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Distribution of Atmospheric SF_6 near a Large Urban Area As Recorded in the Vadose Zone

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Local emissions of SF_6 are of interest for studying their impact on the use of SF_6 as a groundwater-dating tool near source regions as well as for investigating the spatial distributions of (inert) gaseous compounds spreading from urban or industrial centers. A precondition for the use of SF_6 in such studies is the capability to document the temporal and spatial evolution of SF_6 in and around source regions with sufficient resolution. Here we present a time series of SF_6 measurements in soil air at a site (Sparkill, NY) about 25 km north of New York City carried out between May 2000 and January 2002. The data show that, below about 2 m depth, the vadose zone integrates atmospheric SF_6 mixing ratios over time scales greater than 1 month. SF_6 mixing ratios in soil air at these depths match averaged high-resolution atmospheric measurements performed at Lamont-Doherty Earth Observatory in Palisades, NY, located about 3 km south of Sparkill. To a first-order approximation, a simple one-dimensional diffusion model reproduces the measured SF_6 profiles in the vadose zone, suggesting that the soil indeed acts as a low-pass filter for inert atmospheric gases. These findings indicate that measurements of soil air can be used to determine the spatial pattern of SF_6 excess relative to the remote atmosphere for a given region. A transect of soil profiles from Manhattan to the tip of Long Island indicates that emissions from sites close to New York City lead to significant SF_6 excesses (ca. 25% or more) above the clean air mixing ratios over distances of the order of 80 km.

Introduction

Sulfur hexafluoride (SF_6) has been used in recent studies to investigate the dynamics of natural systems including continental waters, the ocean, and the atmosphere. For these studies SF_6 can either be applied as a transient tracer (e.g., refs *1* and *2*) or as a deliberately released tracer (e.g., refs *3*−*5*). One recently developed application is its use as transient tracer for quantification of the spreading and mixing of young groundwater (recharged during the past 20−30 yr) (*1*). These waters generally contain SF_6 that has been added by gas exchange with the soil air at the water table.

In principle, SF_6 should be ideally suited for use in dating of groundwater because it has small natural sources (*6*−*8*), no degradation has been observed in natural waters, tracer studies have found no evidence so far of SF_6 retardation by interaction with aquifer material (*5*, *9*, *10*), it can be detected at very low levels with high precision using a gas chromatograph equipped with an electron capture detector (ECD) (*1*, *11*), and it has increased in the atmosphere at a considerable rate (7−8% yr^{-1}) for the past 20 yr (*6*, *12*). However, for quantitative use of SF_6 as a transient tracer in studies of groundwater movement, the evolution of its mixing ratio at the water table has to be known quantitatively. This requires the knowledge of both the atmospheric mixing ratio and the transfer through the vadose zone to the water table.

Whereas the clean air mixing ratios of SF_6 are fairly well documented (*6*), the perturbation caused by local emissions is less well-studied. Available data indicate that there are significant excesses above clean air mixing ratios in the vicinity of large urban areas (*13*). A good fraction of these excesses are caused by the use of SF_6 by the electrical power industry in high-voltage gas-insulated switchgears (GISs) and transmission lines from where it leaks into the atmosphere (*6*). Since urban centers have high population densities and hence large cumulative demand for electricity, there are also more GISs in and near these areas and more sources delivering SF_6 to the atmosphere. Using a high-resolution time series of atmospheric SF_6 near a large urban area, Ho and Schlosser (*13*) showed that strong local emissions and regional-scale atmospheric mixing cause substantial short-term temporal variability in atmospheric SF_6 mixing ratios. Additionally, these effects cause SF_6 mixing ratios to be, on average, appreciably higher than those in the remote atmosphere (e.g., 102% excess at a site close to New York City in 2000−2001; Figure 1).

To use SF_6 as a groundwater dating tool in these environments, it has to be ensured that there is no or little SF_6 excess above clean air mixing ratios in the recharge area of the aquifer, or the input function has to be defined explicitly. Assuming remote atmosphere mixing ratios in groundwater dating studies for regions with atmospheric excess SF_6 mixing ratios produces apparent groundwater ages that are younger than the actual age or sometimes even prevents the determination of an age. To achieve better understanding of the impact of local emissions on SF_6 mixing ratios around a source region, its distribution has to be measured at multiple locations over time. This task could be accomplished by deploying many instruments that measure atmospheric SF_6 at high temporal resolution. However, such a strategy would require considerable resources, with the potential problem of contaminating the time series by locating the instruments too close to local emission points. Alternatively, natural archives that integrate SF_6 over time scales that are long as compared to the high-frequency variability in atmospheric SF_6 mixing ratios (e.g., weeks to months) could be used. One such potential archive is the vadose zone (e.g., refs *14* and *15*).

