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Some measurements of ground level NO, NO_2 and O_3 concentrations at an unpolluted maritime site

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ABSTRACT

Concentrations of NO, NO_2 and O_3 were measured at ground level at a coastal location in S.W. Ireland, using continuous, chemiluminescence analysis. The results confirm previous measurements of very low background concentrations of nitrogen oxides in background maritime air, $\leqslant$0.2 ppb for NO and 0.4 ppb for NO_2. The transport and removal of NO_2 in a continental air mass is also demonstrated.

In a recent paper we have reported measurements of ground level ozone concentrations at rural locations on an E-W trajectory over the Southern British Isles (Cox et al., 1975). Using measurements of trichlorofluoromethane as an air mass tracer, evidence was found for transport of photochemically produced ozone from the region of emission of the precursor pollutants (nitrogen oxides and hydrocarbons) to remote rural locations. In order to provide more information on the concentration levels and movement of trace gas pollutants in the lower troposphere, the measurements programme has been extended to include the nitrogen oxides NO and NO_2. The chief objectives were to establish the background concentrations of NO and NO_2 at a remote maritime site in S.W. Ireland and to investigate possible transport of NO_x in polluted air masses arriving at this site from continental Europe. The results obtained in 1974 are described in this paper.

1. Site, instrumentation and data collection

The measurements were made at Adrigole, Co. Cork, Eire (51°40′ N 9°45′ W) which is situated on the N side of Bantry Bay, approximately 300 m from the shore. Ambient air was sampled at a height of 2 m above the ground through PTFE tubing. The only local source of NO and NO_2 was very light vehicular traffic passing 50 m from the sampling site and ships passing to and from the oil terminal located at the head of Bantry Bay.

The chemiluminescence instrument for measurement of ozone and the automatic gas-chromatographic system for $CFCl_3$ and other halocarbons have been described (Cox et al., 1975). The nitrogen oxides were also detected by chemiluminescence using a commercial instrument (TECO Model 14B) based on the chemiluminescent reaction of NO with ozone. As with other instruments of this type, NO and total "NO_x" was measured, with programmed interchange between the two modes every 40 seconds. On the present instrument the total NO_x signal was obtained by passage of the sample gas through a stainless steel convertor heated to 680 °C. At this temperature response to NH_3 was insignificant. Most other gaseous nitrogen compounds will be detected in this mode. Tests showed that the response to nitric acid was very low and irreproducible, however, and this is thought to be due to loss of HNO_3 on the sample lines. Spot gas-chromatographic measurements showed that peroxyacetylnitrate concentrations in ambient air at Adrigole were extremely low (<0.1 ppb). It is believed therefore that most of the difference in signal between the NO and NO_x modes was due to nitrogen dioxide and will subsequently be referred to as such.

The output from the NO and NO_x channels of the instrument was sampled into a sensitive ADC and logged on punch tape every 15 minutes, together with the time and the ozone concen-

tration. To overcome problems due to thermal drift in the photomultiplier current from the chemiluminescence detector, the instrument was operated without electrical "back off" of the dark current. Instead the dark current was recorded automatically once per hour by switching off the voltage supply to the ozone generator. The recorded dark current was subtracted from the NO and NO_x recordings in the previous 60 min to obtain the chemiluminescence signal. The response of the entire system was calibrated after setting up, using a standard mixture containing 1.5 ppm NO in pure nitrogen. The absolute limit of detection of the system was approximately 0.2 ppb for NO and NO_2.

After operating the instrument for a period of time it was noted that the signal in the NO channel never dropped below a value of approximately 1.5 ppb, even when the NO_2 was practically negligible and ambient ozone was present in large excess. This background signal in the NO mode is evidently not due to nitric oxide at all since it was present when purified N_2 was sampled through various adsorbents and also when O_3 at concentrations of 1–10 ppm was sampled. When high concentrations of ozone were sampled the signal increased. The chemiluminescence in the absence of NO almost certainly arises from the decomposition of ozone on the surfaces of the reaction cell. The phenomenon is often observed by operators of O_3–NO_x chemiluminescence analysers, but rarely reported; when ambient NO concentrations are low it severely restricts the accuracy with which NO can be measured.

A few analyses for NO_2 using a spectrophotometric method described by Levaggi et al. (1973) were made at Adrigole. The samples were collected over 12-h periods by drawing air at 500 cm^3 min^{-1} through a tube filled with firebrick impregnated with triethanolamine. The trapped NO_2 was extracted in aqueous alkali and measured colorimetrically using a Griess-type reagent. An absorbance of 1% corresponded to 0.4 ppb NO_2.

