Determination of Atmospheric Perfluorocarbon Background Concentrations of fL/L Range at the Western Coastal Area of Korea

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As part of perfluorocarbon (PFC) tracer release experiment conducted at the western coastal area of Korea in February 2001, the background concentration level of perfluorocarbons (PFCs) in the atmosphere was determined by gas chromatography with electron capture detector. Prior to the PFC tracer release experiment in the field, air samples were collected using active samplers and the background concentrations of PFCs were determined. The concentrations of perfluoromethylcyclohexane (C_7F_{14}, PMCH) in the western coastal area of Korea were in the range of 5.8-8.7 fL/L. The mean concentration of the PMCH in the region exhibited no significant spatial and temporal variations. This concentration level is somewhat higher and has larger standard deviation than those of studies previously conducted in USA and Europe on the background concentration levels of PFCs. Because the background concentration of PMCH in Korea is still very low and consistent temporally and spatially, the PMCH tracer can be used suitably for the studies of long-range atmospheric transport.

Keywords : Tracer release experiments, Perfluorocarbons, Perfluoromethylcyclohexane, Perfluorodimethyl-cyclohexane, Background concentration.

Introduction

Great concerns have been raised on the monitoring of atmospheric environment that is essential to evaluate and improve air quality. Since the emission, transport, reaction and removal of airborne pollutants and hazardous materials in the atmospheric environment are well related to the extent of their effect on human health, it is important to understand the full characteristics of those airborne substances. With being as one of valuable analytical tools for elucidating those characteristics, many types of long-range atmospheric transport models have been employed extensively to simulate the transport and dispersion of airborne pollutants and hazardous materials and assess their impact on the atmospheric environment. [1-4]

Even though the transport and dispersion modeling works are very useful for the assessment of the behavior of airborne pollutants, it is crucial to evaluate and confirm the validity and utilities of those models by performing tracer release experiments; in a tracer release experiment, a known amount of tracer gas is released in a controlled way, the released tracer gas is then collected at various sampling sites and its concentration is analyzed. By investigating both temporal and regional variations of observed tracer concentrations and combining the concentration data with meteorological data, tracer release experiment can provide detailed information on the transport and dispersion of gaseous airborne materials. This experiment is also useful to evaluate the atmospheric

dispersion models by comparing experimentally measured data with simulated results from the models.

Sulfur hexafluoride (SF_6) and various perfluorocarbons (PFCs) such as perfluoromethylcyclopentane (C_6F_{12}, PMCP), perfluoromethylcyclohexane (C_7F_{14}, PMCH) and perfluoro-dimethylcyclohexane (C_8F_{16}, PDCH) are tracer gases mostly employed in the tracer release experiments. SF_6 has been used most frequently for short-range tracer experiments due to its relatively high atmospheric background concentration, whereas PFCs have favorably been used for long-range tracer experiments, on a scale of hundreds to several thousand kilometers. There are several properties of the PFCs to make them ideal as tracer gases for long-range atmospheric tracer experiments. Their background concentration is extremely low in ambient air and also they can be detected at the very low concentration level (a few parts per trillion or less) with good accuracy by gas chromatography with electron capture detector (GC/ECD).[1,2,5] In addition, their thermal and chemical inertness, low vapor pressure and limited use in industry are their advantages for the long-range tracer experiments.

A few long-range tracer experiments employing the PFCs were successfully carried out both in United States and Europe, *i.e.* Cross Appalachian Tracer Experiment (CAPTEX)[6] in 1983, Across North America Tracer Experiment (ANTEX)[1,7,8,9] in 1987 and the European Tracer Experiment (ETEX)[2,3] in 1994. Prior to these tracer experiments, studies on the ambient background level of the PFCs were conduct-

ed and it was found that their background concentrations did not show temporal and spatial variations much and were reported to be 3.6 fL/L from ANATEX and 4.6 fL/L from ETEX.[1,10,11]

Although several short range tracer experiments were carried out using SF_6 as a tracer,[12,13] no PFC tracer experiment has been conducted in Korea. Recently, in February 2001, a PFC tracer release field study of around 100-km range was performed over the western costal area in Korea.[14] The western costal region in Korea is a geographically interesting area mainly because of its dense population and many industrial facilities in the area; there have been great concerns on air quality in the area due to the emission of anthropogenic pollutants.[15] In addition, this area is sometimes directly influenced by the western winds from China. Especially, in almost every spring, usually from March to May, Asian dust, originated in central China arid area, flows into this region along the western wind. It is well known that the aerosol concentration increases greatly, one or two orders of magnitude larger than the typical level, when the Asian dust episode occurs. Moreover the compositions of Asian dust particles have been known to be changed during long-range transport from China to Korea. Therefore, Asian dust collected in Korea usually contains not only high concentration of mineral particles but also high contents of some hazardous materials, such as heavy metals, sulfates, and nitrates due to its passage through the industrialized area of China before its arrival to Korean peninsula.[16-18]

Actually, PFC tracer release work in February 2001 was designed and performed as a preliminary study prior to our ultimate long-range tracer release experiment covering China. In addition, its objective was to obtain the transport and dispersion profiles of airborne materials in the western coastal area in Korea and to provide a database for the evaluation of various atmospheric dispersion models.

