



The background atmospheric concentrations of cyclic perfluorocarbon tracers determined by negative ion-chemical ionization mass spectrometry

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Abstract

The background atmospheric mixing ratios for a range of cyclic perfluorocarbons (cyclic-PFCs), widely used in atmospheric dispersion studies, have been measured by gas chromatography-mass spectrometry in negative ion-chemical ionization mode. Background concentrations range from $<1 \text{ fl l}^{-1}$ to $>10 \text{ fl l}^{-1}$, where femtolitre is expressed as parts in 10^{15} (ppqv). Because of their very long atmospheric lifetimes ($>3000 \text{ yr}$) the present day concentrations represent the accumulated emissions from all sources, although significant commercial production did not commence until the 1960s. Cyclic-PFCs are potent greenhouse gases; however, their atmospheric concentrations are currently so low as to make an insignificant contribution to global warming. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Like many other industrial chemicals perfluorocarbons now pervade the global environment. However, unlike many other man-made chemicals they would appear to be relatively benign. Perfluorocarbons exhibit exceptional chemical stability and as such contribute neither to photochemically induced air pollution nor to stratospheric ozone depletion. They are non-flammable, insoluble in water, and essentially non-toxic to the extent that they have been suggested as blood plasma substitutes (Dagani, 1982). It is these desirable properties, coupled with their very low background atmospheric concentrations, that has led to the selection of the fully perfluorinated alkyl-substituted cycloalkanes as almost ideal tracers for atmospheric dispersion studies

(Lovelock and Ferber, 1982; Dietz, 1987; D'Ottavio et al., 1986; Lagomarsino, 1996). Cyclic perfluorocarbon tracers (cyclic-PFCs) have been used successfully in both urban (Draxler, 1989; Draxler and Heffter, 1989; Britter et al., 2000; Cooke et al., 2000, 2001a), and regional scale studies (Ferber et al., 1986; Draxler, 1987; Draxler et al., 1991; Nodop et al., 1998; Green, 1999). They have also been used to locate leaks in underground pipes (Ghafurian et al., 1999; Hassoun et al., 2000). The principal tracers and their properties are listed in Table 1. Cyclic-PFCs are rapidly becoming the tracers of choice due to their extremely low and stable atmospheric background concentrations and relatively few global sources (Ferber et al., 1981). In effect, they are replacing an early popular tracer sulphur hexafluoride (SF_6) (Turk et al., 1968; Dietz and Cote, 1973; Thomsen and Lovelock, 1976). SF_6 has become progressively less useful due to its rapidly increasing background concentration currently approaching about 5 pptv (Maiss

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Table 1
Properties of perfluorocycloalkanes and other tracers

Compound name	Abbreviated name	Molecular formula	B. Pt. (°C)	M. Wt.	Density (kg/l at 25 °C)
Perfluorodimethylcyclobutane ^{a,b}	PDCB	C ₆ F ₁₂	45	300	1.67
Perfluoromethylcyclopentane	PMCP	C ₆ F ₁₂	48	300	1.707
Perfluoromethylcyclohexane	PMCH	C ₇ F ₁₄	76	350	1.788
Perfluoro- <i>o</i> -dimethylcyclohexane ^a	<i>o</i> -PDCH	C ₈ F ₁₆	102	400	1.828
Perfluoro- <i>m</i> -dimethylcyclohexane ^a	<i>m</i> -PDCH	C ₈ F ₁₆	102	400	1.828
Perfluoro- <i>p</i> -dimethylcyclohexane ^a	<i>p</i> -PDCH	C ₈ F ₁₆	102	400	1.828
Perfluoroisopropylcyclohexane	<i>i</i> -PPCH	C ₉ F ₁₈	130	450	1.9
Perfluorotrimethylcyclohexane ^c	PTCH	C ₉ F ₁₈	128	450	1.888
Sulphur hexafluoride	SF ₆		−63.8	146	Gas 6.602 g/l

^aBoth *cis* and *trans* isomers are applicable.

^b1,2 and 1,3 bisubstitution applicable.

^cMultiple geometric isomers applicable.

and Levin, 1994; Geller et al., 1997; Maiss and Brenninkmeijer, 1998). SF₆, along with the very volatile perfluorocarbons, carbon tetrafluoride (CF₄), and hexafluoroethane (C₂F₆), will be controlled substances under the terms of the Kyoto protocol (United Nations, 1997).

