

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/225496101>

Ozone and Nitrogen Dioxide Levels Monitored in an Urban Area (Ciudad Real) in Central-Southern Spain

ARTICLE *in* WATER AIR AND SOIL POLLUTION · MAY 2009

Impact Factor: 1.55 · DOI: 10.1007/s11270-009-0168-8

CITATIONS

19

READS

39

6 AUTHORS, INCLUDING:



[Pilar Martin](#)

University of Castilla-La Mancha

50 PUBLICATIONS 419 CITATIONS

[SEE PROFILE](#)



[Beatriz Cabañas](#)

University of Castilla-La Mancha

64 PUBLICATIONS 434 CITATIONS

[SEE PROFILE](#)



[Florentina Villanueva Garcia](#)

University of Castilla-La Mancha

32 PUBLICATIONS 189 CITATIONS

[SEE PROFILE](#)



[Sagrario Salgado](#)

University of Castilla-La Mancha

47 PUBLICATIONS 317 CITATIONS

[SEE PROFILE](#)

Ozone and Nitrogen Dioxide Levels Monitored in an Urban Area (Ciudad Real) in central-southern Spain

Pilar Martín · Beatriz Cabañas ·
Florentina Villanueva · María Paz Gallego ·
Inmaculada Colmenar · Sagrario Salgado

Received: 3 April 2009 / Accepted: 23 July 2009 / Published online: 25 August 2009
© Springer Science + Business Media B.V. 2009

Abstract This work describes the evolution of NO₂ and O₃ levels from January to December of 2007, covering the four seasonal periods in the urban air of Ciudad Real in the central-southern Spain. The measurements were carried out by means of passive samplers (Radiello® samplers). Eleven samples were collected weekly, placed at different monitoring site locations. The data indicate that the mean levels obtained during this period for O₃ and NO₂ were 38.5 ± 3.5 and 20.8 ± 3.8 µg/m³, respectively. These measurements were compared with other studies in Ciudad Real. Meteorological conditions (temperature, pressure, humidity relative, wind speed and direction) were also investigated.

Keyword Passive sampling · NO₂ and O₃ levels · Urban and rural areas

P. Martín (✉) · B. Cabañas · M. P. Gallego · I. Colmenar · S. Salgado
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Castilla La Mancha,
Avda Camilo José Cela 10,
13071 Ciudad Real, Spain
e-mail: mariapilar.martin@uclm.es

P. Martín · B. Cabañas · F. Villanueva · M. P. Gallego · I. Colmenar · S. Salgado
Laboratorio de Contaminación Atmosférica,
ITQUIMA, UCLM,
Avda. Camilo Jose Cela S/N,
13071 Ciudad Real, Spain

1 Introduction

Urban air pollution problems are frequently associated with the products of combustion in industries, in vehicles and for domestic purposes. Suspended particulate matter, carbon monoxide, sulphur dioxide, nitrogen oxides and ozone (O₃) are common pollutants. Many large cities around the globe exhibit excessive levels of one or more of these pollutants.

Hence, monitoring of air pollution is important and necessary not only to comply with the environmental directives and assess the effectiveness of emission control policies but also to understand the role of the different physicochemical processes in the troposphere.

One of the main problems originated by the air pollution in urban areas is the pollution caused by photochemical oxidants. Amongst these, the O₃ and the nitrogen dioxide (NO₂) are important, which are capable of causing adverse impacts on human health and the environment (Lee et al. 1996; WHO 2000; Mazzeo and Venegas 2002, 2004). Nitrogen dioxide is considered to be an important atmospheric trace gas pollutant not only because of its effects on health but also because (a) it absorbs visible solar radiation and contributes to impaired atmospheric visibility, (b) as an absorber of visible radiation, it could play a potentially direct role in the change in the global climate if its concentrations were to become high enough (WHO 2000), (c) it is one of the major

sources of acid rain (Tang and Lau 1999), (d) it is, along with nitric oxide (NO), a chief regulator of the oxidising capacity of the free troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals, and (e) it plays a critical role in determining concentrations of O₃, nitric acid (HNO₃), nitrous acid (HNO₂), organic nitrates such as PAN (CH₃C(O)O₂NO₂), nitrate aerosols and other species in the troposphere. In fact, the photolysis of nitrogen dioxide in the presence of volatile organic compounds is the only key initiator of the photochemical formation of ozone and photochemical smog, whether in polluted or unpolluted atmospheres (WHO 2000; Varshney and Singh 2003).

Therefore, ozone mainly generated in the photochemical reactions mentioned above is a secondary pollutant. Normally, in polluted areas, it will react with NO and re-form NO₂ and O₂. However, the presence of hydrocarbons (VOCs) in the atmosphere will interrupt this process by being more attractive to the nitric oxide than the ozone molecule is contributing to ozone accumulation. Ozone is also produced by natural sources (trees and thunderstorms for example). It has been found out that the photochemical ozone production in urban areas rises with the NO_x emissions and is less sensitive to the VOC emissions (Sillman and Samson 1995). In areas moderately contaminated, ozone sensitivity to emission of nitrogen oxides depends on the season and on the emission rates (Kleinman 1991).

Monitoring of NO₂ and O₃ is usually carried out using continuous measurement techniques such as chemiluminescence (UNE-EN 14211:2005) and ultraviolet (UV) photometry (UNE-EN 14625: 2005), respectively, that are the reference methods, or active sampling using a pump. However, the continuous measurements are expensive and require continuous maintenance, calibration and electric supply. On the contrary, diffusive samplers for the measurements of O₃ and NO₂ concentrations avoid the need for electric supply or site calibration. Passive samplers are based on free flow (according to the Fick's first law of diffusion) of pollutant molecules from the sampled medium to a collecting medium. These devices can be deployed virtually anywhere, being them useful for mean concentrations determinations.

In the work presented here, a field study of average concentrations of NO₂ and ozone levels have been developed using diffusive passive sampling (Radiello®

samplers) in an urban city of Spain, Ciudad Real, where no permanent air quality monitoring stations existed during measurement period.

