

A new design of groundwater sampling device and its application

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Abstract: Compounds in the atmosphere contaminate samples of groundwater. An inexpensive and simple method for collecting groundwater samples is developed to prevent contamination when the background concentration of contaminants is high. This new design of groundwater sampling device involves a glass sampling bottle with a Teflon-lined valve at each end. A cleaned and dried sampling bottle was connected to a low flow-rate peristaltic pump with Teflon tubing and was filled with water. No headspace volume was remained in the sampling bottle. The sample bottle was then packed in a PVC bag to prevent the target component from infiltrating into the water sample through the valves. In this study, groundwater was sampled at six wells using both the conventional method and the improved method. The analysis of trichlorofluoromethane(CFC-11) concentrations at these six wells indicates that all the groundwater samples obtained by the conventional sampling method were contaminated by CFC-11 from the atmosphere. The improved sampling method greatly eliminated the problems of contamination, preservation and quantitative analysis of natural water.

Keywords: groundwater sampling; improved method; conventional method; tritium; trichlorofluoromethane(CFC-11)

Introduction

Sampling involves the collection of water for analysis. Many techniques are available for collecting groundwater samples. Different techniques should be used for different types of well, different analytes, different types of hydrogeologic settings and chemical compositions of groundwater. The choice of sampling method depends on the study objectives, the class and properties of the monitored chemicals and the hydrogeological characteristics of the site. The overall goal is to obtain representative groundwater without affecting the chemical composition. A variety of sampling devices can be used to remove water from a well. Sampling techniques can be generally categorized as either manual or mechanical. Manual sampling devices include hand bailers and syringe samplers. Hand bailers are commonly used due to their simplicity and low-cost. Mechanical sampling techniques typically involve pumps to lift groundwater to the surface, where the sample is collected. The use of low-flow peristaltic pumps, which can remove water slowly and smoothly from wells, inserted into the bottom of wells, is probably the best approach of obtaining samples to be analyzed for volatile compounds.

The water samples must be put in containers or vials when the groundwater samples are removed from the well to the surface, regardless whether pumps or bailers are used. In this procedure, the samples come into contact with the ambient air and some volatile compounds are transferred between the water and the air. Baehr *et al.* (Baehr, 1999) reported that the concentrations of VOCs in groundwater could potentially increase over time if the atmosphere is the source. Pankow (Pankow, 1986) reported that the concentration of VOCs in groundwater is determined by the atmospheric concentration, the atmospheric pressure and their solubility.

If the concentration of VOCs in the water sample is very low, then the compounds in ambient air will be transferred into the water during sampling or preservation, affecting the results of any analysis. CFCs are the compounds most sensitive to the technique by which groundwater is sampled and analyzed. Several authors have reported that the

contamination of samples by CFCs is due to sampling artifacts and procedures. These include sampling equipment such as tubing (Busenberg, 1992) and materials from which wells are constructed, such as sand installed at the well screens, grout used to seal the borehole annulus and PVC adhesives (Goode, 1998).

In recent years, the USEPA Method has become the standard procedure for sampling groundwater and analyzing it in the laboratory. It recommends the use of a 40 ml VOC sampling vial for sampling groundwater. The water samples are in contact with atmospheric air during sampling and analysis and are therefore contaminated by components in the air. This contamination seriously influences the results of chemical analysis.

Busenberg and Plummer (Busenberg, 1992) suggested the flame-sealing of groundwater samples in glass ampules during field sampling. They indicated that problems of the contamination and preservation of natural water could be solved by isolating the samples from air and sealing the samples in borosilicate glass ampules at the well site for later laboratory analysis. However, their sampling system is expensive and not widely used. This study develops an improved method for collecting water samples, without contamination. Groundwater was sampled at four sites using both the conventional method and the improved method. Samples obtained by each method were analyzed for trichlorofluoromethane(CFC-11) to determine the affect on CFC-11 concentrations of contamination during sampling. The use of the improved method in groundwater sampling was evaluated and comparisons with the conventional sampling method(USEPA Method) were made.

1 Materials and methods

1.1 Site description

Groundwater was sampled from six wells for analysis. These six wells are located at Kanshi Farm, at Kaohsiung "International" Airport Terminal, in the Kaohsiung Economic Processing Zone and in Nanzhi Industrial Park. These four sites are described below.

1.1.1 Kanshi Farm

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A deep supply well (deeper than 200 m), called well S-01 is at Kanshi Farm, a Tai-Sugar field in Tainan, Taiwan, China. A previous study (not published) has shown that the groundwater in this aquifer is relatively old and free of contamination, since the aquifer is confined and isolated from human activity. Waters sampled from this well were initially expected to be free of CFC-11.

