Impact of natural and local anthropogenic SF$_6$ sources on dating springs and groundwater using SF$_6$ in central Japan

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Abstract:

Sulfur hexafluoride (SF$_6$) concentrations in springs and groundwater were measured in the Chubu region of central Japan to evaluate the impact of natural and local anthropogenic SF$_6$ and the validity of SF$_6$ for dating young groundwater in Japan. Sampled water showed detectable concentrations of SF$_6$ at 0.21–125 f mol/L. Most of the mountain springs have SF$_6$ concentration assumed by the dissolution of the clean ambient air in Northern hemisphere. The SF$_6$-based apparent ages for the mountainous springs were estimated at less than 6 years in smaller catchment areas (< 0.5 km$^2$), and ranged from 4 to 32 years in the larger catchment areas located on the Quaternary volcanoes. The SF$_6$ ages for mountain springs were consistent with the scale of groundwater flow and with previously determined $^3$H ages for groundwater in similar settings in Japan, suggesting the loading of natural SF$_6$ in the groundwater is relatively small in the mountainous areas. In the plains, local industrial activities led to high concentrations of SF$_6$ in some of the analyzed groundwater. The results suggest SF$_6$ can be an effective dating tool for young groundwater in Japan, when and where the input of local anthropogenic SF$_6$ is negligible.

KEYWORDS Sulfur hexafluoride (SF$_6$), young groundwater dating, natural SF$_6$, local anthropogenic SF$_6$, the Chubu region in Japan

INTRODUCTION

Information on groundwater residence time is useful for understanding the renewability of groundwater reservoirs and the velocity of solute transport in subsurface aqueous systems. Tritium ($^3$H) has been employed to estimate the residence time of young groundwater (< 50 years old). However, the usefulness of tritium in tracing groundwater residence time is now limited due to its decline to pre-1950 background levels in precipitation. More recently, alternative tracers with dating potential such as $^3$He, $^{85}$Kr, $^{36}$Cl, chlorofluorocarbons (CFCs), and sulfur hexafluoride (SF$_6$) have been successfully employed to estimate the residence time of young groundwater in Europe and America (Kazemi et al., 2006; IAEA, 2006). SF$_6$ and CFCs are considered feasible because sampling procedures and laboratory analysis are much easier for SF$_6$ and CFCs than for $^3$He, $^{85}$Kr, and $^{36}$Cl.

SF$_6$ is a colorless, odorless, nonflammable, nontoxic, and stable gas with excellent electrical insulating and arc-quenching properties (Maiass and Brenninkmeijer, 1988). Significant industrial production of SF$_6$ began in the 1960s, and its concentration in the atmosphere has increased rapidly from 0.03 parts per trillion (pptv) in 1970 (Lovelock, 1971) to 6.8 pptv in 2009 (USGS, 2009). The increase reflects the long lifetime of SF$_6$ (3200 years) in the atmosphere (Ravishankara et al., 1993). Its use as a dating tool is based on the rapid and almost linear 6% annual increase in SF$_6$ in the air in the past 40 years, although dating is constrained from 1970 to the present. The SF$_6$ method is particularly useful in dating very young (post-1993) groundwater (Busenberg and Plummer, 2000; Bauer et al., 2001; Zoellmann et al., 2001; Gooddy et al., 2006). Considering the high velocity of groundwater circulation in Japan (Asai and Tsujimura, 2010), SF$_6$ may be a more useful tracer than CFCs in dating young groundwater. CFCs cannot provide precise ages for very young (post-1993) groundwater because of the declining trend in the atmospheric concentration of CFCs since the early 1990s (IAEA, 2006). However, there is still a paucity or total absence of SF$_6$-based groundwater age data in Japan.

Also, the dating of young groundwater with SF$_6$, in some cases, can be limited by natural terrigenic and local anthropogenic SF$_6$ sources. Busenberg and Plummer (2000) reported many kinds of rocks and minerals can be potential sources of SF$_6$ and the release of natural SF$_6$ is generally higher in fluorite, granite, and hydrothermal deposits. Near urban areas, SF$_6$ emissions from industrial activities such as semiconductor factories, metal processing factories, and power generation plants causes a local rise of SF$_6$ concentrations in groundwater and air (Santella et al., 2008). Direct SF$_6$ addition to groundwater from these sources leads to underestimation or failure of SF$_6$ dating. Locally elevated SF$_6$ in air near urban areas decreases the precision of SF$_6$ dating (IAEA, 2006).

