O$_3$ and CO$_2$ concentrations in a rural area in central Spain

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Abstract

This paper presents the main experimental results of ozone and carbon dioxide concentrations measured in a rural area in the upper Spanish plateau during 2000–2003 from a climatological perspective. Special attention is addressed to characterise the annual cycle and describe the trends observed during the entire period of the study.

Keywords: CO$_2$ annual cycle, O$_3$ annual cycle, CO$_2$ trends, O$_3$ trends.

1 Introduction

Indicators of human influence on the atmosphere during the industrial era have shown that concentrations of atmospheric greenhouse gases and their radiative forcing have continued to increase as a result of human activities. Among the atmospheric components linked to positive radiative forcing, O$_3$ and CO$_2$ are the subject of increasing concern [1]. Experimental evidence has shown that over the last few decades’ background O$_3$ in the troposphere has doubled compared to the pre-industrial years [2]. The impact of global increases in background concentrations appears to be evident in the increase in mean annual concentrations [3]. Conversely, analysis of UK monitoring data, also consistent with reports elsewhere in Europe and the United States, has revealed that O$_3$ peaks have tended to decline over the past decade [4]. Over the two past decades the steadily increasing CO$_2$ trend has been estimated at around 1.5 ppm year$^{-1}$ [5]. Nevertheless, despite the increasing number of monitoring stations around the world, data in rural locations are still sparse. This is especially true in Southern Europe, and specifically in Spain.

In February 2000 we installed the first rural station in the region of Castile and Leon located on the upper Spanish plateau. O$_3$, CO$_2$ and concurrent meteorological variables were measured for almost four consecutive years. The
region covers an area of 100 000 km\(^2\), has a low population density, 200 pp km\(^{-2}\), and agriculture is a major asset. These general features, together with the documented atmospheric cycles associated to the prevailing Iberian low during most of the summer [6], mean the Spanish plateau offers an interesting opportunity to increase current knowledge on O\(_3\) and CO\(_2\) in a representative and non-polluted continental rural area in Southern Europe. The aim of this paper is to present the most salient experimental results obtained from a climatological perspective. Particular attention is given to describing air quality levels, trends observed as well as the annual cycle. Finally, the influence of wind direction on the concentrations of both pollutants is presented and discussed.

2 Description of the site

The station, CIBA, is situated in the geographical centre of the upper Spanish plateau (lat: 41º49’N, long: 4º56’W, alt: 845 m), as shown in Figure 1. The location is a rural cerealist area not disturbed by nearby sources, except the cities of Valladolid (322 000 pp) some 30 km to the SE and Palencia (82 000 pp), located about 40 km to the NE. Hourly O\(_3\) concentrations were measured for almost four consecutive years, from February 2000 to October 2003 using a DASIBI 1008 continuous analyser. The equipment was regularly calibrated using standard methods [7]. CO\(_2\) measurements were performed from February 2000 to December 2004 using a MIR900 continuous analyser. Calibration of zero and span values was regularly performed using bottles of ultra pure nitrogen and CO\(_2\) AIR LIQUIDE standards. All the data were continuously recorded on a DASIBI 8001 datalogger and processed as hourly mean values.

Concurrent meteorological data were available through those routinely measured in a 100 m mast equipped with standard meteorological probes to
measure air temperature, wind speed and direction as well as relative humidity at different levels. The data used in this paper refer to those recorded at the lowest level: 6 m. During the period of study the mean wind speed was 3.5 m s\(^{-1}\), and ranged from 0 to 14.0 m s\(^{-1}\). Mean temperature was 11.9 ºC with extreme values of –9.7 and 35.7 ºC. The prevailing wind directions were NE, SW and W accounting for a frequency of 21.6, 16.3 and 15.4%, respectively.

3 O\(_3\) measurements: results

During the period of study the EC threshold for public information was exceeded four times in July 2003, 91.0 ppb being the highest concentration. The EC threshold for protection of human health, calculated as maximum daily 8 hour means from hourly running 8 hour averages, was exceeded 103 times, of which 4, 25, 26 and 48 took place in 2000, 2001, 2002, and 2003, respectively. Most O\(_3\) air quality indicators tended to show an increasing trend as can be derived from Figure 2, where the annual evolution is shown by means of a box and whisker plot. Each box covers 50% of the data values within the lower and upper quartiles. The whiskers extend out to the extreme maximum and minimum values. Values that fall beyond the whiskers but within three interquartile ranges are plotted as individual points. The horizontal lines and crosses represent the median and mean values, respectively. The annual linear trends, estimated over the first three years for O\(_3\) mean, P\(_{95}\) and P\(_{98}\) percentile values, yielded 0.95, 4.65 and 5.96 ppb, respectively.

