Levels of nitrogen oxides and ozone in Madrid. Study of the nitrogen monoxide/ nitrogen dioxide and nitrogen dioxide/ ozone ratios

R. Fernández Patier, P. Díez Hernandez,
E. Díaz Ramiro, J.M. Fernandez Bayón
Instituto de Salud Carlos III, Centro Nacional de Sanidad Ambiental, Ctra. Majadahonda a Pozuelo Km 2, 28220 Majadahonda, Madrid, Spain

Abstract

During 1992, nitrogen oxides (NO_x) and ozone (O_3) were monitored in Madrid and in the surrounding areas (Loeches), to study the formation and transport of photochemical pollutants from the big cities to around areas. After four campaigns, carried out during the four climatological seasons of 1992, a great difference between the magnitude and the profile of the urban and rural ambients is observed. It stands out the high mean levels of NO (between 71 and 417 ppbv) and NO_2 (between 11 and 89 ppbv) in the city. As well as the high mean level of O_3 (between 9 and 39 ppbv) and the higher proportion of NO_2 in relation to the precursor NO in the rural area. The NO/NO_2 and NO_2/O_3 ratios were calculated for Madrid and Loeches as well as their corresponding hourly profiles, finding greater values in the city for both ratios. Being distinguished therefore, as an emission point of primary pollutants (NO) and Loeches as a point of secondary pollutants (NO_2 and O_3).

1 Introduction

Pollution studies have to be directed towards the formation of photochemical smog, its relation with the formation of secondary compounds as well as the transport and deposition of these in areas at long distances from the emission focus.

In general, the terms oxidant and photochemical pollutant include a great number of secondary compounds originated from primary pollutants, due to the action of direct sunlight (Guderian[1]). These primary pollutans and photochemical oxidant precursors are the NO_x and the volatile organic compounds (VOCs), whereas the most representative of the photochemical

oxidants is O_3.Ozone is indirectly formed in the troposphere by the reaction of sunlight and NO_2.

But, the presence of hydroxyl radicals and volatile organic compounds in the atmosphere, both natural and anthropogenic origins, causes an imbalance in the atmospheric equilibrium, giving origin to higher O_3 concentrations. Other compounds, apart from ozone, are also formed during this photochemical process, as the peroxyacetil nitrate (PAN), nitric acid and hydrogen peroxide, as well as aldehydes, formic acid, secondary particles and a wide variety of short life radicals. The maximum concentration of O_3 that can be reached in polluted atmospheres, not only depends on the absolute concentrations of VOCs and NO_x, but also in their ratio. If this ratio is small, the formation of ozone is directed by the velocity of the reaction and the type of VOCs. However, if the ratio is high the limiting factor is the low concentration of NO_x and therefore, there are less marked differences among VOCs (Dodge[2]).

Not all the VOCs take part in the photochemical reactions in the same manner. It depends on their chemical structure and reactivity. The olefins are highly reactive in the formation of oxidants. The ethylene reacts slower than the longer chain olefins. The paraffin and acetylene hydrocarbons are less reactive but highly toxic.

The objective of this study is to characterize the level of existing precursors in the city of Madrid and the secondary pollutants in a point within the region of Madrid, located at 30 Km from the city in the different climatological seasons and their corresponding ratios.

2. Experimental

During 1992, four 10-day seasonal campaigns were developed.
The two sampling points were situated in:

- Station of precursors: Ministry of Health and Consumption. Madrid
- Station of secondary pollutants: Loeches.

The continuously monitored gases were: nitric oxide (NO), dioxide nitrogen (NO_2) and ozone (O_3). Nitrogen oxides were analyzed by the chemiluminescence technique (ISO 7996[3]) and the ozone by the absorption of UV radiation at 253.7 nm .

3. Results and Discussion

The nitrogen oxides and ozone mean concentrations with their corresponding standard deviations can be observed in Table I.

It should be pointed out that, very frequently, the standard deviation values reach the mean values of the seasonal periods, which is a characteristic of the concentrations of atmospheric pollutants.