In this study, we examine the suitability of the vadose zone as a short-term archive of atmospheric SF_6 at several locations in and around New York City (NYC) as well as a remote location at Winthrop, ME. The sites were chosen to capture the expected large gradients between a city center

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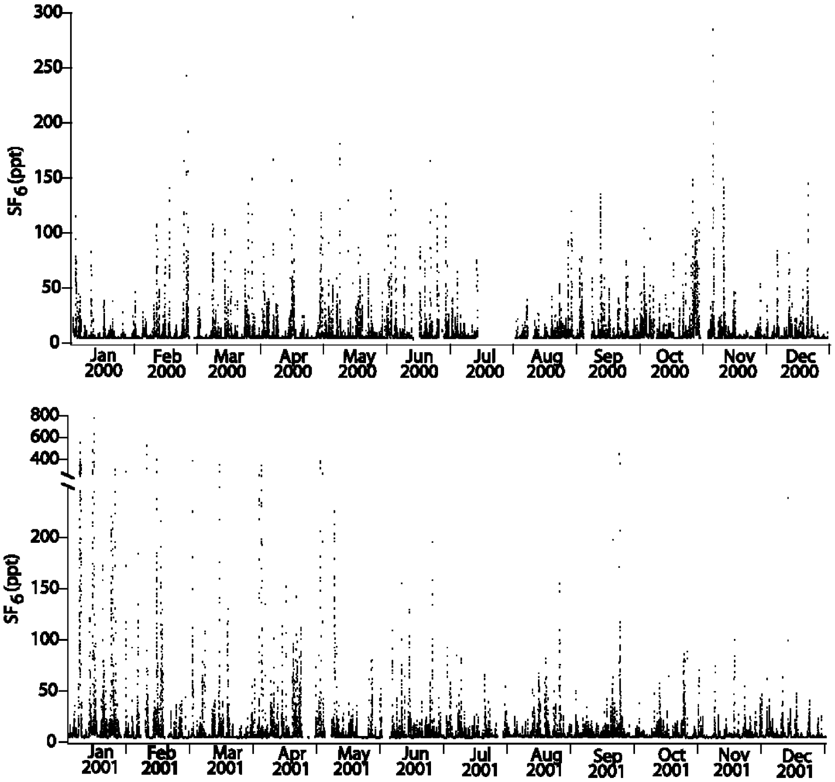

FIGURE 1. Plot of atmospheric SF$_6$ measured at LDEO in 2000/2001.

and a rural site. Additionally, at one site (Sparkill, NY), long-term observations were performed to obtain a comparison to simultaneous high-resolution atmospheric SF$_6$ measurements performed at Palisades, NY. To support our hypothesis, the measurements are compared to model simulations of SF$_6$ profiles in the soil using prescribed (i.e., measured) atmospheric mixing ratios as input to a simple box model. The data show that SF$_6$ measurements in the vadose zone can be used to determine how large an area is affected by local SF$_6$ emissions. This information is important for dating of groundwater as well as for atmospheric mixing studies.

Experimental Section

Sampling Locations. To prove the concept described in the Introduction, SF$_6$ from soil air was sampled at four locations in and around a large urban area (Central Park and Riverside Park in NYC; Palisades, NY; and Sparkill, NY) and at a rural location (Winthrop, ME) (Figure 2). These sites had elevations of approximately 12, 15, 115, 16, and 66 m, respectively. Additionally, a transect stretching from New York City to the eastern tip of Long Island was sampled to estimate the distance over which the SF$_6$ emissions represent a significant perturbation of the clean air values.

