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MULTIVARIATE STATISTICAL ANALYSIS OF METEOROLOGICAL AND AIR POLLUTION DATA IN THE 'CAMPO DE GIBRALTAR' REGION, SPAIN

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Abstract. A complete statistical analysis of meteorological and air pollution data was carried out in the 'Campo de Gibraltar' region (in the South of Spain) from 1999 to 2002. This is a heavy industrialized area where, up to date, very few air pollution studies have been made. The main objectives of the study presented here have been the characterization of the meteorological and (gaseous and particulate) air pollution conditions in the area, and the relations between them. Multivariate statistical techniques, such as Principal Component Analysis (PCA), have been applied to the data. The results show that air quality in the area is highly dependent on meteorological conditions such as wind persistence and direction, dispersion capability of the atmosphere, and humidity content. On average, sulphur dioxide and nitrogen oxide air pollution, mainly caused by fuel-oil combustion and traffic, respectively, is not very high. However, an important number of exceedences of the limits established by the EU Directive 1999 for PM10 (particulate matter with a diameter less than 10 μm) have been observed in some points of the area. A significant percentage of these exceedences (about 22% on average) are likely caused by African dust intrusions, which usually take place from May to August. From gaseous and particulate air correlations, it seems that anthropogenic activities contribute with about 19% on average.

Keywords: nitrogen oxides, particulate matter (PM), PM10, principal component analysis (PCA), sulphur dioxide, total suspended particles (TSP)

1. Introduction

The 'Campo de Gibraltar' is the most southern region of the Iberian Peninsula. It is 584 km^2, and is surrounded by western mountains (a Natural Park called 'Los Alcornocales') that rise up to 700 m, and the Rock of Gibraltar in the South-East, with a maximum altitude of 420 m above sea level (a.s.l.). Its climate is Mediterranean and winds are predominantly easterly and westerly. About 300,000 inhabitants live in the different towns spread in the region (Algeciras, 120,000; La Linea 65,000). It is a very complex scenario, where many stationary sources are present (Figure 1): an oil-refinery and some petrochemical factories close to it, a coal-fired power plant, a fuel-oil power plant, a large steel factory and a paper factory.

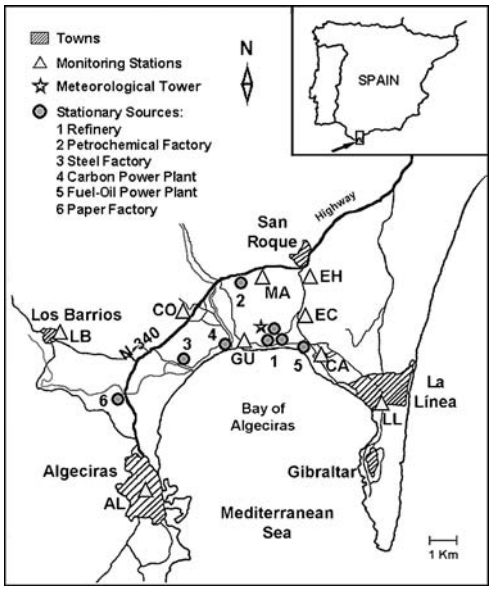

Figure 1. Location of the towns, large factories and the monitoring stations in the 'Campo de Gibraltar'.

Traffic is especially concentrated in the urban areas and the main road of the region (N-340) which surrounds the Bay of Algeciras. The traffic average of this road is approximately 49,046 light vehicles/day and 6,533 heavy vehicles/day. The port of Algeciras, one of the most important ship-trading ports in Europe, is another possible source of particulate and gaseous air pollution in the area. Due to the economic development of the region, many construction activities, which are important particle emission sources, have been carried out lately. In addition, the region is one of the paths that African air masses from Sahara and Sahel deserts take, increasing significantly particulate air concentration in different areas of Spain and Europe (Rodriguez *et al.*, 2001). Therefore, many (particulate) air pollution episodes have been detected by the different monitoring stations that the Environmental Agency of the Andalusian Regional Government has in the region.

It is known that SO_2 and NO_x ($NO + NO_2$), as well as the natural and anthropogenic particulate pollutants, especially, PM10 (particulates with aerodynamic diameters which are less than 10 μm) are potentially toxic to human beings and all living matter (Schwartz *et al.*, 1996; Wilson and Suh, 1997; Goldberg *et al.*, 2000). As a result, and considering the 1999/30/EC Air Quality Directive, there is an urgent need to study the PM10 characteristics and their contributions from various sources in order to control the occurrence of episodic pollution events and decrease the health hazards of PM10.

A study of atmospheric concentration of metals and total suspended particles (TSP) developed in the Campo de Gibraltar from 1982 to 1983 (Usero *et al.*, 1987a),

indicated that TSP level were notably inferior to the former Spanish and EEC air quality standards (TSP maximum daily mean value of 300 μg/m^3). It also showed that a large amount of the V, Ni, Cu, Pb, and Zn concentrations were of anthropogenic origin while the most abundant elements were those commonly associated with soil and marine aerosol. The application of a Chemical Mass Balance (CMB) method to the elemental concentration data (Usero *et al.*, 1987b) revealed that soil dust, marine aerosol and waste burning were the main sources of TSP in the area. However, no studies have been carried out to determine temporal variation of PM10 and gaseous pollutants, and the origin of the different particulate matter episodes. The present work focuses on the statistical analysis of the time series of gaseous and particulate pollutants and their relationship with the different meteorological conditions observed in the Campo de Gibraltar region.