The aims of this work have been, first, to determine average values obtained of NO₂ and O₃ concentrations in the measurement period corresponding to different monitoring points covering almost all the city; second, to compare the results with previous ones determined in the same city from 23 August 2000 to 25 September 2000, using the differential optical absorption spectroscopy (DOAS) technique; third, to establish a relationship between NO_x and ozone levels measured in each period and to relate this with biogenic volatile compounds emissions (BVOCs), according to the physicochemical principles operating in the atmosphere; fourth, to establish the influence of meteorological variables on the measured concentrations and, finally, according to the mean values obtained in each of the sampling points, we analyse the convenience of the situation of fixed monitoring stations in the future in some of the studied zones.

2 Materials and Methods. Experimental Section

2.1 Area of Study

As indicated above, the study was carried out in the urban area of Ciudad Real (Spain). The city has around 65,000 inhabitants and is located in the heart of La Mancha region in central-southern Spain (38.59 N, 3.55 W, at approximately 628 m above sea level) in a fairly flat area, 200 km south of Madrid. With a low presence of industry, traffic is likely to be the most important source of air pollution in this city. Meteorologically, the zone is characterised by very hot and dry summer period with high insulation, variable direction winds and by dry and cold winters, conditions that could play an important role in the evolution of the polluting agents.

In Fig. 1, a map of the city is shown, where the situation of the 11 measurement points can be seen. Samples are sited in town centre (total sampling area of 7.5 km² approximately) with the exception of points 6, 7 and 10 that correspond to rural zones, but in the case of point 10 in the influence zone of a small airport under construction.

Industry next to the city is especially scarce, and the zone is mainly surrounded by rural areas. There is

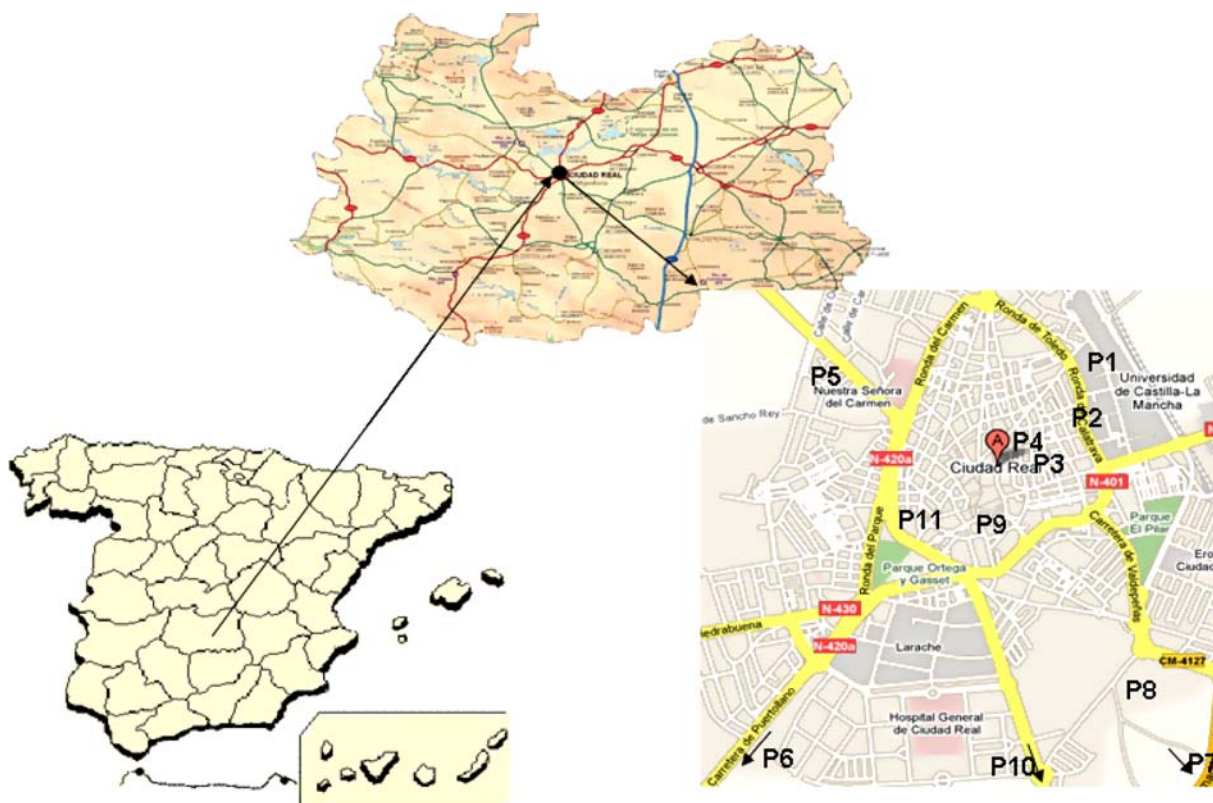


Fig. 1 Situation map of Ciudad Real (Spain) and the sampling points

a petrochemical complex located in Puertollano at 30 km from southwest of Ciudad Real. This complex would affect to increase the NO_2 and O_3 concentrations in the Ciudad Real atmosphere by transporting processes.

2.2 Description of Passive Sampler Employed

One of the most widespread methods for the measurement of ambient NO_2 and ozone concentrations is the passive sampling. Radiello® samplers have been employed (provided by Fondazione Salvatore Maugeri (2003; www.radiello.com)). Radiello passive samplers are different from the axial ones because the diffusion process is radial through a microporous cylinder in which a cartridge with adsorbent material is positioned. Consequently, there is a greater diffusion area, which facilitates the reaction between the gas and the collection cartridge (Cocheo et al. 1999), giving an uptake rate of at least two times higher. Diffusion process can be calculated according to Fick's first law of diffusion provided that

the diffusion coefficient is known (Hangartner et al. 1996).

