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## PERFLUOROCARBON BACKGROUND CONCENTRATIONS IN EUROPE

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**Abstract**—Five studies of the background level of several perfluorocarbon compounds in Europe are here presented together with measurements from the European Tracer Experiment (ETEX). The tracers used during the two ETEX tracer releases were the perfluorocarbons (PFCs); perfluoromethylcyclohexane ( $C_7F_{14}$ , PMCH) and perfluoromethylcyclopentane ( $C_6F_{12}$ , PMCP). Their background concentrations were detected by using both passive and active sampling techniques, to define the spatial and temporal variation of the PFCs over Europe. Also the background variations of four isomers of the PFC compound perfluorodimethylcyclohexane ( $C_8F_{16}$ , PDCH) were studied. The results were compared to other PFC tracer studies in the U.S.A. and Europe. The mean and median values of the measured PFCs were found to vary slightly and randomly in space and time. They were found to be higher and to have a larger standard deviation than the measurements from the American studies. The background concentrations were still found to be low and stable enough for PFCs to be highly suitable for use in tracer studies. The following concentrations were found: PMCP:  $4.6 \pm 0.3 \text{ fl}^{-1}$ , PMCH:  $4.6 \pm 0.8 \text{ fl}^{-1}$ , ocPDCH:  $0.96 \pm 0.33 \text{ fl}^{-1}$ , mtPDCH:  $9.3 \pm 0.8 \text{ fl}^{-1}$ , mcPDCH:  $8.8 \pm 0.8 \text{ fl}^{-1}$ , ptPDCH:  $6.1 \pm 0.8 \text{ fl}^{-1}$ . A study of the correlation between the measured PFC compounds showed a significant correlation between most of the compounds, which indicate that there are no major PFC sources in Europe. © 1998 Elsevier Science Ltd. All rights reserved

**Key word index:** Perfluorocarbons, tracer release, background concentrations, long-range transport.

### 1. INTRODUCTION

A variety of long-range transport models are existing in different European countries, for modelling of gas dispersion over Europe in connection with hazardous releases. The European Tracer Experiment (ETEX) was established to produce a database for evaluation of these dispersion models (Girardi *et al.*, 1997). It was further established to test the emergency preparedness in connection with major accidents. The experiment was jointly organised by the World Meteorological Organisation (WMO), the International Atomic Energy Agency (IAEA) and the Joint Research Centre (JRC) in Italy. ETEX contained two tracer releases, one in October and one in November 1994. The atmospheric tracers were released in Brittany (France), and the outspread measured at 168 meteorological stations in the Central and Northern part of Europe. The gas puff was also detected in the

vertical by three aircraft from the United Kingdom, Germany, and Switzerland. The results from ETEX are described by Nodop *et al.* (1998).

When performing tracer experiments, the background concentrations of the released tracer have to be known. One reason is that the lower the background concentration of the tracer, the less tracer one has to release in order to detect its outspread at locations distant to the source. The second reason is that the background concentration of the tracer should be fairly stable in time and space in order to distinguish the amount of released tracer from its background concentration. Before ETEX, studies of the ambient background level of perfluorocarbons had been performed in the U.S.A. (e.g. Dietz, 1986). No studies had however been performed in Europe. Background concentrations of the released tracers were therefore measured during four passive and one active background study in Europe during 1994. Four of the studies were performed before ETEX started, and one passive study was performed during the second release. Background concentrations have further been deduced from the measurements of the two ETEX releases. The results from all studies

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together with other PFC studies will now be described and discussed.

## 2. DESCRIPTION OF THE TRACERS, THE SAMPLING AND THE ANALYSIS

The tracers chosen for ETEX are members of the perfluorocarbon (PFC) family. The tracer used during the first release (hereafter called Release-1) was perfluoromethylcyclohexane ( $C_7F_{14}$ , PMCH), and during the second (hereafter called Release-2), perfluoromethylcyclopentane ( $C_6F_{12}$ , PMCP). The PFCs are inert, they have a low background level, are easily detectable, and have a limited industrial use (Dietz, 1986). As their background concentrations are low, the amount of tracer that needs to be released is low. This makes them economic in comparison to other tracers like  $SF_6$  and  $CBrF_3$  (Dietz, 1986). All these properties make PFCs suitable for studies of long-range transport of air pollutants. They have already been used with great success in several long-range transport studies in the U.S.A. (Ferber *et al.*, 1986; Draxler *et al.*, 1991).

### 2.1. Sampling procedure

An overview of the five background studies performed in connection with ETEX is given in Table 1. Information about the two ETEX releases and the measurement methods used are also listed. The last column in the table shows the total amount of samples collected, together with the number of samples that were successfully analysed for each study. The samples that were not quantified were those where one was sure that no tracer was present when the tube was exposed (only for the two ETEX releases), they got lost during transport, or they got lost during the analysis procedure. The background concentrations

measured during the Austrian Background Studies (ABS) (Piringer *et al.*, 1997), were sampled by using an active and a passive sampling technique at the eight Austrian stations shown in Fig. 1. Results from the ABS active sampling study are given in Section 5.2. The sampling procedure during this study was the same as the one used for the Release-1 and Release-2 data, and will be described later in this section. The ABS passive sampling study was performed two times, starting at the same days as the ABS active study. Capillary Adsorption Tube Samplers (CATS) which are glass tubes containing an adsorbent element were left exposed to the ambient air for 14 days. The CATS system is described in detail by Dietz *et al.* (1986). The air transport inside the CATS tubes is driven by Fick-Diffusion (Dietz, 1986) and the approximate amount of air sampled is  $200 \text{ ml d}^{-1}$ . The samples from the ABS passive study were analysed at the Brookhaven National Laboratory (BNL). The way to calculate the concentrations from these samples is described in Section 3. Since the study was performed at the same time as the CATS-0 study, the results are included in the concentration data from the CATS-0 study.

Three more CATS studies were performed by the JRC and the BNL at stations in Central and Middle Europe, prior to ETEX. The sampling and analysis techniques were the same as for the ABS passive sampling study, and the analysis was done at the BNL. The tubes were exposed for 14 d in all of the studies. During the first study, CATS-0, background concentrations were measured at 73 of the 168 ETEX stations, shown in Fig. 1. The starting dates of the measurements varied at the different measurement stations, with the first measurement starting on 25 January, and the last ending on 1 April 1994. During the second and third study in October 1994 (CATS-1) and November 1994 (CATS-2), samples were taken at

Table 1. Names, dates, and characteristics for the five PFC background studies and the two ETEX releases performed in 1994. Coll.: Number of samples collected. Ana.: number of samples successfully analysed

Name of study	Type of sampling	Date of sampling	Type of sampling tubes	Adsorbing substance	Analysed at	No. of samples	
						Coll.	Ana.
ABS, active	Active	25-28 Jan 11-14 Feb	Stainless-steel tubes	Carboxen-569	JRC	196	196
ABS, passive	Passive	14 days 25 Jan-8 Feb	Glass tubes	Amborsorb	BNL	20	12
CATS-0	Passive	11-25 Feb 14 days	Glass tubes	Amborsorb	BNL	73	73
CATS-1	Passive	Jan-Apr 14 days	Glass tubes	Amborsorb	BNL	185	174
CATS-2	Passive	7-21 Oct 14 days	Glass tubes	Amborsorb	BNL	185	163
Release-1	Active	14-27 Nov 23-26 Oct	Stainless-steel tubes	Carboxen-569	JRC	4032	3462
Release-2	Active	14-17 Nov	Stainless-steel tubes	Carboxen-569	JRC	4032	2617

