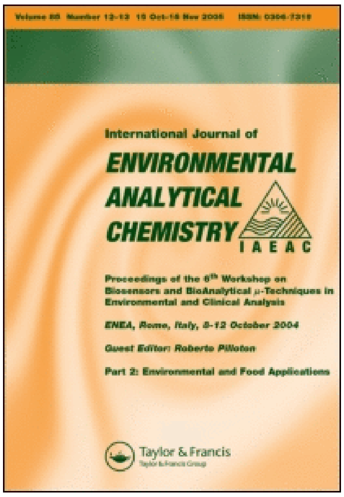

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The Monitoring of Ozone Immissions in Rural and Urban Areas*

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It has been shown, by a statistical study of the concentrations of ozone in air as measured by two monitoring stations—one being situated in an urban and the other a rural area—that photochemical smog episodes do occur.

The ratio O_3 urban/O_3 rural is normally <1. This ratio, however, has been shown to be >1, when certain conditions prevail, notably on days of high solar radiation and low velocity winds. At night-time, in the absence of photochemical reactions, the higher concentrations of ozone observed in town as opposed to the country side has been attributed to air transport phenomena.

KEY WORDS: Ozone, Photochemical smog, Air pollution.

INTRODUCTION

The advent of chemiluminescent instruments for the continuous monitoring of ozone has given rise to a whole series of publications, of results and interpretations about the variation of ozone concentrations measured at different sites at ground level.

Two monitoring stations, one situated in a rural area, the other in an urban area, have been operating in Geneva since 1974. A comparison of the concentrations of ozone as a function of time at these two sites with due regard to the local meteorology and anthropogenic activity should allow one to bring to light photochemical smog episodes, as have been observed in New York[1] and California[2] for example.

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In an area not subjected to any anthropogenic activity, the ozone concentration of the lower troposphere depends on the stratospheric ozone deposits.[3] The latter depend on the height of the stratospheric ozone layer and on the meteorological conditions affecting the transfers between the stratosphere and the troposphere.[4] Certain studies have shown nevertheless, that the concentration of ozone can be correlated with the long distance transport of air masses originating from polluted areas.[5,6] The variation of the height of the mixing layer in the lower troposphere has a great influence on the vertical transfer of ozone. This variation has been studied by means of natural radon activity.[7]

In an urban area, the concentration of ozone near the ground will depend furthermore on the anthropogenic activity, which, as a result of the formation of oxides of nitrogen and hydrocarbons, will lead to the production of ozone by photochemical reactions. Theoretical and empirical models have been established in an attempt to describe the phenomenon.[8]

We believe that there exists in the Geneva basin certain conditions favouring photochemical smog that are statistically significant and are clearly distinguishable from other situations of abnormally high ozone concentrations. We have, indeed, shown that there have been episodes in Geneva when the concentration of oxides of nitrogen, of hydrocarbons, of ozone and of carbon monoxide had daily fluctuations similar[9] to those described by many authors.[10]

EXPERIMENTAL

The town of Geneva is situated at the South-West extremity of the Lemanic basin. She is surrounded on all sides by mountains (Jura, Vuache, Salève) except on her North-East side where she is exposed to Lake Leman (Lake Geneva).

Two monitoring stations, situated one in the town of Geneva (co-ordinates 499,125/117,250), the other (co-ordinates 507,150/126,930), by the side of Lake Leman in an area representative of a rural area, are equipped with the following instruments for the measurement of:

Total hydrocarbons, methane and carbon monoxide	Beckman 6800
Ozone	Beckman 950
Oxides of nitrogen	Meloy 520-2
Sulphur dioxide	Beckman 906
Dust particles	Research Appliance Company (RAC)

A mobile laboratory of ecotoxicology, equipped for the measurement of gaseous pollutants (like the monitoring stations) and meteorological parameters, has been stationed at two well defined urban sites in order to confirm the results obtained by the fixed stations (see Figure 1).

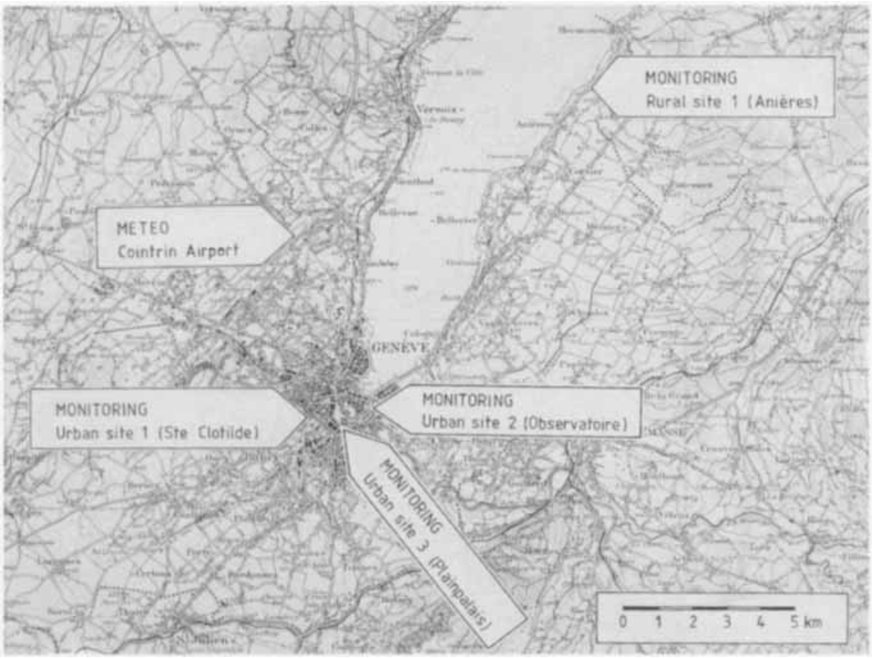


FIGURE 1 Localisation of monitoring sites.

The half-hourly mean concentrations of the pollutants are measured and their values stored on magnetic tapes for treatment on an Univac 1108 computer. Air is sampled at a height of 3 metres above ground level. The speed and direction of the wind are measured on the rural site by means of a Wolfe Anemograph situated at 12 metres above the ground. We also have at our service the synoptic meteorological recordings of the airport of Geneva-Cointrin.