The radial diffusive sampler used consists of a cartridge of 60 mm length and 4.8 or 5.8 mm diameter of 16 mm in diameter. Depending on the polluting compound to be sampled, several different kinds of adsorbing or chemiadsorbing cartridges have been developed. This cylindrical collection cartridge, where the reaction is produced, is housed coaxially inside a cylindrical diffusive body, which restricts the type of molecules that make their way to the collection cartridge and minimises the sensitivity of the system to wind speed (WS) and turbulence. Different kinds of diffusive bodies are available, with like outer dimensions 60 mm length and 16 mm diameter. In this study, the blue diffusive body has been used. It is made of microporous polyethylene 1.7 mm thick and average porosity $25 \pm 5 \mu\text{m}$. Diffusive path length is 18 mm, and it is opaque to light: It is suited to the sampling of light-sensitive compounds. Two cellulose acetate caps are soldered with an epoxy adhesive to the cylinder ends. For

exposition, these components are screwed onto a plane cellulose acetate equilateral triangle equipped with an attaching clip.

The Radiello sampler for measuring nitrogen dioxide and O_3 is based on the principle that NO_2 and O_3 diffuse across the diffusive body towards the absorbing material on the inner cartridge. NO_2 and O_3 in the atmosphere are captured in the sampler as nitrite (NO_2^-) and 4-pyridylaldehyde, respectively. According to the Fick's first law, the quantity of NO_2^- and 4-pyridylaldehyde in the sampler is proportional to the concentration outside the sampler, the diffusion coefficient, the dimensions of the sampler and the sampling time. Concentrations are calculated from the quantity of nitrite or 4-pyridylaldehyde captured in the sampler by means of Eq. 1:

$$C(\mu g m^{-3}) = \frac{m \times z}{A \times t \times D} = \frac{m}{Q_k \times t} \quad (1)$$

where the sampling rate (Q_k) is a constant:

$$Q_k = D \times \frac{A}{z} \quad (2)$$

where C represents the ambient air NO_2 or O_3 concentration measured by the passive sampler (micrograms per cubic metre), m is the quantity of NO_2^- or O_3 captured in the sampler (micrograms) and z , A , t and D denote the diffusion length (metres), cross-sectional area (square metres), sampling time (seconds) and diffusion coefficient (square metres per second), respectively. The theory of the passive sampling method is available in a number of publications (Palmes and Gunnison 1973; Posner and Moore 1985; Harper and Purnell 1987; Krupa and Legge 2000; Gorecki and Namiesnik 2002).

How the diffusion coefficient of the pollutant in the air, the diffusion length and the cross-sectional area are constant, the theoretical sampling rate should be constant. Nevertheless, the diffusion coefficient depends on certain environmental parameters such as temperature and pressure (Brown 2000). These variations have been considered correcting the sampling rate Q_k according to Eq. 3:

$$Q_K = Q_{298} \left(\frac{K}{298} \right)^7 \quad (3)$$

where K is the temperature and Q_{298} is the sampling rate at standard conditions.

For NO_2 , the sampling rate value Q_{298} at 298 K (25°C) and 1,013 hPa is 78 mL min⁻¹. Only in the case of NO_2 is necessary to apply the Eq. 3 to the Eq. 1 to calculate the concentration of nitrite in the ambient air because for O_3 , the sampling rate can be considered linear in the exposure range (10,000–4,000,000) $\mu g m^{-3}$ min⁻¹ and is not affected by humidity or wind speed. The value of Q_k for O_3 is 24.6 mL min⁻¹ (http://www.radiello.com/english/index_en.html).

2.3 Extraction and Analysis of the Samples

Special care was taken when handling the passive samplers. Before and after exposure, the cartridges were kept in airtight containers. After exposure, the sampler's cartridges were transferred to a plastic tube and kept in the refrigerator until the analysis.

2.3.1 Analysis of NO_2 (R&P-Co 2001)

Exposure time was of 7 days. Five millilitres of ultra-pure water was added into the plastic tube with the cartridge inside. The solution was stirred vigorously by vortex for 2 min to allow the nitrite to dissolve in the water. After stirring, the cartridges were removed from the solution. Of the nitrite solution, 0.5 mL was mixed along with 5 mL of sulphanilamide reactive (10 g of sulphanilamide in 100 mL of concentrated HCl and dilute to 1 L with water) and stirred for 5 min. Then, 1 mL of NEDA reactive (250 mg of *N*-(1-naphthyl) ethylenediamine dihydrochloride in 250 mL of water) was added and stirred for 10 min.

The principle of working is the following: NO_2 is chemiadsorbed in triethanolamine as nitrite ion (NO_2^-). During the analysis in the laboratory, the nitrite reacts with sulphanilamide and forms a diazonium compound which reacts with NEDA to form purple azodye which is measured in an UV spectrophotometer at 537 nm (R&P-Co 2001). The concentration of the azodye is proportional to the amount of NO_2 chemiadsorbed over the sampling period (Cocheo et al. 1999). The mass of nitrite in the cartridge is obtained by reference to a linear calibration derived from the spectrophotometric analysis of standard solutions of sodium nitrite.

2.3.2 Analysis of O_3 (R&P-Co 2001)

Exposure time was of 7 days. How the absorbing cartridge contains 1,2-di(4-pyridil)ethylene (DPE) and

it is light sensitive, the cartridge must be stored in a closed tube in the dark. During exposure, the opaque diffusive body of Radiello sampler (of blue colour) protects the cartridge from the light. After the exposure time, the silica gel coated with DPE contained in the cartridge is placed in a plastic tube for extraction. A volume of 5 mL of 3-methyl-2-benzothiazolinone hydrazone (MBTH) solution (5 g MBTH with 5 mL of concentrated sulphuric acid in 1 L of water) is added into a plastic tube containing the silica gel. Then, the plastic tube is hermetically sealed and shaken using a vortex shaker for 1 min. To guarantee a complete reaction, this mixture is left for at least 60 min in the dark at room temperature stirring from time to time before analysis.

