Experimental Evaluation of an Analytical Method for Chlorofluorocarbons (CFCs) in Air and Water Using Gas Chromatography

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가스 크로마토그래피를 이용한 대기와 물시료의 CFCs(chlorofluoro-carbons) 분석법의 실험적 평가

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대기와 물에서의 CFCs (CFC-12, CFC-11, CFC-113)를 분석할 수 있는 시스템을 자체 제작된 퍼지-트랩 추출 장치와 전자포획검출기가 설치된 가스 크로마토그래피를 이용하여 구축하였다. 대기와 물에 대한 시료 채취방법도 확립되었다. 분석 시스템은 실험적으로 최적화되어 최근 대기 시료는 2% 이내, 제주도의 지하수 시료 (CFC-12 농도가 160~180 pg/kg)는 5% 이내의 삼중복시료에 대한 재현성을 보였고, 미국지질조사소 (USGS)의 분석시스템과 교차 분석을 실시하였으며, 10% 오차 범위내에서 일치하였다. 한반도 중부 지역의 세 지점에 대해 19개월에 걸쳐 대기 중의 CFCs를 관측하여 이 지역에서 국지적인 CFCs 근원이 크지 않음을 확인하였다. 제주도의 한 농업용 공공 관정에서 2개월 간격으로 1년 동안 지하수의 CFCs를 관측한 결과 8월까지 지하수의 CFCs 농도가 감소하고 10월 이후에 다시 증가하는 계절적인 변동을 보여 주었다. 이것은 여름철 우기에 발생한 지하수 함양이 수 개월 지연되어 나타난 결과로 볼 수 있으며, 제주도 현무암 대수층의 높은 투수성을 지시한다.

주제어 : CFCs (Chlorofluorocarbons), 환경 추적자, 가스 크로마토그래피, 지하수 연령 측정, 대기 할로겐탄소

CFC (CFC-12, CFC-11 and CFC-113) analytical system for air and water was constructed using a customized purge and trap extraction device and a gas chromatograph with an electron capture detector. Sampling methods of air and water for CFCs were also established. The analytical system was experimentally optimized to result in reproducibilities of triplicates less than 2% for current air samples and less than 5% for groundwater samples with CFC-12 concentration of 160 to 180 pg/kg, and verified with respect to the CFC system in USGS, which showed analytical results were in agreement within 10%. CFCs in air were monitored at three sites over 19-month period in the central part of South Korea, and the result indicates no significant local sources of CFCs in those areas. For groundwater in Jeju Island, CFCs were measured over a year with a two-month interval. The time-series data showed seasonal fluctuations which could be interpreted by the effect of recharge pulse derived from large amount of rainfall during monsoon period with a few month delay, which indicates high permeability of basaltic rocks in Jeju Island.

Key words : CFCs (chlorofluorocarbons), environmental tracer, gas chromatography, groundwater age, atmospheric halocarbons

1. Introduction

Chlorofluorocarbons (CFCs) have been released in the environment entirely by anthropogenic sources and used as environmental tracers in environmental studies (Table 1). CFCs have been widely used as hydrological tracers in groundwater studies since a sampling method by flame-sealed borosilicate ampoules was developed by Busenberg and Plummer (1992). In early studies, only CFCs were used as environmental tracers (Dunkle et al.,

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Table 1. Physical properties of target compounds

| Compound	Formula	CAS-No.	Common name	Formula weight	BP (°C)[1]	VP (atm)[2]	RS[3]
Dichlorodifluoro-methane	CCl_2F_2	75-71-8	CFC-12	120.92	-29.8	6.3	1.0
Trichlorofluoro-methane	CCl_3F	75-69-4	CFC-11	137.36	23.6	1.0	3.6
1,1,2-trichloro-1,2,2-trifluoroethane	CCl_2FCClF_2	76-13-1	CFC-113	187.35	47.7	0.5	1.0

[1]Boiling point (Hohener *et al.*, 2003).

[2]Vapor pressure at 25°C (Hohener *et al.*, 2003).

[3]Relative solubility in water normalized to that of CFC-12 at 25°C. Solubility data from Warner and Weiss (1985) for CFC-11 and CFC-12, from Bu and Warner (1995) for CFC-113.

1993, Cook *et al.*, 1995). Recently, CFCs have been employed in conjunction with $^3H/^3He$ and SF_6 as one of multi-tracers (Ekwurzel *et al.*, 1994, Szabo *et al*, 1996, Plummer *et al.*, 2001, Burton *et al.*, 2002, Burns *et al.*, 2003, Happell *et al.*, 2003).