The 31 counties of the New York Consolidated Metropolitan Statistical Areas (CMSA), which include northern New Jersey, Long Island, southeastern Connecticut, and one county in Pennsylvania, had a population of 21.2 million in 2000. New York City had a population of 8 million in 2000, whereas the population of the two other sampling sites on the west bank of the Hudson River 25 km north of New York City were both smaller. The Orangeburg CDP (census-designated place), which contains both Palisades (41.00° N, 73.91° W) and Sparkill (41.03° N, 73.92° W), had a population of 3388 in 2000. The rural site, Winthrop, ME (44.32° N, 69.96° W), 16 km west of Augusta, ME, had a population of 2893 in 2000, and its nearest neighbor had a population of only 18 560 in 2000.

In addition to the soil air measurements, continuous high-resolution atmospheric SF$_6$ measurements were performed at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University in Palisades, NY.

Soil Air Sample Collection. Soil air samples were collected using a commercially available soil vapor probe, consisting of sections of steel pipe (1.5 cm o.d.) with a retractable stainless steel tip. The tip was connected to a length of stainless steel tubing (3.175 mm o.d.) inside the probe, and soil air was drawn through the tubing. During sampling, the probe was driven into the soil to the desired depth, and the tip was retracted to expose a screen. A 60-mL nylon syringe with a three-way polycarbonate stopcock was connected to the tubing, and 100 mL of air was drawn into the syringe and out of the stopcock in order to flush tubing and syringe. Finally, a 50-mL soil air sample was taken. This sampling method was chosen in preference to permanently installed sampling devices because it allows us to perform rapid surveys in a variety of regions without implementation of extensive infrastructure. Additionally, the method allows adjustment to changing large-scale atmospheric conditions and does not require control of the sampling sites to avoid vandalism of the soil probes. Using a global positioning system (GPS), we can return to each site and obtain another soil profile within a radius of a few meters of the original site.

Each depth was sampled for SF$_6$, and a duplicate sample was taken for every fourth sample. Duplicate samples were collected by first flushing the syringe with 50 mL of soil air and then collecting the actual sample. Consequently, a single soil air sample for SF$_6$ measurement required 150 cm^3 of gas, whereas a duplicate sample required 250 cm^3. The probe was then driven to a greater depth, and the procedure was repeated. Assuming a porosity of 0.3, typical for sand (*16*), the soil volume affected by the collection of one set of samples (including a second 50-mL sample collected for measurement of CFCs that are not discussed here) is about 830 cm^3 for the first set of samples and 1500 cm^3 for the duplicates (i.e.,

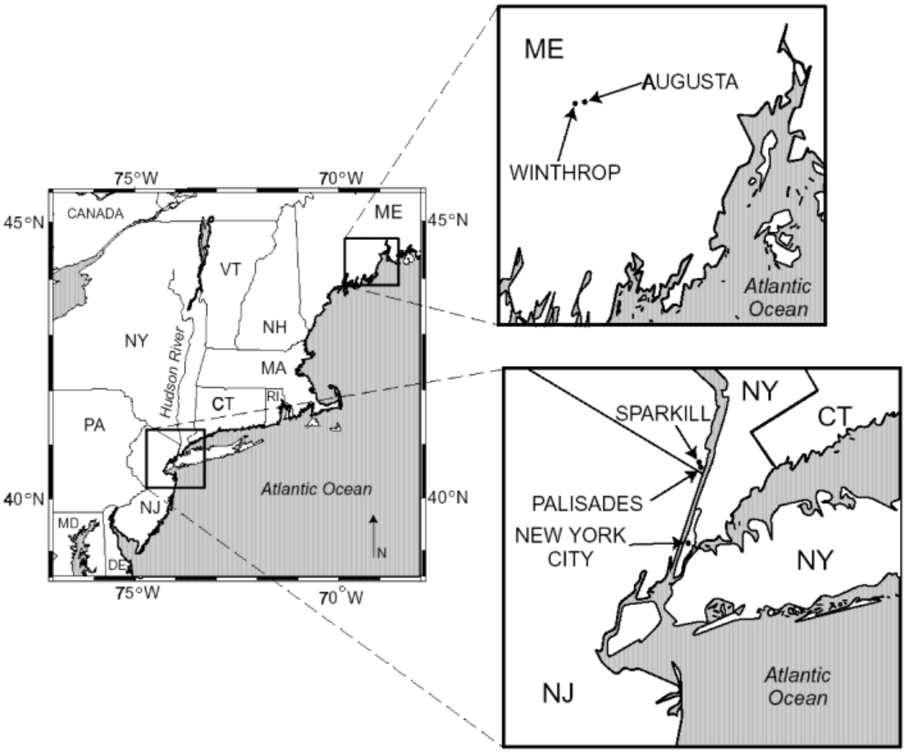

FIGURE 2. Map showing soil air SF_6 sampling locations.

spherical volumes with a radius of about 6 and 7 cm, respectively).