2. Data and Methods

2.1. Description of the area of study

The climate of the 'Campo de Gibraltar' is essentially Mediterranean although it is open to the wet Atlantic air masses which make it very different from the Mediterranean climate of East Spain. Summers are hot while winters are wet and mild. Winter and summer mean air temperatures are 13.8 and 23.0 °C, respectively. The annual precipitation is 772 mm, occurring mainly between October and April. The annual mean surface wind speed is 6.4 m/s, with a monthly minimum of 5.6 m/s in August and a maximum of 7.4 m/s in February. As monthly calm frequency is very low, local air masses are frequently renewed. Winds are predominantly from the E, associated with wet air masses, and from the W, which are drier winds.

2.2. Data and analyses

The study was initiated in January 1999 and continued until December 2002. The meteorological data were mainly obtained from the meteorological tower located in the refinery (Figure 1), on the top of a hill at an altitude of approximately 70 m (a.s.l.). All the meteorological variables considered in this study are measured by sensors installed at 10 m over the ground surface. Wind speed and wind direction are measured by two sensors, an anemometer and a vane, respectively, integrated in a single instrument. Its inertia is very low and speed range is from 0.15 to 46.30 m/s. Air pressure is measured by a solid-state barometer. The operative pressure range is 95,000–105,000 N/m^2. Its accuracy is $\pm$30 N/m^2. Ambient air temperature is measured by a high resolution thermometer with a range of -30 to 50 °C. Direct solar radiation and that from other sources (except from soil surface) are avoided. The hygrometer is a hair hygrometer of synthetic fibres (combined with a thermometer) with a measuring range of 10 to 100%

of relative humidity (and −35 to 70 °C). Its operational accuracy is ±2%. The pyranometer for the measurement of global radiation has a measuring range of 0–1300 W/m^2. Finally, the precipitation transmitter has a maximum measuring range of 2 mm/min with a resolution of 0.005 mm and an accuracy of ±3% until 1.2 mm. Synoptic charts provided by the Met Office were also consulted via Internet (http://129.13.102.67/wz/topkarten/fsfaxbra.html). The meteorological characterization was determined by the statistical analysis applied to the different parameters measured in the tower (surface wind speed and wind direction, temperature, atmospheric pressure, etc.), and other indirectly estimated variables (absolute humidity, mixing height, ventilation factor, etc.). The mixing height (H_m) was estimated from surface data, using the method of Batchvarova and Gryning for the growth of the daytime mixed layer (Batchvarova and Gryning, 1990) and the Benkley and Schulman method for the nocturnal mixing height estimation (Lena and Desiato, 1999). The surface roughness lenght (z_0) was set to 1 m (typical urban value), while the temperature gradient above the mixing layer (γ_θ) was assumed to be 0.05 K/m for H_m values less than 100 m, and 0.005 K/m above 100 m. The equation for the growth of the daytime mixing layer (which is expressed in a basic form by Equation (1)) was solved numerically by Finite Differences Method (FDM).

$$f(H_\mathrm{m})\frac{\mathrm{d}H_\mathrm{m}}{\mathrm{d}t} = g(t) \tag{1}$$

f is a function of mixing height and also depends on different characteristic parameters: Monin–Obukhov length (L), γ_θ and friction velocity (u_*). g is mainly a function of the kinematic turbulent heat flux at ground surface. According to Benkley and Schulman method, the nocturnal mixing height is proportional to wind speed (measured at an altitude of 10 m over the ground surface).

In this study, rotated Principal Component Analysis (PCA) is applied to the meteorological observation data sets, and factors are interpreted as meteorological phenomena that affect the fluctuations in the data. The factors found by PCA do not often have straightforward or unique interpretations. Therefore, in order to clarify the meaning of the components, the most important factors (in terms of variance explained) determined by PCA are subsequently subjected to orthogonal rotation. In this case VARIMAX criterion has been used. By orthogonal rotations, VARIMAX method tries to make the structure of the factor loading matrix simpler. The rotated factor loadings (b_{ij}) are scaled by the square root of the communalities (h_i), getting $b^*_{ij} = b_{ij}/h_i$. Then, the VARIMAX procedure selects the orthogonal transformation that maximises:

$$V = \frac{1}{m}\sum_{j=1}^{p}\left[\sum_{i=1}^{m} b_{ij}^{*4} - \frac{1}{m}\left(\sum_{i=1}^{m} b_{ij}^{*2}\right)^2\right] \tag{2}$$

where m is the number of components and p the initial number of variables. A simple interpretation of this criteria is that maximising V corresponds to spreading out the squares of the loadings on each component as much as possible. Then, it is expected to find groups of large and small coefficients in any column of the rotated loading matrix.

The nine monitoring stations (triangles on the map of Figure 1) used for the half-hourly measurements of SO_2, NO, NO_2, O_3, TSP and PM10 concentrations are controlled by the Enviromental Agency of the Andalusian Goverment. Since the 90's, the Environmental Agency has had about 20 fixed monitoring stations around the area. However, the nine stations selected for the study showed the largest set of validated data during the period of analysis (1999–2002). Furthermore, they cover the different types of environments and surround the main industrial activities in the area. AL and LL are located on a relatively flat terrain of urban areas, with many buildings around. The altitudes of AL and LL are about 20 and 2 m (a.s.l.), respectively. The nearest obstacles are about 5 m. LB is located at the top of a hill of a residential area (far from the center of a small town). Its altitude is about 15 m (a.s.l.). CO and CA are located on a flat terrain (about 8 m of altitude (a.s.l.)) of suburban areas which are close to the industrial sites. MA, EC and GU are located on a rural terrain close to the main industrial factories. Their altitudes are 15, 20 and 3 m (a.s.l.), respectively. Finally, EH is also located on a hill (about 80 m of altitude (a.s.l.)) of a rural area and it is just 20 m from one of the main roads of the region.

