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European Sources of Halocarbons and Nitrous Oxide: Update 1986

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Abstract. Semi-continuous measurements of $CFCl_3$, CF_2Cl_2, CCl_4, CH_3CCl_3 and N_2O were made at Adrigole, Ireland as part of the Atmospheric Lifetime Experiment (ALE). Clean, baseline air from the Atlantic Ocean was measured approximately 70% of the time; pollution events from Europe, for the remainder. The two final years of ALE data from Adrigole give a five-year record from July 1978 to June 1983. This paper extends previous work on the relative enhancements of trace gases during pollution episodes and presents (1) unambiguous identification of elevated levels of N_2O concurrent with halocarbon pollution events, (2) detection of trends in emission of CH_3CCl_3, (3) discovery of seasonal variations in emission of CF_2Cl_2, CCl_4 and CH_3CCl_3, (4) characterization of typical summer and winter pollution episodes, and (5) identification of weather patterns over Europe that are associated with high concentrations of CFCs at Adrigole. Some of these results assume that $CFCl_3$ represents a uniform, well buffered source from the continent. The latter two results are particularly useful in the testing and calibration of three-dimensional chemical transport models. Observed enhancements are marginally consistent with estimates of halocarbon use by the chemical industry. The source of nitrous oxide correlated with halocarbons is 0.8 Tg(N)/yr from Europe alone and represents approximately 10% of the global stratospheric loss.

Key words. Nitrous oxide, halocarbons, regional sources, atmospheric pollution.

1. Introduction

The composition of the Earth's atmosphere is changing today. Emissions of many chemical species into the atmosphere are predicted to have global effects on the air quality of the troposphere, ozone in the stratosphere and the climate (see WMO, 1986 and GTC, 1986 for a review). Interpretation of causes and cures for this increasing pollution of the atmosphere requires knowledge of the major sources for these trace gases.

Local releases of long-lived gases, such as CH_4, N_2O, O_3 and many halocarbons, become globally distributed. These compounds are eventually destroyed by chemical reactions in the atmosphere or at the surface of the Earth. Primary examples of networks for monitoring global air quality are the Atmospheric Lifetime Experiment (ALE: Prinn *et al.*, 1983a) and NOAA's Global Monitoring for Climate Change (GMCC: NOAA, 1986). ALE has analyzed their halocarbon observations, using atmospheric models to infer global budgets and hence to derive sources for these gases. The spatial resolution of emissions determined in this manner is limited since, by definition, baseline stations

sample clean air that is well mixed on scales of 30° latitude by 120° longitude. Furthermore, annual cycles in release of trace gases may be obscured by the seasonal nature of the atmospheric circulation (Prather *et al.*, 1987). There is need for better definition of sources on scales between those of urban plumes and hemispheric averages.

Chlorofluorocarbons (CFCs) have been recognized as 'indicators of air movements' since they were first measured in the atmosphere (Lovelock, 1971). Early work in the British Isles clearly demonstrated the advantage of statistical, correlative analyses of simultaneous measurements of two or more gases ($CFCl_3$ and CCl_4) in an environment with a mixture of background air and pollution episodes (Pack *et al.*, 1977; Penkett *et al.*, 1979; Brice *et al.*, 1982). Semi-continuous measurements have been made at Adrigole, Ireland as part of ALE (Prinn *et al.*, 1983a; Cunnold *et al.*, 1986). Clean, baseline air from the Atlantic Ocean was measured approximately 70% of the time; pollution events from Europe, for the remainder. Analyses of the global budgets for these gases have focussed on the baseline observations from Adrigole and four other sites (Cunnold *et al.*, 1983a, 1983b; Prinn *et al.*, 1983b; Simmonds *et al.*, 1983). A study of the continental sources has been made from the data taken during pollution episodes (Prather, 1985).

This paper presents new information on seasonal and secular trends in the release of $CFCl_3$, CF_2Cl_2, CCl_4, CH_3CCl_3 and N_2O from Europe. The original work of Prather (1985) is updated to include the two final years of ALE data from Adrigole, giving a five-year record from July 1978 to June 1983. This extension of the Adrigole dataset yields (1) unambiguous identification of elevated levels of N_2O concurrent with halocarbon pollution events, (2) detection of trends in the relative emission of different halocarbons, (3) discovery of seasonal variations in emission of CF_2Cl_2, CCl_4 and CH_3CCl_3, (4) characterization of typical summer and winter pollution episodes and (5) identification of weather patterns over Europe that are associated with high concentrations of CFCs at Adrigole. Some of these results presume that $CFCl_3$ can be used as a nearly constant, reference gas, an assumption that is supported by the marketing and use of this gas in Europe over the period of 1978–1983. The latter results are particularly useful in the testing and calibration of three-dimensional chemical tracer models.

Statistical analysis of the ALE measurements is described in Section 2. Derivation of the relative European sources is given in Section 3. The correlation of pollution episodes with weather patterns is shown in Section 4. Section 5 presents conclusions and recommendations for the continued research necessary to define sources for many of these trace gases.

2. Analysis of the ALE Data

Observations of halocarbons and nitrous oxide at Adrigole, Ireland were made

on a semi-regular basis as part of the Atmospheric Lifetime Experiment. The original dataset of three-year duration (7/78–6/81) has been presented in a series of papers (Prinn *et al.*, 1983a; Rasmussen and Lovelock, 1983; Cunnold *et al.*, 1983a; Cunnold *et al.*, 1983b; Prinn *et al.*, 1983b; Simmonds *et al.*, 1983) and subsequently analyzed for pollution and regional emissions by Prather (1985). The five-year record (7/78–6/83) from Adrigole has been described by Cunnold *et al.* (1986; see also WMO, 1986). The original measurements were provided by the ALE Team (R. Prinn, priv. comm., 1986) and are analyzed as follows, in a manner similar to that described in Prather (1985).

(a) Six measurements of volume mixing ratios were recorded for the species $CFCl_3$ (s, denoted as 11s), CH_3CCl_3 (s, MCs), CCl_4 (s, CTs), $CFCl_3$ (p, 11p), CF_2Cl_2 (p, 12p), and N_2O (p), where s and p refer to the different columns used in the gas chromatograph (silicone and Porasil). All six time series are treated independently, even though measurement of $CFCl_3$ was duplicated on each column (11s & 11p). Absolute calibration factors (ξ) are taken from the original ALE papers with the exception of CH_3CCl_3 for which $\xi = 0.8$ is assumed (WMO, 1986).

(b) Volume mixing ratios of species i at four-hour intervals, $F_i(t)$, are calculated by averaging all observations made during the interval. The time series is discrete, with t ranging from 1 (1 July 1978, 0000 H–0400 H GMT) to 10956 (30 June 1983, 2000 H–2400 H GMT).

Table I. Linear trends removed from Adrigole ALE data

Gas	(Abbr.)	1 Jan 1981	Trend	Points	2nd/98th%-ile
$CFCl_3$	(11s)	192.5 ppt [187.5]	8.2 ppt/yr [8.3]	6705	−12/+82 ppt
	(11p)	193.0 [188.4]	8.4 [8.6]	6463	−13/+82
CF_2Cl_2	(12p)	323.1 [318.3]	16.9 [15.0]	6655	−19/+81
CH_3CCl_3	(MCs)	136.1 ⟨128.4⟩	7.7 ⟨7.3⟩	6642	−22/+118
CCl_4	(CTs)	128.4 ⟨127.3⟩	0.5 ⟨0.5⟩	4621	−7/+23
N_2O		307.6 ppb ⟨307.4⟩	1.0 ppb/yr ⟨1.2⟩	4919	−13/+6 ppb

Points are the number of 4 h bins from 7/1/78 to 6/30/83 (10 956 in total) that have reported ALE measurements.
Trends from clean, baseline air at Adrigole are reported for comparison: [...] are from Cunnold *et al.* (1986); ⟨...⟩ are from a linear fit to monthly means of the data labelled as unpolluted by ALE. Percentiles reported are for the residual time series after the linear trend is removed. Offsets (±ppt/ppb) are relative to the mean.

The number of intervals with measurements is noted in Table I. The complete time series for $F_{11s}(t)$ is shown in Figure 1. The other five time series display a similar density of observations during years 4–5, greatly enhancing the datasets for CTs and N_2O that have gaps in years 1–3 (see Prather, 1985, for a figure showing years 1–3 from all six time series).

(c) A least-squares fit to a linear trend is removed from the data and is reported in Table I. The trend must be removed in order to have a stationary time series; it does not necessarily represent a global tropospheric value since pollution events were included (see ALE analyses for atmospheric trends).

(d) The residual distribution of concentrations is sorted, and values which fell above the 98th percentile or below the 2nd percentile were truncated to those respective limits noted in Table I.

(e) A linear trend is again removed from the truncated dataset because the truncation process (d) alters slightly the originally calculated trend (c). The total linear trend removed from the data, $F_i^0 + F_i^1 \times t$, is given in Table I, and the subsequent analysis uses only the residual mixing ratios:

$$f_i(t) = F_i(t) - F_i^0 - F_i^1 \times t. \tag{1}$$

(f) Cross-covariances between two species i and j are computed for a time lag of Δ over a time domain T as

$$CC(i, j, \Delta, T) = \sum_{t \in T} f_i(t) f_j(t + \Delta) \, \delta_i(t) \, \delta_j(t + \Delta) \Big/ \sum_{t \in T} \delta_i(t) \, \delta_j(t + \Delta), \tag{2}$$

where

$$\delta_i(t) = \begin{cases} 1, & \text{if there is a datum for species } i \text{ at time } t, \\ 0, & \text{otherwise.} \end{cases} \tag{3}$$

Due to the discrete nature of the time series, CC is computed for values of Δ equal to 0, ± 4, ± 8, ..., out to ± 720 h (± 30 days). Auto-covariances ($i = j$) and cross-covariances for the entire time series ($T = [1, 10956]$) are shown in Figures 2 and 3. The covariance scales are somewhat arbitrary: for example, if the mean and trend were not removed from the CF_2Cl_2 time series, the origin would be shifted upward about $(320 \text{ ppt})^2 \sim 100\,000 \text{ ppt}^2$.

