Journal of Hydrology (2007) **339**, 93–104

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# Evidence for terrigenic $SF_6$ in groundwater from basaltic aquifers, Jeju Island, Korea: Implications for groundwater dating

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Received 29 June 2006; received in revised form 21 March 2007; accepted 22 March 2007

**KEYWORDS**
Environmental tracer;
Groundwater dating;
CFCs;
$SF_6$;
Tritium;
Volcanic island

**Summary** Measurements of the concentrations of dichlorodifluoromethane (CFC-12), tritium ($^3H$), and sulfur hexafluoride ($SF_6$) in groundwater from basaltic aquifers in Jeju Island, Korea, demonstrate a terrigenic source of $SF_6$. Using a lumped-parameter dispersion model, groundwater was identified as young water (<15 years), old water with negligible CFC-12 and $^3H$, and binary mixtures of the two. Model calculations using dispersion models and binary mixing based on $^3H$ and CFC-12 concentrations demonstrate a non-atmospheric excess of $SF_6$ relative to CFC-12 and $^3H$ concentrations for more than half of the samples. The non-atmospheric excess $SF_6$ may have originated from terrigenic sources in relict volcanic fluids, which could have acquired $SF_6$ from granites and basement rocks of the island during volcanic activity. Local excess anthropogenic sources of $SF_6$ are unlikely. The $SF_6$ age is biased young relative to the CFC-12 age, typically up to 20 years and as high as 30 years. This age bias is more pronounced in samples of groundwater older than 15 years. The presence of terrigenic $SF_6$ can affect the entire dating range for groundwater in mixtures that contain a fraction of old water.


## Introduction

Sulfur hexafluoride ($SF_6$) is a colorless, odorless, incombustible, non-toxic, stable gas with excellent electrical insulating and arc-quenching properties (Maiss and Brenninkmeijer, 1998). $SF_6$ has been used as a conservative artificial gaseous tracer in many groundwater studies through deliberate introduction of $SF_6$-charged water. Upstill-Goddard and Wilkins (1995) used $SF_6$ to evaluate bulk water flow in an artificial geothermal reservoir. In a coastal karst aquifer with freshwater–seawater interfaces, $SF_6$ was used as an artificial tracer to determine groundwater transport rates (Dillon et al., 1999; Dillon et al., 2003). Gamlin et al. (2001) used $SF_6$ to trace surface water from a 9 km reach of a sinking

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0022-1694/$ - see front matter 
doi:10.1016/j.jhydrol.2007.03.011

river to nearby wells. Clark et al. (2005) traced movement of water in a permeable alluvial aquifer from artificial recharge ponds using the gaseous tracers $SF_6$ and $^3He$.

Environmental sulfur hexafluoride ($SF_6$) from atmospheric sources was employed as a dating tool of young groundwater by Busenberg and Plummer (2000). They developed a very sensitive gas chromatography system with electron capture detector to detect low levels of $SF_6$ in groundwater of atmospheric origin and determined the natural background for $SF_6$. Because the $SF_6$ atmospheric history is well known, $SF_6$ has been used as an environmental tracer in multi-tracer studies to estimate ages and mixing properties of groundwater (Plummer et al., 2001). In their study of discharge from springs in the Blue Ridge Mountains of Virginia, USA, reliable ages for young groundwater were obtained by $SF_6$ dating in igneous and metamorphic terrain where terrigenic $SF_6$ had not accumulated because of the young age. CFC ages could not be resolved because of the turnover in air input functions. The $^3H/^3He$ ages of waters from the shallow springs were typically biased 1–2 years younger than the $SF_6$ ages. Because the aqueous diffusion coefficient of He ($6.30 \times 10^{-5}$ cm$^2$/s at 15 °C from Jahne et al., 1987) is seven times larger than that of $SF_6$ ($9.20 \times 10^{-6}$ cm$^2$/s at 15 °C from King and Saltzman, 1995), the waters may have lost some $^3He$ (Plummer et al., 2001) due to incomplete He confinement. Zoellmann et al. (2001) used environmental $SF_6$ to delineate nitrate contamination of groundwater from tertiary basalts in conjunction with $^3H$. Zuber et al. (2005) studied different hydrochemical water types and groundwater mixing in a sandy aquifer in southern Poland using $SF_6$ and $^3H$ where CFCs could not be used for groundwater dating due to contamination of atmospheric CFCs by local sources. Plummer et al. (2003) and Plummer (2005) reviewed applications of $SF_6$ and other environmental tracers to dating young groundwater. Gooddy et al. (2006) studied the Chalk aquifer consisting of microporous and fractured carbonate rocks located in a rural area of southern England using CFC-12 and $SF_6$. They characterized groundwater flow regimes and evaluated the mixing of tracer-free old water and recent recharge, and that of groundwater and surface water near a river.

