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THE FIELD CAMPAIGNS OF THE EUROPEAN TRACER EXPERIMENT (ETEX): OVERVIEW AND RESULTS

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Abstract—As part of the European Tracer Experiment (ETEX) two successful atmospheric experiments were carried out in October and November, 1994. Perfluorocarbon (PFC) tracers were released into the atmosphere in Monterfil, Brittany, and air samples were taken at 168 stations in 17 European countries for 72 h after the release. Upper air tracer measurements were made from three aircraft. During the first experiment a westerly air flow transported the tracer plume north-eastwards across Europe. During the second release the flow was eastwards. The results from the ground sampling network allowed the determination of the cloud evolution as far as Sweden, Poland and Bulgaria. This demonstrated that the PFT technique can be successfully applied in long-range tracer experiments up to 2000 km. Typical background concentrations of the tracer used are around $5-7 \text{ fl}^{-1}$ in ambient air. Concentrations in the plume ranged from 10 to above 200 fl^{-1} . The tracer release characteristics, the tracer concentrations at the ground and in upper air, the routine and additional meteorological observations at the ground level and in upper air, trajectories derived from constant-level balloons and the meteorological input fields for long-range transport models are assembled in the ETEX database. The ETEX database is accessible via the Internet. Here, an overview is given of the design of the experiment, the methods used and the data obtained. © 1998 Elsevier Science Ltd. All rights reserved.

Key word index: Perfluorocarbons, tracer experiment, long-range transport, model evaluation, database.

1. INTRODUCTION

The European Tracer Experiment (ETEX) was established to evaluate the validity of long-range transport models for real-time application in emergency management and to assemble a database which will allow the evaluation of long-range atmospheric dispersion models in general (Klug *et al.*, 1993; Girardi *et al.*, 1997). The objectives of ETEX were to (1) conduct a long-range atmospheric tracer experiment with controlled releases under well-defined conditions; (2) test the capabilities of organisations in Europe responsible for producing rapid forecasts of atmospheric dispersion to produce such forecasts in real time; and (3) evaluate the validity of their forecasts by comparison with the experimental data. This paper presents an overview of the design of the experiment, the methods used and the data obtained. Detailed discussion and analysis of the ETEX data set are given in subsequent papers in this Special Issue.

2. EXPERIMENTAL DESIGN

2.1. General considerations

The European Tracer Experiment was designed as a major field study to simulate long-range transport of a pollutant in

the atmosphere in western Europe. The ETEX experimental phase comprised two separate releases of perfluorocarbon tracer (PFT). Both utilised a total of 168 ground-based sampling sites in 17 European countries, together with three aircraft. Such a large logistical effort required considerable planning spanning two years, briefly summarised as

- definition of suitable meteorological conditions,
- choice of release site,
- choice of ground-level sampling sites,
- choice, construction, validation and deployment of samplers,
- preparation of sampling tubes,
- establishment and validation of analytical procedures,
- establishment of data management protocols,
- co-ordination of the release, sampling and modelling efforts,
- collation, dissemination and archiving of the resultant database.

2.2. Release site

The release location was selected with the aim of maximising the probability of identifying in advance meteorological situations which would ensure the dispersion of the tracer being within the area covered by the ground sampling stations. In order to conduct a tracer experiment over a distance

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of up to 2000 km in Europe, a release site in the western part of Europe was required, with a release occurring in meteorological conditions with a prevailing westerly or southwesterly air flow. The release site used was approximately 35 km west of Rennes, at Monterfil, in Brittany, France. The Monterfil site is the highest flat point in the area, with no obstacles in the vicinity. It is located at $2^{\circ} 00'30''W$ and $48^{\circ} 03'30''N$, 90 m above sea level. The tracer was released from a point 8 m above ground level. The first release occurred on 23 October 1994 and the second on 14 November 1994.

2.3. Tracer compounds

Perfluorocarbon (PFC) compounds are suitable tracer substances for experiments over long distances (Dietz, 1986) and the techniques for their release and determination have been improved by Dietz at Brookhaven National Laboratory (BNL), New York. They were first mentioned by Lovelock and Ferber (1982) and since been used in various experimental studies (Dietz and Cote, 1982; Draxler *et al.*, 1991; Ambrosetti *et al.*, 1998). They are non-toxic, non-depositing, non-water-soluble, chemically inert and environmentally safe. Their vapour pressures are low enough to allow them to be readily sampled onto solid adsorbents. Their industrial use is very limited resulting in low background concentrations in the atmosphere with very little temporal or spatial variation. At ambient pressure and temperature the PFTs are odourless, clear liquids. They were released into the atmosphere by spraying the liquid into a hot air stream, causing it to evaporate. A description of the release equipment is given elsewhere (van Velzen *et al.*, 1997). Two perfluoroalkylcycloalkanes were used as tracers in ETEX. During the first experiment perfluoromethylcyclohexane (PMCH), C_7F_{14} , was released. In the second perfluoromethylcyclopentane (PMCP), C_6F_{12} , was used to avoid cross contamination. Both compounds were manufactured by BNFL Fluorochemicals Ltd, Preston, (U.K.). The purity of the substances is about 98% for PMCP and 99% for PMCH. Some properties of these compounds are given in Table 1.

2.4. Ground-level tracer sampling

To determine the concentration of PFTs in the atmosphere, air samples were taken for subsequent laboratory analysis. Ambient air was passed through stainless-steel tubes, 8 cm long and 6 mm OD, packed in the mid-section with 150 mg of Carboxen-569 (Supelco). The carbonaceous adsorbent was held in place by stainless-steel screens. Carboxen is very hydrophobic with a high capacity for organic compounds. The tubes were manufactured, individually numbered and packed at the JRC Environment Institute, Ispra.

A total of 168 ground-level sampling stations in Europe were used. These stations are operated and owned by the various national Meteorological Services and all linked into the WMO network. The location of the sampling stations is shown in Fig. 1 and listed in Table 2. Each sampling site was equipped with a sequential air sampler. Three different designs were used: the Seibersdorf AS3 (in Austria and the eastern European countries), the Tecora (in Germany) and the JRC-designed and built SAM1 (in all other countries). The sample flow rate was regulated using a critical orifice, with each sampler being calibrated both before and after the experiment. Flow rates of 0.2–0.5 l per minute were used, resulting in total sample volumes of 27–90 l for sampling periods of 3 h. The AS3 samplers were equipped with mass flow controllers and hence allowed more accurate estimation of the total sample volume than for the other instruments. At each site 24 consecutive samples were collected, with the initiation of sampling progressively delayed with distance from the release site, according to the expected arrival time of the tracer plume. Each set of sample tubes contained laboratory blanks and field blanks to account for any passive uptake of tracer during the 72 h total sampling period.

2.5. Aircraft-based sampling

Samples were also collected from three aircraft (the UK-MRF Hercules C130, the Swiss HB-LDT Gulf Stream and the German DO 228) during one day on each of the two experiments. All three aircraft were equipped with Brookhaven Atmospheric Tracer Samplers and used a sampling period of 2 min. Samples were subsequently analysed at Brookhaven National Laboratory. In parallel, the C130 took bag samples, later analysed at the Environment Institute, Ispra, which used sampling times of 30 s, giving a horizontal resolution of around 3 km. In addition the C130 was equipped with Brookhaven's dual trap analyser that allowed determination of tracer concentrations in real time during the flight. This allowed location of the plume about 500 km from the release site, with subsequent direction of the other two aircraft into the plume at downstream distances of 700 and 800 km from the release site.

