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OZONE EPISODES ON THE SWEDISH WEST COAST

Paper presented at the International Conference on Photochemical Air Pollution and its Control, Raleigh, North Carolina, 12-17 September, 1976

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B 337
Göteborg
September
1976

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ABSTRACT

Ozone measurements have been performed in Gothenburg on the Swedish west coast since 1972. On several occasions every summer increased levels of ozone were observed. The highest recorded 1-hour mean was 110 ppb. The high ozone levels coincided in time with increased concentrations of particle-borne sulphur both in and outside Gothenburg and of soot outside Gothenburg. Trajectory studies showed that most of these episodes were associated with transport of air masses from remote industrial areas.

INTRODUCTION

Long-distance transport of air pollutants over western Europe has been the object of extensive research in these countries since around 1970. This work has been focussed mainly on sulphur compounds and their role in the acidification of lakes, running waters and soil. The study of other essential air pollutants such as heavy metals, chlorinated hydrocarbons and nitrogen oxides has been very limited. However, as regards photochemical oxidants a few reports of investigations are available (1, 2). This paper presents results of measurements of ozone and associated parameters performed on the Swedish west coast.

OZONE MEASUREMENTS IN GOTHENBURG

Continuous ozone measurements according to the chemiluminescent ozone-ethylene method have been carried out in Gothenburg on the Swedish west coast since January 1972. Gothenburg is a highly industrialized city (e.g. two oil refineries), with

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a population of half a million. Initially, the purpose of the measurements was to investigate the possible occurrence of locally produced photochemical ozone. Following the results obtained, the measurements were later extended to include long-range transport of oxidants and their precursors.

Only two months after the measurements were started, on the 16th March, the ozone level in Gothenburg rose to above 90 ppb (Figure 1). Although higher peaks have been observed later, this

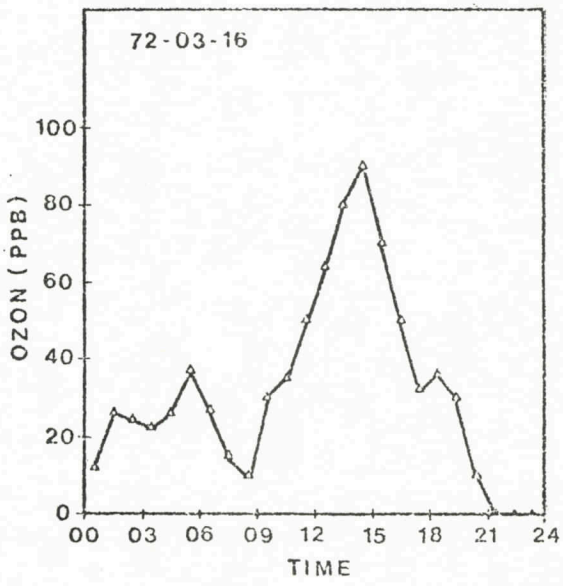

Figure 1. Ozone concentrations in Gothenburg, 16 March 1972

one was remarkable because it occurred so early in the year. March is considered to be a winter month in Sweden; the monthly mean temperature in Gothenburg is +0.7°C. The meteorological conditions and the concentration of other pollutants on this day are shown in Table 1. The data clearly indicate that this ozone peak could not be associated with any natural sources. This is particularly obvious from the concentrations of soot and particle-borne sulphur as well as from the visibility data.

TABLE 1. METEOROLOGICAL CONDITIONS AND CONCENTRATION OF AIR POLLUTANTS IN GOTHENBURG ON 16 MARCH 1972

Wind direction	at 13.00 hrs	SSE
Wind velocity		3 m/s
Temperature		+11.5°C
Relative humidity		54 %
Visibility		7 km (4 miles)
Overcast		No
Ozone	max.1-hour	180 µg/m³
SO_2	daily mean	114 µg/m³
Soot (OECD-method)	daily mean	57 µg/m³
Particle-borne sulphur (X-ray fluorescence)	daily mean	40 µg/m³

In the following months (March-August) of 1972, several similar peaks in ozone concentration above the natural background level were observed. These occurred mostly in the afternoons and early evening hours. However, peaks were observed also at other hours of the day, e.g. early morning. For this period, 1-hour concentrations above 80 ppb occurred on totally 16 days; the highest value recorded was 110 ppb. In subsequent summers (1973-76) similar ozone episodes were observed. However, these episodes were not as numerous as in 1972, and on no occasion did the ozone level exceed 110 ppb within Gothenburg.

