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Artigo

ASSESSMENT OF AIR QUALITY IN VIANA DO CASTELO, PORTUGAL, IN THE SCOPE OF THE POLIS PROGRAMME

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The present paper constitutes a synthesis of the results gotten during the five campaigns of air quality measurement in the years of 2003 and 2004 carried out in the Portuguese city of Viana do Castelo to characterise the reference situation and to accompany the Polis Programme, an urban re-qualification and environmental valorisation plan. The main objective of the monitoring programme consisted of the evaluation of atmospheric pollutants whose levels were susceptible of enhancement in the course of the urbanistic public works. The presented results refer to measurements performed in two distinct places of this city, comprising various consecutive days of acquisition that include, at least, one day of weekend.

Keywords: air quality; meteorological variables; statistical analysis.

INTRODUCTION

Viana do Castelo is a small town in the north of Portugal, capital of the Minho district. It is placed in the right margin of the river Lima, close to the mouth, and extends between the sea and the river, in land almost plan, being protected by the luxuriantly green Sta. Luzia hill. The city has 36546 inhabitants in the 5 parishes of the urban area and a total of 87875 inhabitants in 40 parishes of the municipality. The city has a seaport with naval repairing and construction facilities.

The Polis Programme for the urban re-qualification and environmental enhancement of middle sized cities - of ministerial responsibility - was meant to play a role in the development of new business in areas involving high levels of competences in urban planning, design and renewal of infrastructures and structure-related equipment, as well as providing animation and profitability for areas of excellence, favouring the forming of private partnerships. The project consists of a series of works to modernise or replace outmoded social infrastructures and restore run-down parts of the central, river frontage and park sections of the city to a condition suitable and appropriate to a modern city. It tries to be environmentally friendly, promoting the extension of pedestrian precincts and areas, and be accompanied by appropriate environmental and educational campaigns. The project is part of a nationwide programme strongly supported by the European Union (EU) and the Portuguese Government to promote urban regeneration and renewal in a range of medium-sized cities in the country. The specific objectives of the Viana do Castelo programme are to restore hitherto under-utilised or degraded areas of the city and to render them useable, accessible and convivial to the citizens and inhabitants of the area. It includes several measures to stop cars from circulating at the historical centre, namely by creating new public transport connections from the outskirt, constructing several parking spaces outside the central zone and creating new green spaces in the city and in the city historical centre. The project is accompanied by a rigorous environmental management programme that includes solid wastes, air, water and noise studies, as well as preventive and remedial instruments. Among the adopted environment measures we can cite the watering of the building sites, especially during the foundations' works, the cleaning of shop-windows and pavements twice a week, the washing of the vehicle wheels, the utilisation of drilling, punching, polishing and sawing machines with jets of water and the covering of construction and excavation materials during transportation.

The objective of this work was to investigate the air quality of Viana do Castelo in the scope of the Polis Programme. To this purpose the air pollution levels were measured, with emphasis paid to NO, NO_2, CO, SO_2, O_3, particulate matter (PM_{10} and $PM_{2.5}$) and aromatic volatile organic compounds (benzene, toluene and xylenes – BTX). The occurrence of exceedances of the air quality threshold values was examined, the diurnal profiles were studied and the relationships between each other were explored. The meteorological parameters were also considered in the discussion of the results, as well possible atmospheric pollutant sources, including the construction works within the Polis project.

EXPERIMENTAL

A monitoring programme to determine hourly variation of gaseous pollutants and particulate matter concentrations at two sites in the historical centre of Viana do Castelo subjected to urban re-qualification in the scope of the Polis Programme was conducted in 2003 and 2004, making up five evaluation campaigns (Table 1). Each campaign comprised, at least, two working days and one non-working day (weekend or holiday). The monitoring sites and calendar were selected by the Parque Expo Group, which is the organisation behind all the urban regeneration projects carried out in various Portuguese cities. The locations of air quality monitoring sites are shown in Figure 1.

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Table 1. Monitoring sites and dates

Site	Campaign	Beginning	End
Campo da Agonia	1st Reference situation	0h00 January 23, 2003	24h00 January 25, 2003
	2nd Accompanying of the construction phase	0h00 April 23, 2003	24h00 April 27, 2003
	3rd Accompanying of the construction phase	0h00 October 12, 2003	24h00 October 14, 2003
	4th Accompanying of the construction phase	0h00 April 1, 2004	24h00 April 3, 2004
	5th Accompanying of the construction phase	0h00 October 24, 2004	24h00 October 27, 2004
Largo João Tomás da Costa	1st Reference situation	0h00 January 19, 2003	24h00 January 21, 2003
	2nd Accompanying of the construction phase	0h00 April 29, 2003	24h00 April 04, 2003
	3rd Accompanying of the construction phase	0h00 October 16, 2003	24h00 October 18, 2003
	4th Accompanying of the construction phase	0h00 April 6, 2004	24h00 April 12, 2004
	5th Accompanying of the construction phase	0h00 October 27, 2004	24h00 October 31, 2004

Figure 1. *The historical centre of Viana do Castelo and the two air quality monitoring sites. The shadow area signalises the extension subjected to urban re-qualification and pinpoint the construction works carried out during the last years: 1 – Blocks of flats, commerce, hospital and post-office; 2 – Underground car-park with 1200 places; 3 – Cycling road; 4 – Urban equipment; 5 – Harbour zone; 6 – Marina; 7 – Blocks of flats and other infrastructures; 8 –Liberty Square (underground car-park, library, spectacle and exhibition pavilion, building of the exchequer and employment bureau)*