Recently, concern has arisen over the presence of perfluorocarbons in the environment because they are powerful greenhouse gases with extremely high global warming potentials (GWPs). Like other perfluorocarbons the GWPs of the cyclic-PFCs exceed that of carbon dioxide (CO₂) by a factor of 10³–10⁴. Conversely, their atmospheric mixing ratios are approximately 10^{−9}–10^{−10} (perfluorocarbon tracer/CO₂). Consequently, at present, the effective contribution of the cyclic-PFCs to global warming is negligible. However, perfluorocarbons, in general, have been called the “immortal molecules” due to their long-term persistence in the atmosphere with lifetimes ranging from 3000 to 50,000 years (WMO, 1988). This implies that the current atmospheric burden of perfluorocarbons represents the total of all cumulative emissions from both fugitive and deliberate releases. It is therefore of some interest to determine their current atmospheric background concentrations and rates of accumulation. Furthermore, in addition to their specialized use as tracers of atmospheric dispersion, they have a surprisingly diverse number of other uses ranging from oil and gas well tracing (Ljøsland et al., 1993), as dielectrics in military radar, and applications in the cosmetics industry. Fugitive emissions will clearly be more difficult to quantify as the number of industrial usages expand.

Here we determine the background concentrations for the principal perfluorocarbons which have been deployed as atmospheric tracers using the promising new technique of negative ion-chemical ionization mass spectrometry (NICI-MS). We compare these observations with the historical record of previous measurements and estimate the current global atmospheric burden for each perfluorocarbon tracer.

2. Experimental

The success of these perfluorinated compounds as tracers is due to their relatively facile measurement by gas chromatography with electron capture detection (ECD) (Simmonds et al., 1976; De Bortoli and Pecchio, 1985; D’Ottavio et al., 1986; Lagomarsino and Latner, 1992; Lagomarsino, 1996). Detection of cyclic-PFCs at the sub-pptv level is easily achieved because of their large rate constants for thermal electron attachment, which are close to the diffusion-controlled limit of 3 × 10^{−7} cm³ molecule^{−1} s^{−1} (Christophorou et al., 1984). Detection limits can be further improved to attain the atmospheric background levels in the low femtolitre per litre (fl l^{−1}) range by sample enrichment techniques (D’Ottavio et al., 1986; Lagomarsino, 1996). However, the GC-ECD method introduces the potential problem of interferences from other ubiquitous and more abundant atmospheric halocarbons that also have substantial electron attachment rate constants. To overcome this problem catalytic scrubbers have been used to selectively remove the major atmospheric halocarbons, in conjunction with high-resolution capillary columns to separate the tracers from potentially co-eluting interferences (Lagomarsino, 1996).

An alternative approach for determining the presence of perfluorocarbon tracers with both high sensitivity and high selectivity is to use NICI-MS (Huang et al., 1990). In a pioneering paper Begley et al. (1988) demonstrated that this technique could provide a uniquely selective analytical method for the perfluorocarbons due to the formation of stable molecular anions. The relatively high molecular weights of the cyclic-PFCs (see Table 1) coupled with their relatively low boiling points provides a unique combination of early chromatographic elution with a high mass ion which is very unlikely to be compromised by the presence of co-eluting interferences.

A full description of the analytical methodology used in this work has been reported elsewhere (Cooke et al.,

2001b), and so only a brief description is given here. However, one important change has been the use of a graphitized carbon-based PLOT capillary column, which has the special property of resolving all six possible isomers of perfluorodimethylcyclohexane (PDCH). Previous high efficiency capillary columns were only able to separate four of the six possible isomers (Lagomarsino, 1996; Cooke et al., 2001b).

