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

M.C.M. Alvim-Ferraz*, S.I.V. Sousa, M.C. Pereira, F.G. Martins

LEPAE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Oporto, Portugal

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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.

Keywords: Time-series; Schönbein method; Photochemical production; Meteorological parameters; Seasonal variation

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.

* Corresponding author. Tel.: +351 22 508 1688; fax: +351 22 508 1449.
E-mail address: aferraz@fe.up.pt (M.C.M. Alvim-Ferraz).

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In less polluted environments, ozone is produced in the presence of sunlight (at wavelengths <424 nm), through the photolysis of NO_2:

$$NO_2 + h\nu \rightarrow NO + O \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

where M represents N_2, O_2 or other molecules that can absorb the excess of vibrational energy, allowing the stabilization of O_3. Once formed, O_3 quickly reacts with NO regenerating NO_2:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (3)$$

In the absence of other chemical species this cycle reaches a photo-stationary equilibrium between NO, NO_2 and O_3, without effective ozone formation, and with an ozone concentration proportional to the ratio $[NO_2]/[NO]$. In less polluted environments ozone production may also involve the radicals hydro-peroxile (HO_2) and methyl peroxile (CH_3O_2), intermediate products of CO and CH_4 oxidation:

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (5)$$

These reactions with NO occur when the ratio $[NO]/[O_3]$ is significantly high. The global reactions of oxidation of CO to CO_2 and CH_4 to HCHO are the following:

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \quad (6)$$

$$CH_4 + 4O_2 + h\nu \rightarrow HCHO + H_2O + 2O_3 \quad (7)$$

In polluted environments the photochemical production of ozone cannot be explained solely by the CO–CH_4–NO_x equilibrium, mainly due to the additional presence of volatile organic compounds (VOC). The VOC oxidation cycle disturbs the natural equilibrium NO_x–O_3, allowing alternative paths for the oxidation of NO to NO_2 without consumption of O_3. VOC oxidation mechanisms are mainly induced by OH radical during the day and by NO_3 radical during the night, leading to the production of HO_2 and RO_2 radicals. These radicals are able to oxidize NO to 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:

$$VOC + OH + O_2 \rightarrow RO_2 + H_2O \quad (8)$$

$$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB \quad (9)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (10)$$

$$2(NO_2 + h\nu + O_2 \rightarrow NO + O_3) \quad (11)$$

$$(NO_x + OH +)VOC + 4O_2 + h\nu \rightarrow 2O_3 + CARB + H_2O(+NO_x + OH) \quad (12)$$

where CARB is either a carbonyl species (RCHO) or a ketone (RCRO).

The destruction of ozone is accomplished by chemical and photochemical degradation, by the oxidative cycle of CO and CH_4, and by dry deposition on the soil. The main reactions are the following:

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad \lambda < 310\ \text{nm} \quad (13)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (14)$$

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (15)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (16)$$

$$CO + CH_4 + O_3 + h\nu \rightarrow CO_2 + CH_3OOH \quad (17)$$

Previous studies showed that 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 NO_x for the OH radical. When $[VOC]/[NO_x]$ is high, OH will react mainly with VOC (NO_x limited), generating new radicals and accelerating O_3 production. Under these conditions, typical of rural areas, an increase in NO_x concentration accelerates O_3 formation. When $[VOC]/[NO_x]$ is low, the reaction of OH with NO_x can