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BALANCE OF THE TROPOSPHERIC OZONE AND ITS RELATION TO STRATOSPHERIC INTRUSIONS INDICATED BY COSMOGENIC RADIONUCLIDES

Technical Progress Report

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DISCLAIMER

ABSTRACT

The study of the balance of the tropospheric ozone as a function of atmospheric pollutants and tropospheric transport has been started.

Continuous recordings are available of ozone concentration at three levels (3000 m, 1800 m, and 700 m a.s.l.) of the concentration of the cosmogenic radionuclides Be7, P32, P33, and the CO_2-concentration.

Ozone concentrations > 70 ppb have been observed after stratospheric intrusions as well as in consequence of photochemical reactions in the boundary layer.

An observation sequence, covering now a period of 20 months, is presented of the stratospheric aerosol layer by means of lidar monitoring. Possible errors in the measuring technique are discussed.

A filter photospectrometer for the measurement of the atmospheric total ozone is described, its suitability is checked by a direct intercomparison with a Dobson spectrometer.

1. General Remarks

1.1. Scope of Work, Expenditure of Time and Funds

The research performed under DOE-Contract was in full agreement with the proposed research activities of Modification 8 and Mod. A001 of subject contract.

The full scope of work was performed. Time used by our staff and expenditure of funds were in accordance with the cost estimate in our proposal of July 22, 1977.

1.2. Essential Characteristics

The activities performed within the framework of subject contract can be subdivided according to the following aspects:

i. Continuous recording of the ozone concentration at three levels (Zugspitze 3000 m, Wank 1800 m, and Garmisch-Partenkirchen 700 m a.s.l.).

ii. Continuous aerosol sampling at the station Zugspitze, chemical separation of the cosmogenic radiocuclides Be7, P32, P33 and measurement of their concentration.

iii. Determination of the ozone profile in the boundary layer, assessment of the origin of high ozone concentrations (>70 ppb) by correlation with suitable tracers (Be7 for stratospheric influx, radon decay products for influx of tropospheric origin) and relevant meteorological parameters.

iv. Meteorological evaluation of the radiosonde ascents from eastern USA to eastern Europe for selected long-term periods, calculation of the isentropic trajectories to the measuring station Zugspitze, statistical evaluation

of the tropospheric flow conditions, scientific interpretation of the results.

v. Recording of the CO_2-concentration at the stations Wank and Garmisch-Partenkirchen.

vi. Remote sensing of stratospheric aerosol layers.

Items i, ii, and v serve the purpose of data coverage in terms of the overall subject within the scope of the research project. In this respect the stations Zugspitze and Wank are of importance as bench-mark stations, the station Garmisch-Partenkirchen - in comparison to the mountain stations - is used as urban station.

Item iii represents a first step towards an exact balance of the tropospheric ozone. The question regarding the sources of the tropospheric ozone is handled in detail.

Studies as per v and vi serve to determine a possible affection of the free atmosphere by increased anthropogenic pollution.

Point iv covers the study of the tropospheric transport processes. The results will further our knowledge of the transport of the tropospheric ozone to the lower stratosphere and supplement the works performed on the stratospheric-tropospheric exchange under subject contract, including Mod. 8.

2. Routine Work

2.1. Measurement of the Tropospheric Ozone

The measurement of ozone concentration was continued without interruption at the stations Zugspitze, Wank, and Garmisch-Partenkirchen. No longer failures were experienced. The maintenance schedule set forth in the 76/77 Progress Report proved

a full success.

2.2. Measurement of the CO_2-Concentration

During the reporting period measurements of the CO_2-concentration could be started at the stations Wank and Garmisch-Partenkirchen. The instruments in operation (URAS, manufacturer Hartmann und Braun, Frankfurt) were found to be reliable and are easy to handle.

2.3. Aerosol Sampling and Measurement of the Radionuclide Activity

Aerosol sampling at the station Zugspitze and chemical processing of the samples were continued without any problems. Measurement of the activity of the radionuclide Be7 was carried on continuously. Due to a major malfunction of the liquid scintillation spectrometer the measurement of the radionuclides P32, P33, and S35 had to be interrupted for a longer period (Aug. - Oct. 77). The reason for the length of interruption was that the necessary spare parts were no longer available and thus the liquid scintillation spectrometer had to be completely reconstructed in its digital part.

3. Detailed Meteorological Analysis

The development of a climatology of stratospheric air intrusions was one of the objectives of this work. For this purpose a long-term observation of the transport processes in the troposphere to a given point of the earth's surface was performed to clarify the difference between transport processes on days with intrusions of stratospheric air and such without intrusions. The periods were selected in a manner that possible seasonal effects could fully be covered.

With regard to this aspect three long-term periods have been taken into consideration:

Period A: 20.02.1974 - 25.05.1974 (94 days)
Period B: 20.07.1974 - 20.09.1974 (62 days)
Period C: 01.10.1974 - 08.10.1974 (8 days)

The working material compiled with great expenditure of time (see Progress Report 76/77) is now in the process of being scientifically evaluated. Results will be presented in our Annual Report Part VIII.