The annual cycle of the monthly means is depicted in Figure 3. From this Figure the following main conclusions can be drawn:

![Yearly evolution of O\(_3\) measurements over the four years of study.](image)

The annual cycle is typical of those recorded in Mediterranean countries [8], highlighted by an increase in O\(_3\) during the period of photochemical activity, from April to September, and a decline in winter, from November to February. The maximum and minimum monthly O\(_3\) medians ranged from 41.0 to 27.0 ppb
in April and January respectively. The amplitude of the annual cycle, 14.0 ppb, is in accordance with the results obtained in rural areas of similar altitudes [9]. The minor differences observed from April to August, 2.0 ppb, indicate the presence of a broad spring-summer O₃ peak.

![Figure 3: Monthly means of O₃ concentrations during the whole period of measurements.](image)

The higher outliers and P₇₅, P₉₅ and P₉₈ percentile values were recorded from June to August, peaking in July, when most O₃ episodes and exceedances of the EC threshold for public information are usually reported [10]. The high values also recorded in May and September are indicative of the occurrence of some smog episodes. Specifically, O₃ peaks with concentrations comparable to those recorded in mid summer, up to 83.8 ppb, were systematically observed in September over the four years of measurements, again confirming the strong influence of meteorological factors on O₃ formation [11]. Regarding the lower whiskers and P₂₅ values, it should be noted that the highest values were recorded during spring, from March to May. Of particular interest is the increase observed in April, the month in which the P₂₅ reached the maximum value, 33.7 ppb, being 8.0 and 3.7 ppb greater than those recorded in March and July, respectively. This result indicates that the lower concentrations were greater than those recorded during most of the summer, thus revealing the presence of a generalised increase in O₃. However, it is worth mentioning that this increase, especially during nighttime, can also be partially attributed to the difference in the shape of the monthly nocturnal O₃ levels as can be derived from an examination of the diurnal cycles shown in Figure 4 for some selected months, December, April, May and July. The presence of a vanishing O₃ trend during night-time was a common feature from May to September in contrast to the rather uniform values exhibited during winter and spring (March-April). The nocturnal trend in summer explains the lower percentile values found as compared with those recorded in spring, and specifically in April. Although a description of the diurnal cycles is not addressed in this paper, it may be noted that all were featured by the well-known...
O$_3$ increase during daylight and a decrease during night-time. The wider amplitude of the diurnal cycles during spring and summer is also consistent with the diurnal solar radiation and temperature cycles.

![Graph showing diurnal O$_3$ cycles](image)

Figure 4: Diurnal O$_3$ cycles obtained during some selected months of the year, December, April, May and July.

The results presented suggest the occurrence of two maxima, the first in spring, April-May, and the second in summer, peaking in July since the highest P$_{98}$ values occurred during this month, as pointed out earlier.

Whereas the summer peak occurrence must be attributed to smog episodes favoured by strong solar radiation and high temperatures, the spring peak origin has been widely debated. Observations in many stations across the Northern Hemisphere have also shown variable times of occurrence, typically, from February to May [12]. A summary of the theories proposed has been presented by Monks. One of the most widely accepted is the superimposed contributions of stratospheric-tropospheric exchange, STE, peaking in January-April and O$_3$ produced in the troposphere peaking in April-June. The dominance of each process determines the shape of the spring-summer peak recorded at different measuring sites.

4 CO$_2$ measurements: results

During the entire period of study the mean and median values were 376.3 and 373.8 ppm, respectively, results in accordance with other data reported in the literature. The extreme values ranged from 342.5 to 498.5 ppm. As in the case of ozone, the data exhibited a great inter-annual variability, again showing the important influence of meteorological factors on the concentrations recorded. As derived from Figure 5, most of the statistics, namely the means, median, upper quartiles and outliers, showed a clearly visible annual increase. Taking the median values as a reference, considered to be more representative than the means due to the great variability of the data, the trend obtained was
2.4 ppm year\(^{-1}\), rising from 370 to 376.8 ppm over the four years. The result obtained is slightly higher than others reported in the literature \[13\].

![Box plot showing yearly evolution of CO\(_2\) measurements over the four years of study.](image)

**Figure 5:** Yearly evolution of CO\(_2\) measurements over the four years of study.

The annual cycle obtained is depicted in Figure 6. For interpretation purposes of the seasonal variation, we also include the hourly patterns obtained during some selected months of the year, December, April, May and July (see Figure 7). From these Figures the following considerations can be made.