In this work we also refer to data for NO_x and

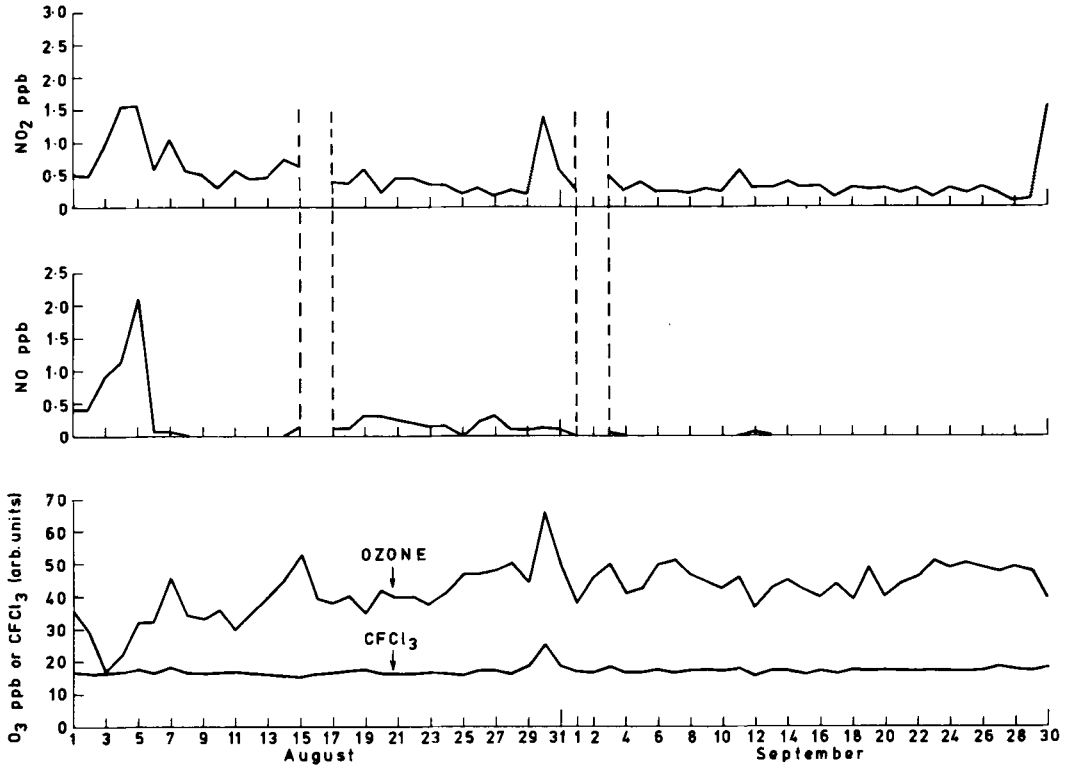

Fig. 1. Daily average ozone, nitric oxide, nitrogen dioxide and trichlorofluoromethane concentrations at Adrigole, August–September 1974.

ozone recorded at Harwell, Oxfordshire (51°35′N 1°19′W). The NO_x measurements made at this site were obtained using an identical chemiluminescence instrument to that used in Ireland, except that the NO_x convertor was of the molybdenum steel type operated at 450 °C. The ozone and meteorological data logging system at Harwell are described elsewhere (Cox et al., 1975 and 1976).

2. Results and discussion

Measurements of NO, NO_2, O_3 and $CFCl_3$ were made during July–November 1974. An essentially complete time series was obtained during the months of August and September and the daily mean values are presented graphically in Fig. 1. The steady, constant $CFCl_3$ concentration over the two month period shows that the air masses advecting over S.W. Ireland during these months were mainly of background tropospheric origin. Only on August 30–31 was there a noticeable increase in $CFCl_3$ above the background level indicating an air mass of continental origin. The ozone recordings showed a similar pattern, i.e. constant at 40–50 ppb for most of the time, but with a noticeable peak on August 30. There was also a period of low O_3 concentration at the beginning of August and this corresponded to higher than normal concentrations of both NO and NO_2. A local source of pollution is indicated here but it has not been located. For the remainder of the period the NO concentration was close to the minimum detectable level (see below). Measurable concentrations of NO_2 were present throughout the period of monitoring. Normally NO_2 was between 0.2 and 0.5 ppb; a noticeable peak was observed on August 30, however, when the $CFCl_3$ data indicated a shift in the air mass origin. The recordings over this period will be considered in more detail later.