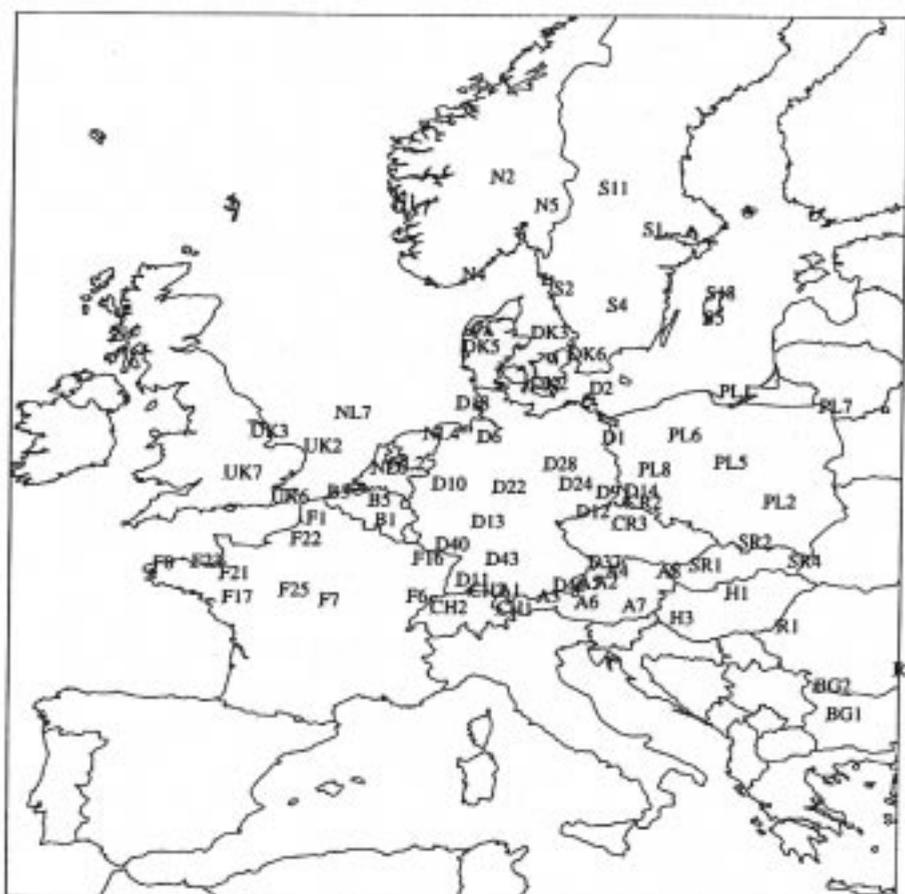


Fig. 1. Map showing the measurement stations used during the Austrian Background Study and CATS-0. For station codes and location, see Nodop *et al.* (1998).

all of the 168 ETEX stations (see Fig. 1 in Nodop *et al.*, 1998). The CATS-2 study was performed during and after the second ETEX tracer release.

During the two ETEX tracer releases, the air samples were taken at all of the 168 ETEX stations. Ambient air was pumped into stainless-steel tubes filled with the adsorbent material Carboxen-569 using samplers of the type SAM1 and AS3. The samplers of the type SAM1 are developed at the JRC, and the AS3 samplers are developed at the Austrian Research Centre at Seibersdorf. The exact air volume entering the tubes during the sampling is given by the flow rate of air pumped onto the tubes, which is controlled by the automatic sampler. The flow rates were 200 ml min<sup>-1</sup>. The samples were taken three hourly from 23 October at 16.00 UTC until 26 October at 16.00 UTC (Release-1), and from 14 November at 15.00 UTC until 17 November 15.00 UTC (Release-2). The samples were analysed at the JRC.

## 2.2. Analysis procedure

The chemical analysis methods used for the passive studies at the BNL and for the active studies at the JRC are similar. A description of the BNL analysis

method is given by Dietz *et al.* (1986). The analysis method and procedure used during ETEX is described by Nodop *et al.* (1998), and can shortly be summarised as follows: The analysis of the approximately 9000 samples collected during ETEX took 2 years. The samples were thermally desorbed and analysed by gas chromatography with electron capture detection. As well as detecting perfluoromethylcyclopentane (C<sub>6</sub>F<sub>12</sub>, PMCP) and perfluoromethylcyclohexane (C<sub>7</sub>F<sub>14</sub>, PMCH), released during the experiment, the JRC and BNL methods also allow the determination of four isomers of perfluorodimethylcyclohexane (C<sub>8</sub>F<sub>16</sub>, ocPDCH, mtPDCH, mcPDCH, and ptPDCH) in a single analysis. Because these compounds were not released, their background concentrations at each site were used for quality control purposes.

## 3. BACKGROUND STUDIES USING A PASSIVE SAMPLING TECHNIQUE

The results from the ABS passive study and the CATS studies are now presented. A comparison of

these studies with the ETEX active sampling is given in Section 6.

### 3.1. Calculation of the concentrations

When analysing the air samples, the resulting peak heights correspond to the amount of tracer found on the sampling tubes. To retrieve the actual air concentrations ( $C(s)$ ) for the different compounds in femtolitre pr. litre ( $\text{fl l}^{-1}$ ), the following equation is used:

$$C(s) = C_{\text{bg}}(s) \cdot \frac{R(s)}{R_{\text{bg}}(s)} \quad (1)$$

where  $C_{\text{bg}}(s)$  is the ambient background concentration of compound  $s$ ,  $R(s)$  is the peak height ratio between the peak height of compound  $s$  and the peak height of ptPDCH.  $R_{\text{bg}}(s)$  is the background value of  $R(s)$ . The rationing of the peak heights towards ptPDCH was done for the following reasons: During the passive tracer sampling, the amount of air entering the tubes during the time of exposure is dependent on two factors: (i) the time of exposure, and (ii) meteorological conditions (e.g. wind and heating effects). The rate with which the PFCs are transported to the adsorbing media is therefore uncertain due to these factors. A method has then been sought to correct the measured PFC concentrations due to uncertainties in the sampling volumes. Dietz (1986) concluded on the basis of background studies in the USA, that the distribution of ptPDCH is close to constant in the atmosphere. Studies performed by Dietz before January 1996 (unpublished), also show close to constant concentrations of ptPDCH, which gives us a reason to assume that this is true also for Europe. The CATS concentrations can therefore be corrected

for errors in the assumed air volume by rationing the peak heights to ptPDCH as shown in equation (1).

