

UNIVERSITY OF SÃO PAULO  
INSTITUTE OF ASTRONOMY, GEOPHYSICS AND ATMOSPHERIC SCIENCES  
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Particulate matter inside residences of elderly in  
the Metropolitan Area of São Paulo

São Paulo

2017



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# Particulate matter inside residences of elderly in the Metropolitan Area of São Paulo

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Thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Sciences in the Institute of Astronomy, Geophysics and Atmospheric Sciences

Major Field: Meteorology

Advisor: Prof. Dr. Fábio Luis Teixeira Gonçalves

São Paulo

2017



I dedicate it to my parents, Maria Helena and Hermenegildo, for all the love, dedication and encouragement along this journey.



“There is no favorable wind for the sailor who doesn’t know where to go.”

Sêneca.





## Acknowledgements

I am extremely grateful to my boyfriend Kaonan for be by my side no matter what, for be my rock. Thanks for the encouragement and help, for the strength and kindness, for patience and love. My gratitude goes also to Keila for receive me so well and for the incentive and patience in the difficult moments.

I am always thankful my parents, my foundation in life, Maria Helena and Hermenegildo, who always invested in my education, for all the support, patience, incentive and love along my life.

I am extremely grateful to the elderly that participated on this project for their time and interest on this research. Thanks for trust me and open their homes to me, for the kindness and desire to help the science, which was essential for the development of this research.

I am grateful to my advisor Prof. Dr. Fabio L. T. Gonçalves for give me the opportunity to work in a so interdisciplinary project and for trust in me to handle a research so different that I was doing before. Thanks for the patience and comprehension.

I am really grateful to Prof<sup>a</sup>. Dr<sup>a</sup>. Adalgiza Fornaro for the intellectual support, for always to find a time to help me, mainly in the difficulties times. Thanks for the advices and friendship.

I am thankful to Prof. Dr. Prashant Kumar and his family for open their home for me, for the kindness and for make my time in Guildford very happy. My gratitude goes especially to Prof. Dr. Prashant Kumar for the teachings, incentives, positive thinking, and the time dedicated to discuss my research.

I am grateful to Prof. Dr. Otto Klemm and the Climatology Group for receive me so well in Münster, for the intellectual support and availability to help me, for make my time happy and productive.

I am grateful to Prof<sup>a</sup>. Dr<sup>a</sup>. Maria de Fatima Andrade and Rosana Astolfo for their support, teachings and willingness to help.

I would like thanks to all my friends, that who hear a lot of complains, gave me support and stayed by my side in the difficulties moments, mainly Luciana Caxa and Rafael Batista for also helped me in the experimental part, and Fernanda Wardo and Benedito Faustinoni Neto for English and presentation support.

I am sincerely thankful to the staffs at University of São Paulo, Surrey and Münster for making more easy my time and adaptation in each university.

I am thankful to CNPq for the grants provided the financial support of CAPES (PROEX, Meteorology Post-Graduation Program at University of São Paulo) and FAPESP (2010/10189-5). My gratitude goes also the collaborative funding received to Universities of Surrey and São Paulo through the UGPN funded projects BIOBURN (Towards the Treatment of Aerosol Emissions from Biomass Burning in Chemical Transport Models through a case study in the Metropolitan Area of São Paulo) and NEST-SEAS (Next-Generation Environmental Sensing for Local To Global Scale Health Impact Assessment) that assisted me to work at the University of Surrey. I am also thankful the financial support of DAAD (German Academic Exchange Service) that assisted me to work at the University of Münster.

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## LIST OF ABBREVIATIONS

AU – Approximately Unbiased p-value

BC – Black Carbon

CETESB – Company Environmental State of São Paulo

*DF* – Deposition Fraction

DL – Detection Limits

GDS – Geriatric Depression Scale

*I/O* – Ratio between indoor and outdoor particulate matter concentrations

MASP – Metropolitan Area of São Paulo

MMSE – Mental State Examination

PCIS – Personal Cascade Impactor Sampler

PM – Particulate Matter

PM<sub>10</sub> – PM < 10 μm in diameter

PM<sub>10-2.5</sub> – PM between 10 and 2.5 μm in diameter

PM<sub>2.5</sub> – PM < 2.5 μm in diameter

PM<sub>1.0-2.5</sub> – PM between 2.5 and 1.0 μm in diameter

PM<sub>0.5-1.0</sub> – PM between 1.0 and 0.5 μm in diameter

PM<sub>0.25-0.5</sub> – PM between 0.5 and 0.25 μm in diameter

PM<sub>0.25</sub> – PM < 0.25 μm in diameter

PMF – Positive Matrix Factorization

qUFP – Quasi-ultrafine particles

rBC – Black Carbon measured by reflectance

RDD – Respiratory deposition doses

WHO – World Health Organization

SPPB – Short Physical Performance Battery

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# Resumo

SEGALIN, B. **Material particulado em residências de idosos na Região Metropolitana de São Paulo**. Tese (Doutorado em Ciências Atmosféricas) - Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, São Paulo, 2017, 119 p.

A população idosa é sensível aos riscos da poluição do ar à saúde. Os idosos passam mais tempo dentro de suas casas, mas há pouca informação sobre a qualidade do ar dentro de suas residências. Os objetivos deste trabalho são caracterizar a massa do material particulado (PM) de diferentes tamanhos em residências de idosos na Região Metropolitana de São Paulo (RMSP) no Brasil; avaliar a influência dos parâmetros meteorológicos e a relação entre PM de ambiente interno e externo; quantificar os íons, elementos traços e *black carbon* (rBC) em partículas quasi-ultrafinas (qUFP) e identificar suas fontes, e estimar as doses de deposição de PM no trato respiratório (RDD). Para alcançar esses objetivos, medimos durante 24 horas as concentrações em massa de PM nos tamanhos 10-2,5; 2,5-1,0; 1,0-0,5; 0,5-0,25 e <0,25  $\mu\text{m}$  ( $\text{PM}_{0,25}$ , qUFP) em 59 residências de idosos na RMSP usando o Personal Cascade Impactor Sampler. O  $\text{PM}_{10}$  é a soma da massa em todos os tamanhos e  $\text{PM}_{2,5}$  é o  $\text{PM}_{10}$  menos o  $\text{PM}_{10-2,5}$ . O  $\text{PM}_{2,5}$  e  $\text{PM}_{0,25}$  contribuíram com 78% e 38% do total de  $\text{PM}_{10}$ , respectivamente. Cerca de 77% e 40% das residências apresentaram maior concentração de  $\text{PM}_{2,5}$  e  $\text{PM}_{10}$  do que aqueles em ambientes externos. Cerca de 13 e 43% das medidas excederam as diretrizes da Organização Mundial de Saúde (OMS) para  $\text{PM}_{10}$  e  $\text{PM}_{2,5}$ , respectivamente. O  $\text{PM}_{0,25}$  excedeu o limiar da OMS para  $\text{PM}_{2,5}$  em 8.3% das residências. As residências com maior concentração de PM em todos os tamanhos estão próximas das áreas de intenso tráfego veicular e não houve precipitação durante a medição. Cerca de 68% das residências têm a maior concentração de massa em  $\text{PM}_{0,25}$ . Analisamos os íons por cromatografia, elementos traços por fluorescência de raios-x e rBC por reflectância. A maior concentração de íons em qUFP foi  $\text{SO}_4^{2-}$  e  $\text{NH}_4^+$ , e os principais elementos traços foram Si e Fe. Cerca de 26% do qUFP é rBC. Algumas residências têm uma alta concentração dos metais pesados tóxicos Cu, Ni, Pb e Cr. Identificou-se 6 fontes de qUFP por fatoração de matriz positiva: emissão de veículos (57%), aerossol inorgânico secundário (21%), solo e construção (7%), pintura de parede (7%), cozimento (5%) e indústria (3%). O RDD para  $\text{PM}_{10-2,5}$  e  $\text{PM}_{2,5}$  foi 20% e 24,6% maior para homens do que mulheres enquanto sentados, respectivamente. O RDD máximo de qUFP e rBC foi na parte traqueobrônquica. É importante o controle de fontes de PM nas residências de idosos para limitar os efeitos adversos à saúde, especialmente partículas finas. Sugerimos considerar o rBC como um poluente atmosférico regulado em termos de ações de controle público para a melhoria da qualidade do ar na RMSP.

**Palavras-chave:** Qualidade do ar interior; Material particulado; Composição química; Residência de idosos; Fontes; Doses de deposição respiratória.



# Abstract

SEGALIN, B. **Particulate matter inside residences of elderly in the Metropolitan Area of São Paulo**. Tese (Doutorado em Ciências Atmosféricas) - Instituto de Astronomia, Geofísica e Ciências Atmosféricas, Universidade de São Paulo, São Paulo, 2017, 119 p.

The elderly population is sensitive to damages caused by air pollution on health. They spend relatively more time indoors, however there is limited information on the air quality they breathe inside their residences. The objectives of this work are to characterise mass of size-segregated particulate matter (PM) in elderly residences in Metropolitan Area of São Paulo (MASP) in Brazil; assess the meteorological parameters influence; evaluate the indoor and outdoor relationship of PM; quantify the ions, trace elements and black carbon (rBC) in quasi-ultrafine particles (qUFP) and identify their sources, and estimate the respiratory deposition doses (RDD). To achieve these objectives, we measured during 24 hours the mass concentrations of PM in different sizes (10–2.5, 2.5–1.0, 1.0–0.5, 0.5–0.25 and <0.25  $\mu\text{m}$  ( $\text{PM}_{0.25}$ , qUFP) in 59 elderly residences in MASP using a Personal Cascade Impactor Sampler. The  $\text{PM}_{10}$  is the sum of all size and  $\text{PM}_{2.5}$  is  $\text{PM}_{10}$  less  $\text{PM}_{10-2.5}$ . The  $\text{PM}_{2.5}$  and  $\text{PM}_{0.25}$  contributed 78% and 38% of total  $\text{PM}_{10}$ , respectively. About 77% and 40% of the residences had higher  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  than those in outdoor environments. About 13 and 43% of the measurements exceeded the World Health Organization (WHO) guidelines for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , respectively. The  $\text{PM}_{0.25}$  exceeded the WHO guideline for  $\text{PM}_{2.5}$  in 8.3% of residences. Residences with higher PM concentration in all size bins are predominantly near the heavy traffic areas during the non-precipitation days. About 68% of residences have the highest mass concentration in  $\text{PM}_{0.25}$ . We analysed ions by chromatography, trace elements by x-ray fluorescence and rBC by reflectance. The major of ions concentrations in qUFP were found to be  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and the major trace elements were Si and Fe. Around 26% of the qUFP is rBC. Some residences have a high concentration of the toxic heavy metals Cu, Ni, Pb and Cr. We identified 6 dominant sources of the indoor qUFP by positive matrix factorization: vehicular emission (57%), secondary inorganic aerosol (21%), soil and construction (7%), wall painting (7%), cooking (5%) and industry (3%). The RDD for coarse and fine particles were found to be 20% and 24.6% higher for male than female elderly during seated position, respectively. The maximum RDD of qUFP and rBC are in the tracheobronchial part. It is important the control of PM sources in the elderly residences to limit adverse health effects of PM, especially fine particles. We suggest consider the rBC as one regulated air pollutant in terms of public control actions for air quality improvement in MASP.

**Keywords:** *Indoor air quality; Size-segregated particles; Chemical composition; Elderly residence; Indoor sources; Respiratory deposition doses.*





# 1. Introduction

Air pollution is any form of substance suspension in the air in a quantity above the usual levels that can cause some inconvenient effect to public welfare, security of humans, animals and plants (CONAMA, 1990; Seinfeld and Pandis, 2016).

The effects of air pollution have been known since ancient times, for example the deaths caused by the smoke from volcanic activity. Nevertheless, volcanic activities are not controllable, but the human activities are. However, only in the 20th century emerged legislations to control air pollution from anthropogenic sources in large scale, due to the major accidents in the Meuse Valley (Belgium - 1930), Danora (United States of America - 1948) and London (England - 1952), when a lot of people died during and after these events (Bell and Davis, 2001; Gomes, 2002). In the metropolitan area of São Paulo (MASP), Brazil, the air pollution studies started when the Environmental Protection Agency (CETESB, *Companhia de Tecnologia de Saneamento Ambiental*) was created, in the late 1970s, due to the increase of the air pollution caused by the local economy development (Andrade et al., 2017).

From these events many studies have been done to evaluate the impacts that air pollution causes on health, especially for respiratory problems (Arbex, 2012). The respiratory system is the part of the human body that is most related to the environment and, due to the large amount of air that an individual breathes, any modification in the composition of the air can be a problem for human health (Souza and Neto, 2011).

Currently, the air pollution is known to have a range of adverse effects on human respiratory and cardiovascular health (Kampa and Castanas, 2008; Brook, 2008; Arbex et al., 2012). In metropolitan areas the increase in the level of atmospheric pollutants due to

industries and mainly the vehicular fleet, becomes an additional risk factor for diseases. São Paulo is an example of a metropolitan area (Section 3.1) with high levels of pollution, which are amplified by meteorological conditions that disfavor dispersion of pollutants, such as thermal inversion, absence of winds and precipitation, solar radiation indices, among others (CETESB, 2012). Several studies prove the effects of air pollution on the health of the population of São Paulo (Saldiva et al., 1994, 1995; Gouveia and Fletcher, 2000; Martins et al., 2001; Franscico et al., 2003; Gonçalves et al., 2007; Bourotte et al., 2007; Olmo et al., 2011; Arbex et al., 2012; Miranda et al., 2012; Pinheiro et al., 2014; Bravo et al., 2016).

Among all the pollutants, the PM is the one which has the greatest impact on the human health, both in short-term and long-term exposures (World Health Organization [WHO], 2006). Although has a high concern about it, there is a huge lack of information over the amount of PM inside the people houses. The concern about air pollution in indoor environments started after 1970, when the buildings and houses were being built to be more efficient thermally and to avoid noise, what made difficult the change of the indoor air with the outdoor environment (Brickus and Neto, 1998). In MASP the studies of indoor air pollution started in 1991 (Gioda and Neto, 2002). However the residential indoor air, and size-segregated PM indoor air are not the focus of the major studies in MASP (Brickus and Neto, 1998; Gioda and Neto, 2002; Andrade et al., 2017). It becomes even more important when we consider the fact that elderly — who are one of the most susceptible groups for air pollution — spend the majority of their time in side their houses.

