmosphere.

Over four annual cycles, CFC 11 and 12 mixing ratios measured at 2 m depth dropped during and slightly after winter to 9 ± 1 and $2 \pm 1\%$, respectively, below the local atmosphere values recorded at LDEO. For CFC 113, lower mixing ratios (by about 7%) were also observed in soil gas during winter but the limited number of data points prevented the difference between the soil and atmospheric observations from being significant (Supporting Information, Table 1). In addition, during 2002, 1,1,1 trichloroethane (TCA), a common solvent, was also measured (Supporting Information, Table 2). Elevated mixing ratios of TCA in soil air at depth indicated contamination of the underlying groundwater, confirmed by high levels in nearby surface waters. TCA values were variable, perhaps due to this contamination. However, a pattern similar to that of CFCs was observed

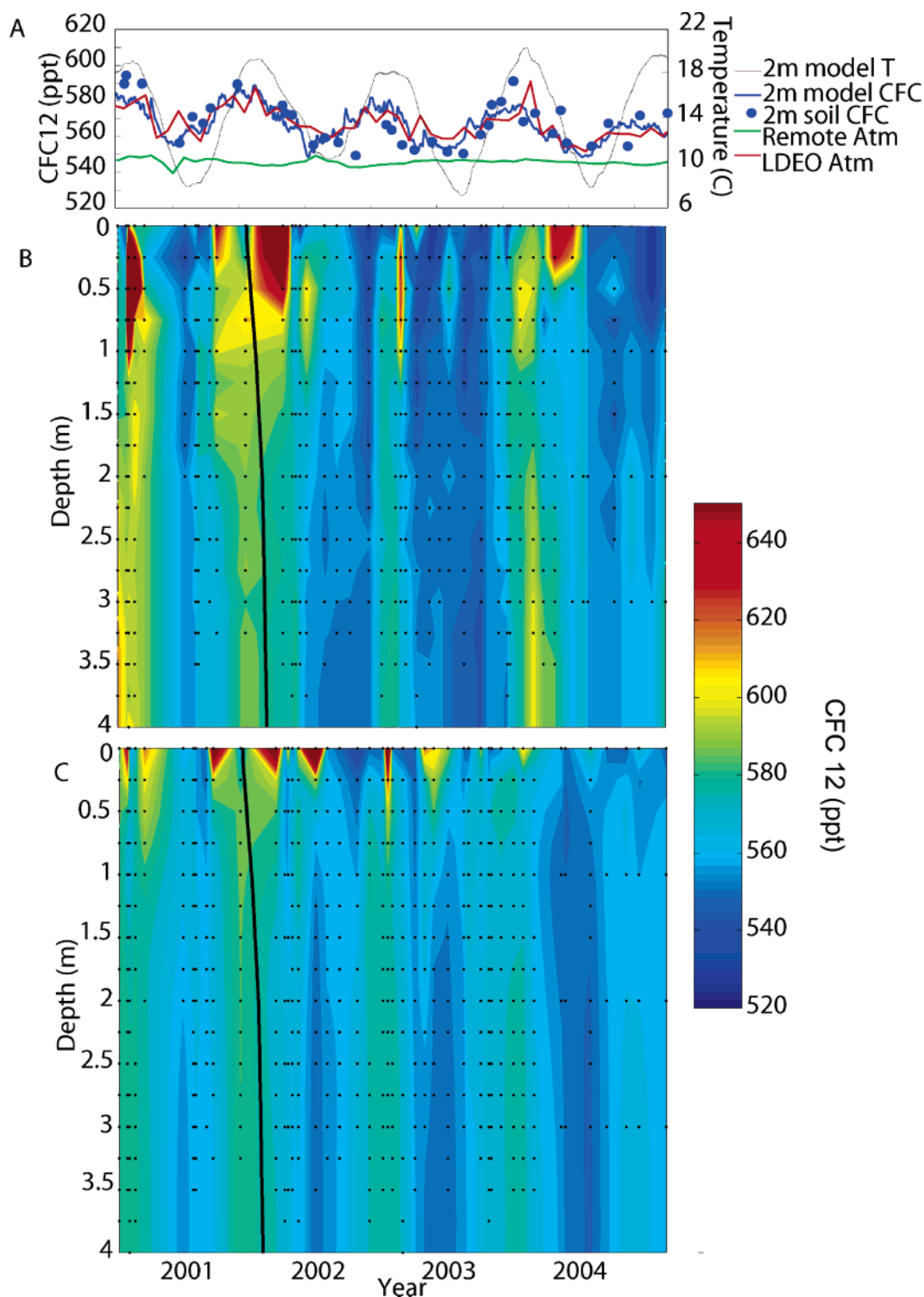


FIGURE 2. CFC 12 soil gas observations and model results. (A) Modeled 2 m soil temperature and mixing ratios compared to observed mixing ratios in soil at Sparkill, the atmosphere at LDEO and in the remote northern hemisphere; (B) time series of all CFC 12 observations at Sparkill; (C) model output sampled at the same time and depth intervals as observations. Solid line at 2001.5 represents the typical diffusive travel time with depth derived from the model.

with higher values in summer and lower ones in winter with the latter falling below atmospheric mixing ratios by around 40%. In contrast, at the same site, sulfur hexafluoride (SF_6), an inert gas of primarily anthropogenic origin, showed soil air mixing ratios very similar to monthly average mixing ratios at LDEO (21).

Deficits in unsaturated zone CFCs similar to those observed at Sparkill were also reported in air samples from a number of vapor wells at sites near Mirror Lake, New

Hampshire (18). Samples collected in winter from multiple locations and depths varied considerably but had, on average, mixing ratios that were 9 and 10% below remote atmospheric values for CFC 11 and 113, respectively, while CFC 12 mixing ratios were close to those of the remote atmosphere. Summer mixing ratios for all CFCs were generally similar to remote atmosphere values. These winter deficits were speculated to be due to increased solubility of CFCs at lower temperatures resulting in increased partitioning into the aqueous phase.