O_3 concentrations were only measured at the LL station, while PM10 at AL and LL sites. TSP and PM10 levels are measured by automatic beta radiation attenuation monitors. SO_2, NO and NO_2, CO and O_3 concentrations are measured by ultraviolet (UV) fluorescence, chemiluminiscence, infrared absorption and UV absorption, respectively. Although the PM10 data were obtained without demonstrating the equivalence with the instrumentation and the current standardised measurement procedures, the quality of the data would be suitable for this study. Recent studies have demonstrated that automatic PM10 instruments (like beta attenuation) underestimate PM10 levels (down to 35%) when compared with the EN12341 reference method (European Comission, 2001). This underestimation, which may also affect TSP in a lesser degree, is due to the volatilisation of semi-volatile species owing to the heating of the sampled air to remove particle-bound water. Therefore, the data presented in this study could include a slight underestimation of the TSP and PM10 measures obtained under the requirements of the 1999/30/EC Directive.

Meteorological and pollutants daily mean values were calculated from more than 80% of the validated hourly values. The different meteorological and air pollutants time series were studied to determine seasonal and mean diurnal variations, the influence of wind direction, and correlations between particulate matter and gaseous pollutants concentrations. Furthermore, the meteorological patterns identified by PCA were correlated with the air pollutants levels in order to study their influence on the air quality of the region.

3. Results and Discussion

3.1. METEOROLOGICAL CHARACTERIZATION

The meteorological variables employed include daily average net radiation (RAD), precipitation (PRC), surface temperature (TMP), wind speed (WSP), sea level pressure (SLP), relative humidity (RHM), absolute humidity (AHM), mixing height (MXH), and the absolute frequencies of the different wind sectors (N, NNE, NE, ENE, etc). The results of applying rotated PCA to the meteorological data of the period 1999–2002 are shown in Table I. Variables with poor communality were finally not considered in the analysis. Only those components associated with eigenvalues greater than unity were extracted. These components explain 72% of the data variability.

TABLE I
PCA analysis using meteorological data (1999–2002)

	MET 1	MET 2	MET 3	MET 4	MET 5	MET 6	MET 7	h^2
TMP	0.93							0.900
RAD	0.82							0.831
AHM	0.75	*0.41*						0.779
NW		−0.78						0.715
NNW		−0.81						0.735
RHM	*−0.40*	0.61						0.674
W			−0.75					0.717
WNW			−0.79					0.789
ESE			0.58					0.566
E			0.59	*0.45*				0.781
WSP				0.92				0.892
MXH	*0.45*			0.80				0.888
SE				*−0.49*				0.556
SSE					0.80			0.705
NNE					0.77			0.647
SSW						0.71		0.553
SLP	*−0.46*					−0.64		0.660
PRC						0.69		0.598
NE							0.76	0.721
ENE							0.74	0.702
% var.	17.4	30.4	43.0	51.9	59.9	66.8	72.0	

Note. Only absolute values greater than 0.40 are shown in the table. Communalities are shown in the last column, while the last row shows the cumulative percentage of variance explained by each principal component.

Different meteorological conditions can be identified: component labelled as MET1 is strongly loaded on TMP, RAD and AHM, and is associated with the thermal low, especially observed during warm periods. It is also characterized by high MXH values and wet conditions derived from evaporation processes. It can be interpreted as the influence of convective turbulence in the area. MET2 shows the contrast between the drier conditions linked to norhwestern winds and the wetter conditions associated with other prevailing winds. MET3 shows the contrast between the most prevailing winds in the area: weasterly winds (W,WNW) and easterly winds (E, ESE). MET4 reflects the influence of high winds and good dispersion conditions, that is, mechanical turbulence. This component is positively correlated with easterly winds (E), while the negative moderate correlation with southeast winds appears to indicate the presence of coastal seabreezes during low wind speed conditions. Although it is difficult to interpret, it seems that MET5 shows the presence of winds from SSE and NNE sectors, usually associated with transitional situations and low wind speeds. MET6 is positively correlated with PRC and SSW winds and negatively correlated with SLP. It seems to represent rain conditions associated with ciclonic winds from the SSW sector. Finally, MET7 seems to reflect the persistence of northeast winds in the area.

3.2. Statistics of TSP (and PM10), SO_2 and NO_2 concentrations

Figure 2 shows a simple statistical analysis of the TSP and PM10 (at AL and LL stations) (Figure 2a), SO_2 (Figure 2b), NO_2 (Figure 2c) and NO (Figure 2d) concentrations recorded in the selected monitoring stations located in the study area during the period between 1999 and 2002. Daily mean levels of particulate matter concentrations are higher at GU, AL, CO, LL and EH stations, which (excluding GU) are located at urban areas or close to the main roads of the region under study. It is worth to note that TSP concentrations at AL and LL must be higher since it is PM10 what is measured at these stations. The annual mean of PM10 at AL and LL stations ranged from 31 to 60 $\mu g/m^3$, and from 34 to 44 $\mu g/m^3$, respectively. Therefore, the maximum annual mean level of 40 $\mu g/m^3$ established by the EU Directive 1999 for human health protection was exceeded in some years of the period under study.