4. Measurement of the Atmospheric Total Ozone

A commercial version of the prototype New Zealand ozone filter photometer (e.g. Matthews et al., 1974*); Basher and Matthews, 1977**) is being run at the Institute for several months. The instrument is specifically designed for the determination of the atmosphere's total ozone content using the well established solar ultraviolet spectrophotometric method.

The photometer measures the intensity of direct sunlight or zenith skylight at 6 wavelengths corresponding to the standard Dobson A, C, and D wavelength pairs. The bands are defined by 6 narrowband interference filters of high transmission. The filters are mounted on a rotating wheel so they are viewed cyclically. Since a complete cycle takes only 0.5 seconds, the 6 measurements are virtually simultaneous. For integration purposes any number of cycles between 1 and 300 can be chosen. To overcome a temperature dependence the rotating filter disc is enclosed in a thermostatically controlled chamber kept at $40 \pm 5^{\circ}C$ for an ambient temperature range of -10 to $35^{\circ}C$.

After having passed the individual filters the light affects a photomultiplier. The photomultiplier current controls an

*) W.A. Matthews, R.E. Basher, and G.J. Fraser, Pure and Appl. Geophys., Vol. 112/6, 931 (1974)

**) R.E. Basher and W.A. Matthews, J.Appl.Meteor., 16, 795 (1977)

oscillator which in turn produces a train of fast, shaped pulses the frequency of which is directly proportional to the current input and, therefore, to the light intensity.

The measurement process is semi-automatic, being initiated by the push of a button and completed a short time later with the display of the results on a digital readout. All six intensity measurements are temporarily stored and are available for display until the next measurement set is initiated. Permanent recording of measurement is manual.

The continuous alignment of the device on the sun is accomplished by an automatic tracking system.

An inherent drawback of this instrumental type originates in the difficulty of accurately despositing the many very thin layers that comprise an interference filter, actually it is not possible to construct filters to the level of precision, repeatability or uniformity ideally desired for the filter instrument (Basher and Matthews, 1977). This means that individual filter instruments may differ among themselves and with Dobson instruments within a few per cent. Therefore, in order to get accurate total ozone measurements any device must be compared with a reliable Dobson instrument. A several days lasting direct intercomparison in spring 1978 at Arosa, Switzerland, showed that our filter instrument was yielding too low ozone values (X) compared to those of the Arosa-standard Dobson (D 101). The ratio of total ozone amount received by both instruments via the AD-wavelength pairs was determined to X_{AD} (filter)/X_{AD} (D101) = 0.933 ± 0.004. This value agrees perfectly with the result obtained by a three month "long-distance comparison" between Garmisch-Partenkirchen and Arosa (bee-line 250 km) in fall 1977 using the daily means and covering an ozone range of 0.200 to 0.400 atm cm.

According to this practical experience it can be stated that the commercial version of the prototype New Zealand narrow-band interference filter photometer can be used with confidence as a total ozone monitor provided a bias relationship is established by a comparison to a reliable Dobson instrument. Weighing approximately 40 lbs. and divided into two easily carried units, the instrument seems to be especially suitable for field measurements. In view of these favourable characteristics it should not be suppressed, however, that no reliable results could be obtained with the instrument from the very beginning. Only when several defects (appearing primarily with the pulse counting system) had been eliminated by our lab the device was working well. With regard to the relatively short time of operation also no decision on the durability and long-term drift of the instrument is possible.

As the instrument has a very sensitive, low noise photomultiplier detector it can also be used for the "Umkehr"-method of determining atmospheric ozone's density with height. In the near future another intercomparison is planned to be conducted at Arosa with concentration on "Umkehr"-measurements. In the long run the instrument is planned to be operated in conjunction with our tropospheric-stratospheric exchange research primarily to get the vertical ozone density profile.

5. Results

5.1. Balance of the Tropospheric Ozone

During the course of the investigation into the balance of the tropospheric ozone the question of the origin of high ozone concentrations in pure-air regions has been tackled as a first partial problem.
The following statement can be made as first tentative result:

Ozone concentrations >70 ppb are caused by subsidence processes in the free atmosphere (in this case the stratosphere is to be regarded as ozone source), and they can also be produced in the boundary layer itself.

In the former case high values of Be7 activity are observed simultaneous in time with the high ozone concentration at the station Zugspitze. Moreover, the meteorological parameters at the mountain stations in such cases behave in a fashion typical of subsidence (e.g. decrease of the relative humidity to values <20%, increase of the potential temperature). The attendant large-scale weather is in such cases characteristic of situations for which there is an increased probability of stratospheric intrusions. The onset of the rise of ozone concentration is at first observed at the highest station (Zugspitze) and with increasing time delay the rise sets in at the lower stations. In case of an influx of ozone within the boundary layer the indices of an influx from the stratosphere, as mentioned in the above, are missing. Besides, these air masses are enriched with high concentrations of the radon decay products Pb 214 and Bi 214 which is indicative of a permanent contact with the ground. The high concentrations are observed at first at the valley station Garmisch-Partenkirchen and arrive at the mountain stations only with the onset of the advancing vertical exchange. The time delay observed during this process is growing with increasing height (Fig. 1).

The question of whether in such cases the ozone is brought in to our area from more distant source regions or whether it is produced locally by photochemical reactions after influx of the necessary trace gases must be left open for the time being. However, this problem will be followed up through further systematic studies.
Short term, extremely high ozone concentrations (> 150 ppb) were not observed during the reporting period.