1.1.2 Kaohsiung "International" Airport Terminal

Two monitoring wells, well MW-52 and well MW-56, which are open to a confined aquifer, are at the Kaohsiung "International" Airport Terminal, located in Kaohsiung, Taiwan, China. The wells are 10.41 m and 10.34 m deep, respectively.

1.1.3 Kaohsiung economic processing zone

One monitoring well (MW-32) is open to a confined aquifer in the Kaohsiung Economic Processing Zone, in Kaohsiung, Taiwan, China. This well has a total depth of 8.23 m and is constructed from 6 in PVC tubing.

1.1.4 Nanzhi Industrial Park

Two monitoring wells (MW-28 and MW-29) were constructed at Nanzhi Industrial Park, located in Kaohsiung, Taiwan, China. These two wells are open to an unconfined aquifer. Wells MW-28 and MW-29 have total depths of 12.21 m and 11.23 m respectively, and both are constructed from 6 in PVC tubing.

1.2 Groundwater pre-sampling work

At least three sampling well volumes of the groundwater were produced using a low flow-rate peristaltic pump to ensure that representative samples were obtained. The conductivity, pH and temperature were monitored until these parameters stabilized (indicating that formation water was being sampled) and then groundwater samples were extracted using a low flow-rate peristaltic pump (at a flow rate of under 0.2 L/min).

1.3 Conventional sampling method

The conventional sampling method, the USEPA Method, recommends the use of a 40 ml VOC sampling vial. The vial was connected to the low flow-rate peristaltic pump using 0.64 cm Teflon tubing. When the vial was filled with the groundwater sample, sealing the vial by a Teflon spacer cap, and leaving no headspace volume. The groundwater sample was in contact with the atmosphere during sampling, constituting an opportunity for contamination. Samples for the analysis of tritium were taken midway through the collection of the CFC-11 samples.

1.4 Improved groundwater sampling method

The improved method involves a sampling bottle, instead of a 40 ml VOC sampling vial. The use of glass bottles maintained the concentration of all compounds over a 34-day period of observation (Reynolds, 1990). The glass sampling bottles had a Teflon-lined valve at each end (Fig. 1). Cleaned and dried sampling bottles were flushed with highly pure nitrogen. Each sampling bottle was connected to a low flow-rate peristaltic pump with 0.64 cm Teflon tubing and flushed continuously about 5 min. Both valves were closed after the sampling bottle was filled with water and no headspace volume remained. The sample bottle was then packed in a PVC bag to prevent the target component from infiltrating into the water sample through the valves. PVC has a diffusivity of about 10^{-17} cm²/s, and so was used to protect

the samples with halogenated hydrocarbons that exhibit low activities (Reynolds, 1990). The bag was sealed after the air was squeezed out. Fig. 1 schematically depicts the improved method for sampling groundwater.

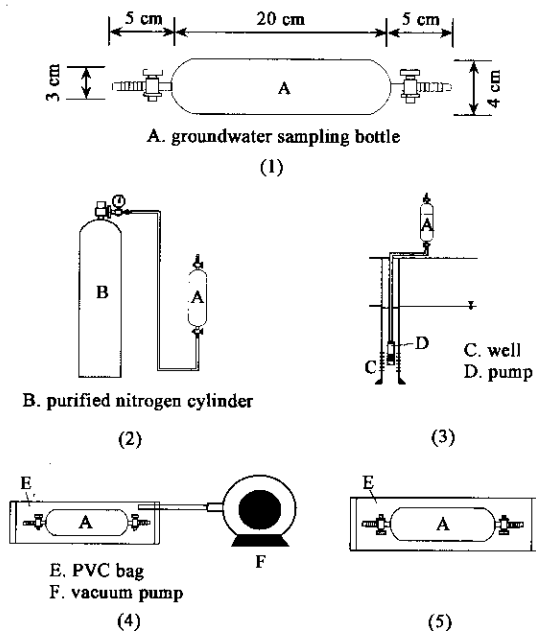


Fig.1 Schematic diagram of the improved method for sampling groundwater (1) sampling bottle required by the improved method for sampling groundwater; (2) flushing the sampling bottle with high-purity nitrogen; (3) using a low flow-rate peristaltic pump to collect groundwater from a well and conduct the water sample to the sampling bottle; (4) squeezing the air out of the PVC bag; (5) sealing the PVC bag

1.5 Sampling QA/QC

Clean and CFC-free tubing, sampling bottles, and new VOC vials were used at each well to eliminate the possibility of cross-contamination. Field blanks and duplicates were taken using both the conventional sampling method and the improved sampling method. Using both of the sampling methods, a 40 ml VOC sampling vial and a sampling bottle were filled with groundwater. Air bubbles were prevented from passing through the sample and no headspace volume was left during sampling and preservation, to ensure that no target compounds would be lost. All samples were placed inside a portable freezer and transported to the main laboratory for quantitative analysis. All samples were analyzed within 14 d of collection to prevent losses from the samples during preservation.