2.6. Chemical analysis

The chemical analysis of the approximately 9000 samples collected was performed at the Environment Institute, Ispra and took 2 yr. No loss of PFCs could be observed from control samples stored over this period and longer. The samples were thermally desorbed and analysed by gas chromatography (GC) with electron capture detection (ECD). As well as PMCH and PMCP, released during the experiment, the method also allows the determination of four isomers of perfluorodimethylcyclohexane, oc, mt, mc and

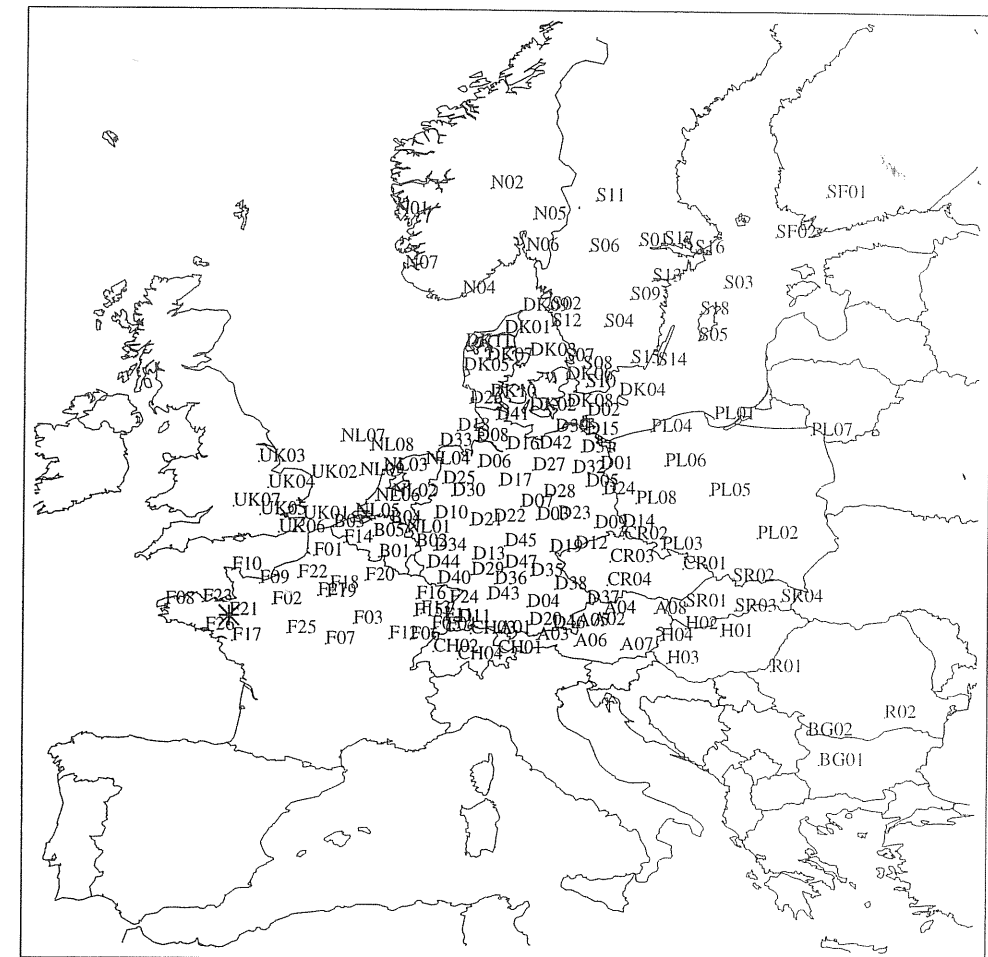


Fig. 1. Map of the ETEX ground-level stations.

ptPDCH in a single analysis. Because these compounds were not released, their background concentrations at each site were used for quality control purposes.

Prior to analysis all samples were dried for 16 h in an oven of $48^{\circ}C$ over Silica gel. No tracer was lost during this process. From the stainless-steel sampling tubes, the sample was thermally desorbed at $340^{\circ}C$ in a DANI 3350 sequential tube desorber into a stream of nitrogen at a flow rate of 25 ml min^{-1} with a cycle time of 7 min. The sample was passed via a heated transfer line at $150^{\circ}C$ to a refocussing trap into the GC system, a Dual Trap Analyser specially built for the detection of perfluorocarbons by Booker, Texas. The trap was rapidly heated to $300^{\circ}C$, injecting the contents of the trap onto the precolumn. The precolumn was a Supelco $45 \text{ cm} \times 3 \text{ mm OD}$, stainless steel packed with 0.1% SP1000 on 80/100 mesh Carbopack C (Supelco). It was held at $160^{\circ}C$ and performed preliminary separation of the perfluorocarbons. Lighter and heavier compounds than the PFCs of interest were eliminated by time set valve switching.

The eluting compounds then passed through a catalytic reactor (SS tube 2 mm ID by 3 mm OD, packed with 5% Palladium on 60/80 mesh Chromosorb P-AW). Here, interfering compounds such as chlorofluorocarbons were destroyed and any remaining oxygen converted to water vapour. A Nafion drier (a permeation drier made from 0.75 mm ID Nafion tubing) was then used to remove any remaining water vapour. The partially separated and now cleaned elutents then passed into the main column (a Booker

$2.25 \text{ m} \times 3 \text{ mm OD}$ stainless-steel column packed with 0.1% SP1000 on 80/100 mesh Carbopack C (Supelco) at $160^{\circ}C$ for final separation.

The separated perfluorocarbons were then finally detected using an electron capture detector at $240^{\circ}C$. This was a Valco design model 140BN with 5 mc ^{63}Ni source. The resultant chromatograms and integrated data were processed by HP Chemstation software.

Gas standards for calibration of the GC were prepared commercially by Airco Industrial Gases (Riverton, NJ U.S.A.), using Brookhaven National Laboratory primary standards. A diluted sample of the standards containing mixtures of PFCs at ppb concentrations was injected onto a normal sampling tube and analysed as described above. The amount of standard, the reproducibility and the estimated quantification limit are given in Table 3.

Typical chromatograms produced by this system are shown in Fig. 2. The peak order is PMCP, PMCH and the four isomers of PDCH. As can be seen, good separation of all the compounds of interest was achieved, especially the baseline separation of the oc and ptPDCH. The time for analysis of one sample was 17 min. Figure 2a shows a standard, Fig. 2b a typical 36 l air sample taken in Europe showing background concentrations and Fig. 2c an elevated peak of PMCP from the tracer released. The response of the ECD was linear up to 1000 fl for PMCH and PMCP. To be able to detect the majority of the lower concentrations with good precision, very high concentrations originating from the release were out of the linear range of the detector.

Table 1. Selected relevant properties of PMCH and PMCP

Physical properties	PMCP	PMCH	PDCH	Units
Boiling range	48	76	102	$^{\circ}C$
Pour point	-70	-30	-70	$^{\circ}C$
Molecular weight	300	350	400	g mol^{-1}
Vapour pressure	368	141	48	mbar
Density	1.707	1.788	1.828	kg l^{-1}
Viscosity	1.049	1.561	1.919	mPas
Surface tension	12.6	15.4	16.6	mN m^{-1}
Specific heat	0.878	0.963	0.963	$\text{kJ kg}^{-1}^{\circ}C$
Expansion coefficient	0.00167	0.00139	0.00104	$^{\circ}C^{-1}$ at $0^{\circ}C$
Conversion factors at $20^{\circ}C$ 1013 hPa	PMCP		PMCH	
	$1000 \text{ fl l}^{-1} = 12.48 \text{ ng m}^{-3}$		$1000 \text{ fl l}^{-1} = 14.56 \text{ ng m}^{-3}$	
	$1 \text{ ng m}^{-3} = 80 \text{ fl l}^{-1}$		$1 \text{ ng m}^{-3} = 69 \text{ fl l}^{-1}$	

