Variación de la concentración de ozono troposférico en la estación de investigación atmosférica "Alejandro de Humboldt" en Mérida, Venezuela (4765 msnm)

Tropospheric ozone concentration at Mérida, Venezuela (4765 masl) atmospheric research station "Alejandro de Humboldt"

Calderón, Silvia [1*]; Iglesias, Margarita[1]; Ramoni, Edinzo[2]; Hoffmann, Josefa[1]; Carrillo, Pedro[1]; Krecji, Carlos[3]; Hochschild, Radovan[4] ; Gross, Berd[4] y Jochen, Gerhard[4]

[1]Laboratorio para la Caracterización Físico-Química y Modelado de la Atmósfera (FIQMA), Universidad de Los Andes.
[2]Departamento de Economía, Facultad de Ciencias Económicas y Sociales, Universidad de Los Andes.
Mérida, Venezuela
[*]silvimar@ula.ve

Recibido: 15-02-2007 Revisado: 07-01-2008

Resumen

Se analizaron estadísticamente los patrones de variación de los promedios anuales, diarios y horarios de la concentración de ozono (O_3) medida entre los años 2005-2007 en la Estación de Investigación Atmosférica "Alejandro de Humboldt" (EIAADH) en los Andes Venezolanos, con el objetivo de encontrar diferencias significativas con respecto a los patrones de variación esperados para un sitio remoto con una atmósfera limpia de elevada altitud. La EIAADH es única en el mundo por estar por encima de los 4000 msnm en el trópico, además ofrece información, hasta ahora no disponible, de gran valor para la correcta interpretación de los cambios atmosféricos en los trópicos. Los valores promedio de las concentraciones de O_3 no mostraron una influencia significativa de emisiones antropogénicas, así como tampoco variaron significativamente con el día del año ni con la hora del día. Las condiciones meteorológicas en EIAADH desde el 2006 fueron correlacionadas con los promedios horarios para identificar la posible influencia de contaminantes transportados desde la ciudad de Mérida y/o estados aledaños. Se determinaron factores de correlación de-0.36, -0.38 y 0.12 entre ozono y año, humedad relativa y dirección del viento, respectivamente. Altas humedades relativas causan la destrucción del O_3 en presencia de bajas relaciones entre las concentraciones de compuestos orgánicos volátiles y óxidos de nitrógeno, características de zonas no contaminadas. La correlación positiva con la dirección del viento, y la existencia de eventos con elevado O_3 fueron asociadas con el transporte de masas de aire desde los llanos durante incendios forestales. El análisis de componentes principales indicó que el O_3 varía principalmente por el transporte desde capas superiores. La sexta componente principal permitió explicar un 6.1 % de la varianza total de los datos en función de correlaciones positivas entre O_3, humedad relativa, año y radiación solar, típicas durante la generación antropogénica de O_3.

Palabras clave: Patrones de variación, emisiones antropogénicas, factores de correlación, análisis de componentes principales.

Abstract

Yearly, daily and hourly average ozone (O_3) concentrations measured during the years 2005-2007 at the Mérida Atmospheric Research Station (MARS) in Venezuelan Andes, were statistically analyzed in order to look for disturbance on their patterns of variation compared to the expected tendencies for a clean environment in a remote site of high altitude. MARS is the highest altitude atmospheric research station in the world, and being in the tropics, it offers valuable data, currently not available, about the atmospheric changes at tropical latitudes. Average values for O_3 concentrations showed no signals of O_3 formation due to anthropogenic emissions, regardless of the hour of the day and the day of the year. Meteoro-

logical data measured in-situ since 2006 was coupled with hourly average ozone to be analyzed through linear correlation factors and Principal Component Analysis. Significant correlation factors of -0.36, -0.38 and 0.12 were found between hourly average concentrations and the year, relative humidity and wind direction, respectively. The ozone destruction at high water vapor concentrations is characteristic of a low VOC/NOx ratio, usually present in unpolluted areas. The positive correlation with the average wind direction and episodes of high ozone concentrations when winds were blown from the Venezuelan plains (Barinas state), suggested the transport of polluted-enriched air masses containing ozone precursors from biomass burning. PCA results suggested that the ozone variation at MARS is mainly driven by vertical transport of ozone-enriched air masses from higher altitudes. Evidence of ozone production due to anthropogenic emissions was found in the sixth principal component due to positive correlations between ozone concentrations and relative humidity, solar radiation and year. These variables were correlated and explained 6.1 % of the total data variance for the 2006-2007 year period.

Key words: Patterns of variation, anthropogenic emissions, correlation factors, principal component analysis (pca).

1 Introducción

In 1999, a Venezuelan, Swedish and German research project helped to establish the Mérida Atmospheric Research Station (MARS) at Pico Espejo (4765 masl). The main research goals were determining the changes in physical and chemical conditions of the troposphere and stratosphere at tropical latitudes, and contributing to the Network for the Detection of Atmospheric Composition Change (NDACC).

MARS is a unique place in the world to study the atmosphere. This station not only allows continuous monitoring of a tropical-high altitude site, but also allows the detection of changes in the atmosphere caused by the Inter-Tropical Convergence Zone motion. Atmospheric research stations at tropical latitudes are scarce and needed to help revealing, once for all, the role of tropics on the planet climate.

MARS has been operating since 2004, and besides the typical meteorological data at ground level, generates ozone concentration, number density, size distribution, light absorption, scattering, chemical composition and mixing state of aerosols at Tropospheric Level; and water vapor, ozone-depleting species mixing ratios at Stratospheric Levels. More information about MARS is available at (Kopp G., 2008).

As a preliminary study, here, we analyzed the temporal variation of ozone (O_3) concentrations measured at MARS to look for differences in the expected behavior of a high altitude and remote site, possibly caused by pollutant transport from the city and/or bordering states (plains around the Venezuelan Andes).

In Mérida, it is vital to watch for all factors that could possibly alter the ecosystems. Due to its natural beauties, it is the one of the most visited cities in Venezuela. As in any other place in the Andes, glaciers at the Sierra Nevada, formed by Picos Bolívar, Espejo, La Concha, Humboldt and Bonpland, have reduced their area from 7 Km^2 in 1925 to 2 Km^2 in 1991 as a consequence of global warming (Schubert, 1999).