		Spring		Summer		Autumn		Winter	
		Mean	Std.dev.	Mean	Std.dev.	Mean	Std.dev.	Mean	Std.dev.
Madrid	NO	104	92	84	93	71	120	417	342
	NO_2	30	9	40	18	11	14	89	38
	O_3	---	---	16	12	11	7	4	3
Loeches	NO	8	13	7	11	14	17	27	33
	NO_2	9	7	12	9	13	9	20	9
	O_3	29	9	39	17	21	12	9	7

Table I.- Mean levels and their standard deviations of nitrogen oxides an ozone in 1992 of Madrid and Loeches (ppbv 20° 101.3 KPa)

As it can be observed, the average NO_x concentrations during the campaigns are much higher in Madrid than in Loeches, confirming the city as a focus of primary pollutants. In relation to NO, the concentrations are between 5 and 12 times bigger in Madrid than in Loeches (except during the winter campaignin which a pollution episode occured). The NO_2 concentrations, also are 3-4 times higher in Madrid than in Loeches, excepting the autumn campaign, where a lower NO_x concentration (NO_2 in particular) was found in Madrid during this campaign. The mean NO and NO_2 concentrations monitored in the rural station are slightly higher than those found in rural areas of the USA (Kelly *et al*[4] and Pratt *et al*[5]), probably due to a greater proximity of our rural station to the city.

The formation of secondary pollutants, in space and time, is clear in the case of O_3, whose concentration in the rural area almost doubles that in the city. It should be noted the ozone mean concentration of 39 ppbv, obtained during the summer campaign in Loeches. The O_3 mean concentrations in the rural point are within the range of those found in the rural zones of the USA (Kelly *et al*[4], and Pratt *et al*[5]). But these are higher than rural areas of France (Zurita & Castro[6]). However, the O_3 mean values observed in Madrid are lower than those found in the same city by Zurita & Castro[6]. This is possible due to the higher sensitivity of our method, though the values now found are in the range of those measured by Rappenglück *et al*[7] in Munich, but very far from the figures mentioned by Kanbour[8] in Baghdad.

In Table II, the NO/NO_2 and NO_2/O_3 ratios for Madrid and Loeches are showed. The calculation of the ratios is made by computing the geometric average of 15 minute data periods of the ratio.

As it can be observed, the NO/NO_2 ratios are greater than 1 and lower than 1 in the urban and rural environments, respectively. Because in the latter point the NO is transformed into NO_2, due to the presence of a great quantity of O_3, as this is an area of secondary pollutants. In Madrid, the large NO contributions sent into the atmosphere makes it difficult to transform all of the NO into NO_2 and hence the fact that the ratio is greater than 1.

		Spring	Summer	Autumn	Winter
NO/NO_2	Madrid	2.34	1.26	2.51	3.56
	Loeches	0.65	0.42	0.24	0.69
NO_2/O_3	Madrid	---	3.31	0.83	20.84
	Loeches	0.25	0.29	0.58	2.80

Table II.- NO/NO_2 and NO_2/O_3 ratios during 1992 in Madrid and Loeches.

The behaviour of the NO_2/O_3 ratios are not homogeneous in Madrid, these are higher than 1 except autumn, when the lower amount of NO are observed. In Loeches, these ratios are less than 1 excepting winter, because of the pollution episode. This indicates that in Loeches, during the most part of the year, the levels of O_3 are higher than those of NO_2.

The annual mean of the ratios, in Loeches, shows approximately 1.7 times more O_3 than NO_2 and 2.2 times more NO_2 than NO. During 1992 in Madrid, on the contrary, the ratios show almost 2.3 times more NO than NO_2 and 3.9 times more NO_2 than O_3.

In Madrid, the concentration of NO is caused by human activity. After 0600LT its level increases to reach a maximum morning peak between 0745LT and 0900LT, and another maximum peak afterwards, though of a lower magnitude, at around 2030LT. The base level of NO in Loeches is much lower than in Madrid, reaching a morning peak between 0800LT and 0830LT, depending on the season. In autumn and winter a new evening maximum is observed, from 1730LT in winter to 1900LT in autumn.