Table 2. List of stations used for tracer sampling

Station code	Station name	Lat. ° "	Long. ° "	Alt. m	WMO Code	Remarks
A01	Bregenz	47 30	09 44	424	11101	
A02	Feuerkogel	47 49	13 44	1618	11155	
A03	Innsbruck Airport	47 16	11 21	578	11120	
A04	Linz	48 14	14 11	297	11011	
A05	Salzburg	47 47	13 03	420	11150	
A06	Sonnblick	47 03	12 57	3105	11146	
A07	Preitenegg	46 56	14 55	1055	11214	
A08	Wien Hohe Warte	48 14	16 21	202	11035	
B01	Dourbes	50 06	04 36	225	06499*	
B02	Elsenborn	50 28	06 11	564	06496	
B03	Koksijde	51 05	02 39	4	06400	
B04	Mol	51 13	05 05	26	06498*	
B05	Uccle	50 48	04 21	104	06447	
BG01	Sofia	42 39	23 23	587	15614	
BG02	Vidin	43 49	22 53	31	15502	
CH01	Arosa	46 47	09 41	1821	06785	
CH02	Payerne	46 49	06 57	490	06610	
CH03	Zürich - Kloten	47 29	08 32	436	06670	
CH04	Jungfrauoch	46 33	07 59	3576	06730	
CR01	Cervena	49 46	17 33	750	11766	
CR02	Liberec	50 46	15 01	400	11603	
CR03	Praha Lidus	50 00	14 27	303	11520	
CR04	Temelin	49 12	14 20	505	11538	
D01	Angermünde	53 02	14 00	55	10291	
D02	Arkona	54 41	13 26	42	10091	
D03	Artern	51 23	11 18	166	10460	
D04	Augsburg	48 26	10 56	463	10852	
D05	Berlin Tempelhof	52 28	13 24	49	10348	
D06	Bremen	53 03	08 48	5	10224	
D07	Brocken	51 48	10 37	1153	10543	
D08	Cuxhaven	53 52	08 42	12	10131	
D09	Dresden-Klotzsche	51 08	13 47	227	10488	
D10	Essen	51 24	06 58	161	10410	
D11	Feldberg	47 53	08 00	1493	10908	
D12	Fichtelberg	50 26	12 57	1214	10578	
D13	Offenbach	50 07	08 44	98	10640	
D14	Görlitz	51 10	14 57	238	10499	
D15	Greifswald	54 06	13 24	6	10184	
D16	Hamburg-Fuhlsbüttel	53 38	10 00	16	10147	
D17	Hannover	52 28	09 42	54	10338	
D18	Helgoland	54 11	07 54	8	10015	
D19	Hof	50 19	11 53	568	10685	
D20	Hohenpeissenberg	47 48	11 01	986	10962	
D21	Kahler Asten	51 11	08 29	859	10427	
D22	Kassel	51 18	09 27	233	10438	
D23	Leipzig-Schkeuditz	51 25	12 14	141	10469	
D24	Lindenberg	52 13	14 07	112	10393	
D25	Lingen	52 31	07 18	26	10305	
D26	List/Sylt	55 01	08 25	29	10020	
D27	Lüchow	52 58	11 08	18	10253	
D28	Magdeburg	52 07	11 35	84	10361	
D29	Mannheim	49 31	08 33	100	10729	
D30	Münster/Osnabrück	52 08	07 42	53	10315	
D31	Neubrandenburg	53 33	13 12	79	10280	
D32	Neuruppin	52 54	12 49	40	10270	
D33	Norderney	53 43	07 09	16	10113	
D34	Nürburg	50 20	06 57	629	10510	
D35	Nürnberg	49 30	11 05	312	10763	
D36	Ohringen	49 13	09 31	277	10742	
D37	Passau	48 35	13 28	408	10893	
D38	Regensburg	49 03	12 06	371	10776	
D39	Rostock-Warnemünde	54 11	12 05	10	10170	
D40	Saarbrücken	49 13	07 07	320	10708	
D41	Schleswig	54 32	09 33	48	10035	
D42	Schwerin	53 39	11 23	68	10162	
D43	Stuttgart-Echterdingen	48 41	09 13	419	10738	
D44	Trier-Petrisberg	49 45	06 40	273	10609	

(continued opposite)

Table 2. (Continued)

Station code	Station name	Lat. ° "	Long. ° "	Alt. m	WMO Code	Remarks
D45	Wasserkuppe	50 30	09 57	925	10544	
D46	Wendelstein	47 42	12 01	1835	10980	
D47	Würzburg	49 46	09 58	272	10655	
DK01	Aalborg Airport	57 06	09 52	3	06030	
DK02	Albuen	54 50	10 58	2	06142	
DK03	Fornaes	56 27	10 58	8	06071	
DK04	Hammer Odde	55 18	14 47	11	06193	
DK05	Hvide Sande	56 00	08 08	3	06058	
DK06	Jaegersborg	55 46	12 32	40	06181	
DK07	Karup Airport	56 18	09 07	51	06060	
DK08	Moen	54 57	12 33	15	06179	
DK09	Skagen	57 44	10 38	3	06041	
DK10	Skrydstrup Airport	55 14	09 16	40	06110	
DK11	Thyboroen	56 42	08 13	3	06052	
F01	Abbeville	50 08	01 50	77	07005	
F02	Alençon	48 27	00 06	141	07139	
F03	Auxerre	47 48	03 33	212	07265	
F04	Bale - Mulhouse	47 36	07 31	271	07299	
F05	Belfort	47 38	06 52	422	07295	
F06	Besançon	47 15	05 59	309	07288	
F07	Bourges	47 04	02 22	166	07255	
F08	Brest	48 27	-04 25	103	07110	
F09	Caen	49 11	-00 27	67	07027	
F10	Cherbourg (Valognes)	49 31	-01 30	61	07039	
F11	Colmar	47 55	07 24	220	07197	
F12	Dijon	47 16	05 05	227	07280	
F13	Epinal	48 10	06 26	340	07173	
F14	Lille	50 34	03 06	52	07015	
F15	Metz/Dma	49 05	06 08	191	07090	
F16	Nancy Essey	48 41	06 13	217	07180	
F17	Nantes	47 10	-01 36	27	07222	
F18	Paris Charles de Gaulle	49 01	02 32	109	07157	
F19	Paris Orly	48 44	02 24	96	07149	
F20	Reims	49 18	04 02	99	07070	
F21	Rennes	48 04	-01 44	37	07130	
F22	Rouen	49 23	01 11	157	07037	
F23	St. Brieuc	48 32	-02 51	136	07120	
F24	Strasbourg	48 33	07 38	154	07190	
F25	Tours	47 27	00 43	112	07240	
F26	Vannes	47 33	-02 45	11	07210	
F27	Trappes	48 46	02 01	168	07145	
H01	Budapest/Lorinc	47 26	19 11	138	12843	
H02	Gyor	47 42	17 41	116	12822	
H03	Nagykanizsa	46 27	16 54	140	12925	
H04	Szombathely	47 16	16 38	220	12812	
N01	Bergen/Flesland	60 18	05 13	50	01311	
N02	Fagernes	60 59	09 14	365	01367	
N04	Kristiansand/Kjevik	58 12	08 05	17	01452	
N05	Oslo/Gardermoen	60 12	11 05	204	01384	
N06	Rygge	59 23	10 47	53	01494	
N07	Stavanger/Sola	58 53	05 38	9	01415	
NL01	Beek/Z.Limburg	50 55	05 47	126	06380	
NL02	De Bilt	52 06	05 11	2	06260	
NL03	De Kooy	52 55	04 47	1	06235	
NL04	Eelde	53 08	06 35	4	06280	
NL05	Vlissingen	51 27	03 36	8	06310	
NL06	Zestienhoven	51 57	04 27	-5	06344	
NL07	J/6-A	53 49	02 57	0	62414	Oil platform
NL08	L7Q	53 33	04 12	0	62405	Oil platform
NL09	P6A	52 46	03 46	0	62409	Gas platform
PL01	Hel	54 36	18 49	1	12135	
PL02	Kielce	50 49	20 42	260	12570	
PL03	Ktodzko	50 26	16 39	316	12520	
PL04	Koszalin	54 12	16 09	145	12105	
PL05	Kolo	52 12	18 40	116	12345	
PL06	Pila	53 08	16 45	72	12230	
PL07	Suwalki	54 08	22 57	184	12195	

(continued overleaf)

Table 2. (Continued)