Although Mérida is a small city and its air quality should satisfy the primary and secondary air quality standards (U.S. Environmental Protection Agency, E, 2008), its population and urban development have considerably grown in the last ten years. As a consequence, vehicle emissions, and all emissions of anthropogenic origin, have increased with a noticeable reduction in the city air quality, especially at the peak hours. In the absence of emission inventories, meteorological and air quality data, it is impossible to know if human activities are already deteriorating the health of natural systems and population.

In order to explore the relation between anthropogenic emissions and the air quality reduction, we initiated with the study of the variability on the O_3 concentration at MARS under different meteorological conditions in a three-year period from 2005-2007.

O_3 is a normal component of the stratospheric chemistry, responsible for absorbing ultraviolet radiation; however at tropospheric level it can behave as an air pollutant if its concentration overpasses the expected value for a clean atmosphere.

The Clean Air Act (1990) established two different standards for ground-level ozone concentration to determine when the ozone exposure can affect the public health and damage animals, crops and buildings. The first ozone standard is not attained when the 3-year average of the fourth-highest daily maximum 8-hour is over 80 ppb; the second one, when there is more than one day per calendar year where the maximum hourly average concentrations is above 120 ppb (U.S. Environmental Protection Agency, 2008).

The World Health Organization (WHO) has found positive correlations between daily mortality and ozone levels in epidemiological time series studies, 0.3 to 0.5% increments in daily mortality for an increment of 10μg/m3 in 8-hour ozone concentration above background concentrations. In 2005, they established as the air quality for ozone a concentration equal to 100 $\mu g/m^3$ for daily maximum 8-hour mean. In days when the ozone concentration reaches this level, the number of attributable deaths brought forward can be estimated at 1-2% for daily exposures above the estimated background of 70 $\mu g/m^3$. At higher ozone

concentration levels higher percentages and more negative health effects are expected; 3-5 % for 100 μg/m^3 with changes in lung function and lung inflammation among healthy young adults, 5-9 % for 240 μg/m^3 with significant reductions in lung function as well as airway inflammation that would cause symptoms and alter performance in healthy adults and asthmatics (World Health Organization, 2005) .

Noxious effects are seen in the presence of high O_3 concentrations. Being a very powerful oxidant, it can cause the reduction of crop yields (Shankar and Neeliah, 2005), to exacerbation of respiratory diseases in sensible groups, such as asthma (Ostro and Chestnut, 1998). At the Pennsylvania forest maximum average hourly ozone concentration between 50 ppb and 100 ppb were positive correlated with foliar stipple injury, premature fall coloration and dropping of leak before the end of the growing season for sensitive trees such as the black cherry and yellow poplar (Comrie, 1994). Such effects are translated into serious economics consequences for agriculture. The Canadian growers faced for many years a severe crop illness in their tobacco crops, known as weather fleck. Tobacco leaves were mainly affected during sunny days with high temperature and dew point, in the presence of smoke. High ozone concentrations at these conditions were later named as a cause of the weather fleck (MacDowell et al., 1964 cited by Heirdorn. and Yap, 1986)

O_3 is naturally present at the troposphere due to vertical transport from the stratosphere. Around 20 % of the total tropospheric O_3 comes through this way (Alvim-Ferraz et al., 2006). Expected concentrations at remotes sites oscillate between 20 and 40 ppbv in a tropical forest (Seinfeld and Spyros, 1997). In clean air, where there is a minimal influence of ozone scavenging and production by pollutants such as NO_x, the altitude can strongly affect the ozone concentration. Remote sites at sea levels show a lower range concentration. For example, southern coast sites in Ontario, Canada during 1976-1981 seasonal patterns for the average hourly ozone concentrations showed highest values of 27 ppb in spring and summer; and the lowest values of 16 ppb and 12 ppb in winter and fall respectively (Heirdorn and Yap, 1986). In remote sites at higher altitude the concentration ranges slightly change. At 1045 m of altitude in the Whiteface Mountain, NJ, USA, during 1989-1993, the highest hourly average ozone concentrations varies from 20 to 36 ppb during high-sun seasons (spring and summer) and from 13 ppb to 19 ppb during low-sun seasons (Brankov et al., 1998).

Episodes of high concentration can be driven by ozone production through a very complex photochemical reaction mechanism between volatile organic compounds (VOCs) carbon monoxide (CO) and nitrogen oxides (NO_x), locally emitted or regionally transported. VOCs, CO and NO_x are produced during fossil fuel and biomass burning. A simplified version of the reaction mechanism will be presented later.

Although statistical analyses cannot offer conclusive details about the physicochemical mechanisms behind chemical pollutant generation and transport; they can certainly identify the intrinsic relations between the variables driving them. A recent study have used statistics to compare 19th and 21th century ozone data looking for signals of anthropogenic contribution to Tropospheric Ozone concentrations. Classical statistics indicated that ozone concentrations measured at Oporto Metropolitan area (41^{o}8'54"N; 8^{o}27'W, altitude of 84.8 m) between 1997 and 2003 were globally 147% higher than those measured between 1861 and 1897. Time-series analyses of both data sets also revealed the appearance of a daily 8-hour cycle, possibly related to human activities(Alvim-Ferraz et al., 2006). Cluster analyses of synoptic-scale ozone-weather data (500-1000 Km), and backward trajectories, have been used to study the in-situ production-destruction ozone cycle due to variation in the meteorological conditions; and the transport of polluted air masses, respectively. Using these techniques (García et al., 2005) identify in the 2000-2003 period that ozone peaks at a rural site around to Valladolid, Spain were caused by local formation mainly driven by temperature during stagnant meteorological conditions. Trajectory-clustering-correlation of filtered time-series of daily maximum hourly average ozone concentrations measured at Whiteface Mountain between 1989-1993 showed that high ozone levels occurred when air masses had traveled over south-east (New York and New England states) and mid-west (Great Lakes areas) (Brankov et al., 1998).

Currently, Venezuela lacks of an atmospheric chemistry and meteorological station network and therefore there is not enough information available to build up air mass trajectories or to identify pattern circulations that help to explain ozone patterns. However, we attempt to use the only information available to offer the first look of the possible anthropogenic influence over the Venezuelan atmospheric chemistry for a rural site at high altitude. Being MARS at tropical latitudes, our results become extremely important to finally understand the influence of tropics on the Earth climate.