2.1. Instrumentation

The analytical instrumentation consisted of a gas chromatograph (model 6890, Hewlett-Packard Ltd., USA) with a mass selective detector (model 5973, Hewlett-Packard Ltd., USA), which can operate in either electron impact (EI) or chemical ionization (CI) mode. For experiments using cyclic-PFCs, the mass spectrometer was operated in NICI and in selected ion monitoring (SIM) mode. The process is a highly selective and sensitive technique for cyclic-PFCs due to the efficient formation of stable cyclic molecular anions. One unexpected benefit of using NICI was that the more abundant chlorofluorocarbons (CFCs) and other halocarbons present in the background atmosphere could not be detected. Although individual CFCs may each have a high electron affinity, most undergo dissociative electron attachment under the NICI conditions used, rather than form stable molecular anions (Knighton et al., 1996). The overall analysis procedure is much simplified by removing the need for high-temperature catalytic scrubbers and/or pre-clean-up procedures. Studies of the sensitivity of the GC/MS system in NICI-SIM mode have been carried out by direct injection of a dilute perfluorocarbon standard via a 100 μ l stainless-steel loop. It was found that 10.6 fg [ca. 7.9×10^{-13} cm³ (v/v)], 9.5 fg [ca. 7.1×10^{-13} cm³ (v/v)], and 18.2 fg [1.2×10^{-12} cm³ (v/v)], of perfluorodimethylcyclobutane (PDCB), perfluoromethylcyclopentane (PMCP) and PMCH, respectively, could be detected with a signal-to-noise ratio of 3:1 when in SIM-mode with selected ions of m/z 300 and 350. To detect background concentrations of cyclic-PFCs at the fl 1 level with high precision, therefore, requires a sample volume of several litres of air (~ 3 l).

An adsorption-desorption system (ADS) was constructed, based on the design described in Simmonds et al. (1995) and Bassford et al. (1998), to achieve analyte pre-concentration, and modified to accept various atmospheric samples. Air samples were cryogenically adsorbed onto a micro-trap, which was maintained at a temperature of -50°C , and filled with 10 mg Carboxen 569, 40–50 Mesh (Supelco, Bellefonte, USA). Under these conditions the cyclic-PFCs present in several litres of air can be quantitatively focused onto the micro-trap without exceeding the theoretical breakthrough volumes (BTV). To ensure that the micro-trap

was clean prior to sampling, it was subjected to four thermal clean-up cycles at 255°C , under a constant flow of helium. The trap is quantitatively desorbed at 255°C in approximately 4 s onto the capillary GC column. The small volume of the micro-trap and the rapid thermal desorption ensures that the enriched sample is transferred to the capillary column with negligible band broadening.

2.2. Calibration

Two gravimetrically prepared primary standard gas mixtures with a stated accuracy of $\pm 1\%$ were purchased from Linde Gases Ltd., UK. The first primary standard (PFC1) contained 20.1 ppm PMCP, 19.9 ppm PDCB, 20.0 ppm PMCH and high ppm levels of CCl_3F (CFC-11, 2296 ppm) and CCl_2F_2 (CFC-12, 4998 ppm). The second primary standard (PFC2) contained 20.3 ppm *o*-PDCH, 20.4 ppm *m*-PDCH, 20.2 ppm *p*-PDCH and high ppm levels of CFC-11, (2298 ppm) and CFC-12, (5001 ppm). The matrix gas was nitrogen (grade 5.0, Air Products) in both cases. Because individual perfluorocarbons are not 100% pure, the actual concentrations in the primary standard were adjusted for isomer impurities present in each perfluorocarbon.

Each primary standard was diluted volumetrically to low pptv (v/v) into a 36-l electropolished stainless-steel cylinder in a single step, using an ultraclean all stainless-steel dilution manifold based on a design developed by the Scripps Institution of Oceanography. This procedure for the preparation of standards has been used successfully as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) Programme (Bullister and Weiss, 1988; Prinn et al., 2000). High purity halocarbon-free zero air (5.5 grade, Air Products Ltd., UK) was used as the diluent gas. This one-step dilution of the primary standard, which also contains CFC-12, and CFC-11 presumes a linear relationship between all species and assigns a concentration to each perfluorocarbon in the mixture relative to the two CFCs for which Scripps maintains absolute calibration standards. A chromatogram showing the separation of the diluted standard PFC1 on the CPSil 5 column is shown in Fig. 1. It should be noted that this column does indicate some resolution of the four possible PDCB isomers. The PFC1 secondary standard was also inter-compared with a perfluorocarbon standard provided by the Environmental Measurements Laboratory (DOE, NY). The two perfluorocarbons (PMCP and PMCH) that were common to the two standards showed excellent agreement with a ratio of PCMP = 1.064, and PMCH = 0.992. The Bristol standard was higher in the case of PMCP, but fractionally lower for PMCH. For determining perfluorocarbon background concentrations the secondary standard is analysed either side of the air sample to minimize any drift or change in performance of the analytical