In order to successfully carry out the PFC tracer field study, it is imperative to develop an analytical system that can determine extremely low concentration of PFCs (in fL/L range) with good accuracy. In addition, it is necessary to confirm that actual atmospheric background concentration of PFCs at the western coastal area of Korea is low and stable. With considering overwhelming amounts of diverse interfering compounds, such as chlorofluorocarbons (CFCs), volatile organic compounds (VOCs) and O_2, in ambient air and extremely low atmospheric PFCs backgrounds concentration, a delicate multi-step analytical system with good sensitivity is required to extract and analyze PFCs specifically from air samples. In addition, great care should be applied during sample handling to avoid contamination. Furthermore, very small difference in PFCs concentrations needs to be accurately determined, because temporal and spatial variations in PFCs concentrations are sometimes very small, especially when tracer release experiment deals with long-range transport and dispersion phenomenon of several thousand kilometers.

In our study, air samples were collected in glass tubes packed with an adsorbent and the samples were thermally desorbed by a rapid heating. The desorbed PFCs were then separated from the other interfering gaseous species before the analysis by GC/ECD in order to meet the requirements mentioned above. Overall 72 air samples were collected from 24 sampling sites over the western coastal area in Korea and analyzed for the determination of PFCs background concentrations.

Experimental Section

Sampler. 24 portable samplers in total were used in this study. Two different designs of the samplers were used: 4 automatic pocket samplers (SKC Inc., USA) and 20 homemade air samplers. The homemade air samplers were developed at Hankuk University of Foreign Studies. It was composed of a micro diaphragm pump, a 6 V battery, a flow meter, a Cajon connector and an ON/OFF switch. In order to make a small size of portable sampler, a tiny micro diaphragm air pump was used. The pump was operated consecutively 48 hrs by using a 6 V battery. Flow meters (Korea Flow Meter Ind. Co.) were calibrated both before and after experiment by using a mass flow meter. Samplers flow rate was regulated in the range of 40-400 mL/min by using a needle valve attached to the flow meter. Stainless steel Cajon fitting was used as a sampling tube adapter. Also the ON/OFF switch was attached to the top of the sampler for the accurate control of exposure time to air.

The performance of the samplers was investigated. When the samplers were operated indoors, flow rates were consistent. However, there were some drifts in the flow rates when the samplers were operated in the field, and their flow rates gradually decreased during 48-hrs operating period. The battery voltage, the weather condition and the sample loading affected the performance of the sampler. Therefore, a drift in the flow rate during field sampling period of about 3 hrs is inevitable and corrected by averaging flow rates before and after the sampling.

Sampling tube. The preparation and handling of sampling tubes to minimize the risk of contamination might be one of crucial processes to measure the extremely low PFCs background concentrations. Sampling glass tubes (11.5 cm long and 4 mm ID) were packed with 170 mg of Carboxen-569 (Supelco, USA), where the Carboxen-569 adsorbent has been commonly used for PFC tracer studies due to its great capacity for organic materials. Prior to use, all the sampling tubes were pre-cleaned by baking them at 400 ℃ for 1 hr using thermal desorption tube conditioning units (Supelco, USA) under the flow of nitrogen gas. Cleaning process was repeated until background concentration for the adsorbent is negligible with inspecting by GC/ECD. The cleaned Carboxen tubes were sealed at both ends with plastic caps, individually numbered and kept in a desiccator.

Samplings. Air samples for the determination of PFC's background concentration were taken during the PFC tracer field study, where PFC gases (PMCH and PDCH) were released at Duckjuck Island located in the Yellow Sea adjacent to Korean peninsula for three consecutive days
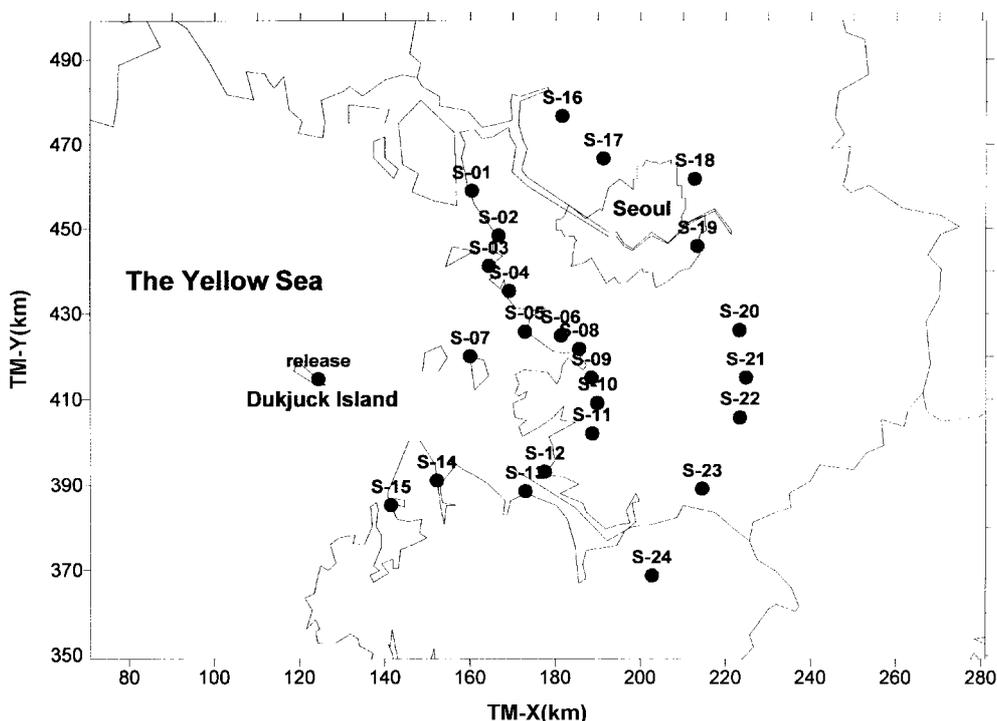
Figure 1. Map of locations of release and sampling sites in the western coastal area of Korea.

