Evolución y comportamiento del ozono estratosférico y superficial en el sudoeste de la Península Ibérica (El Arenosillo)

Evolution and behaviour of the stratospheric and surface ozone in the southwest of Iberian Peninsula (El Arenosillo)

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RESUMEN
La Estación de Sondeos Atmosféricos (ESAt) El Arenosillo es un Observatorio de Referencia Internacional dedicado a la observación y análisis de parámetros atmosféricos diversos, como el ozono superficial y precursores, aerosoles in situ y en columna, ozono estratosférico y radiación solar, y diversos parámetros ionosféricos. En este trabajo se analiza la evolución mensual y diaria con un claro ciclo con máximos en verano y en las horas centrales del día. La dinámica del ozono superficial está fuertemente condicionada por la orografía, las condiciones atmosféricas y las fuentes de precursores. Bajo situaciones de mesoescala se registran episodios de ozono con valores máximos diarios por encima de los 160 $\mu g\ m^{-3}$. Las medidas del contenido total de ozono (TOC) sobre El Arenosillo muestran un marcado carácter estacional, con valores máximos en primavera y mínimos en otoño y en valor promedio, alrededor de 315 Unidades Dobson. Se ha determinado, en base a las observaciones, que durante la década de los 80 se puede observar una acentuada tendencia a la disminución del TOC, estabilizándose paulatinamente durante la década de los 90, para finalmente poder hablar de una tendencia a la recuperación de la capa de ozono en nuestros días.
Palabras clave: Ozono superficial; contenido total de ozono; unidades Dobson; brisa costera; contaminación atmosférica; contaminación fotoquímica; espectrorradiómetro Brewer; espectrofotómetro Dobson; El Arenosillo.

ABSTRACT
Atmospheric Sounding Station (ESAt) El Arenosillo is an International Reference Centre dedicated to the observation and analysis of various atmospheric parameters such as surface ozone and precursors, aerosols in situ and in column, stratospheric ozone and solar radiation, and vari-

ous ionospheric parameters. In this paper the monthly and daily evolution is analysed, with a marked hourly cycle with higher levels in the central hours and in summer months. The surface ozone dynamics is strongly conditioned for the orography (coastal site), atmospheric conditions and sources of ozone precursors. Under mesoscale processes of air masses, surface ozone episodes are recorded with daily maximum up 160 µg m^{-3}. Total ozone content (TOC) measurements at El Arenosillo show a marked seasonality, with maximum peaks in spring, minimum values in autumn and yearly mean around 315 Dobson Units. Based on the observations, it has been determined that a marked TOC depletion can be observed during the 80s, stabilizing gradually in the decade of the 90s to get nowadays a positive trend towards the recovery of the ozone layer.
Key words: Surface ozone; total ozone content; Dobson units; sea-land breeze; air pollution; photochemical pollution; Brewer spectroradiometer; Dobson spectrophotometer; El Arenosillo.

SUMMARY: 1. Introduction. 2. Study area: Atmospheric sounding station – El Arenosillo. 3. Stratospheric ozone. 4. Surface ozone. 5. Relation between stratospheric and surface ozone at El Arenosillo. 6. Summary and conclusions. 7. Acknowledgements. 8. References

1. INTRODUCTION

Ozone is one of the most important atmospheric trace gas species in both the stratosphere and troposphere in terms of human health and climate. While the stratospheric ozone protects life on Earth from the sun's harmful ultraviolet (UV) radiation, the surface ozone is known as an important photochemical pollutant. In the Atmospheric Sounding Station (ESAt) - El Arenosillo ozone measurements are recorded, both in the stratosphere (total column) and in the surface. In this paper the more relevant aspects of stratospheric ozone seasonal variations and trend analysis are presented.

In the section devoted to surface ozone, the monthly and daily evolution that experiment this gas in the lower atmosphere of El Arenosillo is showed as well as the surface ozone dynamics, which is strongly conditioned by factors as orography and emissions of ozone precursors. Finally, the last section is dedicated to discuss the possible relationship between the total ozone and the ozone data collected in the surface.

