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Widespread elevated atmospheric SF_6 mixing ratios in the Northeastern United States: Implications for groundwater dating

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Summary SF_6 is a promising transient tracer for groundwater dating, but elevated levels of atmospheric SF_6 may limit application of this dating method in urban areas. To determine the magnitude of this limitation within the United States (US), this study derives average atmospheric SF_6 mixing ratios from soil air measurements from five major urban areas. All surveyed sites showed SF_6 elevated above Northern Hemisphere clean air levels. In many cases, SF_6 mixing ratios were highest within large cities, but significantly elevated levels persisted hundreds of kilometers beyond the urban centers. Estimated SF_6 emissions from New York city were anomalously large, resulting in average levels over 200% above remote atmosphere values. Emissions from other urban areas included in this study appear to be typical for large cities in the US and maximum observed elevations of SF_6, in these areas, were in the range of 50–100%. These findings imply that caution is needed in choosing an atmospheric input function when using SF_6 as a transient tracer within or near urbanized regions. Within the Northeast US, the assumption of remote atmospheric SF_6 may lead to significant errors in estimation of groundwater ages, especially in the case of an expected future flattening of the atmospheric mixing ratio curve.
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Introduction

SF_6 is an inert gas of predominately anthropogenic origin, used primarily as an electrical insulator in high voltage switching gear and to a lesser extent in the casting of

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reactive metals (Maiss and Brenninkmeijer, 1998). The SF_6 mixing ratio (molar fraction) in the remote atmosphere has increased rapidly over the last several decades to approximately 6 ppt (e.g., Maiss and Brenninkmeijer, 1998; Harnisch and Hohne, 2002), making it a valuable transient tracer (a tracer with a time variable source) for ocean and continental water studies (e.g., Vollmer and Weiss, 2002; Watanabe et al., 2003; Busenberg and Plummer, 2000; Morris et al., 2006; Koh et al., 2007), as well as for studies of atmospheric transport (Denning et al., 1999; Kjellstrom et al., 2000).

For transient tracer applications in aqueous systems, the temporal variability of SF_6 at the air/water interface ('input function'), as well as the temperature-dependent solubility, must be specified. The evolution of SF_6 mixing ratio in the remote atmosphere is well established from continuous measurements (Maiss and Brenninkmeijer, 1998). However, there is evidence that near urban areas, SF_6 mixing ratios can be highly variable on short time scales, and that high SF_6 mixing ratio events of short duration increase the average mixing ratios significantly above remote atmospheric levels (Ho and Schlosser, 2000). In determining groundwater ages, assuming remote atmospheric SF_6 values instead of the elevated local mixing ratios can bias apparent groundwater ages toward younger values, or prevent dating altogether (Ho and Schlosser, 2000). Hence, it is important to determine average atmospheric SF_6 mixing ratios in study areas which are susceptible to SF_6 emissions.

The unsaturated soil zone has been previously demonstrated to integrate atmospheric mixing ratios of chlorofluorocarbons (CFCs) (Weeks et al., 1982; Oster et al., 1996; Severinghaus et al., 1997; Cook and Solomon, 1995; Santella et al., 2006). In a similar fashion SF_6 collected from sufficient depth in the unsaturated soil zone approximates atmospheric values averaged over a period of several months (Santella et al., 2003). This technique has recently been applied to investigate SF_6 mixing ratios in urban areas of the United Kingdom (UK) where only slightly elevated levels of SF_6 were observed (Darling and Gooddy, 2007). In the present study, measurements of SF_6 from the unsaturated soil zone are used to establish patterns of atmospheric SF_6 mixing ratios primarily within the Northeast US. The observed SF_6 levels are examined with respect to their impact on the utility of this promising compound as a transient tracer for groundwater dating near source regions.

Methods

Sampling locations

Soil air samples were collected in five major metropolitan areas: Boston, New York city (NYC), Philadelphia, Washington DC/Baltimore, and Tucson. The population of these five Consolidated Metropolitan Statistical Areas were 5.8, 21.2, 6.2, 7.6, and 0.8 million, respectively, according to the 2000 census (United States, 2000). Soil air was also collected at several remote sites in an attempt to resolve background SF_6 levels (Fig. 1). Most of the soil air sample sites were located in parks or open areas to minimize localized SF_6 sources. Sites were chosen based on the desired spatial resolution to resolve gradients in SF_6 levels, and on local geology. Site locations, elevations, and observed mixing ratios are included by region in Supplemental Tables 1—4.

