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# Source apportionment of atmospheric urban aerosol based on weekdays/weekend variability: evaluation of road re-suspended dust contribution

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**Abstract**

During 1 year, twice per week (one working day and one sunday), 24-h averaged, separated fine and coarse atmospheric aerosol were measured, for total mass and chemical composition, in a suburban site on the outskirts of Lisbon. The relative concentration variability between working days and sundays allowed a better insight into the sources of atmospheric particulate matter. Receptor modelling based on Principal Component Analysis and Multilinear Regression applied to sunday and working day samples revealed marked differences during weekdays, in autumn/winter period. Based on the characteristics of the Principal Components it was possible to conclude that during autumn/winter, a predominant fraction of coarse and fine soil dust provides from anthropogenic activities, being presumably associated with road dust re-suspension by road traffic.


*Keywords:* $PM_{2.5}$; $PM_{2.5-10}$; Weekday variability; Receptor modelling; Road traffic

## 1. Introduction

During the last decades fast urbanization of the world population resulted in increased levels of air pollution from the concentration of industrial and, principally, road traffic activities in urban areas (Fenger, 1999). The problem is particularly important in large metropolis of developing countries where poor planning in urban development resulted in the expansion of suburban dormitories with characteristic increasing road commuter traffic.

Lisbon is the largest urban area in the western Iberian coast, with more than 2.5 million people. Because of lower house prices there has been an enormous expansion of suburban dormitories around the old Lisbon city, with hundreds of thousands inhabitants that every weekday rush in the morning to their jobs in the Lisbon centre and neighbouring industrial areas. Because of poor development of public transports most of the commuting is private road transport, resulting in

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traffic jams and in the constant building of new motorways to respond to the traffic pressure. This behaviour resulted in continuous growing of air pollution levels, in spite of the evolution of environmental performance of new road vehicles.

In the European Union, road traffic currently accounts for the main part of the total organic carbon emissions, more than half of the $NO_x$ emissions and a third of the emissions of volatile organic compounds (Fenger, 1999). Road traffic emissions concerns not only vehicles exhaust but also tire and brake wear and re-suspended dust. Traffic re-suspended particles contains road dust accumulated from vehicle track-out from construction sites, water or wind erosion from nearby areas, tire and brake wear, oil leaks and spills, street repair materials and atmospheric deposition (Clairborn et al., 1995). Vehicles re-suspension is dependent on site-specific characteristics regarding road surface silt content, mean vehicle speed, vehicle weight, number of wheels and moisture or humidity (US EPA, 1985).

In suburban areas, road traffic emissions add to emissions from industrial agglomerates activities, resulting in air pollution levels frequently above legislation limits. Besides ozone and photochemical oxidants during summer episodes, it is particulate matter the major nuisance resulting from urban anthropogenic activities.

The evaluation of the sources responsible for atmospheric particulate pollution is essential to permit a correct action on the control of urban air pollution, but difficult, because of the specific characteristics of particulate pollution. The use of emission/dispersion models to determine source contribution to ambient aerosol contamination in urban/suburban areas is problematic as a result of the large number of traffic, the industrial sources and the complexity of transport and transformation processes at local and regional level. Receptor models are frequently complementary tools to evaluate and quantify particle sources in situations where source/dispersion modelling is difficult, such is the cases associated with fugitive and area or line emissions or atmospheric processes involving gas to particle conversion (Hopke, 1991). However, application of receptor modelling has not resulted in a detailed discrimination of sources and processes contributing to the emission and formation of the aerosol; in general, it results only in the quantification of large source classes. One of the difficulties has been, for example, the clear differentiation between soil dust and road re-suspended dust contribution to the aerosol load, because of the similar composition of both source materials and the common effects of meteorological parameters, such as temperature, humidity and rainfall, on both source strengths. However, receptor modelling can profit from its capability to discriminate sources based on relative variations in concentrations if the strengths of the different sources vary differently in time. In most urban regions road traffic and industrial activities vary substantially between weekdays and sunday, with a strong decrease on the weekend. The comparison between weekday and weekend concentrations is the methodology used in this paper to further differentiate the contribution of different sources, especially road vehicles, to the urban aerosol load in the Lisbon urban area.

## 2. Experimental

### 2.1. Site description

Atmospheric aerosol was sampled in Bobadela, a suburban and industrial area on the North outskirts of Lisbon (latitude 38° 48' 50''N, longitude 9° 05′ 29″W). In recent years, traffic circulation increased dramatically in this area. An important fraction of traffic is commuter traffic, due to the increase of the population living in dormitories located on the outskirts of Lisbon. On the other hand, this area is a corridor, which links the North to the South of Portugal through one motorway (A1) and one main road (EN10); on average, 96,000 motor vehicle circulate daily in these two roads (IEP, 2001).

The sampling station is located 10 km North from the Lisbon centre, in an area of industrial activities, including an urban waste incinerator, a fuel oil power station, a cement factory and several chemical, food and glass factories. More details about APM sources and measurements in this region are given in Almeida (2004) and Almeida et al. (2005).