5.2. Balloon-borne Measurement of the Ozone Height Profile

During the reporting period first balloon ascents with ozone sondes were conducted. Radiosondes of type VIZ, Model 1392 or the corresponding radiosondes with hypsometer, Model 1393, have been launched in conjunction with ozone sondes Model ECC 3-A (manufacturer Science Pump Corporation, Camden, New Jersey, USA). Using 2000 g balloons, altitudes up to 6 mb (ca 35 km) have in general been reached.

Evaluation of ascents is done by desk calculator or via computer. Results are available in tabular form or as plots (Fig. 2). The example shown in Fig. 3 indicates the beginning of a stratospheric intrusion. This is suggested from a twofold tropopause (350 mb and 180 mb) and from an intensive secondary maximum of the ozone partial print in the upper tropopause region.

A first series of daily ozone sonde soundings revealed that it is possible, by means of daily ozone sonde ascents covering the intervals of enhanced probability of stratospheric intrusions, to determine and possibly quantify the stratospheric intrusions together with the influx of the stratospheric ozone into the troposphere.
This aspect will be pursued consistently in the near future.

5.3. Lidar Monitoring of Stratospheric Aerosols

Lidar instrumentation, measuring procedure, and data acquisition and processing have already been described in detail in the preceding reports. Method and data handling have not been changed during the period covered by the present report, whereas the reliability of the lidar system could be improved to such a level that we can take advantage of almost all clear night periods for stratospheric measurements.

During the period July 1977 through June 1978, 29 backscatter profiles of the stratospheric aerosol layer have been determined. Together with the measurements described in the last report, now a period of 20 months since the inception of lidar monitoring in October 1976 can be described. The precision of the stratospheric aerosol measurements and the behaviour of the stratospheric aerosol layer in time and space will be discussed in the following.

5.3.1 Error Discussion

A statement regarding the precision of the lidar measurements only can be made by discussing possible sources of error. An estimate of the following errors will be attempted:

a Statistical error of the photon counts,

b Error resulting from the alignment of profile sections to form a representative profile of the total backscatter,

c Error resulting from the radiosonde uncertainty,

d Additional error, if a standard atmosphere has to be used to compute the molecular backscatter profile,

e Error in the calculation of the molecular backscatter profile which results from disregarding particulate and ozone absorption in the atmosphere.

These errors are plotted versus altitude in Fig. 4. The sum of them is the maximum possible average error when determining the scattering ratio R. R is the ratio of the measured total backscatter to calculated molecular backscatter. The errors a - d influence the result equally towards higher and lower values. Error e is unbalanced and results from an underestimate of the transmission reduction by atmospheric constituents in the calculation of the molecular return. The total

error passes through a minimum at the level of matching, since the errors a, d, and e are zero at the point of matching.

Statistical Error. This random error is a function of the total number of counted photons and 1 σ errors have been calculated. In Fig. 4 this error shows two distinct steps of increase when following the curve from higher to lower altitudes. When receiving signals from below 18-19 km, a neutral filter has to be placed in front of the PMT to reduce the incoming intensity allowing resolution into single photon pulses. At 11-12 km an additional filter has to be applied. The reduction of the counting rate due to the filters leads to an increase of the counting error.

Alignment Error. It is rather difficult to estimate this error. Transmission alterations caused in the troposphere and by cirrus clouds with rather fast changing density produce intensity shifts of the signal received from the individual gate sections of the return profile. Although two of the available ten counting channels overlap, the error introduced by aligning the sections cannot be disregarded. This error is increasing with increasing distance from the matching zone.

Radiosonde Error. This error results from the uncertainty of the density profile deduced from radiosonde data (pressure and temperature). The root-mean-square errors published by Lenhard*) for 1.5 and 0.1 mb pressure steps have been interpolated to match with the 0.5 mb steps used with our radiosonde.

Standard Atmosphere. In the case of actual radiosonde data cannot be made available a standard atmosphere has to be applied. The large number of own radiosonde ascents enabled us to deduce our standard atmosphere, considering seasonal

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*) R.W. Lenard, Bull. Amer. Met. Soc. 54, 691 (1973)

variations. Although matching of measured and calculated return is done in close vicinity to the aerosol layer, the calculated return can deviate considerably from the actual profile when applying a standard atmosphere. The mean-square-deviation of the actual profile from the standard profile at 19 km (average center of aerosol layer) amounts to already 2.5 %, with observed deviations of as much as 6.5 %. If we would have applied the US Standard Atmosphere the average error would have been even larger. To dispense with actual radiosonde data therefore leads to a considerable increase in the uncertainty in lidar data.

Two-way Transmission. To calculate the molecular backscatter the two-way-transmission τ^2 has to be determined

$$\tau^2 = \exp\left[-2 \int_{h_1}^{h_2} \sigma(h)\, dh\right],$$

where σ is the extinction coefficient. Molecules, suspended particles, and ozone contribute to the atmospheric extinction:

$$\sigma = \sigma_m + \sigma_p + \sigma_o$$

In the calculation of the two-way-transmission both σ_p and σ_o have so far been disregarded and the question arises whether this simplification can be tolerated or not.