Station code	Station name	Lat. ° "	Long. ° "	Alt. m	WMO Code	Remarks
PL08	Zielona Gora	51 56	15 32	192	12400	
R01	Arad	46 10	21 19	108	15200	
R02	Bucuresti	44 30	26 08	90	15420	
S01	Fellingsbro-Finnaaker	59 32	15 35	51	02439	
S02	Göteborg-Säve	57 47	11 53	20	02512	
S03	Gotska Sandön	58 24	19 12	12	02584	
S04	Hagshult	57 18	14 08	169	02556	
S05	Hoburgen	56 55	18 09	38	02680	
S06	Karlstad	59 22	13 28	46	02418	
S07	Kullen	56 18	12 27	72	02606	
S08	Ljungbyhed	56 05	13 14	43	02630	
S09	Malexander	58 04	15 14	195	02564	
S10	Malmö-Sturup	55 33	13 22	72	02636	
S11	Malung	60 41	13 43	308	02410	
S12	Nidingen	57 18	11 54	4	02518	
S13	Norrköping	58 35	16 09	33	02099*	SMHI station
S14	Ölands södra udde	56 12	16 24	3	02676	
S15	Ronneby	56 16	15 17	58	02664	
S16	Stockholm-Bromma	59 21	17 57	15	02464	
S17	Västerås-Hässlö	59 35	16 38	6	02446	
S18	Visby	57 40	18 12	42	02590	
SF01	Jokioinen	60 49	23 30	104	02963	
SF02	Utö	59 47	21 23	9	02981	
SR01	Jaslovske Bohunice	48 29	17 40	176	11819	
SR02	Liesek	49 22	19 40	692	11918	
SR03	Lucenec	48 20	19 46	219	11927	
SR04	Milhostov	48 40	21 44	104	11978	
UK01	Manston	51 21	01 21	44	03797	
UK02	Hemsby	52 41	01 41	13	03496	
UK03	Waddington	53 10	-00 31	70	03377	
UK04	Wyton	52 21	-00 07	41	03566	
UK05	Heathrow Airport	51 29	-00 27	25	03772	
UK06	Herstmonceux	50 54	00 20	52	03882	
UK07	Brize Norton	51 45	-01 35	81	03649	

*no WMO code.

Table 3. Amount of standard, reproducibility of standards given as relative standard deviation and the estimated quantification limit (EQL)

PFC	Amount of standard in fl	reproducibility of standards in %	EQL in fl
PMCP	810	0.4	2
PMCH	790	0.5	3
oc-PDCH	26	1.4	12
mt-PDCH	390	1.1	9
mc-PDCH	370	1.4	9
pt-PDCH	41	1.5	15

The setup described here was used for the second tracer release. To cut down on the analysis time, PMCP was not determined in the first tracer release and the GC setting modified accordingly.

2.7. Background concentrations of PFCs

Perfluorocarbons are present in the atmosphere at very low concentrations. In a tracer experiment, only the excess tracer concentration due to the released substance is of interest. Therefore, the spatial and temporal variation of the ambient PFC concentration had to be studied prior to the

ETEX experiment. Altogether four studies were carried out in 1994 to determine the ambient levels of the PFC tracers in Europe (Piringer *et al.*, 1997; Straume *et al.*, 1998). These data were needed to derive the excess concentration of the released tracer, over and above its background concentration. In Europe average background concentrations of 4.5 fl l^{-1} were found for PMCP and 4.6 fl l^{-1} for PMCH.

2.8. Quality assurance and quality control

Quality assurance for such a large and complex experiment as ETEX is essential although very challenging. A number of measures were undertaken to produce a consistent set of results. The procedures of sample handling, analysis and methodology for calculating tracer concentrations due to the releases from a crucial part in the determination of the uncertainty in the data. In the following, the most crucial steps in these procedures are described in more detail.

All steps in the handling of the sampling tubes from preparation to analysis were carefully monitored. Great care was taken to ensure that the location and times of individual samples could be assigned correctly. Sample preparation took place in clean air and all tubes were pre-cleaned by flushing with nitrogen at 340°C for 12 h before being individually sealed at both ends. The tube sets for each release were separately sealed in polyethylene bags and shipped to the sites only shortly before the experiment. To monitor any contamination or passive uptake of tracer a laboratory blank was distributed together with field blanks to each ground-level sampling site. Of the 168 blanks only two

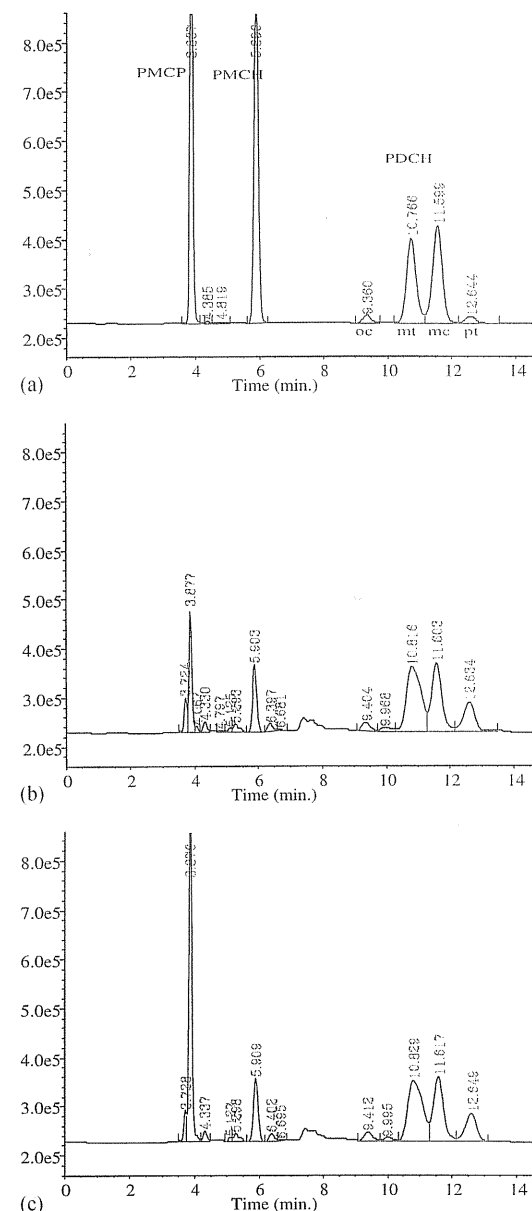


Fig. 2. (a) Chromatogramme of a standard, PMCP, PMCH, oc, mt, mc, ptPDCH, (b) Chromatogramme of a 36 l sample of ambient air, (c) Chromatogramme of a 36 l sample air containing PMCP tracer.

samples showed slight contamination of the PFTs used in the releases.

The field blanks were distributed to account for any passive uptake of tracer during exposure of the sampling tubes to ambient air. They were attached to the side of the air sampler with the bottom cap removed for the entire sampling period of 72 h to act as passive devices. Data obtained from the Capillary Absorption Tube Sampler (CATS), which were used in the previous background studies (Straume *et al.*, 1998), suggest that diffusion uptake amounted to approximately an equivalent sampling volume of 270 ml per day. Calculating the passive uptake of tracer onto the field blanks with a 72 h exposure time at ambient concentrations suggests that about 5 fl of PMCH and PMCP would have been adsorbed passively. As can be seen from Fig. 3 the PMCP

amounts of the field blanks collected during the second release range between 5 and 10 fl. Only at stations with very high concentrations of tracers the uptake could accumulate to 100 fl over the entire sample exposure time. This was the case for the French stations being close to the release point. From these values we can estimate the effect of the passive uptake on the PFT concentrations coming from the active sampling. For a total sample volume of 36 l (90 l for the Tecora sampler) the passive uptake assuming 100 fl l^{-1} in the tracer cloud could lead to an apparent increase in concentration of 1.7 fl l^{-1} (0.7 fl l^{-1}) of PFT considered. For background levels the passive uptake of tracer by the sampling tubes with a value of 0.03 fl l^{-1} (0.01 fl l^{-1}) is negligible. As a result, it was not necessary to make any corrections for passive uptake. Only for one site in France during the second release, a noticeable passive uptake was found.

The concentrations of the gas standards used for calibration had a relative accuracy for each PFT of $\pm 3-4\%$ (Dietz, personal communication). A good agreement was found between PFC standards in use at BNL and dynamic mixtures prepared from permeation tubes. A laboratory intercomparison study conducted with NERI, Risø, showed an agreement of 20% (Ellermann *et al.*, 1998).

Data recovery of the ETEX experiment was very good. Of the total samples distributed to the ground-level network (4032) 3334 were analysed from the first experiment and 2479 from the second experiment. Only 4% of samples were lost in analysis when interfering compounds made tracer quantification impossible. Some samples were lost in shipment and others were not analysed, because the tracer had not reached the area. Very low peak heights for some samples implied problems with sample volume collection or other factors and were discounted.