Sample collection and analysis

Soil air samples for SF_6 analysis were collected at 25 cm depth intervals using a commercial (Arts Machine Shop) soil

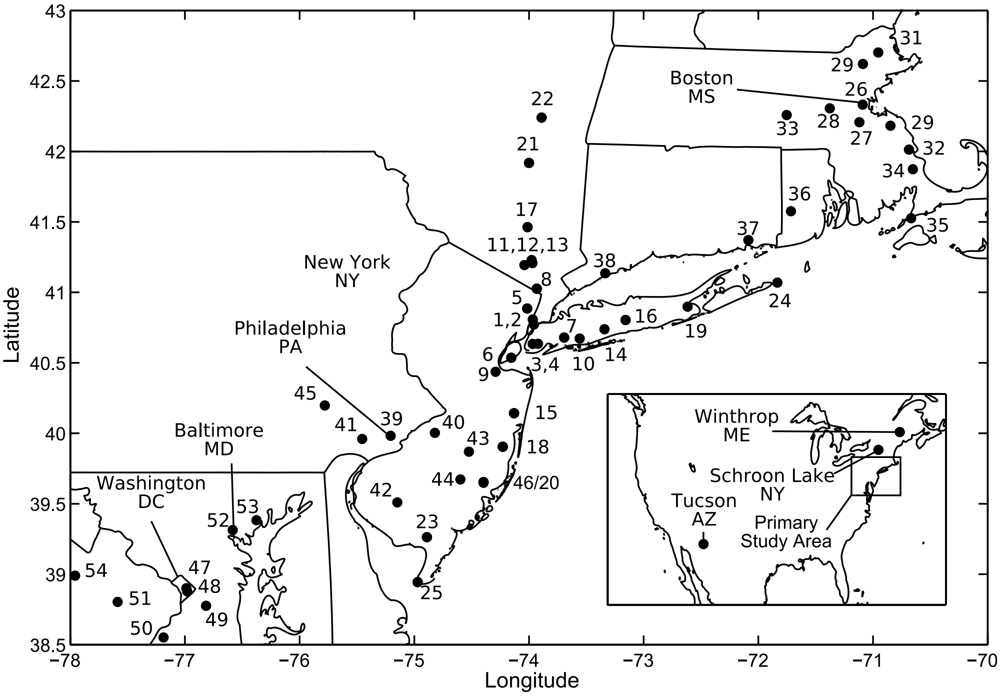

Figure 1 Map showing SF_6 sampling locations (correspond to locations in supplemental Tables 1—4) with names of major US cities and remote sampling locations.

vapor probe driven to the desired depth. Wherever possible, sites with sandy soils were chosen to maximize the depth at which samples could be collected. The length of time over which atmospheric mixing ratios are averaged in soil air depends on depth and the effective gas diffusion rate in the soil. As shown in a previous study at Sparkill, NY, a site with fine-grained sandy soils, SF_6 mixing ratios in samples obtained from 2 m depth or below reflect the average SF_6 mixing ratio over a period of approximately 2 months or longer (Santella et al., 2003). This result is consistent with a gas phase tortuosity of approximately 0.2. Gas diffusion rates for dry and very porous soils may be up to three times as high (Severinghaus et al., 1997). Even in this extreme case, the integration period (mean residence time) for air below 2 m is greater than the time scale of most atmospheric variability, which is of the order of hours to days. At some sites, only profiles shorter than 2 m could be obtained. Hence, values for those sites represent a somewhat shorter time average.

Samples were collected in 60 ml nylon syringes with 3-way polycarbonate stopcocks. First, 100 ml of air was drawn into the syringe and out of the stopcock to flush the probe and syringe. Then, a 50 ml soil air sample was taken. Duplicate samples were taken for every 4th sample. Assuming a porosity of 0.3, typical for sand, the soil volume affected by the collection of a duplicate set of samples is 830 cm^3 (i.e., a spherical volume with a radius of about 6 cm). Disagreements of up to 10% were occasionally observed between duplicate soil air samples when a strong vertical gradient existed in the SF_6 soil air profile. This was attributed to mixing of soil air with high and low SF_6 mixing ratios within the sampled depth interval of the soil column.