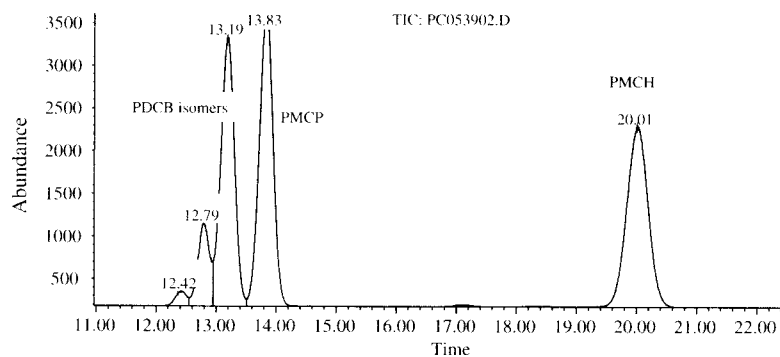


Fig. 1. 30 ml of PFC1 diluted calibration standard with elution order of Cyclic-PFCs on a CP-Sil 5 CB column. Conditions: 100 m \times 0.32 mm i.d. CP-Sil 5 CB column under 1 ml min⁻¹ helium flow. Temperature programme 30 C for 22 min, 20 C min⁻¹ to 150 C, hold 10 min.

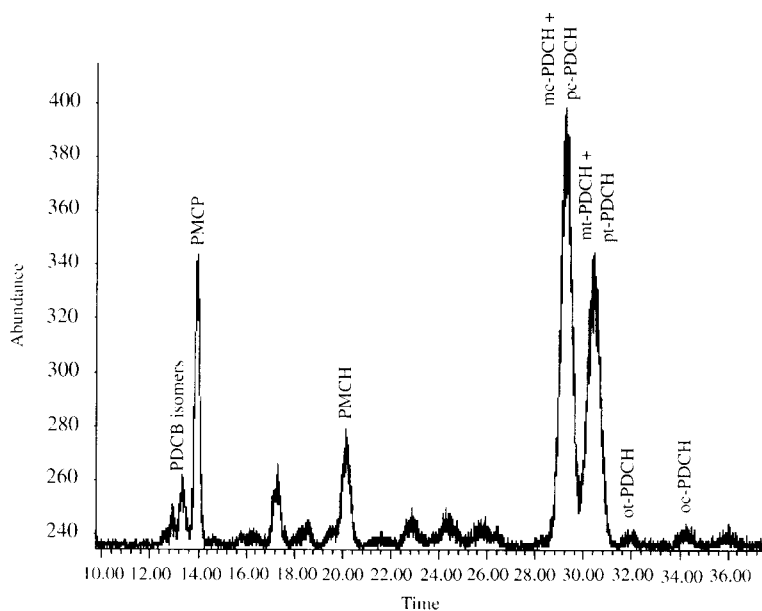


Fig. 2. NICI-SIM chromatogram of 3-L Birmingham (UK) background air. Conditions: 100 m \times 0.32 mm i.d. CP-Sil 5 CB column under 1 ml min⁻¹ helium flow. Temperature programme 30 C for 22 min, 20 C min⁻¹ to 150 C, hold 10 min.

instrumentation. Repeat analyses ($n = 8$) of a standard mixture yielded the following precisions expressed as % relative standard deviation, PDCB (2.13), PMCP (2.86), PMCH (2.26), *oc*-PDCH (2.71), *ot*-PDCH (5.14), *mc*-PDCH (2.53), *mt*-PDCH (2.02), *pc*-PDCH (1.19), and *pt*-PDCH (1.58).

2.2.1. Chromatography

The separation of an ambient air sample (3 l) collected in the city of Birmingham, UK is illustrated in Fig. 2, using a gas liquid wall-coated open tubular (WCOT)

CPsil 5 CB methyl silicone column (0.32 mm \times 100 m, 5 μ m film thickness, Varian Inc., UK). The GC oven temperature was maintained isothermally at 30 C for 22 min, then increased to 150 C at 20 C min⁻¹, and remained there for a further 10 min. Helium (GC+ grade, Air Products Ltd., UK) was used as the carrier gas at a flow rate of 1 ml min⁻¹. Note that only four of the six possible isomers of *ortho*, *meta* and *para* PDCHs and their *cis/trans* isomers are resolved, with co-elution of the *meta/para-cis* and *meta/para-trans* isomers.