The auto-covariances (Figure 2) demonstrate the clear signal of halocarbon pollution events with a duration of several days. The cross-covariances (Figure 3) reveal that elevated levels of all six species occur in phase with one another. Enhanced concentrations of N_2O are clearly correlated with CFC pollution, as seen in Figure 3c, although the auto-covariance of N_2O fails to show such pollution events. Use of the cross-covariances highlights this connection, which is difficult to recover from N_2O alone because of measurement noise. The auto-covariance peak from CFCs is approximately $(10 \text{ ppt})^2 \sim 100 \text{ ppt}^2$; the
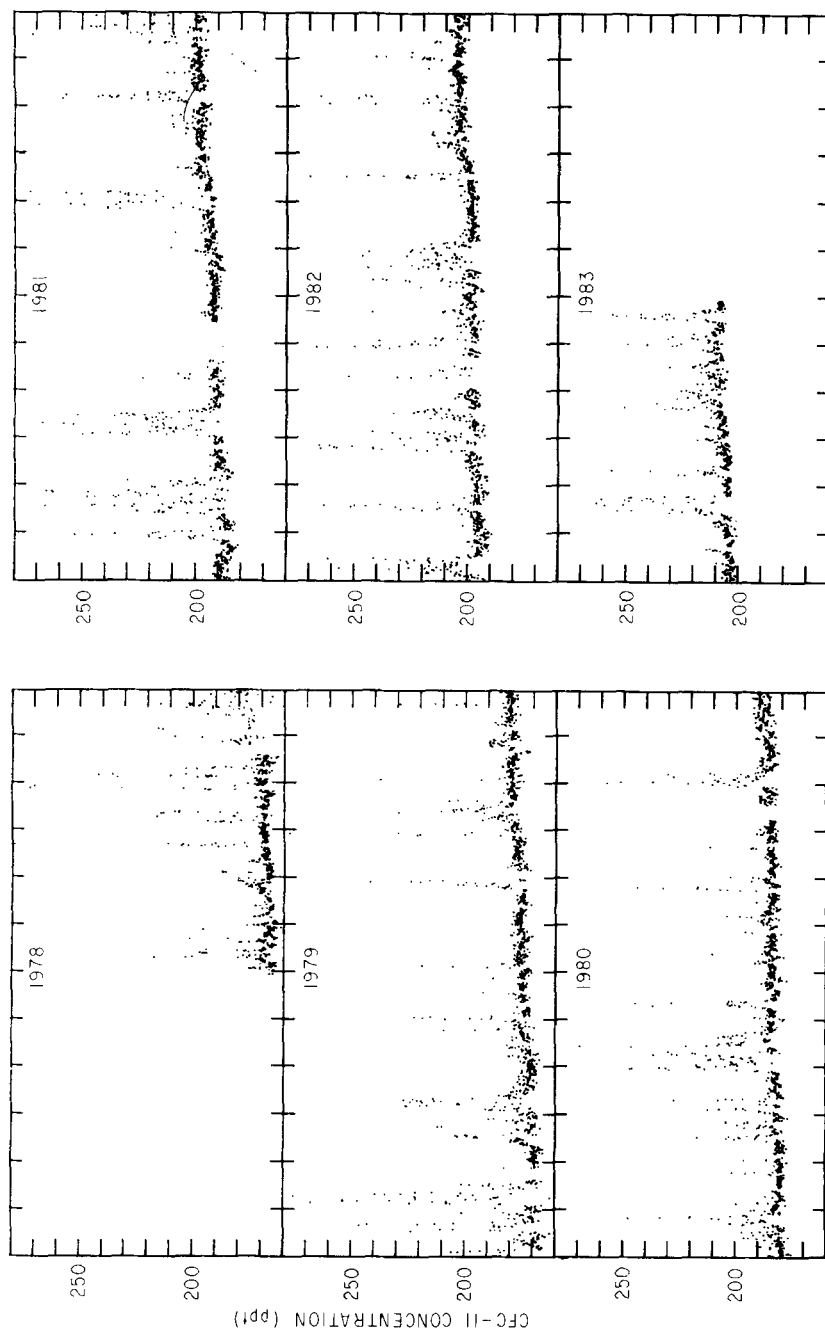
Fig. 1. Time series of ALE observations of CFC-11(s) at Adrigole, Ireland for the calendar years 1978 through 1983. The individual measurements have been averaged into four-hour bins.
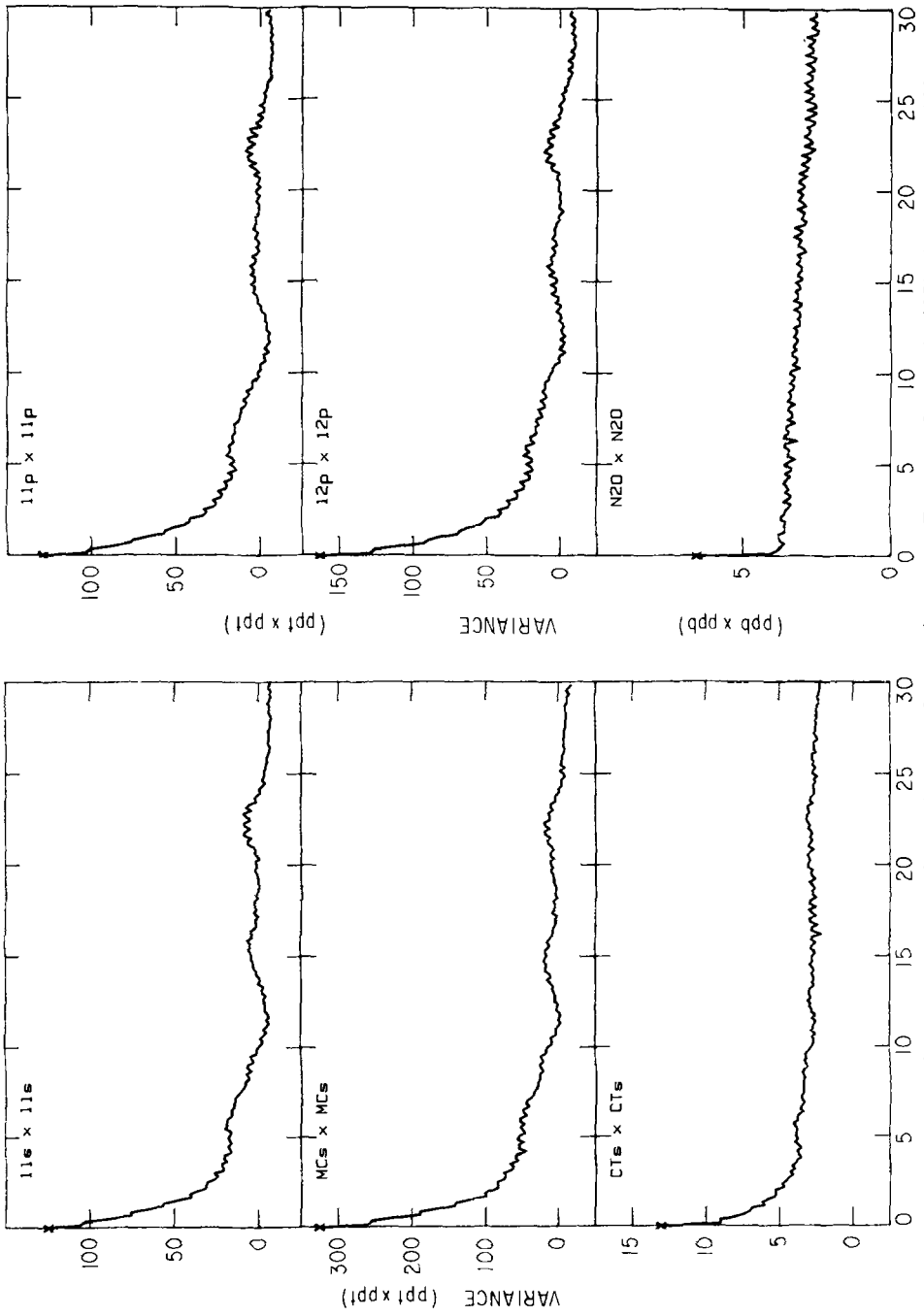
Fig. 2. Auto-covariances of the six measurement series at Adrigole, Ireland for the ALE dataset from July 1978 through June 1983. The lag period varies from 0 (denoted by an 'x') to 30 days.
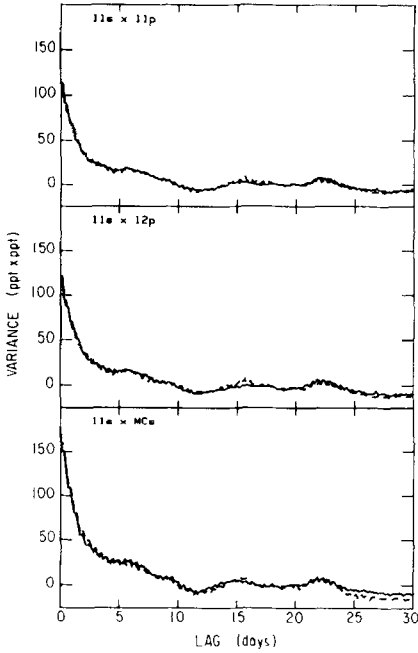
Fig. 3a. Cross-covariances for 11s versus 11p, 12p and MCs at Adrigole. The solid lines refer to positive lags for CC(11s, other gas, Δ, T) as defined in the text; and the dashed lines, to negative values of Δ. The lines connect values every 4 hours.
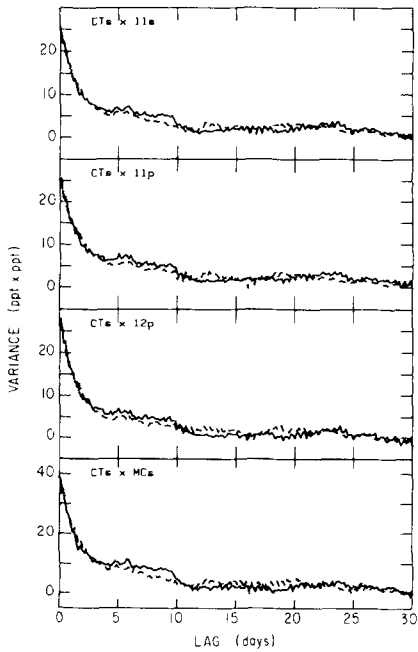

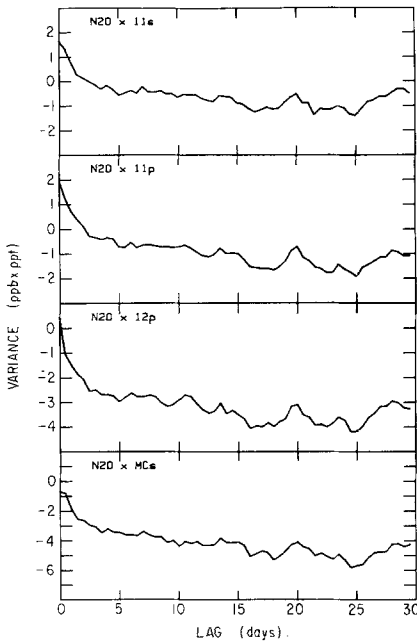Fig. 3b. Cross-covariances for CTs versus the other halocarbon measurements at Adrigole. See Figure 3a.

Fig. 3c. Cross-covariances for N_2O versus the other halocarbon measurements at Adrigole. See Figure 3a. The cross-covariances have been averaged over 12 hour intervals for this figure.

expected signal from N_2O would be 30 times the CFC value (see later discussion), $(300 \text{ ppt})^2 \sim 0.1 \text{ ppb}^2$, which is indiscernible in the auto-covariance for N_2O.

As will be shown later, most of the covariances may be explained by suitable scaling of a single auto-covariance from either 11s, 11p, 12p or MCs. These similarities are expected if the European emissions of $CFCl_3$, CF_2Cl_2, CH_3CCl_3, CCl_4 and N_2O are coherent and maintain relatively constant emission ratios when mixed over a suitable area.