Environmental tracers including CFCs have been applied to age dating of groundwater (Dunkle *et al.*, 1993), interpretation of groundwater flow characteristics (Cook *et al.*, 1995), mixing properties of groundwater and surface water (Plummer *et al.*, 1998), nitrate contamination of groundwater (Böhlke and Denver, 1995), construction and ver-

ification of groundwater flow model (Reilly *et al.*, 1994). In Korea, Koh and Lee (2003) first applied CFCs to investigation of groundwater systems. Koh and Kim (2004) studied groundwater in Jeju island using a multi-tracer approach including CFC-11, CFC-12, and $^3H/^3He$. CFC-11 and CFC-12 in air were monitored for 3.5 years in Gosan, Jeju island from 1995 (Kim *et al.*, 2001). More recently, CFCs in air were monitored on both weekly and monthly basis in Jeju island (Koh *et al.*, 2006). However, to date no study has been carried out for CFC-113 in water and atmosphere in
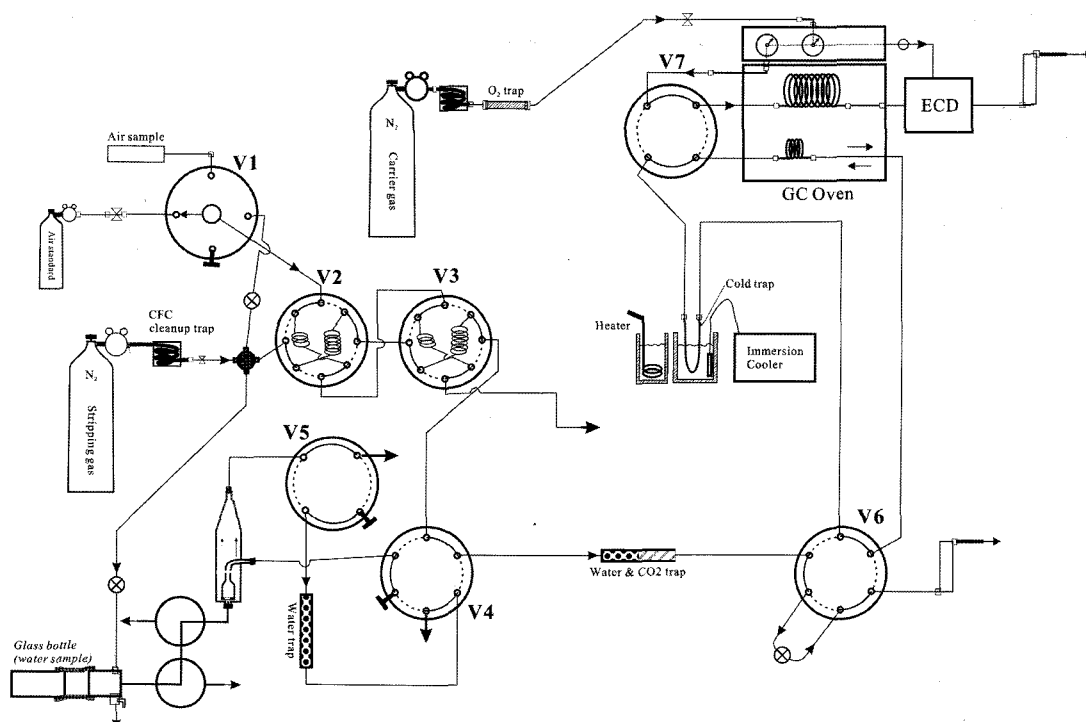
Fig. 1. Schematic flow diagram for CFC analytical system.

Korea.

An analytical method of CFCs in water and air using gas chromatography (GC) was established by Bullister and Weiss (1988). They extracted CFCs by stripping water sample with ultra pure N_2 gas in closed system and trapped them in a cryogenic trap. The trapped CFCs were separated using packed columns and detected with an electron capture detector (ECD).

This study is for the establishment of CFC analytical system for water and air to apply to hydrological studies. Analytical characteristics of CFC-113 as well as CFC-11 and CFC-12 were evaluated using the modified method of Bullister and Weiss (1988) which had been originally designed for measurement of CFC-11 and CFC-12. A sampling method of water using a glass bottle sealed by a metal-lined cap was tested and verified.

2. Construction of CFC analytical system

The analytical system consists of a gas chromatograph with an electron capture detector (ECD) and a CFC extraction device for water samples. The extraction system for water samples was constructed on the basis of the purge and trap system of Bullister and Weiss (1988). The apparatus for water sample introduction was modified from Busenberg and Plummer (1992) and bottle adapter (Teflon) fitted to a glass bottle was installed to minimize atmospheric contact of water sample though the inside N_2 pressure is higher than ambient conditions. The schematic diagram of flow system of the analytical system is shown in Fig. 1. The explanation for the analytical system in this study is only given in case the detail of the system is not sufficient in the original references mentioned above.

2.1. Sampling methods
Air sample
Sampling of air samples was carried out using 850 mL SUMMA metal canister and an Rass-mussen air sampling pump (Biospherics Research Corp.). The metal canisters were evacuated to about 0.1 Pa before sampling. Air samples were pressurized to 30 psi in the canister from the inlet above 2 meters from land surface using stainless steel or Nylon tubes (Böhlke et al., 1999).
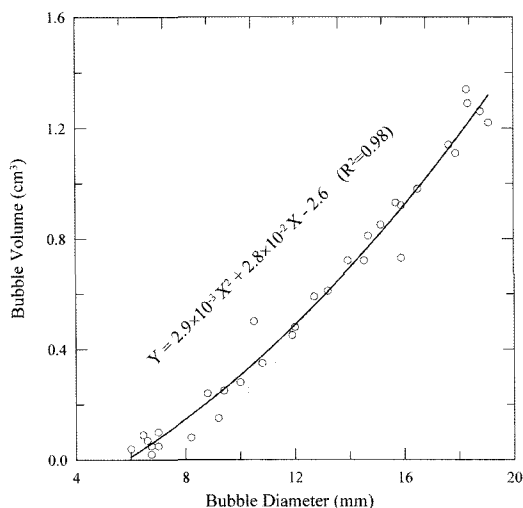

Fig. 2. Empirical relation of diameter and volume of the bubble in glass bottle for water sample.

