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# THE OCCURRENCE OF PHOTOCHEMICAL SMOGFORMATION IN WESTERN EUROPE

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In 1944, photochemical smog was noticed for the first time in the Los Angeles Basin, manifesting itself as vegetation damage, eye irritation, and reduced visibility.

In the early 1950's A.J. Haagen-Smit demonstrated that irradiation of mixtures of nitrogen oxides and hydrocarbons produced products with properties similar to those of atmospheric photochemical smog. The origin of these so called precursors in ambient air may be natural as well as man-made. In areas where photochemical air pollution has now been recognized as being a potential problem, hydrocarbons may be emitted by natural sources (eg. terpenes from vegetation) as well as by human activity, however, the far most important source for nitrogen oxides in those areas being human activity.

A complex range of substances of which ozone is quantitatively the most important, characterize the reaction products. This is the reason why ozone concentrations are often used as an index for the extent of photochemical processes in ambient air. Ambient air, however, may also contain natural ozone from stratospheric origin. These natural concentrations are low, ranging from 0.02 - 0.04 ppm (1) and are subject to seasonal and latitudinal variations. Of importance is the fact that in absence of human activity natural hydrocarbon emissions by vegetation and localized sources such as geothermal areas, forest fires, oil-, gas-, coalfields and natural emissions of nitrogen oxides, mainly by biological processes, have nowhere led to ozone concentrations in excess of the so called natural ones. Other major secondary products formed are peroxyacylnitrates, of which peroxyacetylnitrate or PAN seems to be the predominant member formed in ambient air, aldehydes, solid and liquid particles, hydrogen peroxide, (organic) acids, etc.

For reasons of its non-existence as a product of natural sources, PAN is sometimes considered a better indicator of photochemical smogformation than ozone.

Meteorological factors have been found to be of great importance in areas where photochemical air pollution occurs. These factors include dilution, accomplished by atmospheric turbulence and transport, as well as sunlight intensity, temperature, and humidity. Because photochemistry starts with the absorption of light, the actinic light intensity (290 - 400 nm) is one of the major parameters governing the formation of photochemical smog.

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The radiation received in the lower atmosphere is dependent on solar radiation outside the atmosphere, the suns altitude, the nature and the amount of scattering and absorption in the atmosphere, and the albedo of the surface of the earth. Of these parameters, the suns altitude is probably the most important one.

In figure 1 the daily trend of the UV radiation intensity and the ozone and PAN concentrations are given for each month of 1975 as measured at Delft. From the graphs it can been seen that no smogformation of importance seems to occur before March and after October at the latitude of the Netherlands i.e. 52°N. PAN levels for February and October are extremely low, while in November, December, and January, PAN is almost completely absent im ambient air. Lightintensity data given in figure 1 are so called "volumetric data". Most instruments used to measure radiation intensity measure the combined directsun and scattered sky radiation incident on a horizontal plane. However, a volume of reacting gases in the atmosphere is subject to irradiation from all directions. A cubical arrangement of six horizontal plate physical sensors was used for continuous measurement of the UV radiation intensity. The construction of the instrument was carried out in our laboratories. The performance was identical to the one described by Nader and White (2). The instrument was calibrated against chemical actinometry using the ortho-nitrobenzaldehydemethod (3) as a reference method. Light intensities were expressed as Watt/m$^2$ assuming average energy at 350 nm.

From the zenith angle of the sun as a function of latitude and time of the year it can be concluded that up to 70° northern latitude a sufficient amount of radiation is available for photochemical processes to occur at least during a certain period of the year. At moderate and higher latitudes, the periods become progressively shorter. This means that given a certain distribution density of precursors and certain meteorological conditions, almost any country on earth might now or in the future be faced with a photochemical smog problem.

Research in the field of photochemical air pollution in the Netherlands started about two decades ago. As early as in the 1950's measurements in the Netherlands demonstrated the occurrence of oxidizing components in the "Nieuwe Waterweg" area, which is the heavy industrialized region near the city of Rotterdam. In 1966 semi-automatic measurements, carried out in Delft, once more confirmed the occurrence of elevated oxidant levels in this part of the country. Finally in 1969 systematic ozone measurements with fully automatic equipment began in Delft. From these and other measurements, carried out since that time, it can be concluded that:

I the maximum recorded hourly ozone concentration could reach values of up to 0.25 ppm in this part of the country. Also in other parts of the country concentrations in excess of 0.20 ppm have been recorded;

II the WHO long term goal for 1 hour maximum, 0.06 ppm oxidant as ozone, which is also the legal Japanese oxidant standard could be exceeded on about 75 days of the year (number of violations 300), while the standard set by the Environmental Agency (EPA) of the United States of 0.08 ppm could be exceeded on about 25 days of the year (number of violations 95);

III continuous PAN monitoring at Delft since June 1973 gave maximum peak concentrations up to 20 ppb.