With respect to the NO_2 evolution in Madrid, during the winter campaign, the base level at night, when the emission from cars is lower, is 2 times higher than in spring and summer and 5 times higher than in autumn increasing after 1000LT and reaching a peak at 1400LT, to lower to a base level at 2100LT. During the other campaigns the increase is weaker, but also exists a daily cycle due to the appearance of NO, O_3 and solar radiation.

In relation to NO_2 in Loeches, a maximun appears between 0600LT and 1100LT and another peak lower between 1800LT and 2200LT.

The hourly profile of O_3 in Madrid is related to the appearance of radiation and NO in the air with a maximun between 1000LT and 1800LT and a minimun at 0730LT with a larger magnitude in summer than the other seasons.

In Loeches, there is a rise in all campaigns at 0800LT until they reach maximum steady levels, obtaining an earlier stabilization in spring and autumn than in summer. In the afternoon, when the sunlight begins to disappear the levels of O_3 slowly decrease until the following morning, when the cycle starts again.

The O_3 presents in rural area, due to precursors (NO, VOCs) and sunlight, maximum values between 1200LT and 1900LT, reaching an hourly mean of 87 ppbv between 1300LT and 1400LT on 24 July. These concentrations are very

near to those values of O_3 indicated by the Directive 92/72/EEC[9] that should be informed to the public, and fixed at 180 μg m^{-3} (90 ppbv) for one hour.

The hourly distribution of O_3 maximum values for Madrid and Loeches, coincide with the normal evolution found by different authors, such as Kelly *et al*[4] in USA , Lalas *et al*[10] in Athens , Kanbour[8] in Baghdad and Forteza *et al*[11] in Ravena .

Figures 1 and 2 show the hourly profiles of NO/NO_2 and NO_2/O_3 ratios in Madrid, respectively, in logarithmic scale, so that the magnitude of the ratio is symmetrical, taking 1 as reference.

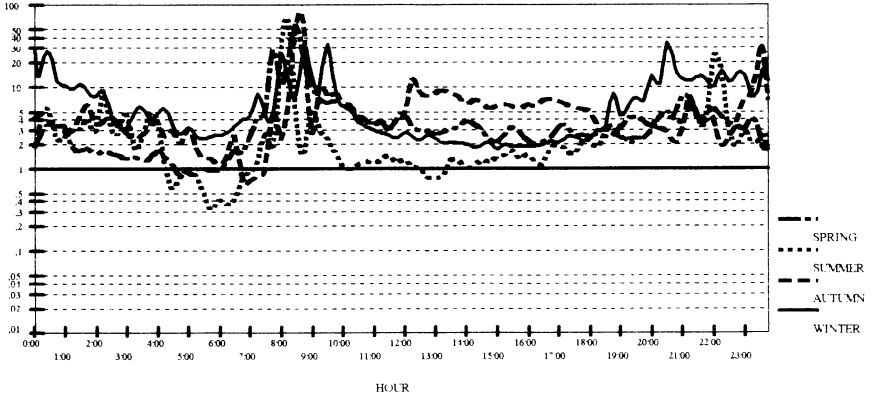

Figure 1.- Hourly profile of NO/NO_2 ratios in Madrid during 1992

It can be observed, in Madrid, the NO/NO_2 ratio is greater than 1 during, practically, most of the day, except for spring and summer, before the beginning of human activity. At these hours, the ratio favours the concentration of NO_2 against NO as the O_3 concentration remains high, after the period of activity of the night before. After the peak morning hour, the ratio is always greater than