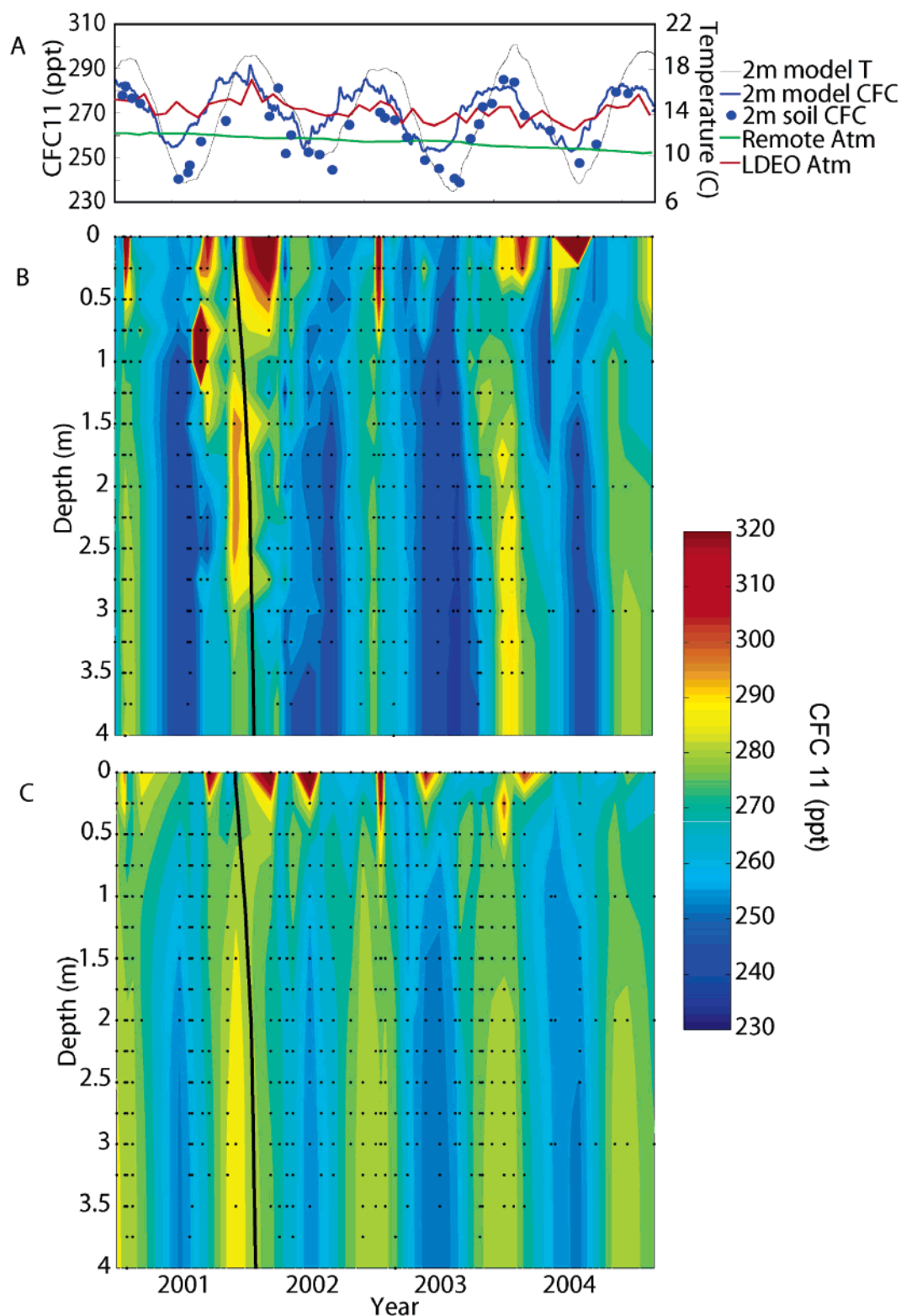


FIGURE 3. CFC 11 soil gas observations and model results. (A) Modeled 2 m soil temperature and modeled mixing ratios compared to observed mixing ratios in the soil at Sparkill, the atmosphere at LDEO and in the remote northern hemisphere; (B) time series of all CFC 11 observations at Sparkill; (C) model output sampled at same time and depth intervals as observations. Solid line at 2001.5 represents the typical diffusive travel time with depth derived from the model.

Solubility effects might also explain the variation seen in the Sparkill time series.

Soil Gas Measurements at Other Sites. Soil gas measurements were made at a number of other sites in and around NYC for CFC 11, 12, and 113 from 2002 to 2003. The purpose of this sampling was to attempt to observe the spatial extent of elevated levels of these gases around NYC. Observation of

soil gas SF_6 levels has been previously established as a method for determining average atmospheric SF_6 mixing ratios (21).

Soil gas mixing ratios for CFC 11 and 12 were, in part, dependent on the distance of the sampling site from NYC (Figure 4 a, b). Data from the Sparkill time series are plotted at 35 km from NYC. Samples taken during the summer and winter seasons at all sites show variability similar to that