2. STUDY AREA: ATMOSPHERIC SOUNDING STATION – EL ARENOSILLO

The Atmospheric Sounding Station (ESAt) (37.1ºN – 6.7ºW, 40 m asl) is located in the coastal area of the southwest of Iberian Peninsula (Mazagón-Huelva). The ESAt develops in five research areas: radiopropagation, stratospheric ozone and ultraviolet, air pollution and meteorology, atmospheric aerosols and characterization of biotechnological applications. In radiopropagation, predictions of the behavior of the ionosphere model for validation of the International Reference Ionosphere (IRI) are made. Total O3 and UV are continuously monitoring, and the observatory regularly hosts international intercomparison calibrations campaigns for Dobson and Brewer in Europe; a laboratory for characterization and calibration of instruments measuring solar radiation is also available. Regarding the air pollution it is being studied the behavior of surface ozone and its precursors in southern Spain (Andalusia), and also several aspects related with the meteorology are analyzed. In the field of aerosols, size distribution, scattering and absorption are being studied. The main tasks in the biotechnological line are the analysis of the influence of UV radiation on crop productivity of strawberry, on biomass production and antioxidant compounds of commercial interest, and on the design of plastics that improve agricultural yields and quality of crops.

3. STRATOSPHERIC OZONE

In this framework, well-calibrated ground-based instruments are essential tools for monitoring the state of the atmosphere and the condition of the ozone layer by means of accurate recording of the total ozone column. Accurate ozone measurements are also required for various scientific and societal applications, such as monitoring and predicting climate change, numerical weather prediction and monitoring and predicting air pollution. In addition, scientific studies have focused on topics such as the global ozone decline and the expected future global ozone recovery (WMO, 2007).

The abundance of atmospheric trace gas constituents and air suspended aerosols can in principle be determined from the spectrum of sunlight measured at the Earth's surface using various mature measurement techniques combined with a thorough understanding of atmospheric radiative transfer under various meteorological conditions and aerosol loads.

The well-established world wide network of Brewer and Dobson spectroradiometers instruments is generally considered as the standard for surface remote sensing of the total ozone column (TOC), being used extensively both for trend studies (e.g. WMO, 2007) as well as for validation of satellite total ozone data.

The Atmospheric sounding station of the Spanish Institute for Aerospace Technology (INTA) at El Arenosillo station, located in the southern part of Spain, is a Global Atmosphere Watch station (GAW #213) where total ozone column measurements have been carried out since 1980 using the Dobson spectroradiometer #120, and since 1997 using the Brewer spectroradiometer #150. Due to the calibrations facilities, good infrastructures and excellent climatology, El Arenosillo host biennial European calibration campaigns for Dobson and Brewer espectroradiometers in cooperation with the Regional Dobson Calibration Centre for Europe and the Regional Brewer Calibration Centre for Europe, what guaranty the performance of the QA/QC (Quality Assurance/Quality Control) recommended by the WMO. The TOC records obtained through the Direct Sunlight (DS) Brewer observations present a relative accuracy of ±1% over extensive time series when the instruments are properly calibrated and regularly maintained (WMO, 2007). Because of their history of excellent maintenance, the Brewer spectroradiometer located at El Arenosillo has an excellent accuracy (Vilaplana, 2004).

3.1 Instruments and database

The total column ozone records are currently an extensive database at El Arenosillo. The instruments used for these measures have been the Dobson Spectrophotometer #120 and the Brewer MK-III Spectroradiometer #150. El Arenosillo is integrated into the global network for the ozone monitoring with the code GO3OS (Global Ozone Observing System) #213 as stated above.

The ozone database with the Dobson spectrophotometer covers since 1980 to present days. The instrument and data are subject to strict quality control. According to the WMO recommendations, the instrument participates in the European calibration campaigns every four years to ensure the quality of data measured by the Dobson in the integrated global network for ozone monitoring. These campaigns were carried out at Arosa (Switzerland) or Hohenpeissemberg (Germany), but since 2007, and due to the close collaboration between the Regional Dobson Calibration Centre for Europe and INTA, the campaigns are running every two years at El Arenosillo.

The Brewer spectrophotometer #150 is operating at the ESAt since the summer of 1997, and its total ozone column measurements are routinely sent to WOUDC. The instrument is characterized and calibrated in UV irradiance at the calibration laboratory available at INTA and participates in the biennial European calibration and intercomparison campaigns organized at INTA in cooperation with the Regional Brewer Calibration Centre for Europe and the World Travelling Standard Reference (Brewer#017).