A relation between ozone and PAN concentrations as was established in Delft for various source areas is given in table 1.

Table 1

Interrelation between ozone and PAN concentrations for areas where the main source of the precursors is automobile traffic and (petro) chemical industries.

| | Main source automobile exhaust | |
|---|---|---|
| | daytime hours | evening and night |
| correlation coefficient (r) | 0.96 | 0.77 |
| ratio of average $O_3$ and PAN concentrations | 45 | 39 |
| regression | $[PAN] = 0.016[O_3]+0.02$ | $[PAN] = 0.028[O_3]-0.13$ |
| | Main source (petrochemical) industries | |
| correlation coefficient (r) | 0.1 | -0.01 |
| ratio of average $O_3$ and PAN concentrations | 30 | 19 |

From table 1 one might conclude that in areas where the major source of PAN and ozone precursors is automobile exhaust, there is a good correlation between ozone and PAN concentrations measured during daytime.

The average ratio $O_3$/PAN measured during daytime is 45, a ratio similar to that measured in Down Town Los Angeles (1). PAN levels are more persistant during evening hours than ozone levels; consequently ozone and PAN concentrations measured during this time of the day are less correlated. In areas where the major source of the hydrocarbon precursors is petrochemical industries the aforementioned correlations are much less strong. Because dilution effects due to dispersion are similar for ozone and PAN, persistance of PAN during the evening and night must be due to:

a) difference in chemical reactivity of both pollutants, and

b) difference in deposition rate at the surface of the earth.

In polluted areas reaction between ozone and NO emitted during the evening rush hour is an important chemical sink for this compound. The reaction rate between ozone and NO is very high, in contrast to the reaction rate between PAN and NO which is far smaller. In relatively unpolluted areas, catalytic destruction or physical quenching at the surface of the earth becomes the predominant sink for ozone. Physical quenching at the surface of the earth for PAN is also less than for ozone (4).

IV semi-continuous total aliphatic aldehyde measurements gave concentrations of up to 0.060 ppm (2 hr. average concentrations expressed as HCHO eq.) during periods of smogformation.

The aforementioned data are of course highly dependent on prevailing meteorological conditions. In table 2 the results of a correlation between maximum hourly ozone concentration, maximum temperature, and average windspeed are given.

Table 2

Correlation between $O_3$ and meteorological parameters. From a linear regression analysis average $O_3$ concentrations were calculated for various maximum temperatures.

| Year | $r(O_3, T_{max}\bar{U})$ | | $\bar{O}_3$ | |
|---|---|---|---|---|
| | | $T_{max}$ 20° | 25° | 30° ($\bar{U}$=3 $msec^{-1}$) |
| 1969-1971 | 0.8 | 0.035 | 0.060 | 0.085 |
| 1972 | 0.7 | 0.060 | 0.080 | 0.090 |
| 1973 | 0.8 | 0.055 | 0.080 | 0.110 |
| 1974 | 0.6 | 0.060 | 0.080 | 0.085 |
| 1975 | 0.7 | 0.050 | 0.075 | 0.090 |

It appears that temperature is the most important single factor, not in itself, but because high temperature indicates the existance of meteorological conditions favourable for the occurrence of photochemical smogformation. In Western Europe these are characterized by an anticyclone over Central Europe, or an extensive high pressure system over Fenno-Scandinavia. Of importance is the fact that the same meteorological conditions then prevail over extensive areas of Europe at the same time, from which one might conclude, that photochemical smogformation should occur over extensive areas of Europe at the same time. Recently data from measurements in Western Europe have confirmed that this statement is a correct one.

As an example the smogformation episode of August 1975 may be given. This episode lasted for more than 15 days, from the end of July to mid-August. Meteorological data and ozone maxima (5) for August 3 and 7 are given in figure 2. Synoptic conditions over Europe during this episode were dominated by a large high pressure area, which was quasi-stationary over the North Sea and Scandinavia. This high gave sunny skies, high temperatures, and low to moderate windspeeds over the entire region. Data from measuring sites in the various countries together with additional aircraft measurements showed that smogformation occurred over an area with an extension of several thousands of square kilometers at the same time. From an airmass trajectories analysis no specific source areas could be indicated (6). It is our believe that this phenomenon will also occur in areas where up to now no measuring data are available, provided meteorological conditions conducive to the process of smogformation prevail. This means not only in areas of Western Europe but in Eastern Europe as well.

In table 3 oxidant concentrations measured alswhere as well as in some Western European countries are given for reasons of intercomparability. In figure 3 the number of hours per year of which the hourly average oxidant concentration equalled or exceeded 0.20 ppm for a locality in California and in Delft are given.