The background concentrations ( $C_{\text{bg}}(s)$ ) in equation (1) for the PFC compounds are defined by Dietz, and are shown in the first row of Table 2. These concentrations are based upon his 1996 values, mentioned above. The background ratio of the peak heights ( $R_{\text{bg}}$ ) are set to the mean value of all station peak height ratios ( $R_s$ ) after applying an iterative scheme that removes the highest and lowest values. The method was used in order to give less importance to unreasonably high or low peak height values, which are not regarded as representative for the overall background in Europe. Assuming a Gaussian law for the distribution of measured peak height ratios around their mean value, the peak height ratios have been iterated by using the following equation:

$$\bar{R}_s - \sigma \leq R_s \leq \bar{R}_s + \sigma \quad (2)$$

where  $\bar{R}_s$  is the mean peak height ratio for all stations considered and  $\sigma$  is the corresponding standard deviation. All stations with an  $R_s$  lower than  $\bar{R}_s - \sigma$  or higher than  $\bar{R}_s + \sigma$  will be taken out of the data set during one iteration. The mean values and standard deviations for the peak height ratios are then updated and used in the next iteration cycle. After two iterations, the values for the mean, median, and standard deviation of the peak height ratio from the CATS studies had stabilised on one level. This median value is taken as the background peak height ratio for each compound in equation (1).

Concentrations from the CATS studies were calculated by applying equation (1). The deviations between the sample concentrations and the mean values

Table 2. Background concentrations from the passive CATS measurements. First two rows: PFC background concentrations  $C_{\text{bg}}$  ( $\text{fl l}^{-1}$ ) and standard deviation  $\sigma/C_{\text{bg}}$  (in % of the background concentration) used for the calculations of the CATS concentrations. Mean values, median values, and standard deviations  $\sigma/\text{mean}$  (in % of the mean value) for the CATS concentrations are given after applying one iteration. Samp. of tot: The number of samples after applying one iteration in percent of the total number of samples

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
$C_{\text{bg}}$	4.7	5.5	0.46	11.8	8.4	5.4
$\sigma/C_{\text{bg}}$	13%	9%	1%	4%	6%	
<b>CATS-0</b>						
Mean	5.0	6.3	0.51	12.4	8.9	5.4
$\sigma/\text{mean}$	38%	41%	30%	19%	19%	
Median	4.7	5.5	0.47	11.8	8.4	5.4
Samp. of tot:	97%	91%	84%	88%	87%	
<b>CATS-1</b>						
Mean	4.9	5.9	0.48	12.0	8.5	5.4
$\sigma/\text{mean}$	17%	16%	15%	6%	5%	
Median	4.7	5.6	0.47	11.8	8.4	5.4
Samp. of tot	89%	97%	95%	99%	99%	
<b>CATS-2</b>						
Mean	4.9	5.6	0.47	12.0	8.4	5.4
$\sigma/\text{mean}$	19%	9%	18%	5%	5%	
Median	4.7	5.5	0.45	11.8	8.4	5.4
Samp. of tot.	93%	85%	96%	98%	95%	

of all the concentrations, normalised by one standard deviation were calculated. These deviations ( $DM_s$ ) are defined by the following equation:

$$DM_s(i) = \frac{C_s(i) - \bar{C}_s}{\sigma_s} \quad (3)$$

where  $C_s(i)$  is the stationwise PFC concentration for compound  $s$ ,  $\bar{C}_s$  is the mean tracer concentration over all stations for compound  $s$ , and  $\sigma_s$  is the corresponding standard deviation. The  $DM_s$  are presented in Fig. 2 for the CATS-1 data set. As can be seen from the figure, the majority of the concentrations are close

to their mean value. At 20 of the 168 stations, concentrations more than one standard deviation higher than the mean value were measured. At 16 of these stations, the high concentrations were found for only one of the PFC compounds, which indicates that they were rather occurring due to contamination or analysis errors than due to local industrial sources. The contamination could have occurred if the tubes were exposed close to a contaminating source at the release site, or if the tubes were not properly closed after the sampling finished. As for the industrial sources, PFC gasses used in industry mostly contain a mixture of several PFC compounds, because to produce pure

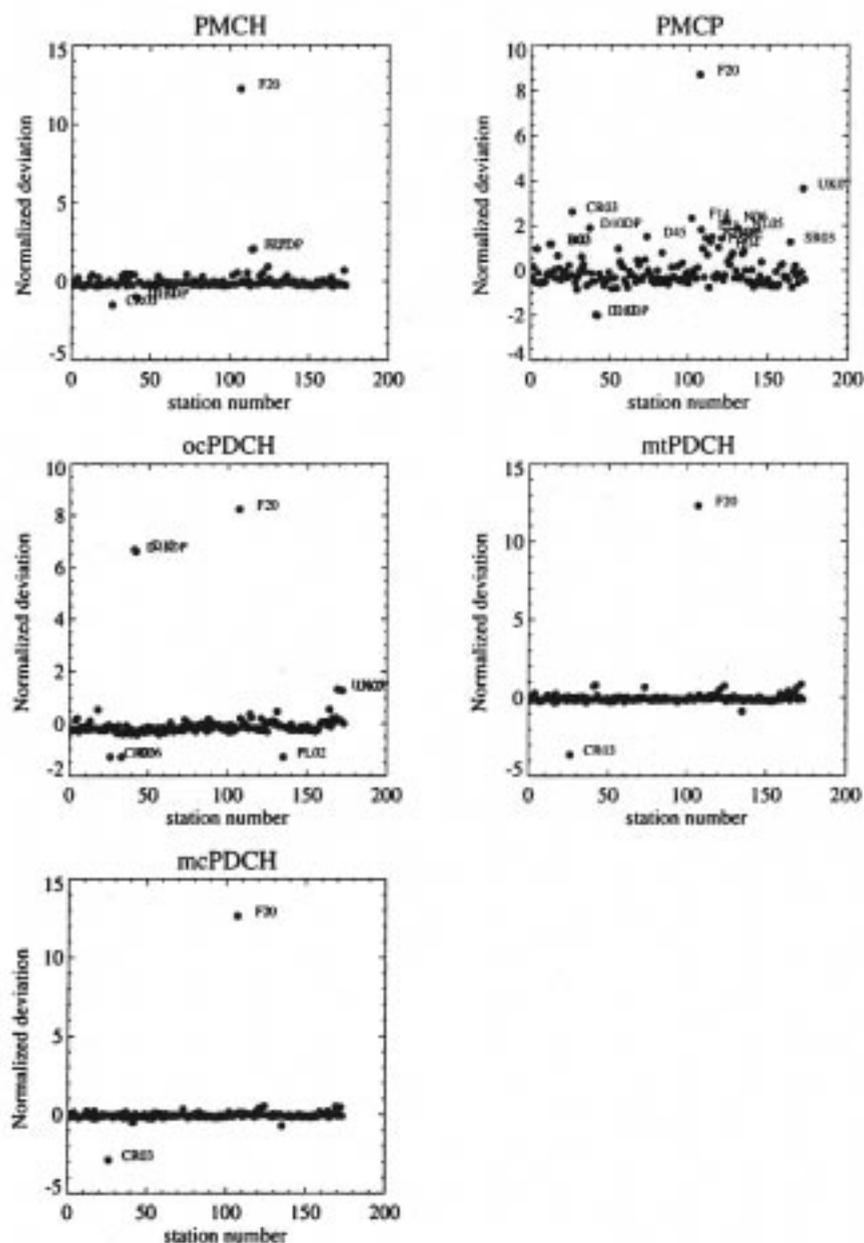


Fig. 2. Deviation ( $DM_s$ ) of the concentrations from the mean value, normalised by one standard deviation from CATS-1. Station names are added when  $DM_s$  is greater than 1 or less than  $-1$ .