### 2.2. Description of the sampling equipment

During one year, ambient aerosol was collected during 24 h periods, twice per week (every sunday and in one weekday chosen sequentially). Sampling was performed with one low-volume and one high-volume samplers, operating side by side. The low-volume sampler, a Gent $PM_{10}$ was equipped with a Stacked Filter Unit (SFU), which carried two

47 mm Nuclepore polycarbonate filters, with 8 and 0.4 μm pore size, in two sequential stages. Upstream of the coarse filter a pre-impactor stage removed particles larger than 10 μm. The air was sampled at a rate of 15–16 l $min^{-1}$, permitting the collection of coarse particles with aerodynamic diameters (AD) between 2.5 and 10 μm in the first filter stage and fine particles with AD < 2.5 μm in the second filter stage. A detailed description of the sampling equipment is given by Hopke et al. (1997) and Maenhaut (1992).

The high-volume sampler 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).

### 2.3. Gravimetric and chemical analysis

Nuclepore and quartz fibre filters were weighed in a controlled clean room (class 10000) before and after sampling, using a semi-micro balance and a micro balance, respectively. $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations were obtained by dividing filter loads by the volume of air filtered.

Samples collected in Nuclepore filters were analysed for elemental contents. The exposed filters were cut with a bistoury into three parts controlled by weight: half was analysed by Instrumental Neutron Activation Analysis (INAA) (Bowen and Gibbons, 1963) with the $k_0$ methodology (De Corte, 1987); a quarter was analysed by Particle Induced X-ray Emission (PIXE) (Johansson and Campbell, 1988); the remaining filter quarter was kept in storage for other eventual measurements, or replicates. PIXE analysis was carried out at a Van de Graaff accelerator, in vacuum and two X-ray spectrum were taken for each of the samples; one with a 1.2 MeV proton beam and no absorber in front of the Si(Li) detector for low-energy X-ray elements and another with a 2.4 MeV proton beam and a 250 μm Mylar® filter to detect elements with atomic number higher than 20. For INAA analysis, filter halves were rolled up and put into a thin foil of aluminium and irradiated for 7-h at a thermal neutron flux of $1.2 \times 10^{13}$ $cm^{-2}$ $s^{-1}$ in the Portuguese Research Reactor. After irradiation the sample was removed from the aluminium foil and transferred to a polyethylene container. For each irradiated sample, two gamma spectrum were measured with hyperpure germanium detectors, one spectrum 2–3 days after the irradiation and the other one after 4 weeks. The $k_0$ method was used and 1 mm diameter wires of 0.1% Au–Al were co-irradiated as comparators.

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

Previously to the sampling campaign, tests of reproducibility within filters and between filters were taken, using parallel sampling with two similar sampling units and measuring the particle species by INAA and PIXE. Results were reproducible to within 5–15%, providing strong support for the validity of the analytical techniques. The details of both sampling and analytical control tests and detection limits are given in Almeida (2004) and Almeida et al. (2003a, 2003b). The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of ±10% (Almeida, 2004; Freitas et al., 2005).

Blank Nuclepore and quartz filters were treated the same way as regular samples. All measured species were very homogeneously distributed; therefore concentrations were corrected by subtracting the filter blank contents.

## 3. Results and discussion

Since meteorological conditions may have influence in the APM concentrations, autumn/winter (21 September–20 March) and spring/summer (21 March–20 September) seasons are analysed separately. Fig. 1 presents the daily average values for temperature, relative humidity and wind speed and daily cumulative values for precipitation measured in Lisbon, during the year 2001 (IM, 2001). Average values for temperature and wind speed are presenting only for days with aerosol sampling (Fig. 1a and b). Data for relative humidity and precipitation is given for all days of the year (Fig. 1c and d) because the dryness status of the soil depends mainly on the precipitation and relative humidity of the days before sampling. Autumn/winter