Seasonal differences in the pollution at Adrigole are shown in the auto-covariances of 11s calculated separately for winter and summer (Figure 4). The winter calculation used all observations in the months of December, January, and February for the time domain T; the summer calculation defined T to be the months June, July and August for all available years. CFC-11 concentrations in winter have about twice the variance of summertime values. They exhibit significant periodicity of 5–10 days, associated with the synoptic repetition of pollution events during winter. Summer covariances show a flat shoulder to time lags of 8 days and no periodic recurrence. The long-term, low-level correlations in summer might be associated with stagnation episodes; this discussion is continued in Section 4 with examination of the sea level pressures.
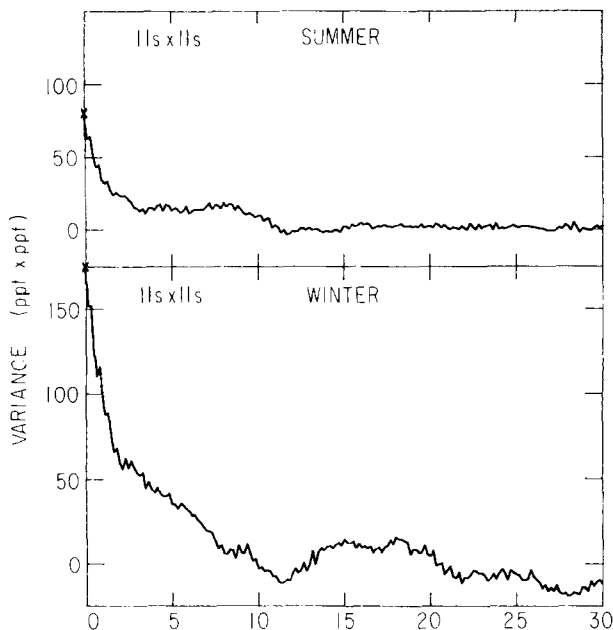
Fig. 4. Auto-covariances of 11s for summers and winters at Adrigole, Ireland. See Figure 2.

The focus here is on time periods of several days, during which the predominantly clean, steady, background concentrations at Adrigole are occasionally augmented by the addition of European emissions of halocarbons and nitrous oxide. Thus, the correlations are limited to the synoptic scale variations and are not influenced by the long-period, interannual variability noted by Cunnold et al. (1986). Quantifying the average variance of pollution events requires determination of the baseline for each covariance in Figures 2 and 3, that is the value of CC in the absence of pollution events.

(g) Baselines for the (i, j) covariance are calculated separately for $\Delta > 0$ and for $\Delta < 0$ ($i \neq j$ only). They are defined as the 16th percentile of the 180 values for $CC(i, j, \Delta, T)$, and subtracted from CC to yield a residual covariance for $\Delta > 0$,

$$cc(i, j, \Delta, T) = CC(i, j, \Delta, T) - 16\text{th}\%[CC(i, j, 4 < \Delta < 720 \text{ h}, T)]. \quad (4)$$

A corresponding set of values is derived for $\Delta < 0$. The uncertainty in the baseline correction is associated with an error term equal to the difference between the 10th and 16th percentiles.

$$ee(i, j, T) = 16\text{th}\%[CC(i, j, 4 < \Delta < 720 \text{ h}, T)] -$$
$$10\text{th}\%[CC(i, j, 4 < \Delta < 720 \text{ h}, T)]. \tag{5}$$

(h) Variances above the baseline are smoothed by averaging over selected ranges in the time lag,

$$\overline{cc}(i, j, R, T) = \sum_{\Delta \in R} cc(i, j, \Delta, T)/N, \tag{6}$$

where the ranges R are defined as follows and N includes both positive and negative Δ. Uncertainty in $\overline{cc}$, denoted by $vv(i, j, R, T)$, is equated to the error in the mean as calculated in the standard manner from the root-mean-squared variance of cc over the range.

R	N	Δ_1 (h)	Δ_N (h)
0	1	0	0
1	6	4	12
2	6	16	24
3	6	28	36
4	6	40	48
5	24	52	96
6	24	100	144
7	24	148	192
8	24	196	240

(i) The relative predictability of a pair of gases may be measured by their coherence, which is defined here as the ratio of their cross-covariance to the square root of the product of their auto-covariances,

$$\overline{cc}(i, j, R, T)/[\overline{cc}(i, i, R, T) \times \overline{cc}(j, j, R, T)]^{1/2}. \tag{7}$$

Coherences are essentially unity (1.00 ± 0.03) for any combination of the major halocarbons (11s, 11p, 12p, MCs) over the ranges $R = 1-7$. At the statistical center of the pollution event $(R = 0)$ values drop below unity $(0.8–0.9)$, indicating that a single measurement of elevated concentrations in an air parcel, *without temporal resolution*, does not properly average over the individual, incoherent emissions of these gases (e.g., Blake *et al.*, 1984). Throughout Europe and the British Isles these gases have many different and independent sources (see WMO, 1986; CEFIC, 1985) whose individual plumes retain some level of inhomogeneity on time scales of 4 h or less, but are effectively well mixed when temporally averaged over periods of 8 h or more. If a wind speed of

5 m sec^{-1} is typical of the air flow across Adrigole, then the spatial scales for coherent sampling are of order 100 km and greater. Coherences for CTs with respect to any of the major halocarbons are notably less than unity (0.85 ± 0.05) over the ranges $R = 1$–7, reflecting possibly a source that is spatially distinct from the other halocarbons. Coherences for N_2O with respect to the major halocarbons are much less (0.22 ± 0.04), in part because the instrumental/sampling variance for N_2O (0.5 ppb^2, note ripples in Figure 2) is larger than the signal which is correlated with the pollution events (0.1 ppb^2), in part because there might be other nearby sources uncorrelated with halocarbons.

(j) The relative source of species i with respect to species j for a given range of time lag from the center of the pollution event is calculated from the ratio

$$ss(i/j, R, T) = \overline{cc}(i, j, R, T)/\overline{cc}(j, j, R, T), \tag{8}$$

with a maximum and minimum value derived from the worst case combination of uncertainties,

$$ss^{max}(i/j, R, T) = \frac{cc(i, j, R, T) + vv(i, j, R, T) + ee(i, j, T)}{cc(j, j, R, T) - vv(j, j, R, T) - ee(j, j, T)} \tag{9}$$

$$ss^{min}(i/j, R, T) = \frac{cc(i, j, R, T) - vv(i, j, R, T) - ee(i, j, T)}{cc(j, j, R, T) + vv(j, j, R, T) + ee(j, j, T)} \tag{10}$$

The form of the denominator in Equations (8)–(10) indicates that it is important to choose a reference species (j) which has the best-defined pollution events and baseline. Therefore, $CFCl_3$ was selected as the reference species, and relative sources quoted in what follows are the average with respect to both 11s and 11p.

Sources of 12, MC, CT and N_2O relative to 11 have been derived from the complete 5-year dataset. Results in Figure 5 show the values of ss for 12/11, MC/11, CT/11, and N_2O/11 for the ranges R of time lags noted above. Error bars encompass half of the extreme range, $\frac{1}{2}(ss^{max} + ss)$ to $\frac{1}{2}(ss^{min} + ss)$. The values of ss are consistent throughout the entire range of R.

Correlative sources given in Table II are derived using the range of time lags $R = 1$–6. These six values of ss are combined with a weighting inversely proportional to their estimated errors and are treated as independent values in order to derive the means reported in Table II. Uncertainties in Table II are based on propagation of known statistical sources of error described above and are intended to represent a 90% confidence interval. In the case of CT and N_2O, data are sparse or missing for the first two years and values of ss for the last three years are used to derive the relative sources given in Table II.

Seasonal differences in the ratio of emissions for 12/11 are seen clearly in Figure 6. The value ss(12/11) for winter, ~ 1.05, is well below the summer
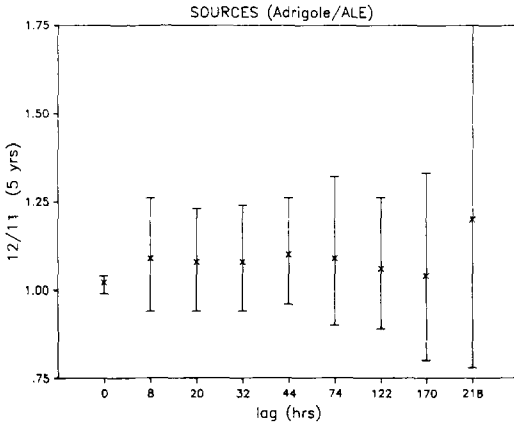
Fig. 5a.   Ratio of CFC-12 enhancements above background air to CFC-11 enhancements as a function of the time lag between the two gases. Values are based on the entire five years of ALE data. The ratio is derived from the cross-covariance of the two gases (see text) and is equated to the relative sources over Europe.
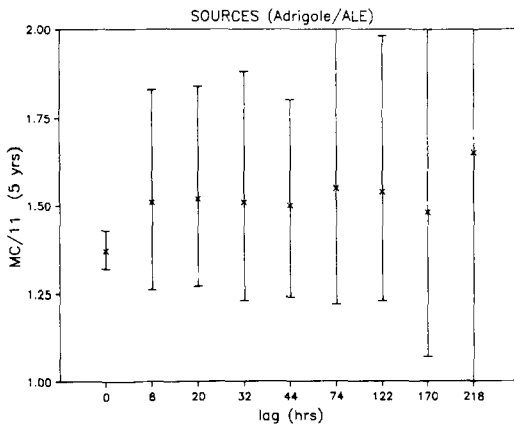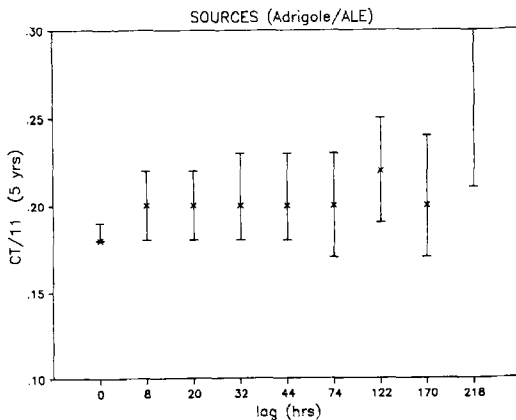

Fig. 5b.   Ratio of Methyl Chloroform enhancements above background air to CFC-11 enhancements as a function of the time lag between the two gases. See Figure 5a.

Fig. 5c.   Ratio of Carbon Tetrachloride enhancements above background air to CFC-11 enhancements as a function of the time lag between the two gases. See Figure 5a.
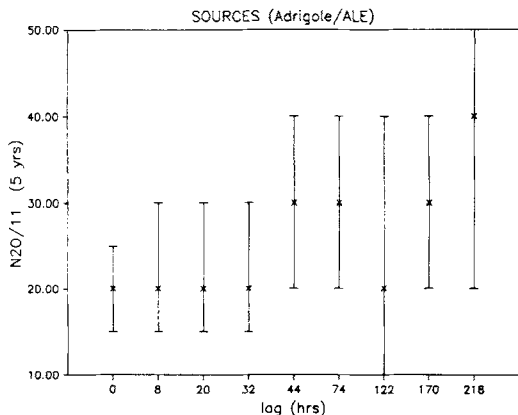
Fig. 5d. Ratio of Nitrous Oxide enhancements above background air to CFC-11 enhancements as a function of the time lag between the two gases. See Figure 5a.