Water sample
Two sampling methods of groundwater for CFCs using copper tube and flame-sealed glass ampoule were previously evaluated by Koh and Lee (2003). In this study, much simpler glass bottle method was employed, which was developed by Reston CFC Lab, U.S. Geological Survey (http://water.usgs.gov/lab/cfc/). Detailed sampling procedure is as follows.

Groundwater was pumped by dedicated submersible pumps or peristaltic pump with Viton tube on the pump head (Koh and Lee, 2003). A glass bottle of 125 mL (4 oz Boston round, Wheaton, 217122) was filled without headspace under submerging condition with flowing water after sufficient flushing and capped by metal cap with aluminum liner (22/400 white metal foil lined closure, SKS bottle & packaging, Inc., Item #: 6021-03). The bottle was checked for no air bubble and sealed by electric tape around the cap. The sampling was done in triplicates at each site.

The glass bottle filled with water sample can have bubbles formed by exsolution of dissolved gases in the sample during storage. Because these bubbles are lost during introduction of water sample to the extraction system, CFCs in the bubbles should be compensated in final analytical results. Volume of the bubble was determined from the measured diameter of the bubble using the equation, experimentally derived in this study, relating
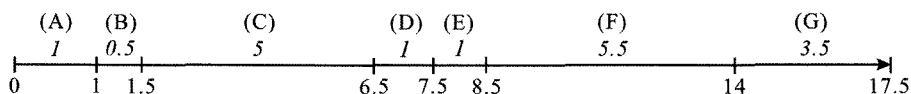
Fig. 3. Time sequence of water-sample analysis in minutes. The analytical sub-procedures are (A) cooling the cold trap, (B) introduction of a water sample, (C) stripping/trapping, (D) heating the cold trap, (E) initial separation, (F) chromatographic run/backflush, and (G) chromatographic run/preparation of next run.

diameter and volume of the bubble (Fig. 2). Because flowing water is not pressurized during the collection of water sample, total pressure is assumed 1 atm in the bubble. Then, amount of CFCs in the bubble was estimated using CFC solubility considering temperature and measured concentration for the injected water, and total CFC concentrations of the sample were compensated by adding these values.

2.2. Purge-trap system

Because atmospheric CFCs have continuously increased from nearly zero until mid-1990s, CFC concentrations in groundwater recharged before 1990s are lower than current level of CFCs in the atmosphere. Thus, extraction and analysis of CFCs in groundwater samples should be done sealed off from the current level of CFCs. Ultra high pure N_2 (99.999%) gas purified by a CFC cleanup trap was used as injection of water sample into the stripper, stripping of water sample and carrier gas for GC system. The CFC cleanup trap was prepared as a 1.5 m SS tubing (1/4" OD) packed with molecular sieve 13X adsorbent (60/80 mesh, Supelco). At first use, it is heated to 300°C for 12 hours with N_2 gas flowing and heated to 300°C for 3 hours for periodic bake-out. CFC peaks in blank run indicate contamination of the cleanup trap, which requires bake-out. CFC cold trap was made by packing 25cm SS tubing (1/8" OD) with Porapak-T (Supelco) and Porasil-C (80/100 mesh, Ohio Valley Specialty Chemicals).

2.3. Gas Chromatography system

A gas chromatograph, (GC-14B-ECD, Shimadzu) was used for detection of CFCs. Carrier gas of N_2 was purified with O_2 trap (OMI-2, Supelco) to remove trace-level O_2. GC analytical columns consist of a GC main column and a precolumn. The GC main column was prepared using 185cm SS tubing (1/8" OD) packed with Porasil-C (80/100 mesh, Ohio Valley Specialty Chemicals) and
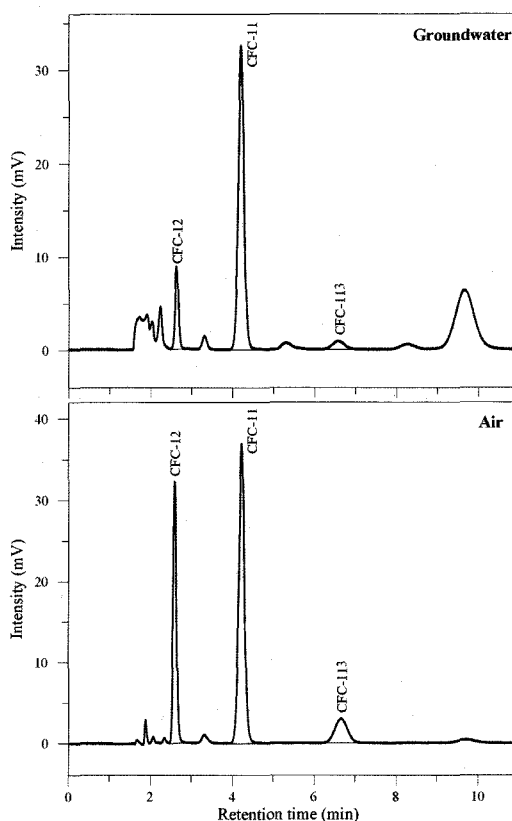
Fig. 4. Chromatograms of CFCs for groundwater and air samples.

precolumn is 16cm SS tubes packed with the same packing material. The columns were activated at 150°C with N_2 gas flowing overnight.