Approximately one-third of the samples from Palisades, NY, was taken using 50-mL glass syringes. Comparison of samples collected in glass and nylon syringes after several hours of storage showed no significant difference in SF_6 mixing ratio. In the nylon syringes, the mixing ratio of SF_6 standard (25.3 ppt) changed by less than 1% when stored for several hours and less than 2% after 2 d. All analyses used in this study were performed within 9 h of sample collection and should not be affected significantly due to storage effects.

Soil Air Sample Measurement. Soil air samples were analyzed for SF_6 by pushing the gas through a drying column of $Mg(ClO_4)_2$ into a sample loop. Subsequently, the samples were injected into a gas chromatograph equipped with an electron capture detector (ECD) by ultra-high-purity (99.999%) N_2 carrier gas. The SF_6 was separated from other gases at room temperature with a molecular sieve 5A column. A standard was analyzed after every 5−10 samples, and consecutive standards were used to bracket the intervening soil air samples. Continuous high-frequency atmospheric SF_6 measurements at LDEO in Palisades, NY, are discussed in Ho and Schlosser (*13*). SF_6 mixing ratios are reported on the NOAA SF_6 scale (*12*).

Results and Discussion

Individual Soil Air SF_6 Profiles. All depth profiles of SF_6 obtained from sites at Central Park, Riverside Park, Palisades, and Sparkill show considerable variability above 1− 2 m depth, reflecting the high temporal variability in atmospheric SF_6 (Figure 3a−d). Below 2 m depth, the SF_6 mixing ratios at Sparkill and Winthrop are relatively constant. For the Palisades, NY, data collected in 2000, the mean SF_6 value below 1 m depth is $\approx$8.7 ± 1.0 ppt. This value agrees well with the year 2000 annual mean of 8.9 ± 0.1 ppt. The annual mean was calculated from almost 38 600 atmospheric measurements at the same site, and the uncertainty is the standard error of the mean, which is similar to the sample handling and analytical error determined from SF_6 data obtained during a period of several hours when SF_6 mixing ratios were low and assumed to be constant. Because of the shallow soils, sampling to a depth greater than 1.5 m was not possible at the Palisades site.

The relatively few measurements of SF_6 from soil gas samples collected in Central Park show a larger excess over the remote atmosphere with mixing ratios of 15.4 ± 1.5 ppt at depths greater than 1m. The SF_6 versus depth profiles obtained from Central Park show significant variation on the basis of location within the park as well as some systematic change with time. Further study is needed to fully understand the Central Park SF_6 mixing ratios. A small number of measurements from Riverside Park also show significant excesses of SF_6. The average SF_6 mixing ratio measured below 1 m was 9.6 ± 1.7 ppt (i.e., significantly lower than those in Central Park), indicating that large spatial atmospheric SF_6 gradients might exist within New York City. Winthrop, ME, on the other hand, had soil air SF_6 values of about 4.8 ± 0.2 ppt at depths below 1 m. These values are very close to the SF_6 mixing ratios in the remote atmosphere at the time of sampling (4.8 ppt in Niwot Ridge, CO). This is likely due to much lower population density and hence fewer point sources for SF_6.

Time Series at Sparkill. To test reproducibility as well as long-term trends that can be compared to the direct atmospheric measurements from Palisades, we established a time series at Sparkill consisting of 34 profiles collected between May 2000 and January 2002 (Figure 4). At this site, the mixing ratio of SF_6 in soil gas at depth tended to be slightly lower than the average atmospheric mixing ratio measured at LDEO. However, the averaged value for all samples below 1 m of 8.7 ± 1.7 ppt is in reasonable agreement with the average of the atmospheric record for 2000−2001 (9.7 ± 0.1 ppt) (Table 1). The large deviation of the average value for the Sparkill soil samples is related to systematic variations of the SF_6 mixing ratio in the soil. The lower SF_6 value in the soil samples from Sparkill as compared to the atmospheric