The principle of working is as follows: The radial diffusive cartridge used for ozone monitoring is filled with silica gel coated with 1,2-di(4-pyridyl)ethylene. Ambient O₃ diffuses through the porous membrane until the cartridge where it is trapped by reaction with DPE. Hauser and Bradley (1966) suggested the probable absorption reaction between O₃ and DPE to form an ozonure intermediate, which upon hydrolysis yields 4-pyridylaldehyde (PA), amongst other products. Later, MBTH reacts with PA to yield the corresponding azide that is a yellow molecule. The absorbance of the solution is measured in the UV spectrophotometer at 430 nm. The mass of PA in the cartridge is obtained by reference to a linear calibration derived from the spectrophotometric analysis of standard solutions of PA. Therefore, the amount of O₃ can be calculated from the amount of PA taking into account that 1 µg of PA correspond to 0.224 µg of ozone.

In all cases, three unused cartridges belonging to the same lot were treated in the same manner as the samples. Then, it was subtracted by the average blank value from the absorbance values of the samples.

3 Results and Discussion

Tables 1 and 2 showed the results of the levels of ozone and NO₂ measured during the campaign.

3.1 Seasonal Trend in Levels of Ozone and NO₂

Figure 2 shows a plot of the mean levels of ozone and NO₂ for all sampling points versus the sampling

period. Each period corresponds to a week of exposure from February to December of 2007.

It can be seen as ozone levels vary throughout the different seasons. In early spring, there are the absolute higher ozone values (periods V and VI with values of 60.9 and 49.1 µg/m³, respectively) although the maximum are typically achieved in summer. On the other hand, the minimum values of ozone were recorded in December (period XL). This change has already been described in literature (Puxbaum et al. 1991) where the increase of ozone concentration in spring is related to the transport of stratospheric ozone towards the top of the troposphere. Other studies (Penkett 1986), however, consider that the peak in the spring season is due to the accumulation of ozone precursors during the winter, as a result of a lower intensity of solar radiation. In spring, these precursors such as nitrogen oxides (NO_x) and volatile organic compounds react to give higher concentrations of ozone in this period. This second hypothesis is supported by the enormous variability of the seasonal lifetime of NO_x, that is, 20 times higher in spring (Lieu et al. 1987).

There are several studies concerning the role and contribution of volatile organic compounds of biogenic origin (BVOCs) in generating O₃. Thus, in Europe, some authors (Vogel et al. 1995) have studied the influence of these BVOCs on ozone concentrations during episodes of high atmospheric temperature in Germany, concluding that the biogenic emissions can contribute between 10% and 20% to ozone concentrations. Other authors using the database project Biogenic Emission in the Mediterranean Area found for the Mediterranean area, where the maximum ozone concentration is around 100 ppbv, that biogenic emissions represent a maximum of 10 ppbv, and this value depends heavily on the dynamic evolution of the regional winds (Navazo et al. 2003).

Our results and previous ones support the importance, respect to the increase of ozone levels, of volatile organic compounds of biogenic origin which have their maximum levels in the spring period as a result of the intense activity of plant species. These BVOCs are mainly isoprene and terpenes but also other oxygenated organic compounds, especially carbonyls and alcohols. Some of them react in the atmosphere with OH and NO₃ radicals with higher rate constants than the most reactive anthropogenic VOCs (Finlayson-Pitts and Pitts 2000). In the

Table 1 Measurements of O₃ in the urban atmosphere of Ciudad Real city and in the airport during 30 January 2007–20 December 2007

Ozone Period	Winter			Spring							Summer														
	I	II		III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	
Points	P1	16.1	34.5	40.1	33.4	60.7	54.6	51.0	62.8	42.8		54.9	48.8	45.2	61.6	44.7	35.4	60.8		68.7	67.3	66.3	68.0		
	P2	10.6	18.9	27.3		57.7	28.9	47.5	45.4	39.2	39.1	36.9	36.7	27.7	52.0	28.7	21.9	38.8		32.0	33.6	33.9	11.0		
	P3	12.3	34.3	34.3	36.7	54.3	29.0	37.3	46.2	51.9	44.7	44.0	44.9	41.5											
	P4	8.9		42.3	42.0	56.6																			
	P5	18.1	45.9	45.7	41.9	62.3	55.5	38.2	50.3	50.2	31.6	51.3	48.3	50.0	50.8	59.6	18.2	36.8		57.1	51.0	57.7			
	P6	14.3	35.3	44.4	39.4	66.2	56.7	56.5	66.2																
	P7	17.2	24.4	37.2	32.0	68.5	62.3	50.3	46.2	46.3															
	P8	19.8	35.9	46.3	47.3		56.9	60.1	53.7		54.2	53.7	44.5	65.8	56.6	46.1	67.8			53.6	63.0	70.0			
	P9							26.2	7.8	11.1	6.2	19.8		32.8	16.3	38.8	28.9			30.5					
	P10												42.9	57.0	47.2	49.1	63.9			59.8	70.1	76.5			
	P11																								
average	14.7	32.7	39.7	39	60.9	49.1	45.9	47.3	40.3	30.4	43.5	46.5	40.7	50.6	45.9	34.1	49.5	–	–	50.3	57.0	60.9	39.5		

Ozone Period	Summer			Autumn																		
	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI	XXXVII	XXXVIII	XXXIX	XL	XLI	XLII			
Points																						
P1	73.0	68.0	59.0	62.2	51.9	36.1	34.5	22.3	29.2	35.3	34.6	33.0	22.3	15.1	14.0	22.2	6.2	7.5	13.7			
P2					45.1	5.0	22.9	12.7	23.7		18.6	27.6	16.2	10.2	7.2	16.0	2.5	6.1	12.5			
P3																						
P4																						
P5		22.7	44.5	55.9	49.9	56.7	34.3	32.1	27.5	36.8	32.6	36.4	22.2	15.5	7.7	15.1	9.1	14.6	14.2			
P6																						
P7																						
P8		76.5	65.7	59.2	50.8	18.6	42.8	29.4	35.5	38.2	20.0	34.9	34.8	29.7	20.2	10.5	13.5	19.4	12.6			
P9																						
P10		63.2	53.7	54.4	51.9	49.9	34.1	33.9	30.3	33.8	33.3	28.5	29.6	29.9	26.4	27.8						
P11					17.6				17.1	28.2	26.8	27.6	13.8	9.4	8.2	16.7	7.2	6.9	8.0			
average	73.0	57.6	55.7	57.9	44.5	33.3	33.7	26.1	27.2	34.5	27.7	31.3	23.2	18.3	14.0	18.1	7.7	10.9	12.2			