3. Background nitric oxide concentration

The nitric oxide recordings were corrected for the background signal from the ozonator on the assumption that during night time, because the ambient ozone was always in excess, the true nitric oxide concentration was in fact zero. The arithmetic mean value from all of the NO data for 1800 hrs–0600 hrs was 1.69 ± 0.13[1] ppb. This was taken as the signal due to the ozonator, which was assumed to be constant throughout the period. This signal was subtracted from the observed readings in the NO channel to obtain the NO concentrations given in Fig. 1.

The mean value of all the daytime NO readings was 1.81 ± 0.10 and the mean daytime nitric oxide concentration was therefore 0.12 ± 0.13 ppb. Although this mean concentration was not significantly greater than the "noise" on our recordings, when averaged over more than 1000 individual pairs of measurements, the NO concentration was significantly above zero according to the "t" test. It is concluded therefore that in background tropospheric air over the north Atlantic, the NO concentration is $\leqslant 0.2$ ppb. Similar values have been measured over the north Pacific ocean by Briehl et al. (1974), using an airborne chemiluminescence NO monitor. These results would tend to confirm the estimate of Robinson & Robbins (1971) for the mean air-concentration of NO over the earth's maritime and polar regions, 0.2 ppb.

4. Background nitrogen dioxide concentrations

Since the NO_2 readings are obtained from the difference in the NO_x and NO channels, they are not expected to be subject to uncertainty due to signals from the ozonator. To check this, the difference between the NO_x and NO channels at the hourly "dark current" readings was analysed. 288 samples taken at random during the measurement period gave a mean value for this difference of 0.07 $\pm$ 0.20 ppb. Thus the "instrumental background" for NO_2 was insignificantly different from zero. Fig. 2 shows a log-probability plot of both the daily average and the maximum hourly average NO_2 concentrations for each day during the August–September monitoring period. Both sets of data show a curved plot, i.e. do not appear to obey a true log-normal distribution. This could be due to the presence of two distinct sources giving rise to different distribution curves. The flat curve at low concentrations is thought to reflect natural NO_2 in background tropospheric air. Superimposed on this is a steep curve originating from emission of NO_2 from local or regional anthropogenic sources. The

[1] Error limits are σ, the standard deviation.

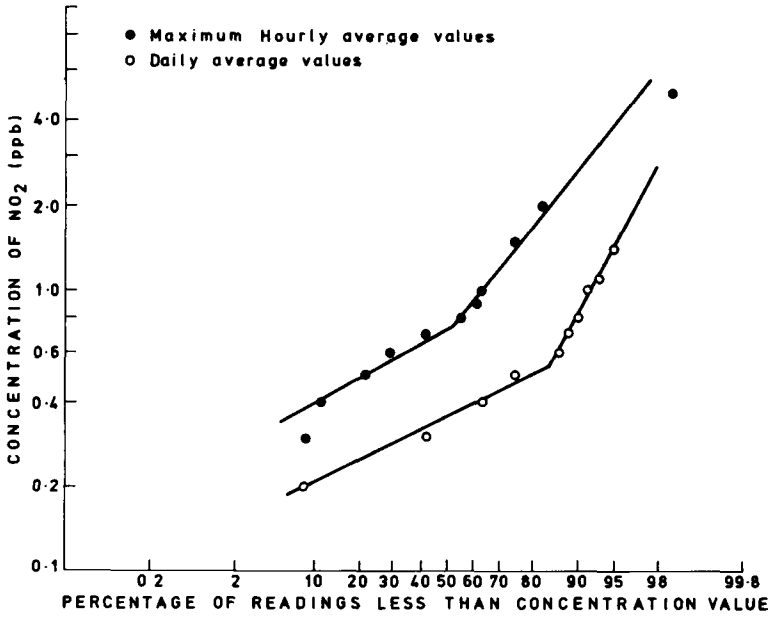

Fig. 2. Log-probability diagram for measured nitrogen dioxide concentrations, Adrigole, August–September 1974.