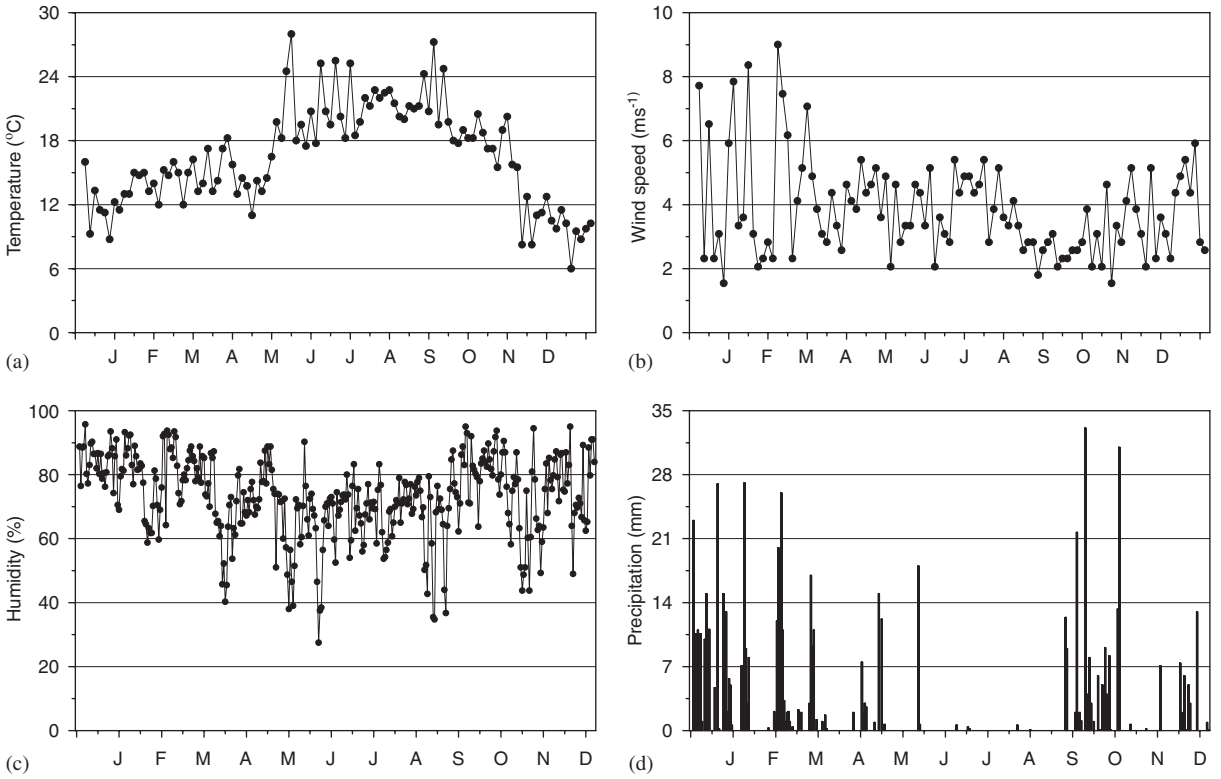


Fig. 1. Daily average (a) temperature (°C) and (b) wind speed ($m\,s^{-1}$) registered in Lisbon for days with aerosol sampling. (c) Relative humidity (%) and (d) cumulative precipitation (mm) registered in Lisbon in all 2001 days (IM, 2001).

seasons were characterized by lower temperatures (average in autumn/winter = 13 °C and average in spring /summer = 19 °C), higher relative humidity (average in autumn/winter = 78% and average in spring /summer = 68%) and higher precipitation (sum in autumn/winter = 549 mm and sum in spring /summer = 123 mm).

### 3.1. Mass concentration

$PM_{2.5}$ and $PM_{2.5-10}$ levels were found in the 3.5–68 $\mu g\,m^{-3}$ and 3.6–71 $\mu g\,m^{-3}$ ranges, respectively. Fig. 2 and Table 1 show that despite shifts in particles concentration levels with time, no clear seasonal trend could be observed for aerosol mass concentrations.

Twenty daily $PM_{10}$ values (with a 28% of daily data coverage) exceeded 50 $\mu g\,m^{-3}$. This value overpass the $PM_{10}$ 24 h limit value of the EU Air Quality directive. Air back-trajectory evaluation using HYSPLIT (Draxler, 1994) indicates that some of these events coincide with long-range transport of air masses from South of Europe and/or North of Africa. These events are highlighted in Fig. 2. The origin of these air masses were confirmed by the chemical characterization of $PM_{2.5}$ and $PM_{2.5-10}$, given the high levels of Al, Si, Fe, Sc, Sm and La (Almeida et al., 2005). As the objective of this paper is to make an evaluation of road re-suspended dust contribution based on weekday and weekend variability, the sampling days with $PM_{10}$ concentration higher than 50 $\mu g\,m^{-3}$ and with South Europe/North Africa origin were removed.

Fig. 2 and Table 2 show a peak in mass concentrations during weekdays, statistically significant, for coarse particles, in autumn/winter period (sign = 0.00 by Mann–Whitney test). The difference in behaviour of the aerosol mass between weekday and weekend can be better visualized through the total mass ratio $PM_{2.5}/PM_{2.5-10}$ that frequently presents clear higher values during sundays owing to lower levels in coarse aerosol concentrations.

### 3.2. PM species

Mann–Whitney test at a significance levels of 0.05 (table not shown) indicates that the concentrations of most of chemical species with usually attributed

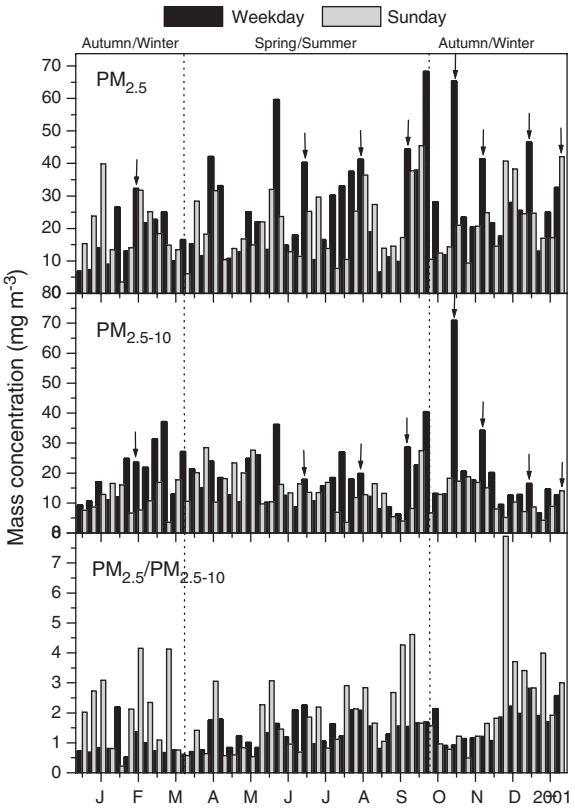


Fig. 2. Weekday/sunday differences for $PM_{2.5}$, $PM_{2.5-10}$ and $PM_{2.5}/PM_{2.5-10}$. The arrows highlight the periods in which both the South of Europe/North Africa episodes occur and $PM_{10}$ concentration exceeded $50\,\mu g\,m^{-3}$.