2 Methodology

2.1 Sampling region description

Mérida is the capital city of the Mérida State in Venezuela. Its metropolitan region concentrates 30.9 % of the state population, 744.986 hab, with a population density of 59.7 hab/ Km^2. The city is located on a plateau at 1630 masl, in the small valley formed by the Chama and Albarregas rivers between the two mountain chains of Sierra Nevada and Sierra de La Culata, both in the Venezuelan Andes. The Albarregas River divides the city in two parts as seen in Fig. 1. There are not chemical or oil industries, being agriculture and tourism the main economic activities. The biggest attraction is the world's highest and largest cable car that travels all the way up to Pico Espejo at 4765

masl, close to Pico Bolivar, the highest Venezuelan mountain (4980 masl). Fig. 1 shows the other four stations of the cable car, Barinitas, La Montaña, La Aguada and Loma Redonda; and the MARS position relative to the Mérida metropolitan region.

As Fig. 1 shows, Mérida 's topography is uneven, and there is a descendant slope from east to west; 100 m of altitude separates Mérida 's downtown from the airport; both connected in straight line by a distance of 2.5 Km. This variable topography causes differences in the predominant meteorological conditions in different parts of the city.

Being in the Andes, Mérida is the Venezuelan coldest state's capital city. Mérida city has an annual average temperature of 19°C and the difference between warmer and colder monthly averages is less than 12°C. Annual air humidity is between 75% and 80%, and the total annual mean precipitation is around 1785 mm, with about 20% in the dry season. Prevailing winds are from W and SW during the dry season and from E and NE during the rainy season.

Even though Pico Espejo is located a few kilometers far from Mérida city, its weather is notably modified by the altitude. At MARS location, climate corresponds to a Páramo thermal floor; annual mean temperature is around 0°C, with sporadic snow events. Prevailing winds are from SE and SW (Foghin-Pillin S., 2002).

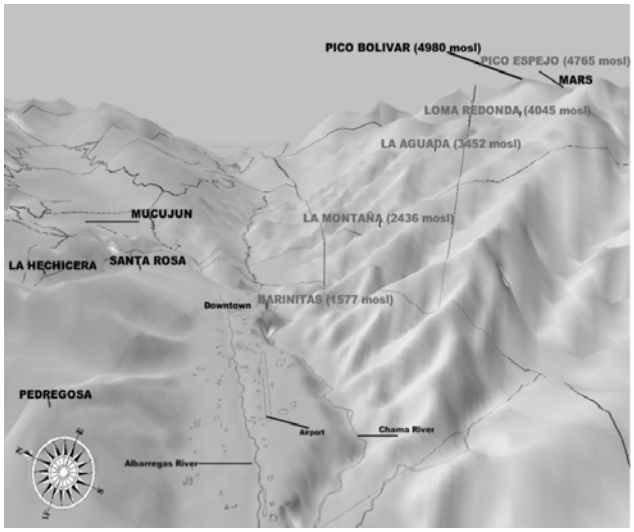

Fig. 1. Three-dimensional view of the Mérida Atmospheric Station at Mérida city obtained from Shuttle Radar Topography Mission Altitude Data (Jet Propulsion Laboratory, 2005) and Venezuelan Map Project, VENRUT (GPSYV, 2008)

2.2 Data preparation

Ozone concentrations were measured daily from April, 2005 to December, 2007 at MARS using an Ultraviolet (UV) Photometry O_3 Analyzer (Model O341M, Ansyco, S.A) with UV-irradiation at 254 nm and a detection limit of 0.4 ppbv.

During three-year period, sampling intervals of 10 sec, 30 sec and 60 sec were used. Arithmetic average hourly concentrations were determined, after elimination of concentrations under the detection limit and missing values. To represent adequately the predominant conditions in the different time periods, average values for hours with less than 75 % of the expected data were neglected and not included in the daily average calculations. Daily average concentrations with less than 65 % of the expected data were also neglected for statistical analyses. Those will be regarded as the completeness criteria from here.

All statistical analyses were done using a 95 % confidence level with MATLAB (6.5) and ORIGINPRO 7.5

3 Results

3.1 General statistics

Values of the daily average O_3 concentrations and valid data for the years 2005-2007 are 26 ± 9 ppb (n_1=211); 24 ± 12 ppb (n_2=210) y 30 ± 6 ppb (n_3=75), respectively. Data for the 2007 failed the completeness criteria proposed in this study. Mean values probed to be significantly different from each other. Daily average O_3 concentrations move in a range from 20-40 ppb, as expected for a remote region of high altitude where ozone scavengers are absent (Brankov E. et al., 1998).

At other latitudes, seasons do have a significant effect on the daily average ozone concentrations. For example, summer peaks, related to higher solar radiation fluxes, are usually observed at places with similar altitude (same atmospheric pressure, approximate 500 mbar) but at northern latitudes (Logan, 1999). Daily average ozone concentrations in a rural site around Valladolid, Spain during 2000-2003 increased during the starting months of the year, reaching a daily mean concentration of 82.5 ppb in July, then decreased reaching a minimum value of 10 ppb approximately in January. Summer maximum were determined by sunny and dry weather conditions favoring photochemical ozone formation (García et al., 2005).

At tropical latitudes, the seasonal cycle comprises just two different periods, the rainy one from May to October equivalent to summer, and the dry one from November to April equivalent to winter at northern latitudes. If there was a seasonal effect on the daily average O_3 concentration, peaks should appear during the rainy season, as seen on Fig. 2 at the end of May and September.

Despite of this apparent increase of ozone during therainy season, the mean values for the rainy and dry seasons proved to be not significantly different from each other at a 95 % confidence level. For the dry season, the mean ozone concentration is 24 ± 14 ppb (n_1=218), while the mean ozone concentration for the rainy season is 28 ± 7 ppb (n_2=278).

Fig. 3 shows the mean, median, lower and upper quartiles of the hourly average O_3 concentrations during 2005-

2007.

In order to look for anthropogenic influences related to changes in the atmospheric transport regime during the day, we performed an analysis of variance on hourly ozone concentrations.

It is known that daily cycles are expected for tropospheric O_3 concentrations in rural sites. Smaller concentrations occur at the early morning and night due to O_3 loss by dry deposition or reaction with nitrogen oxide (NO) at late hours. Higher values at the end of afternoon due to pollutant accumulation and increasing photochemical production rates and/or vertical transport from higher altitudes (Seinfeld and Spyros, 1997).