## Table 3

Ozone concentrations measured in different countries.

| Country | Area | Period | Days over or equal to in the mentioned period | | Maximum (hourly av.) | Source |
|---|---|---|---|---|---|---|
| | | | 0.10 ppm | 0.15 ppm | | |
| U.S.A. | Chicago | 1969-72 | 22 | 5 | 0.20 | (7) |
| | Cincinnati | 1969-72 | 18 | 3 | 0.16 | (7) |
| | Denver | 1969-72 | 42 | 3 | 0.20 | (7) |
| | Philadelphia | 1969-72 | 28 | 1 | 0.15 | (7) |
| | St. Louis | 1969-72 | 15 | 2 | 0.16 | (7) |
| | Washington DC | 1969-72 | 34 | 2 | 0.16 | (7) |
| Japan | Tokyo | 1969-72 | • | 70 | 0.38 | (8) |
| | Osaka | 1969-72 | • | 21 | 0.29 | (8) |
| Netherlands | Delft | 1969-72 | 47 | 5 | 0.25 | |
| U.S.A. | Pasadena | 1964-67 | 401 | 299 | 0.46 | (7) |
| | Los Angeles | 1964-67 | 354 | 220 | 0.58 | (7) |
| Australia | Sydney | 1972-73 | 58 | 15 | 0.28 | (8) |
| Netherlands | Delft | 1973-74 | 14 | 2 | 0.17 | |
| | Eindhoven | 1973-74 | 33 | 6 | 0.22 | (9) |
| United Kingdom | London | 1973-74 | 20 | 1 | 0.18 | (5) |
| | Harwell (Oxfordshire) | 1973-74 | 15 | 0 | 0.14 | (5) |
| Germany | Frankfurt | 1973-74 | 16 | 2 | 0.17 | (5) |
| Canada | Hamilton(Ont.) | 1973-74 | 27 | 2 | 0.15 | (5) |
| | Toronto(Ont.) | 1973-74 | 54 | 2 | 0.16 | (5) |
| Netherlands | Delft | 1975 | 17 | 1 | 0.15 | |
| | Eindhoven | 1975 | 22 | 2 | 0.16 | (9) |
| Australia | Sydney | 1975 | 40 | • | 0.30* | (8) |
| Netherlands (up to Sept.) | Delft | 1976 | 26 | 6 | 0.20 | |

• no data available

* peak concentration

Results of investigations in Western Europe, which are given in national case histories and were presented at an OECD-meeting at Delft (1975), may be summarized as follows:

a) Photochemical smogformation is not a local phenomenon confined to urbanized- and industrialized areas, but may occur over extensive regions of Europe at the same time.

b) Ozone levels exceeding 0.08 ppm are also recorded in rural areas of England, Ireland, the Netherlands, Sweden, and Western Germany, where there are hardly any local sources of precursors. Apart from the local production of some of the precursors, meteorological evidence indicated that this phenomenon may primarily result from the transport of the precursors and to a less extent also of ozone into the rural areas from densily populated- and industrialized regions.

c) In receptor areas, the diurnal trend of ozone may differ from that observed at urban sites. High levels might persist into the night as the nitric oxide and olefinic hydrocarbons emitted during afternoon and evening rush hour traffic are not present to scavenge ozone.
   The persistance of ozone the following day in the rural areas may give rise to even higher ozone levels as a result of meteorological processes and photochemical reactions, taking place during the following day.
   The same might hold for sites situated on the coast, where due to the land-sea breeze circulation system, relatively high ozone levels may persist into the night.

d) In industrialized- and urbanized areas, the highest ozone concentrations do not appear to be found at groundlevel. Although at groundlevel, ozone concentrations may be low, they often increase by factors at higher altitudes within the mixing layer. The lower groundlevel ozone concentrations may be explained by physical quenching at the surface of the earth and by chemical quenching due to reactions with NO and reactive hydrocarbons.
   In figure 4 daily trend graphs for ozone measured at two altitudes on the meteorological observation mast of the Royal Netherlands Meteorological Service are given. At the 200 m altitude measuring site ozone concentrations may not only be much higher than those measured near the surface of the earth, but also persistence of ozone at higher levels is quite obvious.
   From aircraft measurements it follows that depending on the time of the day, even higher ozone concentrations might be measured at higher levels within the mixing layer.

e) One of the major effects of photochemical smogformation in the Los Angeles Basin is a reduction in visibility. Reduction in visibility results up to a great extent by gas to particle conversions eg.:

$SO_2\ (g) \longrightarrow SO_4^{2-}$

$NO_x\ (g) \longrightarrow NO_3^-$

$HC_{(g)} \longrightarrow$ organic aerosols.

In Europe, however, no unequivocal correlation between intensity of smogformation as given by ozone levels, and visibility has been reported, although during certain episodes a clearcut attenuation of the nearground measured volumetric UV light intensity is observed (fig. 5). This observed attenuation cannot be the result of a sorption of light by gaseous pollutants alone, but must mainly be attributed to scattering, absorption, reflection, refraction and diffraction by particles in the polluted layer.

