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Characterizing air particulate matter composition and sources in Lisbon, Portugal

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Abstract The goal of this research is to determine trends and sources of airborne particulates in the centre of Lisbon, by using speciated particulate-matter data and back-trajectory analyses. Results showed that, in 2007, the annual $PM_{2.5}$ concentration exceeded the World Health Organization recommended levels. $PM_{2.5}$ diurnal variability and the ratio between weekdays' and weekends' concentrations indicated that traffic contributed highly to decreasing air quality. Air back-trajectory analysis showed that maritime air mass transport had a significant role on air quality in Lisbon, promoting the decrease of anthropogenic aerosol concentrations.

Keywords Urban aerosols · PM2.5 · Traffic · Airmass back trajectories

Introduction

Ambient aerosols adversely affect human health, visibility and climate. Accurate analyses of the physical–chemical properties of the particles, and the identification of sources of particulate matter and its precursors, are necessary for developing control strategies. Epidemiological studies have consistently shown an association between Air Particulate Matter (APM) pollution and the number of deaths from cancer and cardiovascular and respiratory diseases [1, 2]. There is compelling evidence linking ambient levels of particles and increases in hospital admissions for respiratory and cardiovascular diseases [2–6]. Epidemiological studies have also shown that ambient fine particles ($PM_{2.5}$) are the main responsible for those associations [7].

The project "Atmospheric Aerosol Impacts on Human Health" focuses on the chemical characterization of $PM_{2.5}$ aerosols, with the aim of: (1) analyzing the health risks associated with aerosol exposure; and (2) understanding how the aerosols' chemical composition contributes to those health risks. The study of the associations between the source contributions and the health impacts aims at introducing specific abatement strategies in industrial processes, automobile circulation and city planning, which could decrease the levels of APM and, consequently, decrease the impacts on human health. Results presented in this paper were obtained within this project. A higher number of rhinitis episodes was observed in April (123 cases) and August (27 cases), in a Lisbon basic-school population. The present paper aims at determining trends and sources of particulate matter for these two months.

Experimental

Sampling

During 2007, $PM_{2.5}$ was collected on a daily basis in the centre of Lisbon (38°44′N; 9°8′W). Sampling was done with a Partisol® collector (Thermo Fisher Scientific Inc.), operating at a flow rate of 16 L min^{-1}. Aerosol samples were collected on Teflon™ filters with a diameter of 47 mm.

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Gravimetric analysis

The filter loads were measured by gravimetry using a Mettler® Toledo balance with 0.1 μg readability, placed in a controlled clean room (class 10 000). The exposed filters were cut into two parts: one was analyzed by instrumental neutron activation analysis (INAA) and the other by ion-exchange chromatography.

Chemical analysis—INAA

Elemental characterization of APM was performed by INAA. Each half-filter was irradiated at the Portuguese Research Reactor (RPI; ITN-Sacavém) for 5–7 h, and measured for 4–7 h after 3–7 days and 4 weeks of decay, in high-purity and high-resolution germanium detectors, with an automatic sample changer. A comparator—an Al-0.1%Au disc—was also irradiated and measured for application of the k_0-INAA methodology [8]. The technique has already demonstrated its potential to yield both accurate and precise measurements of APM [9, 10]. All species measured in blank (unexposed) filters were very homogeneously distributed; therefore, concentrations were corrected by subtracting the blank-filter contents.

Air mass back trajectories

For each starting sample date, three-day backward trajectories, ending in Lisbon, were calculated with the HYSPLIT Model [11], at 50 m, 500 m and 1,000 m height, and using the vertical velocity option. According to such trajectories, air masses arriving in Lisbon during the sampling campaign were classified into five main groups: M ≡ Maritime air masses, when backward trajectories indicated an ocean origin, without continental contamination, during the previous 3 days; MT ≡ Maritime transformed air masses, when backward trajectories indicated an ocean origin, with a final re-circulation through the Iberian Peninsula; SC ≡ South Continental air masses, when backward trajectories indicated an African or Southern European origin; N/CC ≡ North/Centre Continental air masses, when backward trajectories indicated an origin in the North or Centre of Europe; and CT ≡ Continental transformed air masses, when backward trajectories indicated an European origin with a final re-circulation through the ocean [13].

Results and discussion

In 2007, $PM_{2.5}$ annual average mass concentration was 19 μg m^{-3}. This value did not exceed the $PM_{2.5}$ limit value of 25 μg m^{-3} defined in the European Union Common Position No. 13/2007 of 25 June 2007. However, results showed that students had been exposed to $PM_{2.5}$ concentrations that exceeded both the World Health Organization and the U.S. Environmental Protection Agency recommended levels of 10 μg m^{-3} and 15 μg m^{-3}, respectively.