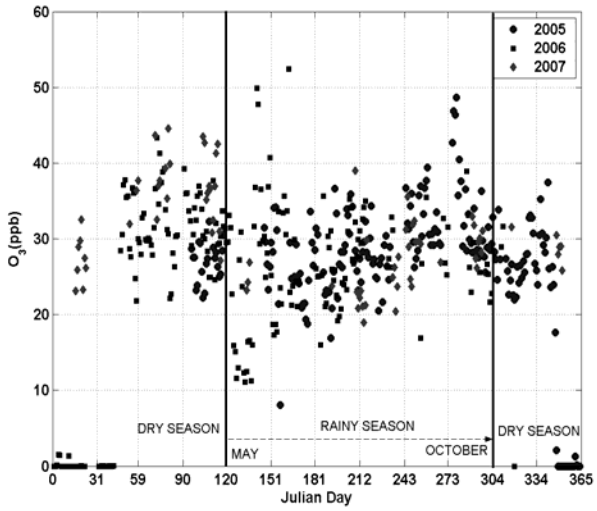

Fig. 2. Average Daily O_3 concentrations per julian day at MARS

At MARS, hourly concentrations for the 24-hour period move alternatively between 20 and 55 ppb with a negative correlation of -0.056 (p=0.0003) between the hour of the day and the hourly average ozone concentration. ANOVA results indicated a significant difference between means at different hours of the day ($p<<0.05$). Minimum values are observed around noon.

These results are not consistent with the expected behavior at a rural site; they look to be more related with those of non-human influenced sites, where ozone daily variation is completely guided by natural atmospheric processes, such as photochemical production and vertical transport, with no influence of polluted air masses ascending from nearby city.

If ozone was photochemically produced due to a pollutant-activated mechanism, it was expected to see higher ozone concentrations when MARS is at the boundary layer, affected by the upslope winds transporting anthropogenic gases from the city. A recent research at Pico Espejo, showed that upslope flow occurs mainly between 10:00 and 19:00, producing maximum values of carbon monoxide, aromatics and halocarbons at noon (Kleiss, 2005). Fig. 3 does not show an increase in ozone concentration between the 10:00 and 19:00 hours. Episodes with O_3 concentrations higher than 60 ppb were observed on May, 21th, and May 22nd, 2006 and June, 12th, 2006, mainly in the morning between the 5:00 and 10:00 hours. They will be studied with more detail in the next section.

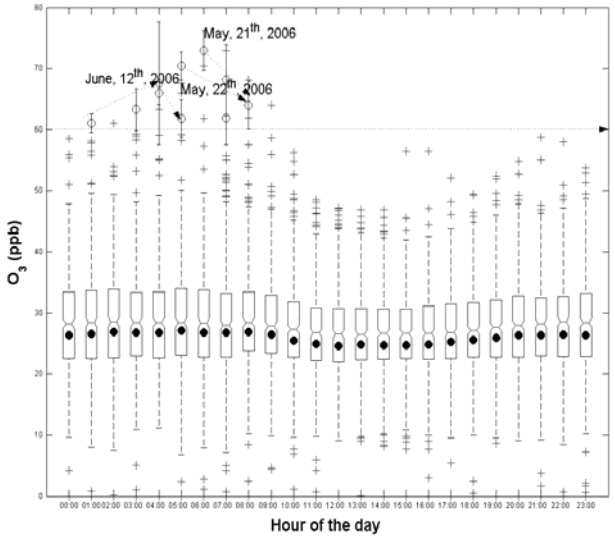

Fig. 3 Average hourly O_3 concentrations per hour of the day for 2005-2007 (mean: black dot, median: red line)

Despite of the last results, we analyzed the relation between the maximum O_3 concentration per hour per day of the week. Each hour, several measurements are done according the sampling time interval (10, 15, or 30 sec). Fig. 4 shows the highest value for each hour, and also the hour at which this value was reached.

In sites affected by anthropogenic emissions, it is common to see reductions in pollutant levels during the weekends; and higher concentrations at working days with maximum values at the peak hours where traffic is heavy. Thus, highest values are measured on working days at noon or at the end of the afternoon (Husar, 1996b).

ANOVA results do not indicate a significant influence of the day of the week on the maximum hourly average ozone concentration at MARS. Also, the maximum hourly ozone concentration did not show relation with the hour of the day. At MARS, the 95th percentile for daily maximum concentrations is always below 60 ppb, while mean values oscillates around 40 ppb.

Average daily maximum hourly ozone concentrations measured during 1991-1995 in urban areas of cities at the West-East Cross-section of the United States, oscillates between 42 ppb and 63 ppb, with peaks of 63 ppb and 62 ppb for Chicago and Detroit respectively; the lowest values observed at New England and South Dakota. In contrast, daily maximum hourly ozone concentrations at the West-East Cross-section vary between 53 ppb to 73 ppb, with peaks of 59 ppb for Kansas City, 63 ppb for St. Louis, 73

ppb for Maryland. Tropospheric ozone background concentrations vary between 35-40 ppb in the whole area (Husar R., 1996a).

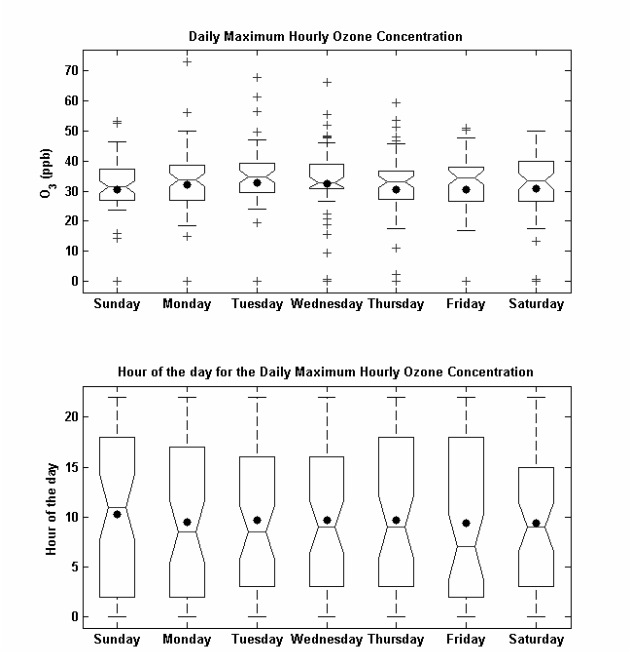

Fig. 4 Average maximum hourly O_3 concentration per week of day and hours at they occurred.

3.2 Correlation analyses

As in any other physical-chemical process, it is expected to have correlation among the variables controlling the production or transport of the pollutant. Meteorological variables such as temperature and solar radiation should affect directly the rates of photo-chemical reactions. In the same way, wind speed and wind direction could be used to identify turbulence or long-range transport of air masses from more polluted areas.