The study was performed by using a mobile air quality monitoring station equipped to measure meteorological variables and atmospheric pollutants in real time (Table 2). The detailed principles of operation and the characteristics of the air quality analysers can be found in the web page of Horiba Instruments (for nitrogen oxides, carbon monoxide and ozone), Verewa (for particles) and Syntech Spectras (for BTX). Briefly, the chemiluminescence method uses the reaction of NO with O_3. A portion of the NO_2 generated as the result of this reaction becomes NO_2*. As these excited molecules return to the ground state, chemiluminescence is generated in the range of 600 nm to 3000 nm. The light intensity is in proportion to the concentration of NO molecules and by measuring it we obtain the NO concentration of the sample. A deoxidation converter changes the NO_2 to NO, which is measured. In other words, the NO_2 concentration can be obtained by the difference between (1) the NO_x concentration measured when the sample gas is directed through a converter and (2) the NO concentration measured when the gas is not run through the converter. The UV fluorescence method operates on the principle that when the SO_2 molecules contained in the sample gas are excited by ultraviolet radiation, produced by a Xe lamp, they emit a characteristic fluorescence in the range of 220-420 nm. This fluorescence is measured and the SO_2 concentration is obtained from changes in the intensity of the fluorescence. The non-dispersive infrared CO analyser uses a solenoid valve cross flow modulation. Fixed amounts of the sample gas and the reference gas are injected alternately into the measurement cell. With the cross flow-modulation method, if the same gas is used for both the sample gas and the reference gas (e.g., zero gas could be used for both), no modulation signal will be generated. This has the great advantage that, in principle, when analysing minute amounts of gas there is no generation of zero-drift. An additional advantage is that the elimination of rotary sectors precludes the need for optical adjustment. A further improvement is that in the front chamber of the detector, the measurable components, including interference components, are detected; in the rear chamber, interference components only are detected. By means of subtraction processing, the actual signal obtained is one that has only very little interference influence. The non dispersive ultra-violet absorption works on the principle that ozone absorbs ultra-violet rays in the area of 254 nm. Measurements are taken from continuous, alternate injections of the sample gas and the reference gas into the measurement cell, controlled by a long-life solenoid valve. The cross flow modulation method is characteristically zero-drift free. A comparative calculation circuit automatically compensates for all fluctuations in the mercury vapour light source and in the detector. The measuring principle of the ambient dust monitors is based on the absorption of the beta rays (electrons) emitted by a radioactive emitter through particles collected from an ambient air flow. The pulse rate of the unloaded filter tape is measured before each collecting cycle, then dust is collected on this precise filter spot

Table 2. Measuring methods

Pollutants	Method
Nitrogen oxide and dioxide (NO and NO_2)	Chemiluminescence
Sulphur dioxide (SO_2)	Pulse fluorescence (UV)
Carbon monoxide (CO)	Non-dispersive infrared photometry
Ozone (O_3)	UV photometry
Inhalable particles (PM_{10})	Beta gauge
Fine particles ($PM_{2.5}$)	Beta gauge
Benzene, toluene and xylenes	Thermal desorption/gas chromatography
Meteorological parameters	**Method**
Wind speed and direction	Ultrasonic anemometry 2D
Temperature and relative humidity	Termo-higrometry
Precipitation	Udometry
Global radiation	Pyranometry

over a pre-defined period, and finally the pulse rate of the loaded filter tape is measured. The difference between the two pulse rates is evaluated in the device and displayed as dust concentration in $\mu g/m^3$. The BTX instrument is a gas chromatograph with a built-in pre-concentration system. Hydrocarbons are pre-concentrated on Tenax GR, desorbed thermally and separated on an EPA624 equivalent column, to reach optimal separation from interfering hydrocarbons. Analysis is done by a photo ionisation detector. The technical description of the meteorological station can be found at the web page of Thies Clima.

RESULTS AND DISCUSSION

All the monitoring campaigns have registered some precipitation and nebulosity. The average temperature values ranged from 9 to 16ºC. The relative humidity was always above 49 and 52% at the Campo da Agonia and João Tomás da Costa sites, respectively. Wind-rose diagrams were constructed to find the predominant wind directions. The air masses in the first site flowed from S, SW and E. The weakest winds corresponded to this last direction, with velocities lower than 1.55 m/s. Winds from S and SW blew mainly with velocities between 3.1 and 5.1 m/s. The calm winds (< 0.55 m/s) represented 7.6% of the acquisitions. At the João Tomás da Costa site, winds were generally from W-SW and E-NE, with velocities in the ranges 3.1-5.1 m/s and 1.5-3.1 m/s, respectively. Winds lower than 0.55 m/s signified 4.2% of the registrations.

Figure 2 compares the average levels obtained in Viana do Castelo and those of other cities around the world for pollutants conventionally measured in air quality networks[1]. Excepting for O_3, in general, concentrations in the Portuguese municipality are in the range of those monitored in other European cities and lower than values registered in America and Asia.

The inter-campaigns levels obtained for the SO_2 do not show an increase after starting of the urbanistic re-qualification (Figure 3). At both sites, the average concentration, hourly maximum and daily maximum did not exceed 4, 36 and 6 $\mu g/m^3$, respectively, situating very far from the legal limits of 20, 440 and 125 $\mu g/m^3$. The average diurnal variation of SO_2 concentrations (Figure 4) shows a prominent peak at around 19-20 hours (local time) at Largo João Tomás da Costa. This increase probably derives from the emissions associated to the naval circulation in the commercial harbour, which is located in front of the monitoring site, on the other margin of the river. This traffic moves solid bulk (cement, china clay, fertilizers and wood chips), liquid bulk (asphalt), general cargo (wood in logs and pallets, aluminium, paper kraft, steel, granite, etc.), and roll-on/roll-off cargo[2].

The NO_2 concentrations do not exhibit a notorious inter-campaigns variation, at both stations. It has been registered inclusively higher levels during the monitoring of the reference situation (Figure 3). The average NO_x concentration recorded at Largo João Tomás da Costa slightly exceeded the limit of 30 mg/m^3 stipulated by the Portuguese legislation to protect vegetation. The average values of NO_2 are approximately 3 times lower than the target of 56 mg/m^3 defined to protect human health. The maximum hourly limit for NO_2 never was surpassed and the monitored values are 3.5 times inferior to the legal one. The pollution roses for the nitrogen oxides (NO, NO_2 and NO_x) measured at Largo João Tomás da Costa (not shown) allowed to verify that there are not significant differences in concentrations when the winds flow from the distinct directions. At Campo da Agonia, the highest values were obtained for air masses from north. The maximisation of levels for this wind direction points out the contribution of traffic in a surrounding trunk road, which constitutes one of the main accesses to the city centre for people coming from north. The average concentration obtained with weak winds is in the range registered in all wind directions. The average level calculated for the other site, together with calm winds, is higher than values measured with stronger wind from various quadrants, which indicates the importance of emission sources close to the air quality monitoring station.

As it was mentioned for other pollutants, the CO values monitored during the urbanistic re-qualification campaigns did not suffer an augmentation when compared with the reference stage. It was noted, inclusively, a decrease of levels at Campo da Agonia, after the first monitoring campaign (Figure 3). The hourly concentrations and 8-h averages are of the same order of magnitude at both stations. However, the maxima observed at Campo da Agonia are approximately the double of those in the other site. The limit value (10 mg/m^3) of CO for the protection of human health was never exceeded in either of the two monitoring sites.