The SF_6 standard used in this study (24.0 ppt) changed by less than ±4% when stored in nylon syringes for one week. Additionally, syringes filled with SF_6-free N_2 contained no quantifiable level of SF_6 after storage for one week. All analyses used in this study were performed within 48 h of sample collection and should not be affected significantly by storage.

Generally, 3 ml air samples for SF_6 analysis were directly injected into a gas chromatographic system and separated from other gases using a molecular sieve 5A column. They were analyzed on a Shimadzu 8A gas chromatograph equipped with an electron capture detector using UHP N_2 as a carrier gas. SF_6 mixing ratios are reported on the NOAA SF_6 scale. Analytical precision of the system was ±1% or better for most of the study. During the period between May 2002 and March 2003 precision was reduced to approximately ±2% due to chromatographic interference of a small, unidentified peak. Calibration standards were run after measurement of approximately six samples. Reproducibility of the standard gas was generally better than ±1%. Reproducibility of duplicate soil air samples averaged ±3% over the course of the study.

Results

Atmospheric time series

Atmospheric SF_6 was measured at high temporal resolution (ca. 12 min) from 2000 to 2004 at the Lamont-Doherty Earth Observatory (LDEO), 25 km north of NYC using an automated GC system (Ho and Schlosser, 2000). The time series is characterized by frequent high mixing ratio events typically lasting for a day or less. Annual average atmospheric levels were 8.9, 10.6, 7.6, 7.3 and 7.5 ppt from 2000 to 2004, respectively. Over this entire time period mixing ratios were on average 82% above remote atmospheric levels and highest mixing ratios were seen when winds were from the south (i.e., from NYC). These pollution events result in a nonstandard, skewed distribution of mixing ratios, a representative example of which (for the year 2000) is shown in Fig. 2. Approximately 80% of the observations fall below the mean.

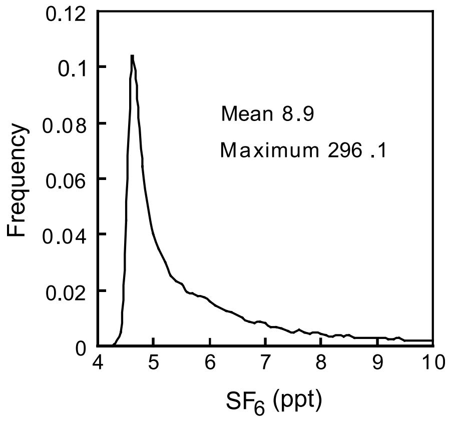

Figure 2 Histogram of LDEO atmospheric SF_6 mixing ratios for the year 2000.

Depth profiles

The SF_6 depth profiles collected at sites near some of the cities discussed below (Fig. 3) have features similar to those reported previously from sites around NYC (Santella et al., 2003). They display variability in the upper meter due to short term (days) variation in atmospheric mixing ratios, and smaller gradients in the SF_6 mixing ratio below soil depths of ca. 1.5–2 m. Other sites had low SF_6 mixing ratios with little variations with depth. At all sites, the SF_6 mixing ratio at depth represent the atmosphere averaged over times of several weeks to several months (Santella et al., 2003).

New York city metro area

Among the areas included in this study, the NYC region was the area sampled most extensively. Hence, spatial and temporal variability of atmospheric SF_6 has been best documented in this region. Most sites were sampled at least twice: once during the periods of May–October, 2001 and then again between May–August, 2002. Several sites were sampled three or more times, and for these sites, the averages of all results obtained in each year are reported. Highest SF_6 mixing ratios were observed in Central Park within NYC, and averaged 16.5 ± 0.6 and 15.9 ± 2.5 ppt (at depths below 2 m) during 2001 and 2002, respectively. This is equivalent to excesses above remote atmosphere SF_6 mixing ratios of 230% and 214%, respectively, (remote SF_6 mixing ratios were 4.8 and 5.0 ppt during 2001 and 2002, respectively; NOAA CMDL, 2005). The SF_6 excesses declined with distance from NYC in all directions (Fig. 4). Minimum mixing