Japan is located in an active tectonic zone and is a heavily industrialized country. Therefore, these additional SF$_6$ sources become important factors in the application of the SF$_6$ dating method to young groundwater in Japan. The present study evaluates the impact of natural and local...
anthropogenic SF$_6$ on dating young groundwater using SF$_6$ in Japan. For this purpose, we measured SF$_6$ concentrations in springs and groundwater samples from the Chubu region in Japan. We discuss the sources of SF$_6$ in groundwater by comparing groundwater and air SF$_6$ concentrations, and by validating the SF$_6$-based age of young groundwater.

**LOCATION OF STUDY AREA AND METHODS**

The study area (Figure 1) in the Chubu region has a mountainous relief with various rock types in the central part, urban nodes in the plains, and industries along the coast. Samples were collected during the dry season (January to March) of 2009 in Aichi, Gifu, Nagano and Toyama prefectures (Figure 1). Fifty nine springs were sampled from the mountainous areas, and samples were collected from 5 springs and 13 wells (groundwater) in the plains. With the exception of 6 springs (No. 42, 43, 74, 75, 76), which were located at the foot of the Quaternary volcanoes, most of the springs in the mountainous area were discharging from small catchments with a surface area of less than 0.5 km$^2$. Annual precipitation in the Chubu region is about 1500–2000 mm in the plains, and about 2000–3000 mm in the mountains (Japan Meteorological Agency, 2001).

The samples were collected with duplicates in 550 mL glass bottles with ethylene propylene rubber seal liner screw caps. Sample bottles were flushed with approximately 3L of the sample water, then filled and capped underwater to prevent contact of the water sample with the atmosphere. A peristaltic pump (Welco model Wpx-1000) was used to take water from wells.

SF$_6$ content in the samples was measured using a purge and trap gas chromatography procedure with an electron capture detector (GC-ECD) at the Geo-Science Laboratory Co. Ltd., Nagoya, Japan. The procedure involved a 400 mL of sample water that was stripped of SF$_6$ by an ultra-pure nitrogen gas. The extracted SF$_6$ was purified and concentrated by two cold traps, and finally injected into the GC-ECD. The precision and the detection limit of the analysis were less than 3% and 0.05 f mol/L, respectively. The detailed procedures of sample collection and analysis followed Busenberg and Plummer (2000) of the U.S. Geological Survey.

**RESULTS AND DISCUSSION**

**SF$_6$ concentration in water samples**

Figure 1 shows the spatial distribution of the sample sites and the associated SF$_6$ concentrations for the spring water and groundwater. The SF$_6$ concentrations of springs in mountainous area showed a small variation (1.5–2.5 f mol/L); two exceptions, samples No. 42 and 77, had lower values of 0.21 and 0.25 f mol/L, respectively.

In the plains, the SF$_6$ concentrations in water samples varied widely. The lower SF$_6$ concentrations, 1.2–1.7 f mol/L, were observed in springs discharging from terrace cliffs of Toyama prefecture (No. 60, 61, 63, 64, 66), and one well in a suburban zone of the city of Nagoya in Aichi prefecture (No. 7). Relatively higher values, 2.0–3.5 f mol/L, were observed in wells located in the Shogawa, Kurobe, and Ohgaki alluvial fans (No. 54, 55, 56, 65, 67, 68, 69, 70, 71, 72). The highest value, 125 f mol/L, was observed at a well located in the urban center of Nagoya city (No. 6).

**Sources of SF$_6$ in groundwater**

The SF$_6$ dating method relies on an assumption that the groundwater keeps the atmospheric SF$_6$ concentration it gains as the aquifer is recharged. However, as mentioned previously, two sources of excess SF$_6$ are probable from the natural matrix of the aquifer and from local industries. Additional SF$_6$ from these sources causes a rise of SF$_6$ concentration in groundwater, leading to underestimation or failure of SF$_6$ dating.

The impact of these extraneous sources of SF$_6$ on groundwater dating can be evaluated by considering two questions: 1) did the groundwater in question have a SF$_6$ concentration within the range of values assumed by the dissolution of SF$_6$ from clean ambient air in the northern hemisphere (clean air), and 2) are the estimated SF$_6$-based
ages consistent with the hydrogeological setting and with the ages derived from other tracers. We used apparent age (piston-flow age) for estimating a SF₆-based age, because apparent age is convenient for comparing of SF₆ concentrations between groundwater and air, and because it is useful for gaining insight into theoretical age distributions (Kazemi, 2006).