Regarding the pollutants diurnal patterns, it is interesting that

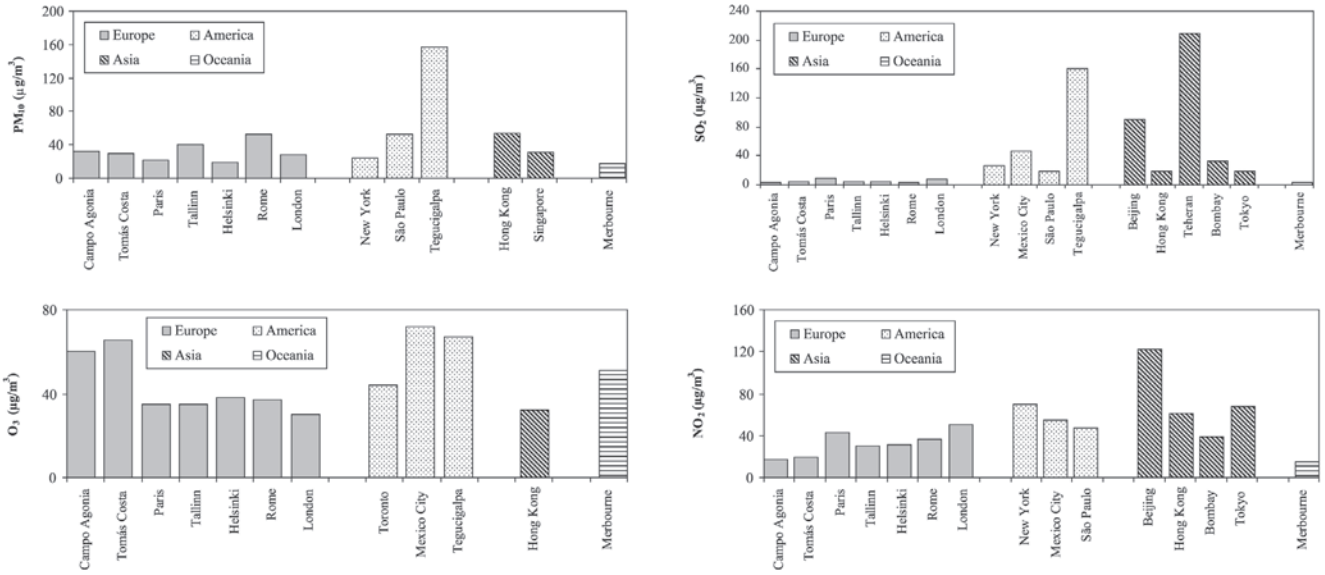


Figure 2. Comparison between the average concentrations obtained in Viana do Castelo and those of other cities around the world for pollutants traditionally measured in air quality networks[1]