PMCH, PMCP, or PDCH isomers is very expensive. During CATS-0, high concentrations were measured at 16 of the 93 stations. Of these, 3 samples contained high concentrations for only one compound, indicating that possible contamination or analysis errors had occurred. For CATS-2, high concentrations were found at 28 of the 168 stations, and at 17 of these high values were found for only one of the PFC compounds. The stations where high values were measured for more than one of the PFC compounds were differing in the three CATS studies. For CATS-0, high values were found at two Austrian stations (A02, A07) (see Fig. 1 in Nodop *et al.*, 1998), one Belgian station (B03), two Czech stations (CR02, CR03), three German stations (D12, D19, D24), three Danish stations (DK02, DK05, DK06), one Norwegian station (N01), and one Dutch station (NL07). For CATS-1 the high values were found at two French stations (F20, F27) and one English station (UK07). For CATS-2 the high values were found at one German station (D13), eight French stations (F03, F07, F08, F16, F19, F23, F25, F27), and one Dutch station (NL02). The high concentrations were not found at the same measurement stations in the three CATS studies, except at F27. There, high concentrations were found for both CATS-1 and CATS-2, but not for the same compounds. They are therefore not assumed to be caused by continuous local sources.

### 3.2. Correction by iterations

The few very high or low concentrations in Fig. 2 biased the mean value of the background concentrations, since the majority of the concentrations are very close to one value. It was therefore necessary to define more representative mean values for the background concentrations, that are not too biased by these few concentrations created by contamination of the samples, analysis errors, or possible industrial sources. This was done by applying the iteration scheme of equation (2) to the calculated concentrations. All concentrations greater than the mean concentration plus one standard deviation or less than the mean value minus one standard deviation were excluded from the data. After applying this iteration scheme one time, the new mean values, median values, and standard deviations (normalised to the mean value) are regarded as representative for the overall background in Europe (Table 2). The mean values are varying with 2–15% from the background concentrations in the first row of Table 2. The standard deviations are varying between 5 and 41% of the mean values. The highest concentrations and variations were occurring for CATS-0, where several samples are assumed contaminated from previous use of the sampling tubes. As is further indicated in the table, 1–16% of the samples were excluded by the iteration procedure.

### 3.3. Correlation

A way to study whether the background concentrations are influenced by local sources is to calculate

Table 3. Pearson correlation coefficients for CATS-0, CATS-1, and CATS-2. # samples: Number of samples considered

	PMCP	PMCH	ocPDCH	mtPDCH
<b>CATS-0, # samples: 71</b>				
PMCH	0.87			
ocPDCH	0.35	0.58		
mtPDCH	0.66	0.88	0.59	
mcPDCH	0.63	0.88	0.77	0.96
<b>CATS-1, # samples: 174</b>				
PMCH	0.81			
ocPDCH	0.38	0.54		
mtPDCH	0.73	0.94	0.72	
mcPDCH	0.74	0.96	0.61	0.99
<b>CATS-2, # samples: 163</b>				
PMCH	0.67			
ocPDCH	-0.05	-0.30		
mtPDCH	0.14	0.10	0.19	
mcPDCH	0.17	0.17	0.34	0.86

the stationwise correlation between them. If there are no local sources of PFCs in Europe, their background concentrations will be evenly distributed in space and time, and the correlation between the compounds will be good. The Pearson correlation coefficients between the different PFC concentrations, prior to the iterations, are presented in Table 3. The table shows a very good correlation (above 0.8) between PMCP and PMCH for CATS-0 and CATS-1, and between mtPDCH and mcPDCH for all three CATS studies. The good correlation between mtPDCH and mcPDCH is expected since they are isomers of the same compound, since they are analysed almost at the same time by the gas chromatograph, and since their background concentrations in the atmosphere are very similar. All compounds in CATS-0 and CATS-1 are further significantly correlated within an error of 1% or better. For CATS-2, the correlations between the compounds are lower and in some cases negative. For 6 of the 10 intercomparisons, the compounds are however correlated within an error of 5% or better. The compounds that are not significantly correlated within this error are PMCP and ocPDCH, PMCP and mtPDCH, PMCH and ocPDCH, and PMCH and mtPDCH. The low and in one case negative correlations found when comparing PMCP to the other compounds, are likely to occur because PMCP was released during the second ETEX release which took place during the first day of CATS-2. The low correlations found when comparing ocPDCH with the other compounds might have been caused by the fact that its concentrations are about 1/10 of the other PFC concentrations. Because of the good correlations found during CATS-0 and CATS-1, the low correlations involving ocPDCH and PMCH during CATS-2 are assumed caused by uncertainties in the sampling and analysis procedure.

### 3.4. Quality control of the data

In order to check whether any contamination of the tubes had taken place, blank tubes were distributed at six sites during CATS-1 and at 15 sites during CATS-2. Data for the blank tubes distributed during CATS-0 are not available. The tubes should have been clean and were not to be exposed to ambient air, in order to check whether contamination of the tubes happened during transport or in the laboratory where they were analysed. All the blank tubes from CATS-1 and CATS-2 showed the presence of low concentrations of one or several of the PFC compounds. In six cases, the concentration of one of the compounds was higher than its background concentration. These high concentrations probably occurred due to analysis errors, since they did not contain the same composition of PFCs as the ambient air. Another possibility is that the blank tubes were contaminated from previous use. One would then however expect to find elevated concentrations for all 6 PFC compounds, which was not the case.

Duplicate tubes were also exposed at 17 sites during CATS-1 and 14 during CATS-2. Concentrations from the duplicate tubes for CATS-0 are again not available. For CATS-1, 3 of 17 pairs of sampled concentrations had a standard deviation of more than 10% of the mean value for PMCH and PMCP. These tubes were located in Austria (A04), Germany (D10), and Sweden (S13) (see Fig. 1 in Nodop *et al.* (1998) for locations). For CATS-2, 7 out of 14 samples had a standard deviation of more than 10% of the mean value for the compounds PMCH and PMCP. These were located in Austria (A04), Germany (D13, D30), France (F08, F20, F21) and in The Netherlands (NL02). These differences between the measured concentrations are occurring because of contamination either from previous use of the tubes, contamination during transport if the tubes were not properly sealed, or contamination during analysis in the laboratory.

## 4. BACKGROUND STUDIES USING AN ACTIVE SAMPLING TECHNIQUE

A description of the concentrations measured during the ETEX releases together with a study of their quality is given in Nodop *et al.* (1998). The background concentrations of all PFC compounds were retrieved from this data set and the results will now be presented.

### 4.1. Measured concentrations

During the active sampling studies, the amount of air pumped into the sampling tubes was controlled by the samplers. The PFC concentrations could therefore be calculated from the measured mass concentrations (from the gas chromatograph), by dividing the mass by the amount of air that had entered the tubes.