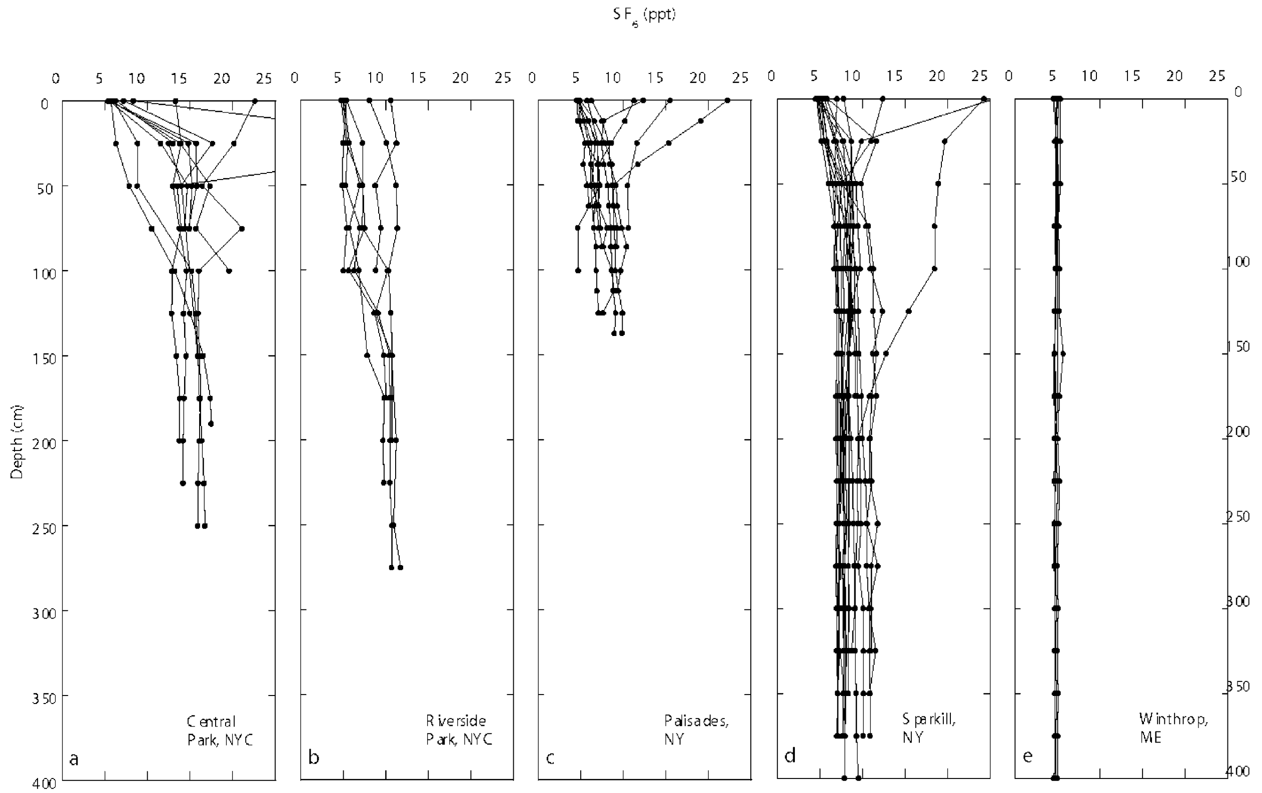

FIGURE 3. Plots of measured SF_6 mixing ratio vs depth for the sites in (a) Central Park, New York City; (b) Riverside Park, New York City; (c) Palisades, NY; (d) Sparkill, NY; and (e) Winthrop, ME. The remote atmosphere (Niwot Ridge, CO) SF_6 mixing ratio at the time of measurement was about 4.8 ppt.