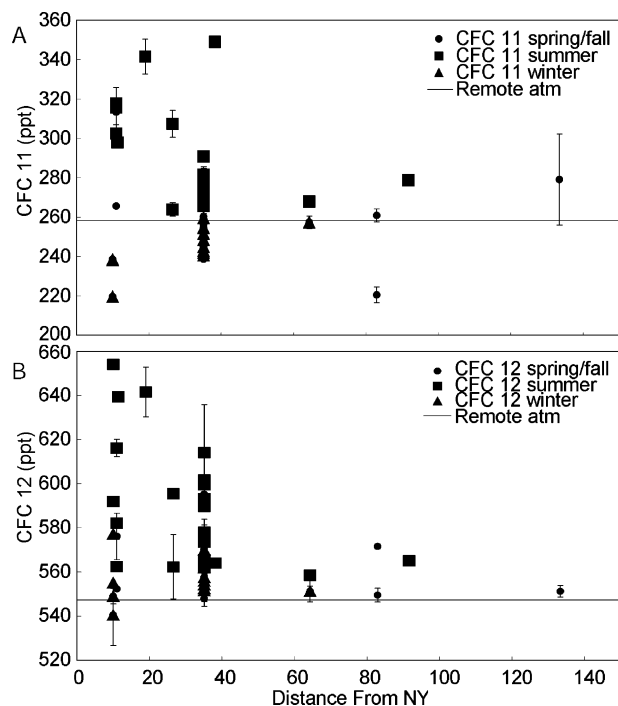


FIGURE 4. Plots showing 2–3 m depth averaged (A) CFC 11 and (B) CFC 12 soil gas mixing ratios with distance from NYC for various seasons, error bars are \pm one standard deviation of depth averaged value.

seen at Sparkill. Data for CFC 113 were too fragmentary to interpret by distance from NYC, but as at Sparkill, low values were more often observed at sites sampled during winter and high values during summer. Unlike for SF_6 , large seasonal variability makes single observation of CFCs in soil gas of limited utility in determining atmospheric levels at individual sites. As a result, these data can only be interpreted in a very generic fashion, CFC mixing ratios decrease as a function of distance from NYC and appear to drop to values close to those observed in the remote atmosphere within a distance of ca. 100 km of NYC.

Modeling of Soil Gas Mixing Ratios. To test whether solubility equilibrium can explain the observed CFC variation, soil gas mixing ratios were modeled for CFC 11 and 12 using a simple 1D diffusion model of the 4 m unsaturated zone at Sparkill. This model reproduces measured SF_6 mixing ratios in soil air at the same site (21). However the original form of the model smoothes the atmospheric input function but fails to reproduce the observed CFC variability in soil air. To reproduce the seasonal cycle, an air/water partitioning coefficient which varies with seasonal temperature fluctuations was included in the model.

Soil temperature and moisture time series were first estimated for the site using the widely applied 1D simultaneous heat and water model (SHAW) (22). Local meteorological data (air temperature, precipitation, solar radiation, daily wind run), site soil properties, and typical parameters for leaf area were used as input for the model which then calculates heat and moisture transport. Model output generally matched soil temperatures observed at 1 m depth in 2000 at Black Rock Forest, 55 km north of Sparkill and one soil temperature profile collected at Sparkill in 2004, although modeled temperatures in warmer periods appear to be uniformly 3 °C higher than the observations. A model run for CFC 11 with temperature linearly scaled to better match observations tested sensitivity of the model to this mismatch. Results obtained with the two temperature models were found to differ by only a few ppt, so the original temperature model results were retained for consistency (Figure 5 a).

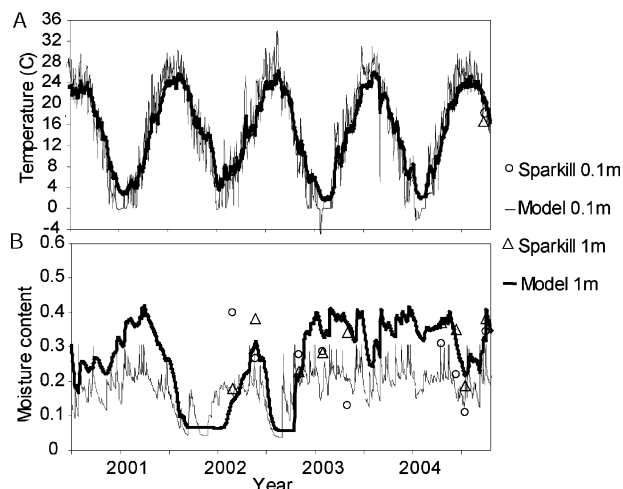


FIGURE 5. Plots of (A) soil temperature and (B) soil moisture output from SHAW model at 0.1 and 1 m depth compared to observations from Sparkill NY.