2.4. Analytical procedures
Analytical conditions

Temperatures of analytical GC columns and ECD were set to 74°C and 315°C, respectively. Carrier gas flow is controlled in the range of 20 to 30 cc/min and flow rate is checked periodically using high resolution digital flow meter (Alltech) within ±0.1 cc/min. Stripping gas flow is set between 70 to 100 cc/min. A surge in gas flow rate

on transition of gas stream to the cold trap was minimized by regulating the gas flow with metering valves. The time frame for analysis of water sample is shown in Fig. 3. For air samples, step B is omitted and trapping time is 3 min in step C.

Extraction of CFCs

Air sample and standard air were injected at ambient pressure to various sample loops whose volumes are accurately measured. Water samples were introduced to the stripper using two 3-way valves pressurized by N_2 purge gas. The intake tube is inserted near the bottom of the bottle to minimize loss of CFCs during introduction of water sample. Stripped water sample was weighed to nearest 0.01 g. CFCs from the water sample were extracted and trapped in a cold trap immersed in a cold bath filled with -30°C (±2°C) isopropyl alcohol (1 L stainless-steel Dewar flask) cooled by a immersion cooler with stirring.

Chromatography

After trapping of CFCs, cold trap was transferred to hot bath maintaining at 97 to 100°C and carrier gas is directed to flow cold trap, precolumn, and GC main column for injection to GC system. CFCs in injected gas stream are initially separated in precolumn and gas flow in precolumn is converted to purge flow (backflush). This prevents slowly eluting compounds from entering the GC
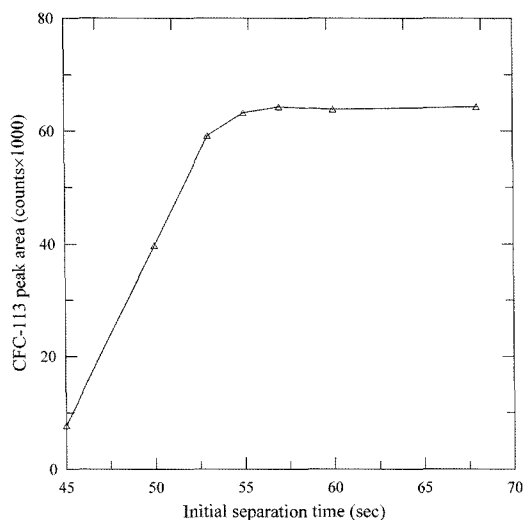
main column, which shortens analysis time and removes possibility of carry-over. Backflush finishes in 15 seconds after CFC-113 peak is fully acquired. Chromatograms for air and groundwater samples are shown in Fig. 4.

3. Optimization of CFC analytical system

3.1. Analytical parameters
Initial separation time in precolumn
During initial separation (IS) of CFCs in precolumn, other compounds than CFCs should be prevented from entering main column to minimize analytical time. To determine optimal IS time, CFC-113 peak areas were compared with varying
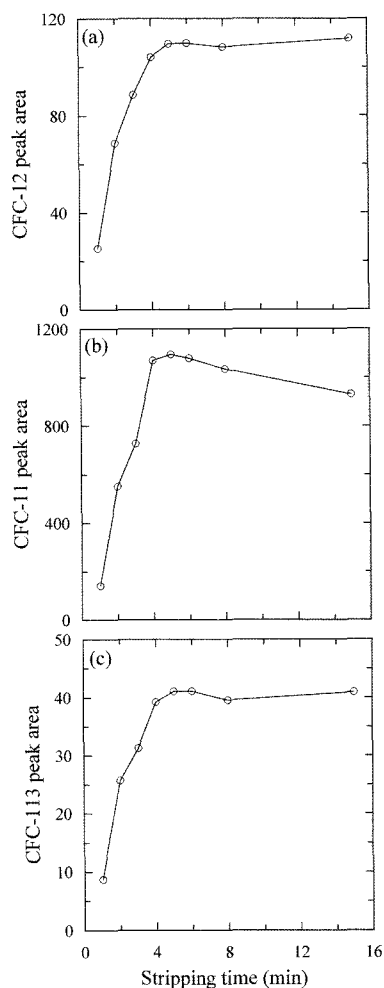

Fig. 6. Peak intensity of CFCs with variation of stripping time in water sample analysis.

Fig. 5. Peak intensity of CFC-113 with variation of initial separation time.

IS time. Because the peak areas were constant after about 60 secs, this time was set to the initial separation time (Fig. 5). To confirm that CFC-113 enters quantitatively the GC main column at the determined IS time, the peak area was compared to that with no backflush. The difference of two measurements was less than 5%, which suggests the determined IS time is appropriate.

Stripping time of water sample

To evaluate extraction efficiency of CFCs from the water sample according to stripping time, clean surface water samples in rural area were analyzed with varying stripping time in the range of 1 min to 15 min. Peak areas increased with the increase of stripping time up to 5 min and leveled off for all of the three CFC compounds (Fig. 6). Stripping

longer than 5 min appears to drive off trapped CFCs from the cold trap because peak areas started to decrease when stripping was prolonged.