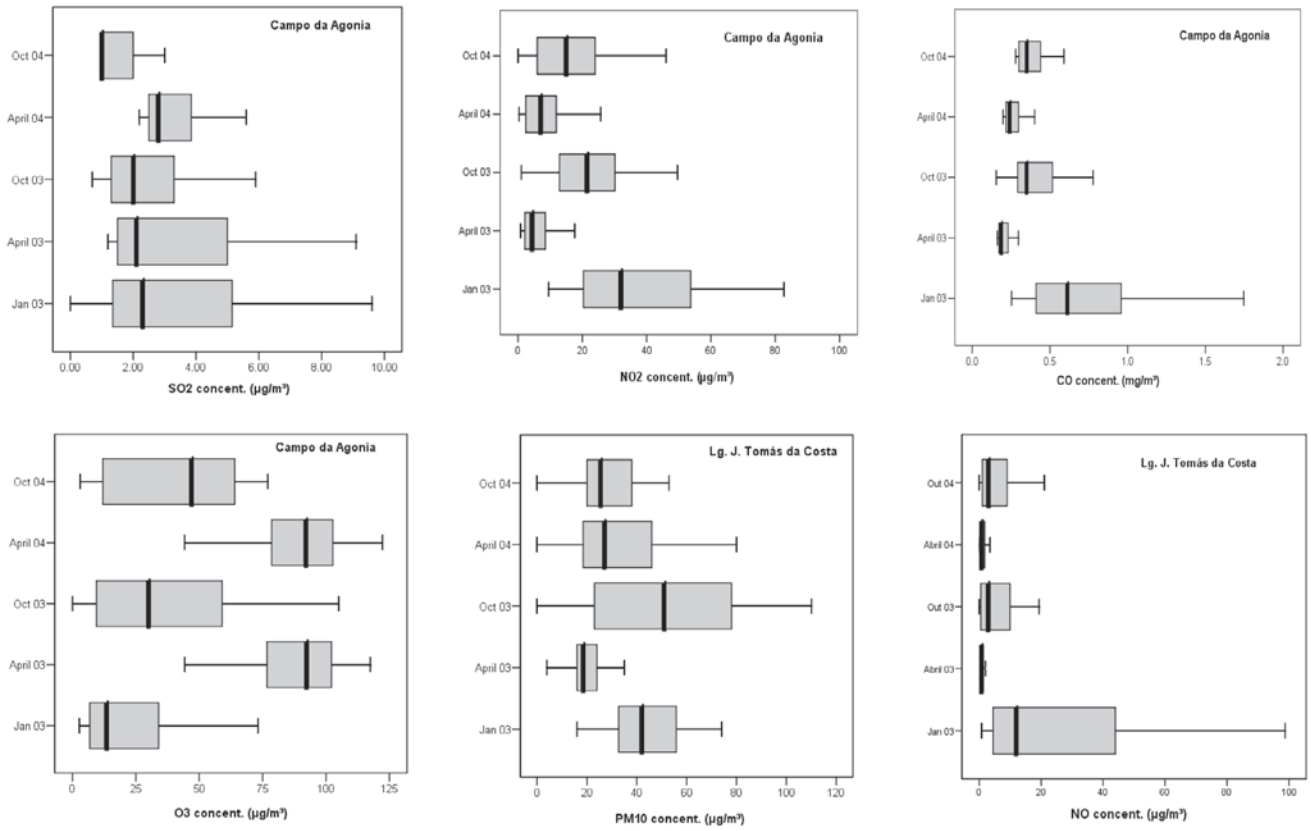


***Figure 3**. The Box-Whisker plots for air concentrations of some atmospheric compounds*

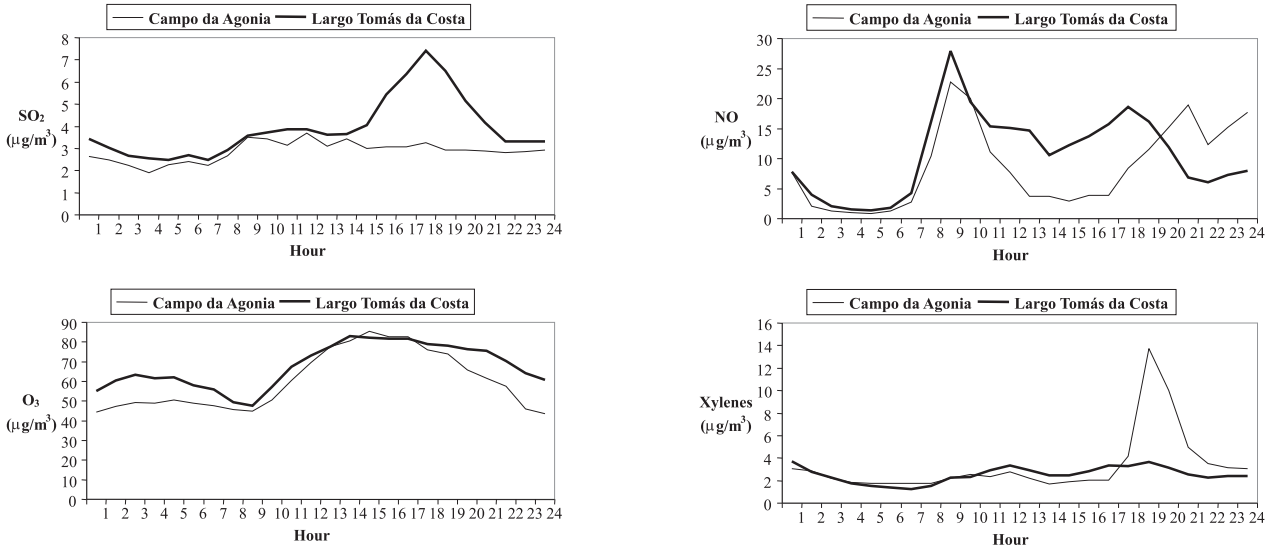


***Figure 4**. Typical diurnal patterns for SO_2, NO, O_3 and xylenes*

NO, NO_2, and CO, exhibit the typical urban daily pattern of primary air pollutants characterised by two peaks, one in the morning and one late in evening, coinciding apparently with the town activities (traffic, open market hours and central heating).

The O_3 levels recorded during the April campaigns (Figure 3) are somewhat higher that those measured in autumn, especially due to more favourable photochemical conditions to the pollutant formation. Ozone is formed in the lower atmosphere (ground level) by a complex series of chemical reactions involving reactive volatile organic compounds (VOC) and NO_x in the presence of sunlight. Because the reactions that form O_3 are driven by sunlight, and because emissions of VOC and NO_x from many sources (for example, vehicles) vary over the course of a day, O_3 concentrations display a characteristic pattern, or diurnal profile, over a typical day. Ozone concentrations are low in the morning hours; it accumulates during the day as emissions of VOC and NO_x undergo reactions, driven by sunlight, that produce O_3. Once the sun sets, O_3 production ceases, and, in an urban area, the O_3 that remains near ground level is either consumed by reactions that are not driven by sunlight, or deposits onto surfaces. Ozone that is not trapped near ground level can be transported significant distances by winds. This set of processes results in a typical diurnal pattern for O_3, shown in Figure 4. It can be seen, however,

that nocturnal O_3 do not decrease towards lower levels as expected. This can be explained by vertical mixing of high ozone concentrations from higher levels or horizontal transportation from rural areas through local and mesoscale wind systems.

The particles originate not only from combustion processes and construction activities, but also from the resuspension of the material deposited on the street and road surfaces. Resuspension of street dust is also influenced by other meteorological factors, *e.g.*, the precipitation, the relative humidity and the wind speed. Resuspension is commonly initiated by traffic-induced turbulence, and it is affected by the properties of the vehicle fleet and street maintenance procedures[3,4]. The average concentrations of PM_{10} and $PM_{2,5}$ in either of the sampling stations are very close and strictly respect the national legislation. It was verified an increase of levels in the course of October 2003, which may be related to building construction in the scope of the Polis Programme (Figure 3). However, in spite of the initiation of new public works in 2004 with potential impact in the atmospheric particulate levels, such as excavations and construction activities for the new municipal library, the peripheral road to by-pass the city centre, and two underground parking places, in fact, a reduction in concentrations was observed in comparison with the previous year. Thus, the registered variation should be interpreted taking into account not only the emission sources, but also the atmospheric dispersion and removal mechanisms. Artiñano *et al.*[5] presented a $PM_{2.5}/PM_{10}$ ratio for Madrid exhibiting a clear seasonal behaviour. Maxima were recorded in autumn/winter, whereas in spring and particularly in the summer months, this ratio dropped to around 0.40. The authors attributed this observation to the nature of the particulate matter, which has a larger crustal/mineral content in summer mainly allocated to the PM_{10} fraction. In winter, and especially during pollution events due to combustion processes that included traffic emissions, the $PM_{2.5}/PM_{10}$ ratio experienced a pronounced increase. At Viana do Castelo, the ratio fluctuated from 0.15 to about 0.7. The higher value was registered in October 2003, probably as a consequence of a pollution event followed by low atmospheric dispersion.

The use of ratios between BTX concentrations allows us to give an estimate of air mass age and origin. Stark changes in these ratios generally imply a change of air mass. Benzene, toluene and xylenes are evident in all motor vehicle-related source profiles, but are present in different proportions in each source-type. These compounds also vary considerably in their relative reactivities and have estimated atmospheric lifetimes ranging from more than a week (benzene) to several days (toluene) to less than 24 h (xylenes)[6,7]. Consequently, these compounds may prove useful in distinguishing among source types and in identifying influences from fresh *versus* aged emissions. There is a difference in the X/T ratios between night time samples (when reactivity is minimal) and daytime samples (when reactivity is maximal), Figure 5. This is consistent with a predominant influence of transported, motor vehicle-related emissions, which are photochemically aged (in a highly variable way) during the day, but which remain relatively unaged in the absence of sunlight. When motor vehicle-related are the dominant sources, the typical values for the B/T ratio range between 0.2 and 0.6[8,9], and this was verified at Viana do Castelo. Studies on vehicular exhaust in general report a ratio of X/T of approximately 0.6. At Viana do Castelo, this ratio presents much greater values, which indicates probable inputs from other sources and particularly from the shipyards.