anthropogenic origin such as Zn, Sb, Cu, Pb, $NO_3^-$, $K^+$, As, V and Ni, in the fine fraction, are lower during spring/summer periods. Lower domestic, industrial and traffic emissions (owing to summertime holidays which are, in Lisbon, traditionally spent in warmer seasons), associated with increasing mixing layer heights and consequent better dispersion conditions (Vecchi et al., 2004), are the probable causes for lower concentrations during warmer months. Moreover, the significant higher level of fine $NO_3^-$ in autumn/winter (sign = 0.00 by Mann–Whitney test) is attributed to the shifting of the $NH_4NO_3$ (s) $\leftrightarrow$ $NO_3$ (g) + $NH_3$ (g) equilibrium to the aerosol phase, for the lower temperatures and higher relative humidities registered on these seasons (Fig. 1). In autumn/winter, regression analysis of $NO_3^-$ vs $NH_4^+$ resulted in $r^2 = 0.83$ and slope = 0.4 (whereas in spring/summer $r^2 = 0.08$). Another difference in nitrate between seasons is the relative amounts of fine and coarse $NO_3^-$. When temperature is high and relative humidity is low (Fig. 1), the $NH_4NO_3$ equilibrium with nitric acid and ammonia favours the gas phase. Sequentially, neutralization of nitric acid by alkaline components of mineral and marine aerosols adds nitrate to coarse particles. The latter is strongly supported by (1) the statistically higher coarse $NO_3^-$ concentration in spring/summer seasons (sign = 0.00 by Mann–Whitney test) and (2) by the Na/Cl excess observed in warm seasons (Almeida, 2004) given that the reaction leading to $NaNO_3$ formation induced Cl volatilization.

Anthropogenically produced $SO_4^{2-}$ is an exception, with $PM_{2.5}$ spring/summer average concentration values almost doubling autumn/winter levels. In warmer seasons, $SO_4^{2-}$ and $NH_4^+$ concentration present a strong correlation ($r^2 = 0.92$ and slope = 1.2, in equivalents $m^{-3}$), which indicates that $SO_4^{2-}$ is mainly present as $(NH_4)_2SO_4$ and/or $NH_4HSO_4$. The spring/summer increase of $SO_4^{2-}$ is probably due to the stronger solar radiation, which speeds up the formation of OH radicals and promotes the formation of secondary sulphates.

Chemical compounds usually associated with natural sources on soil dust, such as Al, Si and Sc, show significantly higher average concentration during the spring/summer months (at least at a confidence level of 85%). This is due to the suspension of dust, which is favoured by dried bare soils in dryer and warmer months.

Fig. 3 shows the ratio weekday/sunday particulate concentrations for chemical elements and compounds in $PM_{2.5}$ and $PM_{2.5-10}$ urban aerosol without the South of Europe/North Africa events. Table 2 presents the significance values from Mann–Whitney test to evaluate the differences between workdays and sundays. It is observed that there is a seasonal effect, with higher differences during autumn/winter periods. The highest ratios are found for mineral species, principally in the coarse particles size range. Table 2 shows that in autumn/winter, the concentrations of chemical elements usually associated with soil dust (Al, Si, Fe, Sc, La, Sm, $Ca^{2+}$ and Mn) were significantly different between weekdays and sundays (at least at a confidence level of 85%). The specific behaviour of calcium concentrations in relation to other mineral species, with weekdays/sundays strong variability for all seasons and size ranges, indicates a probable different origin for, at least, a fraction this element. $Ca^{2+}$ presents a relative weekday enrichment principally for fine particles in autumn/winter months. Moreover, in spring/summer period,

Table 1
Average concentration and standard deviation for PM2.5 and PM2.5-10 species for weekdays and sundays, separated for autumn/winter and spring/summer seasons (ng m$^{-3}$)