An extremely difficult decision which must be made to combat photochemical air pollution is that of setting air quality standards for the precursor pollutants of which the two most important are the reactive hydrocarbons (NMHC) and nitrogen oxides. For ozone, which is responsible for most of the measured oxidants, air quality standards ranging from 0.06 to 0.08 ppm (one hour average) have been set by several authorities. The only way to control the amount of photochemical oxidant, is to limit the amount of NMHC and/or nitrogen oxides emitted in ambient air. How much reduction is needed to insure that ozone concentrations in excess of the standards will not be formed is the key question that have to be answered. If the amount of ozone formed were related simply to the product of the concentration of hydrocarbons times the concentration of nitrogen oxides; $(O_3) = k\ (NMHC) \cdot (NO_x)$, we could assume that eg. a four fold reduction of ozone could be achieved either by a four fold reduction of one of the precursors, or a two fold reduction of both precursors. However, we know that such a formulation is totally inadequate for describing the formation of ozone. We are now aware that for a complex system of multiple competing (radical) reactions, the effects of reduction in concentration of the reacting species may be extremely non-linear.

From results in the field of photochemical air pollution it became clear that on a local basis smaller ozone maxima are predicted, either under conditions of high initial hydrocarbon and low $NO_x$ or low initial hydrocarbon and high $NO_x$. In the former case, high levels of ozone cannot accumulate since the $NO_x$ is rapidly removed as stable products. In the latter case, high initial levels of NO locally will inhibit the formation of ozone, since long reaction periods are needed to oxidize NO into $NO_2$. Furthermore if the initial NMHC/$NO_x$ ratio is sufficiently low, little ozone will be able to form, even at very long irradiation times, for during that period, the hydrocarbons will be substantially oxidized to stable products. This means that there should be an "optimum" ratio of NMHC to $NO_x$ for oxidant formation. Optimum in this respect means the production of the highest oxidant levels with the least quantities of hydrocarbons and oxides of nitrogen i.e. the most undesirable situation from the viewpoint of air pollution. Control strategies for oxidants should therefore be to remove the actual ratio of NMHC to $NO_x$ in a region as far away as possible from the optimum.

## The approach adopted by the USA Environmental Protection Agency (8)

The approach adopted by the USA-EPA is to control hydrocarbon emissions only. Irrespective of the absolute concentrations of the precursors, or their ratio, no reduction in $NO_x$ emissions is required for oxidant control. Reduction in $NO_x$ is only required at a level that will keep ambient $NO_2$ concentrations below the level of adverse health effects.

The EPA strategy is based on the ozone/hydrocarbon relationship derived from aeromatric data, collected mainly in the Washington DC, Denver, Philadelphia, and Los Angeles metropolitan areas. This decision was furthermore based on the concept that less stringent $NO_x$ reduction will enhance the control effects, due to the scavenging effects of NO for oxidants. Based on aeromatric data the EPA considers as crucial to meet the USA air quality standard for oxidant i.e. 0.08 ppm, not to be exceeded more than once per year that the concentration of NMHC should be less than 0.24 ppmC average for morning hours 6.00 to 9.00 a.m.

## The approach adopted by the Japanese Government (8)

The Japanese Government established an air quality standard for oxidants at 0.06 ppm not to be exceeded more than once per year; a level below which no adverse health effects would be experienced. Also an air quality standard for $NO_2$ was established at 0.02 ppm, as a 24 hour average maximum, so as to avoid adverse health effects from nitrogen dioxide.

The believe of the Japanese Authorities was, that abatement programmes to meet the stringent $NO_2$ standard would also contribute to a very high degree to the reduction of photochemical oxidants. Lately, however, an expert committee was set up to propose an air quality standard for hydrocarbons to potentiate the aforementioned approach for photochemical oxidant abatement.

Unilateral reduction of NMHC levels in the Los Angeles Basin have led to increasing ozone levels especially in areas downwind, where the reacting airmass has experienced longer reaction time (10). NMHC control alone delays the production of oxidant, because the conversion of NO to $NO_2$ is slowed down. In the urban environment NMHC reduction will therefore probably lower maximum $NO_2$ concentrations during the day, but will probably result in higher average daily $NO_2$ concentrations since the scavinging effect of photochemistry on $NO_x$ is diminished. Residual urban $NO_2$ will be transported out of the industrialized and urbanized areas into receptor areas, where it will interact with further infusions of organic material and create a greater potential for oxidant formation in downwind airparcels on later times of the day or on subsequent days.

Since oxides of nitrogen and nitrogen containing secondary products such as $NO_2$, nitric acid, (organic) nitrates, nitrosoamines, are harmful pollutants, $NO_x$ abatement may prove to be essential in regional or, in the case of Western Europe, even international control of oxidants.

Finally, the transfrontier aspects of this type of pollution must be stressed, making international cooperation in the field of oxidant pollution abatement a crucial factor.