RESULTS AND DISCUSSION

Thesis

Figure 2 shows the evolution of the monthly mean concentrations of ozone as a function of time. It can be seen, on the one hand, that for the urban site (Ste-Clotilde) the concentration is always lower than for the

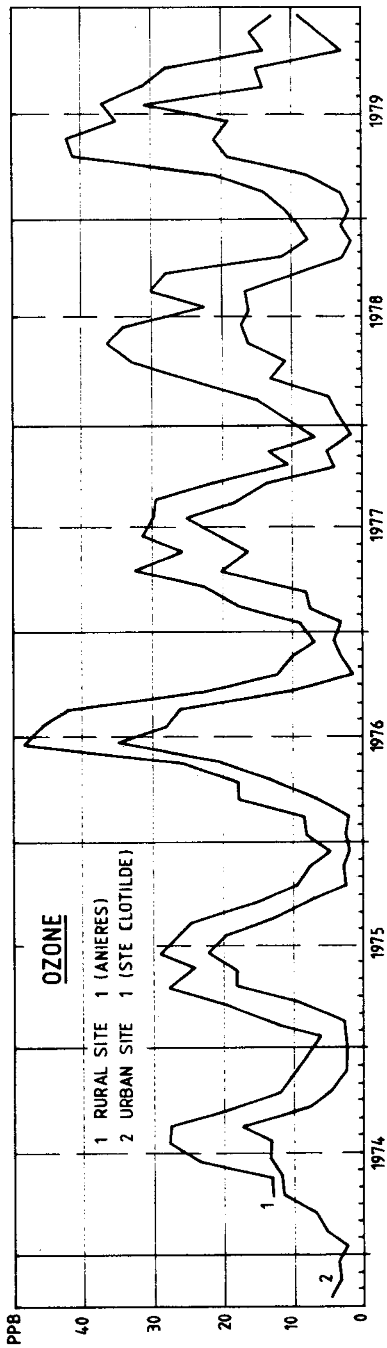


FIGURE 2 Monthly average ozone concentration as a function of time.

rural one and that, on the other hand, the maximum ozone concentrations for the two sites always occur between the months of April and September.

These findings confirm the hypothesis that the variation of the height of the stratospheric ozone layer is a minimum in spring, and that the rate of the dry deposition of ozone is greater in town than in the country.

From these findings we have put forward the hypothesis that the probability of the existence of ozone generated by photochemical reactions in the presence of anthropogenic precursors was a maximum when the concentration of ozone in the urban area was superior to the concentration of ozone in the rural area. The hypothesis equally means that the amount of ozone produced indirectly by the anthropogenic activity is superior to the amount of ozone consumed by dry deposition in the urban area.

On Figure 3 we can see the number of days per month when the ratio urban to rural ozone is greater than 1 for three consecutive measurements made during the day or the night (from 21.00 o'clock to 06.00 o'clock).

Daily period

When $$R_{u/r} = \frac{(O_3 \text{ urban})}{(O_3 \text{ rural})} > 1$$

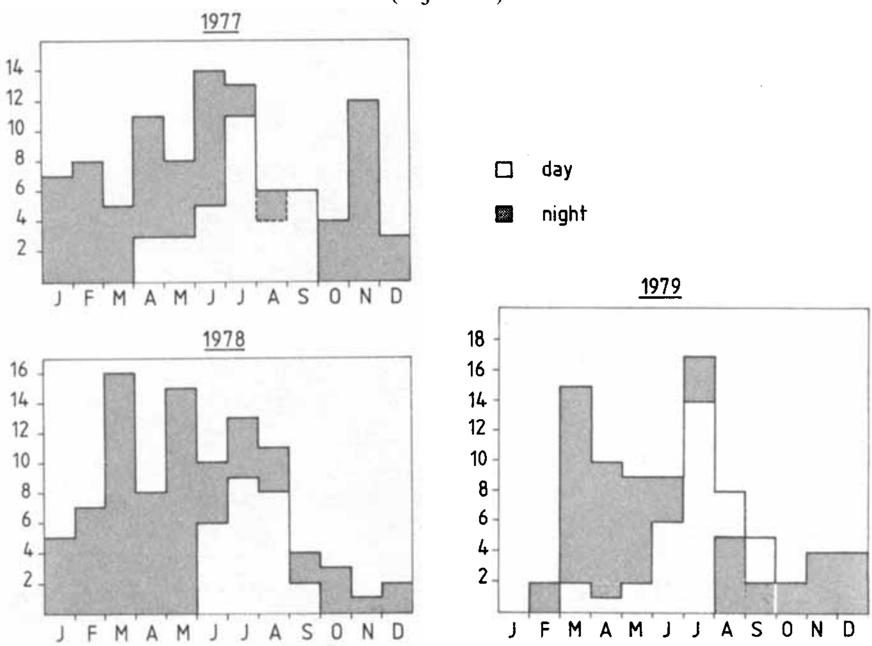


FIGURE 3 Frequency of the number of days for $R_{u/r} = \frac{(O_3 \text{ urban})}{(O_3 \text{ rural})} > 1$.

These ratios reach a maximum during the aestival period, that is to say during the period of maximum insolation. A closer analysis of the distribution of days, when $R_{u/r}$ is >1 during daytime as a function of the days of the week, shows (Figure 4) that there is a maximum on Sundays. But, the only parameter which varies in a cyclic fashion and has a weekly period is constituted by the anthropogenic activity. This fact seems

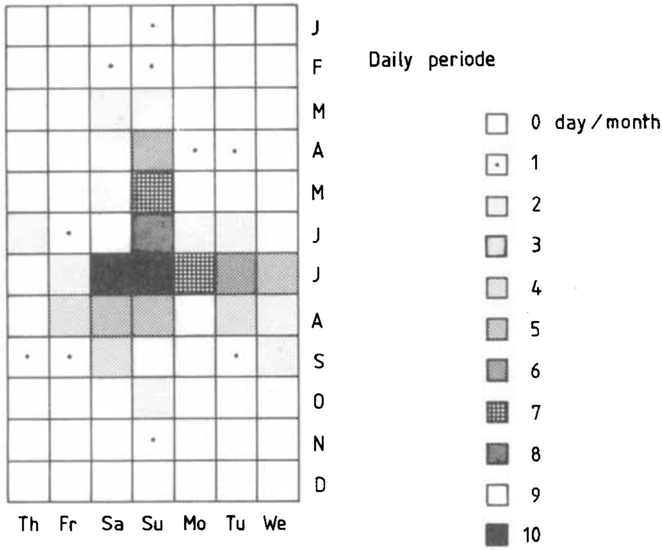


FIGURE 4 Distribution of days for $R_{u/r}=\frac{(O_3 \text{ urban})}{(O_3 \text{ rural}}>1$ as a function of months (1976–77–78–79).

paradoxal since the concentration of ozone increases in town in contrast to the country, especially when the primary pollutants decrease in town. Figure 5 shows that the half-hourly yearly average for total hydrocarbons and oxides of nitrogen are very much lower on Sundays than for the rest of the week, represented here by the Wednesday in town. The phenomenon is similar for dust particles.