The episodes have been evaluated on the basis of meteorological conditions and the concentration of other pollutants. The meteorological conditions during days with high ozone levels showed large variations. For example, the daily maximum temperatures during episodes in 1972 and 1973 ranged from +11.5°C to 31.5°C. The wind velocity also varied considerably (episodes could occur at wind velocities of up to 13 m/s), whereas there

was a clear pattern with respect to wind direction: During nearly all episodes winds were blowing from the sector SE-W. Mostly low or moderate values for visibility were recorded. All meteorological observations were made at Torslanda Airport, 10 km west of Gothenburg (Figure 2).

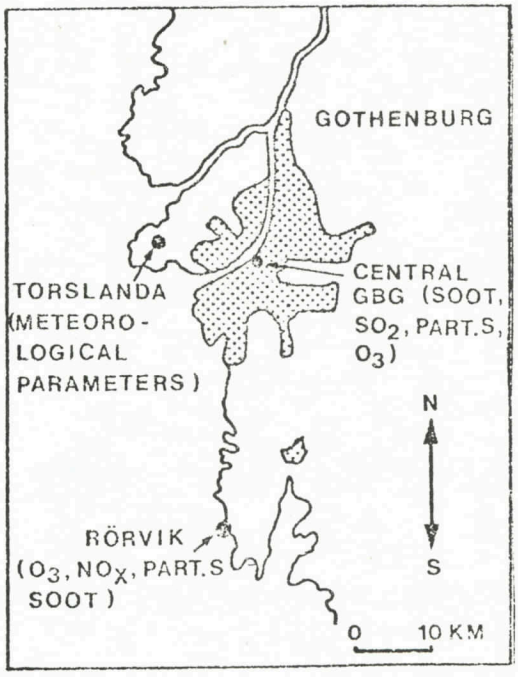

Figure 2. Location of sampling stations for air pollution monitoring and meteorological measurements

Sulphur dioxide, soot and particle-borne sulphur are measured in Gothenburg in a routine network. To determine the origin of the ozone episodes observed in Gothenburg, comparisons were made between daily mean concentrations of these pollutants and peak ozone concentrations. Correlation coefficients were calculated for each month with more than 10 comparable data in the periods March-August 1972 and 1973. No significant covariations for sulphur dioxide and soot were found, but a clear positive relationship was observed for particle-borne sulphur. The correlation coefficients between daily maximum 1-hour ozone mean values and daily mean values of particle-borne sulphur were in the range of 0.30-0.80 in nine out of ten months (Table 2). As

examples of the covariations, plots from August 1972 and 1973 are shown in Figure 3.

TABLE 2. CORRELATION BETWEEN DAILY MAXIMUM 1-HOUR CONCENTRATIONS OF OZONE IN GOTHENBURG (GBG) AND SOOT, PARTICLE-BORNE SULPHUR IN GOTHENBURG AND RÖRVIK. MARCH - AUGUST 1972 AND 1973

		Ozone vs. soot Gbg		Ozone vs. soot Rörvik		Ozone vs. part. S Gbg		Ozone vs. part. S Rörvik	
		r	n	r	n	r	n	r	n
1972	March	0.31	22	0.13	24	0.48	22	0.38	24
	May	-0.21	27	-0.17	27	-0.15	27	0.01	27
	June	0.04	22	0.68	26	0.30	23	0.69	24
	July	0.36	25	0.43	28	0.65	25	0.60	28
	Aug.	0.01	17	0.48	17	0.80	17	0.30	13
1973	April	-0.23	13	0.30	13	0.50	13	0.67	13
	May	0.50	31	0.50	31	0.63	31	0.51	31
	June	0.28	30	0.34	30	0.62	30	0.54	30
	July	0.08	31	0.42	28	0.31	31	0.31	31
	Aug.	0.25	26	0.51	26	0.65	26	0.63	26