Modeled soil moisture also generally matched profiles collected to a maximum depth of 1.5 m in Sparkill at various times in 2002–2004 (Figure 5b), as well as surface moisture values from Black Rock Forest. From soil temperature, solubility coefficients were calculated according to Warner and Weiss (23) and used to determine air/water partitioning for each gas.

SF_6 soil gas mixing ratios produced by this model are almost identical to those of the original diffusion model due to the very low solubility of SF_6 in water (24). To a first order, the modified model reproduces the annual patterns observed in soil gas mixing ratios for CFC 11 and CFC 12 at Sparkill (Figures 2c, 3c). The modeled magnitude of annual variability of the CFC 11 mixing ratios at 3 m depth of around 10% (winter to summer) is close to that predicted by Goode (18) (approximately 9%) using a similar model. The observed rate of change of mixing ratio with depth is also consistent with that predicted by the model (Figures 2b, 3b). The model reproduces some of the interannual variability of the seasonal cycle in the mixing ratio. For example, the winter of 2001–2002 was warmer than that of 2000–2001, and both modeled and observed CFC 11 mixing ratios were higher during this winter. Some of the asymmetry of the summer/winter anomalies is reproduced and can be explained by the generally lower soil moisture content of soils during summer. However, while there is fairly good agreement between observed and simulated CFC 12 mixing ratios for winter, the simulated CFC 11 mixing ratios for winter are consistently higher than those actually observed. The simulations produce deficits of only ca. 6% below local atmospheric levels compared to the observed 9% signal.

The discrepancy between the simulations and observations are most likely due to processes not included in the model. One possibility is that soil/water partitioning, which is constant in the model, changes with temperature and thus affects soil–air mixing ratios. Projecting from studies performed on low organic content aquifer materials (25), it can be expected that the degree of sorption increases from CFC 12, to CFC 11, to CFC 113. We estimated the corresponding soil/water partition coefficients to be 0.0, 0.02, and 0.1, respectively. TCA has a soil/water partition coefficient in saturated low organic sediments of around 0.28 (26). Sorption of neutral compounds is expected to vary with temperature in a manner proportional to solubility (27). Air/water partitioning changed with a 5 °C temperature change by approximately 30%, and similar variability might be expected for soil/water partitioning. The effect this has on soil air

mixing ratios can be tested using a simple mass balance calculation for a closed system.

If equal volumes of air and water with typical CFC mixing ratios in a confined space were equilibrated from a temperature of 15 °C to 10 °C, the air mixing ratio would decrease by approximately 7% and 2% for CFC 11 and 12, respectively. On the basis of their solubility (28, 29), CFC 113 and TCA mixing ratios would decrease by 3% and 13%, respectively. These changes in CFC 11 and 12 mixing ratios are similar to seasonal variation estimated with the diffusion model. The effect of temperature change on an air/water/soil system was calculated in a similar way. Partition coefficients for soil/water, assuming a 30% increase in soil/water partitioning for every 5 °C, were calculated based on those determined by Ciccio et al. (25). A soil phase twice the volume of the air and water phase with soil density similar to that found in Sparkill was assumed. This system results in a decrease in mixing ratios during reequilibration of 10% and 2% for CFC 11 and 12, respectively, and 8% and 30% for CFC 113 and TCA, respectively. The deficit in CFC 11 mixing ratios becomes closer to that actually observed when soil/water partitioning varies with temperature. Being very weakly sorbed, CFC 12 mixing ratios remain unchanged. The expected deficits for CFC 113 and TCA should be more than double due to strong sorption to soils and are comparable to observations from Sparkill. However, no attempt was made to incorporate variation of sorption with temperature into the diffusion model as levels of CFC sorption with varying soil moisture, organic material, and temperature are not well-known.