The concentration variability along the day allowed an insight into the main source of $PM_{2.5}$ [12]. Hourly $PM_{2.5}$ concentrations measured in Entrecampos (about 2 km from the sampling site), by the Air Quality Monitoring Network of the Portuguese Environmental Agency, showed strong diurnal patterns of the $PM_{2.5}$ pollution (Fig. 1a). $PM_{2.5}$ exhibited maximum values in the traffic hours as a consequence of exhaust emissions, tire and brake wear, and resuspension of road dust.

The difference between aerosol concentrations measured in weekdays and weekends allowed an evaluation of the contribution of local anthropogenic activities [14]. Fig. 1b shows that $PM_{2.5}$, NO_3^-, Zn and Sb concentrations were higher during the weekdays. Results, already discussed elsewhere [12], showed that these species are associated with vehicle exhaust (NO_3), tire-brake wear and motor oil (Zn and Sb). The lower number of vehicles in August, due

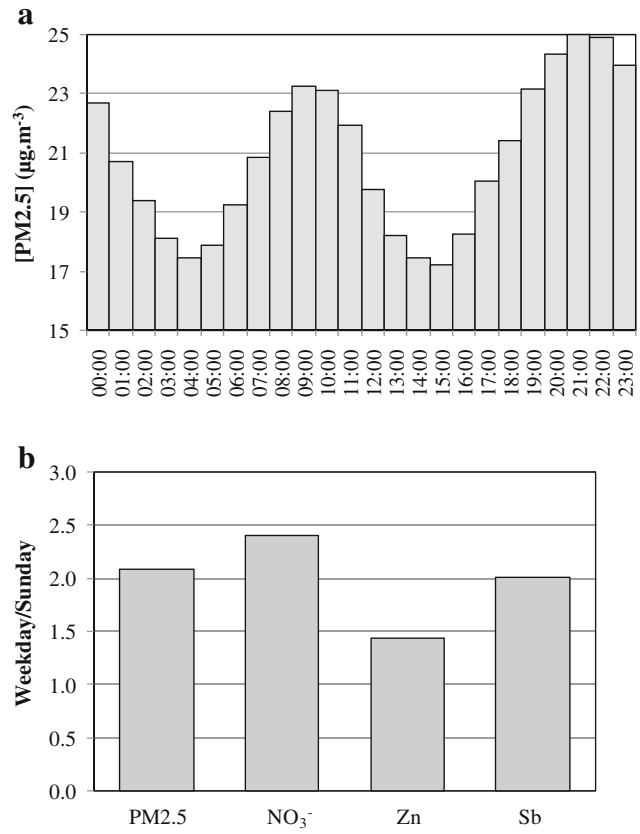

Fig. 1 **a** Mean hourly levels of $PM_{2.5}$ in Entrecampos (μg m^{-3}); **b** Ratio weekday/Sunday concentrations for $PM_{2.5}$ and species associated with vehicles' emissions

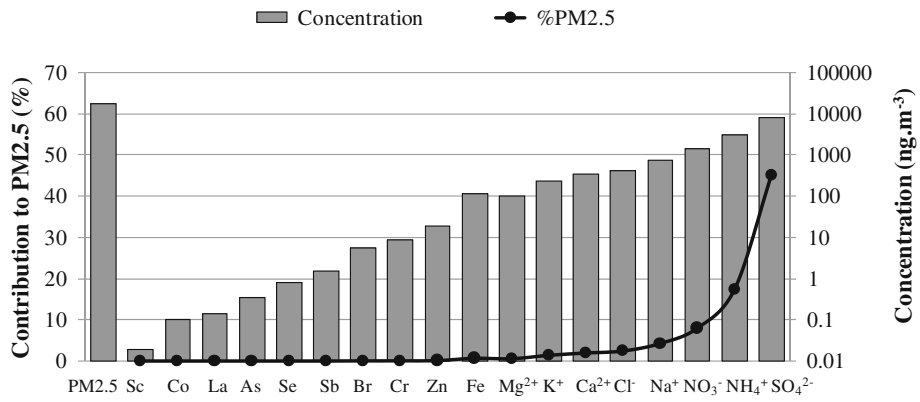

Fig. 2 Average concentrations of $PM_{2.5}$ species (ng m^{-3}) and their contribution for the total mass of $PM_{2.5}$ (%)

to the summer holidays, could explain the lower $PM_{2.5}$ concentrations observed in this month (15 μg m^{-3}) compared with April (21 μg m^{-3}).