## **1.1. Particulate matter (PM)**

Particulate matter (PM) can be liquid and solid particles suspended in the air (Seinfeld

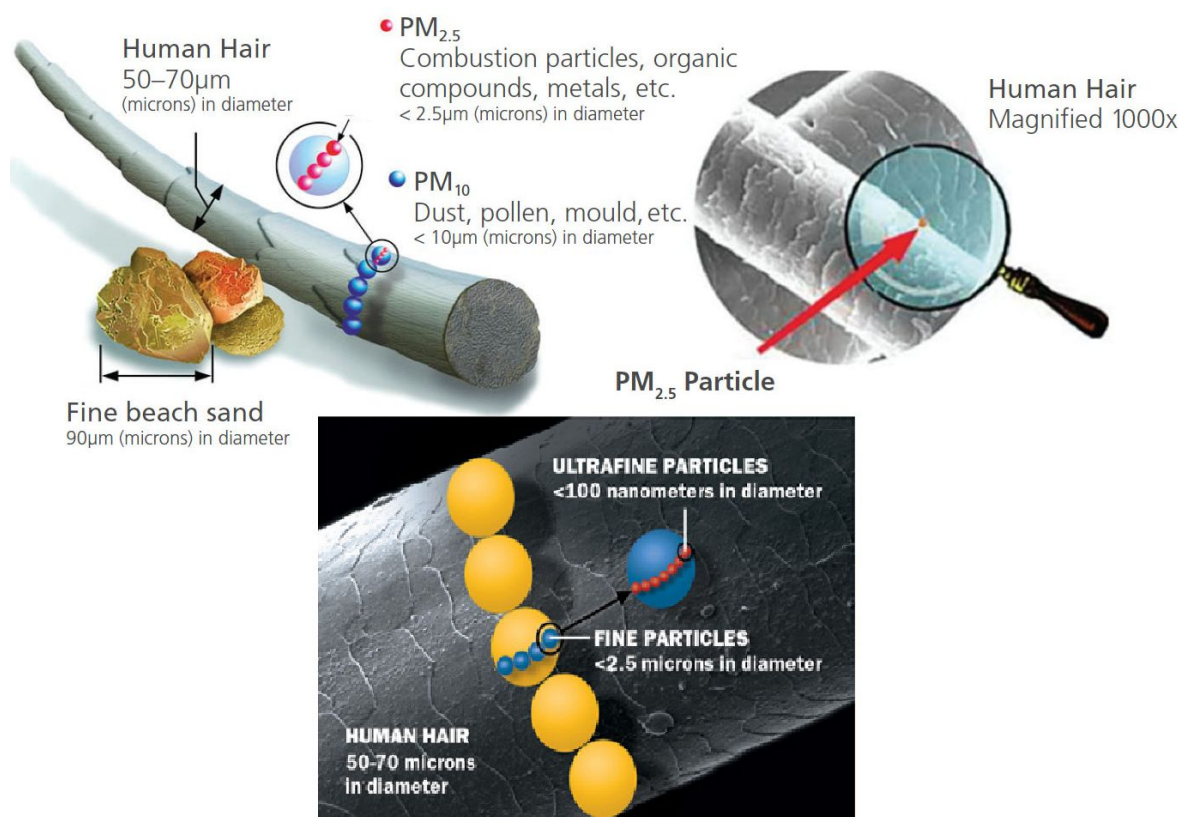
and Pandis, 2016). PM is one of the components of air pollution that can cause problems of visibility, interfere with the solar radiation that arrives at the surface of the Earth, affect plants and animals and cause damage to the human health. The inhalable fraction of PM, which is  $PM_{10}$ , can be divided into coarse ( $PM_{2.5-10}$ ) and fine particles ( $PM_{2.5}$ ; Figure 1). The fine particles also contain particles below 100 nm ( $PM_{0.1}$ , Figure 1), which are referred to as ultrafine particles (UFP; Kumar et al., 2014; Seinfeld and Pandis, 2016). Particles smaller than 0.1  $\mu\text{m}$  in diameter, also referred to as ultrafine particles. The particles with diameters up to 0.25  $\mu\text{m}$ , we refer to as quasi-ultrafine particles (qUFP). The qUFP is an operational definition. This concept has also been utilized in earlier studies (Arhami et al., 2009; Hu et al., 2008; Saffari et al., 2013; Viana et al., 2014).

Particles greater than 10  $\mu\text{m}$  tend to remain in the atmosphere for about one day before depositing in their position in their size (dry deposition), while as 1  $\mu\text{m}$  can remain for weeks in the atmosphere, being withdrawn from the atmosphere by dry deposition or through wet deposition, as they act as a cloud condensation nuclei or they are dragged to the surface by rain (Seinfeld and Pandis, 2016).

The fine and coarse particles generally originate and are transformed separately, are withdrawn from the atmosphere by different mechanisms, have a different chemical composition, and differ significantly from our non-respiratory tract deposition patterns (Seinfeld and Pandis, 2016). This makes the distinction between fine and coarse particles a key element in any discussion of their effects on health.

UFP typically occur in large number of particles while their contribution to the mass concentration is barely noticeable (Kumar et al., 2010; Rivas et al., 2017). On the other hand, coarse particles are low in number but contribute largely to the mass concentration (PM). The

UFP contribute to about 80% of the total number concentrations of the atmospheric particles and the ones with diameter up to  $0.3\ \mu\text{m}$  contribute to over 99% (Kumar et al., 2009, 2010).



**Figure 1.** Illustration of different sizes of particulate matter. Adapted from United States Environmental Protection Agency (EPA).

The UFP are known to have much greater health impacts than their larger counterparts (Martins et al, 2010; Kumar et al., 2011). The fine particles reach the alveoli while ultrafine particles can translocate from respiratory epithelium towards circulation and reach organs such as heart and brain causing adverse effects (Elder et al., 2006; Kreyling et al., 2006; Heal et al., 2012).

The toxic potential of PM is inversely proportional to the particle size. For example, particles with diameters less than  $0.25\ \mu\text{m}$  have higher redox activity (induce oxidative stress

in human cells) than coarse and accumulation modes of particles (Hu et al., 2008). The UFP can also translocate for the bloodstream and achieve other organs such as brain and heart (Elder et al., 2006; Heal et al., 2012). From this perspective, it is very important to study particles of that size range.

In Metropolitan Area of São Paulo (MASP), an ever increasing rate of air pollution due to road vehicles and industries pose significant health risks compared with its surrounding suburban areas (Kumar et al., 2016). In the tunnel experiments in MASP, there was a decrease in the  $PM_{2.5}$  emission factors between 2004 and 2011 (Sánchez-Ccoyllo et al., 2009; Perez-Martinez et al., 2014). However, while light-vehicle emissions have decreased by almost 5 times over the period, the heavy-duty (diesel-powered) emissions were down by half. Then heavy vehicles remain the main source of  $PM_{2.5}$  in the region.

A study carried out in six Brazilian capitals (São Paulo, Rio de Janeiro, Curitiba, Porto Alegre, Belo Horizonte and Recife) showed that São Paulo was the metropolitan region with the highest estimate of the number of deaths associated with outdoor  $PM_{2.5}$ , with 10,000 deaths per year in the MASP (Miranda et al., 2012). However, there is no parallel information about the effects of indoor PM on public health in São Paulo (Miyagusko, 2008; Andrade et al., 2017).

There are uncertainties about the health risk estimates associated with exposure to indoor PM (Lianou et al, 2007) since most of the epidemiological studies are focused on outdoor particles. The urban inhabitants spend up to 90% of their time indoors at home, work or elsewhere (Brown, 1997; Klepeis et al., 2001). Moreover, the concentrations of different PM types vary depending on the type of indoor environments and the quality of the outdoor air surrounding them (Kumar and Morawska, 2013; Salthammer et al., 2016). While the

toxicological and epidemiological studies present evidence of health effects for PM mass concentration (Elder et al., 2006; Kampa and Castanas, 2008; Brook, 2008; Arbex et al., 2012; Heal et al., 2012; Power et al., 2011; Nascimento, 2011; Olmo, 2011; Weuve et al., 2012; Han et al., 2016; Mehta et al., 2016), the effects of different particle sizes on health still require exhaustive assessments. As summarised in Table 1, there are limited studies worldwide that focus on the size-resolved particles in indoor environments and most of the focus usually remains on PM<sub>10</sub> and PM<sub>2.5</sub> (Chao and Wong, 2002; McCormack et al., 2008) or include PM<sub>1</sub> at the maximum (Jones et al., 2000; Goyal and Kumar, 2013; Viana et al., 2014). Studies for indoor elderly environments focusing on size-segregated particles are yet limited. There is a need to characterise the PM concentrations in indoor environments such as the elderly residence that are considered for assessment as part of this work.

**Table 1.** Review of past relevant studies including indoor PM in different size ranges.

Range	Environment type	Key conclusion	Source
PM <sub>10</sub> , PM <sub>2.5</sub> , PM <sub>1.0</sub>	Urban, rural and roadside residences	<ul style="list-style-type: none"> <li>• <i>I/O</i> ratios were greater for fine than coarse particles, and for roadside residences</li> </ul>	Jones et al. (2000)
PM <sub>10</sub> , PM <sub>2.5</sub>	Urban residences	<ul style="list-style-type: none"> <li>• <i>I/O</i> ratios were greater for PM<sub>2.5</sub> than PM<sub>10</sub>;</li> <li>• Residences close to heavy traffic have more PM mass concentration.</li> </ul>	Chao and Wong (2002)
PM <sub>10</sub> , PM <sub>2.5</sub>	Children urban residences	<ul style="list-style-type: none"> <li>• PM<sub>2.5</sub> and PM<sub>10</sub> have mean <math>39.5 \pm 34.5</math> and <math>56.2 \pm 44.8 \mu\text{g m}^{-3}</math>, respectively</li> <li>• Open windows were associated with significantly lower indoor PM</li> </ul>	McCormack et al. (2008)

PM <sub>10</sub> , PM <sub>2.5</sub> , PM <sub>1.0</sub>	Commercial building	<ul style="list-style-type: none"> <li>• PM<sub>10</sub> and PM<sub>2.5</sub> indoor exceed the national standard</li> <li>• <i>I/O</i> is bigger for naturally ventilated places (&gt;1)</li> </ul>	Goyal and Kumar (2013)
PM <sub>2.5-10</sub> , PM <sub>0.25-2.5</sub> , PM <sub>0.25</sub>	School	<ul style="list-style-type: none"> <li>• <i>I/O</i> ratios &gt; 1 if indoor sources influence is greater than outdoor sources; a ratio of &lt;1 indicates the other way around;</li> <li>• PM<sub>0.25</sub> indoor has mean 23.4 µg m<sup>-3</sup></li> </ul>	Viana et al. (2014)

## 1.2. PM and its impacts on elderly health

The susceptibility to air pollution varies with different age groups, socioeconomic status and pre-existing health conditions (Pope, 2000; Peled, 2011; Olmo, 2011). We focused on the elderly population because, among the other population groups, they are growing faster worldwide (Alessandri and Maeda, 2011; United Nations, 2015; Chatterji et al., 2015) and they are a risk group for particles air pollution (Peled, 2011).

The expected trend is the increase from 841 million of elderly in 2013 to more than 2 billion in 2050 when they will surpass the number of children (Chatterji et al., 2015). The recent estimates suggest an increase of 60 years or older population worldwide from 12.3% in 2015 to 21.5% by 2050 (United Nations, 2015). In particular, Brazil is the 5<sup>th</sup> most populous country in the world and almost 30% of its population is expected to cross 60 years, and 6.7% over 80 years, by 2050 (United Nations, 2015). The segment of 80 years or older is the one that registers the highest growth (SMDUSP, 2011). In Brazil, over the last three decades, the population pyramid has been changing from a low developed country to a more developed

country. However, the public health policies have not followed such changes leaving to the elderly submitted to a poor health care. Thus, any effort to improve their life quality is important to those who make the health policies. The researches with focus in elderly people are extremely interesting to the country and any place that are going through for the same changes.

As the elderly population increases, we will expect to see an epidemic of chronic diseases, mainly dementias, cerebrovascular accident, chronic obstructive pulmonary disease, diabetes, heart failure, cancer, and coronary insufficiency (Mathers et al., 2015). In fact, the elderly are more likely to have multimorbidities, either by the senescence process or by the greater exposure to the risk factors and therefore, as commented before, they are a risk group for PM (Peled, 2011). Past study suggest that PM has an highest relative risk for the elderly (Gouveia and Fletcher, 2000) due to their weakened immune system, accumulation of toxic substances over time and pre-existing diseases (Sun and Gu, 2008 ). The air quality standards for  $PM_{2.5}$  or  $PM_{10}$  may not be safe for elderly people and even exposure to much lesser concentrations, compared with the younger age groups, could lead to much higher health risks in elderly because of their lower immunity and less efficient respiratory system (Saldiva et al., 1995; Gouveia and Fletcher, 2000; Peled, 2011; Olmo et al., 2011; Arbex et al., 2012).

Aerosol particles can cause many problems in elderly people such as a change in heartbeat frequency (Holguín et al., 2003), aggravate chronic obstructive pulmonary disease (Osman et al., 2007) and cognitive deficit (Weuve et al., 2012). Past studies suggest association of PM and its compounds with health problems in the elderly such as the acute respiratory inflammation, pneumonia, asthma chronic obstructive pulmonary disease, autonomic cardiac dysfunction, renal and cognitive deficit, and cardiovascular and respiratory



mortality (Saldiva et al., 1995; Liao et al., 1999; Simoni et al., 2003; Holguín et al., 2003; Gonçalves et al., 2007; Halonen et al., 2009; Power et al., 2011; Nascimento, 2011; Weuve et al., 2012; Han et al., 2016; Mehta et al., 2016).

A research in Italy has reported that the elderly people spent significantly more time at home than the other age groups, mainly due to reduced outdoor activities and thereby get exposed to harmful indoor air pollutants for more time (Simoni et al., 2003). Exposure to pollutants based on household estimates can be an excellent measure of personal exposure in retired people (Power et al., 2011), like the majority of the Brazilian elderly who are no longer exposed to the work environment, but to the home environments. For this reason, measurements in such residences are extremely important to assess their air quality.

Also, as summarised in Table 1, there are limited studies about indoor size-resolved particles in where elderly live. For example, Holguín et al. (2003) measured  $PM_{2.5}$  mass concentration for 24 h in an asylum in Mexico. They reported that  $PM_{2.5}$  can interfere with the cardiac frequency of the elderly. Osman et al. (2007) measured  $PM_{2.5}$  mass concentration for about 14 hours in residences in North East Scotland. They discovered higher levels of association of  $PM_{2.5}$  with the worst chronic obstructive pulmonary disease in these elderly. However, the analysis of the different size of PM in the elderly residential environments, covering a full 24 hours diurnal cycle, has not studied in the past researches. Besides the importance of the particles sizes it is also necessary look for its chemical composition and its effect to the health.