Figure 6 shows the half-hourly average of the concentration of ozone as a function of the days of the week for the rural and urban areas. The concentration of ozone is very much higher on Sundays than for the rest of the week. It follows nearly the same profile as the rural area.

In 1972 and 1973 we undertook a series of measurements of the vertical gradient of atmospheric pollutants over the canton of Geneva.[11] Samplings were made by helicopter. The helicopter was equipped with a device which allowed the air samples to be stored in teflon bags for their

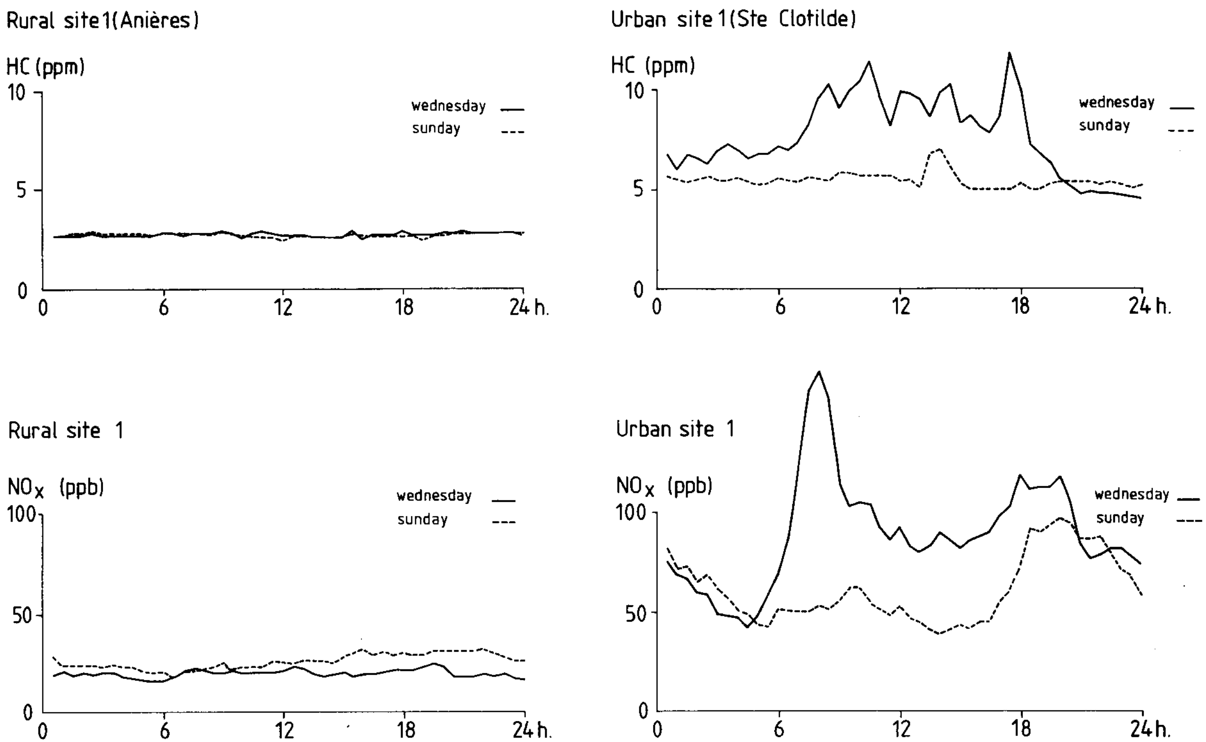
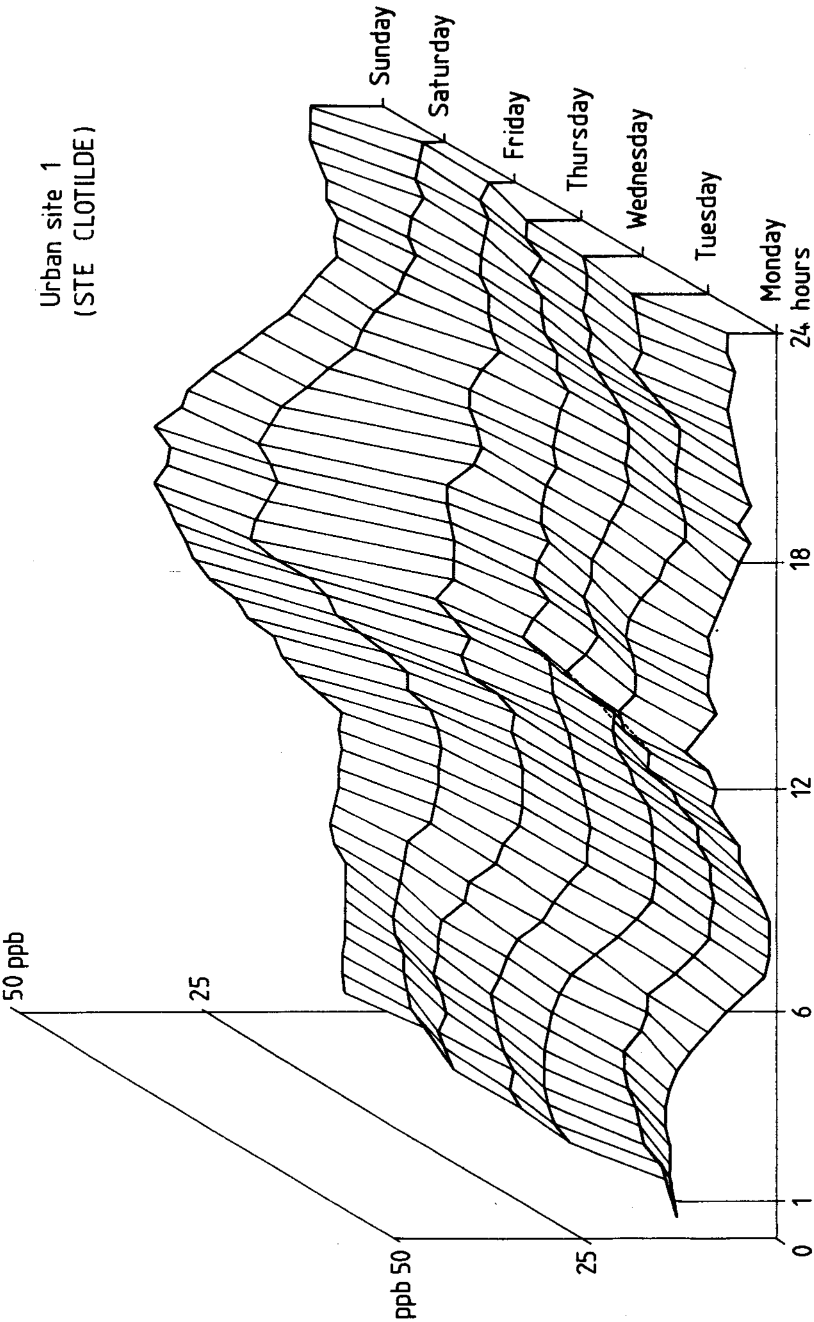