To calculate the contribution of σ_p an average 1977 profile of the particulate backscatter coefficient f_p has been determined basing on 26 lidar profiles

$$f_p = (R - 1)\, f_m$$

where f_p = particulate extinction coefficient,

f_m = molecular extinction coefficient,

R = scattering ratio.

Following the discussion of Russel et al.*) of stratospheric aerosol models, an average backscatter phase function $\frac{P}{4\pi}$ based on the Deirmendjian Haze H model has been applied to calculate the particulate two-way-transmission

$$\tau^2_p = \exp\left[-2 \int_{h_1}^{h_2} \frac{4\pi}{P} f_p dh\right], \quad \text{where } \frac{4\pi}{P} f_p = \sigma_p.$$

The integration has been done for increasing layer thickness starting from 14.4 km, the average height of matching. The resulting %-deviation is plotted in Fig. 4. At the maximum of the aerosol layer at 19 km an underestimate of the measured backscatter ratio of 0.3 % is resulting.

In a similar way the influence of atmospheric ozone has been considered. The stratospheric ozone layer with its maximum at 20 to 25 km height extends with considerable amounts of ozone into the transmission range of interest below the aerosol layer. Again an average ozone profile deduced from own ozone-sonde ascents has been determined and the two-way transmission with an absorption coefficient $\alpha = 2.55 \times 10^{-2}$ [1/cm] (interpolated from data published by Dütsch**) has been calculated.

$$\tau^2_o = \exp\left[-2\alpha \int_{h_1}^{h_2} c \, dh\right]$$

$$\text{with } c = cm_{ozone} \text{ (NTP)/km}$$

The integration again has been carried out with increasing layer thickness above 14.4 km. The resulting %-deviation is

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*) P.B. Russel, W. Viezee, and R.D. Hake, SRI Project 2217, Final Report, Stanford Res. Inst. Menlo Park, Cal. June 1974

**) Meteorologisches Taschenbuch, II. Band, p. 555 Leipzig 1970

plotted in Fig. 4 and exceeds that caused by neglecting particulate transmission at greater heights.

The resulting maximum underestimate in the determination of the scattering ratio by disregarding particulate and ozone optical transmission reduction amounts to 0.6 % at the maximum of the aerosol layer and can presently be neglected by considering the above discussed errors.

A reduction of the overall error can be achieved by reducing error a (higher counting rate), reducing error c (hypsometer sonde), reducing error e (τ^2 calculation including average particulate and ozone profiles), elimination of error d (actual radiosonde data), and elimination of error b (multichannel photon counter, which is under construction).

5.3.2 The Stratospheric Aerosol Layer

During the period of observation maximum scattering ratios ranging from 1.08 to 1.22 have been observed, the average value being 1.14 at an average height of 18.6 km.

In diagram 5 isolines of the particulate backscatter coefficient are presented. The lines have been produced by a smoothing process to eliminate short-time fluctuations. The vertical layer extent was 8 km at the end of 1976, reached almost 12 km in October 1977 and decreased to presently 9 km. The lower boundary varies between 14 and 15 km altitude, whereas the upper boundary shows greater fluctuations and is found between 23 and 26 km. The altitude of the maximum value of the particulate backscatter coefficient is somewhat below the maximum of the scattering ratio and ranges from 17 to 19.5 km. Peak values exceeding 6×10^{-9} $[m^{-1}sr^{-1}]$ have been encountered in January 1977, July to December 1977, and since May 1978. A period of reduced backscatter lasted from February through May 1977.

An error propagation calculation has been conducted to derive the error of the particulate backscatter coefficient considering the above discussed errors. Average errors applying to the altitude levels 18 km and 21 km are given in the following table.

Altitude	Mean square error	
	with	without radiosonde
18 km	± 27 %	± 34 %
21 km	± 23 %	± 46 %

With the above mentioned error reductions an error of 10 % for average backscatter coefficients of 5×10^{-5} $[m^{-1}sr^{-1}]$ can be attained, then allowing the description of short-term variations of the stratospheric aerosol layer.

6. Future Plans

1. Continuation of the measurement of the ozone concentration at three levels (3000 m, 1800 m, and 700 m a.s.l.) for the determination of the ozone profile in the boundary layer and derivation of the balance of the tropospheric ozone.

2. Continuation of the measurement of the CO_2-concentration in the free atmosphere, derivation of natural and anthropogenic time variations by correlation with relevant meteorological parameters.

3. Continuation of aerosol sampling at the station Zugspitze,

determination of the concentration of the cosmogenic radionuclides for the identification of stratospheric intrusions, clarification of the influence of stratospheric intrusions on the balance of the tropospheric ozone.

4. Determination of the influence of trace gases and aerosols on the balance of the tropospheric ozone.

5. Determination of the continuously measured amount of sulfate in the tropospheric aerosol in correlation with the SO_2-concentration.

6. Remote sensing of stratospheric aerosol layers up to 35 km altitude by means of lidar with simultaneous measurement of the aerological ariables through our own radiosonde ascents.

7. Calculation of the isentropic trajectories for the long-term periods described in instant report; classification of the tropospheric flow conditions relative to a climatology of stratospheric intrusions.