CO\(_2\) concentrations tended to increase during spring, from April to June, peaking in May, corresponding to the period of maximum vegetation index at this site. During this period of the year an increase in the higher values (outliers) was a common feature. It then began to decline during summer, July and August, reaching minimum values during most of the winter period, from December to February. It is also interesting to note that during this period of the year the data presented a lower variability than during spring, the extreme greater values being considerably lower than during spring. These results reveal the strong influence of photosynthetic activity on the annual cycle, namely CO\(_2\) uptake during daylight, and respiration of soil and plants during night-time. The interpretation given is fully consistent with the diurnal variation obtained during December, April, May and July (see Figure 7), featured by an increase during night-time and a decline during the day. Moreover, the diurnal amplitude was more pronounced during spring, peaking in May, 20.5 ppm than in July or December, where it dropped to 4.9 ppm. The decrease in central summer might be attributed to the lack of vegetation as well as the high soil temperatures and low soil moisture prevailing at the measuring site, both major driving factors affecting respiration, and consequently, CO\(_2\) emissions. The lower diurnal amplitudes in winter are
consistent with the reduction of respiration due to the low vitality of plants, soil biota and roots during this period of the year.

Figure 6: Monthly means of CO$_2$ concentrations during the whole period of measurements.

Figure 7: Diurnal CO$_2$ cycles obtained during some selected months of the year, December, April, May and July.

The maximum and minimum mean monthly values ranged from 374.3 to 380.0 ppm in January and May, respectively, providing a rather weak seasonal amplitude, 5.7 ppm.

5 Influence of wind direction

Wind direction is considered to be one of the most relevant meteorological variables to identify the relationship between pollutant concentrations and
transport patterns. In this paper the wind rose was divided into the 8 main sectors and the mean concentrations associated to each were determined. Figures 8 and 9 show the results obtained for O$_3$ and CO$_2$ respectively. The central line represents the overall mean value and the lower and upper ones the decision limits at 95% confidence level.

![Figure 8: Influence of wind direction on O$_3$ concentration.](image1)

![Figure 9: Influence of wind direction on CO$_2$ concentration.](image2)

A quick examination of both Figures allows us to conclude the presence of a satisfactory “anticorrelation” between the concentrations of both pollutants recorded at most of the sectors. It should be noted that the NW, SW and W
sectors exhibited the maximum and minimum O\textsubscript{3} and CO\textsubscript{2} means, respectively whereas opposite results were obtained in the N, E and SE sectors.

Since the cities of Valladolid and Palencia are located to the SE and NE of the measuring site respectively, the increase in CO\textsubscript{2} observed in the “polluted sectors”, SE and N, and E sectors might be attributed to the impact of their corresponding urban plume emissions. Taking the overall mean as a reference, the contribution was estimated at roughly 6 and 3 ppm, in the SE, N, and E sectors, respectively. The decrease in O\textsubscript{3} recorded in these sectors appears to be indicative that precursors emissions, and specifically of NO, act as an O\textsubscript{3} sink. The interpretation given is in accordance with the decline in CO\textsubscript{2} observed in the “clean sectors”, W, NW, and SW, in which, as stated earlier, the higher O\textsubscript{3} concentrations were recorded.

6 Conclusions

During the almost four years of study the main indicators of ozone air quality showed a positive trend. The means and P\textsubscript{98} values exhibited an annual increase of 0.95 and 5.96 ppb. CO\textsubscript{2} presented a similar behaviour; the estimated increasing trend being around 2.4 ppm year\textsuperscript{-1}. However, due to the still limited period of study, these results should be considered with caution and future measurements would be required to confirm whether the obtained increasing trend would persist.

The annual cycle of both pollutants has been well characterised. In the case of O\textsubscript{3}, the seasonal variation was typical of that recorded in Mediterranean countries, highlighted by an increase during the period of photochemical activity, from April to September, and a decline in winter. The annual cycle showed a broad spring-summer peak exhibiting very weak differences in the monthly means from April to August, 2 ppb. The annual CO\textsubscript{2} cycle showed a strong influence of photosynthetic activity. CO\textsubscript{2} concentrations increased during the growing season, from April to June, peaking in May, and declined during winter, from November to January. After harvest in mid-summer, CO\textsubscript{2} concentrations again dropped. The seasonal amplitude was also rather weak, 5.7 ppm.

An analysis of the influence of wind direction on the concentrations has enabled identification of the contribution of emissions from the only nearby cities, Valladolid and Palencia, located around 40 km from the measuring site. In the “polluted sectors”, SE, N, and E, namely, those affected by the source location, an increase in CO\textsubscript{2} and a decline in O\textsubscript{3} respectively, were recorded. The “anticorrelation” obtained between both pollutants strongly suggests that gas precursor emissions, and specifically NO, contribute as O\textsubscript{3} sinks at the measuring site.

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References