Regarding SO_2, the highest daily mean concentration levels are found at EC, GU, LL, LB and CA stations, all of them located near the industrial area or, as LB and LL, in alignment with the main stationary sources and the prevailing winds (E-W) direction. SO_2 concentrations are generally under the limits established by the EU Directive 1999 (125 $\mu g/m^3$ of maximum daily mean), although some exceedences were detected at GU, CA, EC and LB stations. Annual mean values ranged from 5 $\mu g/m^3$ at MA site to 31 $\mu g/m^3$ at GU.

In relation to NO_2 levels, the urban AL and LL stations have the highest daily mean concentration values (around 40 and 27 $\mu g/m^3$, respectively), while the rest show mean levels of 20 $\mu g/m^3$, approximately. As a result, it seems that traffic

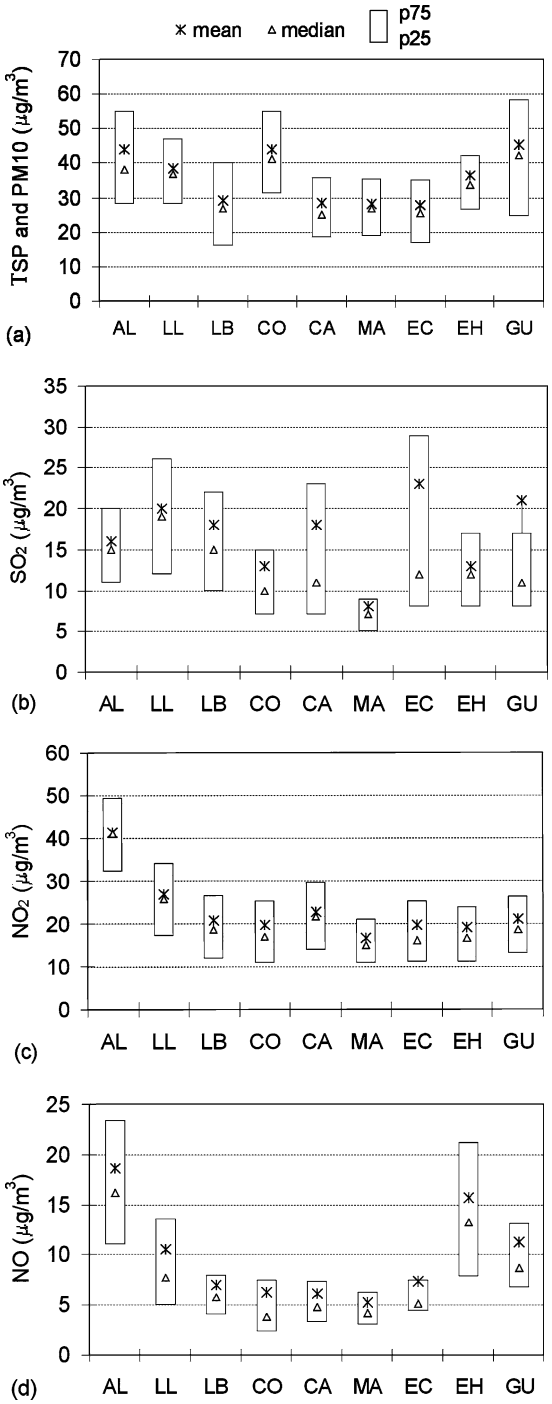

Figure 2. Statistic of (a) TSP and PM10 (at AL and LL stations), (b) SO_2, (c) NO_2 and (d) NO daily mean concentrations in the 'Campo de Gibraltar' region. Period 1999–2002.

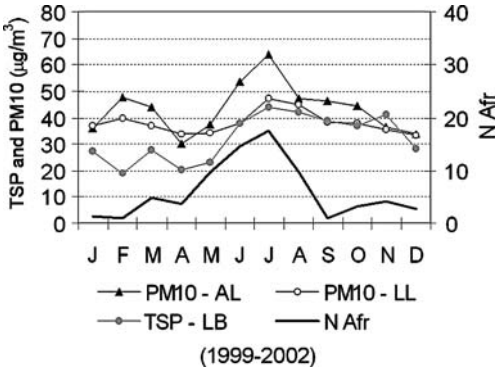

Figure 3. Monthly mean concentrations of PM10 and TSP at urban and industrial sites in the Campo de Gibraltar region. N Afr is the mean number of African dust clouds over the area (from TOMS satellite). Period 1999–2002.

is an important source of NO_2 in urban areas. The annual mean values ranged from 13 μg/m^3 at EC site, to 46 μg/m^3 at AL, close to the maximum of 50 μg/m^3 established by the EU Directive 1999 for 2005, and higher than 40 μg/m^3, maximum limit considered for 2010. NO concentrations were very low in the area. The highest NO daily mean level (110 μg/m^3) was detected at the AL station. Annual mean levels ranged from 3 to 23 μg/m^3 at MA and AL, respectively.

Regarding CO daily mean concentrations, which are only measured at AL station, ranged between 344 and 2,204 μg/m^3. Annual mean levels ranged between 716 and 1,061 μg/m^3. Ozone (measured at LL station) showed annual mean values of 64 μg/m^3, approximately, with very small changes from year to year.