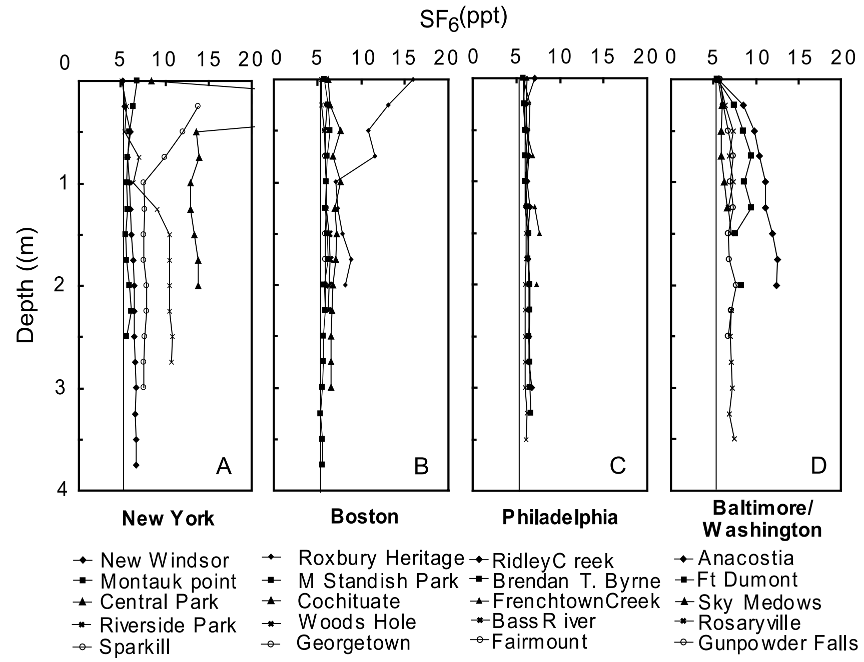

Figure 3 Plots of multiple profiles of SF_6 mixing ratio vs. depth for: (A) New York city NY; (B) Boston MA; (C) Philadelphia PA; and (D) Washington DC/Baltimore MD.

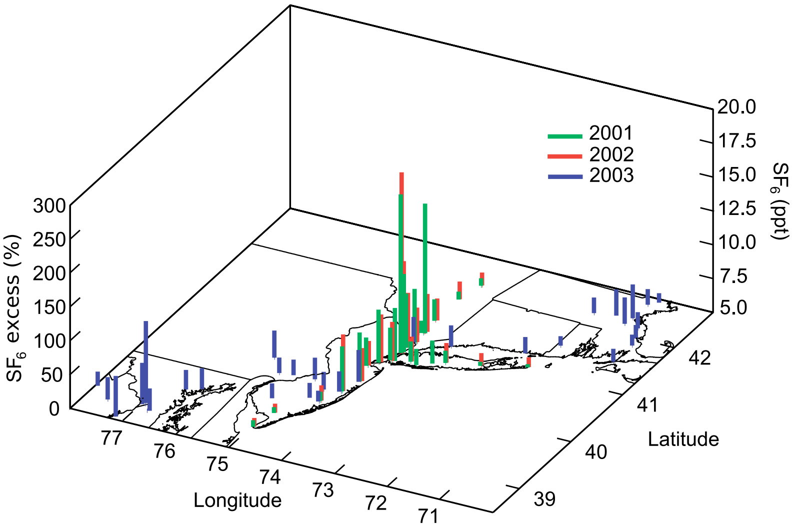

Figure 4 Spatial distribution of SF_6 from a soil depth below 2 m near large cities in the Northeast US. Values observed during 2001–2003 are expressed as mixing ratio and % excess.

ratios were observed at Cape May NJ, 213 km south of NYC. They were 5.4 ± 0.1 ppt (8% above remote atmosphere values) in 2001 and 5.7 ± 0.2 ppt (13% above remote atmosphere values) in 2002.

Boston metro area

SF_6 surveys were conducted in soil air around Boston between June 17 and 24, 2003. Gradients observed in SF_6 soil profiles imply strong temporal variability of atmospheric mixing ratios (Fig. 3B). The maximum mixing ratio of 8.2 ± 0.2 ppt or ~55% excess above the remote atmosphere mixing ratios (below 2 m soil depth) was observed at Roxbury near the Boston city center. SF_6 mixing ratios generally decreased with distance from Boston (Fig. 4), with the most rapid decrease occurring towards the north. However, at all sites in this survey, an SF_6 excess of at least 0.7 ppt, or 15% above remote atmosphere, was observed.