For quality control reasons, at ten measuring sites different samplers were co-located and duplicate sampling was performed. As co-located sampler the Brookhaven Atmospheric Tracer Sampler (BATS) was used and the analysis performed at BNL. Unfortunately, many of these data had to be discarded because sampling protocols were inconsistent regarding sampling times. At the French station Trappes (F27) a valid comparison could be made from 21 data points. The sampling took place in background concentrations and gave for the BATS sampler a mean PMCP concentration and standard deviation of $4.7 \pm 0.8 \text{ fl l}^{-1}$ and for the SAM1 sampler $4.5 \pm 0.8 \text{ fl l}^{-1}$. Subsequently, a new co-location study was conducted at Ispra in 1996 (Bersani and Nodop, 1997), with three samplers each of the type SAM1 and AS3. The results are summarised in Table 4 and show an excellent agreement of 3-7% for the PFCs of interest.

Methodology for calculating the tracer concentrations resulting from the actual release involved many steps. The data from the chemical analysis had to be corrected for the reduced ECD response at high concentrations (loss of linearity). The next corrections were made for the effectively sampled air volume, determined from the flow rate checks after the samplers returned from the experiment and the sampling protocols.

PFT background concentrations were determined in separate studies (Straume *et al.*, 1998) for the whole of Europe. However, these values could not be used in calculating the excess PMCH and PMCP concentrations at each site due to the release. The spatial and temporal variation of the tracer concentration in ambient air during one year and in the whole of Europe, although small, was large compared to the variation of tracer measured during the 72 h experimental period (cf. also Fig 6 and 8). Instead the background concentration was determined individually for each site by taking an average of the concentrations measured prior to the arrival of the tracer plume. Usually 3-5 samples were available for calculation the station background. Examples are shown in Figs 6 and 8. This value plus one standard deviation of the variation of the background concentration (on average 5%) was subtracted from the measured total

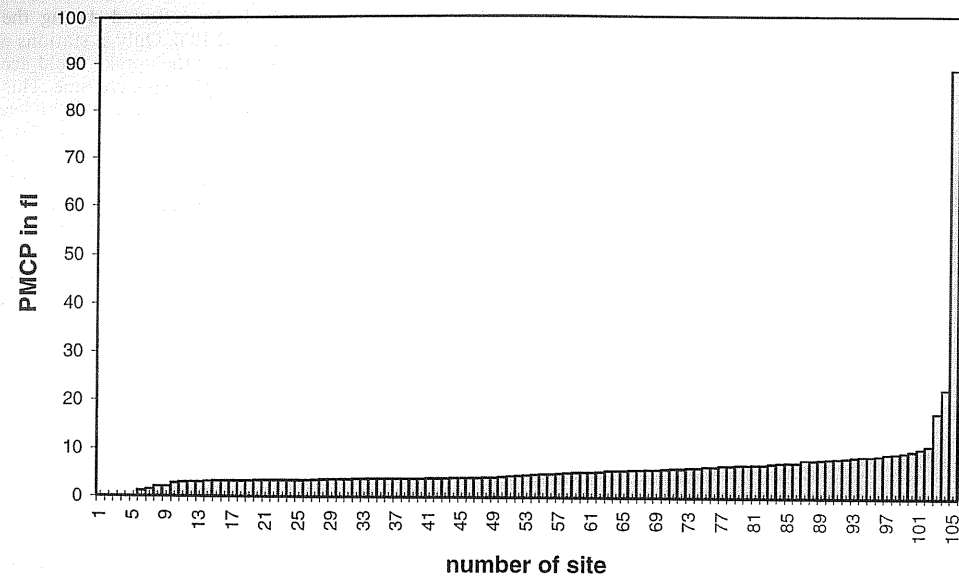


Fig. 3. PMCP levels in field blanks from the second release.

Table 4. PFT concentrations in fl l^{-1} of six collocated samplers at Ispra (number of samples 48)

	PMCP	PMCH	ocPDCH	mtPDCH	mcPDCH	ptPDCH
Mean	8.17	8.75	1.90	13.81	13.56	9.13
Std	0.60	0.52	0.27	0.37	0.42	0.34
Std in %	7.4	6.0	14.2	2.7	3.1	3.7

concentration for each site. These excess concentrations were reported as tracer concentrations and used in the comparison of the experimental data and the calculated concentrations by the various long-range transport models. When this subtraction gave a value of zero or less the data was reported as no tracer originating from the release detected.

Prior to the subtraction of the background concentrations all data was referenced to the ptPDCH background concentration to arrive at a coherent and internally consistent data set. This method was suggested by Dietz (1986) and has been applied to most PFC experimental data in the US (e.g. Draxler *et al.*, 1991). It is a common technique to account for the uncertainties in the sample volume determination. The atmospheric background concentration of ptPDCH is very stable, and hence all stations should measure the same concentration level. Deviations from it could be caused by flow rate variations not being accounted for. Also the concentrations of the other tracers not being released and their ratios to each other represents valuable information to assess the quality of the sample. Therefore, using the ptPDCH background concentration as a reference reduces a lot of variation in the data. An example of the effect of this referencing can be seen in Fig. 4. At D15 (Greifswald, Germany) and CR02 (Liberec, Czech Republic) the 24 samples taken show a very large and random variation of all the PFC compounds. After the normalisation by ptPDCH all other PFT compounds show valid background levels and the elevated PMCP concentration at CR02 can clearly be distinguished as excess tracer originating from the release. For the data of the first tracer experiment a value of 6.24 fl l^{-1} and for the second 5.6 fl l^{-1} was used to ensure comparable data for

PMCP and PMCH. The difference originates from the different GC set-up for the two experiments.

The quantification of the uncertainty of the data is difficult. It depends on the uncertainty in the background level of the PFT used as tracer; the precision and accuracy of the analytical system and the uncertainty in the determination of the exact sample volume (either by flow rates or ptPDCH reference). The data from the "best" sites suggest that the variation of the background levels for all PFC compounds is as low as 2% within the 72 h total sampling period. For most of the sites it is between 5 and 10% for PMCP and PMCH. Co-located sampling showed a precision of 3–7%. The analytical precision is very good for low concentrations of the used tracers (1–2%). But for the very high concentrations measured close to the release site, the uncertainty is very large. Maximum concentrations reported can be by a factor of 2–5 higher, in single cases even more.

3. RESULTS AND DISCUSSION

3.1. The first tracer release

The first tracer release started on 23 October 1994, 16:00 UTC, and ended on 24 October 1994, 3:50 UTC. During these 12 h a total of 340 kg of PMCH were emitted, resulting in an average release rate of 7.95 g s^{-1} . The air stream ($67 \text{ m}^3 \text{ h}^{-1}$) at the top of the chimney (8 m above ground) had an average temperature of 84°C and a velocity of about 45 m s^{-1} .