The average concentrations of BTX did not exceed 1.0, 3.2 and 3.3 μg/m^3 for benzene, toluene and xylenes, respectively. The average diurnal variations for the xylenes at Largo Tomás da Costa are similar to those of NO_2 and CO. At Campo da Agonia, it is

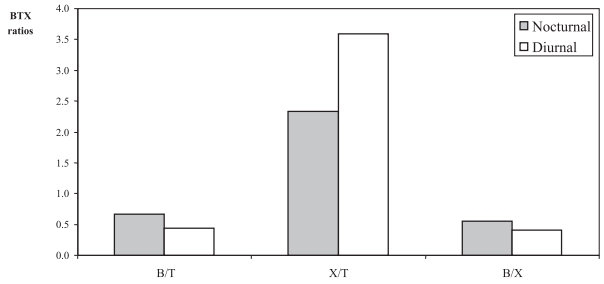
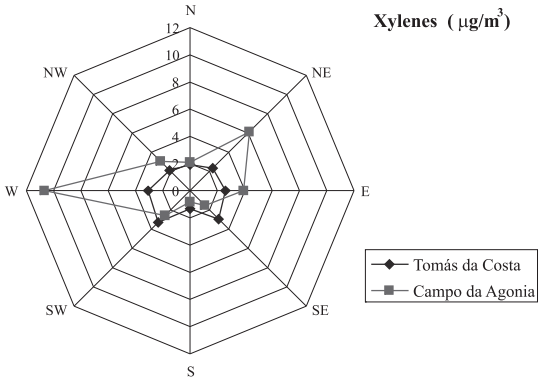


Figure 5. *Average ratios between concentrations of BTX*

clear a peak around 19 hours. The pollution rose (Figure 6) for this site shows higher levels associated with air masses from west. Taking into account that the shipyards are located towards the west with regard to the monitoring site, it is expected that emissions result from inks, varnishes, cleaning products for metallic surfaces and degreaser products, which have xylenes in their constitution. It is curious to note that operations with these products, presumably xylene emitters, occur at the end of the afternoon. Figure 7 compares the benzene levels registered at Viana do Castelo and other cities all over the world[10-28]. Slightly higher benzene levels were registered during the nineties in Europe (2–36 μg/m^3) and Asia (7–31 μg/m^3, excepting Calcutta), whereas concentrations in North America and Oceania were the smallest (≤8 μg/m^3). In North America, catalytic converters to control vehicular emissions are broadly used and result in low ambient benzene[10,29]. On the other hand, in Europe and Asia, the adoption of unleaded fuels in the last decade was accompanied by an augment in the benzene content of gasoline (up to 5%), and catalytic converters are still being progressively implemented[9,10]. Harrison[30] assured that six persons in a population of one million can develop leukaemia when exposed in their lifetime to a benzene concentration of 1 μg/m^3. The average level of 1 μg/m^3 for Viana



	Frequency of wind direction (%)	
Site	**T. Costa**	**C. Agonia**
North	0.3	6.3
Northeast	6.4	24.8
East	24.8	9.8
Southeast	11..5	2.5
South	21.8	9.8
Southwest	23.1	31.6
West	8.0	10.6
Northeast	4.5	4.5
Average conc. with calm winds	**8.5**	**4.3**

Figure 6. *Pollution rose for xylenes and association between wind frequency and different direction sectors*

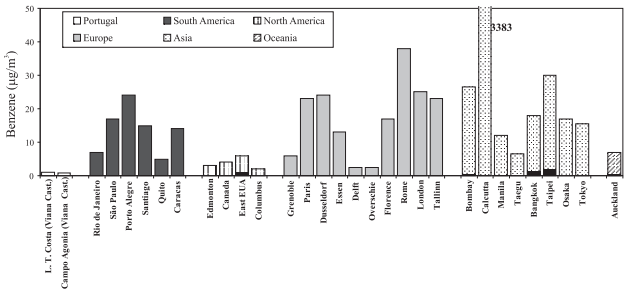


Figure 7. *Average benzene levels for Viana do Castelo and other cities in Latin America[10-12], North America[13,14], Europe[15-22], Asia[9,20,23-27] and Oceania[28]*

do Castelo would lead to a rough estimate of 0.2 extra cases of leukaemia in 36546 persons living in the small metropolitan area.

Figure 8 illustrates the weekly cycles of atmospheric concentrations for various pollutants. Although, weekly changes in the emissions caused by human activities are known to affect the weekly cycle of ambient pollutant concentrations, this emission-concentration relationship is not well elucidated. During weekends, the emissions of anthropogenic pollutants are not noticeably lower compared to those occurring during weekdays, because car traffic does not suffer a visible reduction. This may be attributable to the fact that Viana do Castelo is a tourist destination during weekends because of its shopping, beaches, luxuriant forest, sanctuaries and historical centre. Weekday/weekend differences in ambient levels have been studied, reflecting controversial results[31,32].

Hourly mean values of CO, benzene and toluene were positively correlated (r^2=0.78-0.83), indicating common sources and common dilution processes of fresh emissions. A correlation between benzene and NO_2 was less evident (r^2=0.60), because it is both a primary pollutant (direct emission from combustion) and a secondary one (from the reaction of NO with O_3 or peroxy radicals). The data sets for NO and NO_2 concentration showed a typical relationship described as a power functional curve ($[NO_2]=5.95[NO]^{0.54}$; r^2=0.62). The mathematical function that described the relationship between NO and O_3 was $[O_3]=83.53[NO]^{-0.63}$, r^2=0.53. In the case of low NO concentrations, which means a high O_3 concentration condition, the inclination of the power function curve is larger than the inclination in the case of high NO condition, which means low O_3 concentration conditions. Rich O_3 concentration conditions can oxidise NO easily and produce NO_2 in low NO conditions which caused a larger inclination of the curve. However, under a lean O_3 concentration condition, NO is considered to be hardly oxidised, resulting a lower inclination of the curve[33].

In a further attempt to assess the sources or processes responsible for the observed pollution, Principal Component Analysis (PCA) was applied to the atmospheric compounds and meteorological parameters by using the software package of SPSS. This was performed by utilising the orthogonal transformation method with Varimax rotation and retention of Principal Components whose eingenvalues were greater than unity. Table 4 shows the results obtained for Campo da Agonia. In the total data set, 5 components were extracted, which encompass approximately 81% of the variability of the 17 parameters. The first factor explains about 36% of the total variance and loads heavily on nitrogen oxides, carbon monoxide, benzene and toluene (and inversely for ozone) and is attributed to local road traffic sources. In PC2, the most prominent species were PM_{10} and $PM_{2.5}$. Hence, this factor should be correlated with combustion processes and crustal/mineral sources linked to construction-related activities and resuspension from roads, which generate fugitive dust. PC3 loads on temperature and radiation, contributing to 12.5% of the observed variance. In fact, profiles of these two meteorological parameters play an important role in air quality, influencing atmospheric photochemistry. PC4 most likely represents and industrial source, since it has high loading on SO_2. PC5, with higher factor loading for rain, probably identifies scavenging processes contributing to the wet removal of pollutants. Similar results were obtained for Largo João Tomás da Costa, where traffic was also the source contributing to the maximum explained variance. The extracted components explain nearly 71% of the variability in the original data set. A minor fraction of the variance observed is connected with meteorological parameters.

