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Assessment of Exposure to Airborne Ultrafine Particles in the Urban Environment of Lisbon, Portugal

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Assessment of Exposure to Airborne Ultrafine Particles in the Urban Environment of Lisbon, Portugal

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The aim of this study was the assessment of exposure to ultrafine particles in the urban environment of Lisbon, Portugal, due to automobile traffic, and consisted of the determination of deposited alveolar surface area in an avenue leading to the town center during late spring. This study revealed differentiated patterns for weekdays and weekends, which could be related with the fluxes of automobile traffic. During a typical week, ultrafine particles alveolar deposited surface area varied between 35.0 and 89.2 m²/cm², which is comparable with levels reported for other towns such in Germany and the United States. These measurements were also complemented by measuring the electrical mobility diameter (varying from 18.3 to 128.3 nm) and number of particles that showed higher values than those previously reported for Madrid and Brisbane. Also, electron microscopy showed that the collected particles were composed of carbonaceous agglomerates, typical of particles emitted by the exhaustion of diesel vehicles.

Implications: The approach of this study considers the measurement of surface deposited alveolar area of particles in the outdoor urban environment of Lisbon, Portugal. This type of measurements has not been done so far. Only particulate matter with aerodynamic diameters <2.5 (PM2.5) and >10 (PM10) μm have been measured in outdoor environments and the levels found cannot be found responsible for all the observed health effects. Therefore, the exposure to nano- and ultrafine particles has not been assessed systematically, and several authors consider this as a real knowledge gap and claim for data such as these that will allow for deriving better and more comprehensive epidemiologic studies. Nanoparticle surface area monitor (NSAM) equipments are recent ones and their use has been limited to indoor atmospheres. However, as this study shows, NSAM is a very powerful tool for outdoor environments also. As most lung diseases are, in fact, related to deposition of the alveolar region of the lung, the metric used in this study is the ideal one.

Introduction

Very ultrafine particle materials can enter the body via three main routes: (a) inhalation, (b) ingestion, and (c) dermal penetration. The detrimental health effects of inhaling fine aerosols were recognized long ago and various attempts have been made to minimize exposure, such as the issuing of specific regulations on emissions and objectives for air quality. Current workplace and ambient air environmental exposure limits, which have been established long ago, are based on particle mass. However, this criterion does not seem adequate in what concerns ultrafine particles, as these materials are, in fact, characterized by very large surface areas, which has been pointed out as the distinctive characteristic that could even turn an inert substance into a toxic substance, having the same chemical composition, but exhibiting very different interactions with biological fluids and cells (Oberdörster et al., 1995). Therefore, it seems that assessing human exposure based on the mass concentration of particles, which is widely adopted for particles over 1 μm, would not be adequate in this particular case. In fact, ultrafine particles have far more surface area for the equivalent mass of larger particles, which increases the chance that they may react with body tissues (Kreyling et al., 2002). Thus, a growing number of experts (Donaldson et al., 1998; Oberdörster, 1996) have been claiming that surface area should be used for ultrafine particle exposure and dosing. As a result, assessing workplace conditions and personal exposure based on the measurement of particle surface area is of increasing interest. It is well known that lung deposition is the most efficient way for airborne particles to enter the body and potentially cause adverse health effects. Properties that contribute to the toxic effects of ultrafine particles include solubility, particle morphology, particle size, composition, surface chemistry, surface coatings, and surface area. If ultrafine particles can deposit in the lung and remain there, have an active surface chemistry and interact with the body, then there is a strong potential for exposure and dosing. Oberdörster (2001)
showed that surface area plays an important role in the toxicity of nanoparticles and is the measurement metric that best correlates with particle-induced adverse health effects. The potential for adverse health effects is directly proportional to particle surface area (Driscoll, 1996).

Although the mass concentration of fine particles, namely in the ranges of particulate matter with aerodynamic diameters <2.5 (PM$_{2.5}$) and <10 (PM$_{10}$) µm, has been currently monitored in urban environments in large towns worldwide, very few studies have been made regarding ultrafine particles. Zhiquiang et al. (2000) reported measurements of particles larger than 1 µm in large cities such as Beijing, Paris, Mexico City, New York, Tokyo, and Zurich, whereas Shi et al. (2001) measured particles smaller than 10 µm in Birmingham, Morawaska et al. (2002) monitored ultrafine particles in Brisbane, and Gomez-Moreno et al. (2011) measured ultrafine particle levels in Madrid. All of these studies report concentrations in terms of number of particles per cm$^3$.