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FIGURE 1. Daily trend of the $O_3$ and PAN concentration and the UV (290-400 nm) light intensity measured at Delft, 1975.

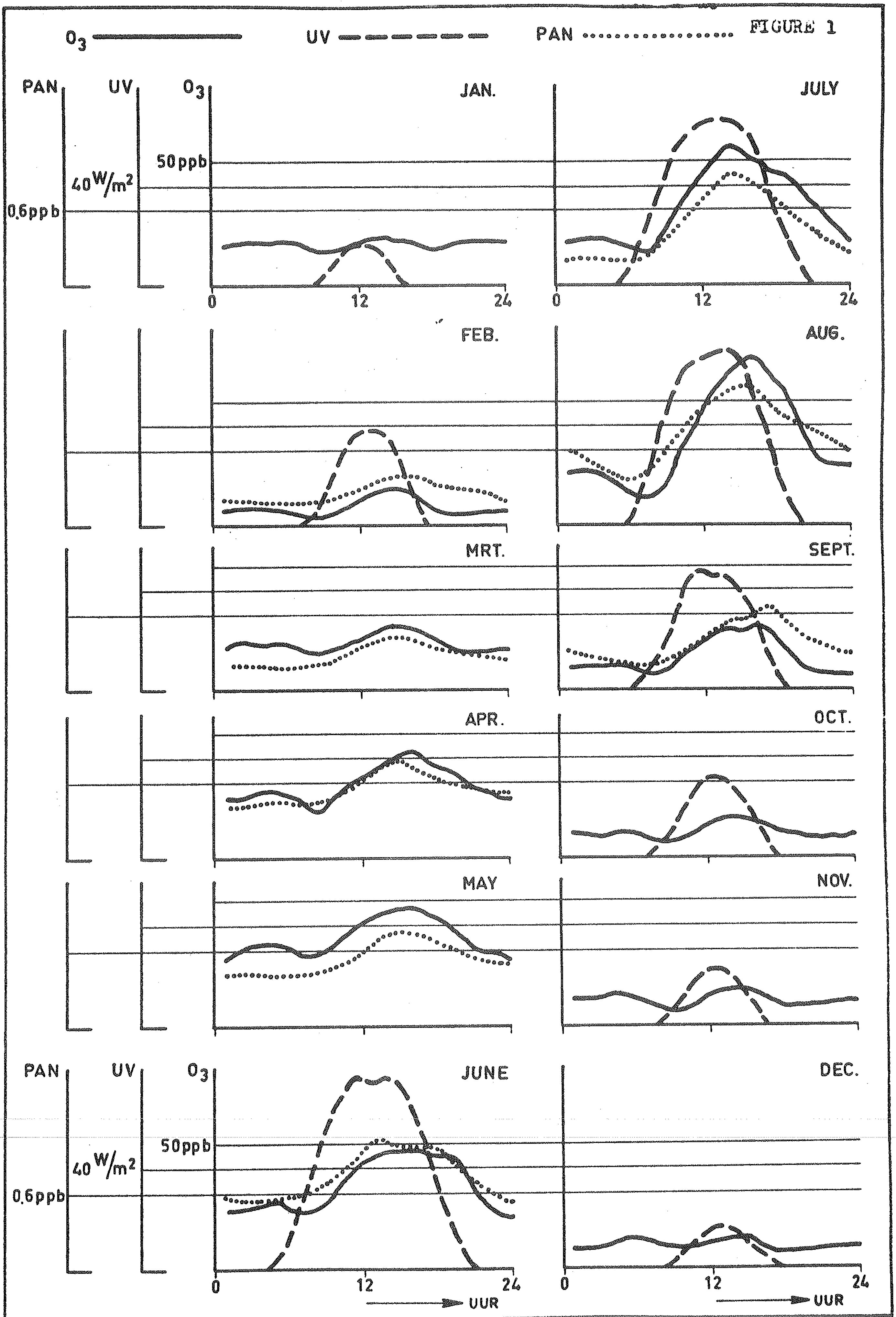
FIGURE 2. Meteorology and $O_3$ maxima in Western Europe, August 1975

FIGURE 3. Number of hours per year of which the hourly average oxidant concentration equalled or exceeded 0.10 ppm at Delft and 0.20 ppm at San Bernadino, California. San Bernadino data from M.D. Zeldin and D.M. Thomas, 1975.

FIGURE 4. Daily trend of the $O_3$ concentration measured at two altitudes at Cabouw, the Netherlands.