CONCLUSIONS

The levels of atmospheric pollutants did not suffer a significant variation when results of the reference monitoring campaign are compared with those obtained during the succession of the Polis Programme. The average NO_x concentration measured at Campo da Agonia slightly exceeded the limit of 30 mg/m³ stipulated by the Portuguese legislation to protect vegetation, in October of 2003, as it was registered in January of the same year during the reference campaign. At Largo João Tomás da Costa, the average values of NO_x, in October of 2003 and during the campaigns of 2004, also surpassed the Portuguese standard of 30 mg/m³. The hourly limit of 280 mg/m³ to protect human health was never exceeded. For both monitoring sites, the daily maxima of 8 hours average of CO and the O_3 highest hourly values were lower than the air quality limit values of 10 mg/m³ and 240 µg/m³, respectively. In October of 2003, at both sites, the average and maximum hourly concentrations of PM_{10} went beyond the annual and daily permissible limits of 45 and 65 µg/m³, respectively. The annual limit stipulated for benzene was never exceeded. In general, the average concentrations of air pollutants obtained in Viana do Castelo are lower than those of other cities around the world. Excepting for SO_2 and O_3, it was not observed a clear pattern with higher levels of atmospheric pollutants on weekdays than on weekends. The diurnal patterns and the observed correlations between the hourly concentrations of NO_x, CO, benzene and toluene indicate a provenience mainly connected to traffic emissions. The pollution

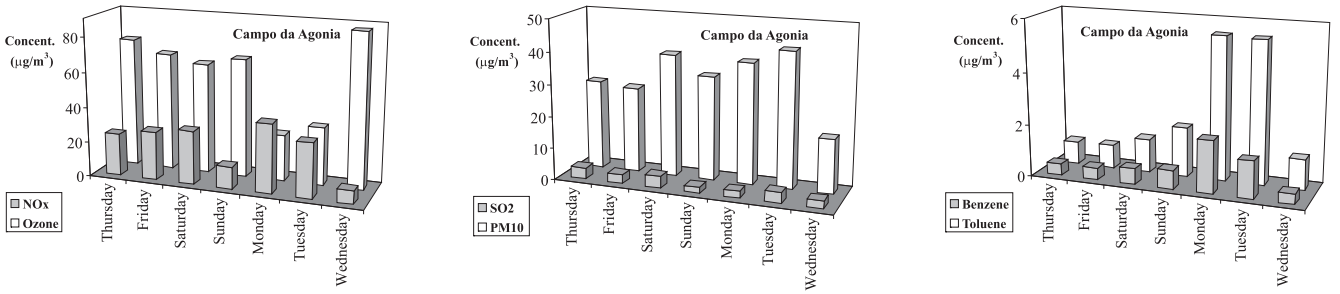


Figure 8. *Average weekly cycles of air pollutants concentrations for one of the monitoring site*

Table 3. National air quality standards of Portugal

Pollutant	Designation	Period	Standard	Legislation
SO_2	Hourly limit to protect human health	Hourly	440 μg/m³, that should not be exceed more than 24 fold a year	DL nº 111/2002
	Daily limit to protect human health	Daily	125 μg/m³, that should not be exceed more than 3 fold a year	
	Limit value to protect ecosystems	Annual calendar and winter (Oct. 1 – March 31)	20 μg/m³	
	Alert limit	3 consecutive hours	500 μg/m³	
NO_2 and NO_x	Hourly limit to protect human health	Hourly	280 μg/m³ of NO_2, that should not be exceed more than 18 fold a year	DL nº 111/2002
	Limit to protect human health	Annual	56 μg/m³ of NO_2	
	Limit to protect vegetation	Annual	30 μg/m³ of NO_x	
	Alert limit	3 consecutive hours	400 μg/m³	
CO	Hourly limit to protect human health	Daily maximum of 8 h average	10 mg/m³	DL nº 111/2002
O_3	Limit to protect human health	8 h	120 μg/m³	DL nº 293/2003
	Limit to inform population	Hourly	180 μg/m³	
	Alert limit	Hourly	240 μg/m³	
PM_{10}	Limit to protect human health	Daily	65 μg/m³, that should not be exceed more than 35 days a year	DL nº 111/2002
	Limit to protect human health	Annual	45 μg/m³	
Benzene	Limit to protect human health	Annual	10 μg/m³	DL nº 111/2002

Table 4. Principal Component Analysis (Varimax with Kaiser Normalization) applied to data from Campo da Agonia

	PC1	PC2	PC3	PC4	PC5
NO	**0.866**	-0.202	0.187	-0.045	0.018
NO_2	**0.779**	0.391	-0.200	0.154	-0.071
NO_x	**0.940**	0.162	-0.048	0.077	-0.040
CO	**0.897**	0.206	-0.213	-0.003	-0.064
SO_2	0.106	0.179	-0.015	**0.886**	0.075
O_3	**-0.816**	-0.214	0.344	0.133	0.059
Benzene	**0.791**	0.312	-0.207	-0.073	-0.019
Toluene	**0.827**	0.436	0.026	-0.047	0.011
Xylenes	0.560	0.531	0.046	0.066	-0.088
PM_{10}	0.213	**0.894**	0.147	0.099	-0.054
$PM_{2.5}$	0.339	**0.852**	0.071	0.075	-0.007
Temperature	-0.060	0.442	**0.714**	-0.107	-0.045
Rel. Hum.	0.402	0.124	-0.430	-0.536	0.336
Wind Speed	-0.432	-0.392	0.333	0.333	0.338
Wind Direct.	-0.474	0.393	0.530	-0.184	0.243
Rain	-0.069	-0.065	-0.108	0.021	**0.927**
Radiation	-0.047	-0.046	**0.845**	0.164	-0.119
Eingenvalues	7.339	2.738	1.426	1.153	1.041
Cumulative % variance	35.8	53.2	65.7	73.6	80.6

Factor loading values >0.70 are in bold.

rose for xylenes points out higher levels when air masses transport the emissions of the shipyards. The civil engineering works of urban regeneration and restoration, building construction, repavement of streets and gardening performed in the scope of the Polis Programme affected only the atmospheric particulate levels, which suffered a weakly increase in October of 2003. It was also noted an influence of meteorological parameters, especially rain scavenging of particulate matter. The data of this study would be useful for future comparisons, after the operation of the new infrastructures in the city, which certainly will cause changes in pollutions levels, over all as a consequence of changes in the traffic flow.

