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ORIGINAL ARTICLE

Measuring air particulate matter in large urban areas for health effect assessment

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Abstract This study deals with Particle Matter (PM) levels in the metropolitan area of Lisbon and shows that EU directive is exceeded in a systematic way, mainly due to the inner city traffic. Results show that it is important to develop an epidemiological study in Lisbon to find a possible association between PM levels, sources and morbidity. Some important issues related with a monitor's representation of regional, sub-regional, and local air pollution exposures to the population in the metropolitan area are highlighted. $PM_{2.5}$ and PM_{10} total mass concentration measured in several places located in both centre of Lisbon and the outskirts are quite well correlated, mainly considering that two measuring methodologies (automatic and gravimetric) were used and areas with different classifications (urban and suburban) were analysed. However, the results imply that a source-oriented evaluation of PM health effects needs to take into account the uncertainty associated with spatial representativity of the species measured at a single sampling station. Temporal correlation across sampling stations, within relatively short separation distances, varied considerably for some important elements (Zn, Sb, Cu, As and Br), indicating that the precision of population exposure estimates for specific elements can vary depending on the species.

Keywords Aerosols · Morbidity · Sources · Sampling · Spatial representative

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1 Introduction

Epidemiological studies have consistently shown an association between PM pollution and the number of deaths from cancer and cardiovascular and respiratory diseases (Pope *et al.*, 2002). There is also evidence linking particulate air pollution and increases in hospital admissions for respiratory (Roemer *et al.*, 1993; Pope, 1991; Burnett, 1995) and cardiovascular diseases (Burnett, 1995; Schwartz *et al.*, 1995). In response to these adverse effects of air pollution, the EU Commission defined limit values for PM_{10} concentrations in ambient air (EU Directive 1999/30/EC) and highlighted the importance of $PM_{2.5}$ because epidemio-

logical studies indicated that the $PM_{2.5}$ fraction may be responsible for the adverse effects of PM_{10} (Pope *et al.*, 2002; Schwartz *et al.*, 1996; Dockery *et al.*, 1993).

In Europe, as well as in the US, gravimetric methods for PM_{10} measurements have been defined as reference methods. These methods are, however, labour-intensive, expensive and therefore not ideally suited for routine compliance measurements. In addition, due to the time consuming analytical procedure, several days are needed from the sampling until the results become available. Therefore, no on-line PM concentrations information can be obtained from measurements with the standard reference methods. These disadvantages could be avoided with automatic on-line monitors, which are already in operation in many monitoring networks. Moreover, monitors provide a far better time resolution, thus, giving also information on the variability of the PM concentrations during the day.

The combination of PM_{10} and $PM_{2.5}$ data from automatic monitors and a limited number of gravimetric PM_{10} and $PM_{2.5}$ values, with their chemical characterization, can be excellently suited to verify the different human responses to different PM levels and composition. On one hand, daily concentrations, provided by automatic monitors, are necessary to avoid problems associated with the timing gap between the cause and the health effect. On the other hand, chemical speciation information can be useful for source-oriented evaluations of PM health effects. In fact, one natural progression of PM health effects research is to conduct a PM source-apportionment using chemical speciation data and to examine the associations between source-apportioned PM and health outcomes, rather than with PM mass overall.

There are several issues that need to be considered in the analysis and interpretation of these data. Firstly, data from automatic monitors cannot be considered equivalent to ones from reference methods (gravimetry based) because of the significantly different measurement methodologies. Secondly, a monitor's representation of regional, sub-regional, and local air pollution exposures to the population in a city or metropolitan area should be evaluated. Health outcomes in time-series air pollution epidemiological studies are aggregated over a wide geographical area. Therefore, it is possible that one single sampling station does not represent each of the sources types for the population exposure. In Lisbon, the morphology of the soil also contributes for significant differences between concentrations measured in different sampling stations. The complex morphology of Lisbon promotes the existence of areas with different dispersion conditions. Regional PM pollution may have smaller errors in exposure estimates than more spatially varying local pollution (Ito *et al.*, 2004).

In this study, we attempt to evaluate the above mentioned issues by analyzing available PM data from six places in the great Lisbon during 2001–2003.

2 Experimental

Table 1 lists the six sites where PM measurements with manual gravimetric method and beta attenuation monitors have been performed and the data available for each station. Fig. 1 shows the geographical position of the sites within the great Lisbon.

Bobadela (BOB), São João da Talha (SJT) and Póvoa de Sta Íria (PSI) sampling stations were placed in a sub-urban area in the outskirts of Lisbon. They were located northeast from the urban centre of Lisbon, being surrounded by high density traffic roads and industrial activities including an urban waste incinerator, a fuel oil

Table 1 Characterization of the sites, available data series and measuring times of gravimetric and beta attenuation method

	Characterization of the site	$PM_{2.5}$	$PM_{2.5-10}$	PM_{10}	Chemical analysis	Measuring time
Olivais (OLI)	Sub-urban			2001–2003		Hourly
Entrecampos	Urban	2002–2003		2001–2003		Hourly
(ENT)	Urban	2002–2003		2001–2003		Hourly
Av. Liberdade	Urban			2001–2003		Hourly
(LIB)	Urban			2001–2003		Hourly
Bobadela (BOB)	Sub-urban	2001–2003	2001–2003		2001–2003	24 h (twice a week)
S. João da Talha	Sub-urban	2001–2003	2001–2003		2001–2003	24 h (twice a week)
(SJT)		(autumn/winter)	(autumn/winter)		(autumn/winter)	
Póvoa de Sta Iria	Sub-urban	2001–2003	2001–2003		2001–2003	24 h (twice a week)
(PSI)		(spring/summer)	(spring/summer)		(spring/summer)	