Cooling temperature of cold trap

When a cold trap is cooled in a cold bath, there is a vertical temperature gradient in the bath though the bath is stirred. To evaluate the effect of cooling temperature on trapping CFCs on cold trap, air standard is measured at three different temperatures of -25, -30, and -35°C at cold bath. Peak areas showed relative differences of 1.4%, 2.1 %, and 0.1 % for CFC-12, CFC-11, and CFC-113, respectively at the three different temperatures. This indicates that trapping of CFCs is not sensitive to cooling temperatures at the range of -25 to -35°C.

Table 2. Peak areas of CFCs in seven runs of air standard for 6 different volumes

	CFC-12					
Analysis date	1cc[1]	2cc	5cc	10cc	15cc	25cc
Jun-02-2005	23175	45285	105313	192929	280480	448851
Jun-10-2005	22690	44184	101588	186408	273297	441351
Jun-24-2005	23042	45268	102980	190103	275050	441215
Jul-08-2005	23412	45652	104373	191794	278717	444619
Jul-15-2005	23514	45656	104501	191506	280869	448765
Jul-18-2005	23033	44940	103351	191699	280357	444412
Jul-19-2005	23701	44971	102253	187716	274316	437049
RSD, %	**1.5**	**1.1**	**1.3**	**1.3**	**1.2**	**1.0**

	CFC-11					
Analysis date	1cc	2cc	5cc	10cc	15cc	25cc
Jun-02-2005	29526	59909	155778	358878	657493	1490287
Jun-10-2005	28368	58583	152749	353042	640678	1437694
Jun-24-2005	29845	60139	155212	353678	637750	1415608
Jul-08-2005	29429	60186	154235	351602	637713	1430248
Jul-15-2005	29422	59592	151872	344927	628122	1404151
Jul-18-2005	28986	59002	152705	349135	632499	1429992
Jul-19-2005	29404	59552	152290	346735	629663	1419608
RSD, %	**1.6**	**1.0**	**1.0**	**1.3**	**1.5**	**1.9**

	CFC-113					
Analysis date	1cc	2cc	5cc	10cc	15cc	25cc
Jun-02-2005	7187	14545	34251	66630	97890	161619
Jun-10-2005	7309	14450	33488	64104	96762	161035
Jun-24-2005	7231	14857	34831	67721	100161	161638
Jul-08-2005	7311	14517	34712	66177	98824	162196
Jul-15-2005	7224	14689	34983	66727	99213	161289
Jul-18-2005	7171	14409	34175	66202	98171	159574
Jul-19-2005	7110	14548	33802	65566	96539	158103
RSD, %	**1.0**	**1.1**	**1.6**	**1.7**	**1.3**	**0.9**

[1]nominal injection volume of air standard at ambient temperature and pressure

3.2. Calibration

A CFC standard for air and water samples was obtained from Oceanic and Atmospheric Research Laboratories, NOAA (National Oceanic and Atmospheric Administration, USA) as natural uncontaminated air. For calibration of the analytical system, six different volumes of the air standard were injected and calibration curves were constructed from the relation of peak areas and injected mass of CFCs (Table 2). To verify reproducibility of the system over a long term period, seven measurements over the period of seven weeks for the six points of standard were carried out. Relative standard deviation (RSD) of peak areas is less than 2% for three CFC compounds, which suggests that the analytical system is very stable. Because the response of ECD is nonlinear and range of peak area is wide, normalized area and normalized sensitivity were used for calibration.

$$x = \frac{A}{A}\cdot M^* \quad \text{and} \quad y = \frac{M}{A}\cdot\frac{A^*}{M^*} \qquad (1)$$

where, x: normalized peak area

y: normalized sensitivity^{-1}

M: number of picomoles in the injected standard, and

A: corresponding peak area

(the starred quantities are for 10cc sample loop)

The relation of normalized peak area (x) and the reciprocal of normalized sensitivity (y) is fitted with a cubic equation where R^2 is greater than 0.99 for CFC-12 and CFC-11 and 0.95 for CFC-113 (Fig. 7).

3.3. Low-level detection

Background CFCs can be detected from various sources of stripping and carrier gases, infiltration of air, contamination from materials of valves and tubing. The signal-to-noise (S/N) ratio in blank run is usually less than 2 for gas blank passing sample loop and less than 4 for water blank passing both sample loop and stripper system. The relatively high S/N ratio for water blank can be attributed to residual water attached to stripper wall after draining stripped sample. At this level of blank, CFCs can be detected in water to the concentrations as low as 1.1, 0.9, and 0.6 pg/kg with sample injection of 30 cm^3 for CFC-12, CFC-11 and CFC-113, respectively.
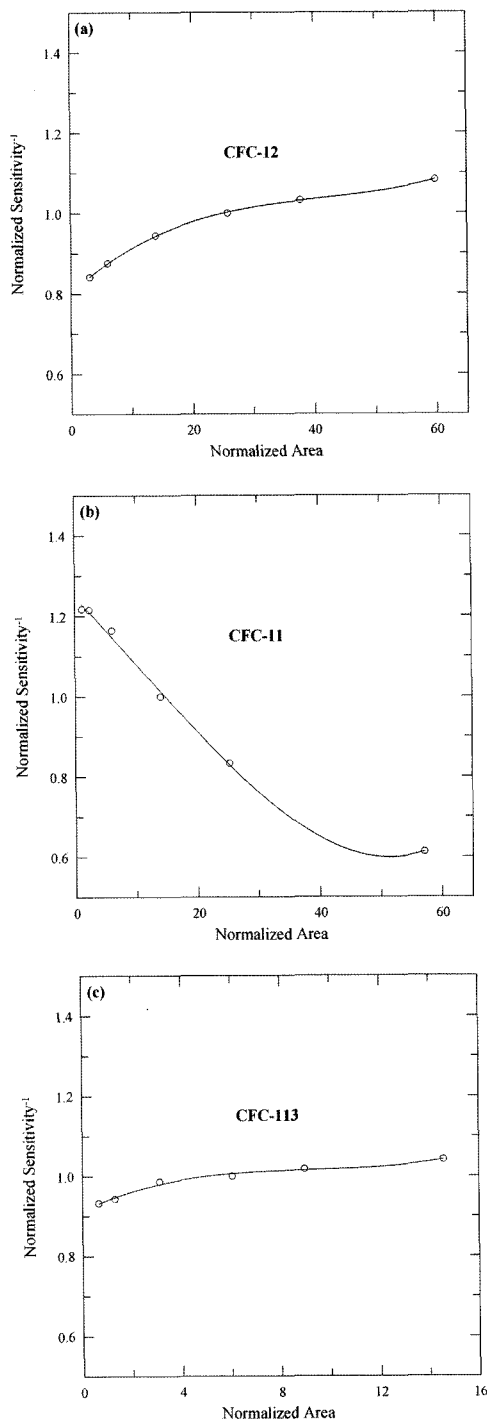