Among the few studies reporting nanoparticles, the study of Ramachandran et al. (2005) assessed ultrafine particles in the urban environment of Minneapolis, Kuhlbusch et al. (2004) measured ultrafine particles in the Ruhr area in Germany, and Ntzniarchistos et al. (2007) monitored ultrafine particles in Los Angeles area. All these last three groups measured ultrafine particle concentration in terms of surface area, expressed as µm$^2$/cm$^3$, which we feel is the most significant metric in what concerns this type of pollutant, particularly bearing in mind the existing relationship between surface area of ultrafine particles and their health effects.

**Materials and Methods**

**Sampling site**

Measurements were made in 56 consecutive days on late spring, from 4 April until 30 May 2011, on a trailer that was located downwind on Av. Columbano Bordalo Pinheiro, a four-lane avenue in Lisbon, Portugal, shown in Figure 1, which is one of the main accesses to the town center coming from West (Benfica) and its surroundings. Through this avenue heavy fluxes of traffic enter the town, consisting of automobiles, trucks, and buses. For comparison purposes, the air quality data on particulate emissions (PM$_{2.5}$ and PM$_{10}$) measured regularly on the only nearby station in Entrecampos (about 1 km east of the sampling site) were also obtained as part of the information made public by the Portuguese Ministry of Environment. Measurements were made during weekdays and also on weekends, during 24-hr periods, every 10 sec. This station is also located in a four-lane avenue of Lisbon, which has similar traffic patterns of the sampling site. Also, a baseline measurement was done inside the trailer at night during 15 min, using a filter.

**Meteorology**

The measurements were made during the dry season, in the absence of rain. Lisbon has a subtropical-Mediterranean climate with mild winter and warm to hot summers. The annual average temperature is 17 °C, 21 °C during the day and 13 °C at night, with an annual precipitation of 725.8 mm, mainly concentrated in autumn and winter months. Summer lasts about 6 months, from May to October. In the measuring period the average daily temperature was 17.4 °C, with a maximum temperature of 21.4 °C during day and a minimum temperature of 13.3 °C at night. The consistency of this weather on a daily basis ensures that representative results were obtained during the duration of this study. Previous studies focused on air pollution episodes in Lisbon area have characterized their driving meteorological conditions as well as their typical atmospheric patterns. In summer, the situation permits the development of mesoscale flows land-sea breeze and upslope-downslope (anabatic-katabatic) flow (Barros et al., 2003), leading to the occurrence of episodic air pollution events. Thus, the worst pollution episodic situations in this region usually coincide with typical summer weather. During the sampling periods no air pollution episodes took place, and no significant Eastern Atlantic Ocean influence occurred in the sampling site, as it is located in the middle of the town, surrounded by tall buildings.

**Automobile traffic**

It is estimated that exhaust gases from automobiles account for 44.0% and 11.7% of NO$_x$ and volatile organic compound emissions, respectively, in Lisbon area, and 12.5% of PM$_{10}$ (Gois et al., 2009). The contribution of exhaust gas emissions to the concentration levels of ultrafine particles has not been quantified previously, but it is expected to be substantial. The automobile traffic fluxes entering and leaving the center of Lisbon have been previously monitored for these main access avenues (Rocha, 2008). It was noticed that the incoming traffic during the morning increases from 400 until 1000 vehicles/hour from 8:00 a.m. to 9:00 a.m. In the afternoon, the opposite flux leaving the town center increases from 800 to 1000 vehicles/hour between 5:00 p.m. and 6:00 p.m. and sometimes reaches 1100 vehicles/hour at 8:00 p.m. during working days. It is also estimated that this traffic consisted of about 40% of diesel versus 60% of gasoline-fueled vehicles.
Measuring equipment

For measuring nanoparticle exposure, a nanoparticle surface area monitor (NSAM) (TSI, Model 3550; xx, xx), was used. This equipment indicates the human lung-deposited surface area of 155 particles expressed as square micrometers per cubic centimeter of air (μm²/cm³), corresponding to tracheobronchial (TB) or alveolar (A) regions of the human lung, according to the International Commission on Radiological Protection (ICRP) deposition model developed by the American Conference of Governmental Industrial Hygienists (ACGIH) (Phalen, 1999).