A calculation of the tracer concentrations, by using previously calculated background concentrations as was done for the passive studies (equation (1)), was therefore not necessary.

During both ETEX tracer releases, 24 three-hourly averaged samples were taken at each of the 168 ETEX stations. As mentioned earlier, the tracer released during Release-1 was PMCH, and during Release-2 PMCP. The data sets will therefore contain concentrations for these compounds that are higher than the ambient background levels. Extra care has therefore been taken to calculate the background concentrations for these compounds.

The first treatment of the measured background concentrations was to calculate the mean values, median values and standard deviations. The deviations between the station concentrations and the mean value normalised by one standard deviation ( $DM_s$ ), as calculated by equation (3), are presented in Fig. 3 for Release-1. No values are given for PMCH, since the data contained concentrations from the released tracer. PMCP was not measured for Release-1. As can be seen from Fig. 3, most of the stations contain measured concentrations within two standard deviations from the mean value. Two standard deviations are chosen because the number of measurements from the ETEX releases was 20–40 times higher than for the CATS studies. For Release 1, 30 of the stations contained concentrations more than 2 standard deviations higher than the mean value. At 14 of these stations high values were measured for only one of the PFC compounds, indicating that contamination or analysis errors probably had taken place rather than a release from an industrial source. The rest of the stations showed high values for several of the PFC compounds. These stations were located in Austria (A02, A03) (see Figure 1, Nodop *et al.*, 1998), Bulgaria (BG02), the Check Republic (CR01, CR02), Germany (D13, D28, D45), France (F21), Norway (N05), Holland (NL07, NL08), Poland (PL04, PL05), Rumania (R01), and the Slovak Republic (SR01). For Release-2 (not shown), concentrations more than two standard deviations higher than the mean value were measured at 17 of the 168 stations. In 9 of these samples, high values were found for only one compound. The stations showing high values for several of the PFC compounds were located in Germany (D04, D13, D23, D28, D45), France (F17), Hungary (H04), and Holland (NL02, NL03).

The samples showing high concentrations for the same compounds in Release-1 and Release-2 were located at: D13, containing elevated concentrations for *oc*PDCH, *mc*PDCH, and *pt*PDCH, D28, containing elevated concentrations for all of the PDCH isomers, and D45, containing elevated concentrations for *oc*PDCH and *mt*PDCH. Local sources might have influenced the PFC background levels on these stations. At station D45 however the high values occur at only one of the twenty-four 3 hourly time steps during both releases, which excludes a local

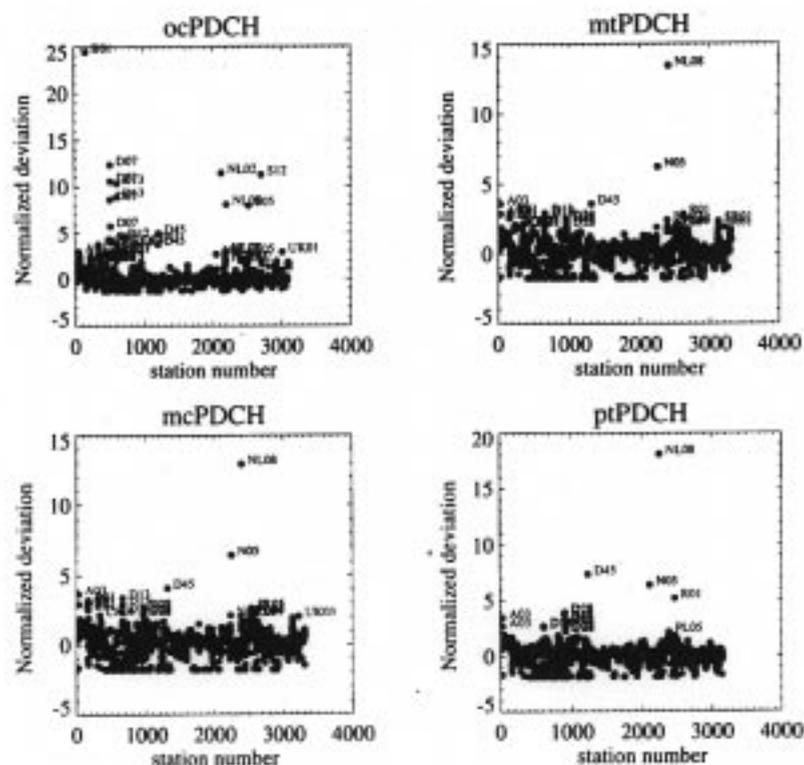


Fig. 3. Deviation (DM<sub>i</sub>) of the concentrations from the mean value, normalised by one standard deviation from Release-1. Station names are added when DM<sub>i</sub> is greater than 3 or less than -3.

continuous source. At D13 and D28 high values are further not found for all of the 24 time steps, which shows that the elevated background levels for the PFC compounds are varying.

#### 4.2. Correction by iterations

An iteration scheme identical to equation (2) has been applied to the Release-1 and Release-2 data sets, in order to give less importance to a few unreasonably high or low concentrations measured. As mentioned in the previous section, a substantially higher number of measurements were taken during Release-1 and Release-2, than during the CATS studies (20–40 times). Therefore, two iterations were performed because of the higher uncertainty involved in the measurements. The results are given in Table 4. For the PMCH concentrations from Release-1 and the PMCP concentrations from Release-2, three iterations were performed to make sure that the released tracer is not present when calculating the background concentrations. The mean and median values stabilised on one level for all PFC compounds after two iterations. The standard deviations varied with 10–20% from the mean values. The number of values excluded from the data set by applying the iterations were about 50% of the total number of samples, which indicates that the criteria of performing two iterations is very strict in this case.

#### 4.3. Correction of the assumed air volume

To eliminate possible biases due to undetected errors in the sampling procedure, also the ETEX data were referenced to ptPDCH. The PFC concentrations were then corrected by dividing them by the factor to which the value of ptPDCH differ from its mean value, by applying the following equation:

$$C_{\text{corr.}} = \frac{C_{\text{uncorr.}}}{(C_{\text{ptPDCH}}/C_{\text{ptPDCH,br}})} \quad (4)$$

where  $C_{\text{corr.}}$  is the corrected concentration,  $C_{\text{uncorr.}}$  is the uncorrected concentration,  $C_{\text{ptPDCH}}$  is the measured ptPDCH concentration, and  $C_{\text{ptPDCH,br}}$  is set to  $6.2 \text{ fl l}^{-1}$  for Release-1 and  $5.9 \text{ fl l}^{-1}$  for Release-2, which are the median values in Table 4. These values are slightly higher than the ptPDCH background concentration given for the CATS studies, which was  $5.4 \text{ fl l}^{-1}$ . The iterative method (equation (2)) was again used on the ptPDCH-corrected data to find a more representative value for the mean and median background concentrations. The results are shown in Table 5. The table shows that the mean values after iterating and referencing the data to ptPDCH (Table 5) are mostly lower than the mean values for the data that were only iterated (Table 4). There are however some exceptions: ocPDCH and mcPDCH for Release-1, and PMCP, mtPDCH, and mcPDCH