Philadelphia region

Between July 3 and 23, 2003 soil air SF_6 profiles were sampled at 8 locations near Philadelphia, PA. At one site (Wharton) samples could not be collected at or below 2 m due to saturated soils. Unlike NYC and Boston, the highest SF_6 levels (7.3 ± 0.2 ppt or 40%) were observed northwest of the city center (at Frenchtown Creek, ~60 km outside Philadelphia) instead of within the city. Within Philadelphia, the SF_6 mixing ratio (6.4 ± 0.1 ppt) was not significantly elevated beyond that of other sites in the vicinity (Fig. 4). Soil profiles in the study area indicate relatively little spatial or temporal variability in the SF_6 mixing ratio. (Fig. 3C).

Additionally, water samples collected from a shallow well at one site approximately 25 km southeast of Philadelphia (39.710°N, 75.058°W; elevation 46 m) contained levels of SF_6 slightly higher than solubility equilibrium with the remote atmosphere (2.2 pmol l^{-1}; equivalent to equilibrium with a soil air SF_6 mixing ratio of 6.2 ppt). Air samples were also collected in 2003 from a number of nearby soil vapor wells screened above the water table at depths of 5–6 m (Baehr et al., 2001). Air samples from these vapor wells contained SF_6 levels between 6.3 and 6.8 ppt (18–29% excess above remote atmospheric levels), i.e., similar to levels observed in more shallow soil air samples collected during the Philadelphia survey.

Washington DC and Baltimore metro area

Between October 22 and 24, 2003, soil gas was collected from 8 locations in and near Washington DC and Baltimore, MD. At five of these sites, samples were collected from below 2 m depth. At three sites, samples were collected only to depths of about 1.23–1.75 m due to dense clay soils. Average SF_6 mixing ratios in the soil air samples at all sites were above remote atmosphere values (Fig. 3D). A maximum SF_6 mixing ratio of 12.3 ± 0.3 ppt was observed at Anacostia in the southeastern quarter of Washington. Another site, Ft Dumont, located less than 3 km from Anacostia had a considerably lower SF_6 mixing ratio of 8.3 ± 0.9 ppt. The lowest SF_6 mixing ratio observed was a 1 m average of 6.4 ± 0.2 ppt at Sky Meadows, located approximately 82 km west of Washington DC. The SF_6 mixing ratios at all other sites were slightly above 7 ppt (around 35% excess) with little variation. Aside from two high SF_6 mixing ratio sites in Washington, no gradient in soil air SF_6 mixing ratios was seen with distance from either city (Fig. 4).

Tucson region

On November 15 and 18, 2003 soil gas SF_6 was measured on samples from two sites in and near Tucson, AZ. One site was near the Tucson city center (32.214°N, 110.922°W; elevation 769 m), the second site was located near Oracle, approximately 56 km to the north of Tucson (32.572°N, 51.580°W; elevation 1127 m). Soil SF_6 mixing ratios observed at both sites were nearly constant with depth. The average SF_6 mixing ratio for samples from below 2 m depth for the site within Tucson was 6.7 ± 0.1 ppt (~27% excess above the remote atmosphere). At Oracle, an average soil SF_6 mixing ratio of 5.4 ± 0.1 ppt (excess above the remote atmosphere: <1%) was observed, close to Northern Hemisphere clean air values.

Remote sampling sites

Soil gas samples were collected at a remote site in Winthrop, ME (44.305°N, 69.977°W; elevation: 66 m) five times between 2000 and 2002. SF_6 mixing ratios were among the lowest observed but increased with time from 4.7 ± 0.1 ppt (0% excess above remote atmosphere values) in 2000 to 5.5 ± 0.1 ppt (6% excess) in 2002. In October 2003, samples were also collected from a remote site near Schroon Lake, NY (43.862°N, 73.756°W; elevation: 256 m). This site is located in the Adirondack Mountain region of New York State, approximately 340 km north of NYC. Average SF_6 mixing ratios observed at 2 m depth were 6.0 ± 0.1 ppt (15% excess).