### **1.3. Chemical composition of PM**

Atmospheric aerosol particles in the urban environment are characterized by different

sizes, and chemical composition (Heal et al., 2012; Kumar et al., 2014). It is the complex mixture of chemical and elemental components that make up the PM, in part, responsible for its toxicity (Brokamp et al., 2015). The PM has a wide chemical composition that varies both in species and in quantity, according to the location of the sources that originate these particles. Urbanized regions are most affected by air pollution due to variety and large numbers of sources. In addition, weather conditions may or may not favor their formation, dilution, removal and transport. In the MASP the winter is dry, with calm winds, predominance of high pressure systems on the continent and frequent thermal inversions near the surface which favors the highest concentration of pollutants in the region. In this season, combined with lower amounts of precipitation, inhalable particulate concentrations can reach values higher than the national air quality standard ( $150 \mu\text{g}\cdot\text{m}^{-3}$ , 24 hours average) and with a higher frequency of occurrences (Miranda and Andrade, 2005). In addition to the increase of  $\text{PM}_{2.5}$  concentrations, it is observed an increase in the Black Carbon (BC) content (Miranda et al., 2012). These atmospheric conditions may favor the formation of new ultrafine particles (Martins et al., 2010).

In contrast to a significant number of studies on the chemical composition of ambient larger particles, there is hardly any study on the chemical composition of qUFP, specifically if it comes to indoor air pollution (Viana et al., 2014). This is comprehensible in light of the high mass concentrations of particles are expected to be in the coarse and accumulation ranges. While the sheer number concentration of qUFP is a good indicator of the potential health effects, the chemical composition of these particles is equally or even more important to be considered in health impact assessment (Saffari et al., 2013).

Airborne urban particles compositions, including those of qUFP, are characterized by

several metals such as aluminium (Al), arsenic (As), cadmium (Cd), lead (Pb), manganese (Mn), and mercury (Hg), which affect the neurological system (Pohl et al., 2011). Likewise, metals such as Al, Pb, Hg, zinc (Zn), copper (Cu) and iron (Fe) have been clearly associated with Alzheimer's disease, which affects elderly people (Lovell et al., 1998; Polizzi et al., 2002; Zatta, 2003; Zatta and Frank, 2007). Exposure to silica (Si) has been associated with kidney disease, lung cancer, rheumatoid arthritis, tuberculosis and pneumoconiosis (Steenland et al., 2001; Attfield and Costello, 2004). Moreover, nickel (Ni) and vanadium (V) together have negative effects on cardiac function and influence in the short-term mortality (Campen et al., 2001).

All these metals are components of qUFP, which are the focus of this study. For example, Hu et al (2008) reported highest concentrations of Na and S in qUFP collected in Los Angeles - Long Beach Harbor. Further, Viana et al. (2014) studied qUFP inside schools in urban environments and found that most chromium (Cr) and Ni (metals with high redox properties) are present in qUFP rather than in larger particles.

The main indoor source of airborne particles is resuspension from vacuum cleaning, soap/cleaning sprays, smoking, incense burning and cooking, mainly frying activities (Vu et al., 2017). Vacuum sweeping, biological and mineral sources produce predominantly coarse particles (Kamnes et al., 1991). Indoor combustion sources (cooking, wood burning, candle burning, fireplace or kerosene heating) produce mainly particles with diameters below 1  $\mu\text{m}$  (Hussein et al., 2006; Kumar et al., 2013). For UFP, cooking was the most important indoor source (Bhangar et al., 2011). Certainly, outdoor air is also a source for indoor PM, which holds especially for qUFP and UFP because they can best penetrate the natural and artificial ventilation systems (Abt et al., 2000). In schools, for example, the indoor qUFP had major

trace elements and ions sources from outdoor (Viana et al., 2014; Table 1). In the MASP, many trace elements with health effects such as BC, Cu, Zn, Pb, Fe and V were associated with vehicular sources (Andrade et al., 2012; Miranda et al., 2012). The PM fraction from the vehicular traffic combustion processes aggravates ischemic heart disease in the elderly (Lanki et al., 2006).

Some studies about indoor air pollution identify various sources of UFP doing measurements specifically for each possible source, human activities and with a focus on the number of particles generated (Table 2). Only one study analysed the source of indoor qUFP based on their chemical composition (Viana et al., 2014; summarized in Table 2). An interesting question is concerned to quantify how large the contribution of vehicular emissions is to indoor air pollution in elderly residences, and to identify the other possible sources for qUFP. Considering that BC is an important component of PM because it is a vehicle marker, affects global warming and causes health damage, it will be highlighted in this study (Section 1.3.1).

**Table 2.** Review of past relevant studies including indoor qUFP and UFP.

<b>PM types</b>	<b>Environment types</b>	<b>Key conclusions</b>	<b>References</b>
UFP	One 32 m <sup>3</sup> full-scale chamber in Hørsholm, Denmark	<ul style="list-style-type: none"> <li>From 11 indoor specific sources tested was the combustion of pure wax candles that produce more number of UFP.</li> </ul>	Afshari et al. (2005)
UFP	One suburban residence in Virginia, USA	<ul style="list-style-type: none"> <li>Complex cooking was the majority source of UFP number, followed by outdoor sources.</li> </ul>	Wallace (2006)
UFP	One laboratory in New York, USA	<ul style="list-style-type: none"> <li>Out of the seven oil tested, soybean, canola, and safflower oil had the lowest generation of particles</li> </ul>	Torkmahalleh et al. (2012)

qUFP	39 Schools in Barcelona, Spain	<ul style="list-style-type: none"> <li>Indoor source for Zn, Cu, Co, Cl<sup>-</sup>, the outdoor source for Sb, Ba, V, Ni, Ca, Al<sub>2</sub>O<sub>3</sub>, Ti, K, Ni, SO<sub>4</sub><sup>-2</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>.</li> </ul>	Viana et al. (2014)
UFP	Two residences in California, USA	<ul style="list-style-type: none"> <li>In electric appliances and cooking pans, the sources of UFP were detergent residue and organics sorbed from indoor air.</li> </ul>	Wallace et al. (2015)
UFP	One laboratory in Piacenza, Italy	<ul style="list-style-type: none"> <li>Burn wood in a manual heaters utensil instead pellet in an automatic produce more UFP with more toxic chemical composition</li> </ul>	Ozgen et al. (2017)

### 1.3.1. Black Carbon

The Black Carbon (BC) is one of the major component of PM<sub>2.5</sub> and its predominant sources are fossil fuel combustion (mainly diesel) for transportation, solid fuels for industries, residential wood and coal burning, biomass open burning (agriculture, forest and vegetation in general) and power plants using heavy oil or coal (Janssen et al., 2012; Bond et al., 2013). Consequently, the BC is an indicator of a PM mixture generated from a wide variety of combustion sources. BC, when present in the atmosphere, can influence climate change and cause harmful effects to health.

The BC is considered a climate forcing because it plays an important role in the climate of the Earth. It absorbs solar radiation by heating the atmosphere and disperses the light by reducing the solar radiation that reaches the surface and it is reflected back into space (Bond et al., 2013). In addition, BC affects cloud processes by changing the number of ice droplets and particles, changes the temperature structure of the clouds and cause melting of snow and ice due to their absorption of solar radiation (Bond et al., 2013; Gonçalves et al.,

2012; Costa et al., 2014).

There is an association of daily variations in BC concentration, as well as in the medium and long term, with changes in health due to cardiovascular mortality and cardiopulmonary hospitalizations (Janssen et al., 2012). The exposure of the elderly to BC is significantly associated with disturbances of the autonomic control of the heart (Schwartz et al., 2005), a decrease in blood pressure (Mordukhovich et al., 2009), cognitive decline (Power et al., 2011) and worsening of preexisting conditions such as coronary heart disease and diabetes (Fang et al., 2012). BC can affect negatively the respiratory system and cognition of elderly people (Jansen et al., 2005; Power et al., 2011). BC combined with iron and nickel has been found to affect the cardioregulatory system (Chang et al., 2007). Short-term human health effects studies show that associations with BC are more robust than those with  $PM_{2.5}$  or  $PM_{10}$ , suggesting that BC is a better indicator of harmful PM from combustion processes (in particular from vehicles emission) than only the mass concentration of PM (Janssen et al., 2012).

Considering the BC climate change effect, it can cause also indirect effects on human health. Climate changes affect the thermal comfort of the population. The thermal stress can cause health effects on the population of São Paulo, such as respiratory morbidity (Gonçalves et al., 2005). The thermal discomfort will increase in São Paulo due to climate changes (Batista et al., 2016) and the elderly can suffer with heat discomfort indoors (Alves, Duarte and Gonçalves, 2016) and cognitive problems (Trezza et al., 2015).

The BC present in  $PM_{2.5}$  is strongly dependent on the distance of the high vehicular traffic routes, with a significant decrease of the concentrations up to 100 m of distance (Ranf et al., 2009). In most urban areas of Brazil vehicles are considered the main source of

emission of pollutants in the atmosphere. Experiments carried out in road tunnels are important in the evaluation of emission factors of pollutants by the real fleet circulating in the region, which also avoids meteorological effects and photochemical transformations. The contribution of heavy vehicles to BC emissions was 29 times higher than that of light vehicles in 2004 and probably can be relatively higher, considering that PM emissions by light vehicles have decreased more significantly (Sánchez-Ccoyllo et al., 2009).

Past studies in the MASP, showed that more than 90% of the BC is present in inside the  $PM_{2.5}$ , with mass concentration maxima at the  $d < 0.094 \mu m$ , and a secondary peak in the accumulation mode,  $d \sim 0.59 \mu m$ , indicating that the BC was originated from primary emissions as ultrafine particles (Ynoue and Andrade, 2004). The mass proportion of BC present in  $PM_{2.5}$  was  $21 \pm 4\%$  in winter and  $28 \pm 10\%$  in summer (Castanho and Artaxo, 2001). More recently, there was an increase in these values, reaching the proportion of  $38 \pm 14\%$  (Miranda et al., 2012). Between six Brazilian capitals (São Paulo, Rio de Janeiro, Curitiba, Porto Alegre, Belo Horizonte and Recife), the highest proportion of BC in  $PM_{2.5}$  was in São Paulo (Miranda et al., 2012). According to the results of several studies, BC was considered a vehicular source marker for MASP. It is a parameter to analyse the effects of particles from vehicles source and their effects on human health. In the best of our knowledge, there are no studies on the effect of BC on health in Brazil, and about BC in  $PM_{0.25}$  in the worldwide.

There are many lack in the research about indoor air quality in MASP. We intend fill these gaps, and the results of this research, together with outdoor air quality information obtained through an official monitoring network, can guide public policies aimed at improving the quality of life of the elderly in the large Brazilian cities.

## 2. Objectives

The main objective of this work is to analyse the particulate matter (PM) inside the residences of the elderly people in the Metropolitan Area of São Paulo (MASP). The specific objectives of this are:

1. Quantify size-segregated PM mass concentration in indoor air of these residences.
2. Assess the influence of outdoor meteorological conditions on the indoor PM concentration.
3. Understand the relationship between the indoor and outdoor (*I/O*) PM mass concentrations.
4. To quantify ions, trace elements and black carbon (rBC) present in quasi-ultrafine particles (qUFP) mass concentration inside elderly residences.
5. To quantify rBC present in qUFP and its relationship with weather conditions mass concentration inside elderly residences.
6. To identify the sources of the qUFP inside elderly residences.
7. Estimate the respiratory deposition doses (RDD) of the size-segregated particles and rBC in different parts of respiratory tract.



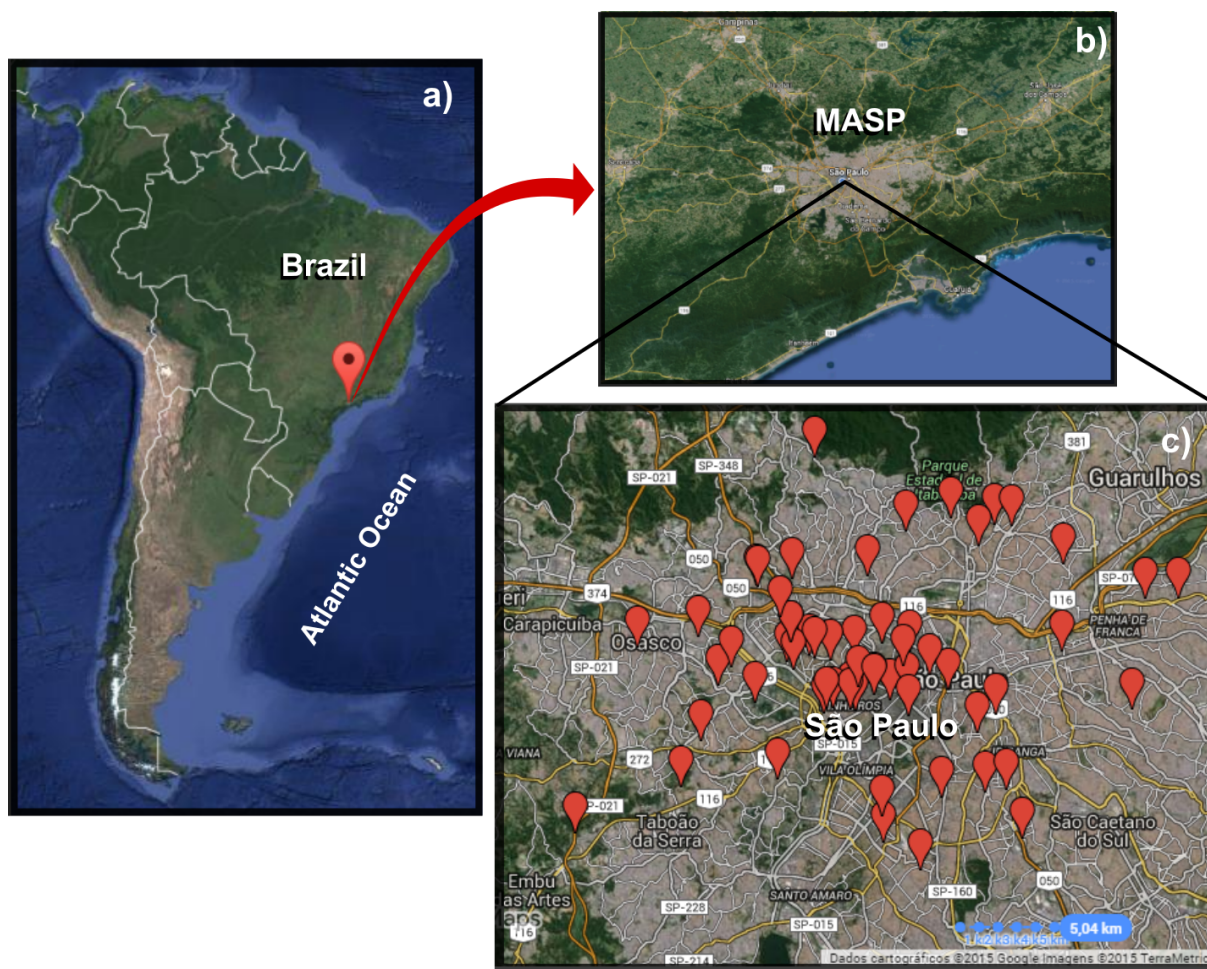
## 3. Methodology

This section describes the data and methods used in the three papers that generated this thesis (Segalin et al., 2016, 2017a,b).