(February 12-14, 2001). The locations of the tracer release site and 24 sampling sites in the western coastal area of Korea are shown in Figure 1. Air samples for the background concentration measurements were taken once a day from 10:00 am to 1:00 pm just before the release of the PFC tracers for field experiments. Air sampling was done with flow rate of about 100 mL/min, resulting in total sampled air volumes of about 18 L for sampling period of 3 hrs. After sampling, Carboxen tubes were sealed at both ends with plastic caps and stored in polyethylene plastic bags individually. Carboxen tubes at each sampling site were also separately stored in polyethylene bags (not to be mixed up with tubes from the other sites) and kept in a desiccator prior to analysis. It was ensured that sampling sites and times corresponding to individual Carboxen tubes were assigned correctly. Overall 72 Carboxen tubes, three for each sampling site, were collected and sent to Hallym University for the analysis.

Refocusing procedure. Samples were thermally desorbed and analyzed by GC/ECD. Since, a variety of compounds as well as the PFCs in the air are adsorbed in the adsorbent, a process collecting mostly PFCs is required prior to the analysis of the sample by GC/ECD. First, sampling tube was purged of oxygen and volatile compounds for 2 min by using nitrogen gas (UHP grade, 99.9999%) with the flow rate of 300 mL/min. No PFCs were lost during this purging process. Although the purging helps to remove some volatile materials and oxygen, many interfering compounds in the atmospheric environment are still adsorbed to the adsorbent. Especially, the compounds sensitive to ECD, such as oxygen, CFCs, sulfur-containing organic compounds and SF_6 should
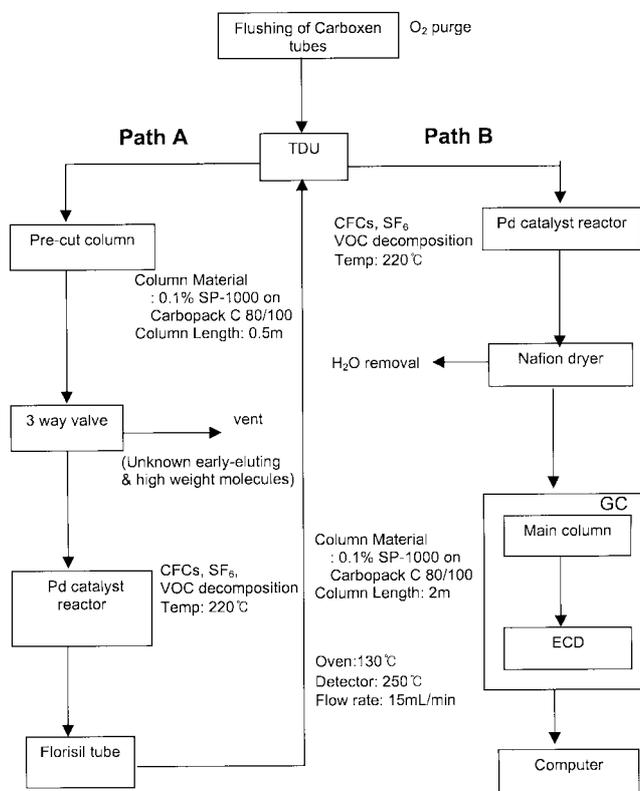

Figure 2. Schematic diagram of PFC analysis system: Path A: refocusing process, Path B: analysis process.

be removed before the analysis of the sampling tube. Schematic diagram of the refocusing process of PFCs is
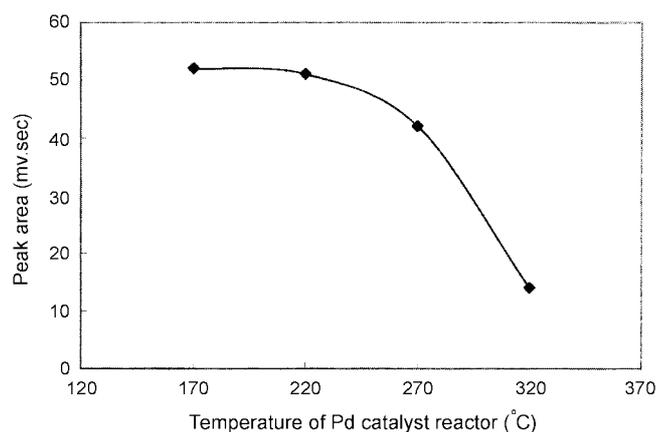
Figure 3. Variation of PMCH peak areas depending on the temperature of Pd catalytic reactor.