8. Critical examination into the impact of solar events on the profile of the atmospheric ozone and the influx of stratospheric ozone into the troposphere by means of daily ozone sonde ascents, and intensified measurement of the total atmospheric ozone during selected periods after solar events.

9. Elaboration of a modified system for submitting relevant measuring data in a new form in future reports.

(Dr. R. Reiter)
Director
Principal Investigator

Legends of Figures

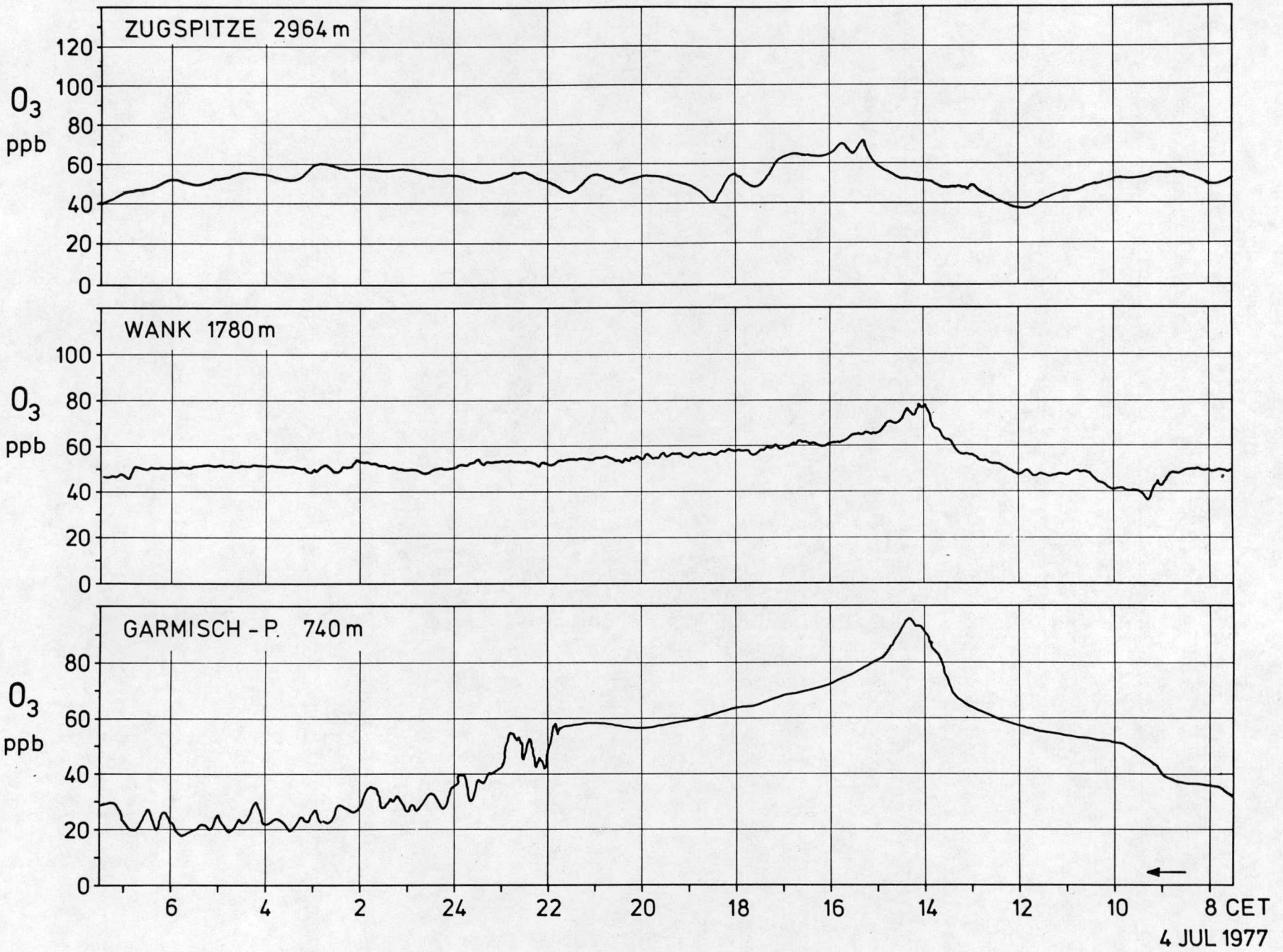
Fig. 1: Recordings of ozone concentration at 3 levels in the case of photochemical production

Fig. 2: Typical ozone (solid line) and temperature (dashed line) profiles observed by balloon sounding

Fig. 3: Ozone and temperature profiles. The beginning of a stratospheric intrusion is indicated by the fine structure of the temperature profile between the 400 mb and 180 mb level