Table II. Enhancements of halocarbons and nitrous oxide relative to $CFCl_3$ (11) in European air

CF_2Cl_2	(12)	1.08 ± 0.04	s
CH_3CCl_3	(MC)	1.52 ± 0.07	s, t
CCl_4	(CT)	0.22 ± 0.02	s
N_2O		30 ± 10	

s Seasonal pattern in relative emissions is found.
t Trend in relative emissions over 5-year period is found.
Units are dimensionless molar ratios, averaged for the ALE Adrigole data from 7/1/78 through 6/30/83. Uncertainties represent the variances and difficulties in determining the elevations above the background for the pollution events (see text) and do not reflect any systematic biases in the sampling of European air at the Adrigole site.

ratio of ~ 1.25. Errors are larger for the summer values because of the lower levels of pollution in summer as noted in Figure 4. The full seasonal patterns of the halocarbon sources are described in the next section.

3. Means, Trends, and Seasonality of Sources

3.1. *CFC-11*

The choice of CFC-11 as the reference gas in the previous section was based on which gas provided the most well defined continuum for the concentrations in background, presumably oceanic air. There are, however, other reasons to select this species as the reference gas. It has a diversity of sources (45% aerosols, 29% rigid foam, 16% flexible foam: CEFIC, 1985) which are likely to provide a
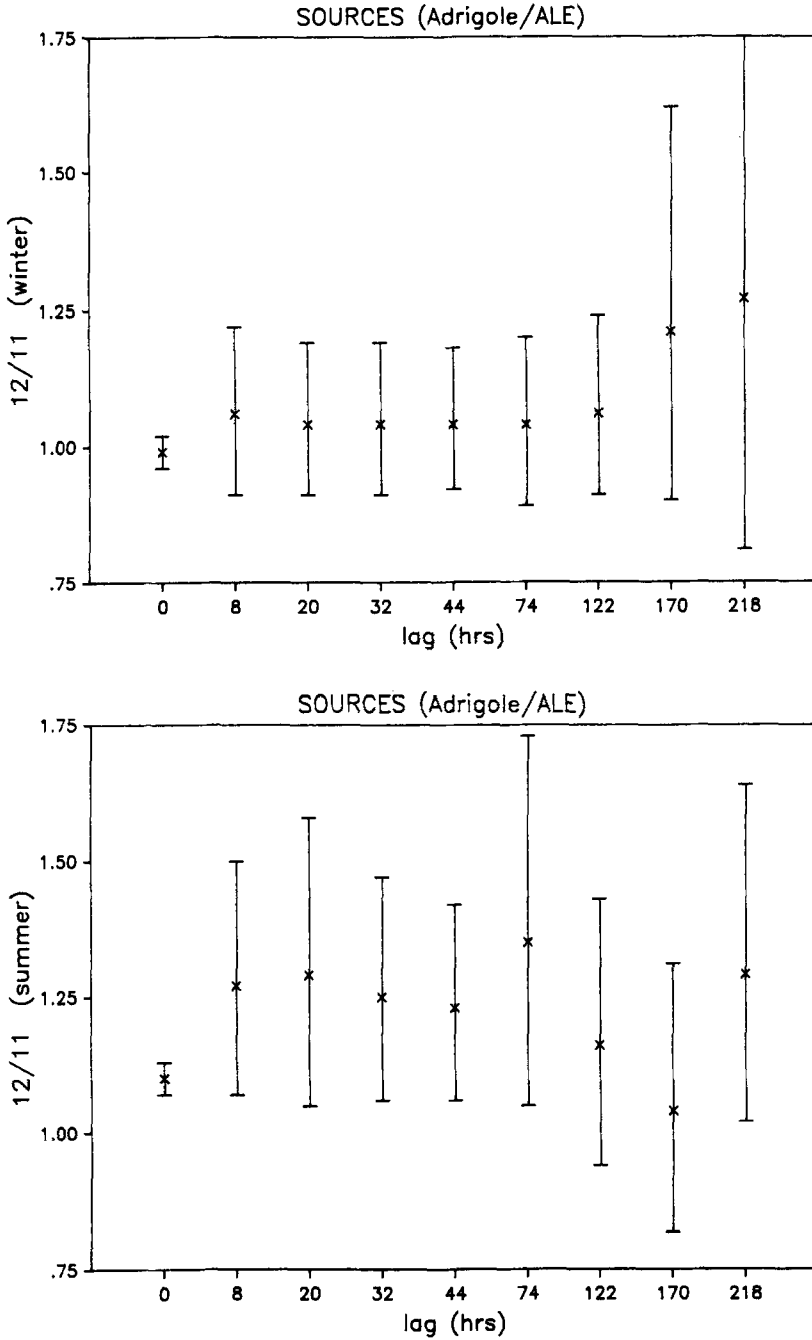
Fig. 6. Ratio of CFC-12 enhancements above background air to CFC-11 enhancements as a function of the time lag between the two gases. Values are based on the five complete winters of ALE data (top panel) and the four complete summers (bottom panel).

uniform rate of emission over the period of this study, 1978–1983. Current levels of production of CFC-11 in Europe were reached in the early 1970s and have remained essentially constant (±10%) between 1978 and 1983, approximately 150 Gg/yr (CEFIC, 1985). The period between sales and emission varies according to use from immediate release (6 months for aerosols) to delays of several years (rigid polyurethane foam, Gamlen *et al.*, 1986). This extended release tends to buffer the emission of CFC-11 over seasonal, interannual and even economic variations. Therefore, CFC-11 will be used as a baseline to determine variations in emissions of the other ALE gases.

3.2. CFC-12

Enhancements of CFC-12 show a well defined mean ratio, 12/11, of 1.08 ± 0.04 for the entire 5-year record (see Table II). This value may be weighted slightly in favor of wintertime emissions when the total variance associated with pollution is greatest (see Figure 6). The relative release of 12 with respect to 11 is shown in Figure 7 and displays no obvious trend over the five winters of ALE data. The winter of 1979/80 has large error bars because anomalously few pollution events were recorded during this period. A strong seasonal modulation of order 25% is seen in Figure 7, with emissions of 12 peaking in summer (Figure 7, JJA).

Uses of 12 are similar to those for 11 with the notable exception of refrigeration (24% of European sales in 1983, CEFIC, 1985). It is suggested here that the seasonal cycle in release of CFC-12 corresponds to the major loss of 12 from large industrial refrigeration systems, that it is associated with mechanical stress and breakage when these systems are first turned, and that it occurs in the late spring or early summer. Such a pattern may be less important over the North American continent where refrigeration and air conditioning are often in use year-round.

If there were a preferential release of CFC-12 during summer, the signal should be seen in the background air of the Northern Hemisphere about 3 months later. The delay is due to a combination of the time required to mix the continental sources throughout the northern midlatitudes and the typical phase lag of 3 months by which concentrations follow sources or sinks. Indeed this signal is seen in the ALE data for the background air at both Adrigole and Cape Meares, Oregon. The maximum occurs in the autumn (September–November) with an amplitude of about 1.7 ± 0.6 ppt, or about 12% of the annual forcing for CFC-12, which is about 15 ppt/yr (Cunnold *et al.*, 1986).

3.3. Methyl Chloroform

Enhancements of MC relative to 11 show a well defined average ratio of 1.52 ± 0.07 for the five-year period (Table II) and exhibit a clear trend with releases increasing over the five winters (Figure 8). The seasonal pattern in MC
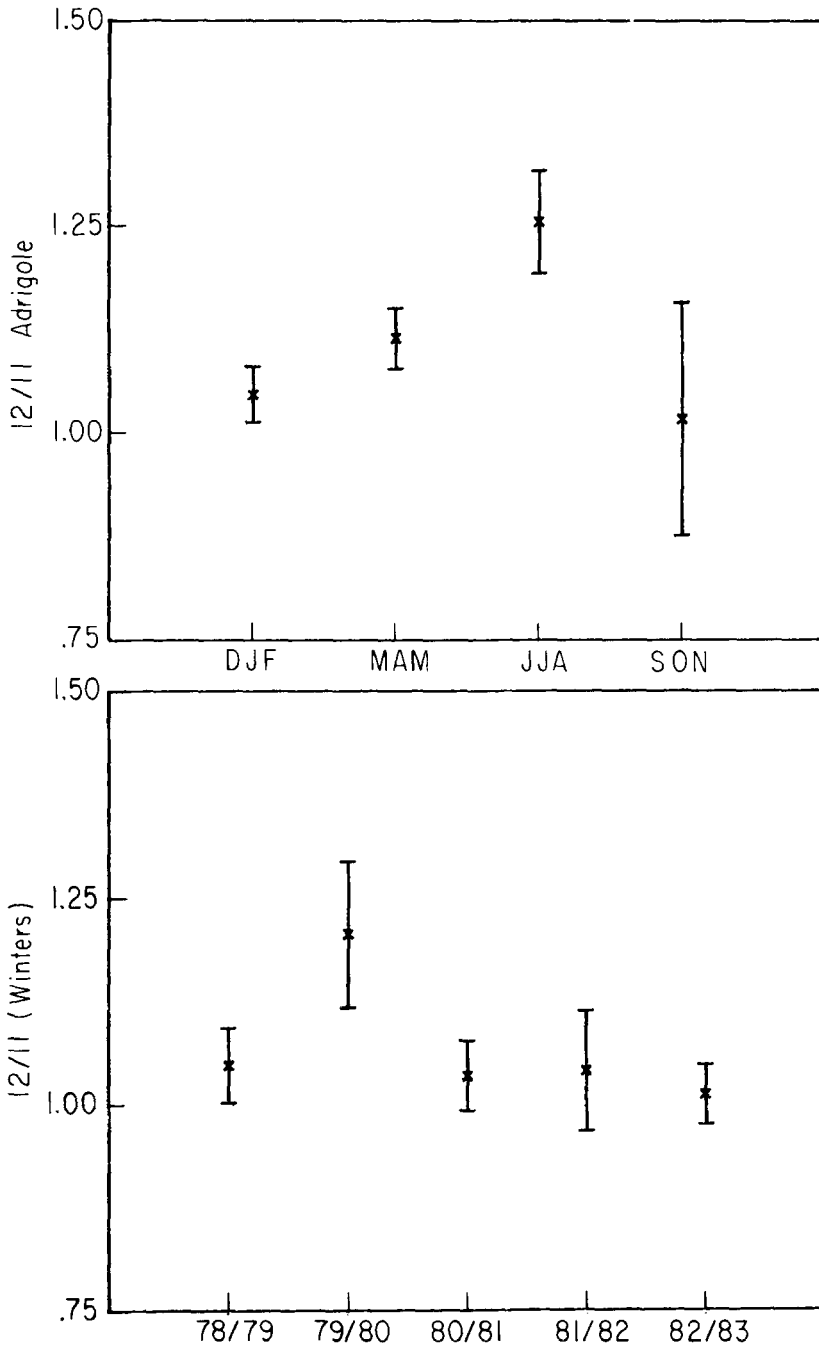
Fig. 7. Seasonal and interannual trends in the ratio of sources CFC-12/CFC-11. The seasonal ratios use all Adrigole data from the appropriate season over the five-year ALE record. The long-term trend shows relative sources derived for the five individual winters.
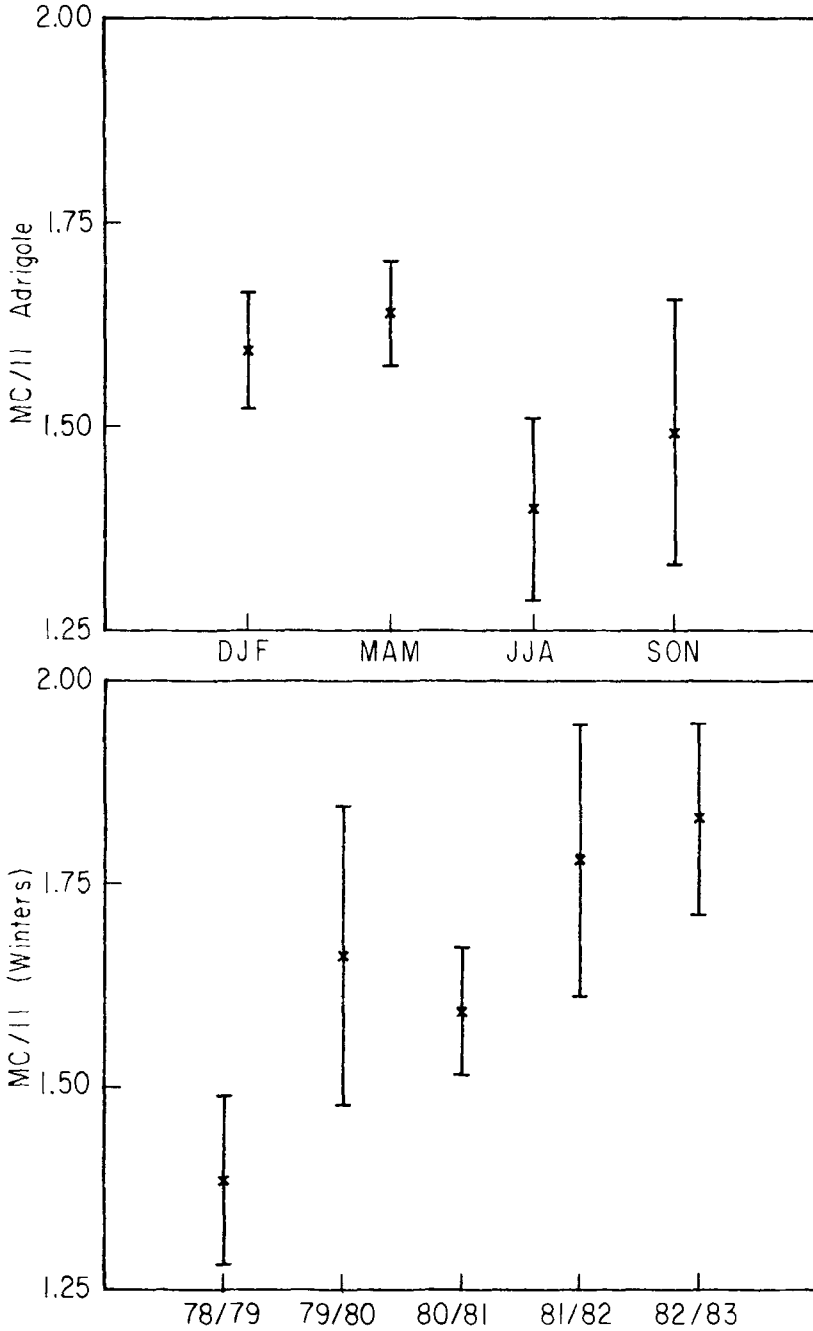
Fig. 8. Seasonal and interannual trends in the ratio of sources MC/CFC-11. The seasonal ratios use all Adrigole data from the appropriate season over the five-year ALE record. The long-term trend shows relative sources derived for the five individual winters.

