Photochemical pollution precursors and ozone in the atmosphere of Cartagena from 1995–1997

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Abstract

This paper presents the results of two years monitoring photochemical pollution precursors in the atmosphere of Cartagena (Spain). Air quality parameters: suspended particulate matter (SPM), SO_2, O_3, NO, NO_2, methane hydrocarbons (MHC), non-methane hydrocarbons (NMHC), and total hydrocarbons (THC), have been measured at five sampling stations. Analysis of variance has shown high spatial and temporal variability on these values at different sampling points. Meteorological parameters from three meteorological towers have been also used to carry out correlation analysis with air quality parameters. A positive correlation between solar radiation and ozone, and between ozone and wind speed show the importance of long distance transport for photochemical pollution precursors.

1 Introduction

In spite of a high decreasing on air pollution levels registered by the automatic control network in the city of Cartagena, one of the most equipped in Spain, some episodic situations have been observed. In order to determine if they are due to photochemical oxidants, efforts have been focused on determining their presence in the atmosphere of Cartagena. For

this purpose, real-time monitored air quality parameters have been controlled on five sampling stations, which measure ozone, nitrogen oxides, sulphur dioxide, and particles, from 1995 to 1997.

Photochemical oxidants are secondary pollutants formed when sunlight irradiates the atmosphere polluted with non-methane hydrocarbons and nitrogen oxides[1]. Chemical aspects related to the photochemical smog synthesis are very complex, and need further investigation. It is widely known that hydrocarbons react with atomic oxygen, ozone, and oxidative radicals such as hydroxy and hydroperoxy, to increase the free radical balance. This free radicals react with another hydrocarbons and oxygenated species, and with nitrogen oxides to produce smog, a mixture of substances such as nitrogen oxides, carbon monoxide, hydrocarbons, aldehydes, ozone, and different organic compounds.

1.1 Chemical processes

Nitrogen oxides are considered one of the main atmosphere components influencing on the formation of photochemical smog, due to the photolysis reaction at wavelengths less than 280 nm, releasing oxygen radical and nitrous oxide. Free radicals carry out the formation of secondary oxidants at the atmosphere. In this sense, hydroxyl and hydroperoxyl radicals oxidise hydrocarbons, beginning important chain reactions in the atmosphere[2,3].

Although in the photochemical oxidation, different inductive compounds take part, mainly those related to reaction mechanism such as NO, NO_2, and O_3, photochemical oxidants daily variations can not be explained by such a simple model. For that reason, high ozone amounts reported in urban atmospheres can not be justified by a reaction mechanism of interaction between NO and NO_2. Other mechanisms have been proposed, such as free radicals generated by organic compounds, R′, RO′, y HCO′, involved on NO_2 formation, and its accumulation parallel to an ozone increased level, both acting as chain reactions beginners.

Many atmospheric processes must be considered heterogeneous processes, since they include reactants transference processes from gaseous to condensed phase, followed up by an homogeneous reaction on condensed phase. Heterogeneous processes related to troposphere chemistry involve the formation of solid or liquid secondary particulate matter within the aerosol, as well as reactions among different aerosol components[2,4].

1.2. Effects on human being of photochemical oxidants

Photochemical oxidants, and, in general, photochemical smog which contains them, exert a negative effect on human being, depending on pollutant concentrations and individual sensibility. It is considered[5] that such as 0.007 ppm (130 $\mu g/m^3$) produces a reduction on athletic efficiency, and at 0.1 ppm, eyes and mucosal irritation occurs. When 0.25 ppm (490 $\mu g/m^3$) are reached, asthma episodes increase. The effects of a ten-days pollution episode at Los Angeles city, during 1979, can be resumed as follows: 87% of interviewed people showed health concern. Out of them, 57% developed eyes irritation, and 25% headache and throat inflammation. Half of patients with chronic respiratory diseases, such as asthma or emphysema, had to be hospitalised, and, finally, sportive competitions had to be stopped on affected areas. For that reason, WHO recommends a safe concentration about 150-200 $\mu g/m^3$.

In addition to the adverse health effects caused by ozone, this pollutant reduces agricultural yields and causes forestry damage[6].