This equipment is based on diffusion charging of sampled particles, followed by detection of the charged aerosol using an electrometer. Using an integral pump, an aerosol sample is drawn into the instrument through a cyclone with a 1 μm cut point. The sample flow is split, with one stream going through a set of carbon and high-efficiency particulate air (HEPA) filters and an ionizer to introduce positively charged ions into a mixing chamber. The other aerosol flow stream is mixed with the ionized stream in a mixing chamber and charged aerosol and excess ions move onto an ion trap. The ion trap voltage can be set to TB or A response. The ion trap acts as an inlet conditioner or a size-selective sampler for the electrometer, by collecting the excess ions and particles that are not of a charge state, corresponding to the TB or A response settings. The aerosol then moves on to the electrometer for charge measurement, where current is passed from the particles to a conductive filter and measured by a very sensitive amplifier, as shown schematically in Figure 2. The charge measured by the electrometer is directly proportional to the surface area of the particles passing through the electrometer.

The equipment was set to alveolar response settings only, as this is the most significant metric.

Particle number concentration and size distribution were measured using a scanning mobility particle size spectrometer (SMPS) (TSI, Model 3034). The system consists of three components: (i) a bipolar radioactive charger for charging the particles; (ii) a differential mobility analyzer for classifying particles by electrical mobility; and (iii) a condensation particle counter for detecting particles. The SMPS (TSI, Model 3034) measures the particle diameter (Dp) (in terms of electrical mobility diameter) between 10 and 487 nm using 54 size channels (32 channels per decade) for number concentrations in the range from 102 to 107 per cm³.

Morphological analysis was conducted using a nanometer aerosol sampler (TSI, Model 3089) to collect particles on a mesh transmission electron microscopy (TEM) copper grid with a carbon/formvar support film, and these samples were analyzed through a TEM microscope (FEI, Model Tecnal G2; xx, xx; 200 kV, twin lens).

Results and Discussion

Measurement results, over a typical week, are presented in Table 1, which also shows calculated values of time-weighted average (TWA) for 8-hr periods, total deposited alveolar area, and dose per lung area. It should be noted that TWA is the average exposure over a specified period of time, usually a nominal 8 hr, which is a parameter frequently used in exposure assessments in indoor environments. Although it is usually not frequently used for outdoor environments, it is useful for further comparisons with indoor exposures. Figure 3 shows the measured alveolar deposited surface area in two typical consecutive weekdays: Tuesday, 10 May 2011, and Wednesday, 11 May 2011. Figure 4 shows the same measurements but on a typical weekend day: Sunday, 8 May 2011.

These measurements exhibited differentiated patterns for weekdays and also for weekend days, as expected, and previously noticed for other urban environments (Morawska et al., 2002; Ntziachristos et al., 2007). As the obtained measurements have shown always similar patterns regarding weekdays and weekend days, other measurements are not shown here. Figure 5, which shows three superimposed weekday patterns (sample 4 = Tuesday, sample 5 = Wednesday, sample 6 = Thursday), shows the similarity of those patterns. On the opposite, Figure 6, which shows superimposed week (sample 3 = Monday, sample 4 = Tuesday, sample 5 = Wednesday, sample
Table 1. Measurement results over a typical week (late Spring, 2011)