FIGURE 5 Half-hourly yearly mean (1978) of different pollutants.



Urban site 1
(STE CLOTILDE)
Sunday
Saturday
Friday
Thursday
Wednesday
Tuesday
Monday
24 hours
18
12
6
1
0
50 ppb
25
ppb 50
25

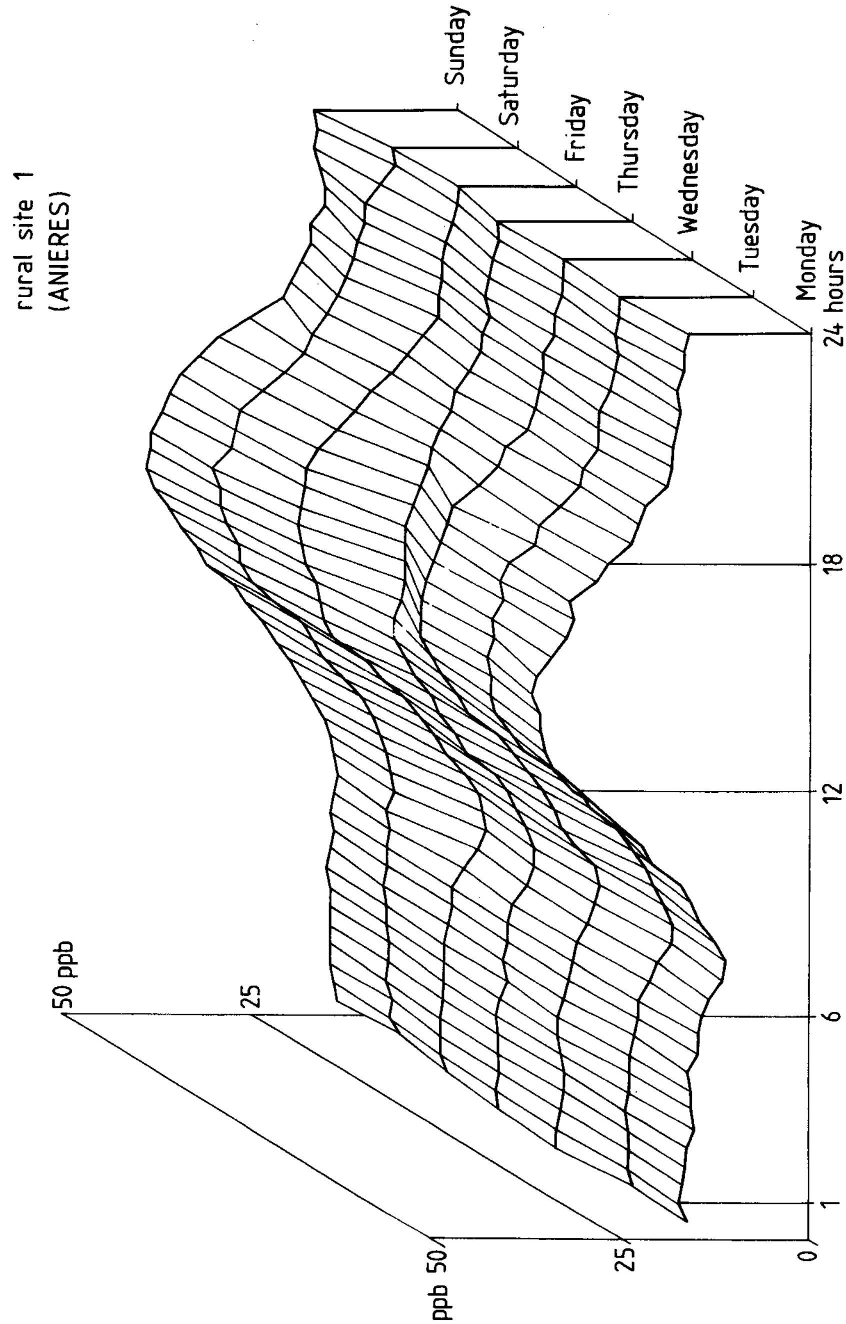


FIGURE 6 Half-hourly mean concentration of ozone (1979) from Monday to Sunday.

subsequent analysis in the laboratory (CO, NO_2, THC). Absorption of SO_2 in tetrachloromercurate solution was done on the helicopter and the spectrophotometric measurements done in the laboratory later. Ozone was monitored in situ by chemiluminescence on board of the helicopter by means of a Beckman 950 apparatus modified for energetic autonomy.