1.6 Chemical analysis of groundwater samples

The CFC-11 content in the samples was analyzed according to the USEPA Method 502 (USEPA, 1983). The analyses were performed using purge and trap (Tekmar LSC 2000, USA), coupled to a gas chromatograph (Shimadzu GC-14A, Japan) that was equipped with an electron capture detector (ECD) to determine the quantity of the CFC-11. Each analysis involved a 5.0 ml water sample. The sample was purged using a stream of N₂ at 40 ml/min for 10 min at ambient temperature. The optimum conditions of the GC/ECD analytical system involved the following; the use of a 3 m long column with an inner diameter of 1/8 in, packed with 25 Octoil-s on celite-545 (170–250 μ); N₂ was used as the carrier gas at 5 ml/min and as the make up gas at 95 ml/min; the temperatures of the oven, injector and detector were fixed

at 30°C, 150°C and 250°C, respectively. The detection limit of the method was calculated to be 0.0072 ng/L, calculated as three times the standard deviation of a sample analyzed nine times.

The conventional method inputs the groundwater sample into the purge and trap concentrator through a gastight syringe. Therefore, the samples were allowed to be in contact with the atmosphere during this procedure. In the improved method, the sampling bottle is directly connected to the purge and trap concentrator, and was thus absolutely isolated from the atmosphere (Fig. 2).

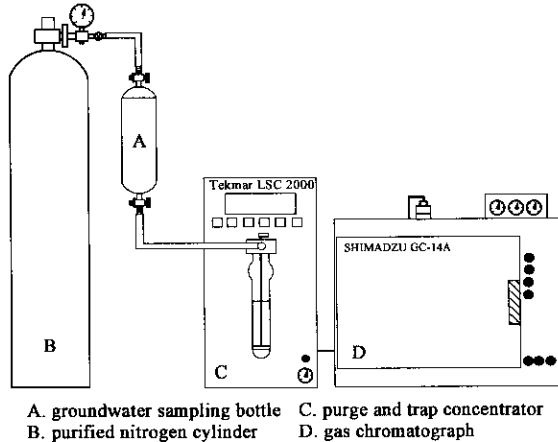


Fig. 2 Schematic diagram of the connection between the sampling bottle and the analytical system

2 Results and discussion

2.1 Relationship between concentrations of CFC-11 and tritium

CFC-11 in the atmosphere is a synthetic organic compound, which has been used commercially since 1931. The concentration of CFC-11 in the lower troposphere varies from 50 pptv to 500 pptv (Thompson, 1979; David, 1998). Normally, the atmospheric concentration is least above the ocean and greatest above urban areas (Thompson, 1979). CFC-11 in the atmosphere is transferred to surface water through precipitation. The Henry constant of CFC-11 is 0.11 atm · m³/mol at 20°C (Pankow, 1986). The equilibrium aqueous concentration of CFC-11 in air at a concentration of 500 pptv is calculated to be 0.618 ppt. Busenberg and Plummer (Busenberg, 1992) reported a CFC model for estimating the groundwater recharge ages, and this model is within 2 years under optimum conditions.

Before atmospheric fusion-bombs were tested in the early 1950s, a steady-state tritium inventory of approximately 3.5 kg was maintained on the Earth's surface as a result of the cosmic-ray. In 1953, the concentration of tritium in precipitation began to increase as nuclear weapons were tested. The concentrations of tritium in groundwater formed before 1953 and uncontaminated by CFC-11 from pollution sources should be under 1 T.U. and CFC-11 should not be detected in this groundwater. However, the concentration of tritium in groundwater formed after 1953 is greater than 1 T.U. and the concentration of CFC-11 therein is usually less than 0.618 ppt (Pankow, 1986; Liu, 1996). Consequently, Busenberg and Plummer (Busenberg, 1992) suggested that tritium data are useful in determining whether the observed

CFC-11 concentration have been modified by contamination.

2.2 Comparison of groundwater sampling methods

Groundwater samples were extracted from well S-01 by both the conventional and the improved methods. A little CFC-11 was detected in samples obtained using the conventional method. The average concentration of CFC-11 was 0.384 ± 0.023 ppt. However, no CFC-11 was detected in samples obtained by the improved method (Table 1). This result indicates that the improved method can isolate the samples from air and prevent them from being contaminated. The same groundwater samples were also analyzed to determine tritium concentration. The concentration of tritium was 0.6 ± 0.3 T.U., indicating that the groundwater around well S-01 was formed before 1953. The concentration of CFC-11 should be less than detection limit according to the CFC model. Between these two methods, only the samples obtained by the improved method can match this result.