Table 4. Background concentrations from the active ETEX measurements. Mean value, median value (both in  $\text{fl}^{-3}$ ), and standard deviation  $\sigma/\text{mean}$  (in % of the mean value) for the CATS concentrations after applying two iterations. Three iterations are applied for PMCH in Release-1, and PMCP in Release-2. Samp. of tot.: the number of samples after two iterations in % of the total number of samples analysed

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
<b>Release-1</b>						
Mean		4.7	0.92	9.3	8.8	6.1
$\sigma/\text{mean}$		20%	16%	12%	12%	12%
Median		4.6	0.91	9.3	8.8	6.2
Samp. of tot.		52%	59%	44%	44%	48%
<b>Release-2</b>						
Mean	4.5	4.6	0.94	9.1	8.6	5.9
$\sigma/\text{mean}$	13%	13%	10%	13%	13%	13%
Median	4.5	4.7	0.94	9.0	8.5	5.9
Samp. of tot.	45%	48%	51%	48%	47%	53%

Table 5. Background concentrations from the active ETEX measurements, corrected for ptPDCH. Mean values, median values (all in  $\text{fl}^{-3}$ ), and standard deviations  $\sigma/\text{mean}$  (in % of the mean value) for the concentrations after two iterations. For PMCH in Release-1 and PMCP in Release-2, three iterations are performed. Samp. of tot.: the number of samples after two iterations in % of the total number of samples analysed

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
<b>Release-1</b>						
Mean	–	4.7	0.98	9.3	8.9	–
$\sigma/\text{mean}$		17%	33%	8%	9%	
Median		4.5	0.87	9.2	8.7	6.2
Samp. of tot.		71%	92%	80%	81%	
<b>Release-2</b>						
Mean	4.6	4.6	0.94	9.3	8.7	–
$\sigma/\text{mean}$	6%	10%	7%	7%	5%	
Median	4.6	4.6	0.93	9.3	8.7	5.9
Samp. of tot.	57%	89%	72%	73%	79%	

for Release-2. For these compounds the mean value was slightly higher when referencing the data to ptPDCH. The median values are all lower in Table 5 than in Table 4, except for the slightly higher values for PMCP, mtPDCH, and mcPDCH in Release-2. In most cases the standard deviations are ranging from 5 to 17% of the mean value, and are more or less unchanged or lower than for the uncorrected data. There is one exception for ocPDCH in Release-1, where the standard deviation is much higher relative to the mean value after correcting for ptPDCH (16% before correction and 33% after). The ptPDCH correction seems in this case to make a larger spread in the concentrations. The number of stations excluded in the ptPDCH referenced data were much lower than for the unreferenced data, because the referencing lowered many of the concentrations down to the mean concentration level. The high number of measurements excluded for PMCH and PMCP are caused by the presence of the released tracers.

#### 4.4. Correlation

As for the CATS studies, the correlations between the different PFCs from Release-1 and Release-2 were

Table 6. Pearson correlation coefficients for Release-1. unco.: correlation for concentrations before correcting for ptPDCH, co. pt: correlation for concentrations after correcting for ptPDCH. # sam: Number of samples successfully analysed

	ocPDCH		mtPDCH		mcPDCH	
<b>Release-1,</b> # sam: 3334	unco.	co. pt	unco.	co. pt	unco.	co. pt
mtPDCH	0.53	0.29				
mcPDCH	0.50	0.27	0.98	0.82		
ptPDCH	0.48	–	0.90	–	0.93	–

calculated, and are given in Tables 6 and 7. No iterations were performed on the data sets. The numbers in the first column for each compound show the correlations of the PFC concentrations before they were corrected for ptPDCH. The second column shows the corresponding values after correction. Correlations for the released tracers in Release-1 (PMCH) and Release-2 (PMCP) are not shown.

Tables 6 and 7 show a varying degree of correlation between the PFC compounds, as was also found for

Table 7. As Table 6, but for Release-2

Release-2, # sam.: 2479	PMCH		ocPDCH		mtPDCH		mcPDCH	
	unco.	co. pt	unco.	co. pt	unco.	co. pt	unco.	co. pt
ocPDCH	0.70	0.30						
mtPDCH	0.81	0.38	0.84	0.66				
mcPDCH	0.87	0.39	0.83	0.69	0.98	0.98		
ptPDCH	0.76	-	0.63	-	0.80	-	0.94	

the CATS studies. For Release-1, the correlation was as expected excellent (above 0.9) between the PDCH isomers: mtPDCH and mcPDCH, mtPDCH and ptPDCH, and mcPDCH and ptPDCH before correcting the data for ptPDCH. The correlation was lower but still significant within an error of 1% when comparing ocPDCH with the other compounds. The lower correlations for ocPDCH are again believed to be caused by its lower concentrations relative to the other compounds. For the data corrected by ptPDCH, the correlations became weaker (0.27–0.82) but were still significant within an error of 1% or better. Before the correction to ptPDCH was done, a few high concentrations for the compared PFCs influenced the calculations of the correlations. When these few high values were lowered, by referencing the data to ptPDCH, the correlations became more representative for the majority of the measurements compared.

For Release-2, the correlation between all compounds was good and significant within an error of 1% (0.66–0.97). When correcting the data by ptPDCH, these correlations became again weaker, for the same reason as was mentioned for Release-1. They were however still significant within an error of 1%.

The varying but significant correlations found during the Release-1 and Release-2 studies, implies that there are probably no major local sources of PFCs in Europe.

## 5. RESULTS FROM OTHER TRACER STUDIES

Several studies of PFC background concentrations have been performed in the U.S.A. and in Europe previous and after the ETEX experiment. Results from some of them will now be presented.

### 5.1. PFC experiments in the U.S.A.

In 1986, Dietz calculated background concentrations of PFCs by analysing air samples taken from an area near by his laboratory at the BNL (Dietz, 1986). In 1989, the Across North American Tracer Experiment (ANATEX) was performed in the USA (Draxler *et al.*, 1991). This was a large perfluorocarbon tracer experiment, where among others background concentrations of PFCs in the U.S.A. were calculated.

Table 8. Background concentrations ( $\text{fl}^{-1}$ ) in the USA (Dietz, 1986, and Draxler *et al.*, 1991). Mean values and standard deviations  $\sigma/\text{mean}$  (in % of the mean value) are given

	PMCP	PMCH	ocPDCH	ptPDCH
Dietz, 1986				
Mean	3.2	4.5	0.30	3.4
$\sigma/\text{mean}$	1%	1%	33%	29%
ANATEX				
Mean	2.1	3.6	0.40	4.3
$\sigma/\text{Mean}$	21%	1%	8%	7%

Table 9. Background concentrations from the active Austrian Background Study, spring 1994. Mean value, median value and standard deviation  $\sigma/\text{mean}$  (in percent of the mean value) are given

	Mean	Median	$\sigma/\text{mean}$
PMCH	5.8	5.7	23%

Table 8 lists the concentrations found from these two studies. The concentrations are 2–15 times smaller than the concentrations found in Europe.