In order to see if this kind of relations were present at our data set we show in Table 1, the correlation matrix between hourly average ozone concentrations and the hourly average values of the most common meteorological variables: dry bulb temperature (T), Relative Humidity (RH), Wind Speed (WS), Wind Direction (WD) and Total Solar Radiation (JT). The variable YEAR was added to verify the negative trend of daily average concentrations from 2005 to 2007.

It was impossible to study the data set for the three-year cycle because average meteorological conditions started to be measured at MARS after March, 2006. P-values for each correlation factor are also registered in the lower diagonal matrix at Table 1.

The average hourly dry bulb temperature at MARS varies during the day coupled to solar radiation. The hourly average dry bulb temperature decreases at night and reaches its maximum at noon, with a mean value is 0.3 ± 1.1 ^{o}C, positively correlated (r=0.65, p<<0.05) with the solar radiation flux. An interesting significant negative correlation (r= -0.36, p<<0.05) occurs between the dry bulb temperature and the wind speed.

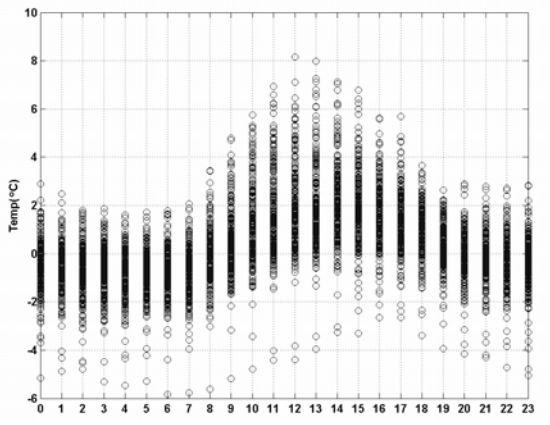

Fig. 5. Dry Bulb Temperature variation per hour of the day for 2006-2007

Table 1. Correlation Factors for meteorological variables and ozone data

r/p	YEAR	T	RH	WS	WD	JT	O_3
YEAR	1	0,04	0,16	0,05	0,00	0,05	0,083
T	0	1	0,18	0,39	0,33	0,65	0,007
RH	*0*	*0*	1	0,08	0,04	0,08	0,514
WS	*0*	*0*	*0*	1	0,11	0,19	-0,04
WD	*0.99*	*0*	*0*	*0*	1	0,06	0,10
JT	*0*	*0*	*0*	*0*	*0*	1	0,008
O_3	*0*	*0,59*	*0*	*0*	*0*	*0,55*	1

As shown in Table 1, there is a significant and positive correlation (0.083) between ozone concentrations and the year. It is known that the tropospheric ozone has increased globally at the planet since the pre-industrial era. Surface ozone concentrations have increased from 10-15 ppb to 30-40 ppb in remote areas of the world (Finlayson-Pitts B. and Pitts J., 1997).

The highest correlation coefficient occurs between relative humidity and O_3 concentrations (-0.514 , p<<0.05). Fig. 6 shows that the lower the relative humidity, the higher the hourly average ozone concentration.

The relative humidity varies strongly during the day as shown in Fig. 7, and has an average value of 85.4 ± 21.9 %. The lowest values are always around noon.

A similar behavior was observed for 19th century ozone data collected at Oporto, Portugal. (Alvim-Ferraz et al., 2006) found a correlation coefficient equal to -0.52 for

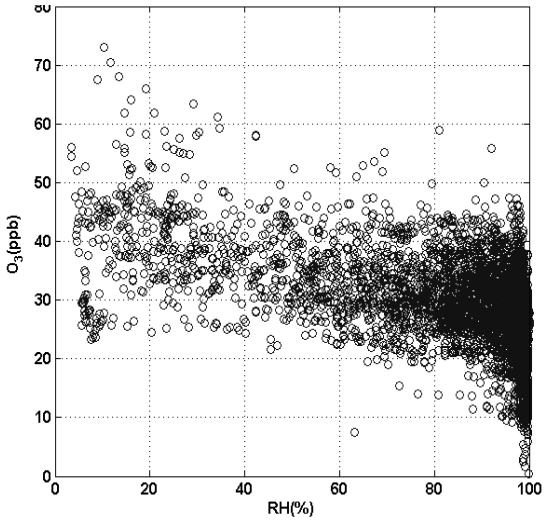

Fig. 6 Variation of the hourly average O_3 concentration in function of Relative Humidity for 2006-2007

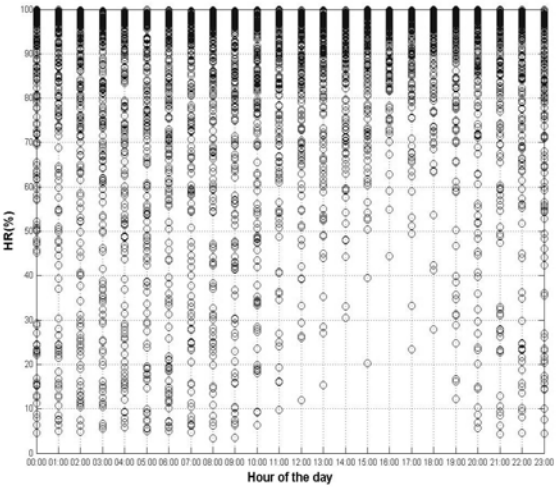

Fig. 7. Average hourly relative Humidity at MARS from 2006 to 2007

both variables; and attributed it to meteorological subsidence, vertical transport of ozone-enriched air masses from the upper troposphere. They also affirmed that ozone destruction overcomes photochemical production in the presence of low NO_x concentrations and high relative humidity

The reaction mechanism proposed by Alvim-Ferraz M. et al. (2006) is shown in detail here.