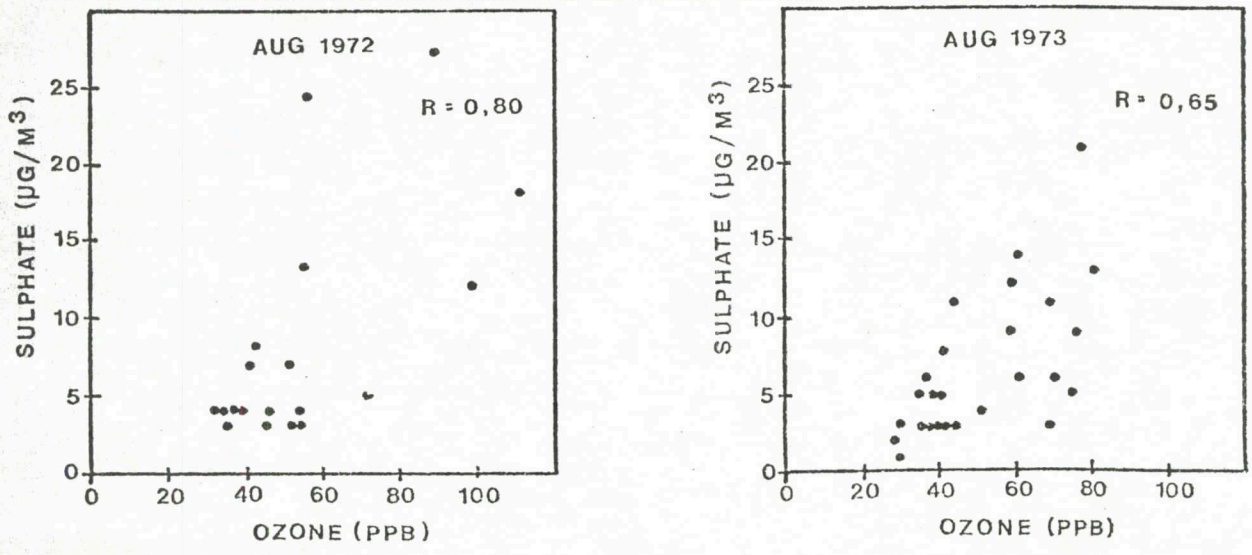

Figure 3. Daily mean concentration of particle-borne sulphur in Gothenburg plotted against maximum 1-hour concentration of ozone in Gothenburg for the months of August 1972 and 1973.

LONG-RANGE TRANSPORT OF OZONE

From other measurements on the Swedish west coast it is known that the concentration of particle-borne sulphur within Gothenburg is mostly a product of long-range transported sulphur. The daily ozone peak concentrations in Gothenburg were therefore compared to the concentrations of soot and particle-borne sulphur sampled at a non-urban coastal station (Rörvik) about 40 km south of Gothenburg (Figure 2). This station is primarily used for long-range transport studies. Soot and particle-borne sulphur have proven to be very useful tracers for long-range transport of air pollutants. Positive correlations for particle-borne sulphur and for soot were observed at this station (Table 2). These results indicated that the observed ozone episodes were not associated with pollutants produced in Gothenburg, but were a result of long-range transported pollutants. To confirm this, 48-hour trajectories were calculated for the days with high ozone concentrations in 1972 and 1973 (3). It was found that in 28 out of 33 cases, the air masses came from the sector E-S-W, having passed over heavily industrialised areas in Great Britain or on the Continent. As an example, the trajectory for the 16th March 1972 is plotted in Figure 4.