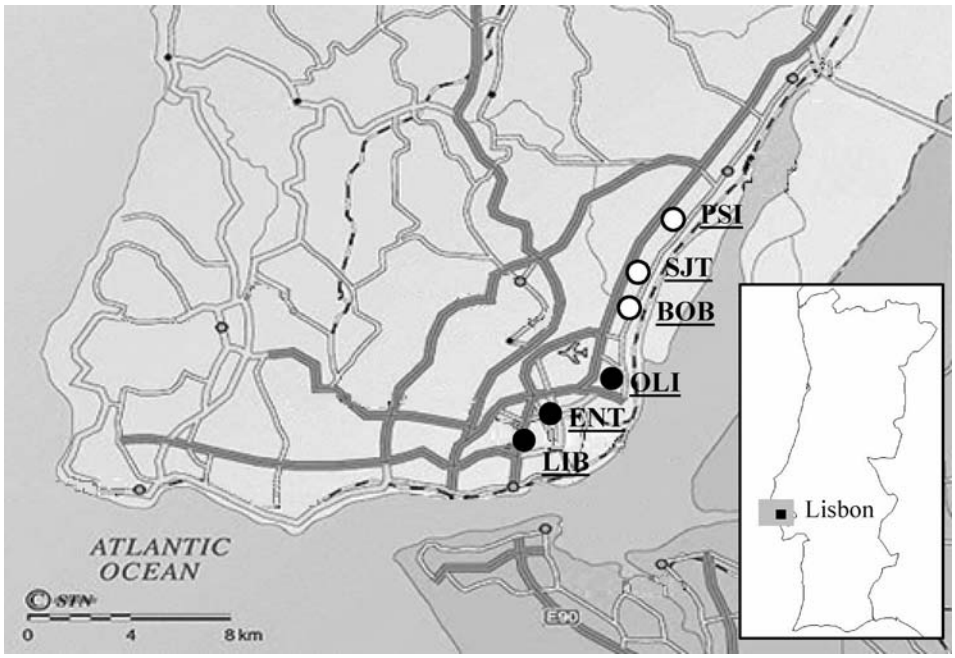

Fig. 1 Localization of sampling sites. Portuguese Environment Institute (IA) automatic data (•) and Technological and Nuclear Institute (ITN) gravimetric data (○)

power station, a cement factory and several chemical, food and glass factories. The sampling was carried out under contract for air quality monitoring of an urban waste incinerator. PM samples were collected twice a week, during 24 h periods. SJT station worked during autumn and winter seasons and PSI station sampled in spring and summer seasons. BOB station collected aerosols samples during the whole period.

Sampling was done with one low volume (Gent PM_{10} sampler) equipped with a Stacked Filter Unit (SFU), which carried, in two sequential stages, 47 mm Nuclepore polycarbonate filters, with 8 and 0.4 μm pore sizes. Upstream of the coarse filter was located a pre-impactor stage. The air was sampled at a rate of 15-16 l min^{-1}, which allowed the collection of coarse particles with aerodynamic diameters (AD) between 2.5 and 10 μm, in the first stage, and fine particles with AD $<$ 2.5 μm in the second stage (Maenhaut, 1992). The filter loads were measured by gravimetry in a controlled clean room (class 10000). The exposed filters were cut into three parts of different sizes: half was analyzed by Instrumental Neutron Activation Analysis (INAA) (Bowen and Gibbons, 1963) with the k_0 methodology (De Corte, 1987); a quarter was analyzed by Particle Induced X-Ray Emission (PIXE) (Johansson and Campbell, 1988); the remaining filter quarter was kept in storage for eventual measurements or replicates.

In Bobadela, during the year 2001, sampling was also made with one high volume sampler, which operated side by side with the Gent sampler. The high volume was equipped with a Sierra PM_{10} size selective inlet and a Sierra single stage impactor plate to separate particles in two size fractions: 2.5 μm $<$ AD $<$ 10 μm and AD $<$ 2.5 μm. This sampler operated at a flow rate of 1.13 m^3 min^{-1}. High Volume aerosol samples were collected on pre-washed and thermally treated Whatman QM-A quartz fibre filters (Tanner *et al.*, 1979).

Exposed quartz fibre filters were used for the determination of water soluble inorganic ions and for measurement of elemental carbon and organic carbon content. For water soluble ions determination, one portion of the filter was extracted with distilled deionised water by ultrasonic and mechanical shaking and filtered through a pre-washed Whatman 42 filter. The aqueous extract was analyzed by Ion Chromatography (Chow and Watson, 1999) (Cl^-, NO_3^- and SO_4^{2-}), Indophenol-blue Spectrophotometry (Weatherburn, 1967) (NH_4^+), Atomic Absorption Spectroscopy (Grohse, 1999) (Ca^+, Mg^{2+}, Na^+ and K^+) and Potenciometry (H^+).

Elemental carbon and organic carbon contents were determined in another portion of the quartz fibre filters with a thermo-optical system, based on the thermal desorption/oxidation to CO_2 with subsequent determination by non-dispersive infrared spectrophotometry (Pio *et al.*, 1993).

The details of sampling and analytical control tests are given in Almeida (2004), Almeida *et al.* (2003a, 2003b) and Freitas *et al.* (2005).

Avenida da Liberdade (LIB), Entrecampos (ENT) and Olivais (OLI) stations belong to the Portuguese Environment Institute (IA) Air Quality Monitoring Network (IA, 2005). The latter consists on several stations distributed in Portugal providing hourly data of the main atmospheric pollutants such as ozone, nitrogen and sulphur oxides, carbon monoxide and particulate matter. Beta-attenuation monitors are used for PM_{10} and $PM_{2.5}$ automatic measurements. A loss of particulate mass could be produced by evaporation of semivolatile compounds during filter collection, due to the air sample heating to remove particle-bound water. IA (2005) quantified the loss of material and therefore, in these stations, PM_{10} results were multiplied by 1.18. Avenida da Liberdade and Entrecampos stations can be regarded as typical urban traffic stations. Olivais station is placed in the outskirts of Lisbon in a sub-urban area.

3 Results

3.1 Limit values exceedances

The EU standards are based on daily and annual limit values for PM_{10} levels that become progressively more restrictive from 2001 to 2010. After January 2005, annual PM_{10} levels should not exceed 40 $\mu g\ m^{-3}$, and the daily mean concentration of 50 $\mu g\ m^{-3}$ should not be exceeded more than 35 days per year. After January 2010, annual PM_{10} levels should not exceed 20 $\mu g\ m^{-3}$, and the daily mean concentration of 50 $\mu g\ m^{-3}$ should not be exceeded more than 7 days per year.