TABLE 1. Mean SF_6 Mixing Ratios and Their Variability in Soil Air at the Five Sampling Sites

location	depth (cm)	mean[a]	σ[a]	N[b]	max/min value	sampling period
Central Park, NYC	>50	15.0	2.2	51	7.9/21.1	3/01–3/02
	>100	15.4	1.5	32	13.3/19.7	
	>200	15.8	1.3	10	14.2/17.5	
Riverside Park, NYC	>50	9.0	2.0	43	4.9/11.8	2/01–2/02
	>100	9.6	1.7	30	5.0/11.8	
	>200	10.7	0.6	10	9.7/11.8	
Palisades, NY	>50	8.2	1.2	50	5.8/10.4	3/00–4/00
	>100	8.7	1.0	16	6.8/9.9	
	>200				no data	
Sparkill, NY	>50	8.9	2.7	454	5.6/39.3	5/00–2/02
	>100	8.7	1.7	384	6.2/18.5	
	>200	8.6	1.2	248	6.8/11.8	
Winthrop, ME	>50	4.8	0.2	53	4.8/5.4	11/00–7/01
	>100	4.8	0.2	43	4.8/5.4	
	>200	4.8	0.1	26	4.8/5.0	

[a] Mean and standard deviation (σ) of SF_6 mixing ratios given in ppt. [b] Number of samples.

measurements at LDEO might be due to small differences in the atmospheric SF_6 mixing ratios between Sparkill and LDEO. Between January and March 2001 when deviation between soil gas and atmosphere was especially high, a snow cover was present at Sparkill for an extended period. One possible explanation for the deviation is that the snow cover and ice lenses that most likely were embedded in it reduced the transfer of SF_6 from the atmosphere to the vadose zone, resulting in SF_6 mixing ratios in the soil gas that were lower than expected under snow-free conditions. In addition to deviations from the annual average, discrete atmospheric SF_6 samples from Sparkill sometimes deviate from atmospheric SF_6 mixing ratios measured at LDEO. Comparison of measured values from depths below 2 m to various running means (30, 90, and 150 d) of the atmospheric SF_6 mixing ratios indicates that the mean time scale for soil air exchange is greater than 30 d (Figure 5).

Model Simulations. Qualitative interpretation of the measured profiles suggests that soil is a good short-term archive for atmospheric SF_6 with the capability of low-pass filtering the high frequencies observed in the atmosphere. However, to check for consistency between our observations and known physical transport through the soil, we used a simple model to test our hypothesis on the basis of numerical simulations. The model is a one-dimensional finite difference model of the vadose zone. Its design is based on the equations for transport in soil similar to those described by Cook and Solomon (*17*) and Weeks et al. (*18*). Weeks et al. demonstrated that such models can be successfully used to estimate soil gas transport (*18*). The model consists of 17 boxes with the

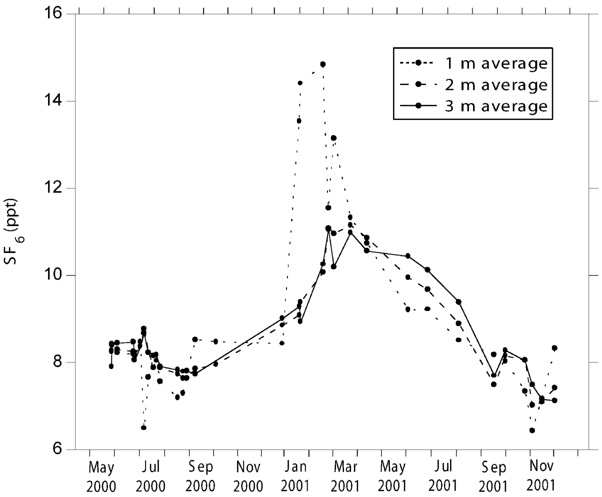

FIGURE 4. Time series of the SF$_6$ mixing ratio in soil gas at Sparkill, NY.

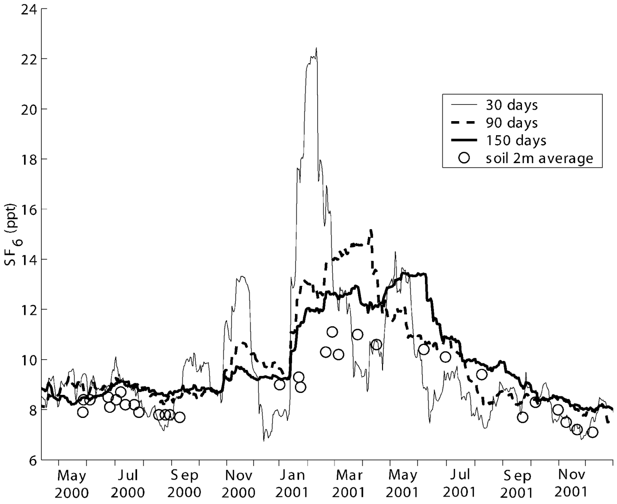

FIGURE 5. Comparison of average SF$_6$ mixing ratios in soil at Sparkill, NY (>2 m depth), with running means (30, 90, and 150 d) of the atmospheric mixing ratio measured at Palisades, NY.