The dominant reaction leading to O_3 formation depends on the equilibrium of the NO_x-CO-CH_4-VOCs reaction cycles. Each cycle will occur and dominate over the others depending on the VOC/NO_x concentration ratio.

$$\left\{\begin{array}{ll} NO_2 + h\nu\left(\lambda < 420nm\right) \rightarrow NO + O & 1.a \\ O + O_2 + M \rightarrow O_3 + M & 1.b \\ O_3 + NO \rightarrow NO_2 + O_2 & 1.c \end{array}\right\} \quad (1)$$

The NO_x reactions shown by Eq.1 do not allow net O_3 formation due to the rapid reaction of the O_3 formed in Eq. 1.b with NO through Eq. 1.c. This happens especially in clean environments where NO_x concentrations are low. In these conditions, carbon monoxide (CO) and methane (CH_4), naturally present in the atmospheric due to biogenic emissions, can also be oxidized to produce O_3 as shown in Eq. 2.

$$\left\{\begin{array}{ll} \mathrm{CO}+2\mathrm{O}_2 + h\nu \rightarrow CO_2 + O_3 & 2.a \\ \mathrm{CH}_4+4\mathrm{O}_2 + h\nu \rightarrow HCHO + H_2O + 2O_3 & 2.b \end{array}\right\} \quad (2)$$

The third path for O_3 formation mainly occurs in polluted environments, where VOCs lead to O_3 accumulation after the NO consumption by the alkylperoxy radicals (RO_2), and peroxyl radicals (HO_2), formed during the VOC oxidation cycle (Eq. 3). CARB indicates carbonyl species (RCHO) or a ketone (RCRO).

$$\left\{\begin{array}{ll} VOC + OH + O_2 \rightarrow RO_2 + H_2O & 3.a \\ RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB & 3.b \\ HO_2 + NO \rightarrow NO_2 + OH & 3.c \\ 2\left(NO_2 + h\nu + O_2 \rightarrow NO + O_3\right) & 3.d \end{array}\right\} \quad (3)$$

Being consumed the NO, it cannot destroy the ozone formed through 1.b and reaction 1.c does not occur.

Once formed by Eqs. 1-3, O_3 can be eliminated by photolytic destruction through Eq. 4.a, by chemical reaction with hydroxyl (OH) and peroxyl (HO_2) radicals through Eqs. 4.b-d; during the CO and CH_4 photolytic oxidation (Eq. 4.e); and finally by dry deposition over surfaces.

$$\left\{\begin{array}{ll} O_3 + h\nu\left(\lambda < 310nm\right) \rightarrow O_2 + O & 4.a \\ O + H_2O \rightarrow 2OH & 4.b \\ HO_2 + O_3 \rightarrow OH + 2O_2 & 4.c \\ OH + O_3 \rightarrow HO_2 + O_2 & 4.d \\ CO + CH_4 + O_3 + h\nu \rightarrow CO_2 + CH_3OOH & 4.e \end{array}\right\} \quad (4)$$

The NO_x and VOC ozone formation cycles (Eqs. 1 and 3) dominate each other depending on the VOC/NO_x ratio.

When this ratio is higher than 12 ppm of C per 1 ppm of NO_x, the O_3 formation is NO_x-limited. The O_3 formed will depend on the NO available to be transformed to NO_2 (Eq. 3.b-c) and on the NO_2 available to finally react through Eq. 3.d. (Finlayson-Pitts and Pitts, 1997). High VOC/NO_x ratio can be observed at rural sites with high biogenic emissions. In these cases, an increase in NO_x produces an increment in O_3 concentrations (Alvim-Ferraz et al., 2006).

At low values of the ratio VOC/NO_x, the ozone formation is VOC-limited. OH radicals tend to react with NO_2 to generate nitric acid (HNO_3), instead of oxidizing VOC

through Eq. 3.a. The final result is less ozone formation, especially when NO_x concentrations decrease, in contrast what it is seen at high VOC/NO_x ratio (Finlayson-Pitts and Pitts, 1997).

Being MARS in a very remote site at a high altitude, air masses should have permanently low NO_x and VOCs concentrations, for a low VOC/NO_x ratio. VOCs from anthropogenic emissions (benzene, toluene, xylene, ethylbenzene, 3-ethyltoluene, trimethylbenzenes, halocarbons, dichloromethane, methylchloroform and carbon tetrachloride) were measured at MARS in 2005 during a sampling campaign between February 16th and 24th. Although concentration peaks occurred at the early afternoon, mainly in the presence of upslope winds, carrying polluted-enriched air masses, the observed concentrations were very low and comparable to those of a remote site (Kleiss, 2005).

In the absence of VOCs, ozone precursors, the ozone formation through the VOC oxidative cycle is very limited; the ozone destruction guided by the water-oxygen oxidative cycle predominates. At high relative humidity values reactions described in Eq. 4 dominate over VOC reactions shown in Eq.3 (Alvim-Ferraz et al., 2006).

On the other hand, wind direction is positive and significantly correlated (0.10, $p<<0.05$) with O_3 concentrations. Fig. 7 shows higher hourly concentrations when the wind direction is between 30 and 270 degrees. Fig. 8 shows that higher hourly ozone concentrations are measured at MARS when air masses from the Venezuelan plains (Barinas State). When the air blows from Mérida city, ozone concentrations show less dispersion and values relatively lower compared to those seen at the north-east and south-east quadrants.

The fact that higher ozone concentrations occur with direct influence of air masses transported from zones with frequent biomass burning events, suggest an ozone production cycle enhanced by VOCs and NO_xs. Ozone peaks out of MARS normal ranges were shown in Fig. 3. These episodes presented O_3 concentrations higher than 60 ppb on May, 21th, and May 22nd, 2006 and June, 12th, 2006, mainly in the morning between the 5:00 and 10:00 hours.

Wind direction on the episode hours varies between 55 and 287 deg with an average of 124 ± 51 deg, while the relative humidity varies between 3% and 50 % with an average of 20 ± 9%. On the other hand wind speed varies between 1 and 7 m s^{-1} with an average of 2.8 ± 1.5 m s^{-1}. Episodes can be seen at Figures 7 and 8 as outliers placed out of the 60 ppb limit, on Barinas' plains directions.

Low humidity and high speed winds favor biomass burnings events, specially in time of the year in states such as Barinas, predominantly formed by plains used for cattle raising, the main economic State's activity.

Biomass burning or fire events from Along-Track Scanning Radiometer Data (ATSR) were already related to VOCs measurements at MARS during the first months of 2005. Fig. 9 shows formaldehyde concentrations at MARS in comparison with fire counts observed around the station during January- March 2005. As it seen, high formaldehyde concentrations coincide with fire counts.