3.2 Ozone daily variation

Regarding seasonal variations, these are not the same over all latitudes. They are very small, almost 0% in tropical latitudes, but can be nearly 50% in the polar latitudes. Seasonal changes at middle latitudes, with the peak in spring and minimum in autumn, are in the order of 25%.

On sites located in the middle latitudes, and especially at high latitudes, there may be very abrupt daily changes, up to 20% from day to day. These changes are linked to the flow of stratospheric winds and variations of the pressure fields. Generally, ozone amounts under anticyclonic situations are lower than during low pressure due to the thinning suffer by the lower stratosphere. These large variations in short periods are therefore closely linked to weather conditions and in particular with the vorticity.

Even the calculation of the total atmospheric ozone presents variations linked to the stratospheric circulation, so that within a year, the total amount varies with amplitude about 10 DU.

There are two cycles well known as responsible of the interannual variations. One is linked to cycles of approximately 11 years of solar activity. In the years of maximum solar activity, ozone in the entire planet could be higher by 2% for the years of solar minimum (about 6 DU). Another cycle is nearly biennially, less comprehensive, and linked to changes in stratospheric circulation on the equator, the so-called QBO (Quasi-Biennial Oscillation). It has also been found that changes appear to be linked to El Niño – South Oscillation (ENSO), abnormal distribution of sea surface temperature and air pressure in the equatorial Pacific.

The ozone seasonal variation mentioned above can be clearly seen for both instruments, Brewer and Dobson (Fig. 1), consisting of maximum values during spring and minimum in autumn. It can be also seen from both spectrophotometers that the standard variation of the data is maximum in spring and minimum in summer, when the measurements are much more regular over mid-latitudes.

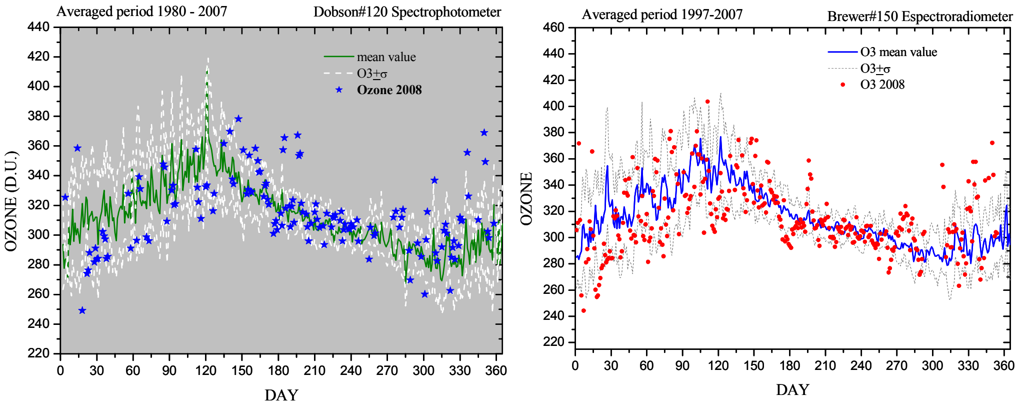

Figure 1. Daily variation of total ozone content at El Arenosillo measured with the Dobson #120 (left) and Brewer #150 (right).

3.3 Trend analysis

One of the more interesting applications that can be carried out is the long term changes over the close to three decades of ozone data observations available at El Arenosillo. For this purpose, it will be presented the Dobson data since 1980 and the Brewer data since 1997.