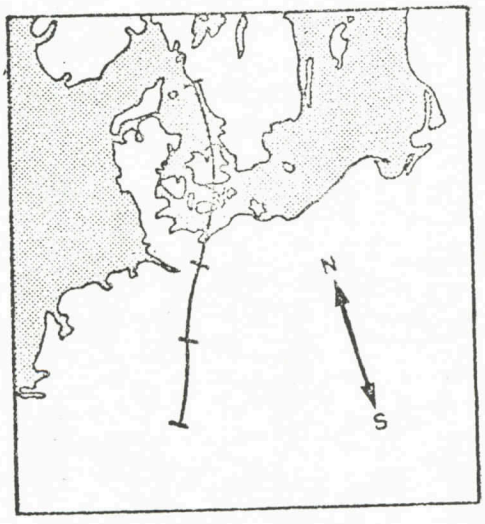

Figure 4. 48-hour trajectory for 16 March, 1972

Comparisons were also made between daily maximum concentration of ozone and particle-borne strong acid measured according to Brosset (4). However, strong acid has not as yet been measured on a routine basis comparable to ozone monitoring and no statistical evaluation is therefore possible. Nevertheless, an examination of the data will show that most of the strong acid episodes are associated with ozone peaks (Table 3).

TABLE 3. COMPARISON BETWEEN CONCENTRATION OF STRONG ACID ON PARTICLES SAMPLED AT RÖRVIK AND MAXIMUM OZONE CONCENTRATIONS DURING THE FIVE MOST ACID EPISODES IN THE SUMMER OF 1975

	H^+ n mole/m^3 Rörvik	NH_4^+/H^+ mole/mole Rörvik	O_3 ppb Gothenburg	O_3 ppb Rörvik
May 19	225	2.8	66	76
29	62	2.4	45	75
Aug. 5	77	1.3	54	130
7	21	2.8	84	151
29	56	3.6	47	-

In the summer of 1975 ozone measurements were also performed at the non-urban station (Rörvik). There, high ozone levels were observed on several occasions. The 1-hour ozone concentration exceeded 120 ppb on 11 days in that period; the maximum hourly concentration was 210 ppb.

There was mostly a close covariation between the ozone levels observed in Rörvik and Gothenburg. However, for most of the time, the level was higher at Rörvik. This indicates that there is no local contribution to the ozone level in Gothenburg. Instead, other pollutants emitted locally partly destroy the incoming ozone. Figures 5 and 6 give examples of ozone episodes

observed at these two stations.