Discussion

Atmospheric time series

Collection of atmospheric grab or integrated samples would be the simplest method to determine atmospheric mixing ratios of SF_6. To estimate the number of atmospheric samples that would be required to accurately resolve annual average SF_6 mixing ratios without the use of a automated GC, the LDEO time series was sub sampled. Twenty-four-hour blocks of data were selected at regular intervals and averaged simulating common integrated flask sampling methods; these one day averages were then averaged by year and compared to the annual average obtained from the entire high-resolution time series. A sampling frequency of at least one integrated sample every 10 days was required to consistently estimate the annual average mixing ratio within 10%. Single grab samples (not integrated) even when collected daily could not consistently reproduce the annual averages observed from all years of the time series within 10% and in over half the years resulted in significant underestimates of annual average mixing ratios. An equivalent sampling frequency might be required for other areas with similarly elevated SF_6 mixing ratios. Hence, soil air sampling, which integrates over a longer time period (Santella et al., 2003), is expected to be a more effective method to define average SF_6 mixing ratios in a study area without the need for extensive resources and intensive sampling efforts.

Observed distribution of SF_6 mixing ratios

Of the five metropolitan areas included in our study, highest mixing ratios were observed within NYC. With the notable exception of Tucson, mixing ratios outside all cities were also elevated, and were almost as high as outside NYC. Only at a few of the most isolated sites did mixing ratios approach Northern Hemisphere remote atmosphere values. Mixing ratios observed in soil near NYC were consistent with atmospheric mixing ratios of SF_6 observed through the high resolution time series at LDEO.

To compare the observed spatial distribution of SF_6 around NYC to known SF_6 emissions in the region, a simple dispersion model was applied. The Industrial Source Complex 3 Short-Term model, a Gaussian plume model, available from the Environmental Protection Agency (EPA) was used to perform these calculations (USEPA, 2005). As SF_6 source distribution was not readily available, the simplest assumptions were used. Electric utility emissions from NYC for 2002 were assumed to be a continuous ground level point

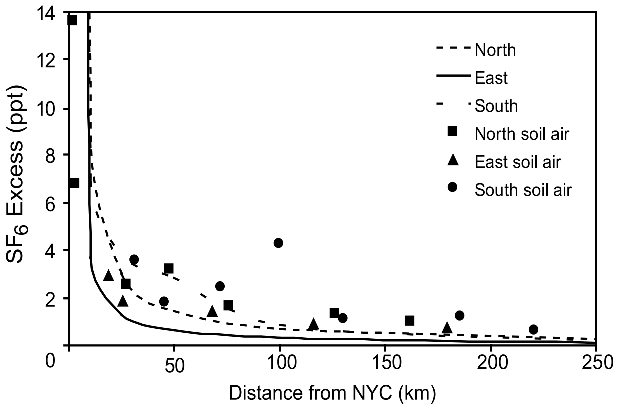

Figure 5 Plot of modeled and observed average SF$_6$ excess above remote atmosphere with distance from center of NYC to the north, south and east.

source, and those from northern NJ were assumed to be a large area source corresponding to the service area of the local electrical utility. Utility emissions are derived from the quantities used to recharge SF$_6$ insulated equipment. Potential emissions from reactive metal processing were neglected as they are a small fraction of electrical utility emissions globally (Maiss and Brenninkmeijer, 1998), and reactive metal casting is not a major industry in the NYC region. Annual average mixing ratios were modeled at strings of receptors to the north, east and south of NYC in line with the soil air sampling locations. This simplified approximation seems to fit the observations reasonably well in all three directions (Fig. 5). Assumption of a point source for NYC results in overestimates of mixing ratios very near the source location as SF$_6$ sources are, in reality, presumably a complicated distribution of point sources. Model results also consistently underestimate mixing ratios for the most distant sites, possibly because of significant contributions of SF$_6$ from outside of the NYC and northern NJ region. However, transport and known emissions from NYC and northern NJ appear to explain much of the variation in observed mixing ratios in the NY/NJ area. Hence SF$_6$ emission estimates (when available) can be useful in evaluating the potential for elevated SF$_6$ mixing ratios within urban areas.