top box representing the atmosphere and the lower 16 boxes representing a 400 cm deep soil zone divided into 25-cm intervals.

The temporal evolution of the SF$_6$ mixing ratios in each of the soil air boxes was calculated using an explicit solution to the advection dispersion equation:

$$\frac{\delta\theta^* c_g}{\delta t} = D^*\frac{\delta^2 c_g}{\delta z^2} - q^*\frac{\delta\theta c_g}{\delta z} \tag{1}$$

where c_g is the SF$_6$ mixing ratios, D^* represents the aggregate diffusion coefficient for the gas and liquid parts of the system, q^* is the aggregate advection, θ^* is an adjustment for gas versus liquid pore space, z is the thickness of each box, and t is time:

$$\theta^* = \epsilon_a + \theta\rho_l K_w \tag{2}$$

$$q^* = q_l\rho_l K_w + q_g \tag{3}$$

$$D^* = D_g + D_l\rho_l K_w \tag{4}$$

$$D_g = D_{g0}\epsilon_a\tau_g \tag{5}$$

In these equations, ϵ_a is gas-filled porosity; θ is volumetric water content; ρ_l is the liquid-phase density; K_w is the liquid/gas partition coefficient of SF$_6$; q_l and q_g are net gas and liquid advection, respectively; D_l is the liquid-phase dispersion coefficient; D_g is the effective gas diffusion coefficient; D_{g0} is the free air diffusivity of SF$_6$; and τ_g is the gas tortuosity.

The SF$_6$ values in the top box were prescribed by quasi-continuous atmospheric SF$_6$ measurements performed at LDEO in Palisades, NY, in the years 2000 and 2001 with a temporal resolution of approximately 15 min. Gaps in the atmospheric data were replaced with the average atmospheric SF$_6$ value for that month. This interpolation scheme was required for approximately 8% of the atmospheric data. A time step of ~14.4 min (1/100th of a day) was selected in order to resolve the atmospheric sampling frequency (ca. 15 min). Atmospheric SF$_6$ values were interpolated linearly between existing data points to a uniform grid.

Within the soil, D_{g0} was chosen to be 0.832 m^2 d^{-1} (*19*), and τ_g depends on the soil type and moisture content with estimates varying from 0.6 for dry, sandy soil (*20*) to 0.19 for finer soils with higher water content (*17*). The latter value was taken to be more typical for the conditions at our sampling sites. Total porosity was taken to be 0.35 in accordance with soil density measurements made at the Sparkill site. Water content for the soil column was prescribed to have a seasonal cycle in volume ratio ranging from ~0.25 in winter to ~0.09 in summer. This was based on soil moisture data collected at a depth of 10 cm from Black Rock Forest, NY, a site ~45 km north of Sparkill. Gas-phase porosity was calculated by subtracting water content from the total porosity. The gas/liquid partitioning coefficient of SF$_6$ was taken to be 132 at 15 °C (*9*). Advection of air and water were set to zero. All other parameters were taken from Cook and Solomon (*17*). To spin up the model, it was run with real-time atmospheric data for the upper boundary layer. These runs covered a period of ca. 4.5 moths before the date at which the first soil measurements were taken.

In general, the simulated SF$_6$ distributions fit the observed data points reasonably well (Figure 6). Deviations between the model results and the observations include a small bias toward higher model values than those measured throughout the time series. The most likely explanation for this deviation is the difference in atmospheric SF$_6$ mixing ratios between Palisades, which is used as the input function, and Sparkill. Additionally, there is a deviation related to the large spike in atmospheric mixing ratios in the winter of 2000/2001. For this event, the model produced higher SF$_6$ mixing ratios in soil air than observed. The effect of snow cover on gas exchange between the soil and the atmosphere was proposed above as a possible explanation.