### 3.1. Site description

The MASP is situated in the State of São Paulo in Brazil (Figures 2a–b). The MASP has a population of about 21 million and is the 12<sup>th</sup> major agglomeration of the world (IBGE, 2016; City Population, 2016; Andrade et al., 2017). This agglomeration includes the city of São Paulo with almost 12 million people (IBGE, 2016) and more than 8.5 million vehicles (DETRAN, 2017). The number of vehicles increases year after year and they are the major source of air pollutants in São Paulo (CETESB, 2015). Despite this, the pollution concentration has decreased in the last 30 years due regulation and change in the fuel, except for ozone and PM<sub>2,5</sub> (Andrade et al., 2017).

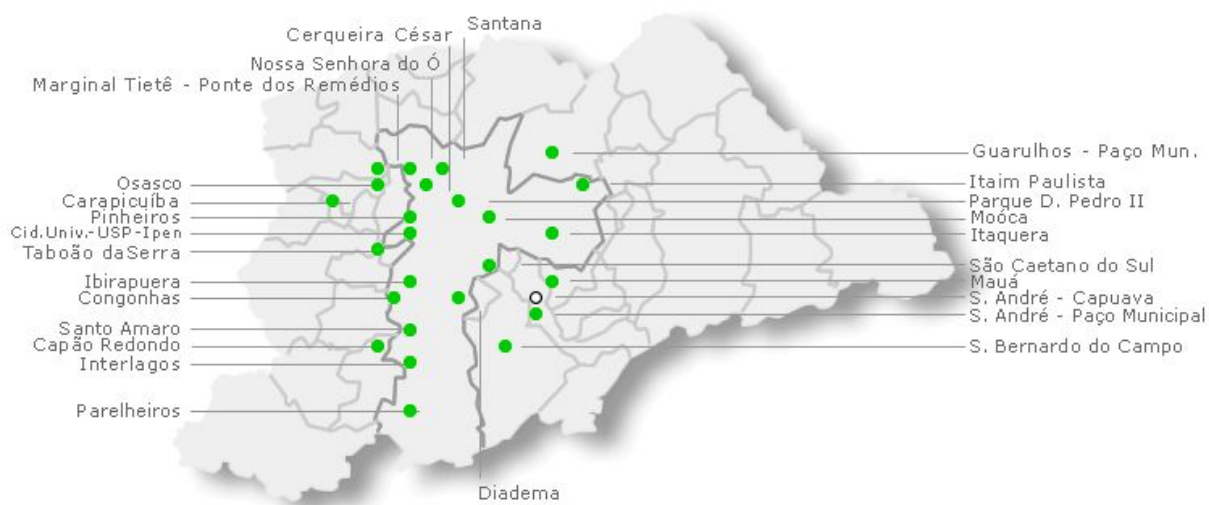
MASP is a subtropical region with hot and rainy summer and dry winter, the annual average of precipitation, relative humidity and temperature are 1409.5 mm, 81.2% and 18.7 °C (Climatological Report, 2016). The pollution levels in the MASP are amplified by weather conditions (e.g., thermal inversion, light winds, little precipitation and high levels of solar radiation) that inhibit the dispersion of pollutants during the winter season (dry season) between June and September (CETESB, 2016).



**Figure 2.** Maps of (a) Brazil in South America, (b) Metropolitan Area of São Paulo – MASP, and (c) locations of elderly residences where indoor PM size-resolved were sampled in MASP. The pictures were taken from Google maps (<https://maps.google.com/>).

The fixed-site air quality monitoring in MASP (Figure 3) is made by automatic monitoring network, run by the Company Environmental State of São Paulo (CETESB). The CETESB is a governmental organization responsible for certifying the quality of air and water in São Paulo. The air pollutants that these stations of CETESB measure are total suspended particles,  $PM_{10}$ ,  $PM_{2.5}$ ,  $SO_2$ ,  $O_3$ ,  $NO_x$ , CO, smoke, benzene, toluene, sulphur, acetaldehyde and formaldehyde (CETESB 2015; CETESB, 2016). About 87% of the air pollution monitored in

the city of São Paulo comes from more than 8.5 million vehicles (CETESB, 2015; DETRAN, 2017). A number of interventions have already been taken to reduce the pollutant concentrations in the MASP but the outdoor levels of PM concentrations still remain over the local standards during most of the time (Kumar et al., 2016).



**Figure 3.** Automatic stations of the network of monitoring from CETESB (green points) in the Metropolitan Area of São Paulo. The pictures were taken from CETESB ([http://sistemasinter.cetesb.sp.gov.br/Ar/php/mapa\\_qualidade\\_rmisp.php](http://sistemasinter.cetesb.sp.gov.br/Ar/php/mapa_qualidade_rmisp.php)).

More than 12% of people living in the city of São Paulo are 60 years and over; this percentage is increasing (Alessandri and Maeda, 2011). In this study, the people are considered as elderly when they cross 60 years of age. We had 60 elderly voluntaries who participated in our work (Section 3.2), being none of them nursing home dwellers. The most part of the elderly in Brazil lives in their own or relatives residences. For example, more than 64% of the elderly are responsible for financial support of the residences in the Brazilian

familiar structure (IBGE, 2000). Besides, the culture of nursing homes in Brazil is either private and very expensive or with bad conditions to live (Quiroga, 2007) and both are shelter especially for debilitated elderly, who do not have the profile for the project selection criteria (Section 3.2). Activities by the residents inside their residences contribute to increased concentration of pollutants indoor (Ferro et al., 2004). The environmental conditions of elderly residences differs from the others because the elderly spend most of their time inside their residences (Section 3.2) while other groups spend much of their daytime away from their residences (e.g., children staying in school and adults at the work). In addition, elderly population does not open their windows often. In this way, the elderly have the greatest exposure to indoor pollutants in their residential environments compared with other age groups.

Figure 2c shows the location of elderly residences in the MASP. A total of 60 samples were collected from 59 elderly residences. These samples were collected from the cities of São Paulo (57), Osasco (2) and Embu das Artes (1), all belonging to MASP. The sampled areas cover more than 62% of the population of the MASP, which has the highest proportion of elderly compared with the rest of the city (Alessandri and Maeda, 2011; IBGE, 2016). Therefore, our study region represents the area with the highest density of the elderly. Out of the total 59 residences studied, 37 were apartments whereas 22 were detached houses; most of this residences were single story with ground-level floor. All these residences were naturally ventilated where the wind and buoyancy-induced flow transported the outdoor pollutants to indoors through open windows and doors, and the Brazilian people usually open the windows and doors. Due to low-income of the population in São Paulo, only a few richest people have central heating or cooling system and less than 2% of the population have air conditioning in

their residences (IBGE, 2004). All MASP residences use liquefied petroleum gas in individual cylinders or piped natural gas for cooking purposes. For provide heating and hot water for shower the residences use electricity (mainly from hydroelectricity).

### **3.2. Study design**

This study was carried out within the framework of FAPESP funded project (2010 / 10189–5), the São Paulo financial support Agency, named as "Human biometeorology: analysis of the effects of environmental variables (meteorological, thermal comfort and atmospheric pollution) and climate change in the geriatric population of the city of São Paulo". This thematic project subsidizes the National Institute of Integrated Environmental Risk Analysis (INAIRA MCT / CNPq FAPESP), as well as the Nucleus of Support for Research on Climate Change at the University of São Paulo (INCLINE).

Within the framework of this project, we selected volunteers from the Faculty of Medicine Clinics Hospital at the University of São Paulo, as per the criteria pre-established by the project team of geriatricians. The main criteria were that the person had to be either 60 years of age or older and should be a volunteer accepting the terms of consent, approved by the Ethics Committee in Research of the Faculty of Medicine Clinics Hospital at the University of São Paulo (number 619274). The additional criteria involved the following (Trezza et al., 2015). The elderly should have four years or more of schooling. They should not be obsessed, depressed, or disabled (on wheelchairs or crutches). All the elderly were submitted to three different tests:

1. Mini-Mental State Examination (MMSE; Folstein et al., 1975)

2. Geriatric Depression Scale (GDS; Sheikh et al., 1991)
3. Short Physical Performance Battery (SPPB; Guralnik et al., 1994).

MMSE is for evaluating cognitive deficit of the individual. GDS is for assessing possible symptoms of depression while the SPPB allows checking the balance deficit. Only the elderly that passed all these conditions and tests were selected to participate as our volunteers. Thus, the studied residences chosen were those where the approved volunteers live.

Initially, we had 88 elderly volunteers. Of which, 11 did not pass in at least one of our criteria and another 14 dropped out due to their sick health. This left 63 elderly houses for our measurements; 3 of them had an error in data set leaving a legitimate data set of 60 elderly. We placed Personal Cascade Impactor Sampler (PCIS) for the collection of size-segregated samples in the living rooms of 60 elderly for 24 hours in each case (more detail in the next section). We collected 60 samples from 59 elderly residences because two volunteers were living in the same residence. Out of 59 elderly residences, six of these residences have a smoker resident. There were 47 female and 13 male volunteers in our 60 elderly; this proportion was expected given that the MASP has relatively more female than male elderly (30%; Alessandri and Maeda, 2011). These 60 elderly stayed 79% ( $18.95 \pm 2.2$  h) of total 24 h of time inside their residences, which is up to ~13% higher time than the elderly studied in Italy (Simoni et al., 2003). These elderly are  $73.9 \pm 5.7$  years old and the oldest is a female 87 years old.

### **3.3. Instrumentation**

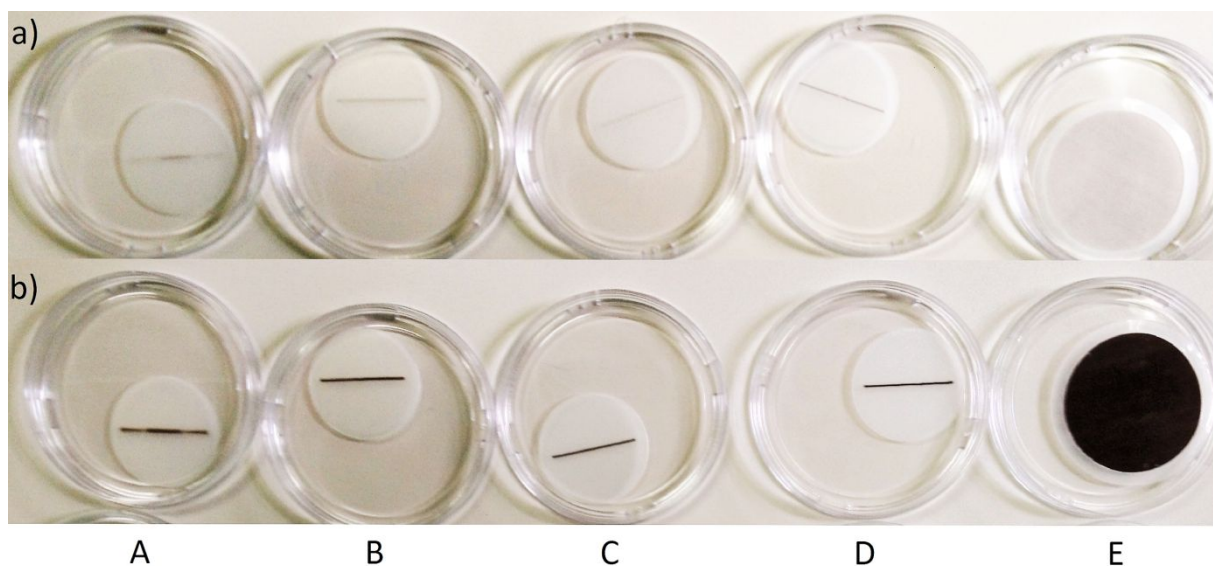
We sampled the PM data with the PCIS, which is a miniaturised cascade impactor. It

has the following four impaction and one post-filter stages: 10–2.5  $\mu\text{m}$  (referred hereafter as A), 2.5–1.0  $\mu\text{m}$  (B), 1.0–0.5  $\mu\text{m}$  (C), 0.5–0.25  $\mu\text{m}$  (D) and <0.25  $\mu\text{m}$  (E; this is a post-filter stage and referred interchangeably as  $\text{PM}_{0.25}$ ). The schematic diagram of the PCIS can be seen in Figure 4 and its further description can be found elsewhere (Misra et al., 2002; Sioutas, 2004). To ensure that the particles are separated precisely in these size-bins, the PCIS must be used with a Leland Legacy Sample Pump (SKC Inc., Cat. No. 100–3000), which runs at a sample flow rate of 9  $\text{L min}^{-1}$ . The PCIS is optimised for this flow rate for 24 h (Sioutas, 2004). The particles were collected on a 25 mm Teflon filter above the cut-off points for A, B, C and D. In order to gather  $\text{PM}_{0.25}$  (E), the PCIS used a 37 mm Teflon filter (Figure 5). Teflon is preferred for collecting such particles since this does not interfere with gravimetric analysis and chemical composition (Misra et al., 2002).



**Figure 4.** Photograph of the Personal Cascade Impactor Sampler (PCIS) and the Leland Legacy Sample Pump (SKC).





**Figure 5.** Example of sampled filters with PCIS indoor elderly residences in the MASP when (a) there was precipitation and (b) there were many days without precipitation on residence close to the avenue with intense traffic vehicular. PCIS stages A, B, C, D and E correspond to  $PM_{2.5-10}$ ,  $PM_{1.0-2.5}$ ,  $PM_{0.5-1.0}$ ,  $PM_{0.25-0.5}$  and  $PM_{0.25}$ , respectively.

Past validation tests have shown that PCIS can collect up to 3.6 mg of fine particles and 0.7 of coarse particles (Sioutas, 2004) and that there is no efficiency loss in the measurement of PM up to 10  $\mu\text{m}$  in environments that have the wind speed up to 2.2  $\text{m s}^{-1}$  (Singh et al., 2003). The PCIS is small and lightweight and can be hung on a person's clothing collar (Figure 4). However, the elderly found inconvenient to carry both the PCIS and the pump due to noise and weight of the pump. For this reason, we placed the PCIS inside their living rooms, where elderly people spend majority of their daily time, at a height of between 0.5 and 1.0 m. Since elderly spend 79% of their total daily time in their residences, our measurements can be considered representative of their indoor exposure.

In order to circumvent contamination and maintain the quality assurance and precision of our measurements, we made an ultrasonic cleaning in the PCIS before each measurement to avoid contamination of samples from one residence to another. We calibrated the pump before



each measurement to avoid variations in the flux with the time of continued use. We also evaluated blank filters (without sample) for all the handling processes and measurement to assess any sign of contamination.