Fig. 4: Error estimate of lidar backscatter measurements

Fig. 5: Time and space variations of the particulate backscatter coefficient of the stratospheric aerosol layer only.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O_3 ppb
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100
80
60
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WANK 1780 m
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GARMISCH - P. 740 m
O_3 ppb
80
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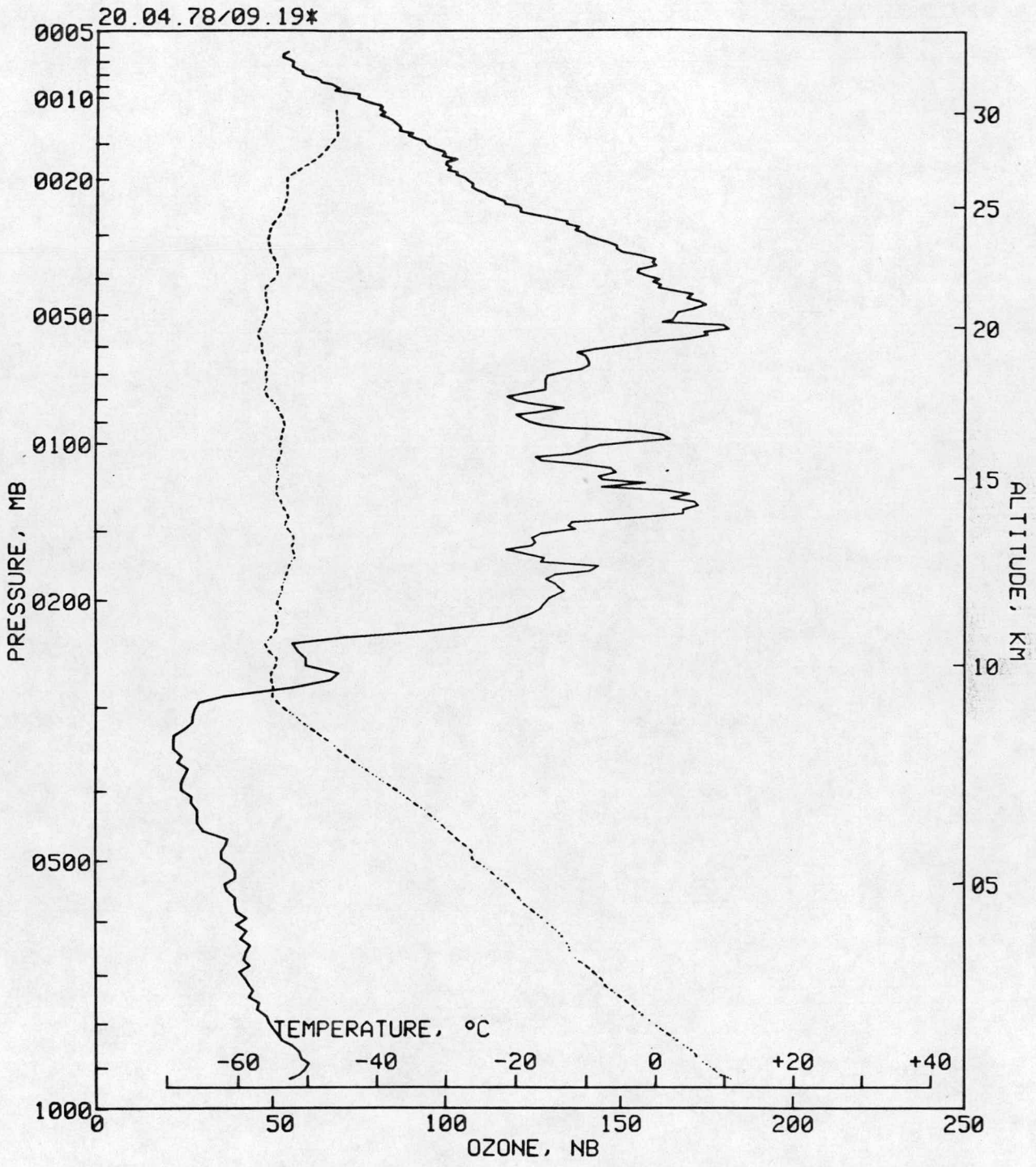
4 JUL 1977