| | $PM_{2.5}$ | | | | | | | | $PM_{2.5-10}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Aut./wint. | | | | Spr./summ. | | | | Aut./wint. | | | | Spr./summ. | | | |
| | Weekday | | Weekend | | Weekday | | Weekend | | Weekday | | Weekend | | Weekday | | Weekend | |
| | Average | SD | Average | SD | Average | SD | Average | SD | Average | SD | Average | SD | Average | SD | Average | SD |
| PM | 14000 | 5500 | 14000 | 6900 | 12000 | 6900 | 13000 | 6600 | 16000 | 17000 | 13000 | 6700 | 16000 | 8100 | 15000 | 6200 |
| $Na^+$ | 170 | 310 | 170 | 390 | 470 | 180 | 470 | 260 | 550 | 750 | 500 | 930 | 1000 | 630 | 1300 | 810 |
| $Cl^-$ | 420 | 480 | 380 | 690 | 220 | 280 | 240 | 380 | 850 | 1400 | 700 | 1600 | 1200 | 960 | 1000 | 1200 |
| $Mg^{2+}$ | 28 | 32 | 24 | 47 | 59 | 21 | 56 | 28 | 72 | 76 | 63 | 88 | 120 | 57 | 130 | 71 |
| Al | 39 | 190 | 27 | 61 | 66 | 53 | 63 | 64 | 120 | 360 | 56 | 100 | 140 | 200 | 130 | 160 |
| Si | 100 | 550 | 58 | 160 | 120 | 130 | 180 | 160 | 320 | 1000 | 170 | 290 | 340 | 480 | 330 | 340 |
| Fe | 120 | 190 | 110 | 71 | 82 | 68 | 62 | 53 | 270 | 600 | 200 | 130 | 180 | 210 | 160 | 140 |
| Sc | 0.0072 | 0.054 | 0.0033 | 0.014 | 0.0091 | 0.011 | 0.0085 | 0.0073 | 0.032 | 0.17 | 0.016 | 0.028 | 0.034 | 0.045 | 0.033 | 0.033 |
| La | 0.053 | 0.15 | 0.037 | 0.063 | 0.047 | 0.042 | 0.041 | 0.035 | 0.12 | 0.44 | 0.089 | 0.084 | 0.12 | 0.13 | 0.10 | 0.1 |
| Sm | 0.0059 | 0.031 | 0.0047 | 0.012 | 0.0075 | 0.0078 | 0.0073 | 0.0059 | 0.028 | 0.09 | 0.011 | 0.017 | 0.023 | 0.028 | 0.021 | 0.021 |
| $Ca^{2+}$ | 440 | 320 | 160 | 68 | 380 | 370 | 260 | 200 | 410 | 180 | 360 | 110 | 400 | 230 | 370 | 120 |
| Mn | 2.3 | 3.1 | 1.7 | 1.1 | 2.0 | 1.4 | 1.8 | 1.3 | 3.7 | 8 | 2.4 | 1.7 | 3.1 | 4 | 2.7 | 2.7 |
| Zn | 21 | 23 | 13 | 17 | 12 | 23 | 4.7 | 8.4 | 21 | 21 | 9.4 | 18 | 8.9 | 13 | 4.6 | 11 |
| Sb | 1.4 | 0.89 | 1.4 | 1 | 0.90 | 1.6 | 0.68 | 2.2 | 1.3 | 1.1 | 1.2 | 0.55 | 0.51 | 0.79 | 0.45 | 0.6 |
| Cu | 4.9 | 3.7 | 6.9 | 3.7 | 3.5 | 2.6 | 2.8 | 3.8 | 6.3 | 5.4 | 6.8 | 3.9 | 4.1 | 3.4 | 2.6 | 2.8 |
| Pb | 7.8 | 12 | 7.1 | 6.5 | 4.5 | 6.7 | 5.5 | 5.9 | 7.6 | 9.9 | 2.7 | 2.5 | 2.9 | 2 | 3.3 | 4.3 |
| $NO_3^-$ | 1329 | 1300 | 1796 | 1300 | 698 | 850 | 647 | 340 | 641 | 360 | 858 | 430 | 1240 | 830 | 905 | 720 |
| $K^+$ | 119 | 100 | 111 | 110 | 80 | 140 | 95 | 150 | 39 | 23 | 29 | 24 | 40 | 19 | 45 | 20 |
| As | 0.32 | 0.26 | 0.37 | 0.45 | 0.10 | 0.12 | 0.079 | 0.21 | 0.12 | 0.35 | 0.086 | 0.06 | 0.061 | 0.13 | 0.064 | 0.27 |
| V | 8.3 | 6.5 | 5.5 | 5.1 | 4.6 | 3.3 | 3.9 | 4.2 | 3.5 | 9.8 | 2.8 | 1.7 | 2.5 | 2.6 | 2.9 | 2.3 |
| Ni | 3.2 | 1.9 | 2.3 | 1.5 | 2.1 | 1.2 | 1.6 | 1.5 | 1.5 | 3.4 | 0.9 | 0.76 | 1.0 | 1 | 1.0 | 0.91 |
| $SO_4^{2-}$ | 2500 | 1200 | 2600 | 1200 | 4000 | 4100 | 4200 | 2800 | 530 | 240 | 370 | 260 | 500 | 360 | 470 | 200 |
| $NH^+$ | 840 | 780 | 1300 | 890 | 1200 | 1200 | 1300 | 920 | 10 | 9.6 | 18 | 20 | 9.3 | 31 | 7.3 | 16 |

this ion also presents concentrations significantly higher in weekdays than in sundays, for fine particles. Nearby cement factory emissions may be the cause for the observed $Ca^{2+}$ concentration values because it is a source dealing with large amounts of dust containing calcium.

Coarse Zn, Pb, As, V, Ni and $SO_4^{2-}$ also present concentrations significantly higher at weekdays in autumn/winter months (Table 2 and Fig. 3).