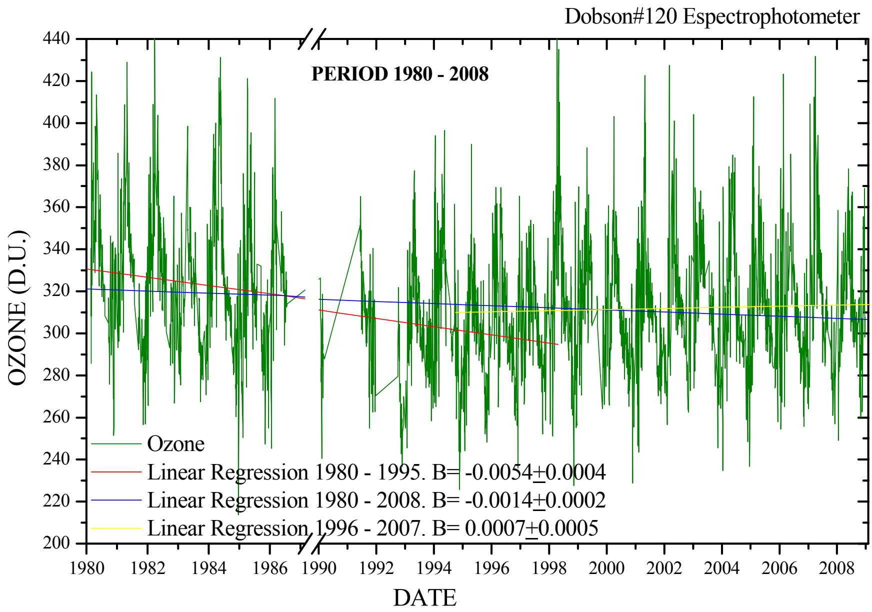

Figure 2. Daily averaged ozone measured at El Arenosillo with the Dobson #120 and trend lines for three different periods.

Figure 2 shows the Dobson data series since 1980 and the trend line over three different periods. The blue line shows the linear regression for the entire observation period, since 1980 until 2008. For this period, the average balance shows a slight decrease of total ozone, which is quantified in an average decrease of 4.78% (15 DU) for the whole period, equivalent to a decrease of 0.16% in annual average.

The red line shows the linear regression for the observation period between 1980 and 1995, which displays more evident deterioration of the ozone layer, the average annual decrease for this period is 0.64%. For the period between 1996 and 2007 (yellow line) the slope of the linear regression is slightly higher than its estimated error, so we can conclude that there is a slight positive trend to the recovery of total ozone amount over these latitudes.

From the Brewer #150 measures (Fig. 3), the results are consistent with those determined by the Dobson spectrophotometer over the last period analyzed, showing a slight positive trend for the recovery of the ozone layer. This positive trend for the ozone layer recovery over mid-latitudes for the last years is consistent with the results obtained by the international scientific community worldwide.

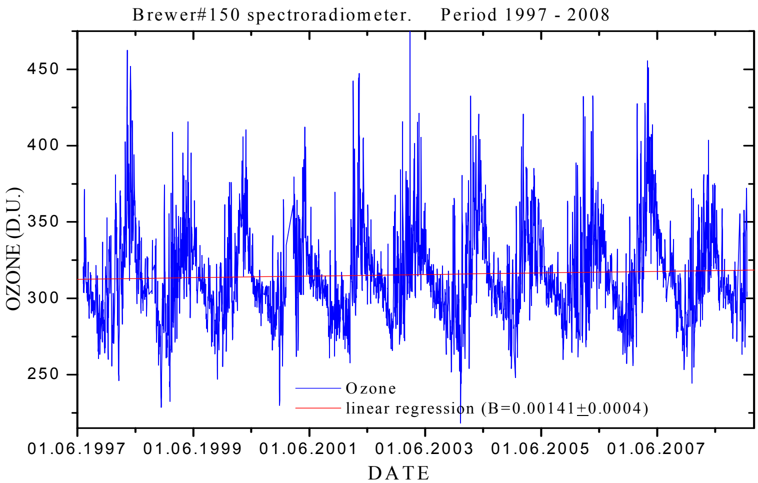

Figure 3. Daily averaged ozone measured at El Arenosillo with the Brewer #150 and trend line for the period 1997-2008.

4. SURFACE OZONE

The levels and variability that shows the surface ozone is studied in many sites around the world from different points of view since this gas is related mainly with the climate change and air pollution (Lelieveld et al., 2009) as well as is used like a trace gas in the studies of the intercontinental transport (Derwent et al., 2008). In the Western Mediterranean Basin and the Iberian Peninsula several studies have been performed in the last years in order to study the surface ozone (Gangoiti et al., 2001; Evtyugina et al., 2006) due to ideal conditions that present this whole area to the formation and accumulation of ozone. In Andalusia (South of Spain) a few works over surface ozone have been performed. Therefore, in 2000 we considered necessary to start the surface ozone measurements at El Arenosillo and the investigations about it. At present, we work in collaboration with the Environment Department of the Andalusia Government and carry out several studied related with the meteorology, ozone precursors and surface ozone in Andalusia (Adame et al., 2008).