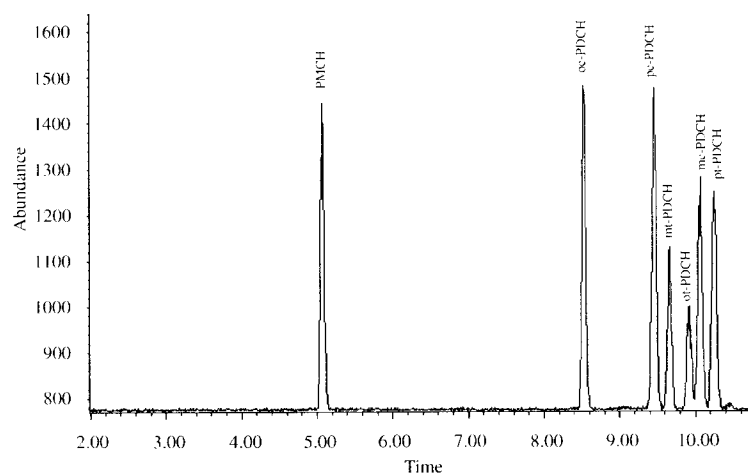


Fig. 3. Resolution of diluted 30 ml of calibration standard PFC2 on CarboGraph 1 PLOT column. Conditions: 30 m \times 0.32 mm i.d. CarboGraph PLOT column under 1.5 ml min⁻¹ helium flow. Temperature programme 30°C for 5 min, 20°C min⁻¹ to 50°C, hold 5 min; 10°C min⁻¹ to 220°C, hold 10 min.

However, using a 30 m \times 0.32 mm graphitized carbon (CarboGraph) PLOT capillary column (Alltech Associates, IL, USA) all six isomers can be baseline resolved as shown in Fig. 3. The temperature profile used to produce this chromatogram was 30°C for 5 min, ramping at 20°C min⁻¹ to 50°C, holding for 5 min, followed by a 10°C min⁻¹ ramp to 220°C and hold for 10 min. The carrier gas was helium at a flow rate of 1.5 ml min⁻¹. New commercial versions of the CarboGraph PLOT columns can be purchased from Lara s.r.l. (Rome, Italy). Methane was used (grade 4.5, Air products Ltd., UK) as the reagent gas for the MS, with the source temperature maintained at 150°C and pressure regulated at 2.1×10^{-4} Torr with the methane reagent gas (corresponding to 40 ml min⁻¹ CH₄ flow).

2.3. Sample collection

Samples were collected in 3.21 electropolished SS canisters, pressurized to about 3 bar, and also in Tedlar bags used in atmospheric tracer dispersion studies (SKC Inc., PA, USA). Tests have indicated that the cyclic-PFCs are stable in the bags for more than 10 months, and appear to be indefinitely stable in the SS canisters (> 5 yr). Preliminary background samples were collected before and after various tracer release experiments as part of the URGENT programme (Cooke et al., 2001a,b), and at various locations in the United Kingdom and Ireland. However, these measurements were limited by the lower resolution of the PDCH isomers on the silicone capillary column. During the later phases of the research we were able to acquire the graphitized carbon PLOT capillary column, thus allowing background determinations for all of the PDCH isomers in air samples collected at the remote

atmospheric monitoring station at Mace Head, Ireland (53°N 10°W). A more detailed description of the sampling site and its climatology has been reported in the TOR network report (Cvitas and Kley, 1994). Samples were collected under clean air baseline conditions with air masses arriving from over the North Atlantic Ocean.

3. Results

Historically observations of the ambient background levels of the cyclic-PFCs have been acquired before and after their deliberate release as tracers during atmospheric dispersion experiments. Background levels of cyclic-PFCs have been reported from studies in the USA (Dietz, 1987; Draxler, 1989; Draxler et al., 1991; Lagomarsino, 1996), and most recently during the 1994 European Tracer Experiment (Piringer et al., 1997; ETEX, 1998; Nodop et al., 1997, 1998).