is the reverse of that for 12 with a 20% reduction in summer (Figure 8, JJA), extending into the autumn (SON). The observed increases in emissions of MC are in conflict with the sales of MC reported by CEFIC (1985) which indicate a constant European usage of approximately 155 Gg/yr from 1979 through 1984.

Methyl chloroform is used predominantly as an industrial cleaning and degreasing agent in the manufacture of metal parts, with some additional applications as a solvent for adhesive and paints. Release of MC is likely to occur during the manufacturing process, and it will not be buffered over the year as for 11 and 12. CEFIC notes that increased efficiency and solvent reclamation has led to level sales of MC in spite of growth in the overall manu- facturing industry. The atmospheric evidence from the Adrigole site points to a 10% increase per annum in MC use over Europe. The minimum in emissions during summer is typical of reductions in industrial capacity expected from the vacation patterns in Europe, whereby entire manufacturing plants shut down in late summer (J. E. Prather, priv. comm., 1987). The observed decrease of 20% could be achieved if the average user of MC ceased emissions for 3 weeks each summer.

The impact of the seasonal variation in release of MC upon the background air of the Northern Hemisphere is similar to that for 12, but reversed in sign. The 20% reduction in emissions should produce an annual amplitude in MC of order $1-1\frac{1}{2}$ ppt with a minimum in late autumn or early winter in the Northern Hemisphere and with no effect in the Southern. This signal has only a small phase difference from that predicted for the photochemical loss of MC by reaction with OH. Based on the observed, presumably photochemical cycle of MC in the southern midlatitudes (Fraser et al., 1985), the corresponding ampli- tude in the northern midlatitudes would be about $2-2\frac{1}{2}$ ppt with a minimum in August–September. Including the seasonal pattern of emissions should lead to a deeper minimum closer to October. Such a cycle is difficult to derive from the current record at the Northern Hemisphere ALE sites. Indeed, variations in industrial use of MC may explain some of the difficulty in deriving a simple photochemical signal from Northern Hemispheric air.

3.4. Carbon Tetrachloride

Observations show clear enhancements of CT when the air over the British Isles contains other halocarbons (Pack et al., 1977; Penkett et al., 1979; Brice et al., 1982). The ratio of excess CT to excess 11 from the ALE Adrigole data is 0.22 ± 0.02 (Table II), consistent with the correlations of 0.07–0.24 reported by Brice et al. (1982) from a few months of data at Harwell, U.K. The smaller amplitude of CT pollution events and the irregular record of ALE data for CT at Adrigole prevent the determination of a trend in emissions. Accordingly, the seasonal pattern for CT releases is not well defined, but CT/11 ratios are

systematically higher during summer (~0.30) than winter (~0.20).

Primary use of carbon tetrachloride is as a chemical intermediate in the manufacture of CFCs, with secondary applications as a solvent or fumigant (CEFIC, 1985). Sources in Western Europe are estimated to be 10 Gg/yr lost to the atmosphere during production of CFCs, with an additional 10 Gg/yr release from the other uses. Eastern Europe is not included in these figures and may contribute substantially to the second category. Chemical plant losses are unlikely to be seasonal, but the diverse secondary applications of CT reflect small end-users where evaporative losses may respond to temperature. The vapor pressure of CT doubles as the temperature increases from 5 to 20 °C, and increased evaporative losses may be the cause of the peak summer emissions of CT.

3.5. *Nitrous Oxide*

Correlation of enhanced levels of N_2O with halocarbons at Adrigole is weak and requires averaging of the entire ALE record. Consequently, trends and seasonal patterns are not derived. The data indicate that 30 ± 10 molecules of N_2O are emitted for each molecule of CFC-11 released over Europe. This result does not depend on a few events; individual years show similar ratios.

4. Meteorology of Pollution Events

Examination of the meteorology over Europe preceding major episodes at Adrigole gives information about the immediate history of air containing enhanced concentrations of halocarbons. The temporal sequence of sea level pressure maps shown here provides a view of the atmospheric circulation which can be used to test the chemical climatology of three-dimensional tracer models. For example, summer and winter produce statistically different pollution events (see Figure 4), and the critical questions are then: Do the seasonal patterns reflect different meteorological conditions? Do they represent the sampling of diverse source regions in Europe? The goal here is not to forecast individual events, but to identify the typical patterns in sea level pressure associated with high levels of CFCs in the boundary layer over Ireland.

In this section the statistical correlative approach is replaced by a linear composite of specific events. The time (GMT) of an event is identified either by the peak in halocarbon concentrations or by the middle point of the event. The entire ALE record from Adrigole has been examined subjectively, and major events which can be defined clearly in terms of elevated levels of halocarbons are identified in Table III. This approach loses the objectivity inherent to the correlative techniques, but does allow for a linear superposition of concentrations and weather patterns which can be more easily interpreted.

A set of 20 summer pollution events and a set of 24 winter events have

Table III.   Midpoint of Adrigole pollution events

Year	Month	Day	Hour	Note	Year	Month	Day	Hour	Note
1978	7	12	0	s	1981	1	30	12	w
	7	14	16	s		2	14	12	w
	9	22	12	s		2	18	8	w
	10	14	12			2	24	0	w
	10	30	0			2	27	0	w
	11	5	20	w		4	4	20	
	12	21	12	w		4	11	0	
1979	1	22	12	w		4	15	4	
	2	6	16	w		8	31	4	s
	2	10	16	w		9	6	20	s
	3	19	12	w		11	7	8	w
	4	8	4			12	23	0	w
	4	11	4			12	30	12	w
	6	3	12	s	1982	1	9	4	w
	8	30	4	s		1	15	8	w
	9	29	20	s		2	18	8	w
	10	14	4			3	27	8	w
1980	1	27	4	w		4	1	12	w
	3	18	20	w		5	11	16	s
	5	2	0	s		5	31	4	s
	5	7	12	s		7	13	8	s
	5	11	4	s		7	22	4	s
	5	16	4	s		7	31	8	s
	6	13	4	s		9	17	12	s
	8	26	16	s		11	8	8	w
	11	2	12	w		12	3	4	w
					1983	2	16	8	
						2	20	4	
						2	23	12	
						4	22	4	
						6	20	20	

'w' denotes events used in winter composite; 's', in summer composite.

been designated in Table III in order to define a composite event for both seasons. The month of February 1981 stands out for its periodic repetition of pollution episodes, which were also recorded at Harwell, England (Brice *et al.*, 1982). The list is by no means comprehensive since there are occasional gaps in the ALE data. Also, winter and summer events in 1983 have not been included because data for sea level pressure were available only through 1982 (W. M. L. Spangler and R. L. Jenne, *Daily Sea Level Pressure Grids, Northern Hemisphere, Jan 1899–Dec 1982*, NCAR, priv. comm., 1986). First, the compositing of the trace gas measurements is presented, and then the corresponding pressure fields are shown.

4.1. *Composites of ALE Data*

The time series of ALE measurements for two winter events, centered on 15 January 1982 and 18 February 1982, are shown in Figure 9. The observations are binned with 4-hour resolution, and concentrations represent residuals with the linear trend (Table I) removed. Both episodes have a duration of several days and happen to have a small peak in halocarbons preceding the main event. The halocarbons clearly co-vary, with the possible exception of CT in the first event. The correlation of N_2O cannot be seen in the individual events because of inherent variance in the measurements at the 3 ppb level.

The winter composite, shown in Figure 10, is derived by averaging the 24 individual series as a function of time lag from the center of the event. The average winter event has a width of about 3 days with peak elevations of about 38 ppt(11s), 40 ppt(11p), 44 ppt(12p), 64 ppt(MCs), 8 ppt(CTs) and ~1 ppb(N_2O). The N_2O enhancement in the composite series would be more apparent if N_2O concentrations in Figure 10 were averaged with a 24 h running filter. These enhancements are consistent with the relative sources derived from the correlative analysis in the previous sections and given in Table II.