2 Materials and methods

Atmospheric pollution control network in the city of Cartagena consists of eleven sampling stations, although for this study, we have processed data from the only five sampling stations monitoring ozone. Figure 1 picks up the situation of these five sampling stations. Nitrogen oxides were determined by chimoluminescence, sulphur dioxide by ultraviolet fluorescence, and ozone by means of ultraviolet absorption methods.

In order to characterise behaviour patterns of studied pollutants, data from 3 meteorological towers were used, the closest ones to the sampling points, these are: T-3 for sampling points called E-1, E-3, and E-5, T-4 for sampling point E-2, and T-1 for sampling point E-4. Figure 1 depicts their situation.

Data collected were statistically analysed using SPSS for Windows software. After data exploration and elimination of non-validated ones, a descriptive statistic was developed. Analysis of variance (ANOVA) was used to define spatial and temporal variations. Different classification criteria, sampling year, sampling point, and wind direction were used.

Correlation analysis allowed us to know the relationships among different air quality parameters and meteorological data.

3 Results

Table 1 picks up average values and standard deviation of valid measurements (N) for each air quality parameter monitored, by year and sampling point.

Figure 1 shows a map of the zone, the sampling points situation, and wind roses for all the years and meteorological towers considered in this study. It also shows concentration roses of air quality parameters at each sampling point. Table 2 picks up range values for wind and concentration roses depicted at figure 1.

ANOVA for each year and sampling point have been graphically represented, with a 95% confidence level interval, for suspended particulate matter, sulphur dioxide, ozone, nitrogen dioxide, and nitrogen monoxide (figure 2). The number of valid data used for each analysis is also indicated.

Correlation analysis developed with air quality data shows positive correlation (p-value=0.000) between nitrogen dioxide and monoxide, and between suspended particulate matter and sulphur dioxide. Nitrogen oxides and ozone shown negative correlation (p-value=0.000). When the correlation analysis was developed with meteorological data and air quality parameters, correlation coefficients (c.c.) greater than an absolute value of 0.100 and less than 0.050 statistic significance level (s.l.) was reached with the following bivariate relationships: relative humidity and ozone (c.c. 0.1381, s.l. 0.000), wind speed range and: nitrogen oxides (c.c. for total nitrogen –0.1729, s.l. 0.000), ozone (c.c. +0.2188, s.l. 0.000), sulphur dioxide (c.c. –0.1330, s.l. 0.000), and suspended particulate matter (c.c. –0.100, n.s. 0.000), and solar radiation and ozone (c.c. +0.2411, s.l. 0.000).

4 Discussion and conclusions

The city of Cartagena, due to high industrial activity and climatic and topographic characteristics, shows one of the highest values for air quality parameters reported in our country, always within the legislated limits[7].

Besides, the abundance of sunny days, with high radiation patterns, involves the best conditions for photochemical oxidants formation, which results on elevated annual average values for ozone at some sampling stations, i.e., E-1. In 1991, due to former problematic situations, the regional authority established an Operative Intervention Plan, with a gradual application of pollution control measures, from decreases emissions to emergency halting of industrial operations.

Wind behaviour differs according to the considered meteorological tower. At T1, situated downtown, North, North-Northeast, and South winds are predominant, meanwhile for T3, situated at a plain area, and T4, at Escombreras valley, winds coming from first and third quadrant are predominant, both with a 30° inclination with respect to T1. This fact is due to the mountain barrier along the coast, open at the south of the city, where the natural seaport is situated. Concentration roses, picked up figure 1, show the sources contribution to air quality levels. In this sense, industrial emissions generated at Escombreras valley, contribute to SO_2, SPM, and NO levels at E-2, and SO_2 levels at E-5. Sampling station E-1, situated at the Northeast of industrial sources, and E-4, situated at the West, show the influence of first and second quadrant for SO_2 and SPM levels.

Figure 2 shows a high spatial and temporal variability on the air quality average values at different sampling stations. The highest ozone levels are found at E-1, farthest from downtown and industrial setting.

Correlation analysis displays a negative correlation between nitrogen oxides and ozone, and the influence of meteorological parameters on secondary pollutant production. Positive correlation between solar radiation and ozone, as well as a tendency of higher ozone concentrations with higher wind speeds, demonstrate an association with long distance transport of photochemical pollution precursors.

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