<table>
<thead>
<tr>
<th>Sampling Conditions</th>
<th>Average Deposited Area ($\mu m^2/cm^3$)</th>
<th>Range of Values ($\mu m^2/cm^3$)</th>
<th>8-hr TWA ($\mu m^2/cm^3$)</th>
<th>Total Deposited Area ($\mu m^2$)</th>
<th>Dose Per Lung Area ($\mu m^2/m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>34.1 ± 5.0</td>
<td>25.5–50.3</td>
<td>1.07</td>
<td>$5.12 \times 10^5$</td>
<td>$6.40 \times 10^7$</td>
</tr>
<tr>
<td>Monday</td>
<td>57.6 ± 5.7</td>
<td>14.7–343.3</td>
<td>172.8</td>
<td>$8.29 \times 10^7$</td>
<td>$1.04 \times 10^8$</td>
</tr>
<tr>
<td>Tuesday</td>
<td>89.2 ± 8.0</td>
<td>27.4–510.5</td>
<td>267.6</td>
<td>$1.28 \times 10^8$</td>
<td>$1.61 \times 10^8$</td>
</tr>
<tr>
<td>Wednesday</td>
<td>87.1 ± 7.5</td>
<td>31.1–421.1</td>
<td>261.4</td>
<td>$1.25 \times 10^8$</td>
<td>$1.57 \times 10^8$</td>
</tr>
<tr>
<td>Thursday</td>
<td>82.2 ± 7.2</td>
<td>23.2–245.7</td>
<td>165.2</td>
<td>$4.72 \times 10^7$</td>
<td>$5.90 \times 10^5$</td>
</tr>
<tr>
<td>Friday</td>
<td>75.0 ± 6.9</td>
<td>17.8–511.1</td>
<td>143.6</td>
<td>$4.70 \times 10^7$</td>
<td>$4.60 \times 10^5$</td>
</tr>
<tr>
<td>Saturday</td>
<td>35.0 ± 4.5</td>
<td>6.91–365.5</td>
<td>107.4</td>
<td>$4.26 \times 10^7$</td>
<td>$3.40 \times 10^5$</td>
</tr>
<tr>
<td>Sunday</td>
<td>34.9 ± 4.0</td>
<td>4.94–252.2</td>
<td>104.7</td>
<td>$4.10 \times 10^7$</td>
<td>$3.20 \times 10^5$</td>
</tr>
</tbody>
</table>

Figure 3. Measurements over two consecutive typical weekdays: Tuesday, 10 May 2011, and Wednesday, 11 May 2011.

Figure 4. Measurements over a typical weekend day: Sunday, 8 May 2011.
In fact, on weekdays, the diurnal profile of the particle surface concentrations shows that in the early night hours, from 12:00 a.m. to around 3:00 a.m., the concentrations have values in the approximate range of the baseline. Some small peaks can be observed around 3:00 a.m., during a short time (15 to 30 min), that can be attributed to the traffic fluxes of garbage collection trucks as well as street cleaning vehicles, both operated on diesel fuel, operating at this period. As particle surface concentrations are clearly influenced by automobile traffic, concentrations clearly start to increase from 5:00 a.m. to 6:00 a.m., thus reflecting traffic entering the center of the town. At these early hours, traffic is mostly constituted by trucks and buses largely fueled by diesel. This traffic fluxes entering the town continues to increase during early morning and reaches a maximal peak around 7:00–7:30 a.m. However, the traffic fluxes usually do not diminish until 9:00–9:30 a.m., which is not shown in the measured concentrations, where a slight decrease can be observed in this period. This is possibly due to an alteration on the traffic profile from the previous hours, which is now mainly constituted by gasoline-fueled vehicles, circulating, at first, at low velocity and, afterwards, in intense and compact traffic jams. These traffic jams are certainly the cause for another concentration peaks appearing around 9:00–9:30 a.m. Concentrations then decrease until new peaks are observed near lunch hour (12:00 p.m.), thus accounting for heavier traffic fluxes, but based on gasoline-fueled vehicles. Concentrations start to rise again during the afternoon, around 5:00–6:00 p.m., accounting for traffic leaving the center of the town. Further on, concentrations are still elevated, compared to baseline, until 9:00 p.m., where other, less intense, peaks are reached. After 9:00 p.m., concentrations drop slowly until 12:00 a.m. and until 2:00–3:00 a.m. of the following day. It can be noticed that this daily pattern is reproducible in the next weekday.

However, in weekend days, concentrations are much smaller, seldom surpassing the baseline, with scattered peaks during all day, more concentrated near lunch hour and early afternoon. During weekend days, there are neither heavy traffic fluxes nor rush hours, which are reflected in the measurements taken. Also during these days, traffic is mainly composed by gasoline-fueled vehicles.

Figure 7 shows the mass concentration variation pattern of PM$_{10}$ measured at the nearby air quality station of Entrecampos, during the same weekdays depicted in Figure 3: although there are some similarities regarding the occurrence of concentration peaks during rush hours, no sound correlation was found between measured alveolar deposited surface area and PM$_{10}$, as the involved metric is completely different as explained previously.