Figure 4. Variation of PMCH peak widths depending on sampling tube inner diameter.

shown in Figure 2, path A.

PFCs which were adsorbed in 4 mm ID Carboxen sampling tube were refocused into 2 mm ID thermal glass tubes packed with 110 mg of 60/100 mesh Florisil (Supelco, USA); the 4 mm ID sampling tube was thermally desorbed rapidly at 350 °C in a thermal desorption unit (TDU, model 890/891, Dynatherm). 5% H_2 (UHP grade, 99.9999%) in N_2 matrix gas (UHP grade, 99.9999%) was used as a carrier gas with the flow rate of 15-20 mL/min. Desorbed gases passed via heated transfer line (150 °C, 1.6 mm OD stainless steel tube) to a precut column. The precut column is a 50 cm × 3.2 mm OD stainless steel tube packed with 0.1% SP-100 on 80/100 mesh Carbopack C (Supelco, USA). Preliminary separation using the precut column is carried out at the column temperature of 130 °C. Compounds that eluted before and after PFCs of interest were vented away by 3-way valve switching. Eluting gas stream passed through a palladium (Pd) catalytic reactor (a 5 cm × 3.2 mm OD stainless steel tube packed with 100 mg of 5% Pd on 60/80 mesh Chromosorb P-AW). In the Pd reactor, some remaining CFCs and SF_6 in the gas stream are decomposed and remaining oxygen is converted to water vapor. However, since the PFC compounds themselves could be destroyed at the catalytic reactor with operating at too high temperature, the dependence of PFC destruction on the reactor temperature was investigated for our analysis set-up. Figure 3 shows the variation of observed chromatographic PMCH peak areas for a certain amount of PMCH according to the difference in Pd reactor temperature. The adequate operating temperature was found to be 220 °C and the catalytic reactor was kept at the temperature (220 ± 3 °C) using a temperature controller. After passing through the Pd catalytic reactor, the eluting gas mostly containing PFCs was refocused to Florisil tube of 2 mm ID. Meanwhile, the precut column was cleaned for the next sample analysis by back-flushing it for 3 min with 300 mL/min flow of N_2 in order to expel some remaining high molecular weight materials. A cycle of the refocusing process in our analysis set-up takes about 15 min.

Although sampling tubes of 4 mm ID were used to increase the sampling efficiency for PFCs, direct analysis of
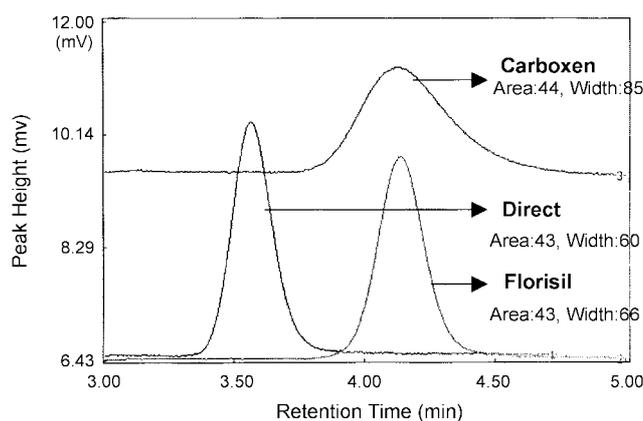
the PFCs from the tubes of this relatively large ID results in broad peaks in the chromatogram. The refocusing process to the 2 mm ID desorption tube increases the resolution of the chromatogram and results in the improvement of data quality. In Figure 4, the effect of the use of the refocusing procedure on the PMCH peak width is shown. A PMCH peak is the narrowest when PMCH is directly analyzed (represented as 'Direct' in the figure) without using either sampling or desorption tubes. When the sampling and desorption tubes are used ('Carboxen' for the sampling tube and 'Florisil' for the desorption tube), delays in retention times are observed due to the time required for the desorption of PMCH from the adsorbents. As the tube ID gets smaller, the chromatogram with better peak resolution can be obtained, even though peak areas are the same.