Daily averages were obtained from PM_{10} hourly data for Olivais, Entrecampos and Av. da Liberdade sampling stations. The number of exceedances of the daily limit value was estimated. In addition, annual arithmetic averages were obtained from the daily values to be compared to the EU directive limit values (Table 2, Fig. 2).

Table 2 Number of analyzed days, PM_{10} annual average concentration and number of days with PM_{10} average concentration higher than 50 $\mu g\ m^{-3}$ in Olivais, Entrecampos, Av. da Liberdade, Bobadela, S. João da Talha and Póvoa de Sta Íria

		2001	2002	2003
Olivais	N	349	360	355
	Average	33	26	26
	No. days > 50 $\mu g/m^3$	65	30	41
Entercampos	N	287	288	364
	Average	41	42	46
	No. days > 50 $\mu g/m^3$	78	85	122
Av. Liberdade	N	360	356	363
	Average	62	59	56
	No. days > 50 $\mu g/m^3$	236	223	192
Bobadela	N	104	104	105
	Average	32	27	27
	No. days > 50 $\mu g/m^3$	10	8	6
S. João Talha	N	47	51	52
	Average	42	44	35
	No. days > 50 $\mu g/m^3$	12	12	7
Póvoa Sta Íria	N	48	53	51
	Average	35	28	30
	No. days > 50 $\mu g/m^3$	9	4	8

As regards the first stage considered by the directive, in the selected urban stations, the 50 $\mu g\ m^{-3}$ daily limit value was exceeded more than 35 times yr^{-1} and the average was higher than 40 $\mu g\ m^{-3}$, during the three years.

In Olivais, the annual limit value established up to 2005 was not exceeded. However, the annual averages concentrations were also very high exceeding the limit value proposed for 2010. The daily limit value was exceeded more than 35 times yr^{-1} in 2001 and 2003.

In Bobadela, PM_{10} average concentrations were above the EU annual PM_{10} standard of 20 $\mu g\ m^{-3}$ targeted for 2010. The EU 24 h PM_{10} limit value of 50 $\mu g\ m^{-3}$ was exceeded more than 7 times in the three years of study. The scenario may be worst because only 104 days per year were analysed in Bobadela. In São João da Talha and Póvoa de Sta Íria with approximately 14% of the year analysed the results indicated that daily limit value was exceeded in both stations (Table 2).

As of today the EU has not put forward any $PM_{2.5}$ limit values. However, the annual average $PM_{2.5}$ mass concentration at Entrecampos (19 $\mu g\ m^{-3}$ in 2002 and 22 $\mu g\ m^{-3}$ in 2003) and São João da Talha (17 $\mu g\ m^{-3}$ in 2001–2003) exceeded the US-EPA standard of 15 $\mu g\ m^{-3}$. Both Bobadela and Póvoa de Sta Íria reached the average of 13 $\mu g\ m^{-3}$ in the period 2001–2003.

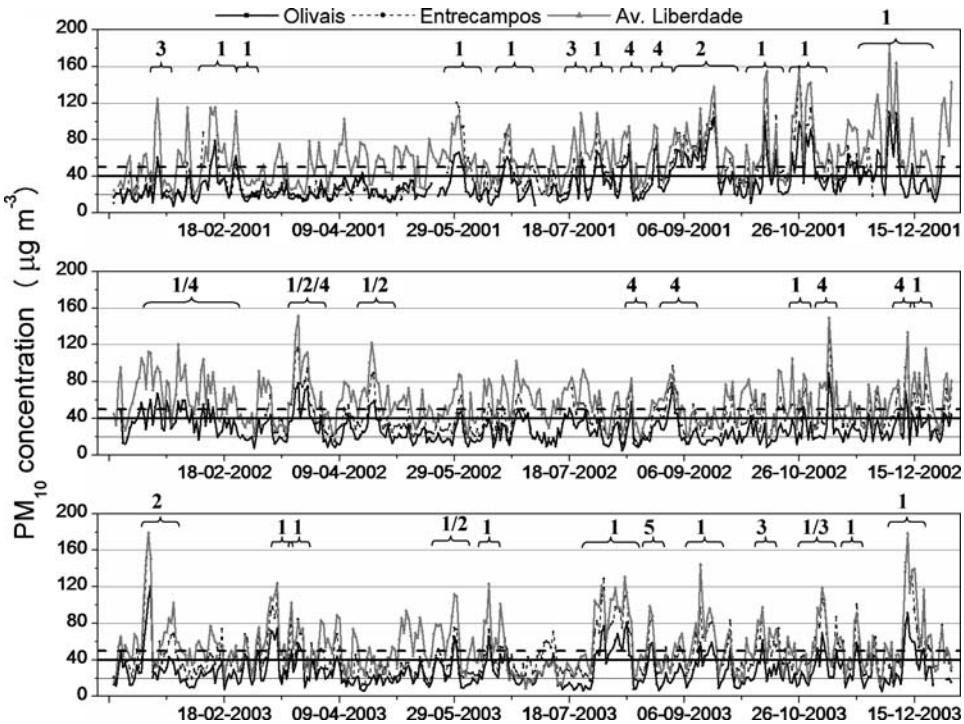

Fig. 2 PM_{10} time series at Olivais, Entrecampos and Av. da Liberdade sampling stations from 2001 to 2003. Backward air masses trajectories identified for scenarios with PM_{10} concentration higher than 50 μg m^{-3} in Olivais - 1 – South Continental, 2 - North/Centre Continental; 3 – Maritime; 4 – Maritime transformed. —24 h EU limit value (50 μg m^{-3}); — EU annual limit value for 2005 (40 μg m^{-3}); — EU annual limit value for 2010 (20 μg m^{-3})

The scenario presented for the sampled stations is very preoccupying mainly for Av. da Liberdade. In the latter, the PM_{10} annual averages for 2001–2003 were higher than all European urban areas and stations placed within street canions analysed by Van Dingenen *et al.* (2004).