All units in micrograms per cubic metre. Each period is 7 days

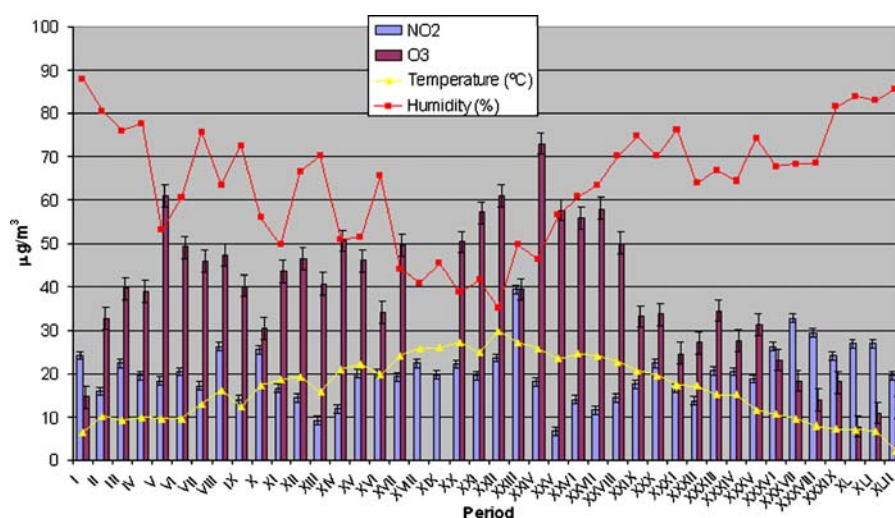
Table 2 Measurements of NO₂ in the urban atmosphere of Ciudad Real city and in the airport during 30 January 2007–20 December 2007

NO ₂	Period	Winter			Spring												Summer											
		I	II		III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII			
Points	P1	18.7	12.3	24.5	15.7	11.3	29.0	12.6	12.5	1.0	22.8	8.7	7.8	3.7	11.6	14.9	14.7	15.5	6.3	12.3	14.4	21.4	22.6	24.0				
	P2	31.1	52.0	41.4	29.1	31.6	38.0	15.6	61.5	24.7	33.9	28.6	25.0	25.4	21.7	69.5	63.2	69.9	42.2	47.0	72.0	44.3	50.6	55.1				
	P3	50.5	17.8	30.2	26.3	28.3	11.0	8.4	38.4	27.8	24.9	15.5	17.2	6.2														
	P4	35.6	15.0	26.0	24.2	44.4																						
	P5	15.9		8.1	16.1	7.6	6.1	6.5	5.6	7.9	14.5	10.2	4.2	2.1	2.4	3.4	4.0	5.3	4.7	13.8	6.2	7.2	8.9					
	P6	5.7	1.8	2.4	8.9	0.4	4.7	6.3	7.4																			
	P7		6.9	32.6	15.7	12.5	25.7	12.6	24.1	5.7																		
	P8	12.0	5.7	14.7		11.0	29.1	4.7	7.7	11.2	9.4	13.9	10.3	10.1	4.0	16.8	16.8	10.2	14.9	17.5	19.1	24.0	30.6					
	P9							69.4	53.1	19.4	47.4	23.4	22.5	16.8	27.6	12.9		14.6	43.4	23.9	17.6							
	P10													0.4	3.0	2.1	1.2	0.1		4.5	3.7	1.2	5.0					
	P11																											
average	24.2	15.9	22.5	19.4	18.4	20.5	17.0	26.3	14.0	25.5	16.7	14.5	9.2	11.7	19.9	20.0	19.3	22.3	19.8	22.2	19.6	23.5	39.6					

NO ₂	Period	Autumn																							
		Summer												Autumn											
		XXIV	XXV	XXVI	XXVII	XXVIII	XXIX	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI	XXXVII	XXXVIII	XXXIX	XL	XLI	XLII					
Points	P1	18.0	12.1	18.8	12.2	8.1	11.7	21.1	19.3	10.6	3.9	12.8	22.6	21.4	41.7	14.3	46.4	9.3	16.1	11.8					
	P2	18.2				49.7	44.7	49.9	36.1	28.8	33.8	33.0	39.7	45.1		41.1	37.7	52.0	36.9						
	P3																								
	P4																								
	P5		1.3	11.2	10.0	3.0	6.6	13.8	5.6	14.1	13.2	18.4	16.8	11.8	28.6	22.0	19.7	47.0	19.9	16.1					
	P6																								
	P7																								
	P8		11.9	20.9	20.7	8.9	20.6	22.3	16.9	12.7	22.7	6.4	11.6	20.6	8.5	26.7	23.7	11.7	10.6	2.3					
	P9																								
	P10		1.3	4.8	3.3	3.1	4.7	4.5	1.7		4.0	3.1	3.2	2.0	1.0	3.0	10.1								
	P11								20.7	2.8	46.3	49.2	18.3	57.3	84.0	69.2	7.0	40.0	36.7	30.6					
	average	18.1	6.7	13.9	11.6	14.6	17.7	22.3	16.7	13.8	20.7	20.5	18.7	26.4	32.8	29.4	24.1	27.0	27.1	19.5					

All units in micrograms per cubic metre. Each period is 7 days

Fig. 2 Evolution of temperature, humidity and NO₂ and O₃ average concentrations of the 11 measured points during the full period



presence of NO_x, BVOCs act as precursors of ozone and/or secondary organic aerosols in the troposphere. Globally, the BVOCs represent about 60% of the total emissions of VOCs.

