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Analysis of the tropospheric ozone dynamics by Lidar

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Introduction

Many attractive results have been recently obtained using the Lidar technique for characterising tropospheric pollution. Most of them were either dedicated to primary pollutants (NOx, SO2, VOC,..) in highly polluted areas (cities, industrial plants,..) or to secondary pollutants, especially ozone, in the free troposphere. The aim of the present study is to compare the photochemical dynamics of ozone under urban and semi-rural conditions, and in particular to observe the effects of large cities on their near neighbourhood.

For this purpose two sets of results were compared, the first obtained during a measurement campaign in the Limmat Valley (Würenlos) nearby Zürich, and the second obtained from a stationary Lidar system implemented in the centre of Leipzig.

Both systems have been previously described in details1,2. They both used Excimer-pumped dye lasers providing few millijoules in the 220-300 nm spectral region in order to detect NO, NO2, SO2, and O3. On the receiver side, the mobile Lidar used a 400 mm telescope and an 8 bits 100 MHz transient digitizer, while the stationary is based on a 610 mm dia. Cassegrainian arrangement and a 10 bits 200 MHz digitizer. The Lidar Station Leipzig further disposes of a very high level software for data analysis and routine measurements, based on a DEC 5000 workstation.

Note that because of reliability and ease to use, we recently implemented in all our Lidar systems high energy (from 100 mJ to 1J) "all solid state" Ti:Sapphire lasers (Elight Laser Systems) instead of the Excimer-pumped dye lasers.

Summer smog in "semi-rural" regions

The Lidar campaign in Würenlos was part of a large scale study on ozone formation in the Limmat Valley, called HOLLA3. The system was placed in a quasi-central position on the Altberg mountain, some 70 m above the Limmat river (figure 1). A highly frequented highway, leading to Zürich, follows the contour of the mountain, well reachable by the Lidar. Figure 1 shows the ozone concentration as a function of time, recorded over three lightpaths: (A) 1.2 km long in total, at 15 m height above the highway, (B) 1.6 km long, 55 m high, and (C) 1.6 km long and 60 m high. A very strong perturbation due to the highway is clearly observable on path (A). Path (A)

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is indeed closer to the highway (only 15 m above) and of shorter length, while the altitude and the longer pathlengths of (B) and (C) reduce the effects of traffic.

These two latter constitute then a reference, where the usual diurnal behavior of ozone concentration is well reproduced. In the morning, low values (20 ppb) are recorded, until solar irradiation rises up, generating ozone up to 110 ppb in the afternoon, by photodissociation of NO2. In the evening, the concentration decreases again, as the sun goes down.

In opposite to this regular behavior, a highly structured pattern emerges for lightpath (A). More precisely, ozone “holes” are observed 4 times a day, exactly at rush hours. This constitutes a direct observation of the dynamics of the NO-NO2-O3 cycle, as it is shown below.
In order to access more precisely the photochemical processes of generation and destruction of ozone, vertical profiles were recorded in a single direction over the highway. For ease of comprehension, ozone concentration is plotted as a function of time for only two different altitudes (figure 2). At 28 metres above the highway, rush hour effects are again well identified. The holes at 1 pm and 6 pm are due to the injection in the valley of high NO concentrations by traffic. NO destroys then O$_3$ and generates NO$_2$. At higher altitude, the drops in ozone concentration at rush hours are weaker (NO concentration is lower) whereas a peak is observed at 3 pm. This is obviously due to the subsequent photodissociation of the NO$_2$ generated at lower altitude before.

**Comparison with the Leighton relationship**

To quantify this direct observation of ozone photochemical dynamics, a comparison between the ozone data with NO and NO$_2$ concentrations has been performed. For this let us recall the origin of the Leighton relationship:

1. $\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}.$ (j$_1$)
2. $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
3. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (k$_2$)

Equ. (1) and (2) is the ozone generation described above while (3) is the depletion mechanism. Since (2) is very fast, the process is determined by the ratio of the rate constants j$_1$ and k$_2$, or (Leighton relationship):

$$[\text{O}_3] \frac{\text{[NO]}}{\text{[NO}_2]} = \frac{j_1}{k_2}$$

Let us note that j$_1$ is dependant of light intensity, and that a special care has to be brought to measure the sun irradiance during the day.

Figure 3 compares the ozone concentration obtained using the Leighton relationship and the measured NOx concentrations with its actual value measured by Lidar. If the agreement is fair from 8 am to 5 pm (still within ± 30 %), it becomes very bad in the night (more than 300 % error !). This shows that oxidation by nitrogen oxides is dominant when solar radiation is strong enough (j$_1$ important) but competitive processes are present. In other words, reactions with other pollutants like VOC's become dominant at night.

![Figure 3: Concentrations of NO, NO$_2$, and O$_3$ and deviations from the Leighton relationship](image-url)
Comparison with urban conditions

A detailed study of the ozone behaviour under urban conditions in Leipzig is performed since summer 1992. Mappings of ozone concentration and vertical gradients have been routinely recorded. The major trend is the unexpected inhomogeneity observed for a secondary pollutant: Since $O_3$ is strongly dependant on the NO concentration, as shown above, strong gradients are still generated.

The example of a vertical profile over Leipzig is shown in Figure 4. Concentrations are plotted at three different altitudes, as a function of time. A fascinating analogy is observed with the "semi-rural" regions. Here again, at lower altitudes, holes are observed at rush hours. Even the afternoon maximum occurs, and is predominant at higher altitudes. Note also that at about 500 metres, the maximum is delayed in time, confirming our statement of diffusion time of the generated NO$_2$.

![Graph](image)

**Figure 4:** Diurnal ozone cycle at 3 different altitudes over Leipzig

The overall trends are however drastically smoothed in comparison with our case model of Würenlos. The reason for this smoothing is of course the complexity of the terrain and the wide spread of the emitter types and locations. The ozone values are furthermore always lower than in the valley near Zürich, probably due to higher NO concentrations. A quantitative analysis is however in this case much more difficult to perform; it needs a long term monitoring of ozone, but also simultaneously at least of NO and NO$_2$.

References