### 5.2. The Austrian active background study, Spring 1994

During the Austrian active sampling study, earlier mentioned in Section 2, ambient air was pumped into stainless-steel tubes filled with the adsorbent material Carboxen-569, by using AS3 automatic samplers. The sampling and analysis method is the same as for the Release-1 and Release-2 data, described in Section 2. The number of samples taken was 196 (Table 1). The measurements were performed 3 hourly for 3 days, and the samples analysed at the JRC. During the study, only PMCH was measured, together with a general concentration for PDCH (no separation of the isomers was done). Therefore, only the results for PMCH are given here. The mean value and standard deviation were  $5.84 \pm 1.34 \text{ fl}^{-1}$ , and the median value was  $5.7 \text{ fl}^{-1}$  (Table 9). The PMCH concentration found during the active ABS study was of the same order of magnitude as the values found during the CATS studies (Table 2).

### 5.3. The ISPRA studies, 1996

During the ETEX campaign, samplers of the type SAM1 and AS3 were used. These samplers were tested in two subsequent studies, where ambient air was sampled outside the laboratory at Ispra (Bersani, 1997).

During the first study, three samplers of the type SAM1 were used. Air was pumped onto the tubes during a period of 25 min per tube. The sampling lasted in total 3 h and 20 min. Two of the samplers had a drift in the flow rate of 1.36% during the total measurement period. The third sampler had a drift of 0.45%. When correcting the data for the drift in the flow rate, only minor changes in the medium tracer concentrations were found. For this short period of time, the changes in flow rates seemed of minor importance.

During the second study, three samplers of the type SAM1 and three samplers of the type AS3 were used. The tubes were exposed for 30 min each, and the total measurement time was 4 h. The first of the SAM1 samplers had a drift in the flow rate of 2.1% of the initial value. For the second sampler the flow rate drifted with 0.75% and for the third it drifted with 10.3% during the total measurement period. The Austrian samplers however had all a constant flow rate. This was due to the fact that the pump was controlled by a microprocessor. Corrections for decreasing flow rates gave only small changes in the mean concentrations.

The measured concentrations from the two ISPRA studies are given in Table 10. The concentrations in row one and three have been corrected by the changes in flow rate only. In row two and four, the concentrations are also referenced to ptPDCH. Equation (4) was used, assuming a constant ptPDCH value of  $5.4 \text{ fl}^{-1}$ . The studies showed background concentra-

tions comparable to the PFC background concentrations found in the CATS and ETEX studies, after referencing the data to ptPDCH. The concentrations of ocPDCH were however much higher in the ISPRA studies. The high values might have occurred because of possible leaks of PFCs from the Ispra laboratory. An intercomparison with the mean values found in Europe and in the U.S.A. is therefore not appropriate. The main finding was however that the flow rates of the automatic samplers of the type SAM1 may drift slightly during a measurement period of about 4 h. A control of drifts in the sampling instruments is therefore necessary, and has been taken into account for the ETEX measurements.

### 6. INTERCOMPARISON OF THE BACKGROUND STUDIES

As was shown in the four passive and two active sampling studies, the standard deviations were high before referencing the data to ptPDCH or by applying iterations. The standard deviations were influenced by a few high concentrations at some of the sampling stations (Figs 2 and 3). The stations that contained high concentrations varied from study to study, which means that continuous local sources of PFCs in Europe are unlikely. There was however one exception. The German station D13 showed elevated concentrations for several of the compounds in as much as 3 of the 5 studies (CATS-2, Release-1, and Release-2). The only compound that was elevated in all of the 3 studies was ocPDCH. No conclusions are however drawn concerning a possible local source at this location.

The different mean values, median values and standard deviations from the three CATS studies, the two ETEX studies and the US studies are plotted in Fig. 4. The results from the ISPRA and active ABS studies are not included because of the low number of

Table 10. Background concentrations from the ISPRA background studies in 1996. Mean values, median values (all in  $\text{fl}^{-1}$ ), and standard deviations  $\sigma$  mean (in percent of the mean value) are given

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
<b>ISPRA-1:</b>						
Corr. flowr.						
Mean	6.1	8.3	1.46	12.2	10.6	7.6
$\sigma/\text{mean}$	25%	95%	15%	21%	21%	14%
Corr. pt						
Mean	4.5	5.9	1.06	8.9	7.8	5.4
$\sigma/\text{mean}$	11%	76%	16%	6%	7%	-
<b>ISPRA-2</b>						
Corr. flowr.						
Mean	8.3	8.9	1.92	14.0	13.7	9.2
$\sigma/\text{mean}$	12%	12%	19%	10%	10%	13%
Corr. pt						
Mean	4.9	5.2	1.13	8.2	8.1	5.4
$\sigma/\text{mean}$	12%	11%	14%	8%	7%	-