This fact could explain the ozone levels background observed all year in rural or urban atmosphere. It can be concluded that the ozone formation in winter period is highly influenced by anthropogenic sources of their precursors, whereas in summer period, biogenic processes at local and regional level will be most favoured.

Respecting NO_x, the main contribution is due to emissions from road traffic, bringing their values keep more or less constant throughout the year, slightly higher in the winter. Last fact can be attributed, as indicated above to the accumulation of ozone precursors during the winter as a result of reduced solar radiation and lower temperature. Having less radiation, NO_x are not photolysed and trends to accumulate.

Finally, it is important to mention that during holiday periods XXIII and XXIV, only sampling points P1 and P2 remained, and therefore, these values are not average values of all sampling points. The empty points in Fig. 2 for periods XVIII and XIX correspond to lost samples.

3.2 Relationship with Climatologic Variables

Attempts were made to relate levels of ozone and NO₂ obtained here with the variables pressure, temperature, humidity and wind. These variables (supplied by Spanish State Agency of Meteorology)

were averaged by each sampling periods and plotted in Fig. 2.

Ozone concentration (in micrograms per cubic metre) showed a slight negative correlation with relative humidity (RH in %) ($[O_3] = -0.62RH + 88.66$) and a positive correlation with temperature (T in degree Celsius; $[O_3] = 0.37T + 2.52$). Periods with higher temperatures and lower humidity usually correspond to higher values of ozone. Thus, for periods V and XIV, values of ozone were higher than expected and this fact could be due to the low humidity of those weeks (53% and 51%, respectively, compared with 61% of humidity in the spring period). Pressure and wind were very variable throughout the year with an average value around of 94–95 kPa and

Table 3 Mean values of NO₂ and O₃ for each sampling point (all period)

Point	NO ₂ (µg/m ³)	O ₃ (µg/m ³)
P1	16.0±1.4	42.5±3.1
P2	41.1±2.4	26.3±2.5
P3	23.3±3.5	39.3±3.0
P4	29.0±5.0	37.5±10.1
P5	11.3±1.4	38.1±2.6
P6	4.7±1.0	47.4±6.3
P7	17.0±3.4	42.7±5.6
P8	14.7±1.1	43.1±3.1
P9	30.2±4.9	21.8±3.6
P10	3.1±0.4	45.5±3.2
P11	38.5±7.1	15.6±2.4

The error is typical error from statistic analysis of data

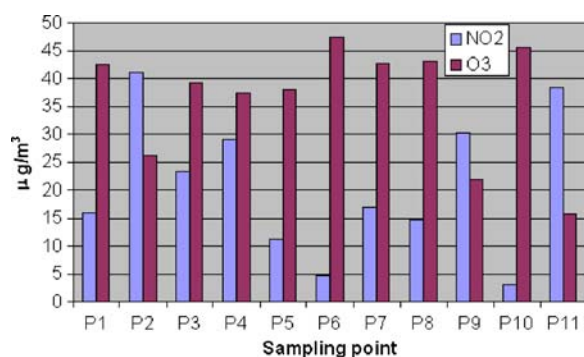


Fig. 3 Plot of average levels of ozone and NO₂ (micrograms per cubic metre) for each sampling point

8 km/h, respectively. An insignificant variation with pressure has been observed. However, wind speed shows a positive correlation (WS in kilometres per hour; $[O_3] = 6.54WS - 15.15$) since higher wind speed often leads to lower NO, and therefore, the loss of ozone is reduced. After analysing the wind rose for each sampling period, it has not found any relation between the levels of O₃ and NO₂ measured in each period with the wind direction; therefore, we can conclude that the transport from contaminated areas such as the petrochemical complex of Puertollano is not important.

Similar variations of ozone concentration with meteorological conditions have previously been reported (Shan et al. 2009).

3.3 Average Sampling Values

Table 3 and Fig. 3 show the average values for each point along the entire sampling period. As it is shown in Table 3, the higher levels of NO₂ correspond to P2,

P3, P4, P9 and P11. These values of NO₂ can be attributed to the intense flow of vehicles on those areas, to emphasise that point P11 is located on the entrance of an underground car parking, which also justifies that this point has a higher average level of NO₂. Points P1, P5, P6, P7 and P8 show lower values than the other sampling points because they correspond to suburban areas. Also to mention that in P10, located in a zone where it was being constructed the Central Airport of Ciudad Real, the lowest concentrations of NO₂ are recorded due to it is in a rural area, where road traffic is lower, and hence, NO_x emissions are very low. Respecting O₃ levels, the highest values are registered in the points that are located in suburban or rural areas except P3 and P4 (although in these points, the period of sampling is very different to the other points, see Table 1)

With the average values of points P1, P2, P3, P4, P5, P6, P8, P9 and P11, a spatial distribution map has been developed for O₃ and NO₂ (Fig. 4) using SurGe Project Manager ver 1.4. As it can be seen, higher values of O₃ correspond to lower values of NO₂ and vice versa. This behaviour is expected considering the inter-conversion of both species according to photochemical cycle of tropospheric O₃ production (Finlayson-Pitts and Pitts 2000).

3.4 Comparison of the Obtained Results with Limit and Threshold Environmental Levels Values

In the case of nitrogen oxides, limit values are set by the RD 1073/2003, transposed the European Directive 1999/30/EC, and are shown in Table 4.