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SUPPLEMENTARY INFORMATION

Additional information on wind roses, $PM_{2.5}/PM_{10}$ ratios, relationships between air pollutants and multiple regression analysis is available free of charge at http://quimicanova.sbq.org.br, as a PDF file.

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ASSESSMENT OF AIR QUALITY IN VIANA DO CASTELO, PORTUGAL, IN THE SCOPE OF THE POLIS PROGRAMME

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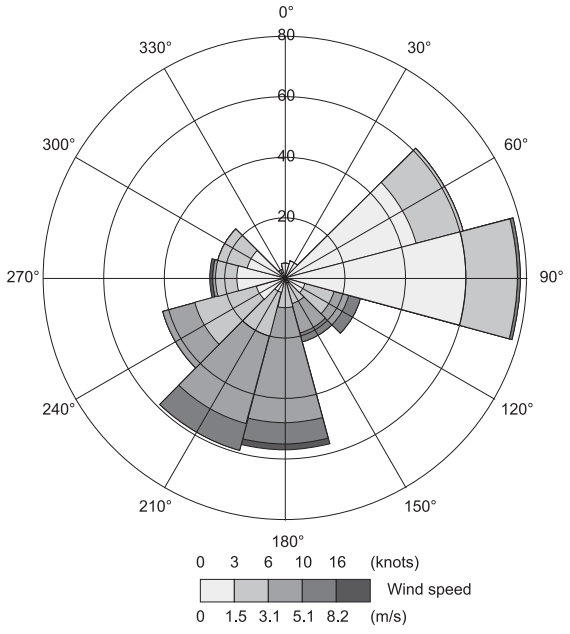
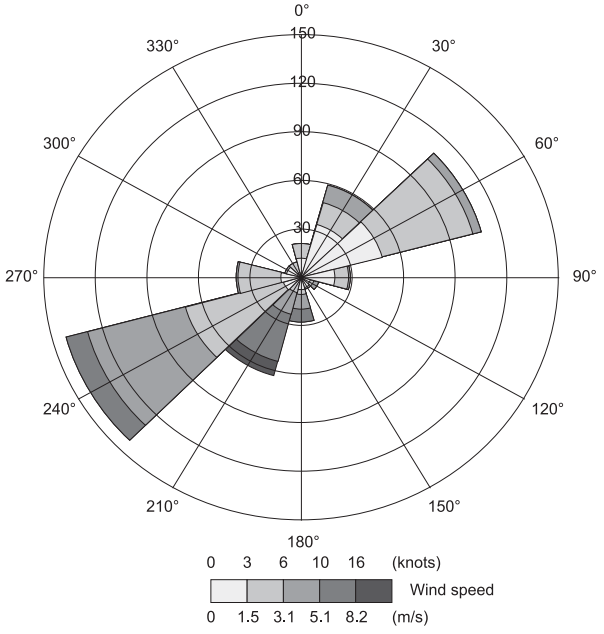


Campo da Agonia



Lg. João Tomás Costa

Figure 1S. *The wind rose plots for the two monitoring sites*

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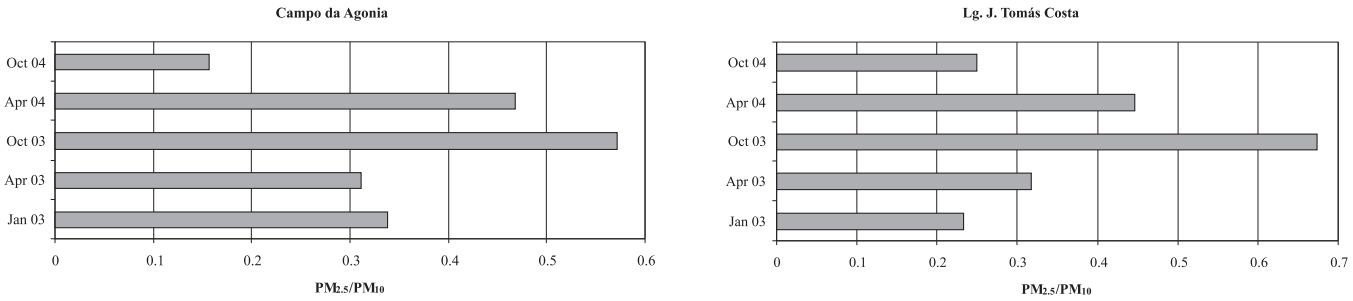

Figure 2S. *$PM_{2.5}/PM_{10}$ ratio for Viana do Castelo obtained during the five campaigns at the two monitoring sites*