### 3.4. Data collection

The samples were collected between a period of May 2014 and July 2015, as per the availability of the elderly volunteers. The samples were collected in March (5), April (6), May (9), June (13), July (15), September (1), October (6), November (4) and December (1). A total of 31 samples were collected in 2014 and the rest of the 29 samples in 2015. In each case, the sampling started during the morning in different hours in accordance with the availability of the elderly, continuously for 24 h in each residence, except for one residence where two elderly were volunteers; we made two measurements on two different dates in this residence. The PM mass concentrations collected on the samples were weighed using a gravimetric method that had a precision scale of 1  $\mu\text{g}$  (MX5; Mettler–Toledo, Columbus, OH, USA). These weights were taken in a room with controlled environmental conditions that had a temperature of  $22 \pm 2^\circ\text{C}$  and relative humidity (RH) of  $45 \pm 3\%$ . For obtaining the  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  mass concentration, we sum the mass concentration of impaction stages A–E and B–E, respectively.

To analyse the meteorological conditions that may have influenced on PM mass concentration we used data of temperature, relative humidity (RH), precipitation and wind speed and direction of the sampling day, obtained from the Meteorological Station of the Institute of Astronomy, Geophysics and Atmospheric Sciences of the University of São Paulo

(IAG-USP), located in the Água Funda, São Paulo (Climatological Report, 2016).

### **3.5. Chemical analysis**

The chemical analysis was made only in the qUFP (E stage of PCIS). The quantity and the structure of PM deposition on the filters in the A-C PCIS stages (Figure 5) make the chemical analysis difficult and even impossible for some technique (Energy Dispersive X-Ray Fluorescence and Reflectance).

#### **3.5.1. Ions and trace elements**

We analysed trace elements present in qUFP using Energy Dispersive X-Ray Fluorescence technique (EDXRF - EDX 700HS; Shimadzu Corporation, Analytical Instruments Division, Tokyo, Japan). The ions analyses were carried out by using ionic chromatography and conductivity detection (Metrohm 850, Herisau, Switzerland). For the aqueous extraction, we placed each Teflon filters in pre-cleaned low-density polyethylene tubes with 10 ml ultrapure water. These samples were shaken for at least 2.5 hours. Thereafter, the solutions were filtered by Millex polyvinylidene difluoride filters (0.22  $\mu\text{m}$  pore size; Millipore, Bedford, MA, USA), followed by ions analyses with ionic chromatography.

All sample analyses were blank-corrected and the trace elements and ions with  $\frac{2}{3}$  or more samples below detection limits (DL) were excluded from this work (Mg, Mn, Se, Sr, Cr, Cd, Rb, V, Sb, As and  $\text{C}_2\text{O}_4^{2-}$ ). For the remaining samples, the compounds with values below DL were replaced by half of the average of their DL (Polissar et al., 1998; Khan et al., 2016). During further data analysis of mass concentrations, we considered some elements to be

present in their oxidized form, for example, aluminum as aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and iron as iron oxide ( $\text{Fe}_2\text{O}_3$ ) (Table 3; Kotz and Purcell, 1987; Hueglin et al., 2005; Beuck et al., 2011).

**Table 3.** Conversion factors for the mass concentration of the trace elements in the frequently form see in the atmosphere.

Elements	Conversion factor	Frequently form
Al	1.89	$\text{Al}_2\text{O}_3$
Si	2.14	$\text{SiO}_2$ and $(\text{Si}_3\text{O}_8)^4$ <sup>a</sup>
P	2.29	$\text{PO}_4^{-3}$
Ti	1.7	$\text{TiO}_2$
Cr	1.46	$\text{Cr}_2\text{O}_3$
Fe	1.43	$\text{Fe}_2\text{O}_3$
Ni	1.0	Ni
Cu	1.25	CuO
Zn	1.24	ZnO
Br	1.0	Br
Pb	1.0	Pb
Ca	2.5	$\text{CaCO}_3$

<sup>a</sup> 50% each (Beuck et al., 2011)

### 3.5.2. Black Carbon (rBC)

In the literature, the terminology "Black Carbon" is used for different measures that vary according to their properties, measurement techniques and related uncertainties, which can cause divergence of results, confusion in the comparison between scientific works and in the use of the term in the legislation of air quality. Due to these facts, Petzold et al. (2013) recommend adequate terminologies to clarify the terms used for BC. In our work we will use measures obtained by reflectance technique and, therefore, we will use the terminology rBC from now on, according to Petzold et al. (2013). We will make comparisons with works that used the same measurement technique.

The rBC mass concentration was quantified by optical reflectance measurements with a refractometer (smoke stain reflectometer model 43D; Diffusion Systems Ltd, London, UK). The rBC concentration (in  $\mu\text{g}\cdot\text{m}^{-3}$ ) was calculated by the empirical equation, valid for the equipment used for our measurements (Miranda et al., 2012):

$$rBC = ((82,794 - (73,206 * \log(m)) + 15,901 * \log(m)^2) * a) / v \quad (1)$$

where:

$m$  is the average of two measures of reflectance carried out on the same filter

$a$  is the area of the filter where there are particles (sampled area) [ $\text{cm}^2$ ]

$v$  is the volume of air sampled [ $\text{m}^3$ ]

## 3.6. Statistical analysis

This section describes the cluster analysis and respiratory deposition doses methods used in Segalin et al. (2017a) and Segalin et al. (2017b) in sequential form, as well as positive matrix factorization used in Segalin et al. (2017b).

### 3.6.1. Cluster analysis

In order to understand the behaviour of size-segregated PM mass concentration in elderly residences, we carried out a cluster analysis by grouping our data. The cluster analysis is used to group a set of data; for example, the data with similarity patterns stay in the same group and referred as a cluster (Wilks, 1995; Maimon and Rokach, 2010). In our study, applying cluster analysis we put the elderly residences with a similar profile of size-segregated PM in a cluster, allowing us to assess the particle behaviour patterns inside

these residences. We used the R package "Cluster", which is an open-source statistical tool, for partitioning (clustering) our data into 5 clusters (Kaufman and Rousseeuw, 1990). We apply this partitioning method in 59 residences. The residence #27 is not added in this analysis due to being an outlier with a significant higher PM mass concentration; otherwise, this could have added far greater weight in the cluster and falsify the representativeness of the groups.

In order to group the elderly residence by mass concentration, trace elements and ions, we choose the *pvclust* package (Suzuki and Shimodaira, 2009) in R programming language for cluster analysis. This algorithm calculates the *p*-value for each cluster in a cluster hierarchy as generated by the *hclust* function. The *pvclust* provides approximately unbiased *p*-value (AU - Shimodaira, 2002) to reduce test bias and the bootstrap probability *p*-value (BP) calculated by multiscale bootstrap resampling (Shimodaira, 2004). We chose AU  $\geq$  95% as a cut point for the clusters because the clusters are robustly supported by the database with this cut point (Shimodaira, 2004; Suzuki and Shimodaira, 2009). For this analysis, the sample #27 was removed because it is an outlier with respect to the mass concentration. We also analysed the meteorological variables for the groups generated by the cluster analyses. We obtain data on temperature, relative humidity, wind speed and precipitation from the meteorological station of Institute of Astronomy, Geophysics and Atmospheric Science (IAG). This station has an average distance of 13.9 km of the residences.

We also calculated the shortest distance between each of the 60 sampled residences and the 27 fixed-site outdoor official air quality monitoring stations (run by the CETESB) in the MASP to find out the closest station to the sampled residences and compare them with the measured indoor concentrations on the same date. The atmospheric concentrations of PM<sub>2,5</sub>

and  $PM_{10}$  from CETESB were obtained by beta continuous ambient particulate monitors (Thermo Scientific 5014i, Electron Corporation, USA).

### 3.6.2. Positive matrix factorization (PMF)

We used the Positive Matrix Factorization (PMF; Paatero and Tapper, 1994) free software by the U.S. Environmental Protection Agency (EPA), version 5.0 (Norris et al., 2014). The PMF is a robust tool to find sources in a particulate matter database (Ogulei et al., 2006a,b; Wallace, 2006; Gietl and Klemm, 2009; Beuck et al., 2011; Amato et al., 2014; Al-Dabbous and Kumar, 2015; Brown et al., 2015; Goel and Kumar, 2015; Khan et al., 2016; Vu et al., 2017). The PMF allows us to decompose the data matrix,  $\mathbf{D}$ , into two matrices  $\mathbf{W}$  and  $\mathbf{H}$  (Cichocki et al., 2009):

$$\mathbf{D} = \mathbf{WH} + \boldsymbol{\varepsilon} \quad (2)$$

where the matrix  $\mathbf{W}$  is the matrix with the proportion of each source in each elderly residence, while the matrix  $\mathbf{H}$  contains the proportion of each ion and trace element in each source, and  $\boldsymbol{\varepsilon}$  is the error matrix. In this way, the inputs of PMF are the mass concentration of the variables for each residence and the uncertainties of their mass concentrations (one advantage of the PMF). The uncertainty ( $\mathbf{S}_{ij}$ ) was calculated with Eq. (3) in accordance with Chueinta et al. (2000), using the estimated measurement error (Eq. 4) from Ogulei et al. (2006a) and the constant  $C = 0.04$ , that produce the best value proximity between of the residual sum of squares ( $Q$ ) and the theoretical value (Ogulei et al., 2006b):

$$\mathbf{S}_{ij} = \sigma_{ij} + C N_{ij} \quad (3)$$

$$\sigma_{ij} = 0.01 (N_{ij} + \bar{N}_j) \quad (4)$$

where  $\sigma_{ij}$  is the estimated measurement error,  $C$  is a constant,  $N_{ij}$  is the mass concentration a  $\bar{N}_j$  is the arithmetic mean of the  $N_j$  values, in the  $i$  sample in  $j$  variable. An extra modeling uncertainty of 5 % was added in PMF model to cover any methodological error (Khan et al., 2016). We categorizes the contributions of elements through value of signal to noise (S/N) as “bad” ( $S/N < 0.5$ ), “weak” ( $1.0 < S/N \leq 0.5$ ) and “strong” ( $S/N \geq 1.0$ ) as suggested by Norris et al. (2014). We further considered as “weak” all those elements with more than  $\frac{1}{3}$  of data below DL (Br, Cr, Ti, Ni and  $\text{NO}_3$ ). For this analysis, sample #27 was also removed.

We chose the number of the factors following the Brown et al. (2015) methodology. They analyse the  $Q_{robust}/Q_{expected}$  value, and when the changes in this fraction became small with the increasing of the factors, the optimal solution is the number of the factors before the change became small. The PMF gave us the  $Q_{robust}$  and  $Q_{expected}$  as follow:

$$Q_{expected} = (S * SS) - ((F * S) + (F * SS)) \quad (5)$$

where  $S$  are the number of the samples,  $SS$  are the strong species and  $F$  is the number of the factors. We run the PMF for 3-8 factors and we found the best solution with 6 factors (Table 4).

**Table 4.** Q-values for PMF runs with 3-9 factors.

<b>Factors</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
<b><math>Q_{robust}</math></b>	551.3	442.6	339.6	259.5	206.9	168.8	134.2
<b><math>Q_{true}</math></b>	551.3	442.6	339.6	259.5	206.9	168.8	134.2

$Q_{\text{expected}}$	663	589	515	441	367	293	219
$Q_{\text{robust}}/Q_{\text{expected}}$	0.83	0.75	0.66	0.59	0.56	0.58	0.61

### 3.7. Respiratory deposition doses (RDD)

We calculated the total respiratory deposition doses (RDD) in the respiratory tract of elderly using the Eq. (6), as used by earlier studies (Azarmi and Kumar, 2016; Kumar and Goel, 2016; Rivas et al., 2017; Kumar et al., 2017):

$$RDD = (VT \times f) \times DFi \times PM_i \quad (6)$$

where  $VT$  is a tidal volume ( $\text{m}^3$  per breath),  $f$  is the typical breath frequency (breath per minute),  $DFi$  is deposition fraction of a size fraction  $i$ , and  $PM_i$  is the mass concentration in different size fractions. The DF is estimated using the Eq. (7), given by (Hinds, 1999), as:

$$DF = IF \left( 0.0587 + \frac{0.911}{1 + \exp(4.77 + 1.485 \ln d_p)} + \frac{0.943}{1 + \exp(0.508 - 2.58 \ln d_p)} \right) \quad (7)$$

where  $d_p$  is the mean diameter and  $IF$  is given by Eq. (8), given by (Hinds, 1999), as:

$$IF = 1 - 0.5 \left( 1 - \frac{1}{1 + 0.00076 d_p^{2.8}} \right) \quad (8)$$

The values of  $VT$  and  $f$  depend on the person gender and physical activity (Hinds, 1999). Considering elderly in an indoor environment, we chose light exercise and seated positions as their physical activities. For light exercise,  $VT$  and  $f$  values are taken as  $9.9 \times 10^{-4}$  ( $12.5 \times 10^{-4}$ )  $\text{m}^3$  per breath and 21 (20) breath per minute for female (male), respectively (Hinds, 1999). For seated position,  $VT$  and  $f$  are taken as  $4.6 \times 10^{-4}$  ( $7.5 \times 10^{-4}$ )  $\text{m}^3$  per breath and 14 (12) breath per minute for female (male), respectively (Hinds, 1999).



## 4. Results and discussion

In this section we present the results of size-segregated PM mass concentration, the influence of outdoor meteorological conditions on the indoor PM concentration, the indoor and outdoor relationship of PM published on Segalin et al. (2017a), the black carbon published on Segalin et al. (2016), the ions and trace elements in qUFP, chemical mass balance and cluster analysis of qUFP, the sources of qUFP submitted as Segalin et al. (2017b). Also we present the results of respiratory deposition doses (RDD) part published on Segalin et al. (2017a) and part submitted as Segalin et al. (2017b).