4.1 Instrumentation and database

The surface ozone concentrations were collected with an analyser based on the absorption of ultraviolet radiation by ozone at 254 nm as the principle of measurement. This ozone analyser has a lower detection limit of 2 μg m^{-3} and was periodically calibrated (every three months) during the study period. Hourly mean ozone data were computed from 10-minute registered values. The period of measurement ozone data used is from 2000 to 2008. Meteorological parameters are being measured at ESAt from 1994 to 2008 which have been used in the studies with surface ozone. Finally, data series of NO and NO_2 starts in 2006. Nowadays, all the instrumentation continues monitoring at the ESAt.

4.2 Monthly evolution

Figure 4 shows the monthly evolution of surface ozone, both for monthly means and for hourly values of maximum, minimum and certain percentiles (99%, 95%, 75%, 25%, 5% and 1%). An extensive description of the behaviour of the surface ozone measured at El Arenosillo and other sites in the area can be found in Adame et al. (2009a). During the first months of the year there is a continual increase in the monthly value of ozone registered due to the increase in the solar radiation and temperature, among other factors. Between April and August the monthly surface ozone remains almost constant with levels higher than 80 µg m^{-3}. Nevertheless, an increase in the maximum levels and 99^{th}, 95^{th} and 75^{th} percentiles is observed during these months.

The highest 1-month averages of surface ozone is reached in the summer months (June to August). The average of monthly maximum measured at El Arenosillo from 2000 to 2008 was 81±6 µg m^{-3} in July. These values in the monthly ozone are similar or higher than those measured in rural sites in the south of Europe (Gangoiti et al., 2001). The ratio between the monthly ozone maximum and the minimum at El Arenosillo is 1.6:1, which is higher than in other rural sites in the Mediterranean region (Kalabokas et al., 2000).

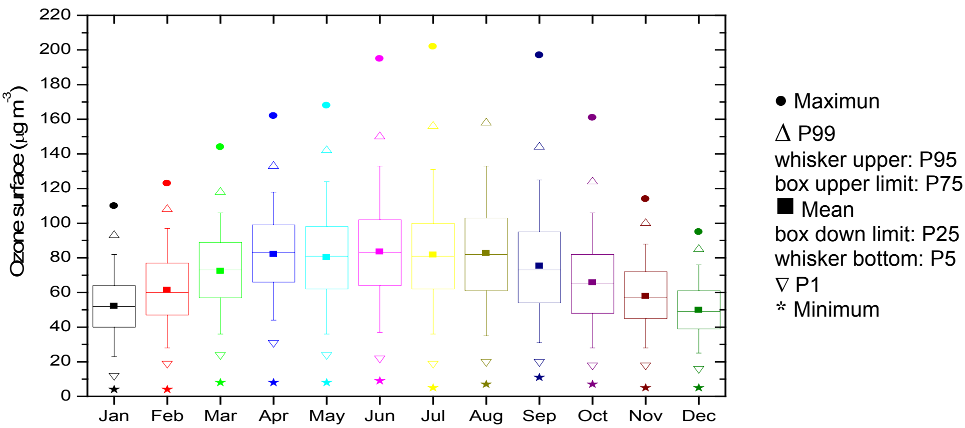

Figure 4. Monthly evolution of ozone surface for monthly means (solid squares) and hourly values of maximum, minimum and 99^{th}, 95^{th}, 75^{th}, 25^{th}, 5^{th} and 1^{th} percentiles. Period (2000-08).

4.3 Daily variation

In Figure 5 the daily ozone cycle, together with NO_2, NO, temperature and relative humidity, is showed for cold and warm seasons corresponding to October-April and May-September, respectively.