Table 2 summarizes the concentrations (in fl l⁻¹) of individual cyclic-PFCs determined during previous background studies and compares them with the North Atlantic baseline results from air samples collected at Mace Head on the West Coast of Ireland, using the newer analytical method of NICI-GCMS. Most obvious in Table 2 are the substantial differences between the different background measurements, depending on sampling year and location. In addition to potential analytical errors and the different timescales over which these background measurements have been acquired, there are several possible explanations for the observed differences in the cyclic-PFC concentrations. First, is the use of different calibration standards, second the co-elution with unknown contaminants, and thirdly the

Table 2
Background atmospheric concentrations of cyclic-PFC tracers (fl l^{-1})

Location and reference	PDCB	PMCP	PMCH	oc-PDCH	pc-PDCH	mt-PDCH	ot-PDCH	mc-PDCH	pt-PDCH	PTCH ^a
USA 1986. (Djetz, 1987)	0.34±0.01	3.22±0.03	4.6±0.05	0.30±0.1	2.2	7.7	0.2	8.2	3.40±1.0	0.07
USA. ANATEX 1987. (Draxler, 1989)		2.09	3.6	0.4					4.34	0.45
USA. MOHAVE (Summer) 1992. (Green, 1999)		6.29±0.43	5.27±0.28	0.56±0.059						0.64±0.16
1993–1994, USA. (Lagomarsino, 1996)		4.15±0.25	3.84±0.17	0.34±0.017				8.41±0.26		
1994, Austria (ETEX) (Piringer et al., 1997)	0.63	5.24	5.9	0.98					5.37	0.59
1994, Europe. (ETEX) (Straume et al., 1998)		4.6±0.3	4.6±0.8	0.96±0.33		9.3±0.8		8.8±0.8	6.1±0.8	
BRAVO, USA, 1999	1.40	5.20	4.80	0.44					5.40	
Mace Head, Ireland (2001)^b	2.70±0.20	6.29±0.22	5.49±0.23	0.73±0.09	6.11±0.44	8.65±0.30	0.65±0.01	10.83±0.01	4.88±0.03	^c

^a Perfluorotrimethylcyclohexane.

^b 30 m × 0.32 mm graphitized Carboplot capillary. Samples collected under clean baseline westerly airflow conditions.

^c Calibration standard unavailable.

Table 3
Cyclic perfluorocarbon background mixing ratios (fl l^{-1}) determined by NICI-GC-MS

	PDCB	PMCP	PMCH	ocPDCH	pcPDCH	mtPDCH	otPDCH	mcPDCH	ptPDCH
SH (1997) ^a , Col. 2	2.83	5.56	5.16	0.69	5.57	7.97	0.65	9.97	4.27
NOAA (1997) ^b , Col. 2	2.73	5.91	5.18	0.75	5.77	8.16	0.70	10.07	4.49
Bristol, UK (2000) ^c , Col. 1	2.46±0.41	6.84±0.96	5.24±1.3						
Birmingham (2000) ^d , Col. 1	3.35±0.72	9.83±0.07	5.66±0.31						
Mace Head, (2000) ^e , Col. 1	2.38±0.3	7.18±0.42	5.23±0.38						
Mace Head (2001) ^f , Col. 2	2.81±0.22	6.43±0.14	5.46±0.31	0.92±0.11	6.13±0.48	8.52±0.18	0.77±0.10	10.73±0.33	4.78±0.21
SH (2001) ^g , Col. 2	2.65	6.17	5.35	0.79	5.75	8.52	0.73	10.30	4.79

Notes: Col. 1 Column 1: 100 m × 0.32 mm 5 μm CP-Sil capillary; Col. 2 Column 2: 30 m × 0.32 mm Carbowgraph PLOT capillary.

^a Sample collected at Cape Grim, Tasmania in 1997.

^b Sample collected at Niwot Ridge, Colorado in 1997.

^c Continuous 2-hourly ambient measurements at Bristol University, 20–24 March, 2000.

^d 4 Samples collected in the Birmingham, UK during 2000.

^e 5 Samples collected at Mace Head, Ireland during 2000.

^f 4 Samples collected at Mace Head, Ireland during 2000–2001, under easterly wind conditions.

^g Sample collected at Cape Grim, Tasmania in 2001.