Influence on Groundwater Ages. These results indicate that changes in water/soil partitioning with temperature can have a significant effect on mixing ratios of soil gases and dissolved levels of CFCs. Within the uncertainty of our observations, there is no evidence for degradation of CFCs in the unsaturated soil zone at this site; CFCs behave conservatively in aerobic soil air as expected. Deviations of mixing ratios from atmospheric levels can be explained by changes in CFC solubility and possibly sorption with temperature. Goode (18) predicted that, assuming constant infiltration, temperature fluctuations at the top of the capillary fringe greater than 5 °C will have a significant effect on groundwater ages. Typically temperature variation of this magnitude occurs at depths less than 3–4 m. Under these circumstances, the nonlinear nature of CFC solubility as a function of temperature causes a greater dissolved CFC concentration than that expected at the average temperature, resulting in younger groundwater ages. Fluctuations in soil air CFC 11 mixing ratios in this study are somewhat larger than predicted by Goode (18), and this may be explained by sorption. However, the seasonal variations in dissolved CFC concentrations are expected to remain similar to those predicted by Goode (18) as additional CFCs lost from the air are taken up by the solid phase. Hence dissolved CFC 11 concentrations will be similar to those predicted by Goode (18), differing from isothermal conditions by 10% or up to a 5 year bias toward younger age in the extreme case of a 20 °C cycle in temperature.

If recharge is episodic, the effect of soil temperature variation on groundwater ages will be different. In the case of Sparkill, from SHAW model results (as well as for many sites in general), infiltration to the water table would be at a maximum during spring. At this site, soil gas CFC mixing ratios are low relative to the atmosphere over most of the spring. This results in lower dissolved concentrations at the water table than would be expected if water reached equilibrium with the atmosphere. CFC 11 mixing ratios at 4 m depth are on average ca. 5% below atmospheric mixing ratios over the spring season. For pre-1990s recharge, equilibrium with this atmosphere results in apparent ground-

water ages 0–4 years older than ideal ages depending on the year of recharge. These low soil air CFC mixing ratios in spring cancel out the increase in dissolved concentrations described previously (18) to different extents depending on the depth of the water table. As described above, a water table at the surface would result in roughly 10% elevated CFC 11 concentrations and younger groundwater ages (18). For a water table at 10 m depth the soil temperature would remain almost constant and the soil air model predicts a seasonal cycle in CFC mixing ratio less than half the size of that for a 4 m water table with a correspondingly smaller effect on dissolved CFC concentration and CFC-derived groundwater age. Seasonal cycles in soil air CFC mixing ratios will have the most significant effect on dissolved CFC concentration and groundwater age in systems with water tables in the range of 2 to 8 m. In practice, deviations in groundwater age may be smaller than expected due to dispersion and gas exchange at the water table after recharge.

Perspective. Mixing ratios of CFCs in soil gas are influenced significantly by seasonal variations in soil temperature, which causes variable partitioning between different phases of the unsaturated zone. The magnitude of this effect is dependent on the solubility and possibly soil/water partitioning of the gases. Results of our study indicate that inclusion of variable soil sorption effects into the model used to obtain these results would be desirable and may be necessary to accurately represent the behavior of compounds with higher sorption coefficients. In an aquifer with a water table shallow enough to experience significant temperature variation, changing CFC partitioning into soil moisture can have a significant effect on dissolved CFC levels and, hence, groundwater age. These biases can significantly increase the apparent uncertainty of CFC tracer ages in shallow aquifers. As different CFCs are affected by temperature variation to different extents, this process adds an additional source of discordance to the suite of CFC tracer ages. Similar effects to those described here might prevent precise reconstructions of atmospheric gas concentrations from soil measurements for other gases with similar or higher solubility.

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Supporting Information Available

Table summarizing TCA and CFC 113 observations and comparison to atmospheric single time point samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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