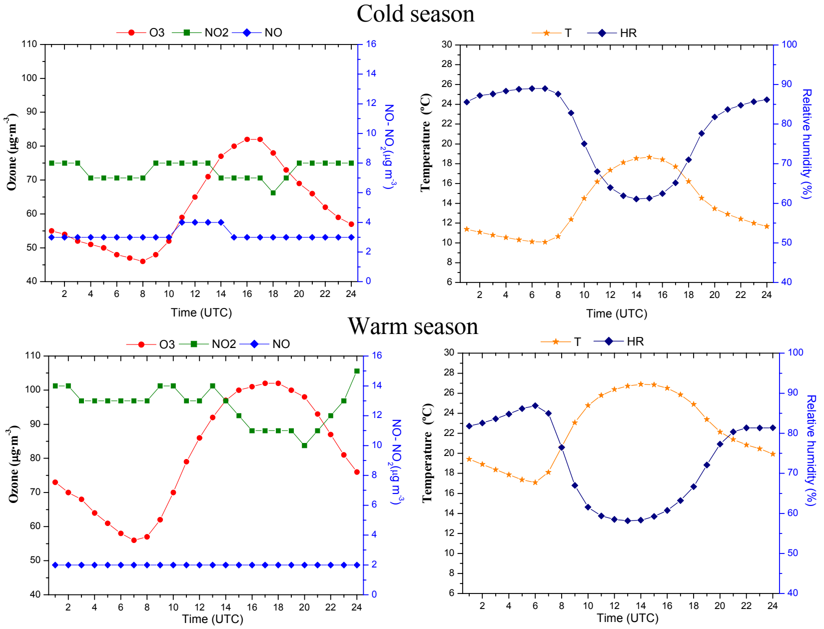

Figure 5. Daily variation of ozone, NO, NO_2, temperature and relative humidity during cold (October to April) and warm (May to September) season.

The lower values of ozone levels occur at night, due to ozone destruction in situ mainly by dry deposition. The effect of titration by NO is not produced due to the lower value of NO recorded at El Arenosillo (Fig. 5). The NO levels at this station remain constant during the day with a value of 2 $\mu g{\cdot}m^{-3}$. The slope of the nocturnal decreasing of ozone is minor in the cold season (temperatures ranging between 10 and 12ºC and 85-90% of relative humidity) and more pronounced in the warm season (nocturnal temperatures up 18ºC and relative humidity lower 95%), in such a way that this decreasing rate seems to be determined by the degree of photochemical ozone production in the previous hours.

Coinciding with the beginning of solar radiation, an increase in ozone values is observed early in the morning. In warm season the average hourly ozone concentration exceeds 95-100 $\mu g{\cdot}m^{-3}$ between 13:00 and 20:00 UTC at El Arenosillo. The contributions to these ozone levels are both photochemical production in situ and transport (of ozone and precursors) from adjacent areas. A decrease in the hourly ozone is observed in the evening, coinciding with the cease of solar activity and slight increase of NO_2 values not caused by emissions but a major atmospheric stability in the surface atmosphere.

4.4 Ozone surface dynamics

In warm season the levels exceed frequently the threshold to protect the human health (120 μg m^{-3} as the maximum daily 8-hour mean) and occasionally the information threshold (180 μg m^{-3} for 1-hour average), both values established in the European Ozone Directive. The causes of these levels could be the emissions of ozone precursors and the meteorological scenarios characteristics of this region.

In the warm season the surface atmospheric dynamic in the southwest of Spain is characterised for wind coming from SW-WSW. The wind registered can be originated by the Atlantic air masses, or due to the mesoscale circulation.

In the study by Adame et al. (2009b), focused in the occurrence and behaviour of the sea-land breeze in this region using the meteorological database of El Arenosillo, it has been detected sea-land breeze with a monthly frequency equal or greater than 35% between June and September, and the maximum value of 50% registered in July. The mesoscale conditions associated with the sea-land breeze favour the formation and accumulation of ozone, hypothesis confirmed by high ozone concentrations recorded at surface.

The land breeze transports the surface ozone and ozone precursors from inland to the coast. The ozone formed during the day reaches the coastline and could form residual layers over the sea. Early in the morning, the start of solar activity ruptures the inversion layer, and begins the formation of both marine breeze and mixed layer which cause that the ozone trapped in the residual layers over the sea to be transported inland. The ozone measured at El Arenosillo early in the morning under a marine breeze scenario could have its origin mainly in the horizontal and vertical transport. The horizontal transport is caused by the sea breeze that brings aged ozone from the sea and the vertical transport coming aged ozone from the residual layers.

5. RELATIONSHIP BETWEEN STRATOSPHERIC AND SURFACE OZONE AT EL ARENOSILLO?

In this section, we present the results of preliminary studies about the possible relationship between the surface ozone and the stratospheric ozone measured at El Arenosillo. Four different scenarios could explain this relationship:

S1. Increase of surface ozone due to stratospheric contribution: in this case, it is produced by a stratosphere-troposphere exchange which reaches the lower layers of the atmosphere.