To compare groundwater and atmospheric SF₆ concentrations, the SF₆ values in groundwater were converted to the equivalent air concentration (EAC) at the time of the recharge, based on Henry’s Law

\[
\text{EAC (pptv)} = \frac{\text{SF}_6 \text{gw}}{\text{K}_H \times (P - P_{H_2O}) \times 1000} \quad (1)
\]

where EAC is the equivalent atmospheric concentration (pptv), SF₆gw is the concentration of dissolved SF₆ in groundwater (f mol/L), K_H is Henry’s Law constant for SF₆, P is the total atmospheric pressure, and P_{H2O} is the water vapor pressure. In this calculation, the parameters of average temperature and average elevation (barometric pressure) are needed for the sites where the groundwater samples were collected (IAEA, 2006). In this study, the water temperature at the time of sampling and topographically determined average recharge elevation (intersection method) was applied to the average recharge temperature and the average recharge elevation, respectively. Busenberg and Plummer (2000) provided the detailed procedure for calculating the EAC.

**Impact of natural SF₆**

The mountainous area in this investigation is located well away from SF₆ sources in the many industries using SF₆ in urban areas. Therefore, the mountain springs discharging from various geological conditions are suitable for evaluation of the impact of naturally occurring SF₆ the water can pick up from rocks and minerals in the matrix of the aquifer.

Figure 2a shows the EAC values for the mountain springs and Figure 2b shows the historical SF₆ concentrations in ambient air in northern hemisphere over time. The EAC values of the springs in mountainous areas ranged from 0.6–7.6 pptv, and 59 out of the 57 springs were in the range of clean air (0.03–6.8 pptv).

Apparent SF₆ groundwater ages for springs in mountainous areas were estimated by comparison of the EAC value for groundwater with historical clean air variation (Figure 2a and b). The size of a catchment area is one of the important factors controlling a residence time of groundwater, because it restricts the maximum scale of the groundwater flow system. Figure 3 shows the relationship between the SF₆-based apparent residence time (SF₆ age) and the topographically determined catchment areas for springs. The SF₆ ages of springs in the mountainous areas can be put into two groups: 1) springs with smaller catchment areas (< 0.5 km²) covered with granites, rhyolite, andesite (Tertiary), metamorphic, shale, sandstone, and limestone, and 2) those of larger catchment areas (> 1 km²) covered with andesite on the Quaternary volcanoes of Mt. Ontake and Mt. Dainichigatake.

The SF₆ ages of springs discharging from small catchment areas (< 0.5 km²) showed short ages of less than 6 years, with no clear relationships between the SF₆ ages and rock types. These small catchment areas in the mountainous regions have high relief and receive a high amount of annual precipitation (2000–3000 mm) resulting in a short circulation time for the groundwater flow which maintains the springs. Sanjo (1987) measured the tritium (^3H) concentration of the base flow within small catchment areas (< 0.5 km²) in mountainous areas in the Kanto region and reported a residence time of about 5 years for groundwater in a non-Quaternary volcanic area. Similar
short residence times (less than several years) was estimated for some mountainous springs in small catchments in Japan, based on the temporal variations of stable isotope data (δD, δ18O, d-excess) (e.g. Asano et al., 2002; Kabeya et al., 2007). Those reported ages agree with the SF$_6$ ages obtained in the present study.

The SF$_6$ ages for springs located at the foot of the Quaternary volcanoes showed a relatively longer duration, ranging from 4 to 10 years in Mt. Ontake and from 9 to 32 years in Mt. Dainichigatake (Figure 3). The residence times of groundwater in the Quaternary volcanoes are generally relatively longer and with larger variations than for springs in non-volcanic areas, reflecting the high capacity for water storage in the volcanic aquifers, large scale groundwater flow, and heterogeneity of the structure and texture within the volcano’s body (Scholl et al., 1996). The residence times of springs in volcanoes in Japan have been estimated using $^3$H, $^3$H/$^4$He, and CFCs (Table I). The $^3$H and CFCs ages estimated for springs in Mt. Ontake are similar with the SF$_6$ age obtained in the present study. Although no comparable data are present for Mt. Dainichigatake, similar age distributions were reported in Mt. Fuji and Mt. Yatsugatake (Table I). Based on these results, the relatively older SF$_6$-based ages observed in springs in the Quaternary volcanoes are consistent with large scale of groundwater flow within the volcanoes.

In the present study, SF$_6$ concentrations in most of the observed springs were within the range of clean air SF$_6$ concentrations (Figure 2), and no clear relationships were observed between the SF$_6$ ages and rock types in the matrix of the aquifer (Figure 3). Also, SF$_6$ ages for springs were consistent with catchment size and previously determined $^3$H ages for groundwater in similar settings in Japan. To better understand the natural SF$_6$ impact, a detailed discussion of the SF$_6$ dating process and a comparison of the observed SF$_6$ ages with observed $^3$H/$^4$He ages are required. Nevertheless, the apparent SF$_6$ ages for springs in the mountainous areas reflect the scale of groundwater flow rather than rock types, suggesting the atmosphere could be the principal source of SF$_6$ and the impact on naturally occurring SF$_6$ on groundwater is relatively small in the mountainous areas.