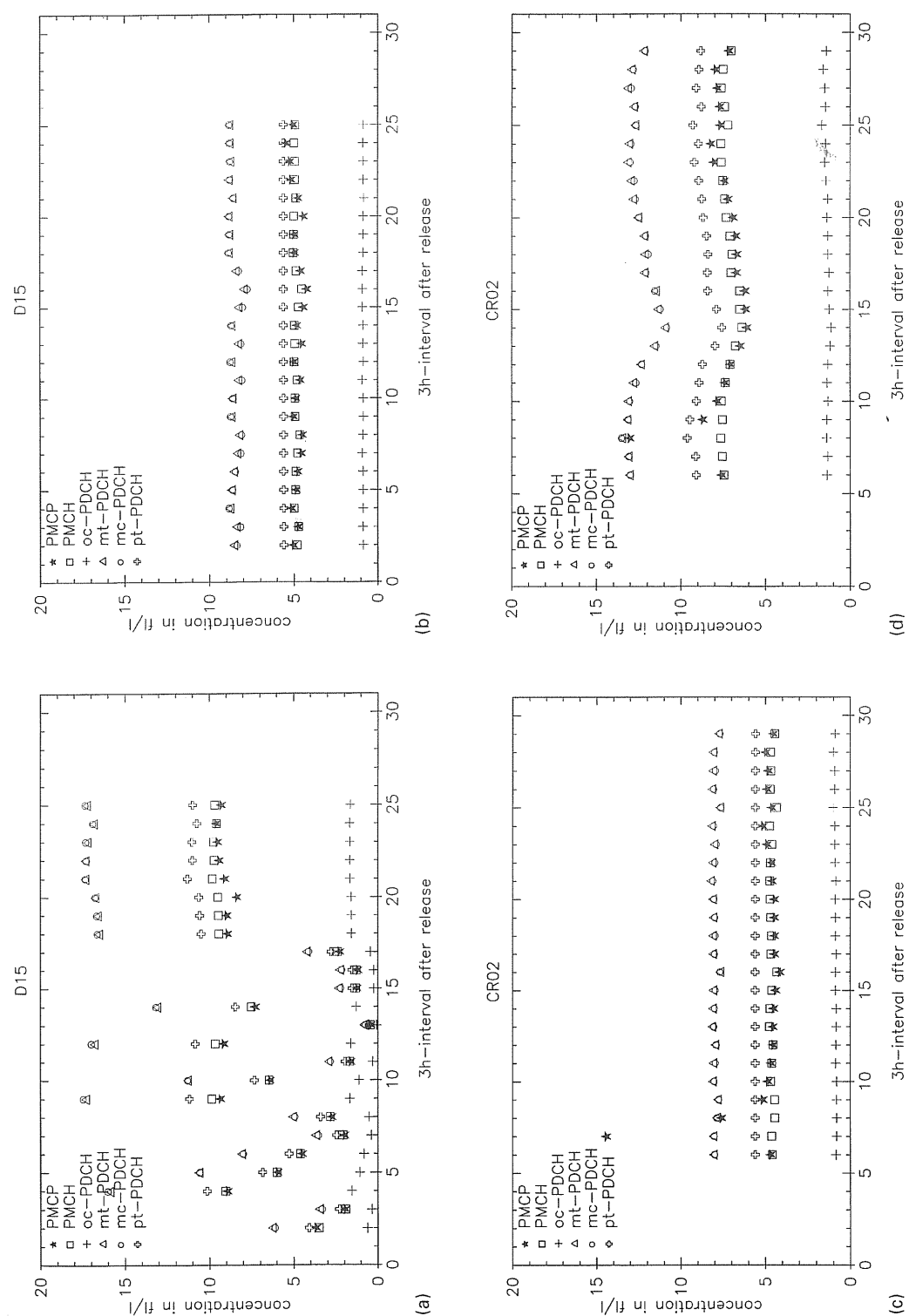


Fig. 4. PFT concentrations at D15 (Greifswald, Germany) and CR02 (Liberec, Czech Republic) before (left) and after (right) the referencing the data to ptPDCH.

The weather situation on 23 October showed a deep low, with its centre east of Scotland, moving north. The cold front had passed the day before and in western Europe southwesterly air flow was prevailing. In the release area the air flow was from the southwest. In the surface layer the wind velocity was 6 m s^{-1} and the temperature was 11°C . The air was unstable and no clear mixed layer height was observed.

From a total of over 4000 samples taken at ground level, 1300 values (32%) showed tracer plume concentrations clearly above background with concentrations in the range 10 to $> 200 \text{ fl}^{-1}$. A total of 1900 (46%) samples gave tracer concentrations within the background noise level and were reported as zero concentrations. Due to quality control procedures, about 180 (4%) measurement values were discarded. Data are available at each site at 3 h intervals for 96 h from the time of release. Figure 5 shows the location of the PMCH tracer 12, 36 and 60 h after the start of the release. The tracer plume traverses Europe in a northeastern direction. After 12 h PMCH could be detected in France and in a few east German sites. After another 24 h later the tracer plume had reached the west coast of Sweden in the north and stretched south to Hungary. The tracer plume covered at this time more or less the entire station network. At 60 h after release, the tracer plume stretched in a broad band from Norway south to Bulgaria and most of the central European stations no longer showed elevated levels. Only a few sites still saw some PMCH from the release.

By looking at the time series of individual stations, the shape of the plume at various distances from the release point can be seen. The PFC concentration profiles during the first release clearly show a decrease in the maximum concentration and an increase in the plume width with distance from the release point. The plume shapes are more or less regular with only one peak. Close to the release site, in France, the concentrations of PMCH measured are well above 100 fl^{-1} at many stations. At Rennes (F21), the site only 30 km away from the release point, more than 850 fl^{-1} was detected. In central Europe tracer concentrations of $8\text{--}50 \text{ fl}^{-1}$ above background were found. At the most eastern stations tracer was detected at only a few fl^{-1} above the ambient levels. In Fig. 6 the total PMCH concentrations, i.e. the plume concentrations including the background concentrations, are represented. At the Austrian site A1 all data show the very stable background value of $4.3 \pm 0.1 \text{ fl}^{-1}$ PMCH, clearly showing that the tracer plume has not reached this site at this time. At the German site D9 the tracer arrived 30 h after the release and the plume traverse lasted 27 h. Further downwind, at the Norwegian site N1 the tracer plume arrived after 60 h and the maximum concentrations were about 20 fl^{-1} , or only half as much as at D9. The end of the plume traverse could not be detected as sampling stopped after 87 h. In

ETEX First Release on 23 October 1994

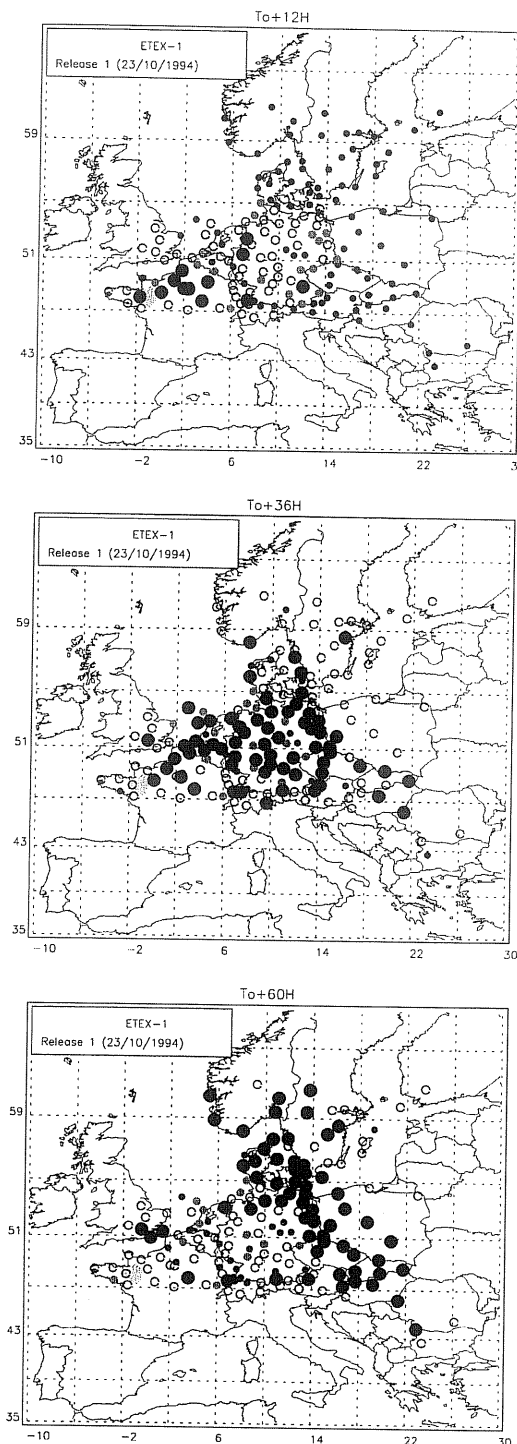


Fig. 5. PMCH detected at ground-level stations in Europe, 12, 36 and 60 h after the first release. Tracer found (●), no tracer found (○), location only (◐), tracer found but uncertain (◑).

Bulgaria, at BG2, more than 2000 km away from the release site, the tracer plume added only 2 fl^{-1} to the background level.