The time series from two summer events, centered on 13 June 1980 and 13 July 1982, are shown in Figure 11. The first period is an example of a long-
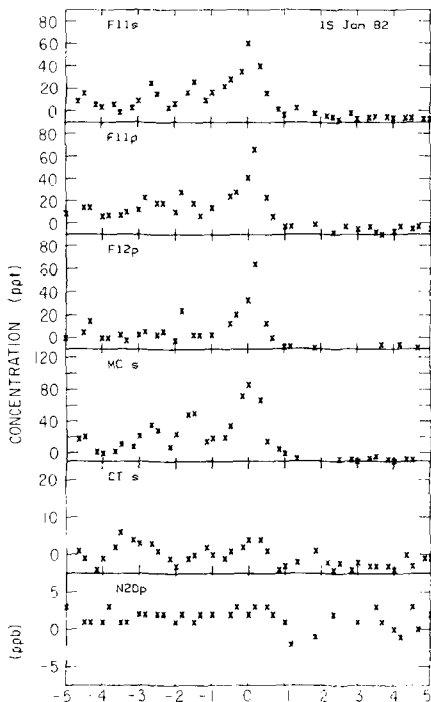

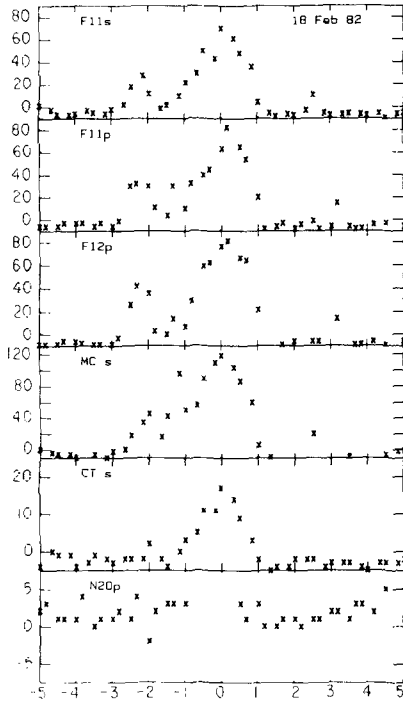Fig. 9a. ALE Adrigole time series centered on 0800 H 15 January 1982.

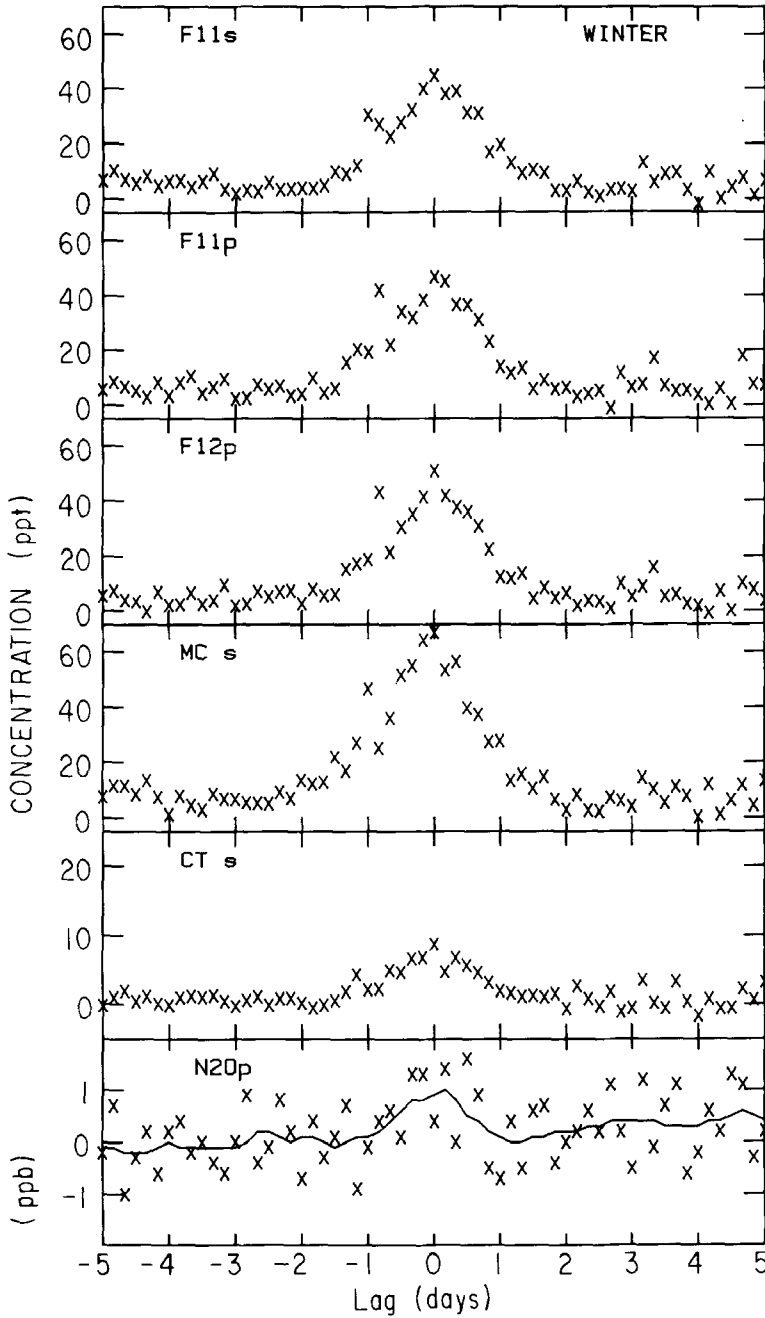Fig. 9b. ALE Adrigole time series centered on 0800 H 18 February 1982.

Fig. 10. Composite of 24 winter pollution events at Adrigole. The solid line indicates the one-day running average of the N_2O composite.
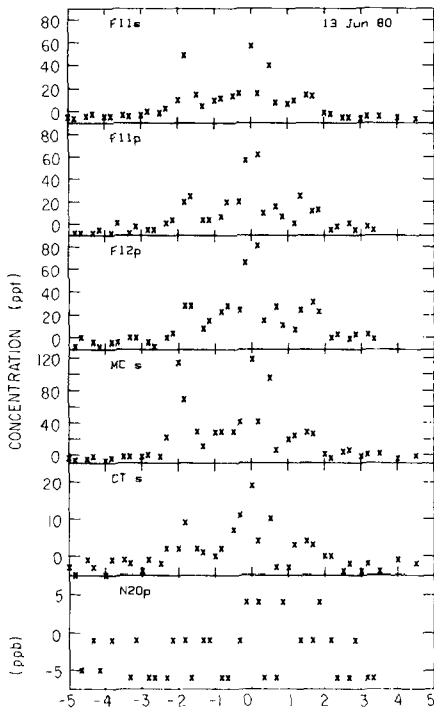
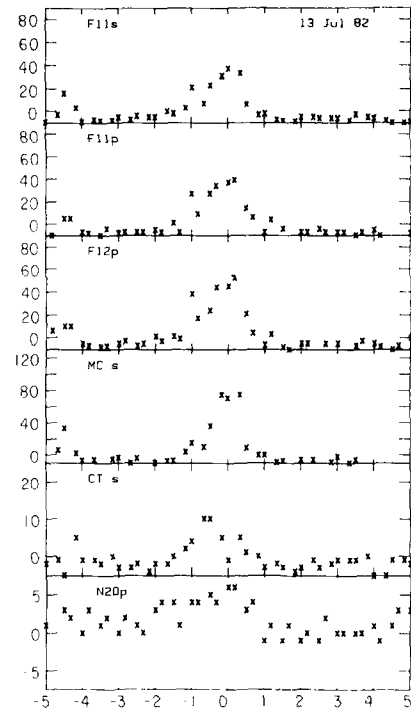Fig. 11a. ALE Adrigole time series centered on 0400 H 13 June 1980.

Fig. 11b. ALE Adrigole time series centered on 0800 H 13 July 1982.

lived summer pollution episode with consistently elevated halocarbon levels for 5 days. The summer composite is shown in Figure 12. Relative enhancements of the different halocarbons during summer episodes are similar to the winter composite. Quantitative results at the ±20% level, however, are difficult to extract from these composites. They cannot be easily used to verify the seasonality of sources derived previously except for the only obvious difference between composites: the larger amplitude of CT during the summer episodes.

4.2. Composites of Sea Level Pressures

Maps of sea level pressure over Europe and the North Atlantic Ocean are shown in Figures 13–17 for the periods discussed above. Background conditions for summer and winter were defined by averaging the pressures from all summer days and all winter days for the period 1978 through 1982. These maps, shown in Figure 13, illustrate the universal pattern of high pressure over the subtropical Atlantic and low pressure centered over Iceland. During winter the North Atlantic low is deeper and more extended, and a high appears over the Urals in western Asia.

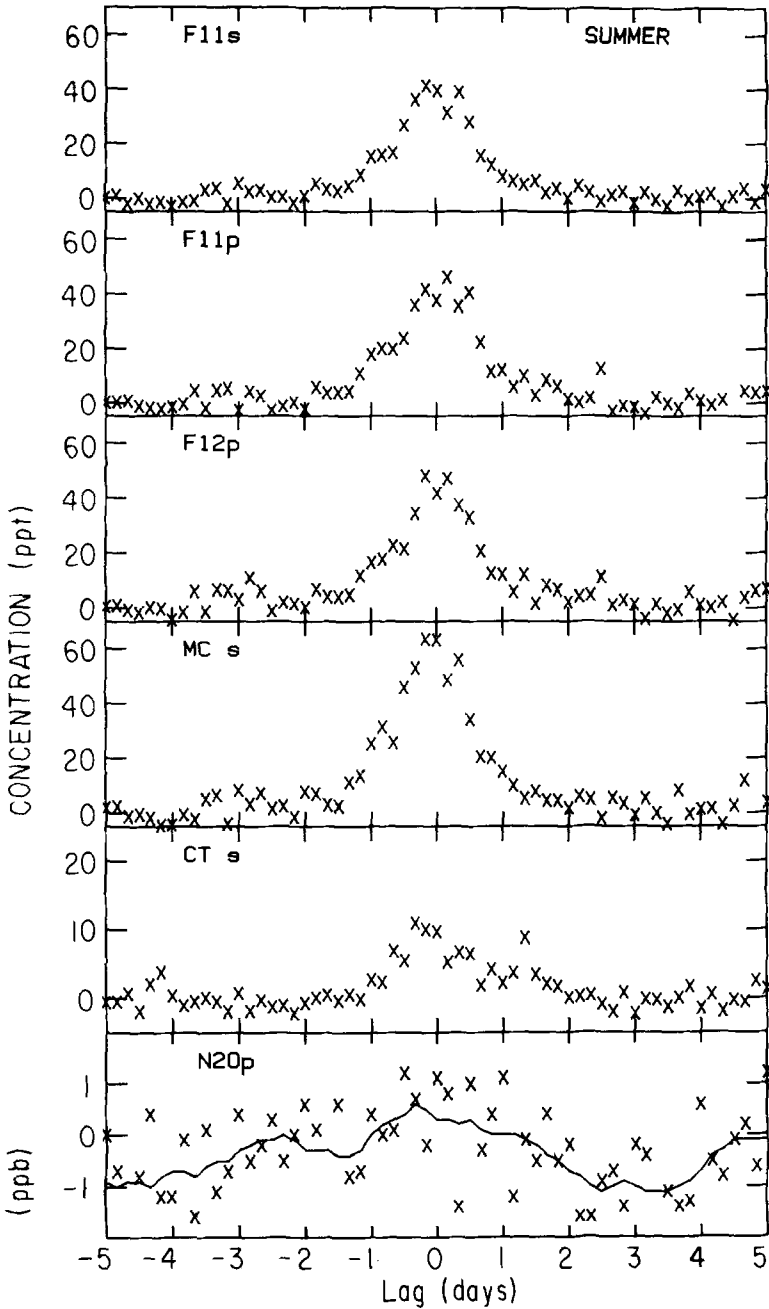The time series of sea level pressure maps for the winter episodes of 15