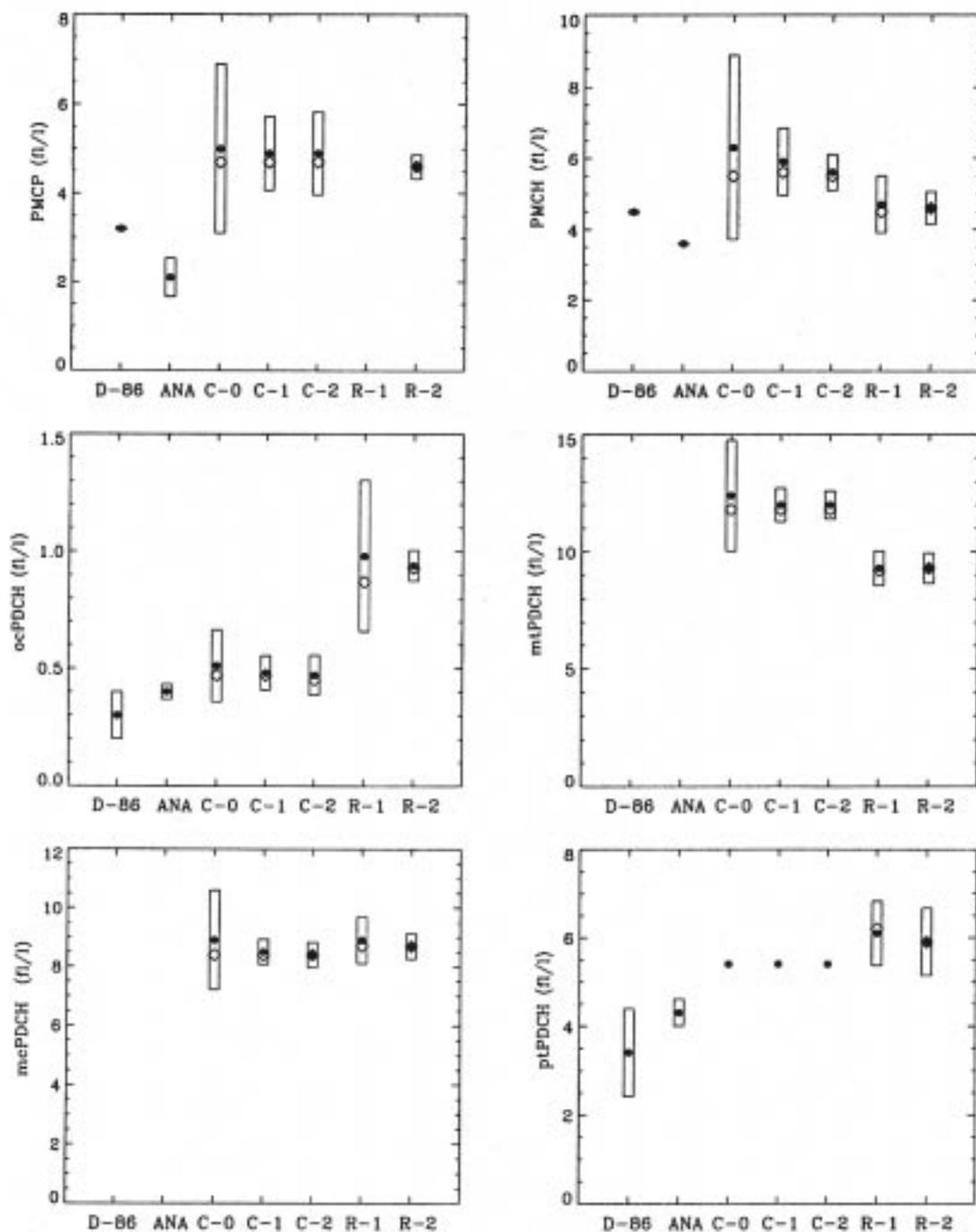


Fig. 4. Box plots comparing the mean values (●), median values (◇) and standard deviations for the American and European background studies for 6 PFC compounds.

measurements. All of the PFC compounds are compared. The concentrations from the CATS (Table 2) and the ETEX (Table 5) studies are corrected for pLPDCH. For the CATS studies, one iteration was performed, and for the ETEX studies, two iterations. As can be seen from this figure, an increasing trend in the background concentrations can be seen for the compounds ocPDCH and pLPDCH, where the

highest values are found during the two ETEX studies. Note however that for the CATS studies, the concentrations for pLPDCH were not measured, but predefined from earlier tracer studies performed by Dietz. For PMCP, PMCH, and mtPDCH on the other hand, the background concentrations are higher for the CATS than for the ETEX studies. For mePDCH, the concentrations found during the

Table 11. PFC background concentrations in Europe from the ETEX study in 1994. The concentrations, Conc. ( $\text{fl l}^{-1}$ ), are calculated as the mean of the median values from the Release-1 and Release-2 measurements. See text for details

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
Conc. ( $\text{fl l}^{-1}$ )	4.6	4.6	0.96	9.3	8.8	6.1
$\sigma$	0.3	0.8	0.33	0.8	0.8	0.8

studies are very similar, and the corresponding standard deviations are low for all except for CATS-0. Even though the CATS-2 study was performed after the Release-1 study and parallel to the Release-2 study, the mean PMCP concentrations were still not higher than during the other CATS studies.

The clear difference in concentrations between the CATS and ETEX studies seems to be connected to the sampling technique used. The background concentrations found during the passive and active studies are varying with 6–27% (ocPDCH is not considered), which still makes both sampling techniques suitable for use in tracer experiments, since variations in both space and time are influencing the data.

The concentrations found during Dietz' study in the 1990s (Table 2) are higher than those found in the 1980s (Table 8). Since the PFCs are inert, and their lifetimes are more than 1000 yr, this could indicate that there has been a rise in the global background concentrations for PFCs over the last ten years.

The majority of the concentrations from all background studies were found to be very close to their median value (50% cumulative value). The most representative level of the background concentrations is therefore set to the median value. It is far from the extreme low and the extreme high concentrations, and it turned out to be lower than the mean values found. We will now suggest a general background value for the six PFC compounds in Europe. When doing so, we have chosen to define the background values as the mean of the median values found from the two ETEX releases only (see Table 5). The reason why we do not include the results from the CATS studies is that the uncertainties in the definition of the actual air volume on the tubes are much higher than when using an active sampling technique. They further contain much fewer measurements than the ETEX data sets. The calculated background values are given in Table 11. The standard deviations are given as the maximum standard deviation found in the two studies. These values are suggested to be considered as the overall background concentration of the PFCs in Europe. The large standard deviation found for ocPDCH during Release-1 is assumed to occur due to uncertainties in the analysis, since the gas chromatograph was optimised to measure more precisely the concentrations of the released compounds. The set-up of the gas chromatographs and the definition of the calibration

curves were more carefully checked for Release-2. This is the reason why the standard deviation reported for ocPDCH probably is too biased by the Release-1 measurements, and it is therefore unrealistically high. The standard deviations are low enough for the PFCs to be suitable for use in tracer studies. This was shown in Nodop *et al.* (1998), where the arrival of the puff at the measurement stations was found to be clearly defined.

## 7. CONCLUSIONS

During the European Tracer Experiment (ETEX) in October and November 1994, two perfluorocarbon (PFC) tracers were released from Brittany, France, and their outspread was measured over Central and Northern Europe. The aim of this study was to detect the background concentrations of the two ETEX tracers together with four other PFC isomers in Europe. The concentrations were measured during four passive background studies, and were further also deduced from the measurements from the two ETEX tracer releases. The PFCs measured were perfluoromethylcyclohexane ( $\text{C}_7\text{F}_{14}$ , PMCH) (used during the first ETEX release), perfluoromethylcyclopentane ( $\text{C}_6\text{F}_{12}$ , PMCP) (used during the second ETEX release), and four isomers of perfluorodimethylcyclohexane ( $\text{C}_8\text{F}_{16}$ : ocPDCH, mtPDCH, mcPDCH, and ptPDCH).

The PFC concentrations measured during the six studies were of the same order of magnitude, but varied somewhat both in time and space. None of the stations showed concentrations more than two standard deviations above the mean value in all studies. In most cases, a significant correlation between the PFCs showed a high standard in the measuring and analysing procedure. These two results make the existence of continuous local source unlikely. The cases when the correlations were low are explained by the natural variation of the background concentrations, or probable sampling, contamination, and/or analysis problems. The European background concentrations of the measured PFC compounds are proposed to be equal to the mean of the median values found for the two ETEX releases. These concentrations are; PMCP:  $4.6 \pm 0.3 \text{ fl l}^{-1}$ , PMCH:  $4.6 \pm 0.8 \text{ fl l}^{-1}$ , ocPDCH:  $0.96 \pm 0.33 \text{ fl l}^{-1}$ , mtPDCH:  $9.3 \pm 0.8 \text{ fl l}^{-1}$ , mcPDCH:  $8.8 \pm 0.8 \text{ fl l}^{-1}$ ,

ptPDCH:  $6.1 \pm 0.8 \text{ fl}^{-1}$ . The standard deviations are representing the highest value from the two studies, except for PMCH. The variations of these background concentrations were found to be low enough for the PFCs to be suitable for use in tracer studies. The ocPDCH compound was found to be less correlated with the other PFCs, probably because of its lower concentrations in the atmosphere. The PFC background concentrations found during Dietz studies in the 1990s were higher than the concentrations found in 1986 and 1989. Since the PFCs are inert, and have a very long lifetime, this might indicate that the global background concentrations of PFCs in the world are increasing.

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