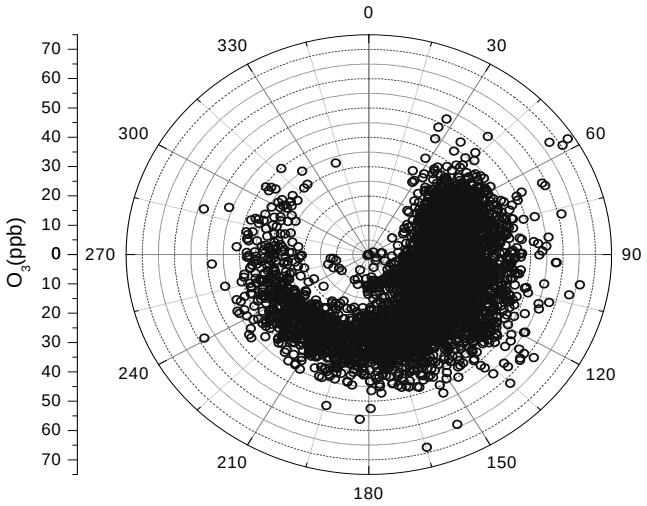

Fig. 8. Variation of the hourly average O_3 concentration in function of Wind Direction

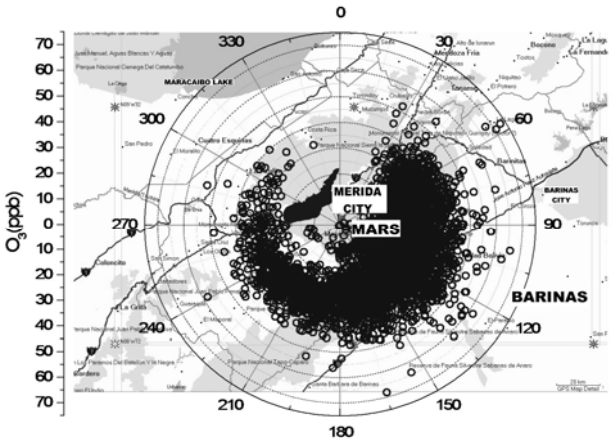

Fig. 9. Detailed description of the influencing areas around MARS. Figure compiled using data from Venezuelan Map Project, VENRUT (GPSYV, 2008; Jet Propulsion Laboratory, 2005)

3.3 Principal component analysis

Whereas correlation analyses helped to reveal the important influence of vertical ozone transport on the variation of hourly ozone concentrations, they did not offer clear information about any possible anthropogenic influence on the variance of hourly ozone concentrations.

Considering that the data variance in an indicator of how the controlling factors affect the ozone destruction-production mechanism, we performed a Principal Component Analysis using the meteorological variables coupled with the year and the hourly average concentrations. The main goal was to identify the correlation among variables that can cause a fraction of the total variance.

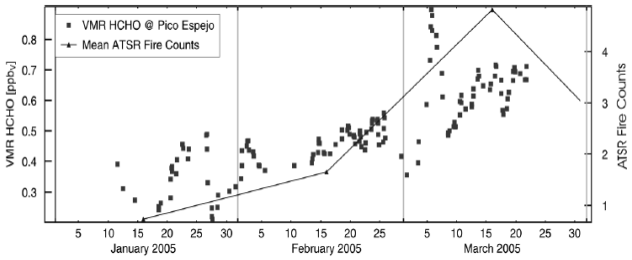

Fig. 10. Formaldehyde concentrations measured at MARS and biomass burning events from January to March, 2005 (Wittrock, F., 2008). (Reproduced with the author permission)

The Principal Component Analysis (PCA) is a statistical technique used to linearly transform a set of data into a significantly reduced domain in which, a smaller number *k* of independent variables is able to retain most of the information in the original *p* variables. This reduced set of k variables, is grouped in p-dimensional vectors to constitute an orthogonal base. The vectors, called Principal Components (PCs), are selected to represent the spatial direction in which the original data show the maximum variance. Inside a PC vector, the higher the vector component associated to a variable; the best this explains the variance. Positive correlations between variables are expected for the vector components of equal sign.

PCA results are shown in the columns of Table 2. Each column represents a PC, together with the variance explained by it, and the cumulative variance obtained.

As it seen, the first PC is able to catch a direction that explains a 28.3 % of the total data variance. The average hourly temperature, the wind speed and the total solar radiation are coupled to each other in this PC, and indicate that the higher the temperature, the higher the total solar radiation and the lower the wind speed. This relation could be associated with the photochemical ozone production cycle dominated daily by the solar radiation and enhanced by the presence of stationary air masses with low turbulence usually seen at low wind speeds. This is obviously the main responsible for local ozone variations. The fact of having the ozone component out of this PC could indicate that the temperature, solar radiation and wind speed equilibrate their effects, introducing just variability on the behavior without causing a significant effect on the ozone production-destruction mechanism. The same behavior is seen for the third, fourth and fifth PCs.

The second PC ties the year, the relative humidity and the ozone concentration to explain a 22.2 % of the total variance, and together with the first PC represent the 50.5 %. This PC indicates how the relative humidity and the ozone concentrations are negatively correlated to each other, and how time, expressed as the number of year, weakens this relation. The lower the relative humidity and the earlier the year, the higher the hourly ozone concentration. As explained in the last section, this behavior is expected during vertical transport when dry and ozone enriched air masses are brought to lower altitudes from the upper atmosphere. The year effect could be associated with a lower number of episodes favoring the atmospheric subsidence at recent years.

The third PC helps to explain the 14. 3 % of the total variance, and when coupled with the latter PCs, represents a 64.8% of the cumulative variance. This PC does not contain the ozone concentration, and indicates that the higher the year; the lower the relative humidity. This suggests that the recent years have been dominated by lower relative humidity values without having a significant effect on the ozone concentrations. This in some way validates the interpretation given to the second PC.

The fourth and fifth PCs explained a 25.2 % of the total variance and could be interpreted as indicators of the transport regime occurring at the MARS station. The fourth one shows a positive correlation between the wind direction and the year, while the fifth component is mainly related to wind speed. The sixth PC helps to explain the 7 % of the total variance, and shows the variable correlation observed in polluted areas when ozone production occurs due to anthropogenic emissions. The PC indicates that the higher the relative humidity and the solar radiation, the higher the ozone concentration.

As it was indicated before, MARS is mainly at the boundary layer during daylight time, when air masses containing ozone precursors, high relative humidity and high temperature values coexist in time favoring the ozone production. This entire picture is enhanced by the increase of anthropogenic emissions caused by the population growth observed in Mérida in the recent years. On the other hand, the anthropogenic ozone production could also occur when air masses transported from the Venezuelan plains (higher wind direction values) reach MARS at the warmer hours carrying higher water vapor, VOCs and NO_x concentrations from biomass burnings.