Table 4
Atmospheric abundance of cyclic-perfluorocarbons in the troposphere

Cyclic-PFC	North Atlantic background air, (Mace Head, Ireland, January, 2001) (Conc. fl l^{-1})	North Atlantic background abundance ^a (metric tonnes)	Background air, USA, 1986 (Dietz, 1987) (Conc. fl l^{-1})	Atmospheric abundance, USA, 1986 (metric tonnes)	Difference Mace Head January 2001-USA, 1986 (metric tonnes)	Growth 1986–2000 (tonnes/yr)
PDCB	2.70	148.04	0.34	18.64	129.40	9.24
PMCP	6.29	344.89	3.22	176.56	168.33	12.02
PMCH	5.49	351.20	4.60	294.26	56.93	4.07
oc-PDCH	0.73	53.37	0.3	21.93	31.44	2.25
ot-PDCH	0.65	47.52	0.2	14.62	32.90	2.35
mc-PDCH	10.83	791.77	8.2	599.49	192.28	13.73
mt-PDCH	8.65	632.39	7.7	562.94	69.45	4.96
pc-PDCH	6.11	446.69	2.2	160.84	285.85	20.42
pt-PDCH	4.88	356.77	3.4	248.57	108.20	7.73

^a Mass of the atmosphere = 5.136×10^{21} g. Molecular weight = 28.9644.

possibility of mis-identification. It is also most likely that the fractional composition of individual perfluorocarbons and their possible isomers has changed over time, with both improvements in their industrial synthesis and methods of purification. In this study we have been careful to determine the fractional compositions of each cyclic-PFC, present in the PFC standards, by analysis of the individual compounds as supplied by the manufacturer. Furthermore, we note that the present day fractional composition of some of the compounds is different from that determined by Dietz in 1987. For example, Dietz reported a pc/pt ratio for the 1,4-PDCH of 0.66, whereas we obtain a pc/pt ratio of 1.3 for a recent sample of the 1,4-PDCH. It is noteworthy that different manufacturers supplied the two samples.

Not all of the species have been measured consistently since the first reported measurements in 1986. It is also

self-evident that with their very long atmospheric lifetimes (> 3000 yr), the most recently determined atmospheric mixing ratios should always be larger than the earlier measurements. From Table 2 this is quite evidently not always the case even allowing for the large uncertainties in the measurements. For example, it is difficult to reconcile the higher background concentration of PMCP (6.26 fl l^{-1}) reported in the 1992 Mohave project, with the lower concentration of 4.6 fl l^{-1} reported in 1994 during ETEX, and the 5.2 fl l^{-1} observed in the 1999 BRAVO project. Similarly, there must be absolute calibration differences for PDCB and oc-PDCH between this study and BRAVO 1999, where background concentrations differ by about a factor of two. With these obvious discrepancies, it is not possible to obtain statistically meaningful chronological trends for individual cyclic-PFCs from the reported values.

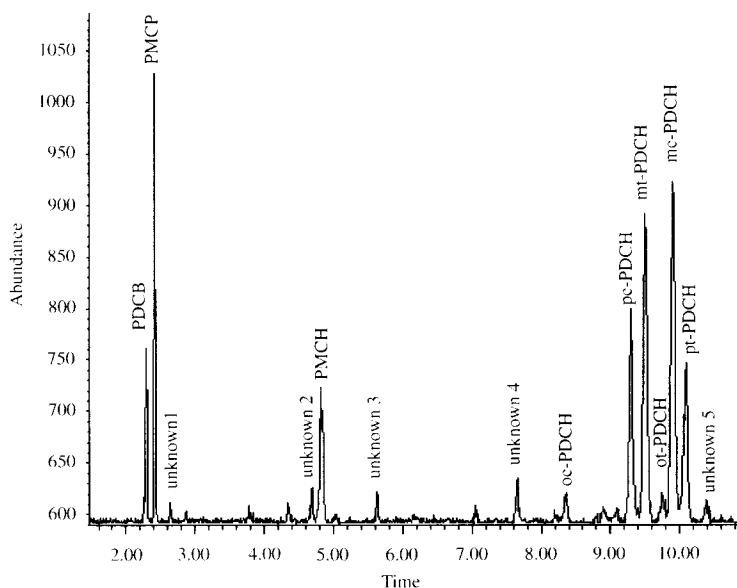


Fig. 4. 3-l ml of Mace Head air analysed on the CarboGraph column. Conditions: 30 m \times 0.32 mm i.d. CarboGraph 1 PLOT column under 1.5 ml min⁻¹ helium flow. Temperature program 30 C for 5 min, 20 C min⁻¹ to 50 C, hold 5 min, 10 C min⁻¹ to 220 C, hold 10 min. Provisional assignments of unknowns: (1) perfluorocyclohexane, (2) perfluorocycloheptane, (3) perfluoroethylcyclopentane, (4) perfluorodimethylcyclopentane, (5) Perfluoropropylcyclopentane.