S2. Increase of stratospheric ozone and a decrease in the surface ozone: the causes could be due to a reduction in the ultraviolet radiation and a minor amount of energy to perform the photochemistry that leads to surface ozone formation.

S3. Reduction of stratospheric ozone and increase in the surface ozone: caused by an increase in the available ultraviolet energy to the photochemistry reactions.

S4. Increase in the levels of surface ozone and increase in the stratospheric ozone: caused by the influence of surface ozone. The stratospheric ozone is the total ozone in the atmospheric column and an increase in the surface layers could cause an increase in the total column if the contribution of the surface layers is in a relevant percentage.

Nowadays, we have started to work in the topic referring to the scenario S1, including in the study the data series of ^{7}Be and ^{210}Pb recorded in the last years at El Arenosillo.

To study the second situation S2, the days with high anomalous values of stratospheric ozone respect to the mean series were selected in the period 2000-2008. After analysing the levels of surface ozone during these days we conclude that peaks of stratospheric ozone do not appear to influence the ozone at surface.

Sudden decrease of stratospheric ozone (third situation, S3) leads in several occasions to an increase of ultraviolet radiation (McCkenzie et al., 1991). However, the surface ozone is not influenced, according to the preliminary results obtained.

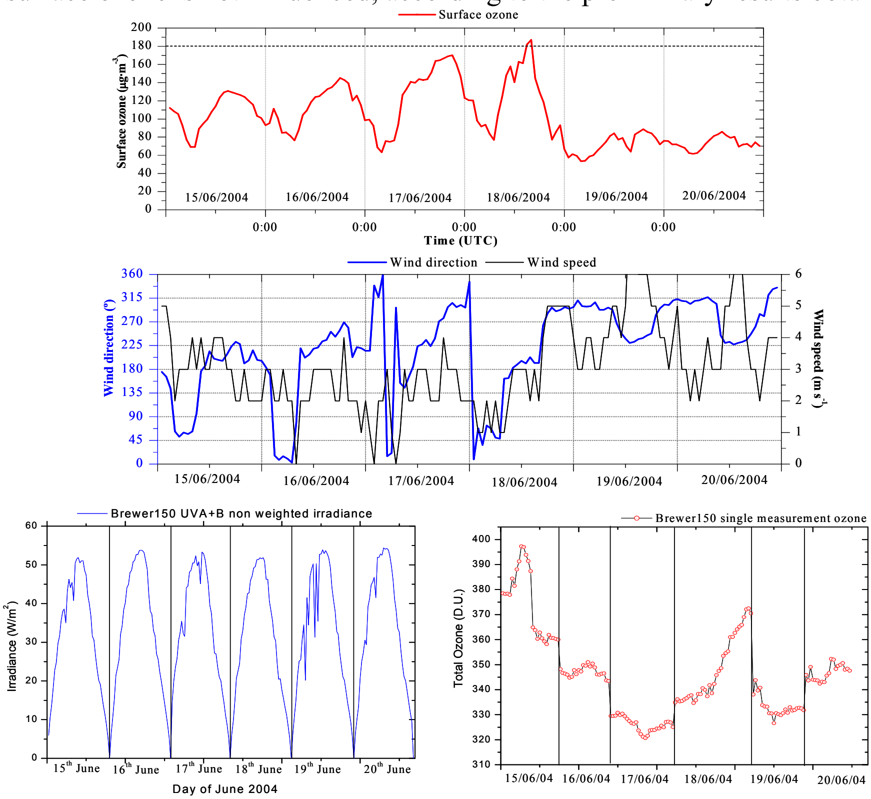

Figure 6. Total and surface ozone, UV irradiance and wind (direction and speed) evolution from 15th to 20th June of 2006.

Figure 6 shows a period with an increase in the levels of surface ozone. Due to the development of sea-land breeze in the study area from 15th to 18th June of 2006 the surface ozone increases at El Arenosillo. During the previous days and under mesoscale processes in the lower atmosphere the ultraviolet irradiance levels are very similar every day with daily maximum around 50 Wm^{-2} (Fig. 6). However, the total ozone presents a decrease trend with values up 390 DU on 15th June and 320-330 DU on 17th June. The surface ozone episode occurs on 17th and 18th June and the behaviour of total ozone does not present a clear influence.

Therefore, concerning the scenario S4 and according to the results obtained in these first works we can summarize that ozone in surface episodes are not clearly connected with changes in the stratosphere. The changes in the surface ozone are mainly influenced by the local meteorological conditions and precursors, and the effect of the stratospheric ozone has a minor contribution.