Fig. 1

Fig. 2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PRESSURE, MB
30
25
20
15
10
05
ALTITUDE, KM
TEMPERATURE, °C
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-40
-20
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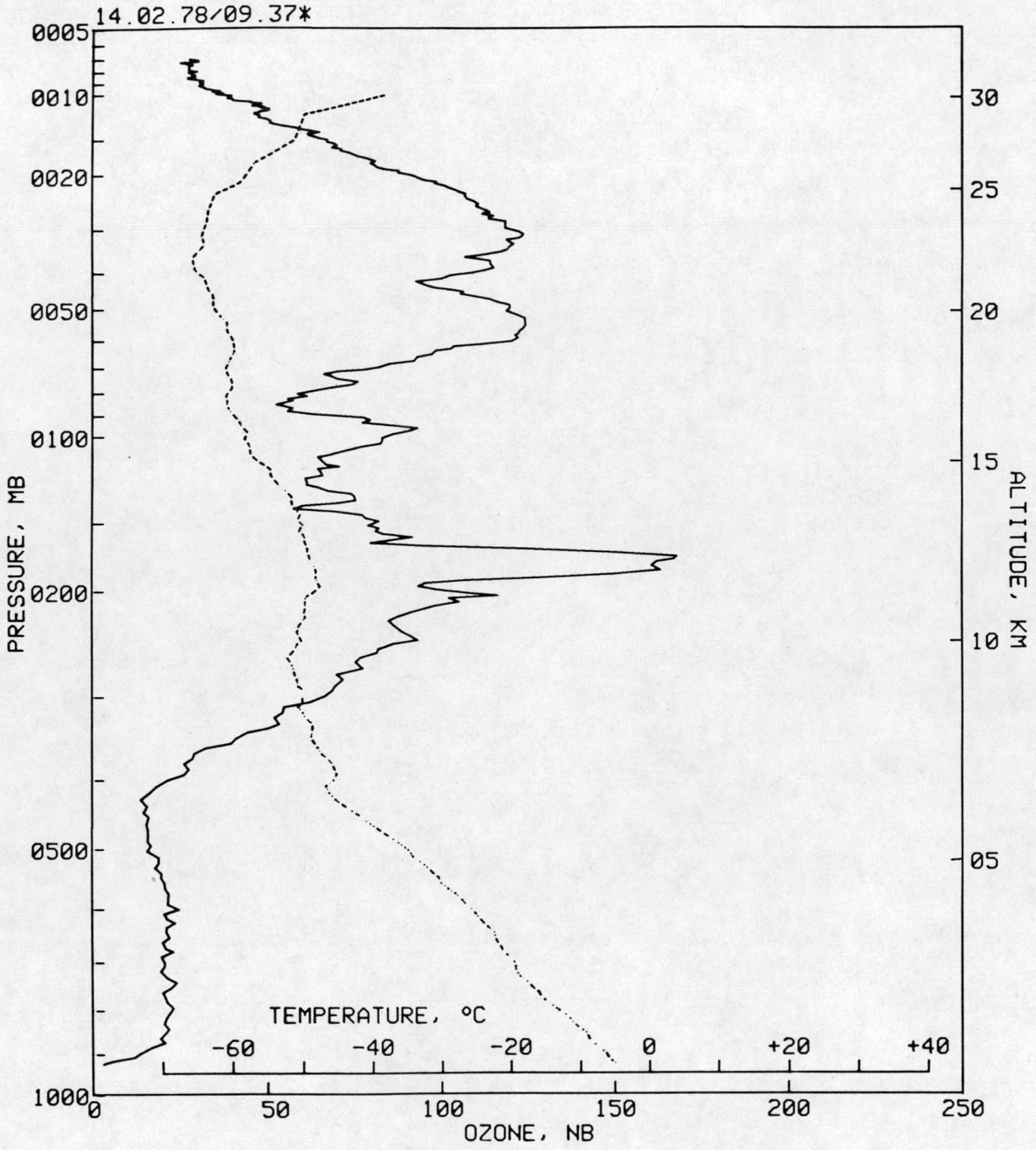
+20
+40
0
50
100
150
200
250
OZONE, NB

Fig. 3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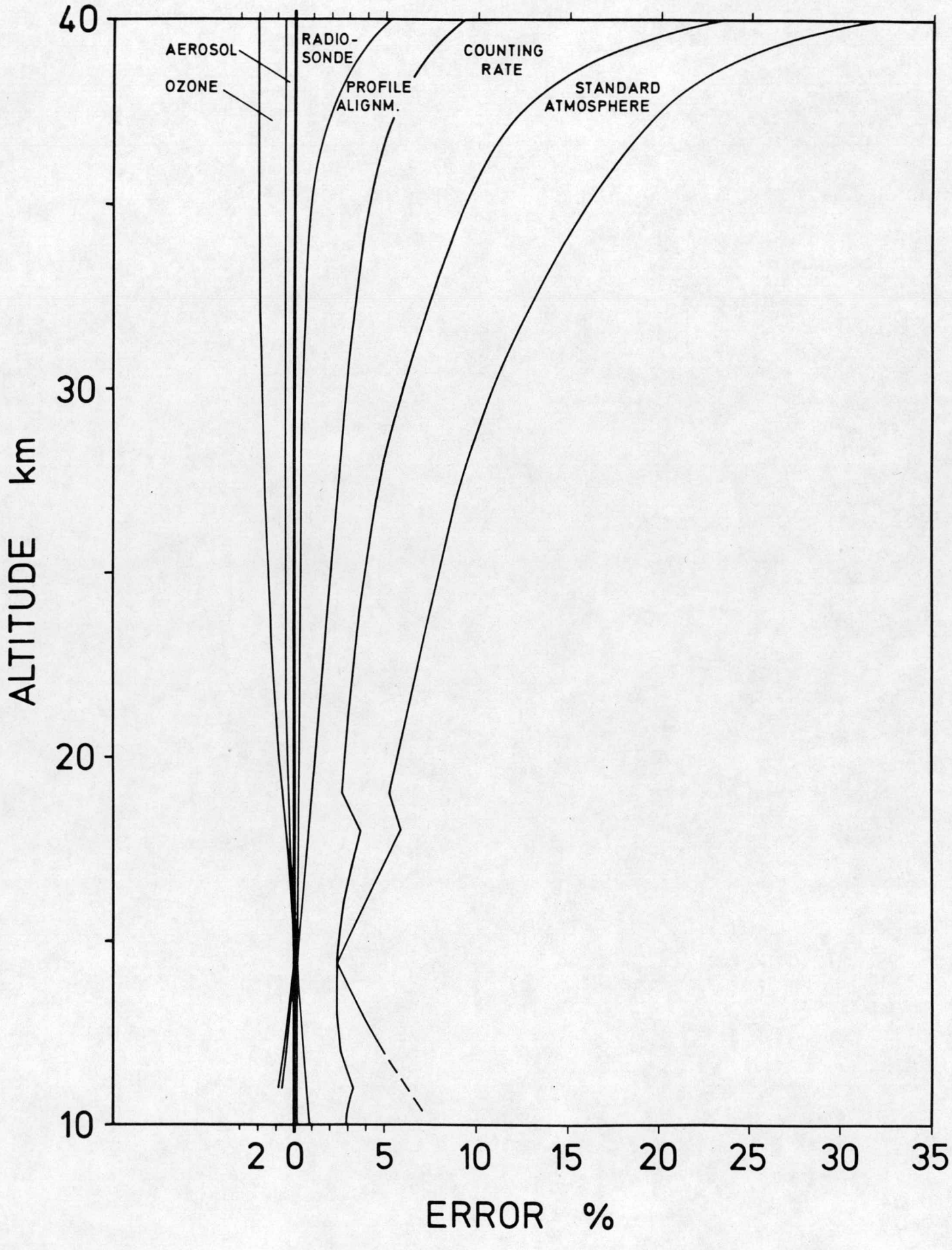
OZONE, NB