Relative higher values of mineral species in weekdays than in sundays, in coarse particles, result surely from the influence of local and regional anthropogenic activities on the production of soil dust. The effect is especially visible during autumn/winter months when, because of colder and wetter weather (see Fig. 1), natural emissions of dust by the action of the wind over bare ground are at a minimum. Several anthropogenic activities, including industrial processes and building construction are possible causes, but the most probable source of antropogenically emitted dust is re-suspension of road dust by road traffic. The latter is an efficient emission process for dust, because the intense road traffic rapidly dries road ground, even in wetter and colder weather conditions. This interpretation for the origin of excess dust during working days is also reinforced by higher levels of Zn in the same periods (sign = 0.01 for $PM_{2.5}$ and sign = 0.00 for $PM_{2.5-10}$ by Mann–Whitney test), which originates from motor oil and tire wear (Sternbeck et al., 2002). In the Lisbon urban area, road traffic is strongly reduced in sundays, due to the absence of commuter traffic and heavy weight vehicles transporting goods and material (Fig. 4). In Av. da Liberdade, one of the main streets of Lisbon (a local that represents average urban road traffic), it was estimated a ratio weekday/sunday of 1.5 (CML, 2001). In the two main highways connecting Lisbon to the northern

Table 2
Significance values from Mann–Whitney test applied to data set in order to evaluate the differences between workdays and sundays for $PM_{2.5}$ and $PM_{2.5-10}$ during autumn/winter and spring/summer seasons

| | $PM_{2.5}$ | | $PM_{2.5-10}$ | |
|---|---|---|---|---|
| | Aut./wint. | Spr./summ. | Aut./wint. | Spr./summ. |
| PM | 0.42 | 0.47 | 0.00 | 0.39 |
| $Na^+$ | 0.42 | 0.78 | 0.62 | 0.84 |
| $Cl^-$ | 0.95 | 0.84 | 0.42 | 0.69 |
| $Mg^{2+}$ | 0.13 | 0.90 | 0.81 | 0.73 |
| Al | 0.08 | 0.91 | 0.01 | 0.90 |
| Si | 0.02 | 0.37 | 0.00 | 0.98 |
| Fe | 0.14 | 0.20 | 0.01 | 0.33 |
| Sc | 0.04 | 0.39 | 0.01 | 0.50 |
| La | 0.15 | 0.48 | 0.03 | 0.52 |
| Sm | 0.04 | 0.62 | 0.02 | 0.54 |
| $Ca^{2+}$ | 0.00 | 0.02 | 0.00 | 0.13 |
| Mn | 0.04 | 0.55 | 0.01 | 0.54 |
| Zn | 0.01 | 0.03 | 0.00 | 0.01 |
| Sb | 0.99 | 0.65 | 0.18 | 0.30 |
| Cu | 0.36 | 0.82 | 0.35 | 0.54 |
| Pb | 0.94 | 0.22 | 0.02 | 0.52 |
| $NO_3^-$ | 0.84 | 0.68 | 0.98 | 0.88 |
| $K^+$ | 0.97 | 0.71 | 0.11 | 0.59 |
| As | 0.55 | 0.84 | 0.02 | 0.59 |
| V | 0.11 | 0.95 | 0.05 | 0.43 |
| Ni | 0.05 | 0.35 | 0.06 | 0.27 |
| $SO_4^{2-}$ | 0.39 | 0.95 | 0.02 | 0.52 |
| $NH_4^+$ | 0.48 | 0.71 | 0.31 | 0.89 |

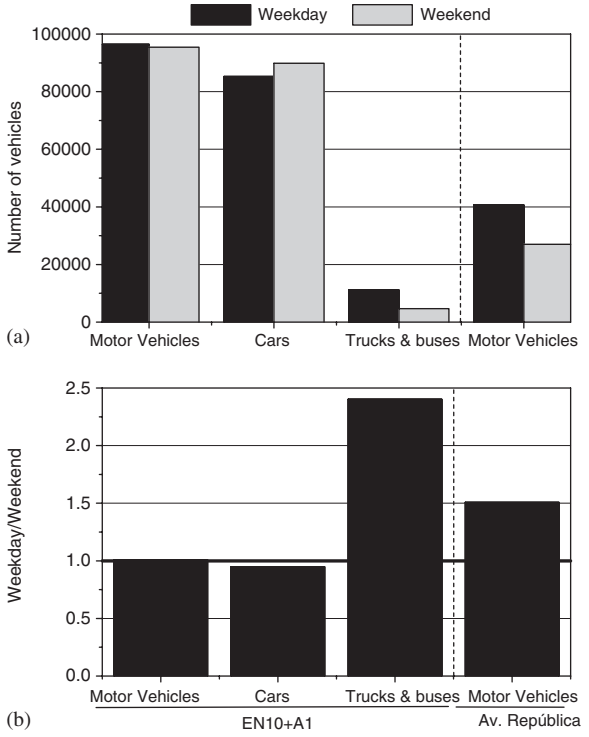


Fig. 4. (a) Average number of vehicles which daily circulate in A1 and EN10 (IEP, 2001) and in centre of Lisbon—Av. República (CML, 2001). (b) Ratio between the number of vehicles circulating in weekday and weekend.