The vertical profiles of the concentration of pollutants show (Figure 7) a decrease up to an altitude of 500 metres. This means that the precursors of photochemical ozone are present in fairly appreciable quantities well

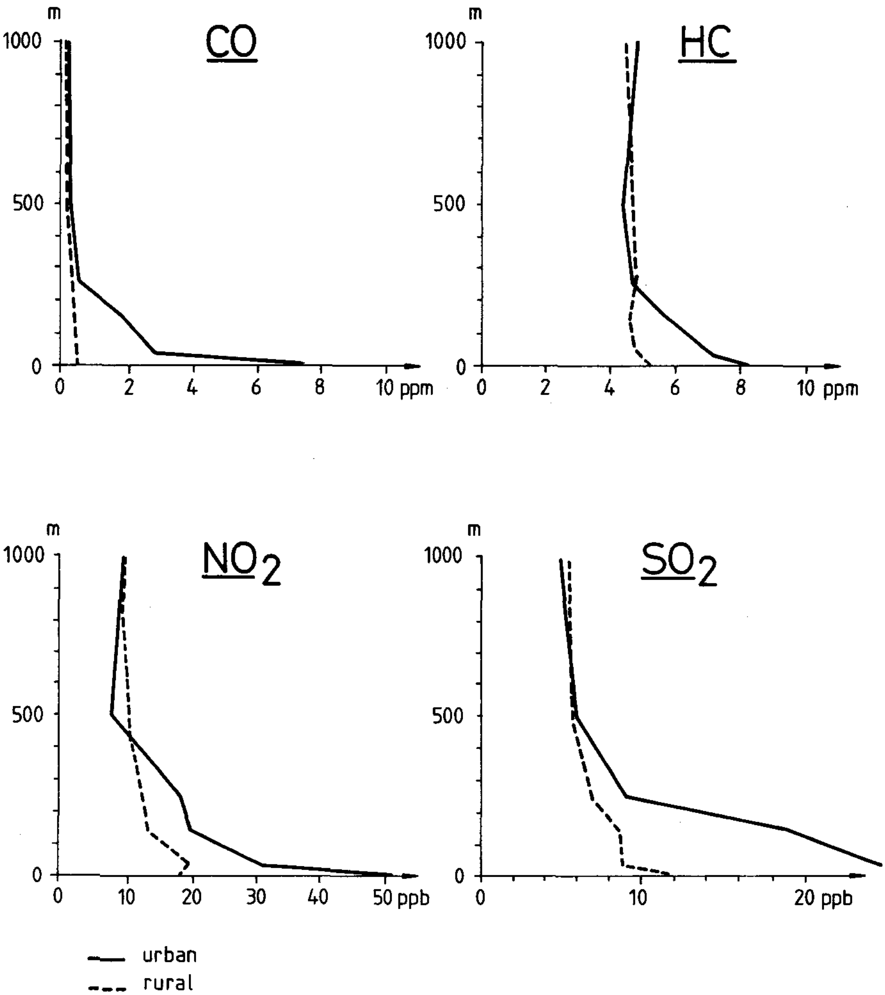


FIGURE 7 Vertical distribution of the various pollutants over Geneva (mean of 22 flights by helicopter).

above the urban areas. The concentration of ozone measured at ground level gives only a punctual information in space; on the other hand, the vertical variation (Figure 8) shows that during periods of strong solar irradiation the maximum for ozone lies between 100 and 500 metres.

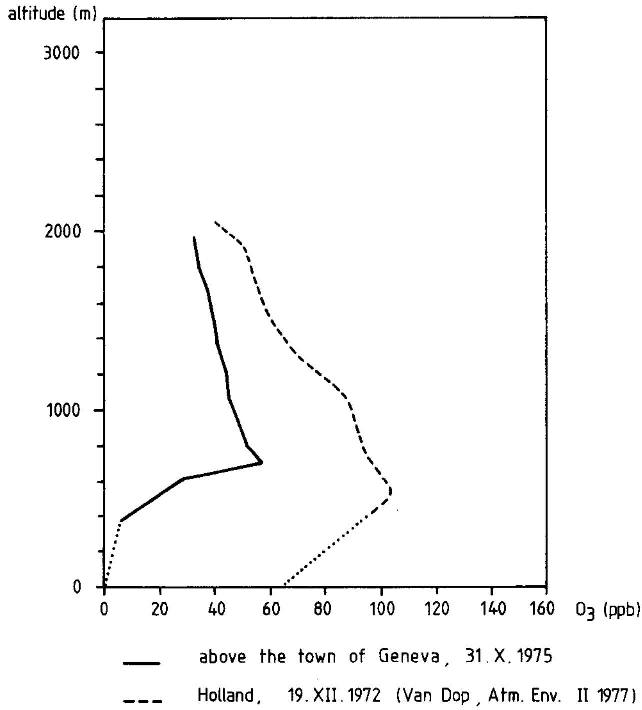


FIGURE 8 Vertical variation of ozone for a very sunny day——above the town of Geneva—31.X.75----Holland, 19.XII.72 (Van Dop, Atm.Env.II 1977).

Based on these facts, one can elaborate a coherent scheme for the vertical distribution of ozone in agreement with the measured ozone values at ground level. It is represented in (Figure 9). Under normal conditions, the dry deposition of ozone, greater in the urban zone, leads to a lower concentration than in the rural zone. At the time of a strong irradiation, the amount of ozone produced cannot, in any case, compete with the high deposition and the ratio urban to rural ozone is always less than 1. On the other hand, when the deposition of ozone is less, for example when there are fewer primary pollutants emitted at ground level, the concentration of ozone in the urban area can be greater than that in the rural area.

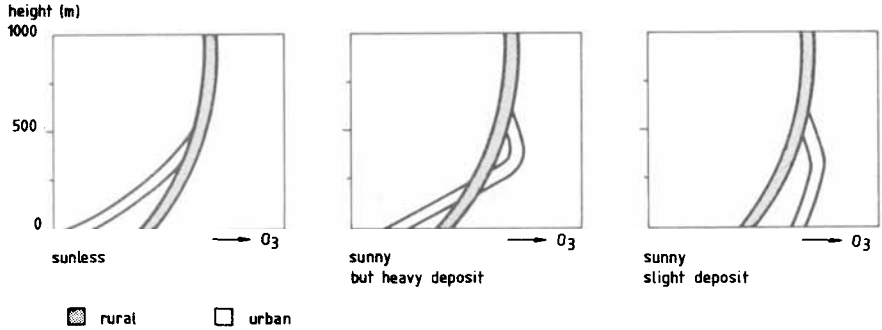


FIGURE 9 Scheme of the vertical variation of the concentration of ozone.