The concentrations of tritium in samples obtained from wells MW-52 and MW-56 were 3.5 ± 0.3 and 3.4 ± 0.3 T.U., respectively. These concentrations of tritium may have been generated by the infiltration of precipitation into the groundwater system after 1953. The average concentration of CFC-11 in samples obtained from wells MW-52 and MW-56 using the improved method were 0.202 ± 0.021 and 0.224 ± 0.030 ppt (Table 1). The groundwater at this site was thus recharged, around the 1970s, according to the CFC model. However, the average concentrations of CFC-11 in samples obtained from wells MW-52 and MW-56 using the conventional method were 0.474 ± 0.115 and 0.449 ± 0.135 ppt. This result indicates that the improved method can prevent the samples from contamination.

The average concentration of CFC-11 in samples obtained from well MW-32 by the conventional sampling method was 0.611 ± 0.136 ppt. The average concentration of CFC-11 obtained using the improved method was 0.231 ± 0.021 ppt (Table 1). The improved method clearly solves the problem of contamination. The groundwater in this site was thus recharged in the 1970s. The concentration of tritium was 2.8 ± 0.3 T.U., indicating that water infiltrated into the groundwater system after 1953.

The concentrations of CFC-11 in samples obtained by the improved method from wells MW-28 and MW-29 in Nanzhi Industrial Park were measured to be 3.442 ± 0.101 and 16.254 ± 1.811 ppt (Table 1). The average concentrations of CFC-11 obtained using the conventional method were 3.607 ± 0.157 and 15.473 ± 1.928 ppt. However, the concentration of CFC-11 in the rainwater collected in Nanzhi Industrial Park was measured as 0.863 ± 0.097 ppt. It indicates that the groundwater samples of this site should not be contaminated by CFC-11 from atmosphere during the sampling procedure. Hence, the concentrations of CFC-11 in samples obtained by both sampling methods were similar and high. Moreover, the concentration of CFC-11 of the groundwater samples in this site were too high to be of atmospheric origin and so were most likely to be attributable to contamination by a point source, such as leakage from an underground storage tank/pipeline or an industrial waste dump (Plummer, 1998).

The analysis of CFC-11 concentrations at these four sites indicates that all the groundwater samples obtained by the

conventional sampling method, were contaminated by CFC-11 from the atmosphere. The improved sampling method solved the problems of contamination, preservation and quantitative analysis of natural water. These results concerning CFC-11 were consistent with tritium data. Furthermore, the improved

sampling method is simpler and cheaper than the ampule-filling system (Busenberg, 1992). The conventional and improved methods differ by 10 to 20 years in determining the age of young groundwater using CFC-11 concentration.

Table 1 Trichlorofluoromethane concentrations in groundwater samples taken from different wells in different locations

Well No.	Kansi Farm	Kaohsiung "International" Airport Terminal		Kaohsiung Economic Processing Zone	Nanzhi Industrial Park	
	S-01	MW-52	MW-56	MW-32	MW-28	MW-29
CFC-11 conc. for conventional method, ppt	0.384 ± 0.023	0.474 ± 0.115	0.449 ± 0.135	0.611 ± 0.136	3.607 ± 0.157	15.473 ± 1.928
CFC-11 conc. for improved method, ppt	ND	0.202 ± 0.021	0.224 ± 0.030	0.231 ± 0.021	3.442 ± 0.101	16.254 ± 1.811
Tritium level, T.U.	0.6 ± 0.3	3.5 ± 0.3	3.4 ± 0.3	2.8 ± 0.3	4.2 ± 0.4	3.8 ± 0.3

Note: ND, non-detectable (< 0.0072 ppt)

3 Conclusions

The conventional groundwater sampling method (USEPA Method) allows the groundwater sample to be in contact with the atmosphere during sampling, constituting an opportunity for contamination. This study demonstrates this phenomenon in relation to the sampling and analysis of CFC-11 in groundwater at different sites. An improved groundwater sampling method was developed and validated for quantifying very low concentrations of CFC-11 in groundwater. Most importantly, the method can cheaply and simply sample groundwater without allowing it to become contaminated when the background concentration is high. The analytical results concerning CFC-11 indicate that the concentrations of samples obtained using the conventional method were two to three times higher than those of obtained using improved method. This difference generates an error from 10 to 20 years in the dating young groundwater using the concentration of CFC-11 therein. Consequently, isolating samples from air that contains target compounds is very important.

In this study, tritium concentrations of all groundwater samples confirm that reasonable concentrations of CFC-11 were obtained using the improved method. Tritium data are useful in determining whether the observed CFC-11 concentration had been modified by contamination.

Acknowledgements: The authors would like to thank the financial support for this research under Contract No. NSC 83-0402-E006-070.

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(Received for review December 20, 2004. Accepted March 7, 2005)