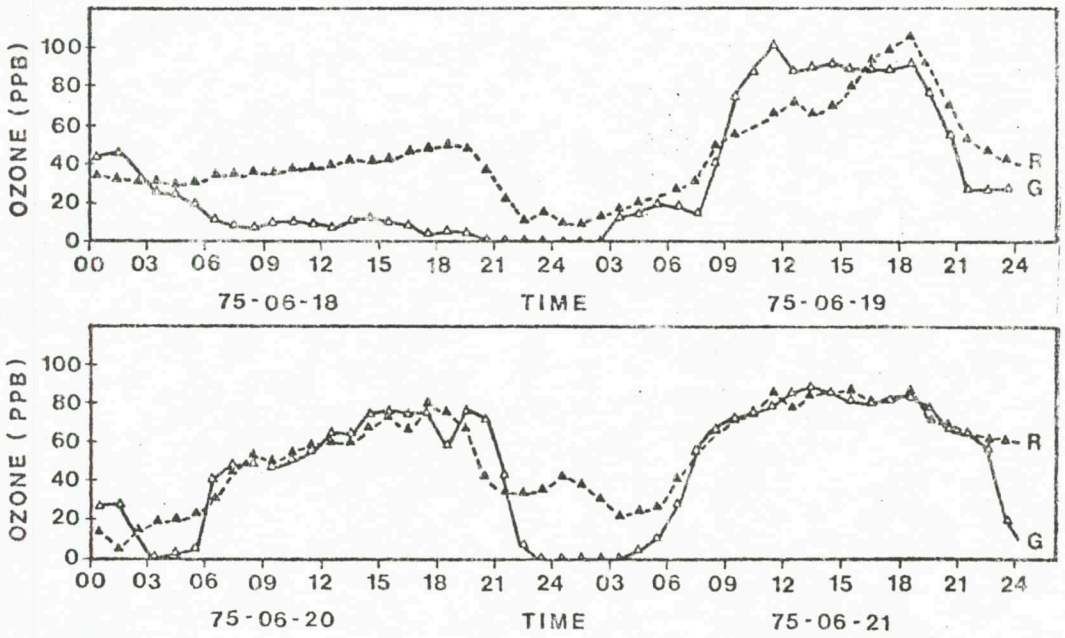

Figure 5. Ozone concentration in Gothenburg and Rörvik, June 18-21, 1975

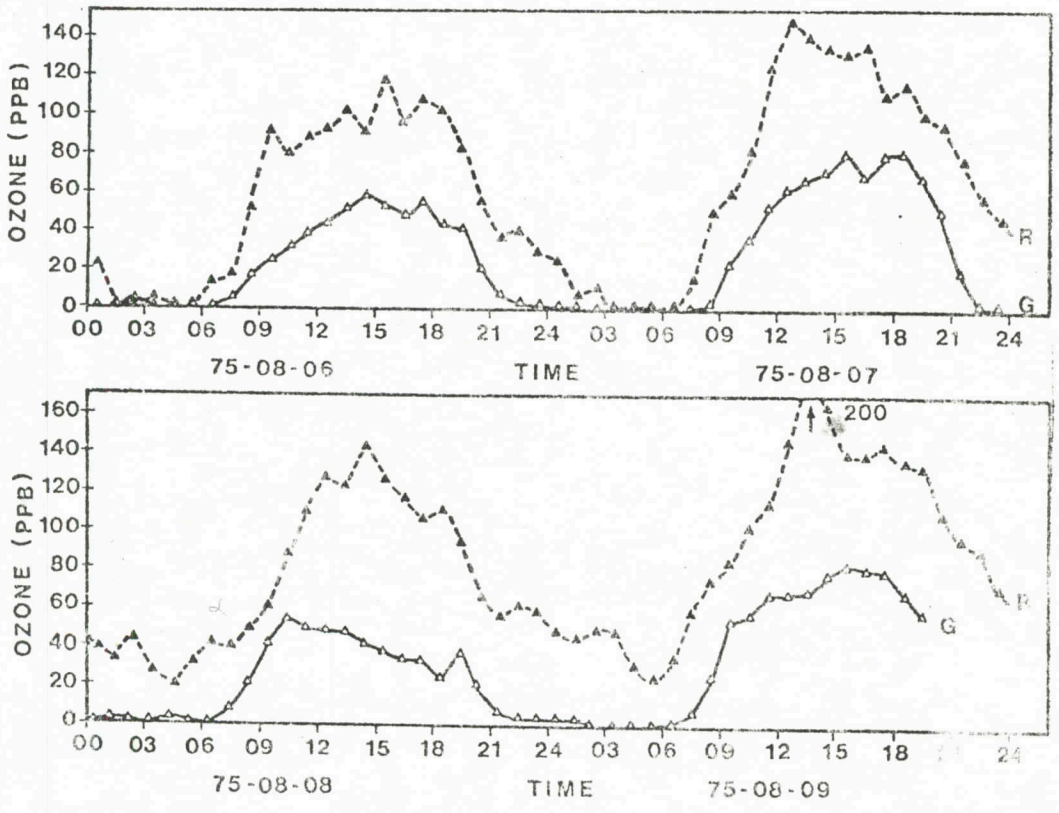

Figure 6. Ozone concentration in Gothenburg and Rörvik, August 6-9, 1975

In a further investigation of the cause of the ozone episodes, continuous measurements of nitrogen oxides were carried out during the summer of 1975 at Rörvik. The levels of nitrogen monoxide as well as nitrogen dioxide were in the range of 1-10 ppb. Despite the small variations in concentration, positive relationships could be seen between the early morning concentrations of NO_x and maximum ozone levels. Figures 7 and 8 are examples of the variation pattern.