PFCs analytical system. PFCs analysis system is composed of a Florisil tube, a TDU, a Pd catalyst reactor, a Nafion dryer, GC/ECD and data manipulating system (see a diagram in Figure 2, path B). The Florisil tube is desorbed at 300 °C for 3 min in TDU. The carrier gas is 5% H_2 in N_2 matrix gas with the flow rate of 15 mL/min. Eluting gas passes through the transfer line (1.6 mm OD stainless steel tube) and enters into Pd catalytic reactor for the final elimination of remaining CFCs and SF_6, and for the conversion of remaining oxygen to water vapor. Water vapor is removed from the analysis system when the gas stream passes through Nafion dryer (MD-050-12S-2, Perma Pure Inc., USA). After that, PFCs are separated in a main column (2 m × 3.2 mm OD stainless steel tube packed with 0.1% SP-100 on 80/100 mesh Carbopack C, Supelco) and detected by ECD ([63]Ni source, 15 mCi). The temperature of the main column is kept at 130 °C in order to separate all PDCH isomers in a reasonable time. Narrow 1.6 mm OD stainless steel tube is used for transfer line in our analysis system in order to minimize peak broadening occurring during the transfer. Chromatographic data is acquired by using Autochro-WIN data system (Younglin Instrument Co. Ltd., Korea).

All the operational parameters of the PFCs analysis system, such as the flow rate of carrier gas and the temper-

ature of column were optimized for the analyses of PMCH as well as four isomers of PDCH, namely oc-, mt-, mc- and pt-PDCH, in a single analysis. pt-PDCH was used for the quality control purpose because it is well known that its background concentration is consistent both temporally and spatially.[19] A cycle of the PFCs analysis process takes about 15 min (30 min to complete the analysis of one sample).

In order to check the validity of the PFC analytical system, three samplers were co-located at a sampling site (Hallym University, Chuncheon, Korea) and the measured PMCH background concentrations were compared. Relative standard deviation of the obtained PMCH concentrations was less than 5%. However, no duplicated samples were collected during the field study in the western coastal area of Korea.

PFC gas standards. Three PMCH (Aldrich Inc., USA) gas standards of 1.161 ± 0.012 ppm, 10.63 ± 0.11 ppb and 101.9 ± 1.0 ppt were prepared in the division of Chemical Metrology and Materials Evaluation, Korea Research Institute of Standards and Science (KRISS). Preparing gas standards for each PDCH isomer was not possible since only technical grade of the PDCH isomer mixture (the percentage of each isomer is unknown) was available. Therefore, the mixture of PDCH isomers was used only for the qualification purpose.

Results and Discussion

PMCH calibration curve. For the calibration, a known amount of PMCH standard gas was taken by a gas tight syringe and injected into an 1 L Tedlar bag (Supelco, U.S.A.) filled with UHP N_2 gas. Gas in the Tedlar bag was adsorbed to Carboxen sampling tubes by using the portable sampler. The Carboxen tubes were analyzed in the same way as the sampling tubes collected for the background study. Figure 5 shows the calibration curve for the PMCH standard gas. ECD response to PMCH is linear in the range of 10-5000 fL of PMCH. Detection limit of PMCH to ECD is about 5 fL and the relative standard deviation of ECD response to PMCH is about 4%.

Calculation of PMCH concentration. As mentioned earlier, among several PFCs analyzed by GC/ECD, the quantitative determination of background concentration was possible only for PMCH. To calculate the background concentration of PMCH from the estimated sample volume, a following equation is used:

$$C = M/V \qquad (1)$$

where C is the actual PMCH background concentration in the unit of fL/L, M is the measured PMCH volume in the unit of fL and V is the actual air volume drawn into the sampling tube in the unit of liter. The sampled air volume is obtained with multiplying average reading of flow rate by sampling time.

However, this nominal air volume might not be the correct air volume drawn into sampling tube. There were some variations in the flow rate during the sampling period of 3 hrs. The uncertainty for the sampled air volume needs to be compensated for and a methodology to correct for the tube-
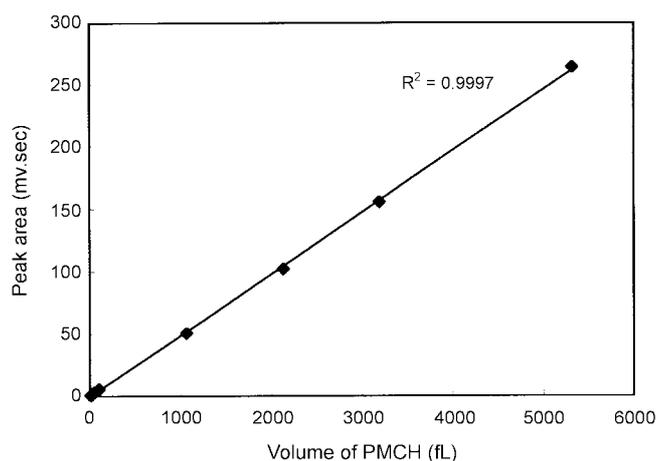

Figure 5. Calibration curve of PMCH standard gas.

to-tube variations of the sampled air volume was proposed and applied in a few previous works.[2] Briefly stating, since the background concentration of pt-PDCH was known very much consistent with spatial and temporal variations,[19] pt-PDCH could be used as a reference material for the determination of actual sampled air volume for each sampling tube. When obtained pt-PDCH background concentration by using nominal air volume was inconsistent with the known, a correction factor (the ratio between the measured and the known background concentrations of pt-PDCH) was applied to correct for its inaccurate estimation of the sampled air volume.