In Table 3 we summarize all of our background measurements using the NICI-GC-MS method of analysis. Where measurements were obtained using the CP-Sil column we only report background measurements for PDCB, PMCP, and PMCH, due to inadequate resolution of the PDCH isomers. With the higher resolution CarboGraph capillary column, background concentrations were determined for all cyclic-PFCs and their isomers. Although much of the variability listed in Table 3 is within the stated uncertainties for a range of samples collected at a given location, for some locations only a single sample was available for analysis. There are several important observations from this study.

First, the background measurements obtained at all of the Irish locations have similar concentrations. In fact, all of the samples collected in 2001 (compare MH 2001 in Tables 2 and 3), under either a westerly or easterly airflow, lie within the reported measurement uncertainties. Piringer et al. (1997) also noted that background concentrations during ETEX showed no apparent systematic dependence on meteorological parameters.

Second, measurements of PMCP are the most variable with the highest concentrations observed in the city of Birmingham, UK, which also recorded some of the highest background concentrations for PDCB and PMCH.

Third, concentrations of background air samples collected in 1997 in the Southern Hemisphere (Cape Grim, Tasmania) are consistently lower than those also

collected in 1997 in the USA (Niwot Ridge, Colorado), which is consistent with the major sources being in the Northern Hemisphere.

Given the extremely low concentrations being measured, and the different analytical methods employed between this study and the other historical data, it is perhaps unsurprising to find such differences. In this study we expect our most accurate measurements to be those obtained with the higher resolution CarboGraph PLOT capillary and the additional selectivity of the NICI-GCMS. In Fig. 4, we show the excellent separation of a 3-l sample of clean oceanic air collected on the West Coast of Ireland on the CarboPLOT column. It is of interest to note that in addition to the major cyclic-PFCs, there are several, as yet unidentified, minor compounds present in the background atmosphere. From their retention times and ion masses we suggest that they are various mixed perfluoroalkyl-substituted cycloalkanes and their isomers, formed as by-products during the vigorous fluorination synthesis of the parent hydrocarbons, which may also contain impurities (Moldavsky and Furin, 1998). For example, by noting the ion fragments it is possible to recognize the loss of various alkyl substituents, such as methyl (loss of CF_3^+ , $m/z = 69$), ethyl (loss of C_2F_5^+ , $m/z = 119$), and propyl (loss of C_3F_7^+ , $m/z = 169$), from the molecular ion. In addition, loss of F [M-19] and F_2 [M-38] can be observed. We have provisionally assigned identifications to some of these unknown compounds, although

currently they cannot be verified due to the absence of authentic standards. While it is relatively straightforward to determine analytical precisions for these measurements it is much more difficult to estimate systematic uncertainties in the preparation of standards. By combining all of the uncertainties in the calibration and analytical procedures we estimate that the overall uncertainty in these observations ranges from about 5% for the more abundant compounds such as the *m*, *p*-PDCH isomers to 14% for the *o*-PDCH isomers. To more accurately validate these observations requires the development of an internationally recognized calibration scale for these compounds. Furthermore, future measurements would benefit from more intercalibration exercises between the different groups making these measurements.

Based on the January 2001 background concentrations determined at Mace Head, Ireland (shown in Table 2), we estimate in Table 4 the global atmospheric burden for individual cyclic-PFCs, assuming that these compounds have been preserved without loss since their first date of commercial manufacture in the 1960s. These abundances range from about 50 metric tonnes (t) for the *cis* and *trans* isomers of 1,2-PDCH, respectively, to approximately 790 t, and 632 t, for the *cis* and *trans* isomers of 1,3-PDCH, respectively. To put these abundances in perspective we note that the present day combined atmospheric abundance of CF₄, C₂F₆ and SF₆ is about 1500 metric kilotonnes (kt), which compares to a total atmospheric abundance from the accumulation of all cyclic-PFCs of only 3 kt.

Comparing the differences in calculated abundances between the first reported measurements in 1986 (Dietz, 1987) with air recently collected at Mace Head, Ireland (January 2001), and assuming a linear growth rate over the 14-yr interval, we calculate that these cyclic-PFCs have grown at rates varying between about 2 yr⁻¹ (*oc*-PDCH) and about 20 yr⁻¹ for the *pc*-PDCH.

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