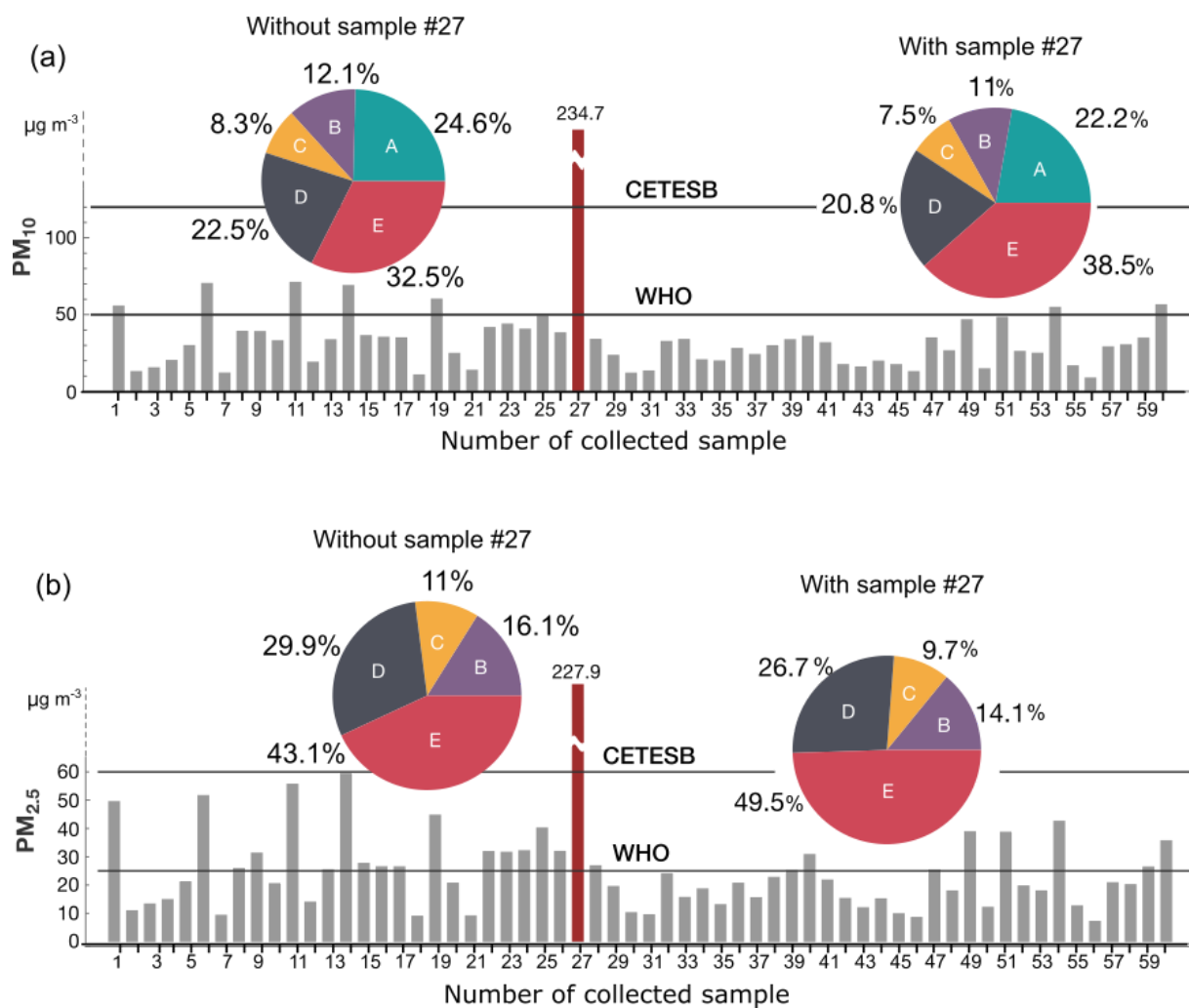
### 4.1. Size-segregated PM mass concentration

This section was published on Segalin et al. (2017a).

Figure 6 shows the mass concentration of  $PM_{10}$  and  $PM_{2.5}$  in elderly residences and the percentage in each of the PCIS stages present in  $PM_{10}$  (Figure 6a) and  $PM_{2.5}$  (Figure 6b). Fine particles were found to dominate (77.8%) of total  $PM_{10}$  mass concentrations inside the elderly residences, leaving a difference of 22.2% for coarse particles (see A in pie graph, Figure 6a, without the sample #27). The fraction of fine particles inside the elderly residences is much higher (~18%) than those in the outdoor environment of the MASP where  $PM_{2.5}$  contribution to  $PM_{10}$  is ~60% (CETESB, 2015). On the other hand, the  $PM_{0.25}$  is a dominant fraction of fine particles, contributing up to about 50% of  $PM_{2.5}$ , suggesting their origin from fuel burn by vehicles. Results of our previous work showed that the black carbon measured by reflectance (rBC; tracer of fuel combustion) was more than 26% of the  $PM_{0.25}$  measured in these elderly

residences. These results indicate a significant contribution from vehicular emissions inside our studied residences due the majority of them being close to streets with intense road traffic.

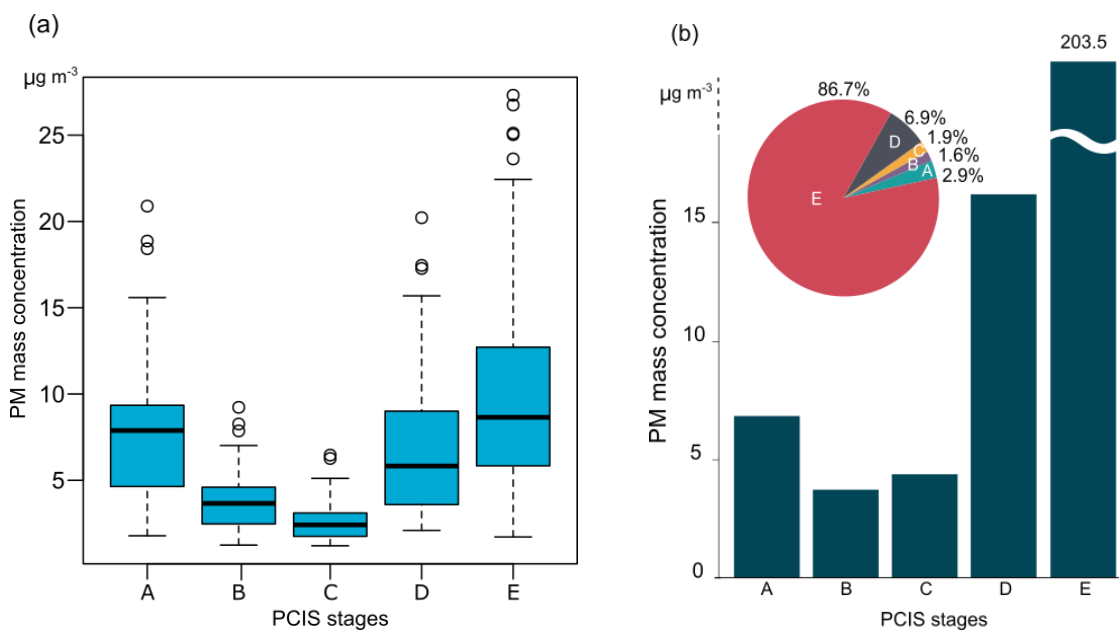
The distribution of PM in elderly residences is asymmetric, except for  $PM_{0.5-1.0}$ , with a greater variability in  $PM_{0.25}$  (Figure 7a). For example, our mean  $PM_{10}$  and  $PM_{2.5}$  were found to be 35.2 and 27.4  $\mu\text{g m}^{-3}$ , respectively (Table 5). The mean mass concentration of  $PM_{0.25}$  was found to be 13.6  $\mu\text{g m}^{-3}$ , which is 1.7–times higher than the coarse particles ( $PM_{2.5-10}$ ; Table 5). Comparisons with the literature indicate our mean  $PM_{2.5}$  (27.4  $\mu\text{g m}^{-3}$ ) to be lower than those found in an indoor asylum in City of Mexican (35.1  $\mu\text{g m}^{-3}$ ; Holguín et al., 2003). Since the asylum building was smoke-free, Holguín et al. (2003) speculated that the high  $PM_{2.5}$  mass concentration come from diesel buses that were parked close to the asylum. Likewise, the mean  $PM_{10}$  and  $PM_{2.5}$  in our studied elderly residences were also found to be lower than those in indoor children residences (Table 1; McCormack et al., 2008), mainly due to cooking and more frequent smoking than those in elderly residence. Our  $PM_{0.25}$  mass concentration was similar to those found in indoor schools (Viana et al., 2014), as summarised in Table 1. The smoking-free environment in both these studies was a similarity that might have made our results comparable but we could not find any other specific reason behind this coincidental similarity.



**Figure 6.** Mass concentrations of (a) PM<sub>10</sub> and (b) PM<sub>2.5</sub> in elderly residences, sampling performed for 24 hours with PCIS. The lines represent the São Paulo State air quality standards (CETESB) and the WHO guidelines. The red columns show the highest PM<sub>10</sub> and PM<sub>2.5</sub> concentrations in the sample #27. The pie chart represents the percentage of each PCIS stage: A, B, C, D and E, corresponding PM<sub>2.5-10</sub>, PM<sub>1.0-2.5</sub>, PM<sub>0.5-1.0</sub>, PM<sub>0.25-0.5</sub> and PM<sub>0.25</sub>, respectively, and including the sample #27 only on the left side.

**Table 5.** Mean and standard deviation of PM in elderly residences, considering and not the sample #27 (Figure 7b), and residences with or not smoker during the sampling.

PM sizes	With sample #27	Without sample #27	Mean difference <sup>1</sup> (%)	Smoking residences	No smoking residences (no #27)
PM <sub>2.5-10</sub>	7.83±4.25	7.85±4.29	0.2	4.66±2.73	7.99±4.42
PM <sub>1.0-2.5</sub>	3.86±1.71	3.86±1.72	0.1	2.34±1.32	3.93±1.75
PM <sub>0.5-1.0</sub>	2.66±1.22	2.63±1.21	1.1	2.01±0.93	2.6±1.2
PM <sub>0.25-0.5</sub>	7.32±4.59	7.17±4.48	2.1	6.89±2.30	7.02±4.41
PM <sub>0.25</sub>	13.6±25.7	10.4±6.32	23.7	11.3±2.73	10.0±5.92
PM <sub>10</sub>	35.2±37.5	31.9±18.0	9.6	25.5±12.4	31.6±17.7
PM <sub>2.5</sub>	27.4±29.1	24.0±12.4	12.4	21.4±8.87	23.6±12.2



**Figure 7.** Size-resolved particle mass concentrations (a) for the entire sample sets, except the (b) sample #27 that showed the highest concentrations of PM<sub>0.25</sub>. A, B, C, D and E are PM<sub>2.5-10</sub>, PM<sub>1.0-2.5</sub>, PM<sub>0.5-1.0</sub>, PM<sub>0.25-0.5</sub> and PM<sub>0.25</sub>, respectively.

The pie graph in Figure 6 shows the percentage of each PCIS stage in PM<sub>10</sub> and PM<sub>2.5</sub>,

<sup>1</sup> Mean difference between samples with and without sample #27.

with and without sample #27. There is a significant difference in mean concentrations when we considered sample #27 (see pie graph with sample #27 in Figures 6a and 6b). This sample is highlighted in Figure 7b due to its highest mass concentration to  $PM_{10}$ ,  $PM_{2.5}$  (highlighted in red in Figures 6a and 6b) and  $PM_{0.25}$  (Figure 7b) that changes the overall mean of proportions, mean and standard deviation of mass concentration significantly (Table 5). For example, almost 90% of contribution for  $PM_{10}$  in sample #27 came from  $PM_{0.25}$  and 8% from  $PM_{0.5-0.25}$  (Figure 7b). The mean difference between mean mass concentration for all fractions of PM, with and without sample #27, was higher for the fine particles, especially  $PM_{0.25}$ . The sample #27 increased 23.7% in  $PM_{0.25}$  mean mass concentration but showed a little influence on the mean of coarse particles and  $PM_{1.0-2.5}$ .

The highest concentrations in sample #27 point to an interesting source. This residence was next to a construction site where the construction activities were active during the measurement period, indicating an escape of particles from this site and infiltrating from outdoor to indoor in this residence through openings of doors (and windows) during their movement in and out from the home. These results also show that the mass concentration of fine and coarse particles from the construction can appreciably change. Azarmi et al. (2016) found that  $PM_{10}$  and  $PM_{2.5}$  in constructions can be until 120% and 11% higher during the work than no work, respectively. They showed that  $PM_{10}$  and  $PM_{2.5}$  mass concentration decreased with the increase of the distance of the emission from construction and, in a few 100 m the mass concentration can be half of its value. However, the residence #27 was about 50 m away from the construction, what can explain the high mass concentration inside the residence.

The differences between indoor coarse and fine particles (Figure 7b) could be because of the decay rate  $PM_{10}$  concentrations decrease exponentially faster with the distance than

PM<sub>2.5</sub> (Azarmi et al., 2016). Furthermore, windows were closed during the construction inhibiting the penetration of coarse particles, but very fine particles (PM<sub>0.25</sub>) could still infiltrate indoors through the residential shells such as cracks and fissures (Abt et al., 2000). The effects of traffic influence in sample #27, compared with the rest of the samples, can be disregarded because of the lowest proportion of rBC (i.e., 0.9% of the PM<sub>0.25</sub> mass) being found in this sample (see Section 4.4).

We also investigated the influence of cigarette smoking in indoor elderly residences since such a smoke can contribute notably to very fine particles (e.g., PM<sub>0.25</sub>) than residences without a smoker (Table 5). We have about 10% residence with a smoker during the measurement (Table 5). However, there were no smokers during the measurements of sample #27, eliminating the effect of smoking as a reason for high PM<sub>0.25</sub>.

We used both the CETESB (2015) and the WHO (2010) guideline values for comparison with our daily averaged data inside the elderly residences (shown by two different lines in Figure 6). The CETESB standard values (daily mean PM<sub>10</sub> and PM<sub>2.5</sub> as 120 and 60 µg m<sup>-3</sup>, respectively) are higher than WHO guidelines (daily mean PM<sub>10</sub> and PM<sub>2.5</sub> as 50 and 25 µg m<sup>-3</sup>, respectively) since CETESB intends to adopt the WHO guidelines over the time in future (Kumar et al., 2016). Only one residence exceeded the CETESB's standards (the aforementioned sample #27) whereas 13% and 43% of the residences exceeded the WHO's PM<sub>10</sub> and PM<sub>2.5</sub> guidelines, respectively. In fact, the PM<sub>0.25</sub> fraction itself exceeded the WHO's PM<sub>2.5</sub> guidelines on 8.3% (5 residences) of the total occasions in the elderly residences (see Section 4.4), showing the significantly high mass concentration of finer sized particles.

The highest values of PM<sub>10</sub>, without the residence #27 (Figure 7b), were 70.1, 69.6 and 68.2 µg m<sup>-3</sup>; these are up to about 20 µg m<sup>-3</sup> above the WHO's guidelines. Likewise, the

highest values of  $PM_{2.5}$  were 59.5, 55.8 and 51.8  $\mu\text{g m}^{-3}$ ; all of them exceeding by over two–times the daily WHO guideline of 25  $\mu\text{g m}^{-3}$ . The above results allow concluding that the elderly in the MASP have disproportionately high concentrations of fine particles in their residences, where they spend almost 80% of their total daily time.