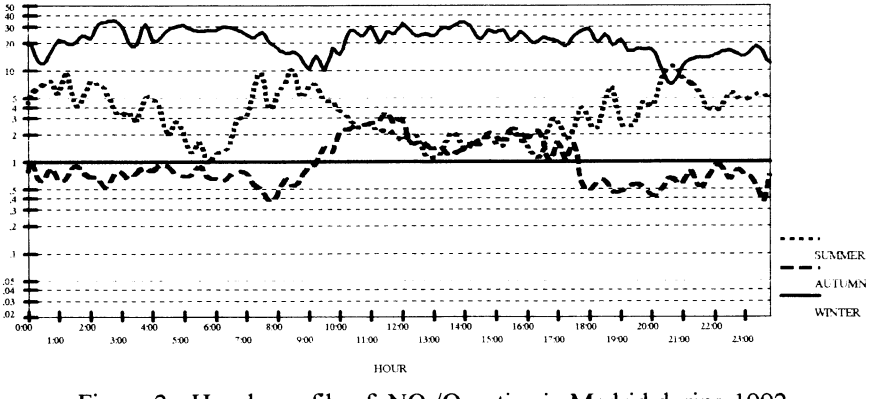

Figure 2.- Hourly profile of NO_2/O_3 ratios in Madrid during 1992

1, but in summer from 1000LT to 1400LT, there is a state of equilibrium of the NO and NO_2 concentration, to rise in the evening peak again, in a cyclic manner. This second maximum is present in all the seasonal profiles and ranges from 1730LT to 2300LT, depending on the season.

The NO_2/O_3 profile in Madrid shows the ratio greater than 1 in the summer and winter campaigns. In autumn, however, the ratio is lower than 1, excepting the subsequent hours to the peak hour, where the primary pollutants are transformed by sunlight. In winter and autumn, the ratio decreases during the human activity hours. But, in summer and during the peak morning and evening hours, the ratio increases due to a greater availability of ozone.

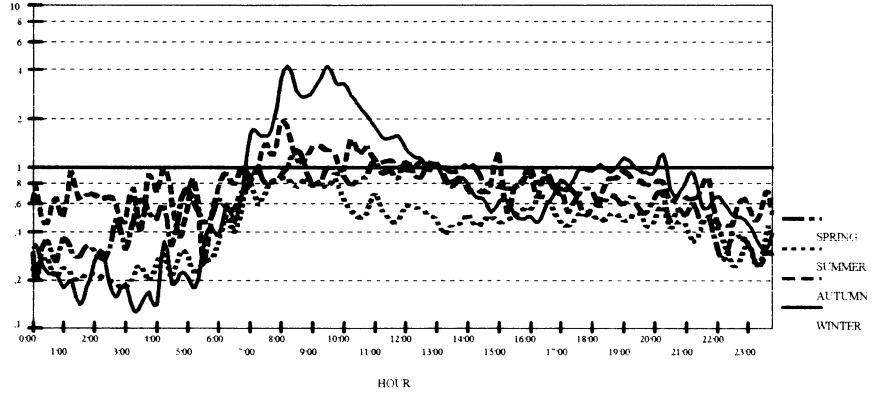

Figure 3.- Hourly profile of NO/NO_2 ratios in Loeches during 1992.

Figure 3 shows the NO/NO_2 profile for Loeches. The values are lower than 1 for all campaigns, except for autumn and winter during the human activity hours, that is from 0630LT to 1300LT approximately, when an increase in the ratio values is produced, due to a rise in NO. The smaller amount of O_3, because of the radiation, causes a lower NO_2 level compared with NO at these hours.

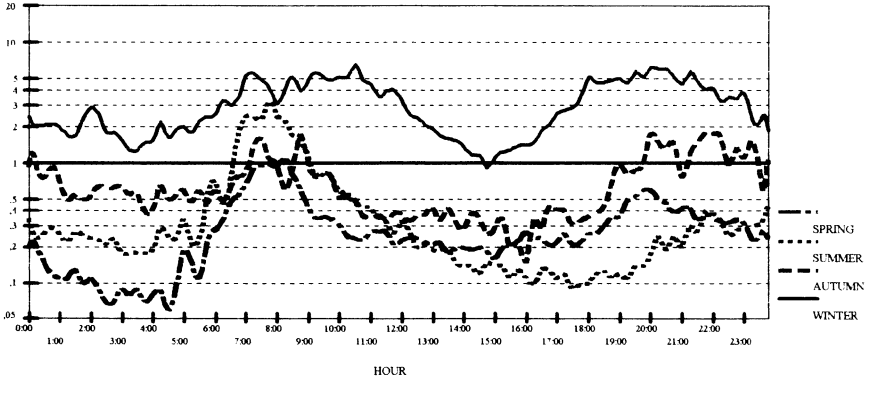

Figure 4.- Hourly profile of NO_2/O_3 ratios in Loeches during 1992.