Three other Portuguese urban cities also presented high PM_{10} concentrations. In 2003, Porto, Coimbra and Aveiro presented a PM_{10} average annual concentration of 43 μg m^{-3}, 50 μg m^{-3} and 43 μg m^{-3} and the 50 μg m^{-3} daily limit value was exceeded 115, 140 and 100 times, respectively (IA, 2005).

The mentioned urban and sub-urban areas contain a large concentration of people and therefore, they exhibit both the highest levels of pollution and the largest targets of impact. Understanding the impact of these PM levels in the human health and controlling air pollution in these areas becomes urgent. In order to evaluate the impact of these concentrations on health, it is essential the knowledge on the chemical composition, sources and origin of atmospheric suspended particles.

3.2 PM sources

Principal Component Analysis followed by Multilinear Regression Analysis (PCA/MLRA) (details of the method are given in Almeida *et al.*, 2005) applied to Bobadela PM_{10} chemical data (measured in 2001) showed that natural sources (sea and soil dust) on average account for 44% of the PM_{10} levels (Fig. 3).

In South European regions, such as Portugal, in addition to anthropogenic sources, the ambient aerosol has an important contribution from natural dust, due to local emissions from bare soil, and an influence of episodic African dust transport outbreaks (Almeida *et al.*, 2005; Rodríguez *et al.*, 2001). Moreover, the Portuguese coastal areas have an important input of marine aerosol (Pio *et al.*, 1996; Almeida *et al.*, 2005). This is due to the geographic position of Portugal (at the extreme southwest of Europe) and to the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean.

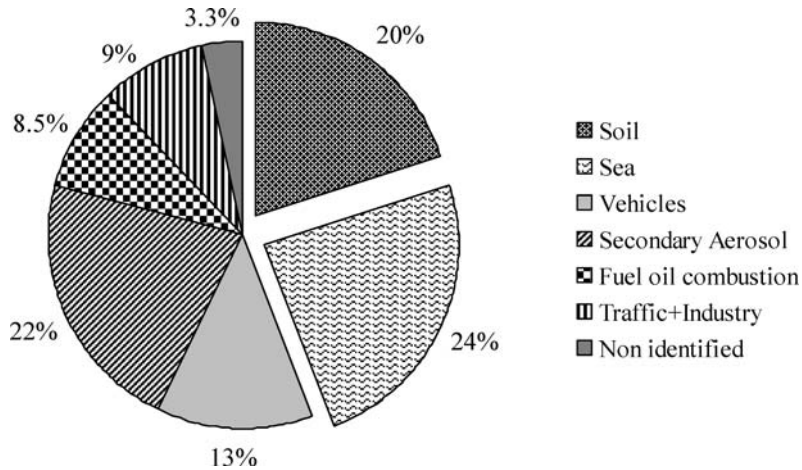

Fig. 3 Average source contribution in Bobadela station for the year 2001

PCA/MLRA focused on traffic and on non-mobile combustion processes emitting sulphur and NOx, which conduce to the formation of secondary aerosols as the main anthropogenic sources contributing to PM_{10}.

The concentration variability along each day permitted an insight into the main source of atmospheric particulate matter. Hourly PM concentrations showed strong diurnal patterns of the PM pollution in the three urban stations (Fig. 4). PM exhibited maximum values in the traffic hours as a consequence of exhaust emissions, tires and brake wear and re-suspension of dust, since it is possible to observe the pattern for both $PM_{2.5}$ and $PM_{2.5-10}$ (Fig. 4). In a previous work (Almeida *et al.*, in press) a PCA/MLRA applied to Sunday and working day samples revealed marked differences during weekdays mainly for coarse particles. Based on the characteristics of the Principal Components it was possible to conclude that a predominant fraction of coarse and fine soil dust provides from anthropogenic activities, being presumably associated with dust resuspension by road traffic.

Figure 2 showed the PM_{10} time series plots for Av. da Liberdade, Entrecampos and Olivais. No clear structure could be observed in the seasonal variations of PM_{10}. Several high pollution episodes could be seen simultaneously in the three stations suggesting that they were connected with regionally and long-range transported air masses. A back trajectory-based method and a few chemical analyses were used to identify the likely PM provenance for such days.

Four days backward trajectories were calculated with the Hysplit Model (Draxler, 1994) for days whose PM_{10} concentrations exceeded the EU daily limit value in Olivais, because the other two sampling stations were more influenced by local sources. According to the backward trajectories, air masses were classified into five main groups: 1—South Continental air masses—if backward trajectories indicated an African or southern Europe origin, 2—North/Centre Continental air masses—if backward trajectories indicated an origin in the North or Centre of Europe; 3—Maritime air masses—if backward trajectories indicated an ocean origin, without continental contamination, during the previous 4 days; 4 - Maritime transformed air masses - if backward trajectories indicated an ocean origin, with a final re-circulation through the Iberian peninsula; and 5 - Continental transformed air masses - if backward trajectories indicated an European origin with a final re-circulation through the ocean. This analysis showed that most of simultaneous events coincided with long-range transport of air masses from Africa or Southern Europe, usually enriched in soil material. The twice a week analysis of Fe for Bobadela samples supported this conclusion. Figure 5 shows that all events associated to South Continental air masses presented high concentrations of Fe, which is a typical soil element.

3.3 Spatial correlation between stations

The comparison between sampling stations can give an insight on the origin (both local and non local) of the particles and on the monitor's representation.