The seventh and last PC indicates that temperature increments are tied to low total solar radiation values. This is not related to a physical and possible behavior.

Table 2. Principal Components and explained variance for the meteorological and ozone data

pc	1	2	3	4	5	6	7
YEAR	0,02	0,30	-0,56	0,70	-0,31	0,02	-0,08
T	0,64	-0,12	-0,07	-0,03	0,16	-0,27	-0,69
HR	-0,19	-0,66	0,03	0,21	-0,11	0,60	-0,34
WS	-0,39	0,21	-0,16	0,13	0,84	0,10	-0,23
WD	0,30	-0,06	0,61	0,64	0,25	-0,03	0,26
JT	0,54	-0,10	-0,42	-0,14	0,29	0,45	0,46
O_3	0,15	0,63	0,33	-0,13	-0,15	0,60	-0,27
%var	28,31	22,19	14,29	13,43	11,79	6,95	3,03
%cumvar	28,31	50,51	64,79	78,23	90,02	96,97	100,0

4 Conclusions

Yearly, daily and hourly averages of O_3 concentrations for the 2005-2007 year period were analyzed for patterns. Ozone concentrations varied in the range expected for a remote site not affected by anthropogenic emissions. Exceptions to this behavior were observed at specific days of 2006 when air masses could have been transported from the South-East of MARS containing volatile organic compounds and nitrogen oxides from biomass burning in the bordering states.

Correlations factors and results from a Principal Component Analysis (PCA) of the meteorological data coupled with the hourly ozone concentration and the year, suggested that ozone concentration at MARS increases mainly during episodes of vertical transport of dry and ozone enriched air masses from the upper atmosphere. Evidence of ozone production due to anthropogenic emissions was found due to positive correlations between ozone concentrations and relative humidity, solar radiation and year. These variables were correlated and explained 6.1 % of the total data variance for the 2006-2007 year period.

5 Acknowledgments

We would like to express our gratitude to Sistema Teleférico de Mérida and to INPARQUES for their friendly support.

References

Alvim-Ferraz M, Sousa S, Pereira M and Martins F, 2006, Contribution of anthropogenic pollutants to the increase of tropospheric ozone levels in the Oporto Metropolitan Area, Portugal since the 19th century, Environmental Pollution, Vol. 140. pp. 516-524.

Brankov E, Trivikrama R and Steven P, 1998, A trajectory-clustering-correlation methodology for examining the long-range transport of the air pollutants, Atmospheric Environment, Vol. 32, No. 9, pp. 1525-1534.

Comrie A, 1994, A synoptic climatology of rural ozone pollution at the three forest sites in Pennsylvania, Atmospheric Environment, Vol. 28, No. 9, pp. 1601-1614.

Finlayson-Pitts B and Pitts J, 1997, Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles, Science, Vol. 276, No. 5315, pp. 1045-1052.

Foghin-Pillin S, 2002, Tiempo y clima en Venezuela: Aproximación a una geografía climática del territorio venezolano, Consejo Editorial de la Universidad Pedagógica Experimental Libertador, Caracas, p.159

García M, Sánchez M and Pérez I., 2005, Ground level ozone concentrations at a rural location in northern Spain, Science of the Total Environment, Vol. 348, pp. 135-150.

GPSYV, 2008, Proyecto mapas de Venezuela en GPS. Caracas, Venezuela, www.gpsyv.net.

Heirdorn K and Yap D, 1986, A synoptic climatology for surface ozone concentrations in southern Ontario 1976-1981, Atmospheric Environment, Vol. 20, No. 4, pp. 695-703.

Husar R, 1996a, (September 16, 1996), Spatial Pattern of Daily Maximum Ozone over the OTAG Region, In: VT DEC Air Trajectory Analysis of Long-Term Ozone Climatology Retrieved February 2nd, 2008, from http://capita.wustl.edu/OTAG/reports/-otagspat/otagspat.html.

Husar R, 1996b, (September 16, 1996), Weekly Pattern of Ozone over the OTAG Region, In: VT DEC Air Trajectory Analysis of Long-Term Ozone Climatology Retrieved February 02nd, 2008, from http://capita.wustl.edu/otag/Reports/otagweek/otagweek.-html.

Jet Propulsion Laboratory, 2005, Shuttle radar topography mission, National Aeronautics and Space Administration (NASA).

Kleiss B, 2005, Pico Espejo: when is it in the free troposphere? MARS-Meeting of 26th August 2005. Karlsruhe, Germany, http://www-imk.fzk.de/asf/mira/Merida/MARS-Meeting-050826/MARS_050826_Kleiss.pdf.

Folkard W, 2008, Formaldehyde concentrations at the Merida Atmospheric Research Station and fire events during 2005, Personal Communication sent to: P. Hoffmann on June, 2008

Kopp G, 2008, (June, 18th, 2007), The Merida Atmospheric Research Station, In: Remote sensing of stratospheric trace constituents using millimeter wave radiometry retrieved March, 19th, 2008, from http://www.imk.fzk.de/asf/mira/Merida/-MARS/mars.htm.

Logan J, 1999, An analysis of ozonesonde data for the troposphere: Recommendations for testing 3-D models, and development of a gridded climatology for tropospheric ozone, Journal of Geophysical Research, Vol. 104, No. 16, pp. 16115-16149.

Ostro B and Chestnut L, 1998, Assessing the health benefits of reducing particulate matter air pollution in the United States, Environmental Research, Vol. 76, No. 2, pp. 94-106.

Schubert C, 1999, Glaciers of Venezuela, United States Geological Survey Professional Papers. SATELLITE IMAGE ATLAS OF GLACIERS OF THE WORLD. GLACIERS OF SOUTH AMERICA, USGS P 1386-I, pp. 1386-I.

Seinfeld J and Spyros P, 1997, Atmospheric chemistry and physics: air pollution to climate, Wiley, John & Sons, Incorporated, p.1360

Shankar B and Neeliah H, 2005, Tropospheric ozone and winter wheat production in England and Wales: A Note Journal of Agricultural Economics, Vol. 56, No. 1, pp. 145-152(148).

U.S. Environmental Protection Agency, 2008, (March 17th, 2008), National Ambient Air Quality Standards (NAAQS), In: Air and Radiation Retrieved March 19th, 2008, from http://www.epa.gov/air/criteria.html.

World Health Organization, 2005, WHO air quality guidelines global update 2005. Meeting Report. Bonn, Germany, World Health Organization. EUR/05/5046029: 30.