Fig. 12. Composite of 20 summer pollution events at Adrigole. The solid line indicates the one-day running average of the N_2O composite.
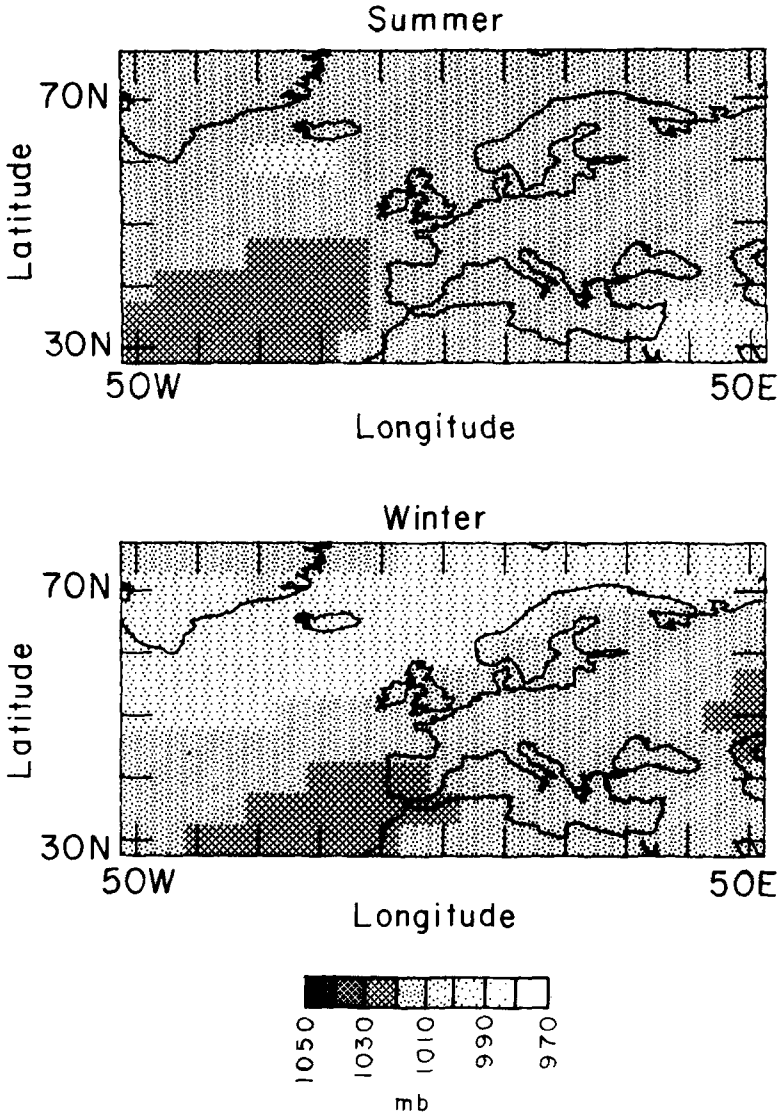
Summer

Winter

Fig. 13. Sea level pressure maps for average summer (top) and winter (bottom) conditions.

January 1982 and 18 February 1982 are shown respectively in Figures 14a and
14b, beginning 3 days before the event and ending 3 days after. The January
episode occurs as a deep low develops immediately to the west of Ireland
and a high ('blocking anticyclone') builds over Eastern Europe. These condi-
tions lead to southeasterly flow and to the backwash of European air over
Adrigole (Pack *et al.*, 1977; Brice *et al.*, 1982). The February event
is more complex and is not amenable to such a simple interpretation. The
composite map from the 24 winter episodes is shown in Figure 15. At ±3 days
from the center of the composite event, the map closely resembles the winter

control (Figure 13). By day −2 a high pressure region builds rapidly over Scandinavia and central Europe; this pairs with a low over the Atlantic, west of Ireland; the pattern fades by day +2. At the center of the episode (day 0), the air passing over Adrigole has circulated through Eastern Europe, central Europe and England.

The summer meteorology is clearly different from that of winter. Pressure maps for the two individual summer episodes are shown in Figure 16. The only obvious similarity between these two is the appearance of a high pressure region north of the British Isles. The summer composite is quite asymmetrical about the center of the episode (day 0). A high building over the British Isles is visible already by day −3, and pressures have returned to the summer control conditions by day +2. As the high strengthens and moves northward, the circulation over Adrigole will change from predominantly oceanic origin to continental. An interesting feature of summer episodes is that they may be predictable several days in advance.

The composite pressure maps describing halocarbon pollution episodes at Adrigole provide a new test for the chemical climatologies simulated by three-dimensional tracer models (e.g., Prather *et al.*, 1987). They clearly identify Europe as the source of halocarbons at Adrigole and support the assertion that the pollution events integrate over a substantial fraction of the continent. Nevertheless, the composites are only averages, cannot describe individual pollution episodes, and may not be representative of all cases (such as the 18 February 1982 event).

The difference in climatologies, between summer and winter, leaves open the possibility that seasonal variations in relative sources inferred above may actually represent alternate regions of Europe emitting a different mix of halocarbons. The interpretation preferred here is that the sampling of European emission at Adrigole is comprehensive and representative: (1) the time scale of pollution (±5 day lags) implies that the correlated emissions occur over large scales; (2) the development of events implies that the source of Adrigole air sweeps over most all of Europe during both summer and winter; and (3) the pressure patterns clearly implicate the main industrial regions of Europe as the source, rather than Scandinavia, Africa, or the Western Hemisphere. These points may be tested with three-dimensional tracer models which are able to reproduce the chemical climatology along with the seasonal characteristics of the meteorology.

5. Regional and Global Budgets

The correlative observations from Adrigole yield relative sources for the halocarbons and nitrous oxide without use of a detailed model for the atmospheric circulation and mxing of chemical tracers. A measure of the absolute emissions from Europe would require calibrated three-dimensional tracer models,
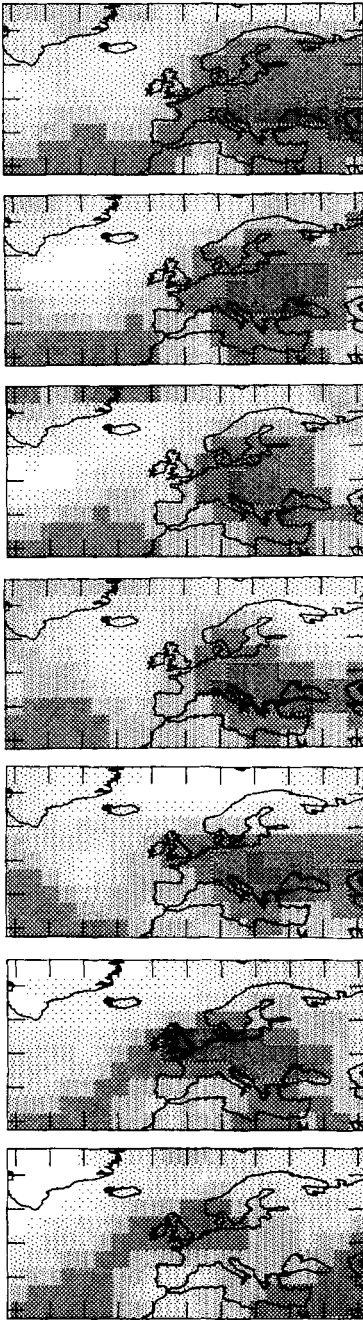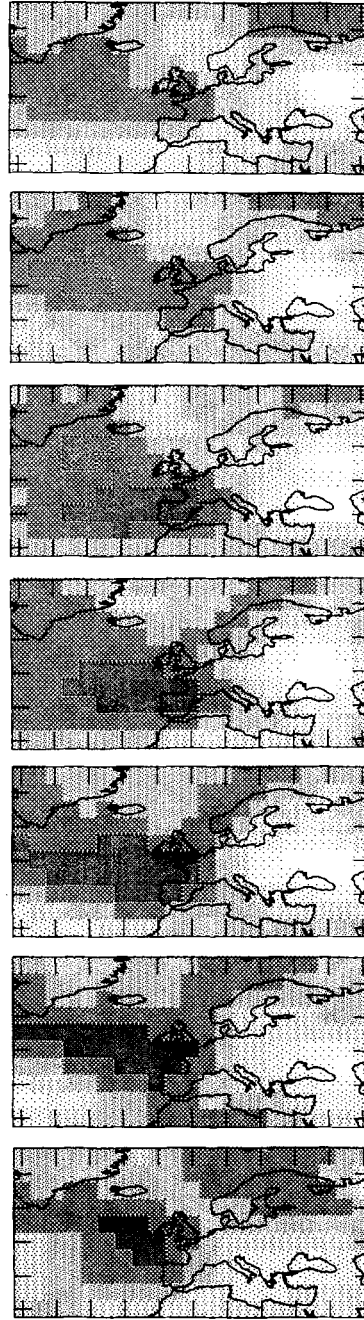
Fig. 14a.   Sea level pressure maps for the week 12–18 January 1982. Day numbers preceding (–3, –2, –1) and following (+1, +2, +3) the center of the pollution episode (day 0 = 15 January 1982) are denoted by each map.

Fig. 14b.   Sea level pressure maps for the week 15–21 February 1982. Day numbers preceding (–3, –2, –1) and following (+1, +2, +3) the center of the pollution episode (day 0 = 18 February 1982) are denoted by each map.