A study of the meteorological conditions prevailing when the ratio urban to rural ozone is greater than 1 during the day, shows that 80% of the time these conditions are characteristic of an anticyclone. In Geneva, this situation is indicated by a strong solar irradiation low winds.

Smog episode example: From the 19th to the 21st of June 1974 the meteorological and solar conditions were favourable to the formation of a photochemical smog (Figure 10). During that period, the concentrations of ozone at the urban station were much higher than those at the rural station: solar activity approximated twelve hours per day, easterly winds were of low intensity. A thin cloud cover favours photolytic reactions. The general meteorological conditions are typical of a stable anticyclone.

The daily evolution of the 19th, 20th and 21st of June is shown on Figure 10. Between 11.00 and 22.00 o'clock, the ratio urban to rural ozone ($R_{u/r}$) is greater than 1, even when North-Westerly/Westerly winds are blowing at ten knots. The cloud cover recordings, every three hours, are weak or null.

Indeed, for relatively constant hydrocarbon concentrations in the neighbourhood of 10 ppm, we find in town, during the period of solar activity, a relatively important formation of nitrogen dioxide shortly after the emission of nitric oxide. The formation of nitrogen dioxide is followed by a decrease in the concentration of nitric oxide. The increase in the concentration of ozone hardly follows that of nitrogen dioxide. The trend for the nyctemeral variations generally accepted to date is observed: At sunrise, an increase in the concentration of carbon monoxide, nitric oxide hydrocarbons. Nitrogen dioxide and ozone, in low concentrations, then appear under the action of solar radiation. About mid-day, the concentration of nitric oxide is a minimum if there are no emissions. The values of ozone reach maximum. In the afternoon and early evening the concentration of ozone is high. Increases are observed in the

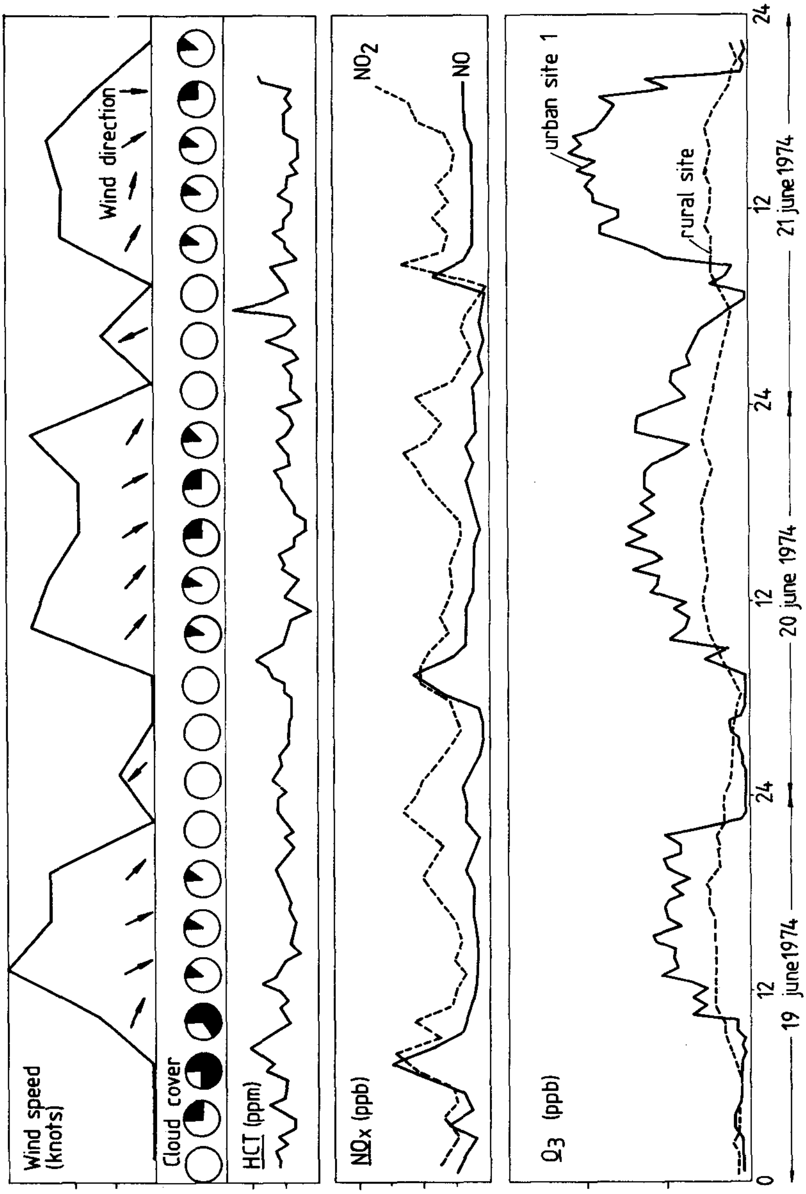


FIGURE 10 Evolution of concentration of ozone and various parameters for "smog episode".

concentration of nitric oxide late in the afternoon and at night. They are due to the pendular traffic. Nitric oxide is then oxidized to nitrogen dioxide by ozone whose concentration falls down to normal levels during the night.

Nightly period

The distribution as a function of the days of the week for nightly periods when the ratio urban to rural ozone is greater than 1 is unpredictable. There is consequently no correlation similar to the one for the exceedings during the daily periods. We can assume that the photochemical yield is zero at night. A priori, the higher concentration of ozone in town cannot therefore be attributed to this type of reactions.

A regular observation of the hourly profiles of the concentrations of ozone has shown us that it was dependent on the wind regime. We have established wind roses for nightly periods for Geneva-Cointrin and our rural station, taking into account only the wind measurements when the ratio urban to rural ozone was greater than 1. Their comparison with the wind roses for total nightly periods shows (see Figures 11 and 12) that there is a correlation between the South-Westerly winds and the exceedings of the concentration of ozone for the urban area as opposed to the rural area. The most probable cause that can account for this phenomenon resides in the fact that stratospheric ozone associated with the disturbances from the South-West, reaches the urban zone and is partially destroyed while passing over the town; the concentration of ozone in the rural area following the wind blowing from the urban zone is consequently lower. It can be seen that the nocturnal ratios urban to rural ozone are not associated with the aestival period but with the period when the atmospheric ozone layer is at its lowest.