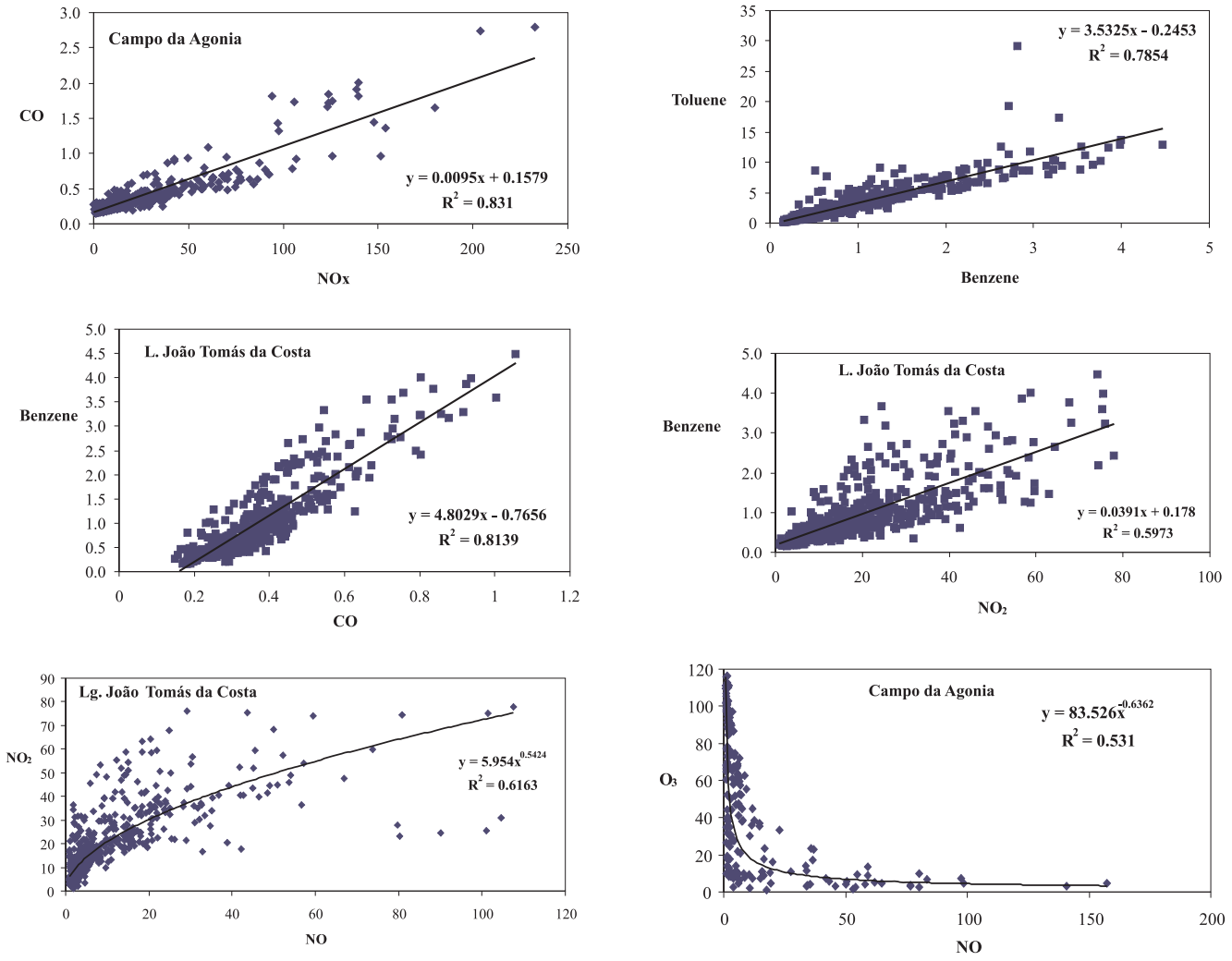

Figure 3S. *Some relationships between air pollutants*

Multiple regression analysis was applied to the gaseous and particulate atmospheric compounds to verify the relationships between the monitored levels and meteorological factors. Some of the regression equations that were obtained, as well the respective statistic parameters, are given in Table 1S. If the *t* values associated with each one of the variables and the *F* observed value are higher (absolute value) than the critical values for the respective degrees of freedom (d_f), then the calculated coefficients have statistical predictive significance. As seen from the equations, only 19 to 43% of atmospheric pollutants depend on meteorological variables.

Table 1S. Multiple regression analysis (least square method), $y = a_1 x_1 + a_2 x_2 + b$, where y is the dependent variable (air pollutants), x_1 and x_2 are the independent variables (meteorological parameters), a_1 and a_2 are the coefficients of regression and b is the constant of regression (significance level = 5%)

Equation	r^2	t_1	t_2	d_f	t_{crit}	F_{obs}	F_{crit}	Site
NO_2 = -0.2154 (T) + 0.5228 (RH) – 4.5916	0.3361	-3.22	0.45	403	1.65	50.99	3.04	Campo da
O_3 = 10.2260 (T) + 3.87701 (WS) – 18.3208	0.4259	12.22	8.68	405		150.21		Agonia
NO_2 = -4.2800 (T) – 1.1260 (WS) + 42.7200	0.3187	-10.85	-5.35	405		94.74		
O_3 = 4.7014 (T) + 0.0337 (Radiation) – 4.2279	0.2646	7.70	3.28	333		59.92		
Toluene = 0.0552 (T) - 0.1503 (RH) – 0.5412	0.2248	3.68	-0.70	331		23.99		
Benzene = 0.0207 (T) - 0.0531 (RH) – 0.1755	0.2860	4.43	0.80	333		33.14		
Toluene = -9.57×10^{13} (RH) + 0.0541 (WS) – 0.1520	0.2250	0.27	3.52	330		19.16		
Benzene = -4.47×10^{13} (RH) + 0.0202 (WS) – 0.0539	0.2864	-0.41	4.42	330		26.48		
Toluene = 0.0552 (T) - 0.15031 (HR) – 0.5400	0.2248	3.67	-0.70	331		23.99		
Benzene = 0.0580 (WS) – 0.2345 (Rain) + 1.4932	0.2261	0.89	-9.69	333		59.64		
Toluene = 0.0469 (WS) – 0.2345 (Rain) + 1.4930	0.2260	0.88	-9.69	333		59.64		
PM_{10} = -5.6979 (T) + 2.7000 (WS) + 8.8840	0.1904	-8.18	7.27	405		42.63		
NO_2 = -3.1321 (T) + 0.9165 (WS) + 14.0801	0.2103	-11.13	5.07	549	1.65	73.10	3.03	Lg. João
NO_2 = -3.4004 (RH) + 0.2072 (WS) + 1.5940	0.2513	-12.21	5.48	548		61.30		Tomás Costa
O_3 = 7.1557 (T) + 2.2441 (WS) + 14.5461	0.3303	14.60	7.12	549		135.37		
CO = -0.0333 (RH) + 0.0023 (WS) + 0.0126	0.2452	-12.38	6.35	548		59.33		
CO = -0.0303 (T) + 0.0050(WS) + 0.3598	0.1897	-11.05	-2.85	549		64.25		
SO_2 = -0.5464 (T) + 0.6343 (WS) – 4.1255	0.2767	-7.11	12.84	549		104.99		
SO_2 = -0.4889 (RH) - 0.0444 (WS) + 0.4892	0.2997	-6.36	-4.25	548		78.19		
SO_2 = 0.8728 (Radiation) - 0.0044 (T) – 8.1795	0.2400	11.07	-4.27	477		76.27		
Benzene = -0.1884 (RH) – 0.0215 (WS) + 0.0942	0.3139	-10.36	11.50	476		72.58		
Toluene = -0.7219 (RH) + 0.0849 (WS) + 0.3694	0.2996	-9.85	11.26	476		67.87		
Xylenes = -0.5162 (RH) + 0.0616 (WS) + 0.3571	0.2173	-7.52	8.73	476		44.06		
PM_{10} = -0.0536 (RH) + 0.4298 (WS) + 3.6146	0.2086	-0.14	8.00	548		48.16		
$PM_{2.5}$ = -1.2311 (RH) + 0.2607 (WS) + 2.2407	0.2047	-4.82	7.52	548		47.00		