

# Contribution of anthropogenic pollutants to the increase of tropospheric ozone levels in the Oporto Metropolitan Area, Portugal since the 19th century

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*Compared to the 19th century, the current ozone concentrations are 147% higher at Oporto, Portugal.*

## Abstract

The main purpose of this study was to evaluate the contribution of anthropogenic pollutants to the increase of tropospheric ozone levels in the Oporto Metropolitan Area (Portugal) since the 19th century. The study was based on pre-industrial and recent data series, the results being analyzed according to the atmospheric chemistry. The treatment of ozone and meteorological data was performed by classical statistics and by time-series analysis. It was concluded that in the 19th century the ozone present in the troposphere was not of photochemical origin, being possible to consider the respective concentrations as reference values. For recent data a cycle of 8 h for ozone concentrations could be related to traffic. Compared to the 19th century, the current concentrations were 147% higher (252% higher in May) due to the increased photochemical production associated with the increased anthropogenic emissions.

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## 1. Introduction

Increased tropospheric ozone levels have been affecting human health, climate, vegetation, materials and atmospheric composition. Respiratory and ocular damage are the most significant effects on human health. Concerning climate, a temperature increase is expected to be related to the tropospheric ozone increase, because it is a greenhouse gas. In vegetation it causes leaf injury, growth and yield reduction, and changes in the sensitivity to biotic and abiotic stresses.

During the pre-industrial era, the ozone found in the troposphere came essentially from the stratosphere, through intrusion of stratospheric air. Recent estimates indicate that stratospheric–tropospheric exchanges only account for 20% of the current total tropospheric ozone, because now it is mainly produced by complex photochemical reactions involving solar radiation and anthropogenic pollutants (Marenco et al., 1994). Hence increased tropospheric ozone levels of photochemical origin can be correlated with the increased emissions of anthropogenic pollutants.

Photochemical ozone is formed by reactions involving solar radiation and anthropogenic pollutants (methane, non-methane volatile organic compounds, carbon monoxide) in the presence of nitrogen oxides.

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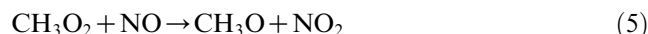
In less polluted environments, ozone is produced in the presence of sunlight (at wavelengths  $<424$  nm), through the photolysis of  $\text{NO}_2$ :



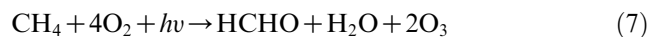
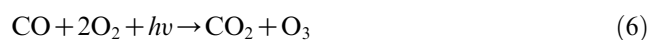
where  $M$  represents  $\text{N}_2$ ,  $\text{O}_2$  or other molecules that can absorb the excess of vibrational energy, allowing the stabilization of  $\text{O}_3$ . Once formed,  $\text{O}_3$  quickly reacts with  $\text{NO}$  regenerating  $\text{NO}_2$ :



In the absence of other chemical species this cycle reaches a photo-stationary equilibrium between  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ , without effective ozone formation, and with an ozone concentration proportional to the ratio  $[\text{NO}_2]/[\text{NO}]$ . In less polluted environments ozone production may also involve the radicals hydro-peroxide ( $\text{HO}_2$ ) and methyl peroxide ( $\text{CH}_3\text{O}_2$ ), intermediate products of  $\text{CO}$  and  $\text{CH}_4$  oxidation:

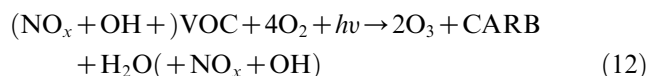
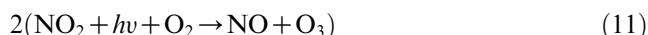
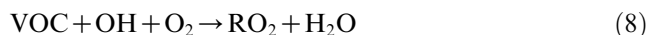


These reactions with  $\text{NO}$  occur when the ratio  $[\text{NO}]/[\text{O}_3]$  is significantly high. The global reactions of oxidation of  $\text{CO}$  to  $\text{CO}_2$  and  $\text{CH}_4$  to  $\text{HCHO}$  are the following:



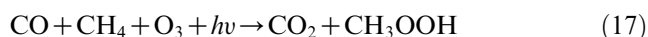
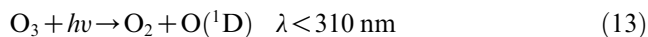
In polluted environments the photochemical production of ozone cannot be explained solely by the  $\text{CO}-\text{CH}_4-\text{NO}_x$  equilibrium, mainly due to the additional presence of volatile organic compounds (VOC). The VOC oxidation cycle disturbs the natural equilibrium  $\text{NO}_x-\text{O}_3$ , allowing alternative paths for the oxidation of  $\text{NO}$  to  $\text{NO}_2$  without consumption of  $\text{O}_3$ . VOC oxidation mechanisms are mainly induced by  $\text{OH}$  radical during the day and by  $\text{NO}_3$  radical during the night, leading to the production of  $\text{HO}_2$  and  $\text{RO}_2$  radicals. These radicals are able to oxidize  $\text{NO}$  to  $\text{NO}_2$  avoiding reaction (3), and leading to the accumulation of ozone through reactions (1) and (2). These mechanisms explain the high concentrations of ozone in polluted areas, since the radiation is high enough to initiate the

photodissociation process. The reactions involved can be simplified as follows:



where  $\text{CARB}$  is either a carbonyl species ( $\text{RCHO}$ ) or a ketone ( $\text{RCRO}$ ).

The destruction of ozone is accomplished by chemical and photochemical degradation, by the oxidative cycle of  $\text{CO}$  and  $\text{CH}_4$ , and by dry deposition on the soil. The main reactions are the following:



Previous studies showed that  $\text{NO}_x$  emissions are mainly responsible for ozone formation in rural areas, whilst VOC are responsible in urban areas (EEA, 1998). There is a competition between VOC and  $\text{NO}_x$  for the  $\text{OH}$  radical. When  $[\text{VOC}]/[\text{NO}_x]$  is high,  $\text{OH}$  will react mainly with VOC ( $\text{NO}_x$  limited), generating new radicals and accelerating  $\text{O}_3$  production. Under these conditions, typical of rural areas, an increase in  $\text{NO}_x$  concentration accelerates  $\text{O}_3$  formation. When  $[\text{VOC}]/[\text{NO}_x]$  is low, the reaction of  $\text{OH}$  with  $\text{NO}_x$  can

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