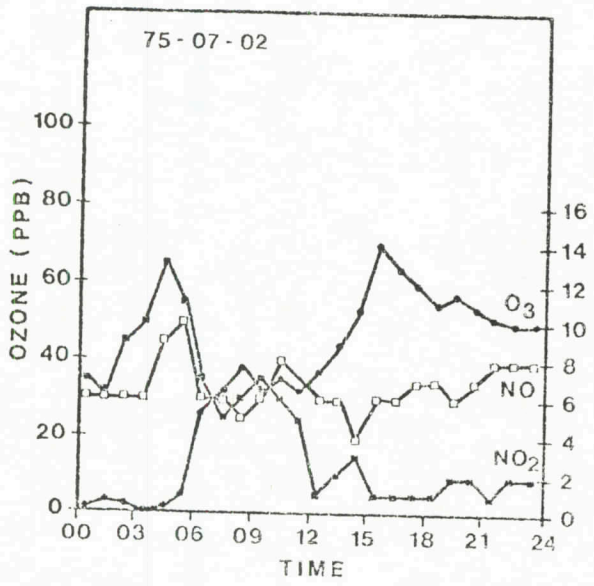

Figure 7. 6 August 1975

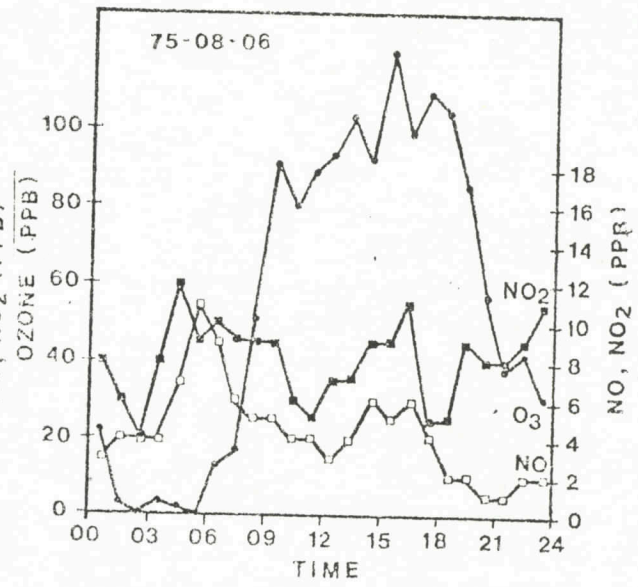

Figure 8. 2 July 1975

Variations in concentrations of ozone and nitrogen oxides at Rörvik.

DISCUSSION

From our measurement data as well as from those collected in other countries in western Europe, it is clear that several ozone episodes occur every summer over large areas in Europe. The impact of these episodes is not known and no investigations have as yet been carried out in Sweden to clarify this. It is very likely that these ozone peaks cause damage to vegetation,

but no such effects have as yet been observed. One reason for this may be that plant injuries on the Swedish west coast are often assumed to be caused by sea spray.

As regards effects on human health, complaints about photochemical smog were made on one occasion (28th May 1973) in Gothenburg to the local Board of Health. The concentration of ozone in Gothenburg that day was 80 ppb at its highest. No data from areas outside the city are available. This episode was associated with very high concentrations of an aerosol consisting of sulphuric acid and ammonium sulphate (5, 6).

One question that arises when studying the simultaneous occurrence of high ozone levels and high concentrations of acid sulphate aerosols is: Does ozone play any role in the oxidation of sulphur dioxide in the long-range transported air masses? The question is very justified considering the correlations observed between ozone and sulphate. In winter, the sulphate in the frequent episodes resulting from long-range transported pollutants is formed through catalytic oxidation. In summer, this process is less likely because of, among other things, low relative humidities. The summer aerosols also differ from the winter aerosols in several other respects, e.g. size distribution and acidity. These differences indicate that sulphates are formed by different mechanisms and that ozone or oxidants are compounds that might play a role in sulphate formation.

It is well known that the reaction between ozone and sulphur dioxide in the gas phase is a very slow reaction and of minor importance for the oxidation of SO_2. However, according to experiments by Penkett (7), oxidation by ozone in the liquid phase might be possible. The acid aerosols normally occurring in connection with ozone episodes contain a water phase even at rather low relative humidities. Research on this reaction mechanism is in progress.

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