NYC was by far the largest SF$_6$ source of any city considered even given its large population (Table 1). These high emission rates have been attributed to intensive use of SF$_6$-insulated equipment in NYC and its ageing condition (NESCAUM, 2004). Known SF$_6$ emissions from utilities in Baltimore, Washington DC, Boston and Tucson appeared typical of large US cities, and were only ~0.8, 1.8, 4.1, and 0.5% of NYC emissions, respectively. Emission estimates for Philadelphia were not available, but are expected to be similarly low. When applied in a dispersion model similar to that described above, emissions from the five other cities reproduced or overestimated SF$_6$ mixing ratios observed within a few kilometers of the cities. However, city emissions alone dramatically underestimate the mixing ratios observed at sites most distant from the city centers. SF$_6$ sources in the Northeastern US appear to raise the SF$_6$ mixing ratio significantly over the entire region. Elevated levels of SF$_6$ observed near Winthrop, ME and Schroon Lake, NY, both remote from large cities, support this hypothesis. The impact of distant urban sources of SF$_6$ on these remote areas is not surprising as previous studies of atmospheric transport have highlighted the influence of urban pollution on these areas (Schichtel and Husar, 2001; Wishinski and Poirot, 2004).

The regional nature of the elevation in SF$_6$ mixing ratio observed outside of cities in the northeast is reinforced by comparison of the distribution of atmospheric SF$_6$ observed in this study with troposphere SF$_6$ mixing ratios modeled by Atmospheric General Circulation Models (AGCMs) from 1993 global emissions (Denning et al., 1999). Many AGCMs predicted troposphere SF$_6$ mixing ratios in excess of the remote Northern Hemisphere average by 10—20% over most of the Northeastern US, in agreement with the excesses observed outside of large cities in this study. The southwestern region of the US, including Tucson, was modeled as having a lower excess of 3—10%. SF$_6$ mixing ratios observed in soil gas outside of Tucson were in fact among the lowest observed in our study. SF$_6$ levels observed by Darling and Gooddy (2007) are also within the range of modeled levels of SF$_6$

Table 1 SF$_6$ emissions from electrical utilities

Location	Time period	kg SF$_6$/year	Population 2000	kg SF$_6$/1000 people
New York city NY	2002	101,604	8,008,278	12.7
Pittsburgh PA	2002	5849	334,563	17.5
San Francisco CA	2002	4989	776,733	6.4
Chicago IL	2001	2224	2896,016	0.8
Washington DC	1998—2000	1814	572,059	3.2
Boston MA	2002	1361	589,141	2.3
Austin TX	1999	1179	656,562	1.8
Baltimore MD	1999	803	651,154	1.2
Tucson AZ	2002	544	486,699	1.1
Springfield MO	2001	156	151,580	1.0
San Antonio TX	2001	131	1,144,646	0.1
Sacramento CA	2001	23	407,018	0.1
US (EPA 2002)	1999	719,484	281,421,906	2.6
US, Canada (Maiss 1998)	1995	635,026	312,702,998	2.0
United Kingdom (all sources)	1999	49,895	58,886,000	0.8

in the southern UK, which varied from 5–30% excess (Denning et al., 1999).

The low SF_6 levels reported by Darling and Gooddy (2007) contrast with elevated levels observed at almost all locations in the present study despite the focus of both studies on large urban areas with similar populations. Koh et al. (2007) also observed low SF_6 mixing ratios in agreement with Northern hemisphere background values in a moderately developed region in South Korea. Lower mixing ratios observed in the UK are most likely due to lower SF_6 emissions. UK per capita emissions of SF_6 from all sources (AEA, 2007), are less than half of those in the US (Table 1). Emissions for individual cities in the UK are expected to be reduced compared to similar sized US cites in the same proportion. In addition NYC, which is central to the current study area, has unusually large SF_6 emissions from its electrical distribution system. Factors such as degree of atmospheric dispersion may also have an impact, although southern UK average wind speeds are not very different from those in the Northeast US, implying that local levels of dispersion may also be similar. As SF_6 emissions data are often compiled by governments and industries, understanding local and regional levels of $SF_{6,}$ emissions can be an important and relatively simple step in evaluating the potential for elevated levels of atmospheric SF_6.