Table 1. *Results of colorimetric analysis for NO_2 in air samples collected at Adrigole, May 1974*

Date	Day/Night	NO_2 ppb
26–5	d	1.4
26–5	n	<0.2
27–5	d	1.0
27–5	n	0.7
28–5	d	0.5
28–5	n	0.6

mean = 0.70 ppb

geometric mean of the daily average concentrations is 0.34 ppb and of the maximum hourly values 0.80 ppb. The latter is expected to be higher than the mean of the daily average concentrations since in addition to instrumental noise the NO_2 concentrations will be modulated diurnally due to the photochemical process:

$$NO_2 + h\nu = NO + O$$
$$O + O_2 + M = O_3 + M$$
$$NO + O_3 = NO_2 + O_2$$

Table 1 shows the results of the colorimetric analysis of the NO_2 samples collected on the adsorbent. All samples were collected for 12 h either during the day or overnight. No obvious difference between daytime and nighttime is evident on these few results. The air masses were maritime-polar during the period of measurement and the results confirm the conclusion based on the chemiluminescence measurements, i.e. background NO_2 concentrations are substantially less than 1 ppb at this location.

There is rather more available information regarding background NO_2 compared to NO. Nearly all reports refer to measurements made using colorimetric wet-chemical methods, some of which have been subject to much criticism (Axelrod et al., 1976). In 1962, O'Connor reported measurements of NO_2 concentrations made in western Ireland which apparently showed a seasonal variation; 0.34 ppb Spring, 0.22 ppb Autumn. Our values are in remarkably good agreement with these values measured 15 years ago and also with the measurements of Junge (1957) on Hawaii, taken in 1956 ($\leqslant$1 ppb) and Lodge et al. in the mid Pacific in 1960 (95% of all samples <1 ppb). The recent suggestion (Goldman, 1975), based on data gathered on Hawaii, that the upper air background NO_2 concentration may have increased markedly since 1956 is in conflict with our measurements and is probably erroneous, as others have pointed out (Axelrod et al., 1976).

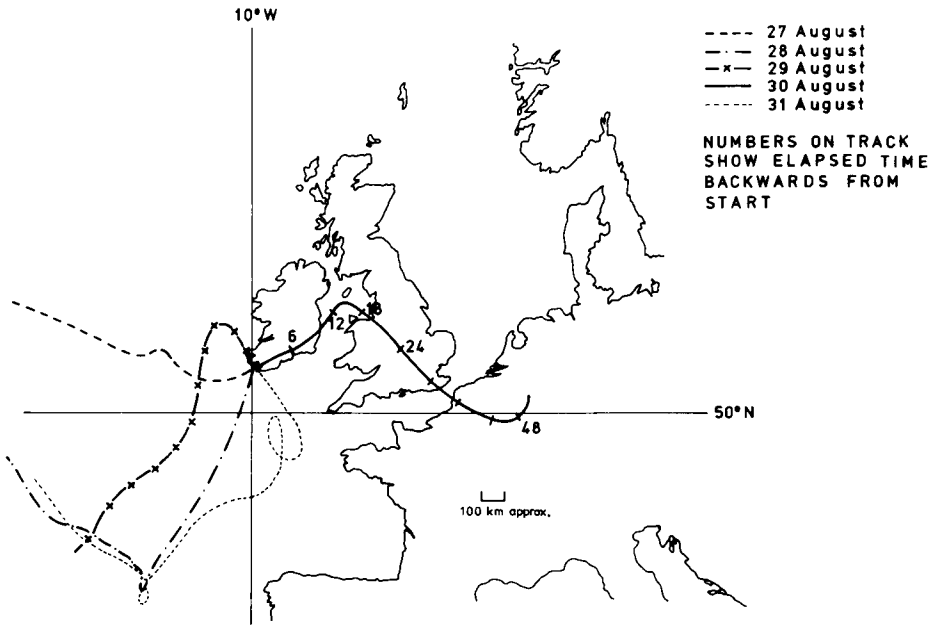

Fig. 3. Backtrack trajectories 1200 hrs August 27–31, 1974, Adrigole.