6. SUMMARY AND CONCLUSIONS

The annual evolution of surface ozone at El Arenosillo (37.1ºN– 6.7ºW, 40 m asl) shows an increase in its levels in the first months and concentrations almost constant (around 80 µg m^{-3}) from April to August with a decrease in the last months of the year. The surface ozone presents a marked daily cycle, nevertheless the records of NO show constant values during the day and slight differences in the case of NO_2. The ozone episodes have been detected at El Arenosillo under sea-land breeze scenarios, mainly in the warm season (May-September).

It is shown the total ozone content (TOC) measurements at El Arenosillo since 1980, witch is the longest series in Spain. The TOC over our latitudes shows a marked seasonal variation, with peaks in spring and minimum in autumn. Long-term analysis shows a strong ozone depletion in the 80’s and signals of recovery in recent years.

The relation between stratospheric and surface has been analysed under four possible scenarios. The preliminary results indicate that in this coastal area does not appear a clear relation between the stratospheric and surface ozone. The causes could be due to the mechanisms of formation, elimination and transport are completely different in these two regions of the atmosphere.

7. ACKNOWLEDGEMENTS

To Elvira Zurita, our great friend.

8. REFERENCES

ADAME, J.A., A. LOZANO, J.P. BOLÍVAR, B. DE LA MORENA, J. CONTRERAS & F. GODOY (2008). Behaviour, distribution and variability of surface ozone at an arid region in the South of Iberian Peninsula (Seville, Spain). *Chemosphere*, 70, 841-849. doi: 10.1016/j.chemosphere.2007.07.009.

ADAME, J.A., J.P. BOLÍVAR & B. DE LA MORENA (2009a). Surface ozone measurements in the Southwest of the Iberian Peninsula (Huelva, Spain). *Environ. Sci. Pollut. Res. (accepted).* doi: 10.1007/s11356-008-0098-9.

ADAME, J.A., E. SERRANO, J.P. BOLÍVAR & B. DE LA MORENA (2009b). On the tropospheric ozone variations in a coastal area of the southwestern Europe under mesoscale circulation. *J. Appl. Meteorol. Clim*. (*in press*).

DERWENT, R.G., D.S. STEVENSON, R.M. DOHERTY, W.J. COLLINS & M.G. SANDERSON (2008). How is surface ozone in Europe linked to Asian and North American NOx emissions?. *Atmos. Environ.*, 42, 32, 7412-7422.

EVTYUGINA, M.G., T. NUNES, C. PIO & C.S. COSTA (2006). Photochemical pollution under sea-breeze conditions, during summer, at Portuguese West Coast. *Atmos. Environ.,* 40, 6277-6293.

GANGOITI, G., M.M. MILLAN, R. SALVADOR & E. MANTILLA (2001). Long-range transport and recirculation of pollutants in the western Mediterranean during the Project regional cycles of air pollution in the West-Central Mediterranean Area. *Atmos. Environ.,* 35, 6267-6276.

KALABOKAS, P.D., L.G. VIRAS, J.G. BARTZIS & C.C. REPAPIS (2000). Mediterranean rural ozone characteristics around the urban area of Athens. *Atmos. Environ.,* 34, 5199-5208.

LELIEVELD. J., P. HOOR, P. JÖCKEL, A. POZZER, P. HADJINICOLAOU, J.P. CAMMAS & S. BEIRLE (2009). Severe ozone air pollution in the Persian Gulf region. *Atmos. Chem. Phys*., 9, 1393-1406.

MCKENZIE, R.L., W.A. MATTHEWS & P.V. JOHNSTON (1991). The relationship between erythemal UV and ozone, derived from spectral irradiance measurements. *Geophys. Res. Lett.*, 18, 2269-2272.

VILAPLANA, J.M., (2004). Measurement and analysis of ozone and UV solar radiation at El Arenosillo-INTA (Huelva, Spain) (in Spanish). Ph.D. thesis, University of Valladolid, Valladolid, Spain, 247 pp.

WORLD METEOROLOGICAL ORGANIZATION (2007). Global Ozone Research and Monitoring Project, *Scientific Assessment of Ozone Depletion: 2006* (Geneva, Switzerland), Tech. Rep. #50.