3.3. Seasonal pollutant variations

Figure 3 shows the seasonal variations observed in PM10 monthly concentrations measured at AL and LL urban-industrial sites and TSP monthly concentrations at LB residential-industrial site. The mean number of African dust clouds over the area, calculated from TOMS satellite images, can also be seen in Figure 3. These PM10 seasonal variations are similar to those experienced in the rural Mediterranean environments (Rodriguez *et al.*, 2002), with increases in summer, which are usually related to African dust intrusions and soil dust resuspension. However, the increases at the urban sites (AL and LL), especially during winter months, are likely to be anthropogenic due to the moderate positive correlation observed between PM10 and NO_x concentrations. The observed winter/summer (W/S) concentration ratios ranged from 0.42 to 1.08, with a mean station value of 0.82.

Although the seasonal pattern shown in Figure 3 has not been observed in the rest of the TSP series, a high similarity between daily means has been detected during some months of the period between 1999 and 2002 at the majority of

monitoring stations. This reflects that external and regional (emission and/or meteorological) factors, as the influence of clean Atlantic or dust loaded African air masses, may strongly rule particulate air pollution in the area. In fact, African dust intrusions, which have been detected using TOMS maps of UV-radiation absorbing aerosol index (Herman *et al.*, 1997) and considering the correlation between the different TSP local series, seem to be very frequent in the area under study. TOMS maps from 1999, 2000 and 2002 show that the higher number of clouds over the area takes place from May to August (about 80% of total). However, 2001 showed a different pattern, with a higher number of clouds from October to December (about 60% of total). The influence of Atlantic air masses was observed from the study of UK Meteorological Office synoptic charts of pressure at sea level.

No seasonal trends were observed for the SO_2 series. SO_2 monthly concentration levels remained nearly constant at AL, LL and LB stations throughout the year, while a higher variability was observed in the rest of the monitoring stations. The observed winter/summer (W/S) concentration ratios ranged from 0.67 to 1.40 (with a mean value of 0.89).

The monthly trend of NO and NO_2 did not repeat itself from year to year. W/S concentration ratios ranged from 0.72 to 1.44 for NO_2 (with a mean value of 1.05), and from 0.65 to 1.68 for NO (with a mean value of 1.15). According to Bower *et al.* (1991), the measured NO_2/NO_x ratio is a convenient variable of the extent and completeness of atmospheric oxidation processes. The annual NO_2/NO_x ratio was approximately 0.68, with a minimum of 0.66 in December and a maximum of 0.71 in June. Consequently, a very slightly enhanced oxidation process is detected during the summer period.

The patterns of CO and O_3 monthly mean concentrations have been shown in Figure 4. CO concentrations were smaller during summer months, which is likely due to a decrease in traffic emissions together with a higher dispersion capacity of the atmosphere during that period. O_3 shows a monthly evolution very similar

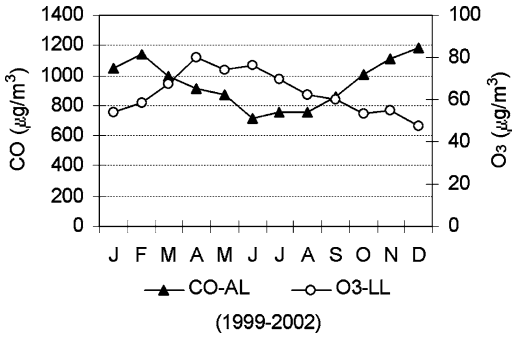

Figure 4. Monthly mean concentrations (1999–2002) of CO and O_3 at urban and industrial sites in the 'Campo de Gibraltar' region.

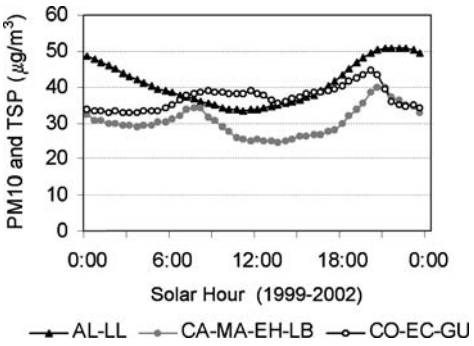

Figure 5. Diurnal variations of 1/2-h average PM10 and TSP concentrations at the same (solar) hours at different sites in the 'Campo de Gibraltar' region. Averaging Period: 1999–2002.

to that found by other authors in points at latitudes similar to LL station (Dueñas *et al.*, 2002).

3.4. Diurnal pollutant variations

Figure 5 shows the overall diurnal average variations for TSP and PM10 concentrations during the period between 1999 and 2002. Three similar but different trends have been detected: PM10 concentrations at AL and LL stations have a slow changing trend, with greater values at night, especially around 22:00 solar time, and a marked decrease which approximately takes till noon, approximately; TSP concentrations at CA, MA, EH and LB stations show a similar behaviour with faster changes and two peak concentrations in the early morning and around 21:00 in the evening, which are likely caused by traffic and plume impacts in some cases; finally, TSP concentrations at CO, EC and GU stations show an increase during daytime, probably due to the influence of the different and continuous anthropogenic activities developed in the industrial area. In summary, the worst particulate air pollution conditions seem to occur in the first morning and night hours at the majority of the stations. Diurnal variations during weekdays and at weekends were studied separately in order to determine the influence of traffic on particulate air pollution. The results showed that, no matter which day it was, the trend was almost the same, but with lower hourly levels at weekends, especially during daytime. This seems to reflect a strong influence of meteorological and orographical conditions, while daily mean levels seem to depend mainly on the emission rates.