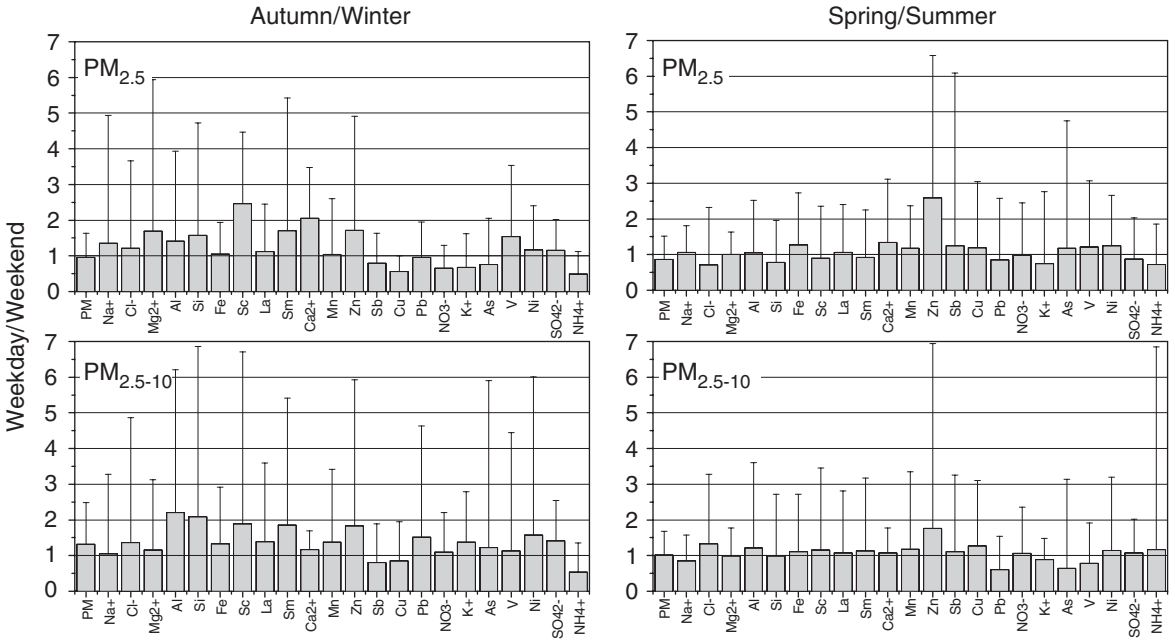


Fig. 3. Weekday/sunday ratio for $PM_{2.5}$ and $PM_{2.5-10}$ species discriminated by autumn/winter and spring/summer seasons.

of Portugal (A1 and EN10), which go through the sampling site area, the traffic of passenger cars does not change appreciably during weekends, because these two roads are used by Lisbon population during weekends to get out of the city in weekend holidays. But even in these roads the intensity of truck traffic decreased 58% during weekends (IEP, 2001).

### 3.3. Source apportionment

Aerosol source identification was further performed by Principal Component Analysis (PCA) followed by Varimax rotation applied to the full set of samples. To assess quantitatively the contribution of each source group for weekday and sunday $PM_{2.5}$ and $PM_{2.5-10}$, a Multi Linear Regression Analysis (MLRA) was applied to the experimental data, using $PM_{2.5}$ and $PM_{2.5-10}$ concentrations as dependent variables and as independent variables the principal component factor scores, calculated by introducing a fictitious sample with null concentrations for all variables (Thurston and Spengler, 1985).

Six main chemical profiles sources contributing to $PM_{2.5}$ were identified. The first factor represents the crustal contribution, given that it is defined by typical soil elements, such as Al, Si, Sc, Mn, Fe, La and Sm. The second factor is associated with fuel-oil combustion defined by Ni and V. The third factor represents the marine aerosol, as deduced from the high $Na^+$, $Cl^-$ and $Mg^{2+}$ loading factors. The main components defining the fourth factor are $SO_4^{2-}$ and $NH_4^+$, which derive from gas to particle conversion processes of products of the $SO_2$ oxidation and $NH_3$. The fifth factor is correlated with Zn, Cu and Sb, which are associated with coal combustion and traffic (mainly tires and brake wear rather than