Figures 8 and 9 show the measured size distribution measured with the SMPS analyser: Figure 8 shows $D_p$, the electrical mobility diameter and number of particles on a typical weekday, corresponding to an average diameter of 16.9 ± 1.46 nm and an average number of particles (d$N$/dlog$D_p$) of 4.53 × 10$^4$ per cm$^3$. Figure 9 refers to a typical weekend day, corresponding to an average diameter of 128.6 ± 1.97 nm and an average number of particles of 7.5 × 10$^3$ per cm$^3$. The observed differences, during week- and weekend days, are consistent with a majority of gasoline-fueled vehicles during weekend compared to weekdays.
where diesel-fueled vehicles (trucks and buses) are in considerable higher number. Figure 10 shows the evolution of the median values of number of particles and \(D_p\) for each day of the week, as computed from the number size distribution spectra measured by the SMPS. Each point is the mean between all days of this study and the error bars represent the respective standard errors of all readings corresponding to each day of the week.

Figure 11 shows a TEM image of ultrafine particulate collected using the nanometer aerosol sampler, during a weekday. As expected (Ramachandran et al., 2005), the collected particles seem to be composed of carbonaceous agglomerates of irregular shape, similarly to vehicle exhaust particles from diesel-fueled vehicles.

It should also be noted that the measured deposited surface area is within the same order of magnitude as the values measured by Kuhlbusch et al. (2004) in the Ruhr area, of 30–45 \(\mu\text{m}^2\)/cm\(^3\) and by Ntiziachristos et al. (2007) in Los Angeles area, of 38–71 \(\mu\text{m}^2\)/cm\(^3\). In what concerns number of particles, Morawska et al. (2002) measured 6330/cm\(^3\) on weekends and 8010/cm\(^3\) on weekdays for Brisbane, whereas Gomez-Moreno et al. (2011) measured 2000–19000/cm\(^3\) on weekdays in Madrid, which means that the measured number of particles in this study is considerably high. In spite of this, the evolution pattern, noticed by Morawska et al. (2002), on the number of particles and its diameter during weekdays and weekends was again observed in this study, as shown in Figure 11.

In what regards the measured levels of deposited alveolar surface area, it should be noticed that outdoor levels, during weekdays, show considerable increases from the baseline, from 160% to 260%. This clearly points out for high exposures to
ultrafine particles in the urban environment of central Lisbon, as also indicated by the measured total deposited area and dose per square meter lung area mentioned in Table 1, when compared to baseline. Therefore, the time-weighted average (TWA), also presented in Table 1, which was calculated from the sampling period for a total exposure of 8 hr, is also considerably higher than baseline. This observation is an indicator of a strong potential for occurrence of lung-related diseases due to the exposure to high doses of ultrafine particles in this urban environment.

Conclusions

Previous studies (Fissan et al., 2007; Kuhlbusch et al., 2000; Ntziachristos et al., 2007) confirmed evidence that diffusion chargers are useful and reliable instruments for measuring ambient aerosol concentrations in different environments and that their signal can be combined with the number concentration of particles to provide an estimate of the mean diameter in real time.

This set of measurements is the first stage of a study on airborne ultrafine particles in the urban atmosphere of Lisbon. The study clearly demonstrated the existence of ultrafine particles due to automobile traffic, which could be confirmed by the measurements of size distribution and morphology of sampled particles. Also, this seems to be consistent with observations of ultrafine particle concentrations in other major towns. Mainly during weekdays, observed concentrations can be as high as 2.6 times the measured baseline level.

It should be noted that, although measured parameters such as the deposited area and the dose per lung area are elevated when compared with baseline values, mainly for weekdays where automobile traffic is more intense, they cannot, at this stage, be ascertained as toxicity indicators. Nevertheless, they point out for important contamination of potentially hazardous particles released from automobile traffic in urban environments. Data obtained in this study is basic information allowing for understanding the relationship between exposure to ultrafine particles in urban atmospheres and health affections, which can be taken as the basis for epidemiologic studies. As ultrafine particles can have a significant lifetime in urban air, possible effects on health cannot be neglected.
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References


About the Authors