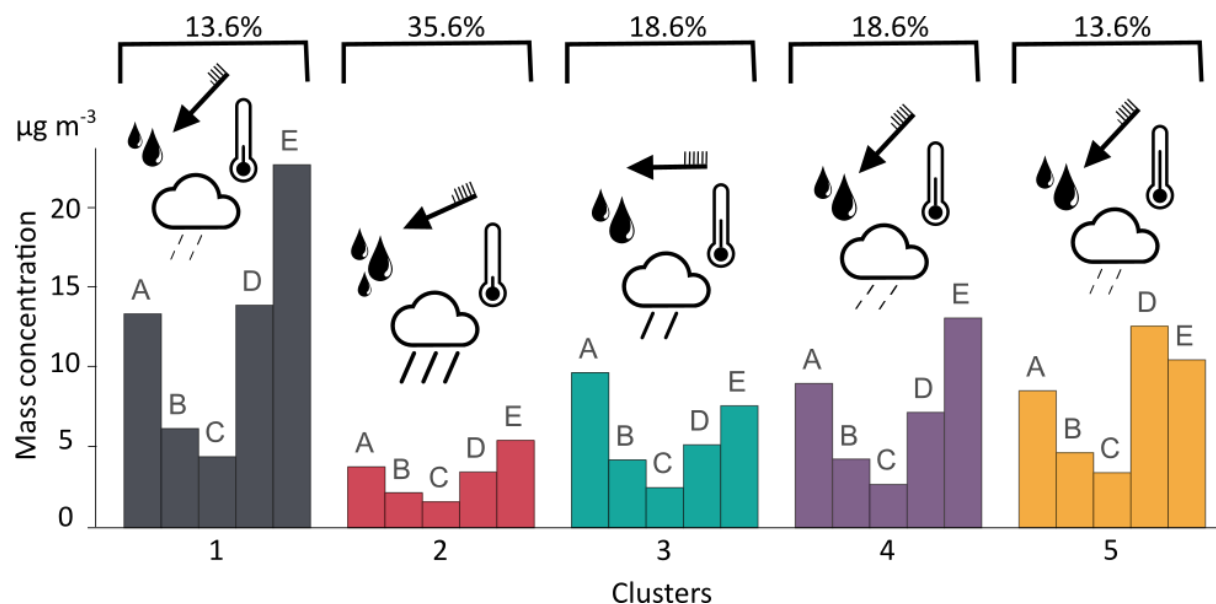
## **4.2. Influence of outdoor meteorological conditions on the indoor PM concentration**

This section was published on Segalin et al. (2017a).

In order to understand the PM mass concentration behaviour in elderly residences, we clustered our samples into five groups (Figure 8). These clusters were chosen because they represent better the different PM behaviours seen in the residences. The cluster 1 represents the residences (13.6%) with a higher concentration of PM in all sizes. These are residences near to intense vehicular traffic and these samples were collected in days without a precipitation. The cluster 2 represents the measurements made during the precipitation events. This cluster had the minimum mass concentration in all PCIS stages and describes the most part of the residences (35.6%). All these measurements were made during the days when there was precipitation.

The cluster 3 has the residences with more coarse particles (stage A) than the other PM sizes, mainly due to wind speed being higher during the measurements that would have favoured the resuspension of coarse particles (Harrison et al., 2001; Kumar et al., 2015). The cluster 4 has the same profile like as the cluster 1, but with less mass concentration, whereas the cluster 5 has a different profile with the maximum concentrations in  $PM_{0.5-0.25}$  (stage D).

All the clusters present low mass concentration in the  $PM_{0.5-1.0}$  (stage C). The major part of the residences (67.8%) presents a peak of concentration in  $PM_{0.25}$  (stage E), indicating much higher formation and infiltration of finer sized particles in elderly residences.



**Figure 8.** Clusters of the elderly residences. The brackets represent the percentage of residences in each cluster. A, B, C, D and E are  $PM_{2.5-10}$ ,  $PM_{1.0-2.5}$ ,  $PM_{0.5-1.0}$ ,  $PM_{0.25-0.5}$  and  $PM_{0.25}$ , respectively. The cloud, thermometer, raindrops, and the arrow represent the precipitation, temperature, relative humidity, and wind direction and speed, respectively. The interpretation of these qualitative symbols can be seen in Table 6.

Figure 8 shows the behaviour of size-segregated PM in indoor elderly residences, indicating the highest values of  $PM_{0.25}$ ; the same trend was also observed in outdoor urban environments. The highest concentration of outdoor  $PM_{0.25}$  can be expected due to the contribution of elemental and organic carbon (Singh et al., 2003) and sulfates (Freitas and Solci, 2009), which are generated through combustion process and gas-to-particle conversion (Seinfeld and Pandis, 2016). Likewise, our 26% of indoor  $PM_{0.25}$  was represented by rBC (Section 4.4) that consisted mainly the elemental carbon (Seinfeld and Pandis, 2016),



explaining these highest concentrations in indoor elderly residences.

**Table 6.** Meteorological mean parameters for the clusters in Figure 8. Mean precipitation ( $P$ ) in all residences for each cluster, percentage of precipitation days ( $P_{\text{days}}$ ), days without the precipitation before the sampling period (days without P), relative humidity ( $RH$ ), wind speed ( $U$ ) and direction ( $WD$ ) and temperature air ( $T$ ) measured in the IAG station – USP, for sampling period with PCIS in the elderly residences.

Cluster	1	2	3	4	5
P (mm)	0.62	5.0	1.4	0.14	0.68
$P_{\text{days}}$ (%)	25.0	86.4	54.5	27.3	25.0
Days without P	3.3	0.8	2.0	2.0	5.5
$RH$ (%)	72.4	85.9	77.3	75.4	79.2
$U$ ( $\text{m s}^{-1}$ )	4.4	5.6	6.0	5.6	5.4
$WD$	NE	ENE	E	NE	NE
$T$ ( $^{\circ}\text{C}$ )	18.3	17.8	19.1	18.6	20.2

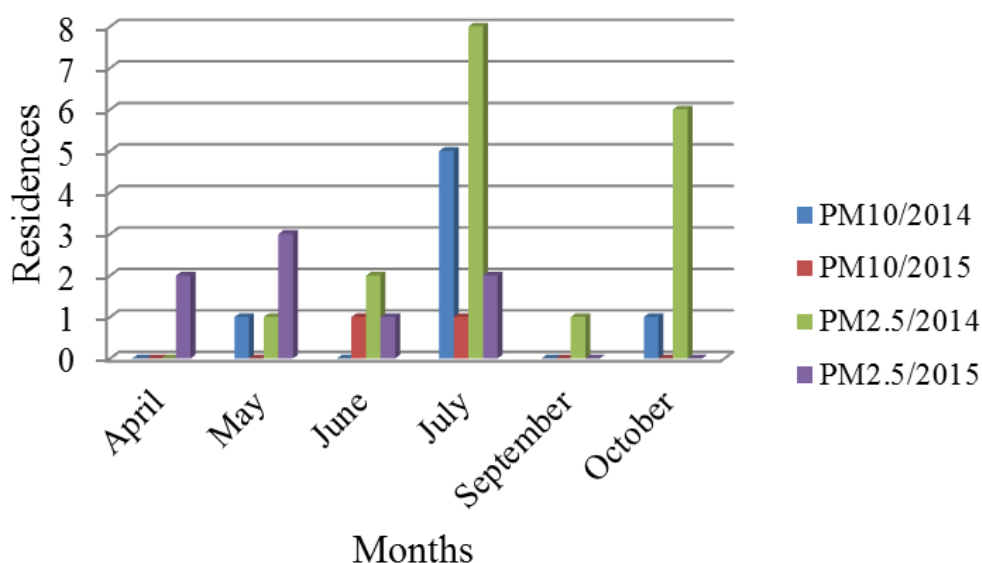
Table 6 shows the mean meteorological parameter in each cluster (Figure 8), taken from the IAG station (Climatological Report, 2016), which had a mean distance of 13.9 km from the studied residences. All the measurements in cluster 1, and about 64% of the residences in clusters 3 and 4, were sampled in winter (May–July). About 59% of residences in cluster 2, and only 25% in cluster 5, were sampled during this period. At this time of the year, the weather conditions are mostly dominated by the temperature inversions, neither wind

nor precipitation, which are not favourable for dispersion of air pollutants (CETESB, 2015; CETESB, 2016). The cluster 2 represents the most part of samples in days with more strong precipitation than other clusters (Table 6, the most intense precipitation was in summer and spring. Usually, there are more intense events of precipitation in the MASP between November and March each year, which represents the rainy season (Liebmann et al., 2001; Climatological Report, 2016).

Nevertheless, indoor  $PM_{10}$  and  $PM_{2.5}$  mass concentration in 13% and 43% of the elderly residences crossed WHO guidelines, respectively (Figure 6). The majority of these exceedances were noted during the months of July and October (Figure 9). In July, which represents a winter month, high-pressure weather system (i.e., anticyclones) caused thermal inversions in the lower atmosphere and reduced the wind speed (CETESB, 2015). In October, which represents a spring month, an atmospheric blocking caused by abnormal activity of subtropical anticyclone of the South Atlantic was observed on the MASP (CETESB, 2015). During both these months, the weather conditions were favourable to trap the PM close to the surface to result in increasing mass concentration in the region (Sánchez-Ccoyllo and Andrade, 2002).

We also assessed the difference in exceedances between 2014 and 2015. Almost 78% and 70% of the  $PM_{10}$  and  $PM_{2.5}$  in elderly residences exceeded WHO guidelines in 2014, respectively (Figure 9). During the period from May to September of 2014 (covering the winter), there were 5% additional days with unfavourable dispersion conditions higher than 2015 (CETESB, 2015; CETESB, 2016). This occurred mainly due to stable weather conditions during the winter that limited the dispersion of pollutants and hence increased the PM concentrations (Climatological Report, 2016; Sánchez-Ccoyllo and Andrade, 2002).

Furthermore, there was relatively higher precipitation in June (14.4%) and July (69.2%) of 2015 compared with 2014 (Climatological Report, 2016), which might have also contributed to reduce the PM concentration in 2015. The higher PM concentration in the outdoor environment in 2014 might have resulted in increased indoor PM concentration when windows and doors are open or by infiltration through openings, and in turn leading to higher exceedances of indoor PM over the WHO guideline values in 2014 than those in 2015.



**Figure 9.** Number of residences that exceeded WHO guidelines in 2014 and 2015.

### 4.3. Indoor and outdoor relationship

This section was published on Segalin et al. (2017a).

The *I/O* ratio is widely used since this provides a direct relationship between the PM

mass concentrations in indoor and outdoor environments (Chen and Zhao, 2011). We calculated the distances between the residences and CETESB's station to find the closest station to each residence. After this, we take the  $PM_{10}$  (Table 7) and  $PM_{2.5}$  (Table 8) data from these stations to the same period of sampling in the residences with PCIS. The stations with less than 16 hours of valid diurnal measurements were excluded (CETESB, 2015). Due to this criterion, eight residences had their closest station with invalid data to the sampling period with PCIS, and therefore we used the second nearest station.

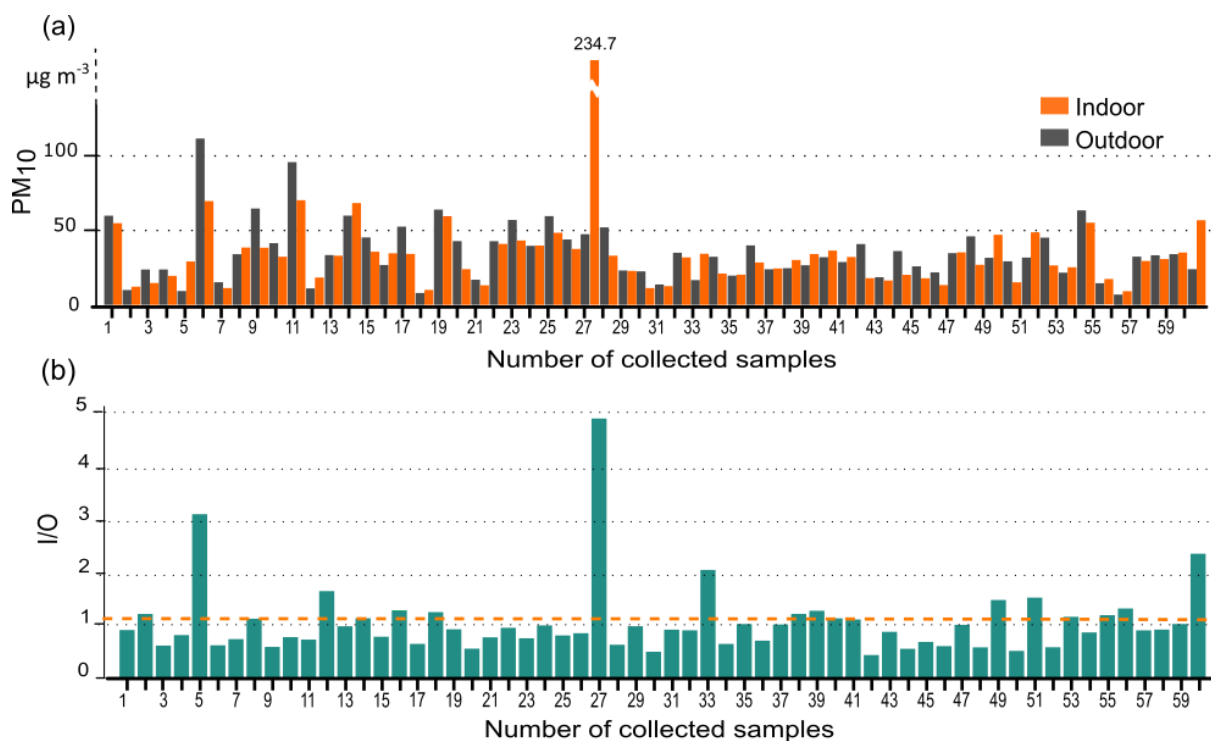
**Table 7.** The number of elderly residences closest to each CETESB's stations and the mean distance from the nearest station for  $PM_{10}$ .

CETESB's station	Number of residences	Mean distance (km)
Capão Redondo	1	6.78
Carapicuíba	1	3.79
Cerqueira César	12	1.57
Congonhas	5	2.59
Guarulhos Paço Municipal	2	6.28
Marginal Tietê Ponte dos Remédios	8	3.02
Moóca	3	2.88
Osasco	3	3.92
Parque Dom Pedro II	3	2.70
Pinheiros	9	1.64
São Caetano do Sul	3	5.22
Santana	6	4.78
Taboão da Serra	2	3.41

Figure 10a shows the indoor and outdoor  $PM_{10}$  mass concentration measured for all the 60 residences. About 40% of residences had the indoor  $PM_{10}$  higher than those outdoors. Among these residences, 6 had precipitation event during the sampling period. A possible explanation to high indoor  $PM_{10}$  compared with outdoors, may be due to the fact that the elderly closed the windows during the rain hours. The elderly residences have only natural ventilation and their *I/O* mean is 1.06 (Figure 10b). Goyal and Kumar (2013) showed *I/O* ratio for  $PM_{10}$  in kitchen and canteen with natural ventilation as 1.33 and 1.47, respectively. In our elderly residences, the *I/O* rate is lower, presumably because of the measurements being carried out in the living room with no direct sources of  $PM_{10}$  emissions. The highest *I/O* was found for the sample #27 due the construction. If we overlook the sample #27 from the calculations, the *I/O* becomes 0.99, showing almost similar concentrations of indoor and outdoor  $PM_{10}$ .