A similar approach was employed to estimate the actual air volume drawn into sampling tube in this study. Since all the manufacturers stopped making pt-PDCH of high purity, it was impossible to quantify pt-PDCH background levels in this study. Therefore, the chromatographic peak area of pt-PDCH per one liter of the sampled air (the unit peak area of pt-PDCH) was used as a reference value for the correction of air volume. The unit peak area of pt-PDCH was obtained by averaging all the air samples analyzed for the determination of PMCH background concentration (54 samples in total). Correction factor (R) for each sampling tube was obtained as followings.

$$R = A'/A \qquad (2)$$

where A' is the measured unit peak area of pt-PDCH for each sample and A is the average unit peak area of pt-PDCH obtained from all the samples. Now, the actual air volume (V) was retrieved from the nominal air volume (V').

$$V = R \times V' \qquad (3)$$

After correcting for the air volume for each sampling tube by applying the correction factor, the actual PMCH background concentration was determined by equation (1).

PMCH background concentration. This study on the determination of PMCH background concentration was performed as part of PFC tracer release experiment conducted over the western part of Korea in February 2001. Prior to the release of the tracers (PMCH and PDCH), the background
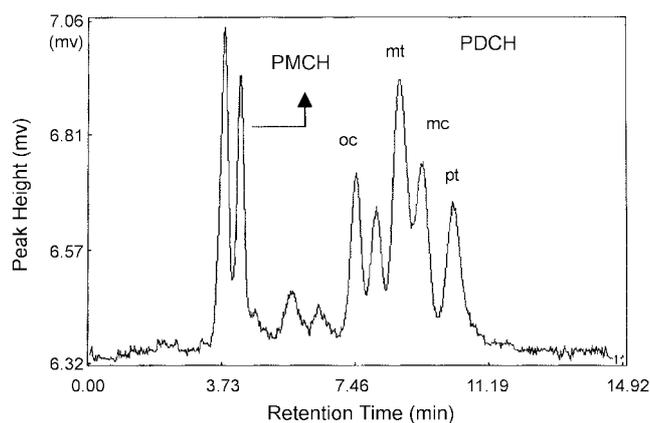
Figure 6. A typical chromatogram of PFCs collected in ambient air.

concentration of PMCH had to be determined in order to estimate the optimal amount of the tracers to be released, which depends mainly on the scale of tracer field study. A preliminary study on the PMCH background concentration level was carried out in Chuncheon, Korea. More than 30 samples were collected and analyzed at Hallym University in Chuncheon during January 2001. A typical chromatogram obtained in this study is shown in Figure 6. Elution is in the order of PMCP, PMCH and four isomers (oc-, mt-, mc- and pt-) of PDCH. By optimizing carrier gas flow rate and column temperature, good separation of the four PDCH isomers was achieved. PMCH background concentration in Chuncheon, Korea, was measured to be 7.4 ± 0.8 fL/L. A comparison between data uncorrected and corrected for the air volume is shown in Table 1. After the correction, relative standard deviation (RSD) decreases from 14% to 10%.

During the PFC tracer release experiment over the western coastal area in Korea, samples for the determination of PMCH background level were collected once a day before the release of PFCs tracer. At the 24 sampling sites, three samples were collected daily for three consecutive days. Daily PMCH background concentrations at the sampling sites, mean values and standard deviations are shown in Table 2. Some samples were lost during the analysis, mostly in the refocusing procedure. Also, all the sampling tubes at sites from 19 to 24 were found to be heavily contaminated by PFC and all the data from those sites were discarded. The sampling sites 19-24 were managed by a group that was in charge of the trace release and thus had kept several tens of kilograms of PFC tracers unopened in the laboratory. Sampling tubes were sent to the group a day before the scheduled field experiment. However, the field experiment was delayed for a week due to unsuitable weather condition.

Table 1. PMCH background concentration in Chuncheon, Korea

	Mean (fL/L)	σ	RSD (in %)
Uncorrected	7.46	1.06	14
Corrected	7.39	0.77	10

Table 2. Daily PMCH background concentrations at the sampling sites in the western coastal area of Korea

Sites	Sampling date			Mean for 3 days
	February 12, 2001	February 13, 2001	February 14, 2001	
S-1	7.62	7.23	–	7.42
S-2	7.18	4.94	6.99	6.37
S-3	6.99	7.38	–	7.18
S-4	6.62	8.00	–	7.31
S-5	5.79	7.53	7.66	6.99
S-6	–	5.91	8.61	7.26
S-7	7.55	7.70	6.42	7.23
S-8	5.87	6.18	6.73	6.26
S-9	6.37	5.05	7.44	6.29
S-10	6.61	5.87	6.49	6.32
S-11	6.76	7.53	5.48	6.59
S-12	7.91	7.61	5.90	7.14
S-13	6.31	6.32	6.69	6.44
S-14	8.15	8.25	7.69	8.03
S-15	7.91	8.02	7.70	7.88
S-16	6.16	7.96	8.30	7.47
S-17	6.68	6.02	8.66	7.12
S-18	6.56	8.56	8.31	7.81
Mean	**6.88**	**7.00**	**7.41**	**7.10**
σ	0.73	1.08	1.10	0.60
RSD (in %)	10.55	15.48	14.90	8.38