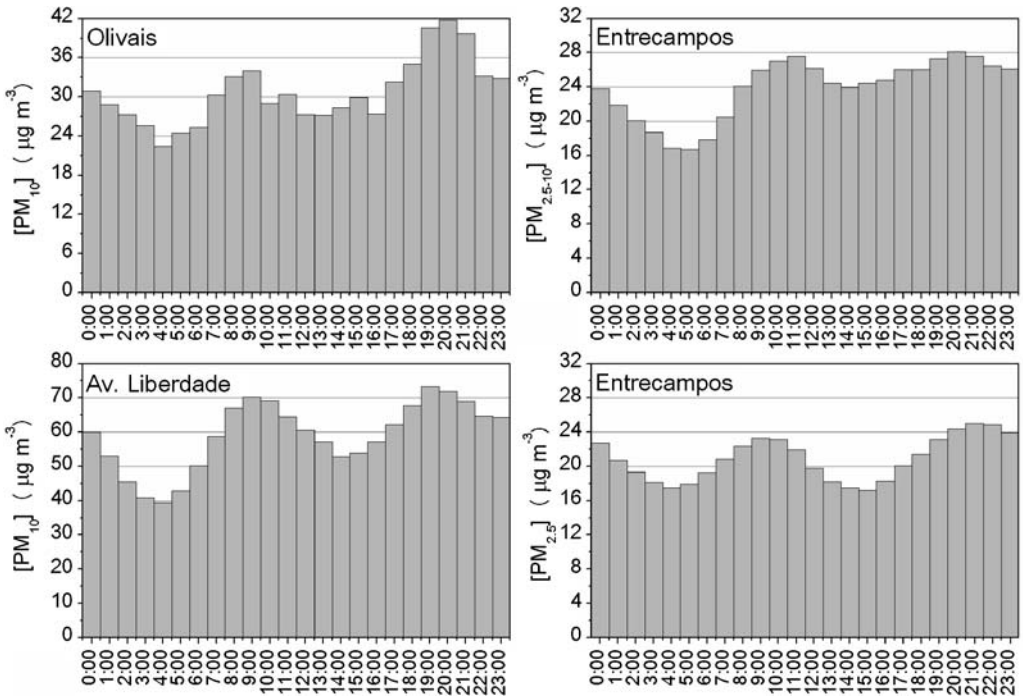

Fig. 4 Mean hourly levels of PM_{10} in Olivais, Entrecampos and Av. da Liberdade (recorded from 2001 to 2003) and $PM_{2.5}$ in Entrecampos (recorded during the year 2003)

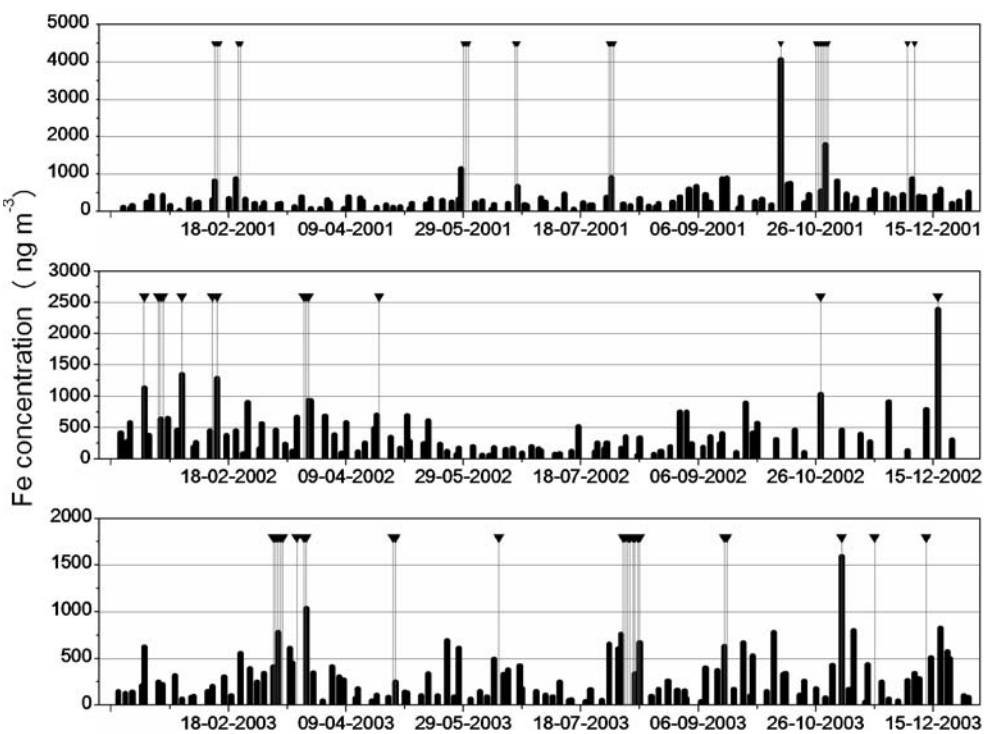

Fig. 5 Fe time series at Bobadela from 2001 to 2003. South Continental trajectories marked for events identified at Olivais in Figure 2

There are two components of any differences between measurements made at two sampling stations: one is the temporal correlation of the measurements and the other is the quantitative difference in concentration. Measurements can be excellently correlated over time and simultaneously can have large differences in concentrations. From an epidemiological point of view, the former is important for the strength of association, while the second is important for the effect size (risk per $\mu g\ m^{-3}$).

Figure 6 presents the correlations between PM_{10} concentration in Olivais with the PM_{10} measured in the two urban stations (Av. da Liberdade and Entrecampos). The regression analysis displayed a slope of 1.3 indicating that Entrecampos and Av. da Liberdade presented higher concentrations of PM_{10}, as expected, since traffic is more intense in these two places. Furthermore, the correlation coefficients showed a quite close connection between the stations.

The combination of data from automatic monitors with gravimetric PM_{10} and $PM_{2.5}$ values, and their chemical characterization, can be excellently suited to verify the effects of PM levels and composition in human health. However, in this combination, PM_{10} and $PM_{2.5}$ total concentrations should be comparable.