WINTER

+3

+2

+1

0

-1

-2

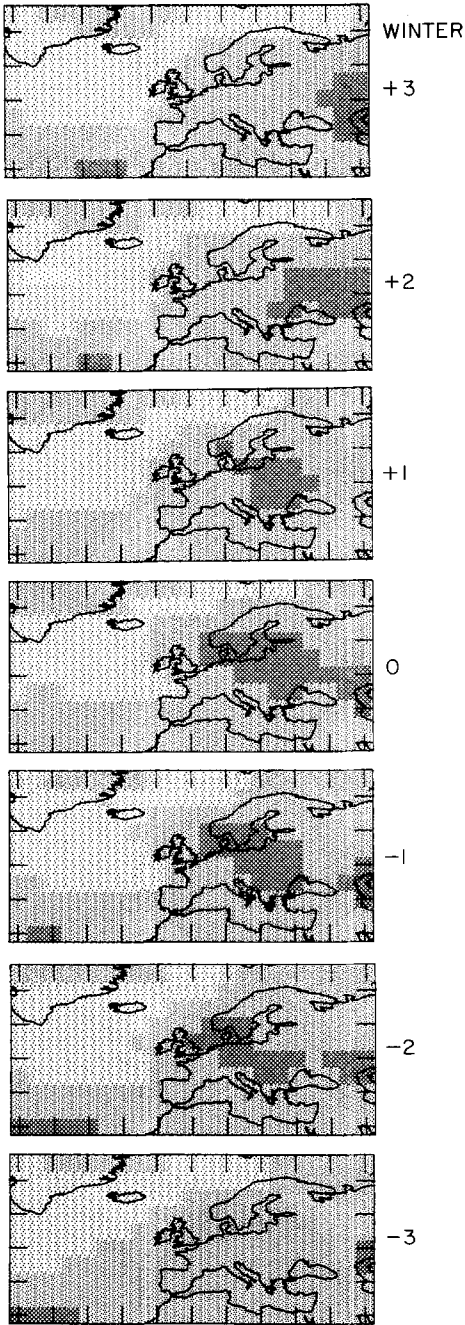-3

SUMMER

+3

+2

+1

0

-1

-2

-3

Fig. 15.   Composite of sea level pressure maps
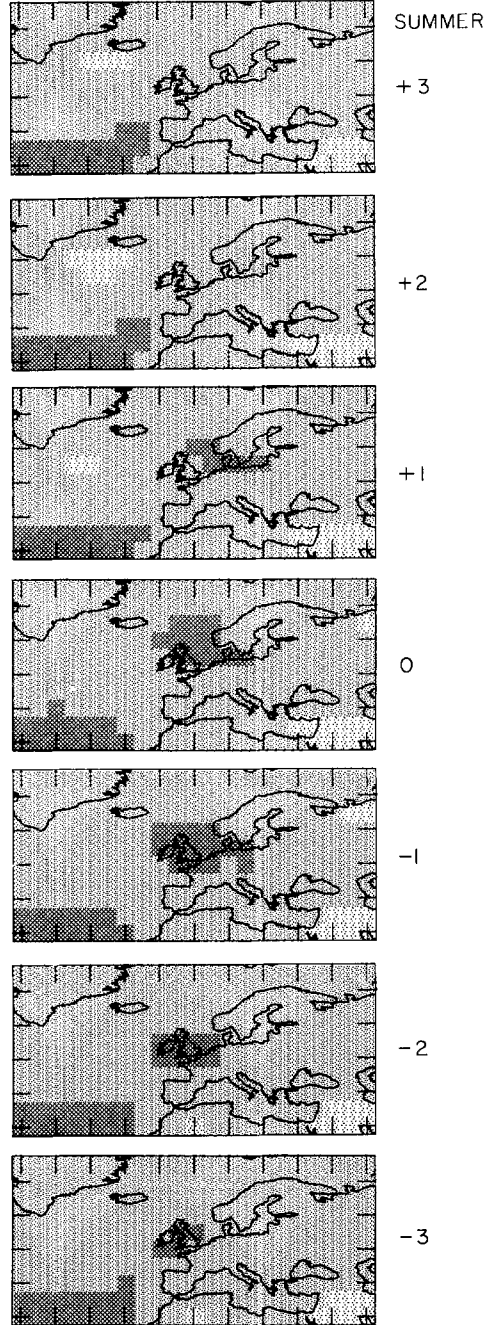for 24 winter pollution episodes at Adrigole.

Fig. 17.   Composite of sea level pressure maps
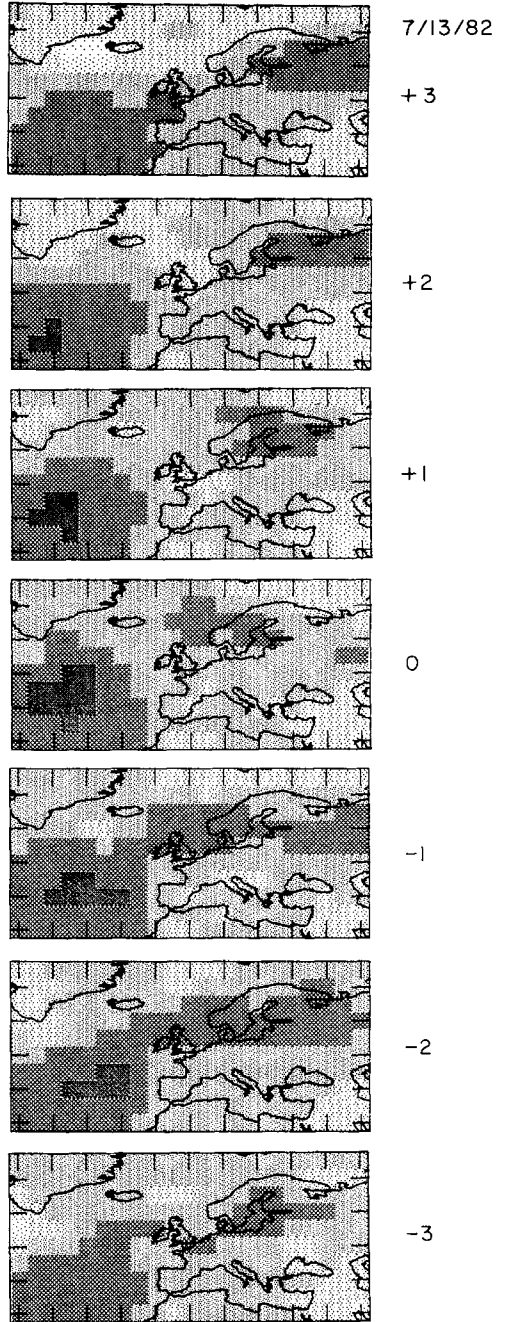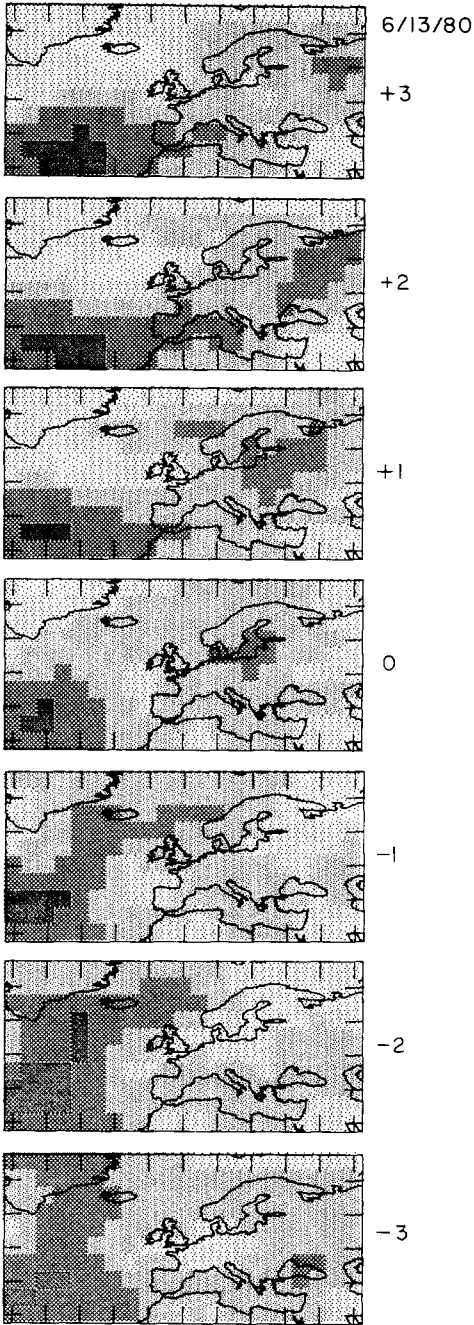for 20 summer pollution episodes at Adrigole.

Fig. 16a. Sea level pressure maps for the week 10–16 June 1980. Day numbers preceding (–3, –2, –1) and following (+1, +2, +3) the center of the pollution episode (day 0 = 18 June 1980) are denoted by each map.

Fig. 16b. Sea level pressure maps for the week 10–16 July 1982. Day numbers preceding (–3, –2, –1) and following (+1, +2, +3) the center of the pollution episode (day 0 = 13 July 1982) are denoted by each map.

which currently are under development (GTC, 1986). This analysis focusses on the consistency between reported sources and measured correlations during pollution episodes.

Estimates of global and European releases of the ALE gases during the period 1978–1983 are given in Table IV. Values are derived from a variety of sources, ranging from ALE estimates of the global budgets to reports of sales by the chemical industry (CEFIC, 1985; CMA, 1985; see also WMO, 1986). Sources of N_2O from combustion of nitrogen-rich fuel (mainly coal) are based on the analysis of Hao *et al.* (1987). The relative sources given in Table IV are in units of g(gas)/g(CFC-11); the observed molar ratios of Table II have been converted to mass ratios. Results derived here from the ALE data are in clear disagreement with the budgetary estimates for halocarbon use in Europe.

Emission of CFC-12 relative to CFC-11 is estimated to be 1.42 g(12)/g(11) globally, with only half that value, 0.78, for Europe. The observed ratio at Adrigole, 0.95, exceeds budgetary estimates, but is still less than the global average. A similar situation applies to methyl chloroform: the global ratio, 2.1 g(MC)/g(11), is twice as large as the European value of 1.02; and the observed ratio, 1.48, falls between the two. According to the chemical industry, Europe is a disproportionately large user of CFC-11 (more than 1/2 of the global budget) relative to other halocarbons (less than 1/3 of the global budgets for 12 and MC). Values used here for European sales of MC have been corroborated recently (P.M. Midgley, priv. comm., 1987). Therefore, a plausible explanation of this discrepancy would be the reduction in CFC-11 emissions in Europe by 25% through export goods such as aerosols (45% of total use). The inferred emissions of carbon tetrachloride also cannot be explained by the industrial losses and solvent use reported for Western Europe, but in this case, they are likely to include significant contributions from Eastern Europe. The European source of N_2O, 0.8 Tg(N)/yr, represents 25% of the global emissions associated with combustion (Hao *et al.*, 1987) and 10% of the integrated stratospheric losses.

Table IV.   Estimated global and regional sources (Gg/yr) of halocarbons and nitrous oxide for the period 1978–1983

Gas		Global	g/g(11)	Europe	g/g(11)	Observed
$CFCl_3$	(11)	265		153		
CF_2Cl_2	(12)	375	1.42	120	0.78	0.95
CH_3CCl_3	(MC)	550	2.1	156	1.02	1.48
CCl_4	(CT)	120	0.45	20	0.13	0.25
N_2O		3200	12.0			5

Units are Gg (10^9 g) per year for halocarbons and Gg(N)/yr for N_2O.
Global emissions for halocarbons are from the ALE analyses (see also WMO 1986); N_2O estimates are from Hao *et al.* (1987).
European emissions include Australia, New Zealand and South Africa (CEFIC, 1985).
Observed ratios (g/g) are derived from molar ratios in Table II.

An important priority for future measurements is to expand and refine the N_2O data and to include correlative CH_4 observations. Such a program would help define the globally important sources of these gases associated with human activity in Europe and the rest of the world. Of equal importance is the inclusion of new chemical species important to climate and air quality such as CFC-113, CFC-22, the halons, and non-methane hydrocarbons. Twice-daily sampling for at least three years would be required to produce a useful chemical climatology for these gases at a site like Adrigole.

Acknowledgements

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