Consequently, sampling tubes used at the sites 19-24 were stored in the same building, although not in the same room, with bulk PFC tracers for a week. This incident emphasizes extremely careful handling of sampling tubes to avoid contamination, because we are dealing with very small amount of PFCs in ambient air (a few parts per trillion). Since we did not see any contamination for the samples at the other sites, this could be the only explanation for the source of such heavy contamination.

Daily PMCH background concentrations in the western part of Korea are in the range of 5.8-9.5 fL/L. The average PMCH background concentration for the three sampling days is 7.1 ± 0.6 fL/L and the relative standard deviations for each day are in the range of 11-14%. This RSD values are higher than that obtained in Chuncheon. It is likely that the uncertainty in the data for the 18 sampling sites will be larger because sample collections can be more influenced by the diversity of sampling circumstances and by the different skills of sampling people. Daily average PMCH concentrations show a trend of small elevation with the progress of the tracer release experiment. Since this small increase in PMCH concentration is within the range of its standard deviation, this trend could not be regarded significant. However, the possibility of actual increase in the PMCH concentrations cannot be excluded. As mentioned earlier, this study was carried out as part of the PFC release experiment. During the tracer release experiment, about 3 kg of the PFC tracers were released each day after the samples for the
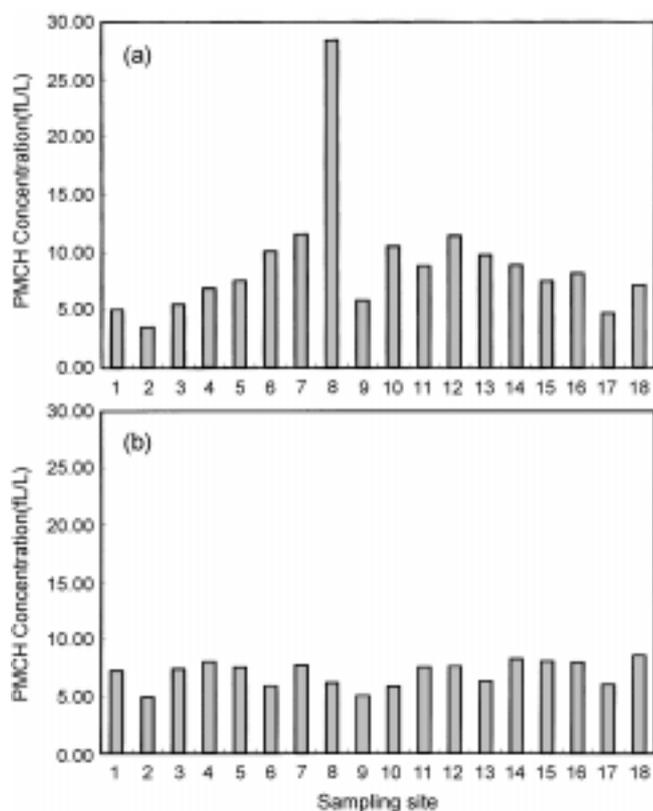
Figure 7. PMCH background concentrations at sampling sites (collected on Feb.12, 2001). (a) Uncorrected for flow rate fluctuations (b) Corrected.

Table 3. PFC background concentrations (fL/L) observed in ANATEX, ETEX and this study

	PMCH	oc-PDCH	mt-PDCH	mc-PDCH	pt-PDCH
ANATEX					
Mean	3.60	0.40	11.7	–	4.34
σ	0.03	0.03	2.57	–	0.32
RSD (in %)	1	8	22	–	7
ETEX					
Mean	4.6	0.96	9.3	8.8	6.1
σ	0.8	0.33	0.8	0.8	0.8
RSD (in %)	17	34	9	9	13
This study					
Mean	7.1	1.12*	2.78*	1.92*	1.57*
σ	0.8	0.25	0.53	0.26	0.26
RSD (in %)	11	22	19	13	17

*Mean values for PDCH isomers are for chromatographic peak areas.

ANATEX experiment in the United States and ETEX in Europe, which are listed in Table 3. The reason for the higher PMCH background concentration in this study is not clear. However, it is quite probable that the actual elevation of PMCH background concentration can be observed because PFCs have very long lifetime in the air due to their chemical inertness, and thus the actual increase of concentration with elapsed time can be expected; the PMCH background concentration measured during ETEX tracer experiment performed in 1994 was reported to be higher than that measured for ANATEX experiment in 1986 (4.6 *vs* 3.6 fL/L). Also, a subsequent PFC background level study conducted in Ispra, Italy in 1996 (ISPRA) after ETEX campaign showed the increased PMCH background concentration of 5.9 fL/L.[10] Since our present study is the latest measurement for the PFC background level, the measured PMCH background concentration of 7.1 fL/L might be due to the actual increase in atmospheric PFC concentration.