Fig. 4 Maps of O₃ and NO₂ spatial distribution. Units in micrograms per cubic metre

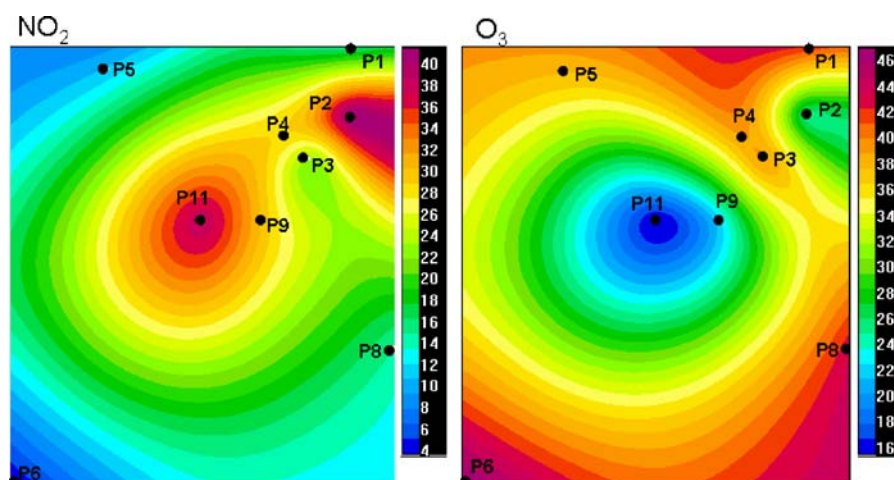


Table 4 Limit values for nitrogen dioxide and oxides of nitrogen

	Averaging period	Limit value	Margin of tolerance	Date by which limit value is to be met
Hourly limit value for the protection of human health	1 h	200 $\mu\text{g}/\text{m}^3$ NO ₂ , not to be exceeded more than 18 times a calendar year	50% on the entry into force of this Directive, reducing on 1 January 2001 and every 12 months thereafter by equal annual percentages to reach 0% by 1 January 2010	1 January 2010
Annual limit value for the protection of human health	Calendar year	40 $\mu\text{g}/\text{m}^3$ NO _x	50% on the entry into force of this Directive, reducing on 1 January 2001 and every 12 months thereafter by equal annual percentages to reach 0% by 1 January 2010	1 January 2010
Annual limit value for the protection of vegetation	Calendar year	30 $\mu\text{g}/\text{m}^3$ NO _x	None	19 July 2001

Limit values must be expressed in micrograms per cubic metre. The volume must be standardised at a temperature of 293 K and a pressure of 101.3 kPa

According to the RD 1796/2003 that transposed the European directive 2002/3/EC, threshold values for ozone are shown in Table 5.

Levels of ozone and NO₂ obtained during the campaign are within the allowed values. However, comparing the average annual values, which are shown in Table 3, and threshold limit values, which appear in Tables 4 and 5, there are some relevant data.

The values obtained for NO₂ in points P2 and P11 slightly exceed the annual limit value for the protection of vegetation (30 $\mu\text{g}/\text{m}^3$) and human health (40 $\mu\text{g}/\text{m}^3$). For ozone levels, only the point P6 with a value of 47.4 ± 6 $\mu\text{g}/\text{m}^3$ exceeds the threshold limit value (40 $\mu\text{g}/\text{m}^3$ calendar year) that imply damage to materials.

Annual average values obtained in this work for NO₂ and ozone are consistent with other studies

developed in towns with similar atmospheres to Ciudad Real city (Navazo et al. 2003)

3.5 Comparison with the Levels Measured by DOAS in the 2000/2001 Marketing Year

Bibliographic data about levels of NO₂ and O₃ in Ciudad Real city are virtually non-existent except for a study conducted in 2001, about the seasonal trend in levels of gaseous pollutants (ozone, NO₂ and SO₂) by means of a DOAS system (Saiz-Lopez et al. 2006) during the period of 21 July 2000 to 23 March 2001. The study area was the campus of the University of Castilla La Mancha. Values were also monitored through a mobile station of the Regional Air Quality Network (RAQN) in a different point (Porzuna road;

Table 5 Values threshold for ozone according to the RD 1796/2003

	Level	Report for each year
Information threshold	180 $\mu\text{g}/\text{m}^3$	For each day with exceedance(s): date, total hours of exceedance, maximum 1 h ozone and related NO ₂ values, when required
Alert threshold	240 $\mu\text{g}/\text{m}^3$	For each day with exceedance(s): date, total hours of exceedance, maximum 1 h ozone and related NO ₂ values when required
Health protection	120 $\mu\text{g}/\text{m}^3$	For each day with exceedance(s): date, 8 h maximum
Vegetation protection	AOT40=6,000 $\mu\text{g}/\text{m}^3\text{h}$	From May to July
Forest protection	AOT40=20,000 $\mu\text{g}/\text{m}^3\text{h}$	From April to September
Materials	40 $\mu\text{g}/\text{m}^3$	Calendar year

Saiz-López et al. 2006). These sampling points are coincident with points P1 and P5, respectively, of our campaign. The average values of NO₂ and O₃ in the study of Saiz et al. (50 and 27 g/m³, respectively) are different from those obtained by passive samplers and are shown in this study (16 and 42 µg/m³, respectively). But this difference may be partly attributable to the period of sampling, which in the case of Saiz et al. are not include the months of the main ozone production, from May to July, whilst in this work are included. However, these results seem to agree that the highest values of NO₂ are registered in the sampling points of the centre (DOAS and P1) compared with the points of the suburban areas, RAQN and P5.

4 Conclusions

- Ozone levels recorded in Ciudad Real area in 2007 through the use of passive sensors, with average values of 38.5 ± 3.5 µg/m³ for O₃ and 20.8 ± 3.8 µg/m³ for NO₂ are below the threshold values. Then, it can be assumed that air quality in the considered area is high.
- The seasonal distribution of ozone concentrations seem to be related to levels of BVOCs, reaching maximum values during periods in which plants have a more intense activity (spring and early summer).
- The highest values of ozone are obtained in suburb areas, where the influence of road traffic is lower.
- The highest values for NO₂ are obtained in the central areas of the city, where the influence of vehicles is higher.
- There is an inverse relationship between levels of ozone and NO₂.
- There have not been found a clear relationship between meteorological variables and levels of O₃ and NO₂ obtained.
- This is to emphasize that points P2 and P11 are probably the most indicated points to install permanent monitoring stations for NO_x.
- Another important point is to control the airport area (P6), with an annual level of ozone above the threshold value. It is important to mention that these values will probably suffer variations when the airport is operating completely. Therefore, it

would be necessary to control this point in order to see the influence of the airport in the contaminants levels in the area.