Recent results from other urban sites

The mobile laboratory has been in operation since the end of last year. We have studied two sites in town:

Urban site 2: The site is situated in the town centre, on a promenade which is above two main roads with heavy traffic.

Urban site 3: The site is situated on a wide stretch of ground reserved for recreational purposes.

In a general way, the examination of the hourly profiles of ozone at these two sites confirm the observations at site 1.

I. The hourly profiles at the rural and urban sites are qualitatively similar. This means that the ozone measured at this time of the year

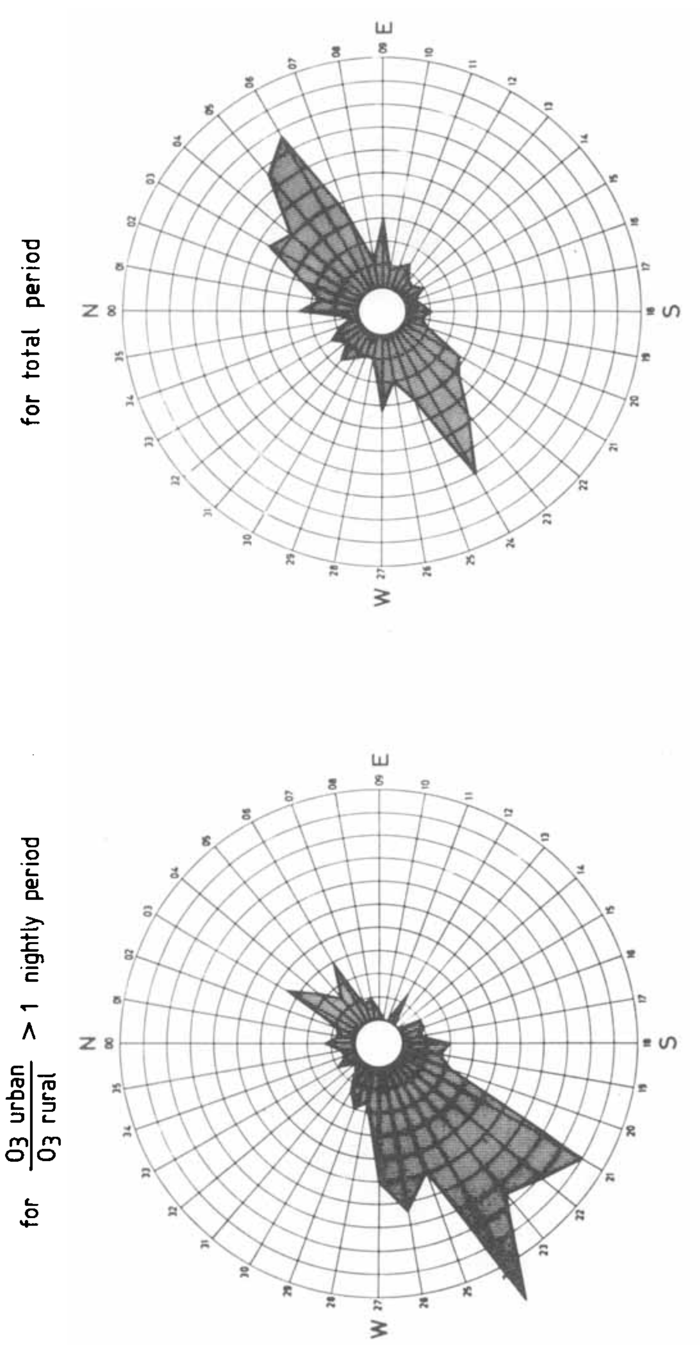


FIGURE 11 Wind roses for Cointrin Airport (1978).