**Impact of local anthropogenic SF$_6$**

Figure 2a shows the EAC values for water samples in the plains area, along with the historical SF$_6$ concentrations of clean ambient air in the northern hemisphere (Figure 2b). The 5 springs (No. 60, 61, 63, 64, 66) discharging from the terraces in Toyama prefecture showed relatively low EAC values, 3.6–5.9 pptv, which is within the range of clean air. About half of the groundwater in the plains showed 10–30% higher EAC values than the upper limit of clean air variation, with anomalous values as high as 400 pptv, which is about 60 times the peak concentration of atmospheric EAC, observed in the groundwater from the urban center of Nagoya city. These observations suggest that either local industries and/or rock in the matrix of the aquifer are additional sources of SF$_6$ in groundwater within the plains.

Alluvial gravel which maintains groundwater in the plains area consists of rock types carried from the mountainous areas, where the impact of natural SF$_6$ was not remarkable. Also, the IAEA (2006) reported SF$_6$ levels in water derived from clastic sediments are lower than in samples from pristine fresh rocks. On the other hand, the plains host many industries such as semiconductor factories, metal processing factories, and power generation plants, which release SF$_6$ into the secondary environment. Such anthropogenic sources of SF$_6$ may account for the observed excessive SF$_6$ in some groundwater samples in the plains.

The addition of SF$_6$ from the local industries to the groundwater may have been generated by the following mechanisms. Elevated SF$_6$ concentrations in air near urban areas may be the source of dissolved SF$_6$ in the groundwater. SF$_6$ used in some processes in factories is added directly

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**Table I. Estimated residence times for springs from the Quaternary volcanic aquifers in Japan, based on $^3$H, $^3$H/$^4$He, CFCs, and SF$_6$ methods.**

| Volcano      | Tracer | Residence time | Reference     |
|--------------|--------|----------------|---------------|
| Fuji         | $^3$H/$^4$He | 4–11 y | Mahara et al., 1993 |
| Fuji         | $^3$H   | 30 y       | Yoshioka et al., 1993 |
| Yatsugatake  | $^3$H   | 1–60 y     | Kakiuchi and Marui, 1994 |
| Yatsugatake  | CFCs   | 20–30 y    | Asai and Tsujimura, 2010 |
| Ontake       | $^3$H   | < 20 y     | Asai et al., 2009 |
| Ontake       | CFCs   | <10 y      | Asai and Tsujimura, 2010 |
| Dainichigatake | SF$_6$ | 9–32 y   | This study |

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into the groundwater aquifer. Santella et al. (2008) reported concentrations of SF$_{6}$ in air over large urban centers in the United States are about twice that of clean air. Similar elevated SF$_{6}$ air concentrations were also observed in the urban area of Tokyo, Japan (Komine et al., 2003). So, the SF$_{6}$ concentrations exceeding documented atmospheric SF$_{6}$ concentrations by 10–30%, which were observed in some groundwater samples, might be explained by dissolution of SF$_{6}$ from urban air. SF$_{6}$ concentrations at the remarkable level of 400 ppt recorded in groundwater sample from the urban center of Nagoya city is considered to be caused by direct intrusion from local industry.

Input of excessive anthropogenic SF$_{6}$ from local industrial activities caused a high concentration in some groundwater in the plains. This suggests local anthropogenic SF$_{6}$ may limit the usefulness and accuracy of measuring SF$_{6}$ to date young groundwater within the plains of Japan.

**CONCLUSIONS**

This study investigates the applicability and accuracy of using SF$_{6}$ as a dating tool for young groundwater in the Chubu region in Japan. The observed SF$_{6}$ in most springs in mountainous areas were of atmospheric origin where the impact of natural SF$_{6}$ is relatively small. Input of excessive anthropogenic SF$_{6}$ from local industrial activities was observed in some groundwater in the plains. The SF$_{6}$-based apparent ages for the mountainous springs were estimated at less than 6 years in small catchment areas (< 0.5 km$^2$), and 4 to 32 years in the Quaternary volcanic area. The SF$_{6}$ ages obtained were consistent with the scale of groundwater flow and with previously determined $^{18}$O ages for groundwater in similar settings in Japan.

The present study investigated only representative water samples in the Chubu region, and the SF$_{6}$ ages were determined under simple conditions. To understand the validity of the SF$_{6}$ dating method in Japan will require collection of long term SF$_{6}$ data in various water samples, application of a groundwater mixing model, monitoring of atmospheric SF$_{6}$, and comparison of SF$_{6}$ age with $^{18}$O/$^{16}$O aging methods. The results of this study suggest the SF$_{6}$ method can be an effective dating tool for young groundwater in Japan, when the input of local anthropogenic SF$_{6}$ is negligible.

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