$PM_{2.5}$ levels were mainly due to anthropogenic particles derived from local sources and long-range transport [13]. According to Fig. 2, the most abundant species in $PM_{2.5}$ (concentrations generally higher than 1 μg m^{-3}) were SO_4^{2-}, NH_4^+, NO_3^-, Na^+, Cl^-, Ca^{2+}, K^+, Mg^{2+} and Fe; 18 % of the $PM_{2.5}$ mass was not explained by the measured species. The lack of mass closure (i.e. constituent concentrations not adding up to the gravimetrically-measured amount) was partly due to unmeasured species, namely black and organic carbon, which in Lisbon are mainly associated with vehicular traffic [13, 15]. SO_4^{2-} and NH_4^+—which derive from gas-to-particle conversion processes, from SO_2 oxidation and NH_3 neutralization—contribute to 45 % and 17 % of $PM_{2.5}$ mass, respectively. These ions presented a strong correlation (0.97) which indicated that SO_4^{2-} was mostly present as ammonium sulfate. NO_3^- represented on average 8 % of the $PM_{2.5}$ mass (Fig. 2).

Due to the geographical position of Lisbon, on 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, maritime influence was very important for the aerosol characteristics. Figure 3a shows that lower concentrations of SO_4^{2-}, NH_4^+, NO_3^- were associated with Maritime trajectories due to the transport of these clean air masses from the Atlantic Ocean. SO_4^2, NH_4^+, NO_3^- presented lower concentrations in August (7104, 2528 and 1120 ng m^{-3}, respectively) than in April (9015, 3749 and 1780 ng m^{-3}, respectively) due to the more frequent influence of maritime air masses to the site. Sea-spray ion concentrations (Na^+, Cl^-, Mg^{2+}) accounted for 7.3% of the total $PM_{2.5}$ mass (Fig. 2). Figure 3b shows that higher concentrations of Na^+, Cl^-, Mg^{2+} were associated with maritime trajectories. However, regardless of air-mass origin, the concentrations of these ions are higher in Portuguese coastal areas than in more continental European regions [13].

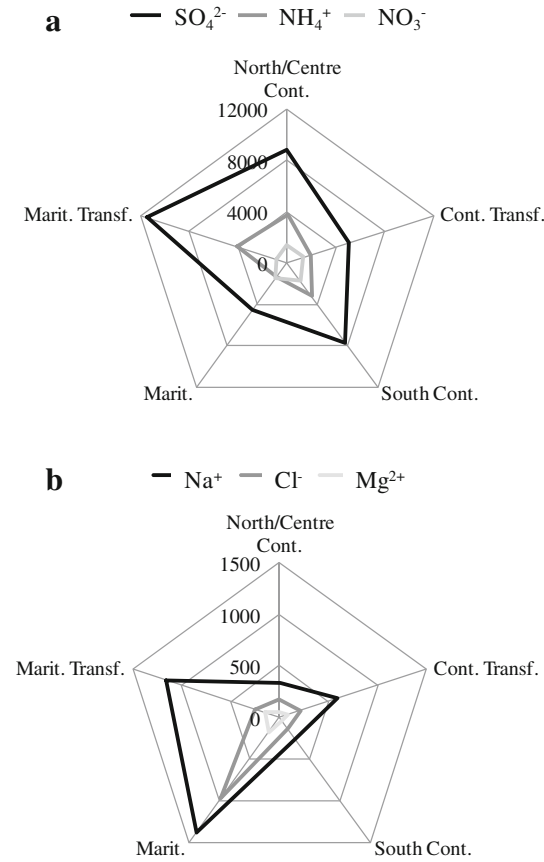

Fig. 3 **a** SO_4^{2-}, NH_4^+ and NO_3^- and **b** Na^+, Cl^- and Mg^{2+} average concentrations discriminated by air-mass type (*Marit.* Maritime air masses; *Marit. Transf.* Maritime Transformed air masses; *North/Centre Cont.* North Centre Continental air masses; *Cont. Transf.* Continental Transformed air masses; *South Cont.* South Continental air masses. All values in ng m^{-3}

Conclusions

$PM_{2.5}$ composition was investigated in order to identify the main sources of $PM_{2.5}$ variability during April and August 2007, in the centre of Lisbon. $PM_{2.5}$ levels were mainly due to anthropogenic constituents, SO_4^{2-}, NH_4^+ and NO_3^- being the most abundant species in $PM_{2.5}$. The concentration variability along the day and the ratio between weekdays and Sundays showed traffic to be an important source of particles in this area. Back-trajectory analysis indicated maritime air-mass transport as having a significant role on air quality in Lisbon, by promoting a decrease of anthropogenic aerosol concentrations. Air-pollution abatement strategies as well as public-health enhancement policies should focus on traffic and on non-mobile combustion processes emitting SOx and NOx, which mostly contribute to the formation of secondary aerosols.

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