Fig. 7. Normalized calibration curves for CFCs.

Table 3. Replicate analysis of low-level CFCs in a groundwater sample

Replicate No.	Analysis date	CFC-12	CFC-11 (pg/kg)	CFC-113
1	Dec-16-2005	7.4	15.1	2.0
2	Dec-19-2005	7.8	12.6	0.4
3	Dec-20-2005	8.1	17.6	2.4
4	Dec-21-2005	7.9	15.2	2.8
5	Dec-21-2005	7.2	16.9	2.2
6	Dec-22-2005	7.3	11.7	2.4
7	Dec-22-2005	7.3	11.7	2.4
Average		**7.6**	**14.4**	**2.1**
Standard deviation		**0.4**	**2.4**	**0.8**

Detection limit of the analytical system can be determined by measuring seven replicates of the water sample which is expected to have negligible CFCs over at least 3 days using the equation (Snyder, 2004);

$$MDL = 3.14 \times s \tag{2}$$

where, MDL=method detection limit, and
s=standard deviation of the replicate analysis

To set a criterion for reliability of low-level analysis, a groundwater sample with low level CFCs was analyzed for seven replicates (Table 3). The sample has low ^3H concentration of 0.1 TU, which was reported in Koh *et al.* (2006) as sample FW11. The low ^3H indicates that the sample was recharged before 1950s when atmospheric CFCs were negligible compared to those in modern air. The signal-to-noise (S/N) ratios of the analytical results were higher than the S/N ratio of 3 to 5 usually used for MDL determination. However, it is not practical to spike a sample with CFCs to such a low level, the results were used for a practical quantification limit (PQL) for low-level detection, which is determined for CFC-12, CFC-11, CFC-113 as 1.1, 7.6, 2.4 pg/kg, respectively using the analytical results and the equation (2). Considering the PQL, the recharge year of groundwater can be dated to about 1950, 1960, and 1970 using CFC-12, CFC-11 and CFC-113, respectively for recharge temperatures of 10 to 20°C.

3.4. Verification

To evaluate biases of the constructed analytical system, CFC analytical results obtained from our system for air and water were compared with those measured at Reston CFC Laboratory (USGS) for duplicates or triplicates of the same samples (Table 4). For air samples, differences in results were less than 5% for CFC-12 and CFC-11 and 10% for CFC-113. The differences in results for water samples were less than 10% except for the samples with negligible CFCs.

4. Application of CFC analytical results

4.1. Atmosphere

Atmospheric CFC levels were measured at two rural areas of Yesan (126°51'14.1", 36°38'45.9") and Boeun (127°33'31.4", 36°27'51.8"), and one urban area at KIGAM in Daejeon (127°21'44",

Table 4. Comparison of CFCs analytical results by this study and USGS for the same samples in duplicate or triplicate

Site	Sample type	KIGAM[1] Concentration[3] CFC-12	CFC-11	CFC-113	Standard deviation CFC-12	CFC-11	CFC-113	USGS[2] Concentration[3] CFC-12	CFC-11	CFC-113	Standard deviation CFC-12	CFC-11	CFC-113	Difference[4], % CFC-12	CFC-11	CFC-113
Boeun (2004)	Air	575	263	83	-	-	-	552	256	78	3.9	1.2	0.9	4.1	2.8	6.7
Boeun (2005)	Air	541	258	186	1.5	0.4	0.3	545	251	171	2.1	2.6	1.4	-0.7	3.0	8.7
Yesan (2005)	Air	541	257	-	2.1	0.1	-	541	251	-	5.5	0.9	-	0.1	2.6	-
Jeju Island #1	Water	8.2	39.9	1.7	1.8	7.5	0.6	4.1	50.8	2.6	1.2	2.2	2.6	99	-21	-35
Jeju Island #2	Water	267	567	71.2	2.4	5.7	1.9	286	604	73.8	5.7	18.2	2.6	-6.7	-6.1	-3.6
Jeju Island #3	Water	169	437	41.4	3.4	7.0	1.7	180	436	39.8	0.4	0.4	0.9	-6.3	0.2	4.1
Jeju Island #4	Water	287	719	77.4	6.3	7.2	1.7	308	766	76.9	1.5	0.7	1.6	-6.7	-6.2	0.6

[1]Analytical results in this study.
[2]Analytical results by the Reston Chlorofluorocarbon Laboratory in USGS.
[3]pptv for air samples, pg/kg for water samples.
[4]Difference of two measurements by KIGAM and USGS.