$SF_6$ has many advantages as an environmental tracer in comparison to CFCs. $SF_6$ does not react with the substrate or sorb onto aquifer organic matter and apparently does not biodegrade, even in highly reducing environments as is the case with chlorofluorocarbons (Busenberg and Plummer, 2000). Contamination of groundwater from non-atmospheric anthropogenic sources of $SF_6$ is less likely than contamination with CFCs. $SF_6$ is mainly used as an electrical insulator in high-voltage switches and transformers and as a blanket gas in the melting operations of magnesium metal production (Maiss and Brenninkmeijer, 1998), but $SF_6$ is not present in any commonly used household products. In addition, $SF_6$ does not readily sorb into rubber and polymers; therefore, groundwater is less likely to be contaminated with $SF_6$ from contact with these materials during sampling. Atmospheric concentrations of $SF_6$ are expected to continue to increase into the 21st century (Ko et al., 1993). This enables $SF_6$ to be continuously used as a hydrologic tracer in the future, which is not the case for CFCs that have atmospheric mixing ratios that have decreased from the 1990s. The dating range with $SF_6$ applies to water recharged in 1970 to the present.

Dating of young groundwater with $SF_6$ can, in some instances, be complicated by natural terrigenic sources of $SF_6$, such as from some diagenetic, igneous and volcanic fluids, presumably within fluid inclusions in mineral grains (Harnisch and Eisenhauer, 1998; Harnisch et al., 2000; Busenberg and Plummer, 2000), and by addition of excess air during recharge (Busenberg and Plummer, 2000). Furthermore, urban air can be elevated in $SF_6$ from local and regional sources (Ho and Schlosser, 2000; Santella et al., 2003).

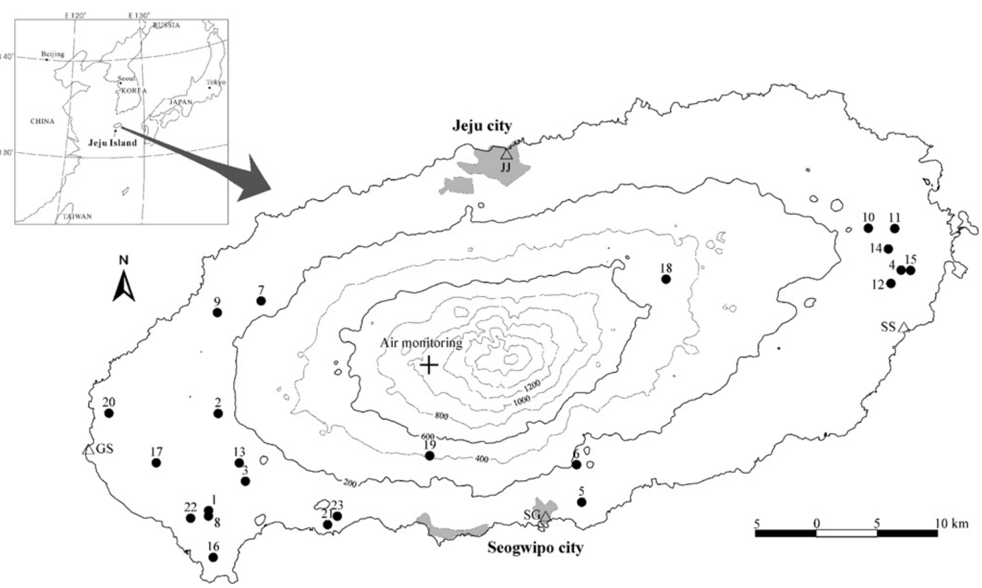


**Figure 1** Location of groundwater sampling sites. A cross shows the site of air monitoring for CFCs and $SF_6$. Numbers on the contour lines are altitudes in meters above mean sea level (Korean geodetic vertical datum was established in 1916 based on measured sea level at Incheon Port). Triangles are meteorological stations of Korea Meteorological Agency, where JJ = Jeju, GS = Gosan, SG = Seoguipo, and SS = Seongsanpo. Shaded areas locate the two major cities of Jeju and Seogwipo on the island.