Acknowledgments The authors gratefully thank to Foundations of UCLM for supporting a part of this work.

References

- Brown, R. H. (2000). Monitoring the ambient environment with diffusive samplers: theory and practical considerations. *Journal of Environmental Monitoring*, 2(1), 1–9.
- Cocheo, V., Boaretto, C., Cocheo, L., & Sacco, P. (1999). Radial path in diffusion: The idea to improve the passive sampler performances. In V. Cocheo, E. De Saeger, D. Kotzias (Eds.), *International Conference Air Quality in Europe. Challenges for the 2000's*. Venice, Italy.
- Finlayson-Pitts, B. J., & Pitts, J. N. (2000). *Chemistry of the upper and lower atmosphere: Theory, experiments and applications*. San Diego: Academic.
- Fondazione Salvatore Maugeri (2003). Instruction manual for Radiello sampler, version 1/2003. <http://www.radiello.com>.
- Gorecki, T., & Namiesnik, J. (2002). Passive sampling. *Trends in Analytical Chemistry*, 21(4), 276–291.
- Hangartner, M., Kirchner, M., & Werner, H. (1996). Evaluation of passive methods for measuring ozone in the European Alps. *Analyst*, 121, 1269–1272.
- Harper, M., & Purnell, C. J. (1987). Diffusive sampling—a review. *American Industrial Hygiene Association Journal*, 48(3), 214–218.
- Hauser, T. R., & Bradley, D. W. (1966). Specific spectrophotometric determination of ozone in the atmosphere using 1, 2 di(4-pyridyl) ethylene. *Analytical Chemistry*, 38, 1529–1532.
- Kleinman, L. I. (1991). Seasonal dependence of boundary layer peroxide concentration: the low and high NO_x regimes. *Journal of Geophysical Research*, 96, 20721–20733.
- Krupa, S. V., & Legge, A. H. (2000). Passive sampling of ambient, gaseous air pollutants: an assessment from an ecological perspective. *Environmental Pollution*, 107, 31–45.
- Lee, D. S., Holland, M. K., & Falla, N. (1996). The potential impact of ozone on materials in the UK. *Atmospheric Environment*, 30, 1053–1065.
- Lieu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W. (1987). Ozone production in the rural troposphere and its implications for regional and global ozone distributions. *Journal of Geophysical Research*, 92, 4194–4207.
- Mazzeo, N. A., & Venegas, L. E. (2002). Estimation of cumulative frequency distribution for carbon monoxide concentration from wind-speed data in Buenos Aires (Argentina). *Water, Air and Soil Pollution: Focus*, 2, 419–432.
- Mazzeo, N. A., & Venegas, L. E. (2004). Some aspects of air pollution in Buenos Aires City. *International Journal of Environment and Pollution*, 22(4), 365–379.

- Navazo, M., Durana, L., Alonso, J. A., García, J. L., Ilardia, M. C. y Gangoiti, G. (2003). Caracterización de compuestos orgánicos volátiles atmosféricos en áreas industriales, urbanas y rurales de la C.A.V 1995–2003.
- Palmes, E. D., & Gunnison, A. F. (1973). Personal monitoring device for gaseous contaminants. *American Industrial Hygiene Association Journal*, 34, 78–81.
- Penkett, S. A. (1986). The spring maximum of photo oxidants in the Northern Hemisphere. *Nature*, 319, 655–657.
- Posner, J. C., & Moore, G. A. (1985). Thermodynamic treatment of passive monitors. *American Industrial Hygiene Association Journal*, 46(5), 277–285.
- Puxbaum, H., Gabler, K., Smidt, S., & Glates, F. A. (1991). One-year record of ozone profiles in an Alpine Valley (Zillertal-Tyrol, Austria ,600–2000 m a.s.l). *Atmospheric Environment*, 25(9), 1759–1765.
- R&P-Co. (2001). *Radiello® Model 3310 passive sampling system. Passive gas sampling system for industrial indoor/ outdoor and personal exposure assessment*. East Greenbush: Rupprecht & Patashnick.
- Saiz-López, A., Notario, A., Martínez, E., & Albadalejo, J. (2006). Seasonal evolution of levels of gaseous pollutants in an urban area (Ciudad Real) in central-southern Spain: A DOAS study. *Water, Air and Soil Pollution*, 171, 153–167.
- Shan, W., Yin, Y., Zhang, J., Ji, X., & Deng, X. (2009). Surface ozone and meteorological conditions in a single year at an urban site in central-eastern China. *Environmental Monitoring Assessment*, 151, 127–141.
- Sillman, S., & Samson, P. J. (1995). Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environment. *Journal of Geophysical Research*, 100, 11497–11508.
- Tang, H., & Lau, T. (1999). A new all-season passive sampling system for monitoring NO₂ in air. *Field Analytical Chemistry and Technology*, 3(6), 338–345.
- UNE-EN 14211 (2005). Ambient air quality. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence.
- UNE-EN 14625 (2005). Ambient air quality—standard method for the measurement of the concentration of ozone by ultraviolet photometry.
- Varshney, C. K., & Singh, A. P. (2003). Passive samplers for NO_x monitoring: a critical review. *The Environmentalist*, 23(2), 127–136.
- Vogel, B., Fiedler, F., & Vogel, H. (1995). Influence of topography and biogenic volatile organic compounds emission in the state of Baden- Württemberg on ozone concentrations during episodes of high air temperatures. *Journal of Geophysical Research*, 100, 22907–22928.
- WHO (2000). *Chapter 7.2 Ozone and other photochemical oxidants. Air Quality Guidelines-Second Edition*. Copenhagen: WHO Regional Office for Europe.

Further Reading

www.jccm.es/medioambiente
www.radiello.it
www.troposfera.org