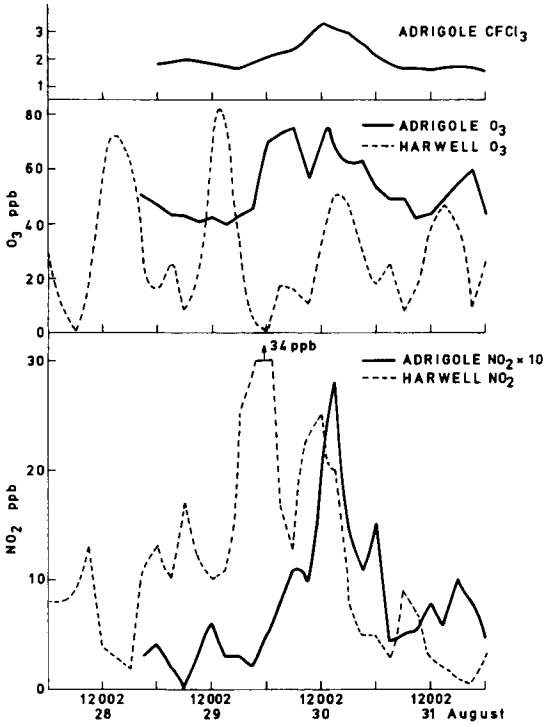

Fig. 4. Concentrations of nitrogen dioxide, ozone and trichlorofluoromethane at Adrigole and Harwell, August 28–31, 1974.

Robinson & Robbins (1971) suggested a value of 0.5 ppb for mean air concentration of NO_2 in maritime and polar regions and our results lend support to this.

5. Transport of NO_2 in polluted air

The $CFCl_3$ measurements indicated only one incidence when polluted air advected over S.W. Ireland, on 30th August when the NO_2 concentration showed a distinct increase over the background levels. Backtrack trajectories for 1200 hrs GMT computed in the same manner as that described previously (Cox et al., 1975), for the period August 27–31, are shown in Fig. 3. It will be seen that all air masses were maritime in origin except for that arriving on August 30. The latter air mass had passed over the southern English Midlands 24 h previously and over the lower Rhine valley 48 h previously. The detailed time histories of the O_3 and NO_2 concentrations for Adrigole and Harwell for August 28–31 are shown in Fig. 4.

Comparing firstly the ozone levels we see that maximum ozone concentrations reached at both sites were similar but the Harwell data showed a marked diurnal variation which was absent at Adrigole. The daytime O_3 concentrations were elevated at Harwell on August 28 and 29, but not on the 30th or 31st. At Adrigole O_3 was only significantly above background on August 30, and the backtrack trajectory and $CFCl_3$ data are consistent with an anthropogenic source, as we have postulated before.

The NO_2 concentrations at Harwell were at least an order of magnitude higher than at Adrigole. Assuming the Harwell data to be representative of the air present over the southern English Midlands at a given time it will be seen with reference to the backtrack trajectory for 12 hrs August 30 that the NO_2 concentration in the air mass had declined from 10 ppb at 1200 hrs on August 29 to 2 ppb at Adrigole 24 h later. This decline is presumably due to dilution and/or physico chemical removal processes. In this respect it is of interest to note that the half-life for oxidation of NO_2 to nitric acid by reaction with hydroxyl radicals

$$OH + NO_2 (+M) = HNO_3$$

is about 10 h, based on the consensus value for the rate constant at ambient temperatures (1.0×10^{-11} cm^{-3} $molecule^{-1}$ s^{-1}, Hampson & Garvin, 1975) and observed hydroxyl radical concentrations (3×10^6 molecules cm^{-3}) in the surface atmosphere in N.W. Europe (Perner et al., 1976). Thus gas-phase oxidation alone could adequately explain the apparent loss of NO_2 from the air mass under consideration. However, there is insufficient observational information in the present work to draw any firm conclusions regarding the overall lifetime and fate of NO_2 in continental air.

The results confirm that continental air contains more NO_2 than maritime air, as has been found by others (Axelrod, 1976; Breeding et al. 1973). The geometric mean NO_2 concentration at Harwell was 4.7 ppb from measurements taken over 5 months in the spring and summer, 1974 (Cox et al., 1976). There was undoubtedly some influence of motor-traffic sources on these measurements, however. We are unable to provide any estimate of the relative proportions of anthropogenic and natural NO_2 in continental air masses, either in S. England or after transport to S.W. Ireland.

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НЕКОТОРЫЕ ИЗМЕРЕНИЯ КОНЦЕНТРАЦИЙ NO, NO_2 и O_3 НА ПОВЕРХНОСТИ ЗЕМЛИ В НЕЗАГРЯЗНЕННОМ МОРСКОМ МЕСТЕ

Измерялись концентрации NO, NO_2 и O_3 на поверхности земли на берегу моря в юго-западной части Ирландии. При этом использовался непрерывный хемилюминисцентный анализ. Результаты подтверждают данные предыдущих измерений очень низких фоновых концентраций окислов азота в фоновом морском воздухе-меньше $0.2 \cdot 10^{-9}$ для NO и $0.4 \cdot 10^{-9}$ для NO_2. Также определены перенос и удаление NO_2 в континентальной воздушной массе.