Diurnal trends for SO_2 show a typical increase during daytime (Figure 6). At night, mixing height has the lowest values; so that, ground impacts of the SO_2 clouds near the main stationary sources with stacks around 110 and 220 m high are less probable. However, during daytime the strong thermal convection causes the plume abatement which leads to higher ground concentration levels. Diurnal variations and daily mean levels during weekdays and at weekends showed slight

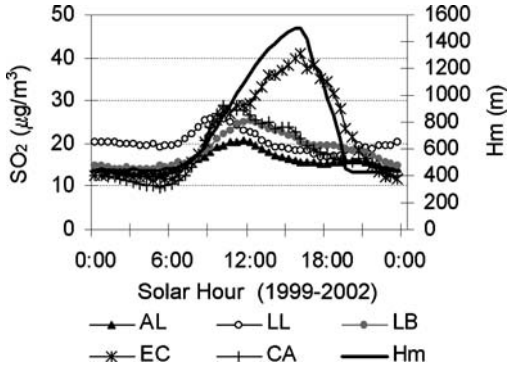

Figure 6. Diurnal variations of 1/2-h average SO_2 concentration at the same (solar) hours at different sites in the 'Campo de Gibraltar' region and estimated mixing height (H_m). Averaging Period: 1999–2002.

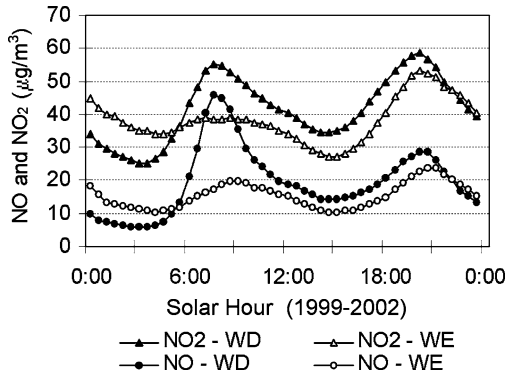

Figure 7. Diurnal variations of 1/2-h average NO and NO_2 concentration at the same (solar) hours at AL site during working days (WD) and weekend (WE). Period of analysis: 1999–2002.

differences (except at AL and CO), pointing out the industrial combustion sources as the main contributing sources to SO_2 in the area.

Figure 7 shows the NO and NO_2 diurnal concentration variations at AL monitoring station. A similar trend has been observed in the rest of stations. The highest NO peak concentration takes place at dawn during week days, likely due to a higher traffic intensity. In fact, a significant decrease and a delay of about 1 h in this first peak is measured during the weekend. A second but smaller peak is observed at about 20:00 solar hour, which coincides with the second highest increase in traffic intensity and a decrease in the dispersion capacity of the atmosphere as inferred from the modelled mixing height values. NO_2 shows a similar trend, with two peaks at the same hours. A cumulative effect of these gaseous cannot be disregarded once a slightly positive trend is observed in their daytime hourly measurements. It is worthy to note that, in the night-time, NO and NO_2 concentration levels during

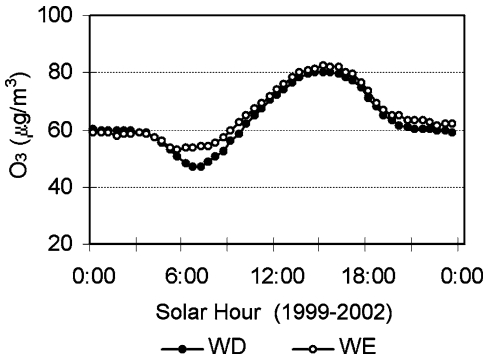

Figure 8. Diurnal variations of 1/2-h average O_3 concentration at LL site during working days (WD) and weekend (WE). Period of analysis: 1999–2002.

weekends are higher than on weekdays, probably due to an increase of traffic intensity around the bars and restaurants close to the monitoring station. An increase in PM10 concentration was also measured in the weekend night-time. The time evolution of CO 1/2 h mean levels is very similar to that observed for NO_2.

Figure 8 shows the diurnal variation of O_3 at LL monitoring station. As it was already detected by other authors (Dueñas *et al.*, 2002; Viras, 2002; Bhugwant *et al.*, 2001), a minimum value appears in the early hours of the morning (here at about 7:00 solar hour), caused mainly by the high injection of NO from traffic emissions which reacts with ozone producing NO_2. This depletion is not so pronounced during the weekend because NO levels are significantly smaller at that time (see Figure 7).

3.5. Effect of wind direction

The analysis of the influence of wind direction on the different pollutant average concentrations has been summarised in Table II. From the maximum to minimum average concentration ratios (spatial mean value of 1.5, with a standard deviation of 0.16), it can be seen that air particulate concentrations are less dependent on wind direction than the rest of pollutants. This result seems to show that the main contributing sources to particulate air pollution in the area are more spread out. In contrast, from the same max/min ratios for SO_2 (spatial mean value of 3.7, with a standard deviation of 2.03) and the sector of maximum average concentration for each monitoring station, it can be seen that the main contributing sources are located in the centre of the area, what is likely to be the refinery and the nearby petrochemical industries. Results for NO and NO_2 concentrations are very similar, with a general decrease in average concentrations for the prevailing wind sectors (E and W), for which wind speed is usually higher.

Regarding O_3 (measured at LL monitoring station), the max/min ratio is about 2.2, with the maximum measured for Easterly and cleaner air masses.