Table 5. Analytical results of CFCs for air samples

Collection date	Site	Concentration (pptv)			RSD[1] (%)		
		CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113
01-Apr-05	Yesan	541	257	-	0.4	0.0	-
22-Sep-05	Yesan	530	243	79	0.5	0.4	0.3
16-Dec-05	Yesan	523	249	79	0.2	0.2	0.4
03-Jun-05	Daejeon	541	259	-	0.1	0.1	-
15-Nov-05	Daejeon	555	249	82	0.1	0.0	1.8
16-Dec-05	Daejeon	526	253	94	0.0	0.3	0.2
29-May-04	Boeun	575	263	83	one result	one result	one result
03-Jun-05	Boeun	541	258	-	0.3	0.2	-
22-Sep-05	Boeun	543	242	81	0.1	1.0	0.9
16-Dec-05	Boeun	526	253	80	0.2	0.3	0.5

[1]Relative standard deviation of triplicate analysis otherwise noted.
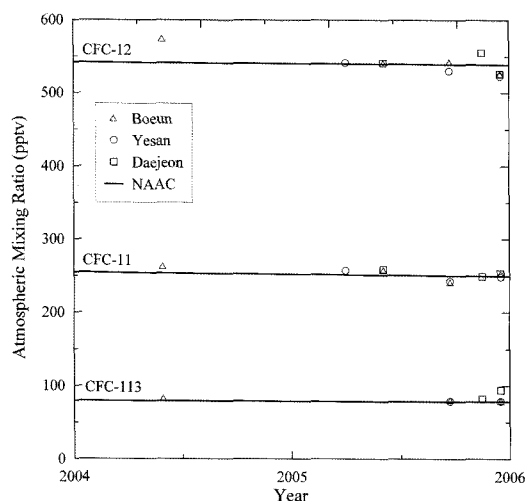
Fig. 8. Measured CFCs in air from the sites of Yesan, Boeun and Daejeon. Solid lines are North America Air curves (NAAC) for comparison.

36°22'34") to check for input history of CFCs in the Korean Peninsula. The site of Yesan is surrounded by agricultural land use and small scale of residence and the site of Boeun is in the forest with negligible human influence which belongs to conservation area for drinking water protection zone. The sampling site in Daejeon is located in the Daedeok Science Complex, north the downtown area. Uncertainties of measured atmospheric mixing ratios of CFCs were less than 2% (Table 5). The atmospheric CFC concentrations measured at the three sites conformed to those of North America air (*http://water.usgs.gov/lab/software/air_curve/*)

prepared by Reston CFC Laboratory (Fig. 8). This suggests that local sources of CFCs are negligible and North America air curves can be used for determination of groundwater age in those areas. For the Daejeon site, the conformity of measured atmospheric CFCs to the global level indicates that local excess of atmospheric CFCs is not significant near the large metropolitan area.

As indicated in the North America air curves of CFCs, the decreasing trend of atmospheric CFCs in global scale greatly limits the dating range of groundwater by CFCs. The atmospheric levels of CFC-11 and CFC-113 started to decrease in 1993 and 1995 respectively. The growth rate of atmospheric CFC-12 significantly slowed after 1992 though the level actually increased to 2000. Thus, CFC dating should be applied to groundwater recharged before 1990s and it has no discriminating ability for water recharged after that.

4.2. Groundwater

CFCs in groundwater were determined for a irrigation well of the eastern area (well A) in Jeju Island which was collected every two or three months for one year to investigate seasonal variation of groundwater ages (Fig. 9). Uncertainties of measured concentrations of CFCs in the groundwater samples are less than 5% for most of measurements (Table 6). The well is located in areas with agricultural land uses and an altitude of 150 m a.s.l. CFC concentrations in groundwater from the well decreased during June to August suggesting decrease of younger- water component,
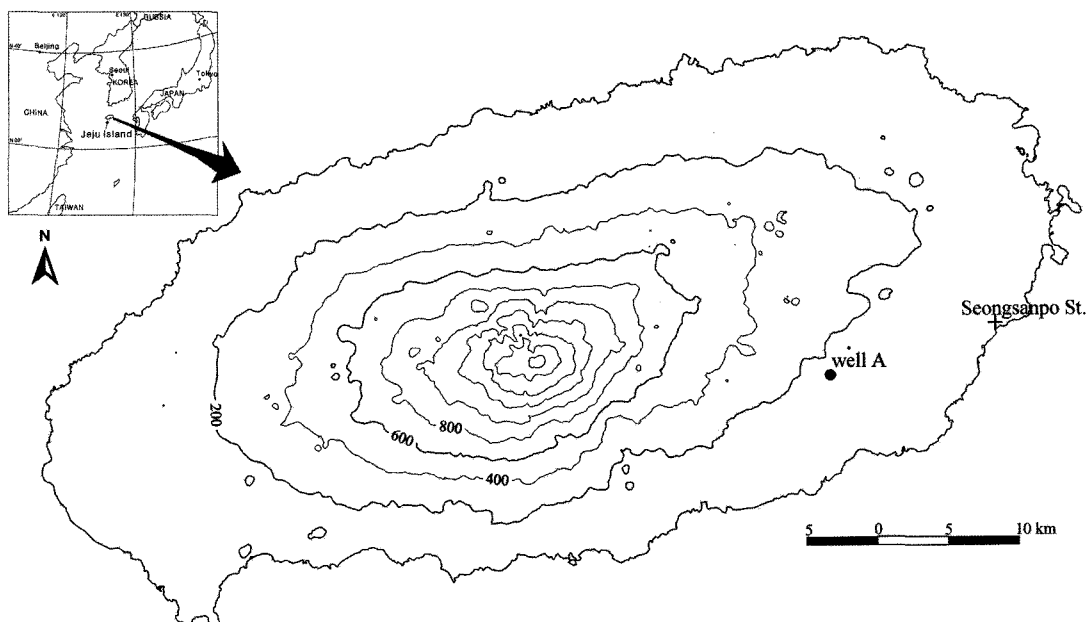
Fig. 9. Location of a well for CFC measurements and a nearby meteorological station.