Another possibility for its currently observed high values of the background concentration could be related to the uncertainty involved in the correction procedure used to assess the sampled air volumes. Without knowing the accurate pt-PDCH background concentration, the application of the correction factor by referencing to pt-PDCH could induce some deviation from the true concentration. For example, the measured apparent background level of PMCH for ISPRA was 8.3 fL/L. However, after applying the correction factors referenced to pt-PDCH, the PMCH concentration turned out to be 5.9 fL/L.[10]

The RSD of PMCH background concentration obtained in this work is larger than those of ANATEX and ETEX studies. There might be several factors influencing the uncertainty in the data: the site-by-site variation in the background level, the precision and accuracy of the analytical system and the uncertainty in the determination of the exact sampling volume. The higher RSD than those from the other researches may mostly be attributed to the manual control of the PFC analytical system employed in our study. The PFC analysis systems used in ANATEX and ETEX experiments

background measurement were collected. Therefore, there is a possibility of the actual increase of daily PMCH background levels due to the remaining PMCH, released in the pervious day, in the atmosphere. However, the daily variations of PMCH concentrations at each sampling site are rather random. No data at a sampling site shows a higher concentration than two standard deviations above its average value, implying that there exists no local emission source for PMCH in this region.

The PMCH background concentration at each sampling site on February 13, 2001 is shown in Figure 7. For the comparison, PMCH concentrations with and without correction for the sampled air volume are shown together (Fig. 7 (a) *vs*. (b)). Remarkable improvement of the data quality is achieved for the data obtained in the western coastal area, when compared to that in Chuncheon. Variation in the magnitudes of the correction factors for the data collected in the coastal area is much larger than that at Chuncheon, where samples were collected in a more controlled way. It was also observed that there was a good correlation between the performance of a sampler and its corresponding correction factors. Samples collected by the sampler with better performance usually required smaller correction on their air volume. In general, commercialized automatic samplers needed smaller correction.

Average PMCH background concentration in this work is somewhat higher than the previously reported ones, such as

were developed to carry out the automatic analysis. They constructed fully automatic PFC analysis systems in order to analyze several thousands of samples collected from the extensive PFC field studies, which were performed on the vast area covering several thousands of kilometers. In this study, however, all the analytical operations, such as setting of flow rate of carrier gas and valve switching, were done manually. It is expected that automation of the analytical system would certainly improve the reproducibility of data. The other reason might be the uncertainty involved in the analysis, since the sensitivity of the gas chromatography was optimized to measure the expected high PFCs concentration for the samples from the PFC release experiments.

Although it was unable to determine background concentrations of PDCH isomers in this study, the relative abundance of the four PDCH isomers in ambient air was investigated. In general, the ratio of the unit chromatographic peak areas for the four PDCH isomers (oc-, mt-, mc- and pt-PDCH) in the air showed quite a constant values of approximately 1:3:2:1.5 (see Table 3), implying rather constant distributions of the four PDCH isomers in the air. This relative abundance, however, does not accurately reflect the proportion of their actual concentrations because the response of each isomer to ECD should be somewhat different from others.

Conclusion

An analytical technology to detect very low concentrations of PFCs in the atmosphere was developed by using GC/ECD. The analytical system was utilized for the study on PMCH background concentration in the western coastal area of Korea. The study was carried out as a part of PFC tracer field experiment performed in February 2001. Air samples were collected at 18 sampling sites located at the western coastal area in Korea and PMCH and four isomers (oc-, mt-, mc- and pt-) of PDCH were analyzed. Determined PMCH background concentration was 7.1 fL/L with a relative standard deviation of 8.4%. Also, PMCH background concentration in Chuncheon, Korea was found to be 7.4 ± 0.8 fL/L.

The measured PMCH concentration is higher than those of the previous researches conducted in USA and Europe. The higher PMCH background concentration observed in this study might reflect an actual increase in its background concentration with elapsed time due to its chemical inertness and/or be due to the application of "somewhat overestimated" correction factors for the sampled air volume. In this work, it was demonstrated that pt-PDCH was very useful reference material to correct for the sampling volume fluctuation and to improve the quality of field data remarkably. Relatively worse reproducibility observed in the data can be mainly attributed to the manual operations employed in our PFC analysis system.

The PMCH background concentration in the western coastal area in Korea was found to be fairly consistent temporally and spatially. In addition, during this field study,

the possibility of PFC emission from local sources was excluded. Even though the background concentrations of the four isomers of PDCH were not quantified in this study, the concentrations of PDCH might be very low and the relative abundance of PDCH isomers in the air seems to be quite consistent. Therefore, it is possible to use PMCH and PDCH at the same time as multi-tracer for a long-range atmospheric transport studies.

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