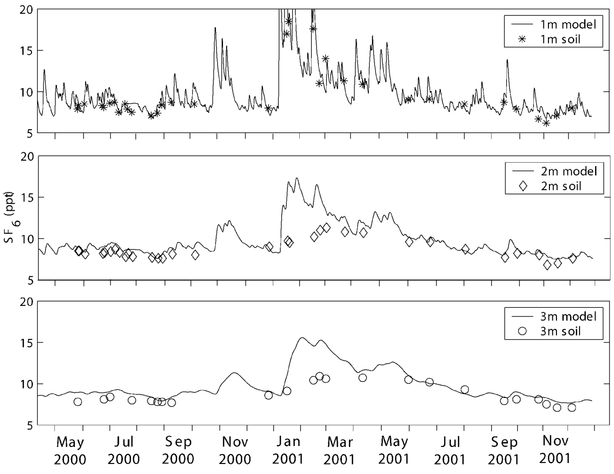

FIGURE 6. Comparison of measured (symbols) and simulated (lines) SF$_6$ mixing ratios at Sparkill, NY, for three depths.

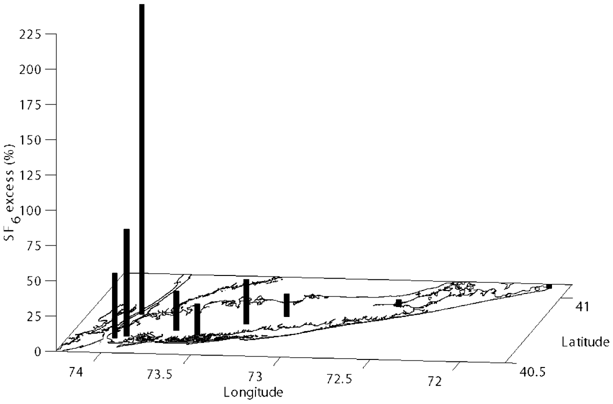

FIGURE 7. Map of soil gas SF_6 excess measured along a transect from New York City to Long Island.

The model is not sensitive to advection or diffusion in the liquid phase because of the low solubility of SF_6. Model runs with a recharge flux of 0 and 0.5 m yr^{-1} resulted in soil gas mixing ratios that differed by less than 1%.

The relatively good agreement between the simulated and the observed soil SF_6 profiles using typical values for soil properties suggests that vadose zone is a viable short-term archive for inert gases. Diffusion also appears to be a dominant process in controlling soil SF_6 mixing ratios. Although simultaneous measurement of more variables such as temperature, pressure, soil moisture, etc. may refine the study, we expect that the main conclusions from this work will remain valid.

Spatial Patterns. A sampling transect extending from Central Park to the eastern tip of Long Island was performed to obtain insight into the scale of the SF_6 excesses observed at LDEO/Sparkill and New York City. The measurements were performed between June and August 2001. The data clearly reveal the large-scale nature of the persistent SF_6 excess above remote atmosphere values (Figure 7). The excess values range from more than 200% in Central Park to about 20% at a distance of roughly 80 km from the center of New York City. This example shows that, in the case of New York City, the use of SF_6 in groundwater dating is limited within a radius of more than 80 km. Similar studies in the proximity of other large urban and industrial centers will determine if the persistently high SF_6 values in and around New York City are an exception or a typical feature.

Perspectives. The vadose zone integrates atmospheric SF_6 mixing ratios over time scales greater than 1 month. SF_6 measurements in soil air at depths greater than 1−2 m were found to generally correspond to averaged direct measurements of atmospheric mixing ratios. A simple physical model can be used to describe the main features of the observed SF_6 mixing ratios in the vadose zone, validating our concept that soil is a short-term archive for inert atmospheric gases with low-pass filtering capability. Hence, a relatively small number of measurements of soil air might be used to determine the possible presence and spatial pattern of atmospheric SF_6 excesses for a given area relative to remote regions. Further work is required in order to develop this method for practical applications, but preliminary work indicates that it is effective. Measurement of SF_6 mixing ratios in the vadose zone and atmospheric air could also be used to better understand gas transport in the unsaturated zone. This would allow comparison of expected and measured soil gas mixing ratios for inert as well as reactive gases.

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