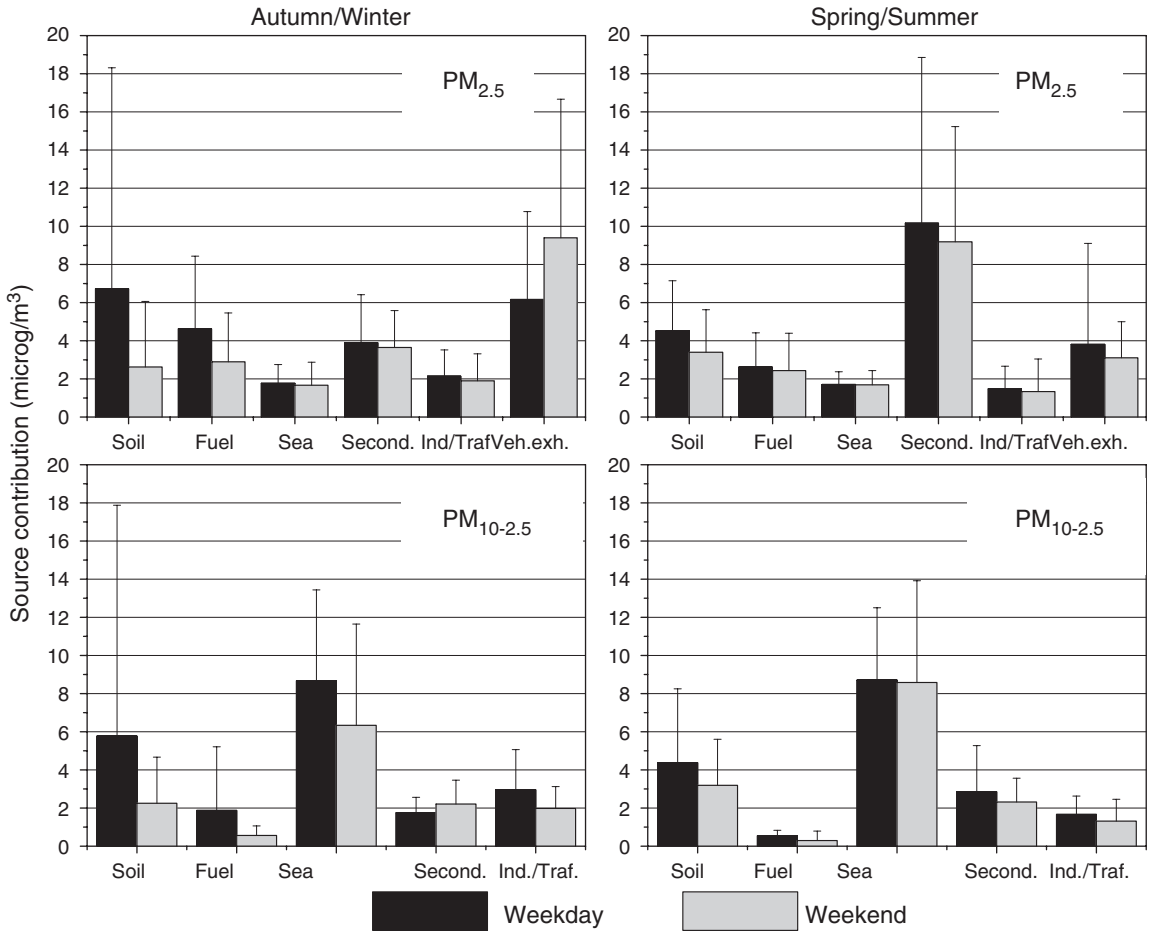


Fig. 5. Weekday/sunday differences for $PM_{2.5}$ and $PM_{2.5-10}$ source contribution discriminated by autumn/winter and spring/summer seasons.

combustion processes). The chemical profile of the sixth factor is mainly defined by $NO_3^-$, which derives from gas to particle conversion processes of products of the $NO_x$ oxidation, and it is expected to provide mainly from vehicle exhaust. In the coarse fraction, a similar source profile was identified. The major exception was the source correlated with $NO_3^-$, which was not identified, being this ion correlated with the secondary aerosol, in this size range. Details of source apportionment are given in Almeida (2004) and Almeida et al. (2005).

Fig. 5 compares source contributions calculated by PCA/MLRA for weekdays and sundays. The comparison confirms the observations and conclusions taken from the direct concentrations analysis: the larger differences between weekdays/weekends occur during autumn/winter periods for soil dust. The levels of soil dust are on average two (in coarse particles) to three (in fine particles) times higher, in working days, during colder months. Fig. 5 highlights the importance of the road traffic activity for PM characteristics as result of re-suspended particles from road dust.

Also noticeable is the variation in contribution of sources from fuel combustion that present 1.5–2.5 higher values during working days, in the autumn/winter period.

Fig. 5 shows much weaker variability between working days and sundays during spring/summer periods, although there is also a tendency for higher source contributions during working days, principally for the dust-related source. The lower impact of decreasing weekend anthropogenic activities during warmer months is presumably related with better dispersion conditions during this period of the year, associated with higher source emission of natural dust by the action of the wind, which is favoured by the warmer and drier weather. In summer, there is possibly a more important input from regional sources that weakens the effect of the weekend local source variability. Presumably, in colder months, there is a higher contribution of local and urban sources to the aerosol load.

## 4. Conclusion

The difference between aerosol concentrations measured in weekdays and weekend days allowed to evaluate the contribution of local anthropogenic activities to the urban aerosol load.

In weekdays, there is clear increase in the concentrations of Al, Si, Fe, Sc, La, Sm, $Ca^{2+}$ and Mn elements, which are associated with mineral aerosol; and Zn results mainly from tires and motor oils. During weekdays, soil contribution was on average 2.6 times higher, in autumn/winter and 1.3 times higher in spring/summer. This variability shows that, at least during the colder/wetter period of the year, most of the soil-derived dust is produced by anthropogenic activities, presumably resulting from road dust re-suspension by road traffic.

Road traffic activity has therefore a predominant contribution to the particulate contamination of the suburban atmosphere in Lisbon, either in the form of fine particles, as a result of direct and precursor emissions from engine combustion, or as coarse particles produced from tire and break wear, or re-suspended from road dust.

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