TABLE II
Ratios between the maximum and minimum pollutant average concentrations measured for the different wind sectors

	TSP, PM10		SO_2		NO_2		NO	
	max/min	S_{max}	max/min	S_{max}	max/min	S_{max}	max/min	S_{max}
AL	1.7	NNE	1.8	SE	1.4	NNE	2.3	NNW
LL	1.4	NNE	2.8	NW	2.8	SW	3.9	SW
LB	1.3	ENE	2.6	SE	2.9	SE	2.3	SE
CO	1.6	SE	2.5	ESE	3.2	SSE	3.4	N
CA	1.3	NNW	4.4	WNW	3.3	S	3.0	S
MA	1.5	E	2.9	SSE	2.0	S	2.1	NNW
EC	1.7	SSE	8.0	W	2.3	S	1.6	S
EH	1.3	NNW	2.7	SW	2.4	S	2.2	SW
GU	1.3	SSE	6.0	E	2.2	S	2.2	NNW
Mean	1.5	–	3.7	–	2.5	–	2.6	–
Std. Dev.	0.16	–	2.03	–	0.62	–	0.71	–

Note. Wind sector for which the maximum average concentration is measured (S_{max}).

3.6. CORRELATIONS BETWEEN GASEOUS AND PARTICULATE AIR POLLUTANTS

In order to study the relations between the different gaseous air pollutants and TSP (and PM10) concentrations, the correlation coefficient (r^2) was daily measured for all stations during the period under analysis. Table III shows the annual average number of days with a correlation coefficient greater than 0.4 (moderately strong correlation) for the different pairs of air pollutants. Absolute numbers are not very high, in part due to the fact that only the days with at least 80% of the data available were considered in the analysis. Therefore, relative percentages (in brackets) are more meaningful. In general, these values are also very small, even at the stations close to the industrial area. Correlations between TSP and NO_2 are the most frequent at the 'Campo de Gibraltar', especially at urban stations (AL and LL). Higher values of strong NO_x-Paticulate Matter (PM) correlations (around 180 days per year, 49%) were found in a study performed in many cities of the UK (Deacon *et al.*, 1997).

Considering the high daily correlation observed between CO and NO_2 concentrations (0.63 ± 0.25, mean annual value $\pm$ standard deviation), the results point to traffic as the most probable contributing source to particulate air pollution at the urban area of AL (at least during these days of strong correlation).

TSP and SO_2 correlations are more frequent at EC station, which is very near to the petrochemical factories. For days with a strong correlation between these two pollutants, a simultaneous increase in TSP and SO_2 concentrations is observed during daytime, probably due to the gaseous and particle plume abatement caused

TABLE III

[c]Annual average number of days (relative percentage in brackets) with a correlation coefficient greater than 0.4 between the corresponding gaseous air pollutant (SO_2, NO_2, NO, and CO) and TSP[a] (or PM10[b]) nm: not measured. [d]Annual mean number of exceedences. [e]Annual average number of exceedences with moderately high particulate-gaseous correlation. [f]Annual average number of exceedences under African dust intrusions. [g]Annual average number of exceedences under African dust intrusions and high particulate-gaseous correlation (relative percentages in brackets).

	SO_2^c	NO_2^c	NO[c]	CO[c]	Nsup[d]	Ngas[e]	NAfr[f]	Ngas+Afr[g]
AL[a]	27 (10)	59 (22)	24 (10)	49 (18)	110	38 (33)	13 (14)	13 (9)
LL[a]	29 (13)	62 (21)	20 (7)	nm	65	10 (16)	16 (23)	8 (14)
LB[b]	13 (5)	41 (18)	14 (6)	nm	12	4 (33)	5 (37)	1 (8)
CO[b]	13 (5)	29 (11)	11 (5)	nm	39	8 (16)	10 (24)	2 (9)
CA[b]	8 (3)	9 (3)	3 (1)	nm	7	1 (10)	4 (34)	0 (0)
MA[b]	11 (4)	24 (8)	9 (4)	nm	5	0 (11)	1 (6)	0 (0)
EC[b]	38 (14)	27 (11)	13 (5)	nm	8	1 (20)	3 (15)	1 (5)
EH[b]	6 (3)	25 (10)	6 (2)	nm	17	3 (12)	5 (26)	0 (1)
GU[b]	10 (4)	18 (9)	8 (4)	nm	100	18 (18)	24 (24)	13 (12)
Mean	17 (7)	33 (13)	12 (5)	–	40	9 (19)	9 (22)	4 (6)

by the typical convective activity of these hours. Furthermore, westerly winds, for which this site is under the influence of the industrial area, were prevailing during those days.

3.7. PM10 AND TSP EXCEEDENCES AND PARTICLE-GASEOUS CORRELATIONS

The annual mean number of exceedences at the different stations has been shown in the last columns of Table III. The PM10 maximum daily mean established by the 1999/30/EC Directive for 2005, that is, 50 μg/m^3, was considered in the analysis of PM10 exceedences. Considering that the coarse fraction (PM10) is about 83% of the ambient aerosol, a maximum of 60 μg/m^3 was taken for TSP daily concentrations. A similar fraction has been measured in a study of the size distribution of the urban aerosol in Seville (Fernandez *et al.*, 2001). The contributions of African dust intrusions and anthropogenic activities on particulate air pollution have been studied from TOMS satellite observations and moderate correlations between gaseous and particulate air concentrations, respectively. As it can be seen in Table III, the maximum number of exceedences allowed by the EU Directive for 2005 (35 per year) was surpassed at AL, GU, LL and CO stations. An important percentage of the exceedences can be attributed to African dust intrusions (22% on average). In fact, the highest values of exceedences take place between May and September, when Saharan dust intrusions and particle resuspension are likely to occur. A significant spatial correlation between the different particulate concentration series has been measured during these events.