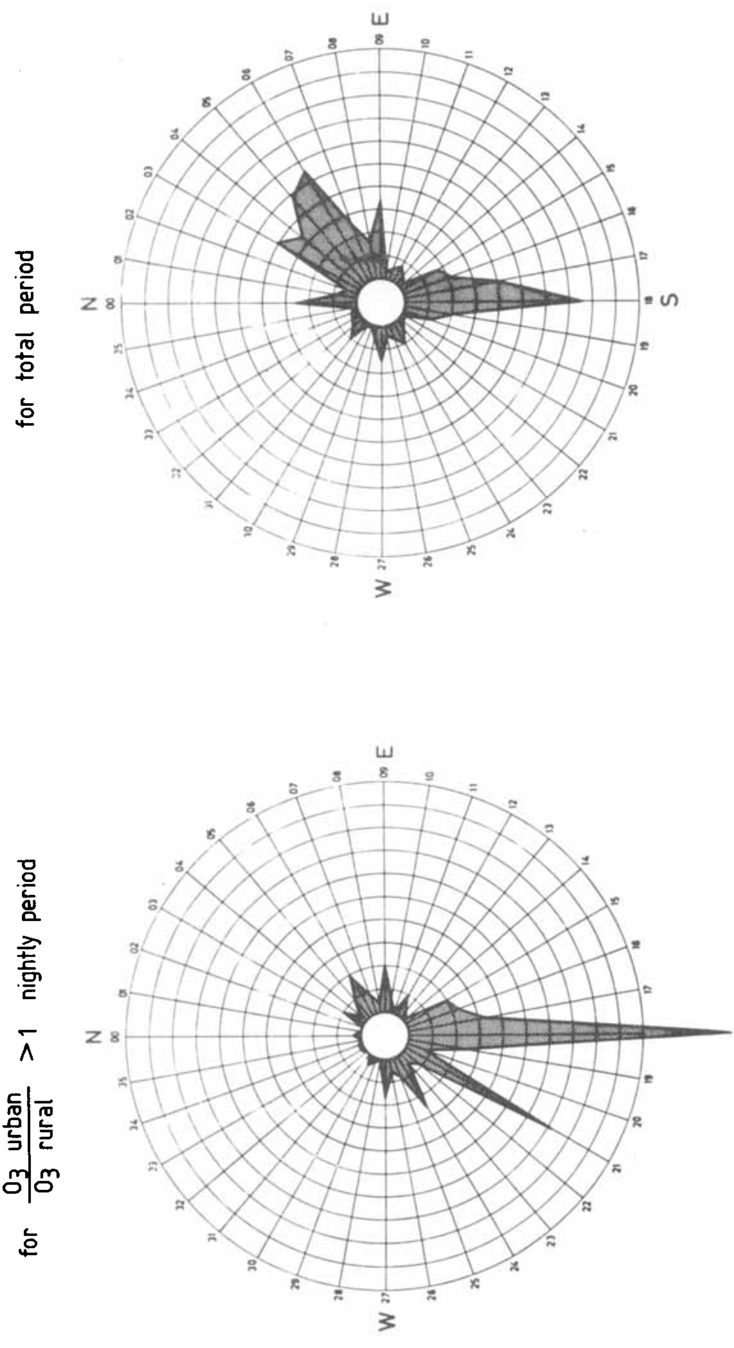


FIGURE 12 Wind roses of rural site 1 (1978)

(between February and May 1980) comes from the stratosphere; the stratospheric deposit is quasi-homogeneous over the studied territory.

II. Quantitatively, it is seen that the elimination processes of ozone are more pronounced in town. Comparatively the profile of the rural site is always the higher. Among the urban sites, site 2 is higher than site 1 and site 3 is similar to site 1.

We have equally looked for the periods for which the ratio $R_{u/r}$ was greater than 1.

Between February and mid-May 1980, there has been only a period of a few hours during which the concentration of ozone in the country was lower than that in town at night. This happened on the 11th of March 1980. Figure 13 shows the hourly profiles for ozone and it can be seen that between midnight and 06.00 o'clock the concentration in town is greater than in the country. The meteorological chart which gives the situation at 01.00 o'clock G.M.T. indicates at that time a perturbation associated with the South-Westerly wind regime. This fact confirms, as will be seen later, findings established on statistical bases: the exceedings at night, when the ratio urban to rural ozone is greater than 1, are associated with winds from a Westerly direction.

CONCLUSION

The measurements of the concentration of ozone on rural and urban areas show, undoubtedly that there is formation of ozone in an urban area by photochemical reactions under conditions of strong solar radiation.

The comparison of the concentrations of ozone enables one to bring to light the simplest elements of a model which will allow one to know the causes for the variation of ozone concentrations at ground level. Unfortunately, most of the time there is a superposition of the different causes of production, consumption and dilution of ozone which makes it impossible to describe in a rational manner the observations made at ground level.

In order to specify certain terms of the model, some parameters should be known at all times, such as:

the vertical variation of the concentration of ozone,

the concentration of total oxidants,

the concentration of certain compounds characteristic of photochemical smog such as PAN.

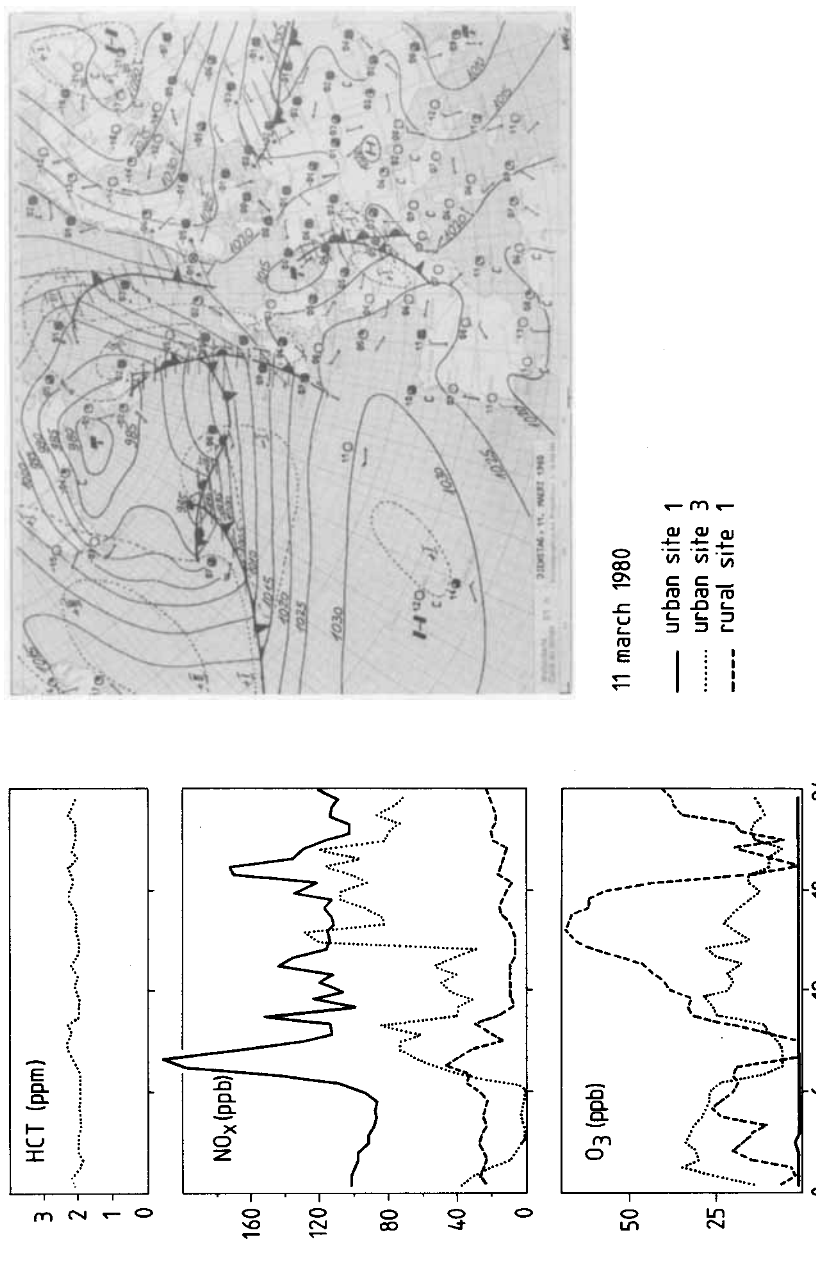


FIGURE 13 Evolution of ozone, NO_x and HCT concentration for a typical south westerly flow wind.

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