FIGURE 5. Daily trend of UV (290-400 nm) light intensity measured at Delft, 1976

FIGURE 1



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|---|---|---|---|---|
| IG-TNO | BUITENLUCHT | | RAPP G | NR. TG |

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| | |
|---|---|
| NETHERLANDS | CONC. — 0.10 ppm |
| ITALY | CONC. — 0.08 ppm |
| GERMANY | CONC. — 0.09 ppm |
| SWEDEN | CONC. — 0.12 ppm |
| ENGLAND + IRELAND | CONC. — 0.11 ppm |
| FRANCE | CONC. — 0.20 ppm |

7/8-8-75

| | |
|---|---|
| NETHERLANDS | CONC. — 0.12 ppm |
| ITALY | CONC. — 0.08 ppm |
| GERMANY | CONC. — 0.09 ppm |
| SWEDEN | CONC. —<0.08 ppm |
| ENGLAND | CONC. — 0.15 ppm |
| FRANCE | CONC. — 0.13 ppm |
| AUSTRIA | CONC. — 0.10 ppm |

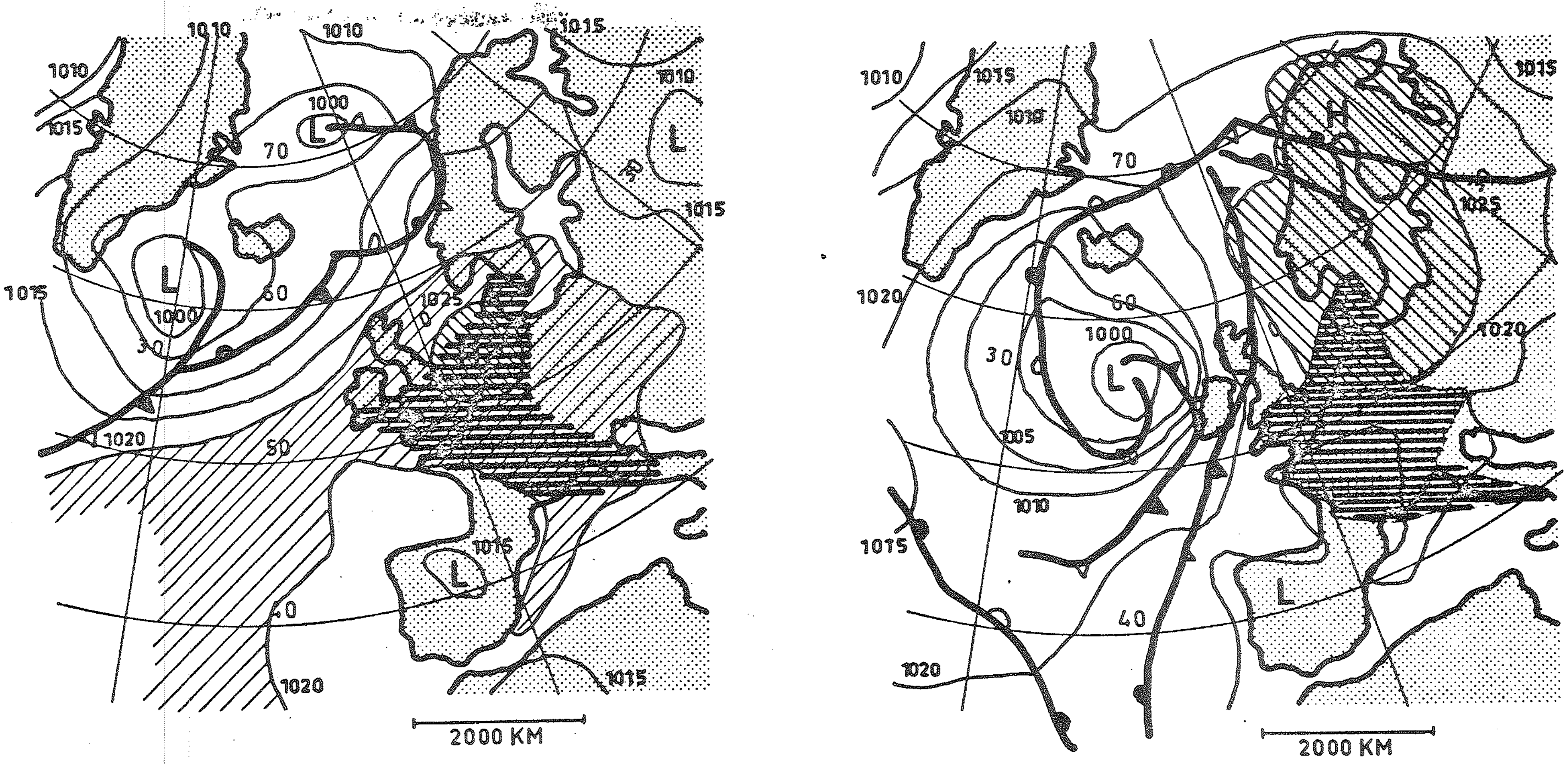
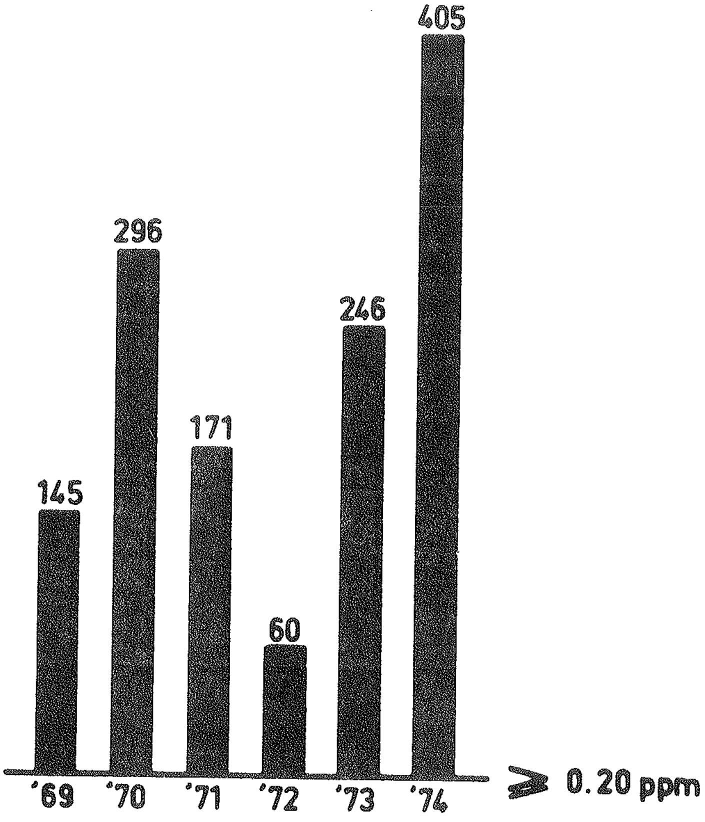
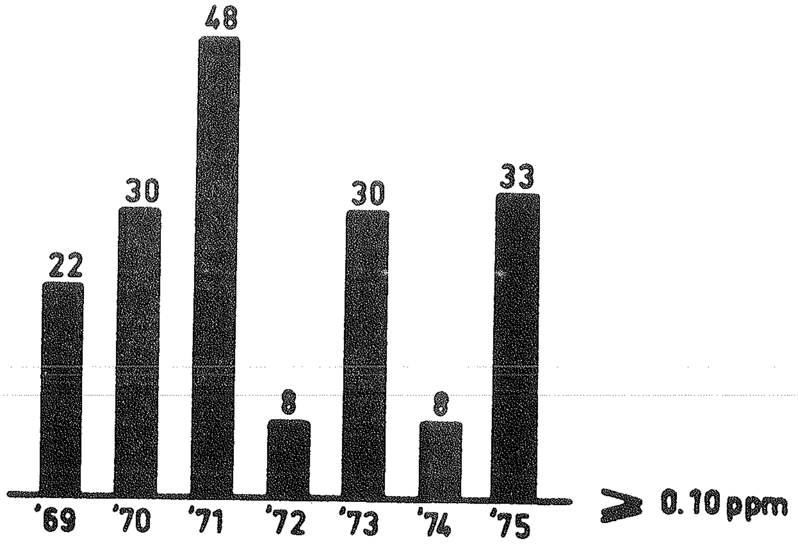


