Study of the $O_3$-NOx relationship in different periods of the year

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Abstract

The processes involved in producing and transporting ozone ($O_3$), the main component of the photochemical smog, have proved to be complex. From the scientific point of view, ozone gas is the combined result of complex physical and chemical transformations. Photochemical oxidizers as ozone are not emitted directly into the air, but are formed when nitrogen oxides (NOx) and hydrocarbons are combined having solar radiation as propellant. These gases are emitted by different sources such as vehicles, power plants and industries where combustion processes take place.

The aggressiveness of the pollutant ozone depends on its concentration in the air, which is a function of the amounts of the precursor gases present and local and seasonal weather conditions.

This work studies the ozone level variations in different periods of the year and the relation with nitrogen oxides concentration analyzed in the town centre, where the influence of motor vehicles on the quality of ambient air is noticeable. It is observed there is a direct relationship between the periods of maximum ozone concentrations and the presence of strong solar radiations.

During the studied period, which involved three years, numerous episodes have been determined in which the levels have exceeded the standards accepted by regulations. They occur at the peak concentrations of the precursor gases and during the times of maximum solar radiations.

Keywords: ozone, photochemical pollutant, exceedences.
1 Introduction

The ozone is a colorless, invisible and nicely smelling gas. Its molecule formed by three oxygen atoms is very reactive when combined with other chemical elements, oxidizing and corroding the materials, in consequence. At certain concentrations it also irritates the mucous membrane of living creatures.

The ozone which is found in the atmosphere layer nearest to the earth surface, up to an altitude of 10 km, is the tropospheric ozone. Part of it is of natural origin, known as bottom value, formed by the nitrogen oxides naturally present in the atmosphere and the volatile organic compounds mostly sent out by the aromatic plants and the one resulting from the intrusions of stratospheric ozone (23% of the total) and the one formed in the electrical discharges of a storm.

The ozone formed by anthropogenic activities is a secondary pollutant not emitted directly into the atmosphere but formed by photochemical reactions among its precursors, activated by solar light. As a consequence high levels are found at the end of spring and the beginning of summer [1].

The “Secretaría de Política Ambiental de la Provincia de Buenos Aires“ standing normative establishes an ozone concentration of 0.12 ppm, for 1 hour, for the ambient air quality.

The objective of this work is to study the ozone level variations in the different seasons of the year and its relationship with other contaminants analyzed in the San Nicolás city centre where the influence of motor vehicles on the quality of ambient air is noticeable.

San Nicolás has 160,000 inhabitants, a large number of industries and a traffic flow that reaches 50,000 vehicles including public and private transportation [2]. It is located in the North of Buenos Aires Province in Argentina.

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2 Experimental

The ozone and NOx concentrations were measured by means of a monitoring system with two measuring remote stations connected by cell phones to the system of data acquisition in a computer where they were stored and processed.

The gases were analyzed by Environcels sensors. These electrochemical sensors for gaseous diffusion possess excellent stability in an extensive range of ambient temperatures. Each sensor is composed of four electrodes, one active electrode and a contra electrode that realize the detection, a reference electrode for each gas, and a fourth electrode that compensates the temperature variation. The complete description of the monitoring system, including the sensors measurement ranges sensitivity to each pollutant was mentioned in a previous work [3].

The data obtained from stations are average hour values of the contaminants concentration levels. The studied period was three years long.
The meteorological data (temperature, rainfall, wind course and velocity, humidity and atmospheric pressure) were determined by means of a Davis Weather Monitor II station. This was placed in the Faculty campus.

3 Results and discussion

The analysis performed during the period of time in study allows verifying the direct relationship between the solar radiations and the ozone levels. Figure 1 shows that the highest ozone levels occurred during the months with highest temperatures. Moreover, this relationship can be clearly observed during the day with maximum ozone concentrations in the hours of higher solar radiation [4].

![Figure 1: Monthly averages of ozone in the town centre.](image1.png)

![Figure 2: Number of exceedences according to the time of the day.](image2.png)
During the studied period several situations of alarm, that is concentration of ozone that exceeds the air quality standard, were detected. This standard can’t be surpassed more than once a year. Taking into account the number of times the ozone concentration exceeds the value fixed by legislation, it can be observed that larger amount of exceedences occur between 14.00 and 17.00 as it can be seen in figure 2. In this figure the number of times that the standard was exceeded according to the time of the day during the three years analyzed is shown.

In the town centre the flow of motor vehicles (one of the main producers of NOx and hydrocarbons) is evident, mainly at working times. The ozone levels increase in accordance with the levels of the precursor gases, when the meteorological conditions are adequate for its formation. In such conditions, the ozone levels increase during the hours of greater flow of vehicles, according to the larger concentration of the precursor gases. A slight temporary running can be generally noticed which is necessary for the formation of the gas under study.

The model of photochemical smog, formed as a result of urban transport pollution, considers eleven main pollutants taking part of twelve chemical reactions [1, 5]. The reactions that show NOx as O3 precursors are the following:

\[
\begin{align*}
\text{NO}_2 + h\nu & \xrightarrow{K_1} \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \xrightarrow{K_2} \text{O}_3 + \text{M} \\
\text{NO} + \text{O}_3 & \xrightarrow{K_3} \text{NO}_2 + \text{O}_2
\end{align*}
\]

where M represents a third molecule that absorbs the energy excess and stabilizes the ozone molecule formed.

Figure 3 shows the values of a certain month, February 2000, expressed as daily averages where the direct relationship between ozone and its precursors can be observed. This is a typical behavior in late spring and summer.

![Figure 3: Ozone and NOx levels as daily average.](image-url)
Figure 4: Ozone and NOx levels as monthly average.

Figure 4 shows the monthly average levels of O$_3$ and NOx corresponding to the studied period. It can be observed that NOx levels in January and February are relatively inferior than the levels corresponding to the rest of the year due to the holiday time. However, in spite of that, the ozone levels are the highest in the period under study, owing to the fact that it is in these months when solar radiations are greatest.

4 Conclusions

The present work has studied the pollution levels caused by the presence of ozone as secondary pollutant and of its precursor gases, the nitrogen oxides, in San Nicolás city, Argentina.

It has been observed there is a direct relationship between the periods of maximum ozone concentrations and the presence of strong solar radiations.

During the period under study, numerous episodes have been determined in which the levels have exceeded the standards accepted by regulations. They occur when the precursor gases concentrations increase notoriously and during the times of maximum solar radiations.

The only way to avoid or diminish the high levels tropospheric ozone is to decrease the emission of its precursor gases, which are produced by motor vehicles and industries.

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References