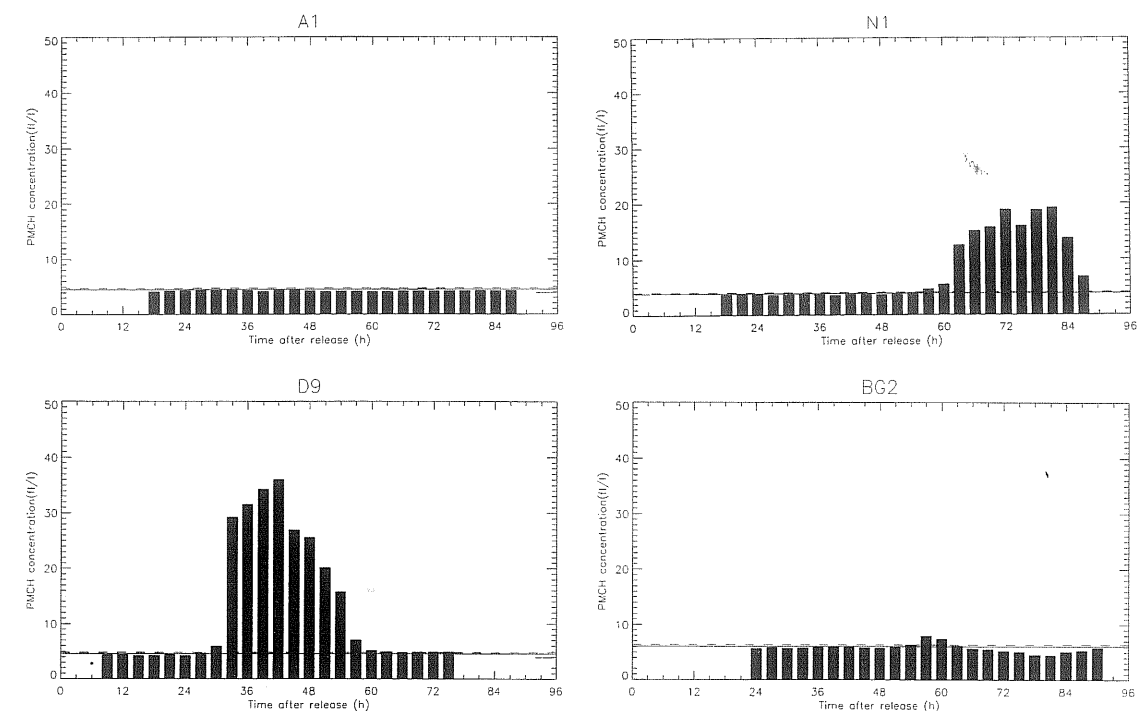


Fig. 6. PMCH concentration profile at A1 (Bregenz, Austria), D9 (Dresden, Germany), N1 (Bergen, Norway) and BG2 (Vidin, Bulgaria) during the first release. Lines indicate background concentration (solid) and uncertainty (dashed).

3.2. The second tracer release

The second tracer release started on 14 November 1994, 15:00 UTC and ended on 15 November 1994, 2:45 UTC. During these 12 h a total of 490 kg of PMCP was emitted, resulting in an average release rate of 11.56 g s^{-1} . The air stream ($71 \text{ m}^3 \text{ h}^{-1}$) at the top of the chimney had an average temperature of 73°C and a velocity of about 50 m s^{-1} .

The weather situation on 14 November showed a deep low, with its centre between Iceland and Norway, moving slowly eastwards. The associated cold front curved from Denmark towards the Channel and the Azores. At the release site there was a very strong south-westerly wind (12 m s^{-1}) of very stable and mild (14°C) warm sector air. The stable layer extended to 400 m height. During the release there was a slight drizzle. The cold front passed the site towards the end of the release and after the passage of the front the wind at ground level decreased rapidly.

Compared to the first release, much less tracer was found. Of the total number of data points obtained only 13% revealed elevated PMCP concentrations. Due to quality control procedures, about 200 (5%) measurement values were discarded. Not only were fewer non-zero values calculated, but also the concentrations were much lower. Even close to the release site in France, the maximum concentrations reached only 200 fl^{-1} of PMCP for two data points. Figure 7 shows those ground-level stations at which PMCP

was detected 24, 48 and 72 h after the release. After only 24 h the tracer plume had reached Poland, suggesting a very high transport speed. After 48 h tracer shows up again in eastern France and southern Germany and another 24 h later elevated PMCP concentrations were measured only at single stations rather than over larger areas. The tracer plume does not seem to have had such a regular shape then the one from the first release. At many sites tracer was found intermittently, rather than in a continuous sequence of samples as might be expected from the traverse of a plume with first increasing and then decreasing tracer concentrations. This can also be seen from the Fig. 8 which shows the concentration time series at stations in France, Poland and the Netherlands. In Caen (F9), PMCP tracer was detected as early as 6 h after the release start with concentrations of 200 fl^{-1} . However, after 60 h another peak shows up with concentrations of 15 fl^{-1} of PMCP. Note that the concentrations of the first 7 samples are elevated due to passive uptake (apparent at about 8.5 fl^{-1}), as discussed earlier. The double peak structure can be seen also in stations in the Netherlands (Fig. 8, at NL1), Belgium and Germany. However at another French site, F3, the tracer plume arrived later (at 24 h) and formed a single peak shape. As an example of a site far down wind, the PMCP concentrations at PL2, in Poland are shown. The released tracer adds about 1.5 fl^{-1} of PMCP to the background level arriving only 27 h after the release.

ETEX Second Release on 14 November 1994

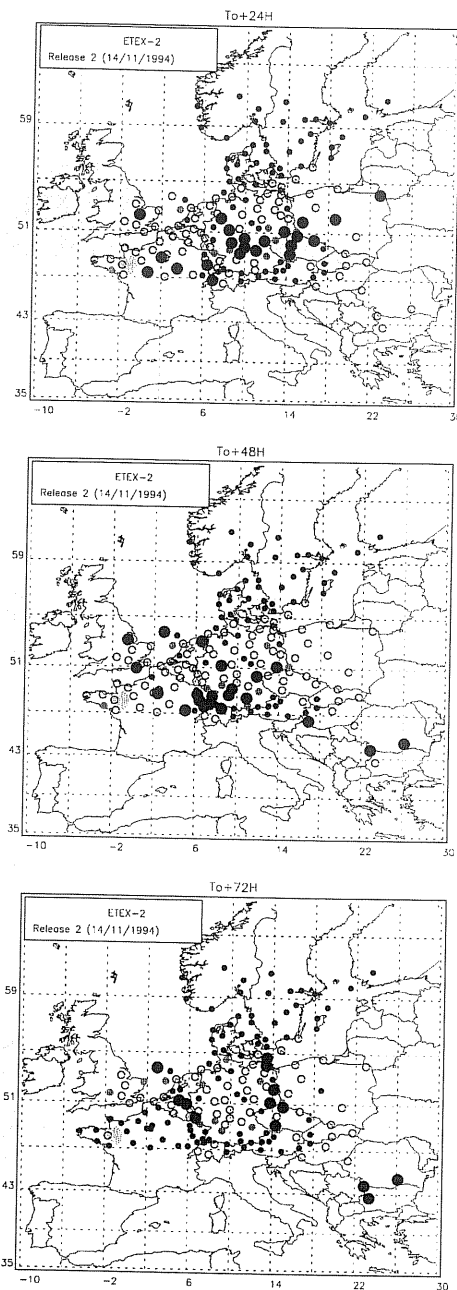


Fig. 7. PMCP detected at ground-level stations in Europe, 24, 48 and 72 h after the second release. Tracer found (●), no tracer found (○), location only (◐), tracer found but uncertain (◑).

3.3. Aircraft-based tracer results

On the day after the tracer was released three aircraft collected samples. On the 24 October the MRF aircraft flew a north-south traverse at altitudes between 220 and 900 m above ground at about 400 km distance from the release point. The PMCH concentrations of the bag samples for five runs are shown in Fig. 9. In the centre of the plume concentrations are

as high as 600 fl^{-1} and moves from 9:00 to 16:00 UTC north eastwards. During the second release, unfortunately, no tracer could be detected. At present the aircraft data has not been fully evaluated and still preliminary.