Also, Figure 4 represents a different NO_2/O_3 profile from that found in Madrid. In spring and summer the ratio is higher than 1 at peak hours, from 0630LT to 0900LT, with the lowest values at night. The greatest O_3 concentration is found during these two seasons. In autumn, at the end of the day, the ratio is greater than 1, caused by the simultaneous increase in NO_2 and decrease in O_3. In the winter campaign and in agreement with the lowest radiation season, the NO_2 levels are higher than those of O_3 during, practically, all day.

4. Conclusions

According to the obtained results, it can be deduced that there is a different degree of concentration of photochemical pollutants between the city and the rural zones nearby.

The concentrations of NO and NO_2 are higher in Madrid (urban) than in Loeches (rural), while those of O_3 are higher in the rural station than in the urban station, having reached an O_3 hourly mean of 87 ppbv in Loeches.

The NO/NO_2 ratios are higher than 1 in Madrid and lower than 1 in Loeches, representing primary and secondary pollutant areas, respectively. With regard to the NO_2/O_3 ratios, these are not homogeneous for Madrid and for Loeches these are smaller than 1 (excepting the winter campaign, which was climatologically anomalous).

The NO, NO_2 and O_3 hourly profiles in Madrid are different from those in Loeches, as in its evolution as in their magnitudes and proportions.

Thereby, the study of the NO/NO_2 and NO_2/O_3 hourly profiles could be used to determine the primary or secondary photochemical nature of a sampling station.

5. Acknowledgements- This work is part of a research project financed by the Regional Plan of Research of the Community of Madrid C221/91: "Formation, transport and deposition of photochemical smog in the area of the Autonomous Community of Madrid". Also, the authors would like to thank all the Area of Atmospheric Pollution of the National Centre of Environmental Health .

6. References:

1. Guderian, R., *Air pollution by photochemical oxidants*, Springer Verlag, Berlin, 1985.
2. Dodge, M.C., Combined effects of organic reactivity and NMHC/NO_x ratio on photochemical oxidant formation- a modelling study, *Atmospheric Environment*, 1984, **18**, 1657-1665.
3. ISO 7996. *Ambient air-Determination of the mass concentrarion of nitrogen oxides- Chemiluminiscence method.*
4. Kelly, N.A., Wolff, G.T. & Ferman, M.A., Sources and sinks of ozone in rural areas, *Atmospheric Environment*, 1984, **18**, 1251-1266.
5. Pratt, G.C., Hendrickson R.C., Chevone B.I., Christopherson D.A., O'Brien,M.V. & Krupa, S.V., Ozone and oxides of nitrogen in the rural upper-midwestern U.S.A., *Atmospheric Environment*, 1983, **17**, 2013-2023.
6. Zurita, E. & Castro, M., A statistical analysis of mean hourly concentrations of surface ozone at Madrid (Spain), *Atmospheric Environment*, 1983, **17**, 2213-2220.
7. Rappenglück, B., Kourtidis, K. & Fabian, P., . Measurements of ozone and peroxiacetil nitrate (PAN) in Munich, *Atmospheric Environmet*, 1993, **27B**, 293-305.
8. Kanbour, F.I., . Variation of ozone concentrations in tue ambient air of Baghdad. *Atmospheric Environmet*, 1987, **21**, 2676-2679.
9. Directive 92/72/EEC: Commision of the European Communities. Council Directive of September 21, 1992 on atmospheric pollution for ozone (DOCE 297 13.10.1992 1-4) 1992.
10. Lalas, D. P., Asimakopoulos, D.N. & Deligiorgi, D.G., Sea-breeze circulation and photochemical pollution in Athens, Greece, *Atmospheric Environment*, 1983, **17,** 1621-1632.
11. Forteza, F., Strocchi, V., Giovanelli, G., Bonasoni, P. & Gergiadis, T., Transport of photochemical oxidants along the northwestern adriatic coast, *Atmospheric Environment*, 1993, **27A**, 2393-2402.