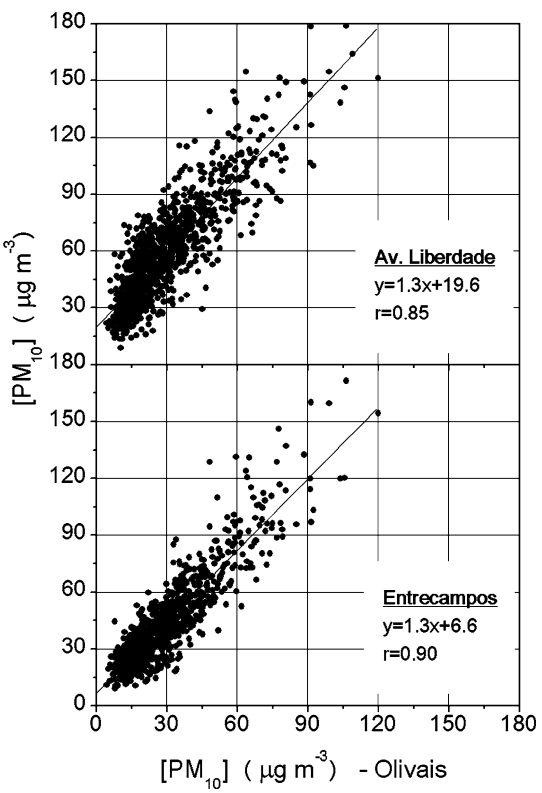

Fig. 6 Comparison between PM_{10} concentrations measured in Olivais, Entrecampos and Av. da Liberdade

Figure 7 compares Bobadela manual gravimetric measurements with the automatic beta-attenuation data used in IA stations. Bobadela $PM_{2.5}$ and $PM_{2.5-10}$ concentrations were summed in order to calculate the PM_{10} levels. Considering that adding to the discrepancies associated with different measurement methodologies, the stations are placed in different areas of the great Lisbon, PM measurements obtained with the automatic monitors fitted well with those performed with the gravimetric method. Olivais is the station closer to Bobadela. Regression analysis of Bobadela PM_{10} concentration vs. Olivais PM_{10} concentration presented a correlation of 0.85 and slope of 1.04. As expected Av. Liberdade and Entrecampos have higher concentrations. The correlation between Entrecampos and Bobadela is better for $PM_{2.5}$ than for PM_{10}. Finer particles have higher residence times and can originate from un-local sources. Owing to the gravity effect, coarse particles are rapidly removed from the atmosphere by sedimentation reflecting more the local sources (for instance particles ressuspension attributed to vehicles circulation).

The excellent correlation between the stations show the importance of regional sources, long range transport and meteorology (precipitation, temperature, humidity) in the concentrations of PM.

Particulate matter is a chemically non-specific pollutant, and may originate or be derived from different emission source types. Thus, its toxicity may well vary depending on its chemical composition. If the PM toxicity could be determined based on source types, the regulation of PM might be implemented more effectively.

Differences between 21 $PM_{2.5}$ and $PM_{2.5-10}$ components measured across—Bobadela, S. João Talha and Sta Iria Azóia were examined (Figs. 8 and 9).

The main constituents of the soil (Al, Si, Sc, Fe, La and Sm) showed consistently high temporal correlation ($r > 0.8$) and equivalent levels across the three sampling stations. These chemical elements are highly influenced by long range transport of dust from South of Europe and North of Africa. Besides being associated with soil material, Ca presents poorer correlations between stations and high concentrations in PSI. This was attributed to the cement production placed a few kilometers north of PSI sampling station. Besides being

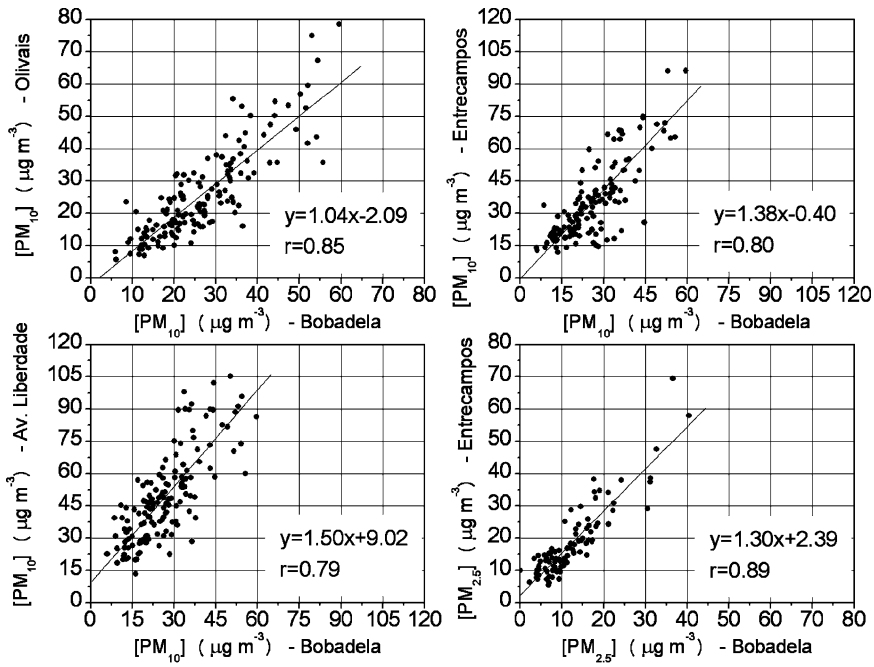

Fig. 7 Comparison between PM_{10} and $PM_{2.5}$ concentrations measured in Bobadela with gravimetric method and in Olivais, Entrecampos and Av. da Liberdade with authomatic method

principally associated with soil, Ti also provided from anthropogenic sources (Almeida, 2004). Correlations between stations showed low values ($0.5 < r < 0.8$) for this element.

Marine aerosol, represented by Na and Cl, shows a range of correlation from high ($r > 0.8$), in coarse fraction, to moderate ($r > 0.7$), in fine fraction. Chemical industry placed in this region was probably the origin of the poorer correlation for Na in fine fraction.

Previous studies (Almeida *et al.*, 2005) showed that, in coarse fraction, K was associated with sea salt spray (soluble fraction) and soil (insoluble fraction). Correlations between stations presented values higher than 0.8 for this element in $PM_{2.5-10}$. In the fine fraction, K was mainly associated with traffic and combustion sources and, therefore, correlations were lower.

Once considered the principal traffic tracer, with the implementation of unlead gasoline, Pb is no longer associated with this source. Pb showed consistently high temporal correlation ($r > 0.8$) between stations showing a non local origin.

Sulfur—the component of the secondary aerosols—showed a range of correlation from high in fine fraction ($r > 0.8$) to moderate in coarse fraction ($r > 0.6$).