Table 6. Analytical results of CFCs for groundwater samples

Sample	Collection date	Concentration (pg/kg)			RSD[1] (%)		
		CFC-12	CFC-11	CFC-113	CFC-12	CFC-11	CFC-113
Well A	20-Jan-05	178	479	44	3.9	3.9	6.0
	19-Apr-05	173	470	43	0.7	0.7	0.6
	20-Jun-05	169	472	43	3.7	2.1	7.6
	29-Aug-05	156	389	36	2.7	2.9	1.9
	11-Oct-05	166	536	44	2.2	5.1	4.1
	09-Dec-05	162	434	46	1.5	1.8	2.6

[1]Relative standard deviation of triplicate analysis otherwise noted.
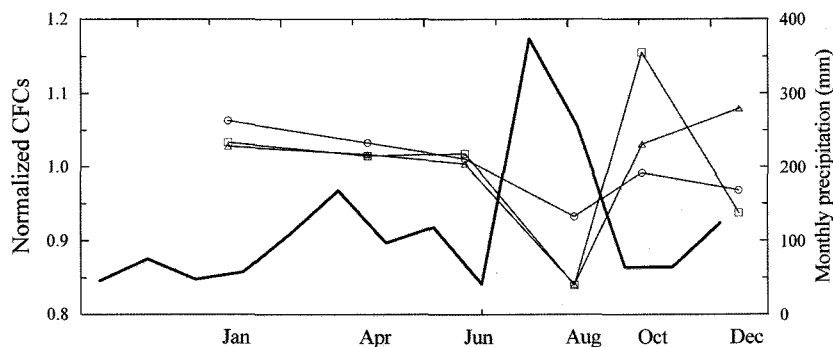
Fig. 10. Variation of normalized concentration of CFCs to yearly averages in groundwater from well A in eastern area of Jeju Island during the year of 2005 where open circle is for CFC-12, open square for CFC-11, and open triangle for CFC-113. Monthly precipitations at Seongsanpo station were shown as a thick solid line for comparison with the variation of CFC concentrations in groundwater from well A.

and CFC concentrations increased in October to recover a yearly trend. This seasonality in CFCs was compared to monthly precipitation measured at nearby stations (Fig. 10). From the comparison,

it appears that increase of CFC concentrations in October is attributed to that heavy rainfall in July and August that generates a recharge pulse and resultantly increases fraction of younger water in groundwater with about two-month delay. For the evaluation of the time delay in recharge to the wells from high rainfall during monsoon period, more frequent sampling for CFCs are needed. However, this result indicates that variation in rainfall is propagated to the wells within a few months, which is relatively fast considering thickness of unsaturated zone. This corresponds to that in Jeju Island, soil covers have a low capacity to delay infiltration of rainfall and basaltic rocks have high permeability (Koh et al, 2005).

5. Summary and conclusions

An analytical system for CFC-12, CFC-11 and CFC-113 in air and water samples was constructed using a customized purge and trap extraction system and a gas chromatograph with an electron capture detector. Air samples were collected using pressurized metal canister method. For groundwater samples, glass bottle method with metal lined caps was employed, which is much simpler than flame-sealed ampoule method and correction method for the loss of gas bubbles was also established. The analytical system was experimentally optimized for various procedural parameters to result in reproducibilities of triplicates less than 2% for current air samples and less than 5% for groundwater samples with CFC-12 concentration of 160 to 180 pg/kg, and verified with respect to the system in the Reston Chlorofluorocarbon Laboratory in USGS, which showed analytical results are in agreement within 10% for both air and water samples. CFCs in air were monitored at three sites over a year in the central part of South Korea, which indicates the level of atmospheric CFCs conforms well to North America Air curve suggesting no significant local sources of CFCs in those areas. For groundwater from a irrigation well in eastern area in Jeju Island, CFCs were measured bimonthly over a year. CFCs in groundwater showed seasonal fluctuations which can be interpreted by the effect of recharge pulse derived from high rainfall during monsoon period with a few month delay, which indicates high permeability of basaltic rocks in Jeju Island.

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