Fig. 4


40
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ALTITUDE km
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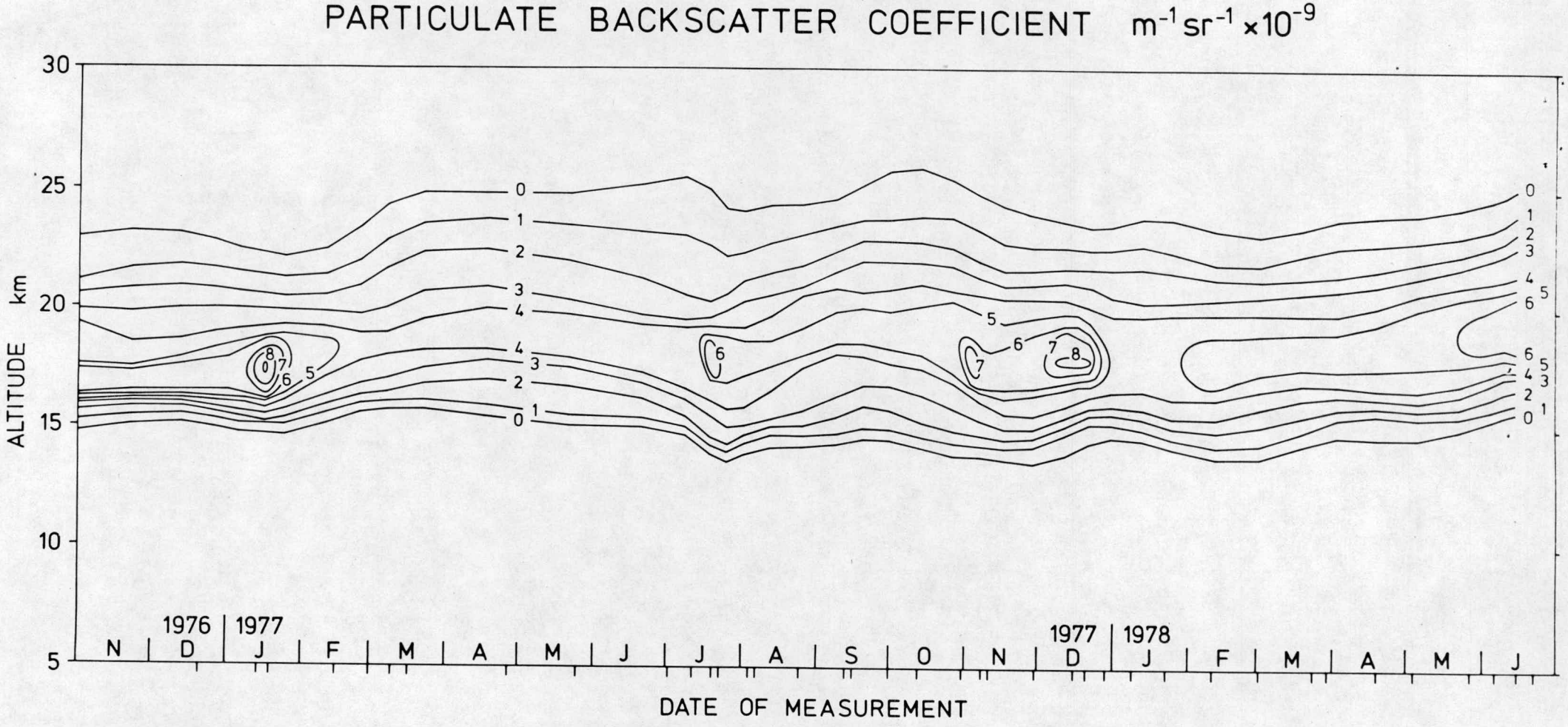
2 0 5 10 15 20 25 30 35
ERROR %


PARTICULATE BACKSCATTER COEFFICIENT $m^{-1}sr^{-1} \times 10^{-9}$
ALTITUDE km
30
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1976
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1977
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DATE OF MEASUREMENT

Fig. 5