The main constituents of fuel oil combustion, Ni and V, showed poor correlations principally in coarse fraction, being the concentrations higher in PSI. This is probably due to the fuel oil power plant placed some kilometers north from PSI station. The higher correlations ($r > 0.6$) observed in fine fraction could be attributed to regional sources.

Sb, Cu, Zn, As and Br associated with combustion processes and traffic (mainly tires and brake wear, rather than combustion processes) showed poor correlations between sampling stations and higher concentrations in SJT. This is probably due to the proximity (<100 m) of this station to a motorway.

The poor correlation with SJT for Se is attributed to the sudden increase of Se concentrations (400 times) by the end of 2001 (values not shown in Figs. 8 and 9). The observed anticorrelation and a winds study showed that there was an important local source of Se (Freitas *et al.*, 2005).

During 2001, a complete PM characterization was made in Bobadela. PCA analysis indicated that elemental carbon, organic carbon and NO_3^- are associated with traffic (Almeida *et al.*, 2005), which is the most important source in the centre of Lisbon. Therefore, in this urban area these species could have a great weight for the impact of PM in human health. It is essential to understand their distribution in the city to analyse the spatial representativity of their measurements.

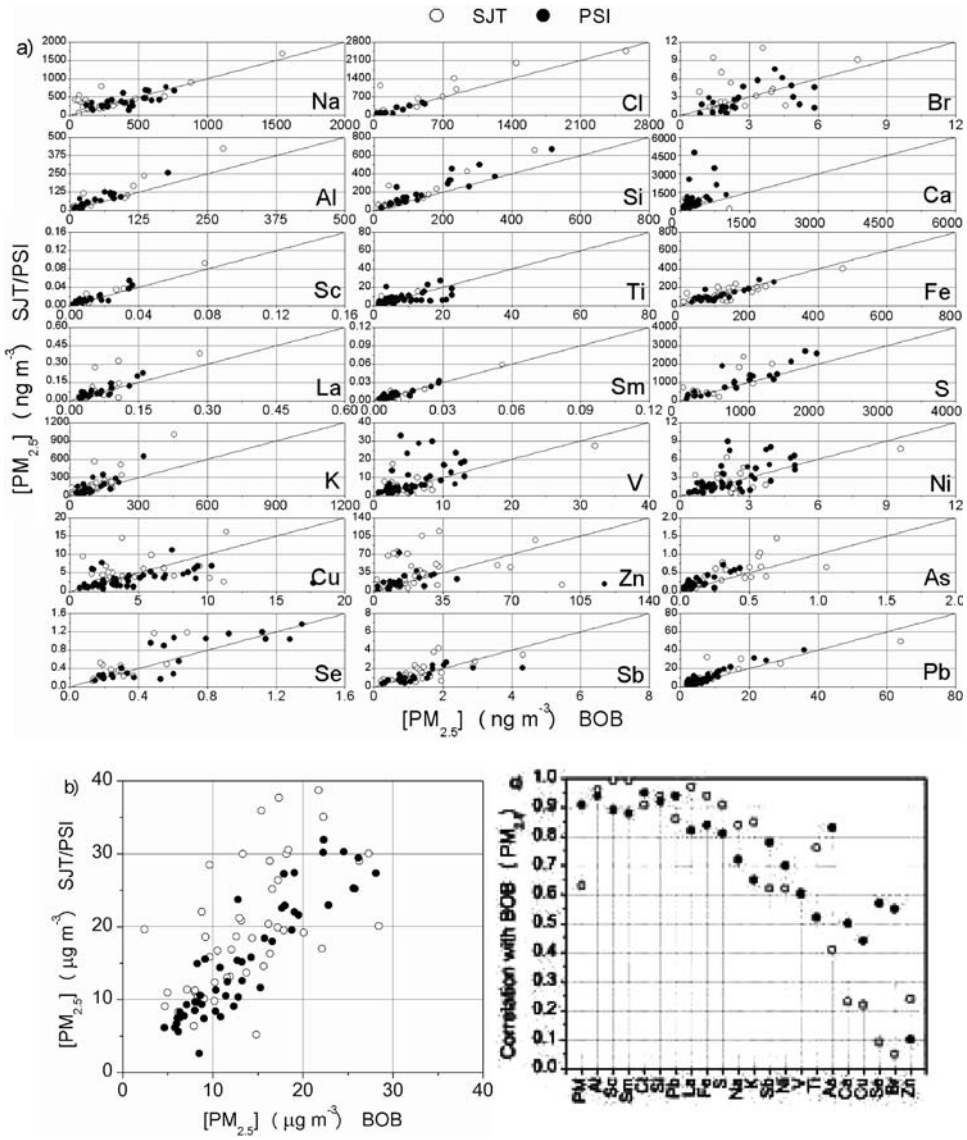

Fig. 8 Comparison of $PM_{2.5}$ components (a) and total mass (b) across 3 sampling stations. Correlations of $PM_{2.5}$ components and total mass (c)

However, comparisons between stations are not possible for these species because they only were measured in Bobadela.

In order to understand the contribution of the vehicles for the atmospheric characteristics in different places of the city, attention was paid to carbon monoxide (CO) measured in the stations Olivais, Entrecampos and Av. da Liberdade. Hourly CO concentrations measured in the three stations exhibited maximum values in traffic hours confirming the association of this gaseous pollutant with exhaust emissions. As expected concentrations of CO were higher in Entrecampos and Av. da Liberdade since traffic is more intense in these two places. Correlations between stations showed low values for CO ($r = 0.52$ for Avenida da Liberdade vs Olivais; $r = 0.72$ for Olivais vs Entrecampos and $r = 0.44$ for Av. da Liberdade vs Entrecampos). These results stand out that the influence of traffic is not uniform in Lisbon and probably the concentrations of element carbon, organic carbon and NO_3^- also vary significantly within the city.