About 19% of the exceedences takes place during days with a significant correlation with, mainly, NO_2 concentrations, showing the anthropogenic origin of these events. Approximately, 6% of the exceedences occurs under the joint influence of anthropogenic activities and African dust intrusion, making environmental pollution worse.

3.8. Influence of meteorological parameters on atmospheric concentration

Finally, a correlation analysis between the different air pollutants daily mean concentrations and the meteorological components (MET) explained in a former section has been performed (Table IV). This analysis could be helpful to determine if the different meteorological conditions lead to low or high air pollution levels at the stations under study. As a summary, and considering the correlations with a statistical significance equal or greater than 95%, the following conclusions could be extracted:

- PM10 or TSP concentrations increase during the thermal low, for prevailing wet easterly winds and, in general, for low wind speeds.
- Whatever the meteorological conditions, SO_2 concentrations show a clear dependence on wind direction, increasing at each station for winds from the petrochemical factories.
- Regarding NO and NO_2 concentrations, there is a clear dependence on wind direction, although weaker than for SO_2. In general, high speed (easterly wind) conditions lead to lower NO and NO_2 concentrations and viceversa.

TABLE IV

Correlation coeficients (with a statistical significance greater than 95%) between TSP[a] (or PM10), SO_2[b], NO_2[c] and NO[d] daily mean concentrations and the different meteorological components indentified by PCA (from 1999 to 2002)

	MET 1	MET 2	MET 3	MET 4	MET 5	MET 6	MET 7
AL	+[a] 0[b] 0[c] +[d]	− + − 0	+ + + −	0 − − −	+ + + −	− − − 0	− + 0 0
LL	+ + + −	+ − − −	+ − − 0	− − − 0	0 − − +	− 0 0 0	0 0 0 0
LB	+ 0 0 0	+ + + +	+ + + +	− + − 0	− + + 0	− 0 − −	+ 0 + 0
CO	+ 0 + −	0 + 0 −	+ + + 0	0 + − −	+ + + 0	+ − 0 0	0 − 0 0
CA	+ + + −	+ − − −	+ − − −	0 + − −	− − − 0	0 − 0 0	− − − 0
MA	+ + − 0	+ − − −	+ + 0 0	0 0 − −	0 + + +	− 0 + 0	0 − − 0
EC	+ + − −	0 − − −	0 − − −	0 + − −	+ − 0 0	+ + 0 −	− − 0 0
EH	+ − 0 +	0 − − −	+ + − −	− − − −	+ + 0 0	0 + 0 0	0 − 0 0
GU	+ + 0 0	− + + −	+ + + +	+ + + −	+ + + +	+ 0 0 0	− + 0 +

Note. '+' means positive correlation; '−' means negative correlation, and '0' means that no significant correlation was observed (statistical significance less than 95%).

From the global number of positive and negative correlation coefficients, it seems that there is a significant relative increase of air pollution under conditions labelled as MET1 (thermal low), MET3 (persistent E winds) and MET5 (NNE and SSE winds), and a decrease under MET2 (wet non-westerly winds) and MET4 (high speed winds).

3.9. Environmental management

It seems that a significant percentage of airborne PM exceedences comes from natural events (e.g., African dust intrusions, soil dust resuspension by wind). These events are natural and, in some cases, inevitable. However, dust resuspension caused by wind and human activities (e.g., traffic) could be reduced by water spraying of roads and by the growth of green plants around them. There is also a need to identify the main sources of PM and quantify their contributions more precisely by using a receptor modelling. This would allow the implementation of specific techniques to reduce air pollution.

As air quality in the area, especially in terms of SO_2 and NO_x levels and probably in other toxic chemical elements and organic compounds, seems to be highly dependent on wind direction, the determination of new urbanization areas should take this into account, avoiding locations in the path of the industrial plumes.

Finally, and as a new approach recently proposed in other areas (Chaulya, 2005), the development of a suitable green belt, with species with a real capacity of air pollution reduction surrounding the different pollution sources, would be an interesting measure to improve air quality in the region.

4. Conclusions

Different meteorological conditions have been identified from the PCA applied to meterorological data from 1999 to 2002: summer thermal low, wet conditions associated to non-northwesternly winds, W or E prevailing wind conditions, mechanical turbulence conditions and its contrast with wind transitions, and precipitations associated to SSW winds.

Air pollutant concentrations in the area are not very high, although, considering the EU Directive 1999 requirements for 2005, some exceedences have been detected in PM10 series and SO_2 concentrations at urban stations and near the industrial areas, respectively. In general, PM concentrations have an annual trend with higher values during summer, when African dust intrusions and local resuspension are more frequent in the area. The analysis of diurnal variations shows that the worst particulate and NO_x air pollution conditions seem to occur in the first morning and night hours at the majority of stations. Regarding SO_2 concentrations, they increase during daytime, due to convective activity, and present a clear wind direction dependence, pointing to the refinery and the petrochemical facilities as

the main contributing sources. From the analysis of the influence of wind direction on PM concentrations, it seems that the main PM contributing sources are external or spread over the area.

In conclusion, the analysis of TOMS satellite observations and gaseous-particulate matter correlations allowed to infer that a significant part of PM exceedences was likely to come from African dust intrusions (about 22%) and anthropogenic activities (19%, approximately).

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