FIGURE 2

FIGURE 3





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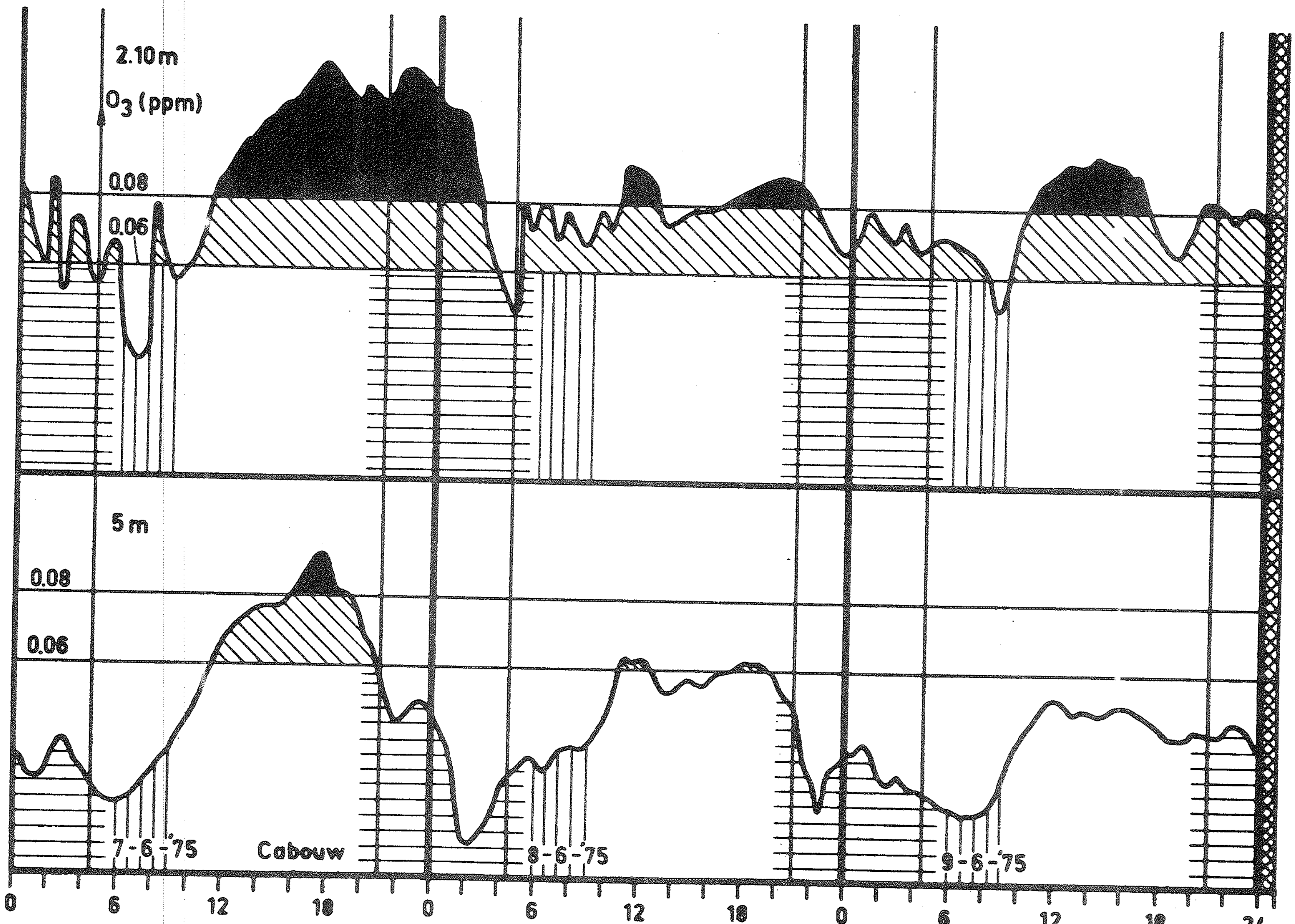
2.10m
$O_3$ (ppm)
0.08
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IG-TNO

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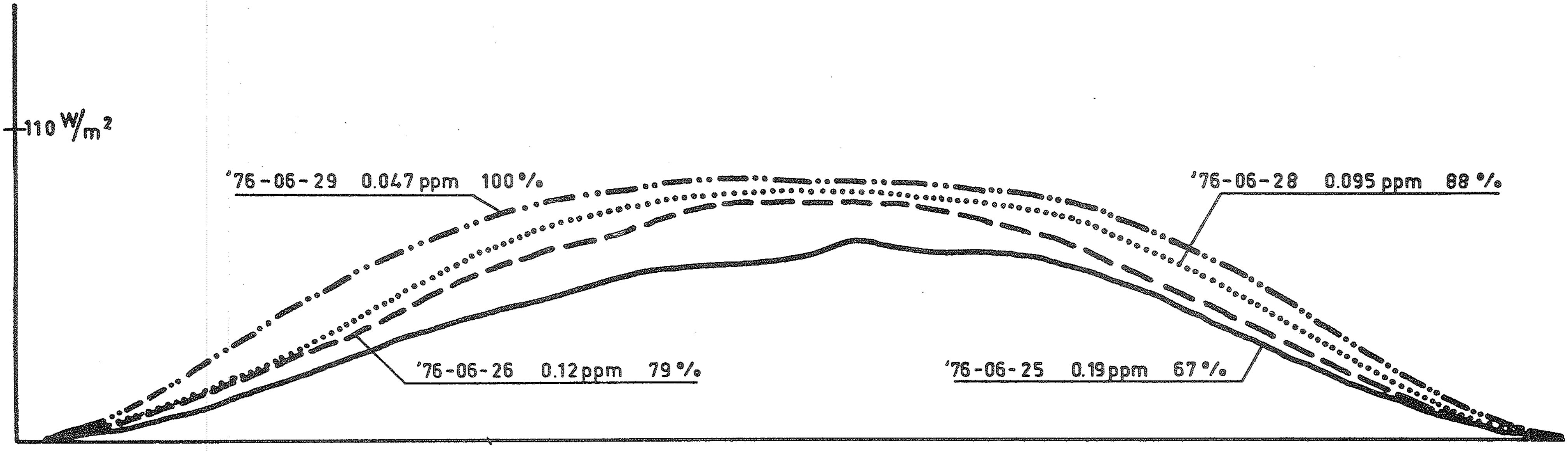

FIGURE 5