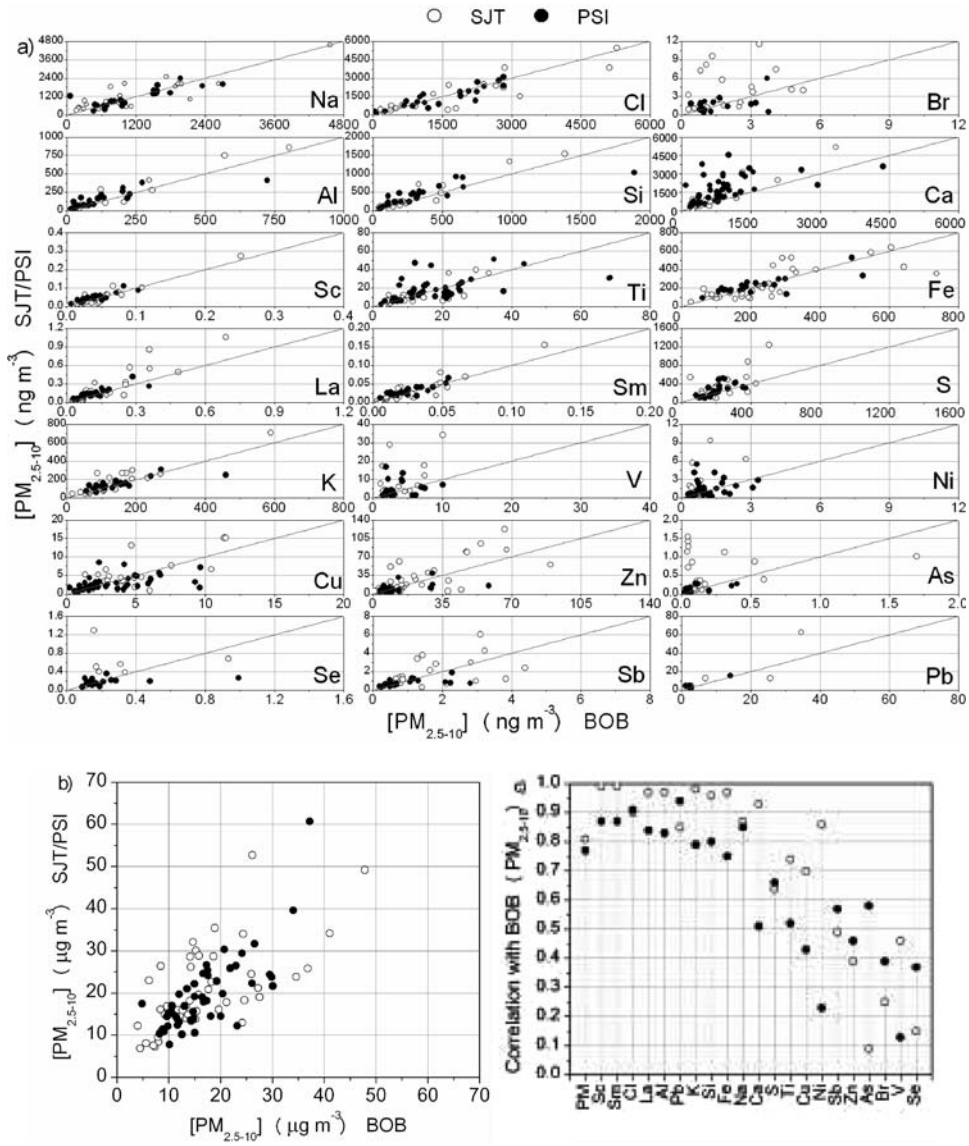

Fig. 9 Comparison of $PM_{2.5-10}$ components (a) and total mass (b) across 3 sampling stations. Correlations of $PM_{2.5-10}$ components and total mass (c)

4 Discussion

The above results indicate that daily fluctuations of the sources types represented by some species could not be precisely estimated for population exposure for a larger geographic boundary. Thus, if one single sampling station data is used to estimate the entire city population exposure, the potential health effect of individual PM species with low station-to-station correlation would be underestimated or overestimated compared to PM species that have high station-to-station correlation.

Figures 8b,c and 9b,c show a good correlation between stations for total PM_{10} and $PM_{2.5}$ concentration whereas Figs. 8a,c and 9a,c present poor correlations for some species (Sb, Cu, Zn, As and Br). This occurs because well correlated species have higher weight for total mass. According to Almeida (2004) in Bobadela sulphate, soil and marine elements accounted for 32% of $PM_{2.5}$ and 40.1% of $PM_{2.5-10}$ total mass, whereas the sum of V, Ni, Cu, Zn, As, Se, Br and Hg accounts for 1.2% of $PM_{2.5}$ and 1.8% of $PM_{2.5-10}$. Consequently, clear effects of PM on human health could be difficult

to discern when PM total mass is considered and speciation is not taken into account. In fact, PM total concentration can mask the potential health effect of some species present in particles, that besides having a lower contribution for the total mass, can have an important role in the health impacts of the PM. A particular case is the high concentrations registered in Fig. 2, which are associated with particles, enriched in soil material as Al, Si, Fe, Ca, Sc, La and Sm, transported from the South of Europe and North of Africa. Further studies should evaluate the impact of these events versus the impact of episodes with lower PM total concentrations using particles enriched in more toxic species provided from local sources.

5 Conclusion

As a result of a preliminary study carried out in the metropolitan area of Lisbon it is possible to observe that the EU directive is exceeded in a systematic way in the centre of Lisbon due to the traffic inside the city. Since it is worldwide recognized that PM air pollution has a relevant impact in human health, it was considered important to analyse the implications of these levels (and sources associated) for the health of the population living in Lisbon.

Important issues need to be considered in the analysis and interpretation of environmental data for this propose. These issues are related with a monitor's representation of regional, sub-regional, and local air pollution exposures to the population in the metropolitan area.

$PM_{2.5}$ and PM_{10} total mass concentration measured in several places located in both centre of Lisbon and in the outskirts are quite well correlated, mainly considering that two measuring methodologies (automatic and gravimetric) were used and areas with different classifications (urban and suburban) were analysed. However, results of our study implies that a source-oriented evaluation of PM health effects needs to take into consideration the uncertainty associated with spatial representative of the species measured at a single monitor. Results showed that the temporal correlation across sampling stations, within relatively short separation distances, varied considerably for some important elements (Zn, Sb, Cu, As and Br), indicating that the precision of population exposure estimates for specific elements can vary depending on the species.

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