Limitations of the methodology

The primary requirement of the observational method applied in this study is the necessity of a porous unsaturated zone at least 2 m thick. This requirement can generally be met at a wide variety of locations, but occasionally might limit application of the method. Additionally, there is the potential for temporal and spatial variation in atmospheric SF_6 mixing ratio if the sampling site is close to an SF_6 source. For example, SF_6 excesses observed at five sites near NYC differed by more than 15% between the 2001 and 2002 surveys (supplemental Table 1). Greatest variation is generally observed at sites with higher mixing ratios, as they are closer to sources and influenced to a larger degree by changes in emission strength. At three of these locations Haverstraw (next to a power plant), Allaire, and Double Trouble, SF_6 mixing ratios in soil air were on occasion significantly higher than regional trends, presumably due to the influence of nearby sources. Similarly, high mixing ratios observed at Anacostia in Washington DC and a sharp gradient between Anacostia and Ft Dumont may be due to the proximity of a power station, located approximately 0.5 and 2.5 km from Anacostia and Ft Dumont, respectively. These anomalies clearly demonstrate that caution is needed when interpreting single soil profiles, which may be influenced significantly by local sources of SF_6. However, even single soil profiles can serve as a qualitative indicator for the presence and rough magnitude of excess SF_6 concentrations in a specific area. If single soil profiles were to be interpreted as representative of entire regions and applied in groundwater dating, a significant bias might result in apparent groundwater ages. However, when considering a number of sites together, as in this study, the impact of temporal and spatial variability in SF_6 emissions, on mixing ratios is minimized.

Implications for SF_6 as a transient tracer for groundwater dating

The high SF_6 excess observed previously around NYC (Ho and Schlosser, 2000; Santella et al., 2003) appears not to be unique. Mixing ratios observed around other US cities are elevated, although somewhat less dramatically, unlike cities in the southern UK (Darling and Gooddy, 2007). Most sites sampled showed some SF_6 excess, implying that caution is necessary before assuming background SF_6 mixing ratios near developed regions in the US. The age bias resulting from a constant SF_6 excess of 10% or less is 1–2 years (Ho and Schlosser, 2000), similar in magnitude to the error in age determination due to groundwater sampling and analysis. In the areas surveyed in this study, SF_6 excesses in the range of 10% were observed only at a few locations. SF_6 excesses of 20% or less were observed at only six of 25 sites in the NYC region. In the other areas surveyed, excesses of 20% or less were found at 11 of 32 sites. Hence bias in apparent groundwater ages of more than 2–5 years and negative ages for very recent recharge are expected at greater than half the investigated sites.

These findings imply that assumption of remote atmosphere mixing ratios will significantly limit the application and accuracy of SF_6 dating methods in some urban areas. These elevated levels are of particular concern as the highest atmospheric SF_6 excesses in the current study were found (as expected) in and near large urban areas with high population density, exactly where transient tracers such as SF_6 may be of most use in addressing groundwater management and contamination issues (e.g., Morris et al., 2006). However, observations from the UK indicate that SF_6 levels are not always elevated even in major urban areas. The presence of a significantly elevated SF_6 will depend on local and regional emissions strength as well as average rates of atmospheric dispersion. Considering recent observations and estimates of SF_6 distribution by Denning et al. (1999) it would appear that significant portions of the Northeast US, Europe and Asia have potential for SF_6 levels more than 10% over Northern Hemisphere background. Hence it is particularly important to examine SF_6 levels at sites where application for groundwater dating is planned. In the case where significantly elevated levels of SF_6 exist, this could in theory be overcome by estimating an adjusted local atmospheric input function for SF_6 (Bauer et al., 2001; Zoellmann et al., 2001) but further study is needed to determine the practicality of this approach in various settings.

Conclusion

Measurement of SF_6 mixing ratios in soil gas has been shown to be useful for observing average atmospheric SF_6 levels over a wide geographical area with greater spatial resolution than practically possible by collection of atmospheric time series. Soil gas measurements seem especially well suited for screening for excess SF_6 at sites for which groundwater dating is planned and for estimating its potential effect on groundwater ages at sites in urbanized regions. In environments affected by atmospheric SF_6 excesses measurement of SF_6 in soil gas sampled with a frequency on the order of months, might be used to define a local input function. Reconstruction of the atmospheric SF_6 mixing ratio that has been low-pass filtered in the unsaturated soil zone could facilitate the application of SF_6 as a transient tracer in studies of groundwater circulation and mean residence times.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhydrol.2007.10.031.

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