3.4. Meteorological database and tracer data

During and after the experiment meteorological information on the state of the atmosphere was collected, vital for the interpretation of the measurements and the modelled outspread from the experiments. The database contains both ground and upper air observations collected from the time of the tracer release and three days ahead. The ground observations contain sonic anemometer soundings taken from the release site. Further, they include synoptic weather observations from the 168 stations where the tracer gas concentrations were measured. Synoptic weather observations from 80 additional sites in France were also collected from the area near the site of release. The upper air data contains radiosonde, SODAR and constant volume balloon soundings from the release site. Radiosonde data from all WMO radiosonde sites in Europe are also stored for the period from October to December 1994. Further SODAR soundings from 10 nuclear power plants in France are stored for a period of 3 days after each release. The data bank also contains selected meteorological fields from the ECMWF analysed data archive. Data are available at the surface and at four upper levels for the day of the tracer release plus the next 3 days. At the surface pressure, total cloud cover, 10 m wind and 2 m temperature is retrieved. At the upper levels (1000, 850, 700, 500 hPa) geopotential, temperature, wind speed and humidity is given. The database is described in Straume and Nodop (1997).

4. CONCLUSIONS

The experimental data collected for the first and the second tracer release form two different data sets. Despite the fact that they were both planned to take place in similar meteorological conditions the results from both experiment are very different. The tracer plume originating from the first release looks like what one in general thinks of how a plume should look: in its centre high concentrations, falling off to the edges, covering a small area in the beginning and with more time extending over larger areas while being transported away from the release point. However, for the second experiment, high tracer concentrations show up at several isolated stations. The "cloud" is apparently broken up into several parts moving at different speed and in different directions. Also the concentrations are much lower and detected at fewer sites in the ground-sampling network. The experimental data and the modelling results of the real-time and post-release-time are extensively

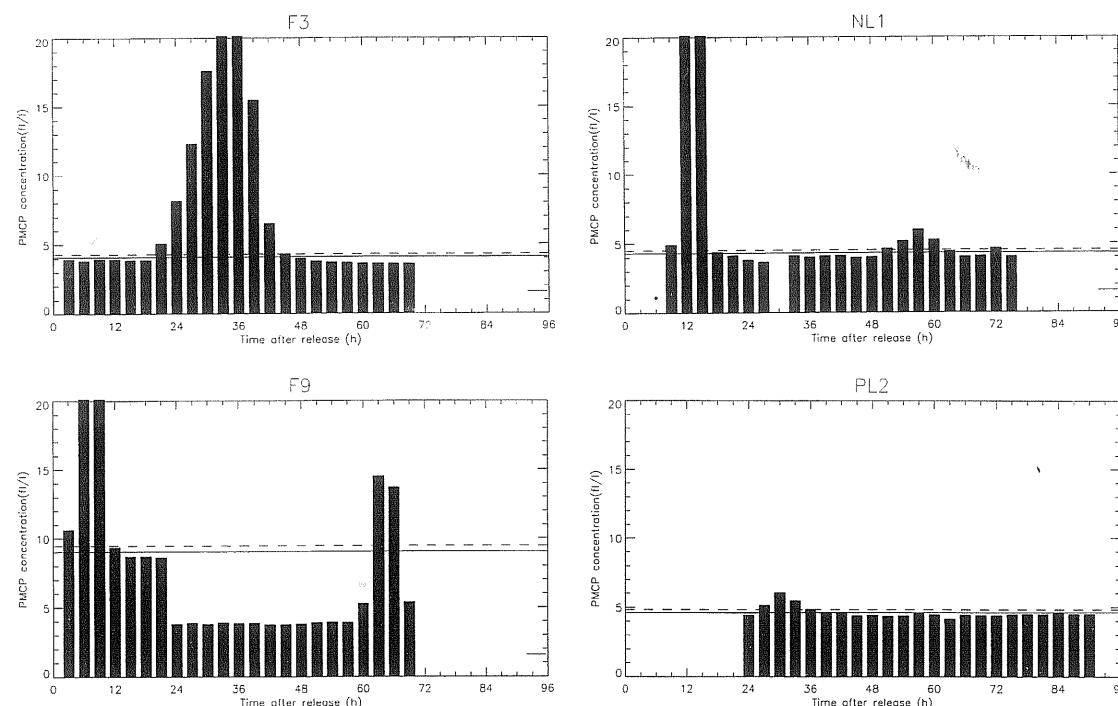


Fig. 8. PMCP concentration profile at F9 (Caen, France), F3 (Auxerre, France), NL1 (Beek, The Netherlands) and PL2 (Ktodzko, Poland) during the second release. Concentrations above 20 fl^{-1} are cut off. Lines indicate background concentration (solid) and uncertainty (dashed).

ETEX 1st Experiment (24.10.1994) MRF - Bag Samples (30 s filling time) - 400 km distance from release point

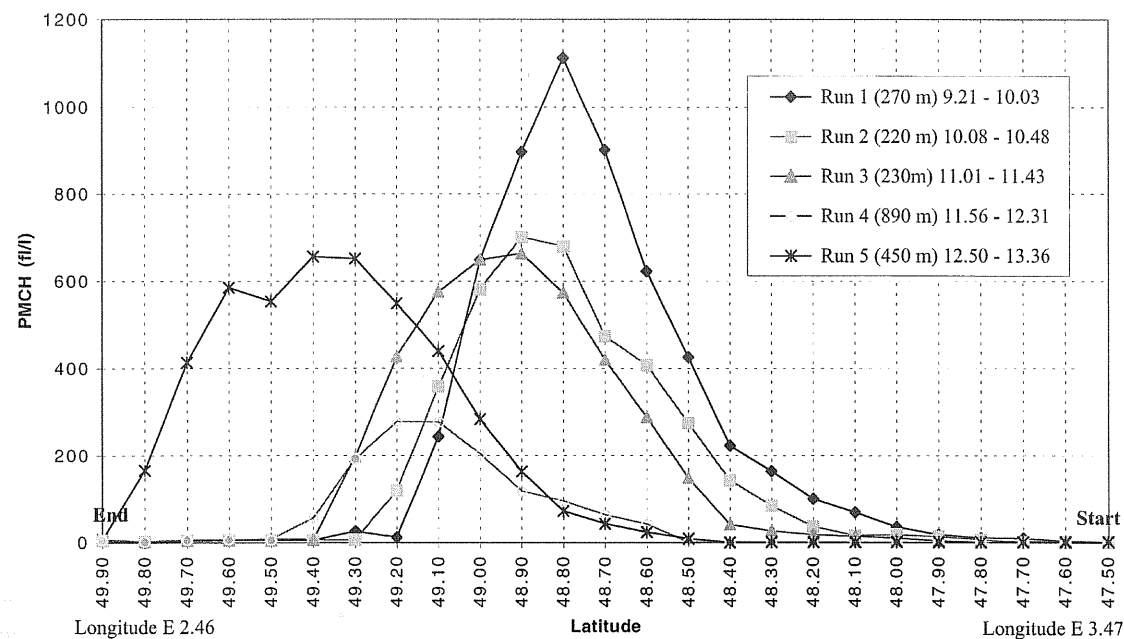


Fig. 9. Airborne concentration 400 km downwind of the release site in a north-south travers on 24 October 1994.

discussed in the Proceedings of the ETEX Symposium (Nodop, 1997).

ETEX provides a unique experimental database for validating long-range atmospheric dispersion models.

The meteorological data and the tracer data are on the Environment Institute's ftp server and can be accessed through the WWW (<http://www.ei.jrc.it/etex>). The results presented here are based on the data

set presently made available to the ETEX community. The quality control of the ETEX data set is a continuing endeavour, and includes an on-going independent external audit, and a final, validated, data set will be available once this is completed.

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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 (C₇F₁₄, PMCH) and perfluoromethylcyclopentane (C₆F₁₂, 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 (C₈F₁₆, 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 ± 0.3 fl l⁻¹, PMCH: 4.6 ± 0.8 fl l⁻¹, ocPDCH: 0.96 ± 0.33 fl l⁻¹, mtPDCH: 9.3 ± 0.8 fl l⁻¹, mcPDCH: 8.8 ± 0.8 fl l⁻¹, ptPDCH: 6.1 ± 0.8 fl l⁻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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