**Table 8.** The number of elderly residences closest to each CETESB's stations and the mean distance from the nearest station for  $PM_{2.5}$ .

CETESB's station	Number of residences	Mean distance (km)
Cidade Universitária USP – IPEN	31	5.68
Itaim Paulista	3	11.81
Marginal Tietê Ponte dos Remédios	26	5.61

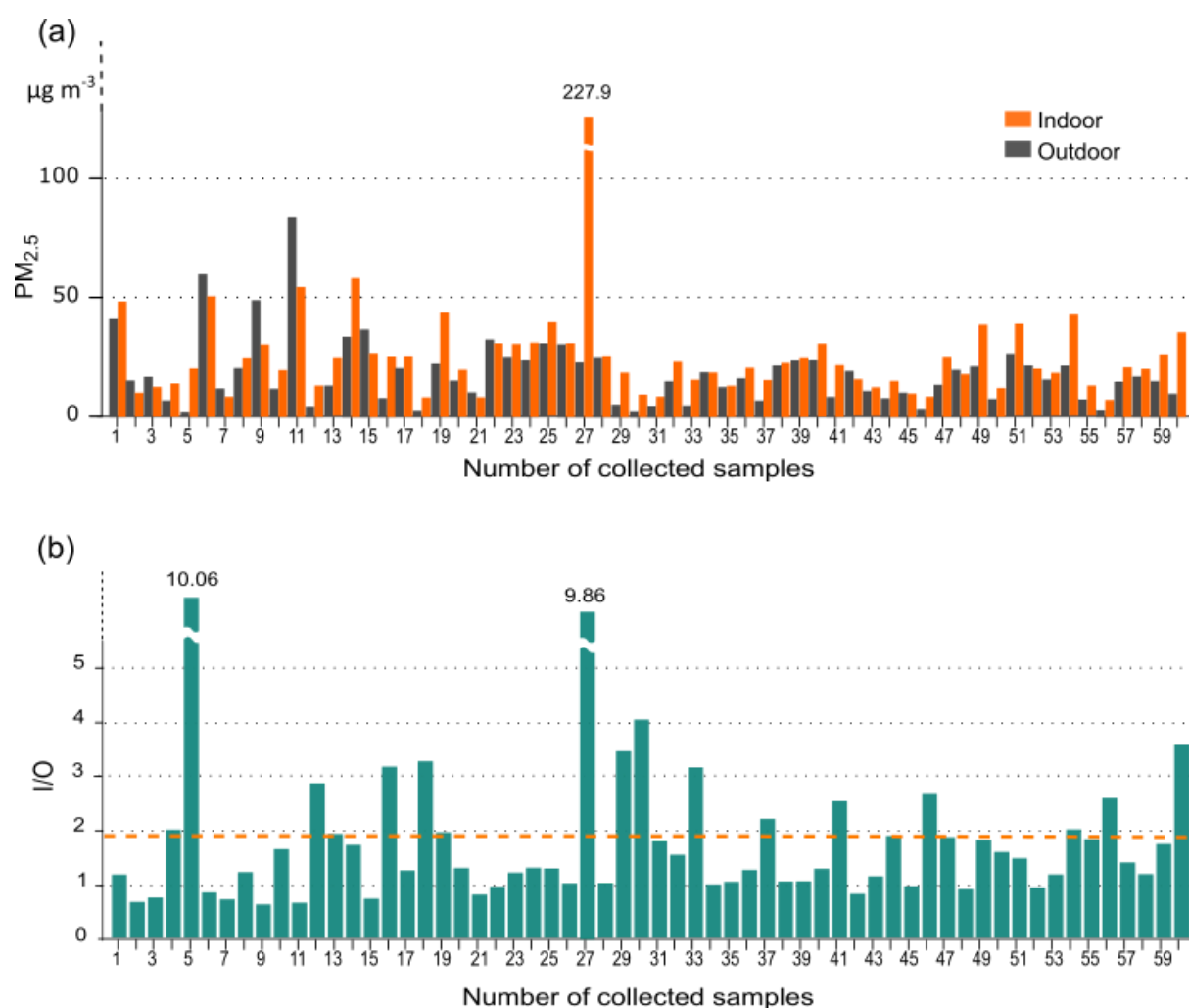


**Figure 10.** PM<sub>10</sub> mass concentration (a – indoor) in elderly residences and (a – outdoor) in its valid outdoor air quality stations (CETESB) and (b) PM<sub>10</sub> indoor/outdoor rates (*I/O*). The dashed line represents the mean *I/O*.

As for the PM<sub>2.5</sub>, about 77% of elderly residences have more PM<sub>2.5</sub> mass concentration than the outdoors (Figure 11a). The *I/O* for PM<sub>2.5</sub> was found to be 1.89, higher than the PM<sub>10</sub>, probably due to the effect of internal sources such as cooking and smoking on fine particles in the studied residences (Chao and Wong, 2002). These results also suggest that there are more production and/or penetration of fine particles inside the residences, coupled with greater deposition of coarse particles indoors compared with outdoors (Jones et al., 2000). The *I/O* ratio for PM<sub>2.5</sub> presents 2 peaks at the samples #27 and #5 (Figure 11b).

Chen and Zhao (2011) reported very high *I/O* ratios for PM<sub>2.5</sub> in the presence of indoor combustion sources and smoking; however, this was not the case in residences #5 and #27.

The higher  $I/O$  ratios for sample #5 can be due to vehicular emissions since this residence was between two large avenues with intense road traffic (Av. Consolação and Av. Nove de Julho) where 21.3% of  $PM_{0.25}$  was found to be rBC (see Section 4.4). Therefore, the vehicular traffic seems to have made important influence to bring the observed differences in  $PM_{2.5}$  mass concentration. The residence #27 had a high  $I/O$  ratio for  $PM_{2.5}$  due to the construction work and the emissions from heavy construction machinery appear to have contributed to the observed difference (Azarmi et al., 2016; Azarmi and Kumar, 2016).



**Figure 11.**  $PM_{2.5}$  mass concentration (a – indoor) in elderly residences and (a – outdoor) in its valid outdoor air quality stations (CETESB) and (b)  $PM_{2.5}$  indoor/outdoor rates ( $I/O$ ). The

dashed line represents the mean  $I/O$ .

In order to understand the indoor/outdoor relationship between the mass concentration of  $PM_{10}$  and  $PM_{2.5}$ , we established correlations in the form of Pearson and Spearman coefficients. The Pearson's coefficient evaluates the linearity between variables (Wilks, 1995) whereas the Spearman's coefficient evaluates an increase or decrease in one variable as a function of another variable (Wilks, 1995). As can be seen from Table 9, the Pearson's coefficient was low for both the  $PM_{10}$  and  $PM_{2.5}$ . These relationships suggest that there is no linear relationship between indoor and outdoor PM. However, Spearman's coefficient is higher than Pearson's coefficient, suggesting that indoor mass concentration of PM can increase or decrease non-linearly with the outdoor PM mass concentration. This is possible since the sources of particles are usually different in indoor and outdoor environments (Jones et al., 2000).

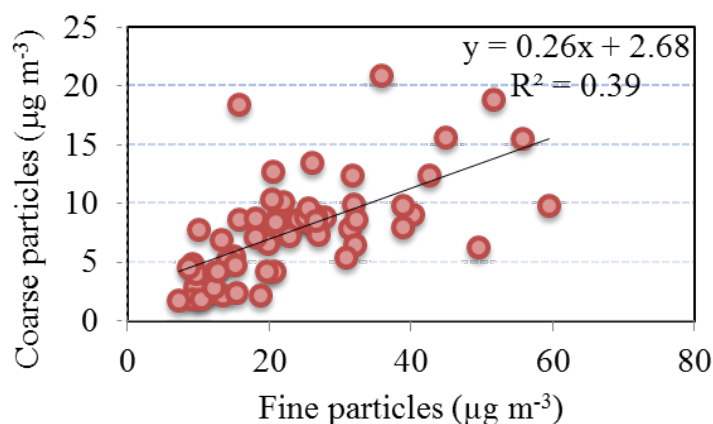
**Table 9.** Correlation between  $PM_{10}$  and  $PM_{2.5}$  from indoor (elderly residences) and outdoor (CETESB's station) environments.

	Pearson's coefficient	Spearman's coefficient
$PM_{10}$	0.474	0.737
$PM_{2.5}$	0.349	0.776

Likewise, the relationship between coarse and fine particles inside the elderly residences was found showing a low linear correlation ( $R^2 = 0.39$ ; Figure 12). The comparison of our results with the literature suggests the similar nonlinear relationship between coarse and fine particles, with a low  $R^2$  value between  $PM_{2.5}$  and  $PM_{10-2.5}$  being  $<0.30$  (Wilson and Shu, 1997). Such a correlation is expected due to the fact that the formation and removal processes



of fine and coarse particles in the atmosphere are different (Heal et al., 2012; Seinfeld and Pandis, 2016).



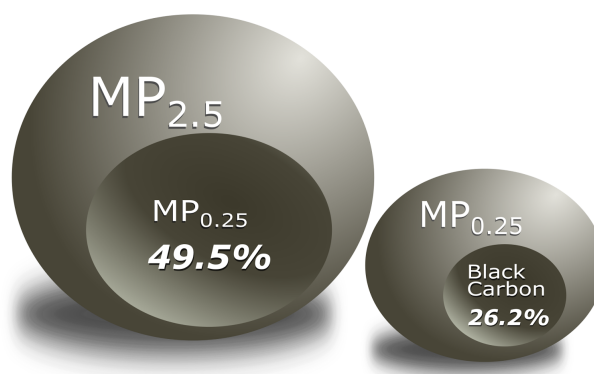
**Figure 12.** The relationship between coarse ( $PM_{2.5-10}$ ) and fine ( $PM_{2.5}$ ) particles sampled in elderly residences in MASP.

#### 4.4. Black Carbon (rBC)

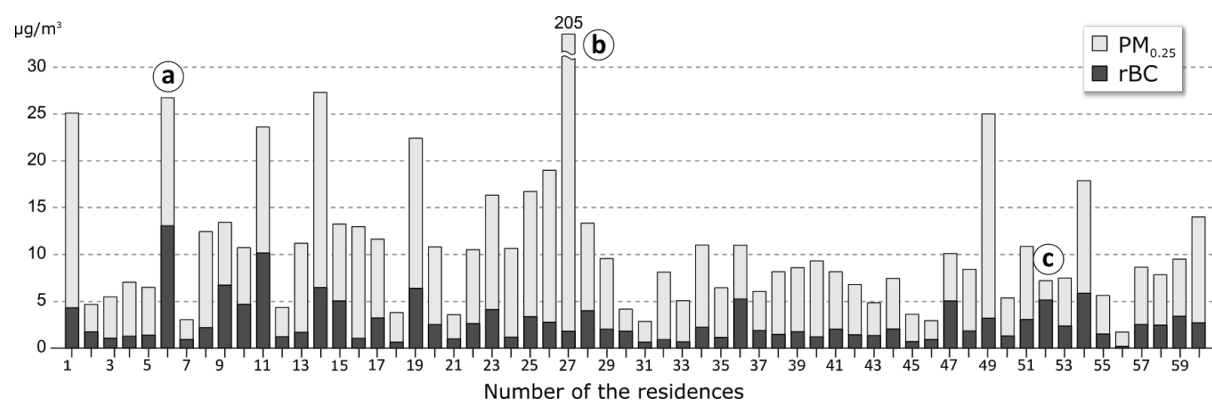
This section was published on Segalin et al. (2016).

As it has been shown in the Figure 6b, 49.5% of  $PM_{2.5}$  sampled in the residences was composed by  $PM_{0.25}$  (Figure 13). The mean  $PM_{0.25}$  in the residences was  $13.6 \pm 25.7 \mu\text{g m}^{-3}$  (high standard deviation values are due to an extreme case) and rBC was  $2.8 \pm 2.3 \mu\text{g m}^{-3}$ . As seen in Figure 7b, the highest concentration of  $PM_{0.25}$  was  $203.5 \mu\text{g m}^{-3}$ , due construction works about 50 m from the residence of the elderly. It is noteworthy that this sample had the lowest proportion of rBC (0.9%) with  $1.81 \mu\text{g m}^{-3}$  (Figure 14, letter b). After 6 months we performed a new sampling with PCIS (residence #43) in the same residence of residence #27 (Figure 14, letter b), but referring to another elderly resident of the house. The mass concentration of  $PM_{0.25}$  and the proportion of rBC in  $PM_{0.25}$  were different, with  $4.8 \mu\text{g m}^{-3}$  and

27.7%, respectively. This reinforces the influence of the construction work on the initial sampling (residence #27). Figure 15 shows the images of the sampled filters containing low (Figure 15a) and high (Figure 15b) concentration of Black Carbon.

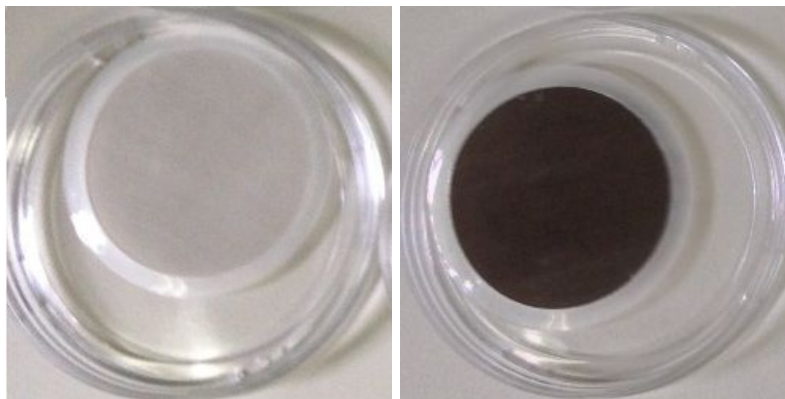


**Figure 13.** Proportion of PM<sub>0.25</sub> mass concentration in PM<sub>2.5</sub> (left) and proportion of Black Carbon in PM<sub>0.25</sub> (right) measured during 24 hour in the residences of the elderly in the MASP.



**Figure 14.** Mass concentration of PM<sub>0.25</sub> (total: gray plus black) of the 24-hour samplings in the elderly residences, and the proportion of rBC present in the PM<sub>0.25</sub> of these residences (in black). The residence #6 (letter a) represents the highest mass concentration of rBC, #27

(letter b) the largest mass value of  $PM_{0.25}$  and #52 (letter c) the highest proportion of rBC in  $PM_{0.25}$ .



**Figure 15.** Examples of the  $PM_{0.25}$  filter appearance after sampling in the residences of the elderly. The photo on the left came from a residence that is distant of intense vehicular traffic and it was during a very rainy day, and the photo on the right came from a residence near the heavy vehicular traffic route and it was in a day without rain.

There is no national or international standard threshold for  $PM_{0.25}$ , and outdoors measurements of such small particles are not made by regulatory agencies, such as CETESB, in the state of São Paulo. Despite this,  $PM_{0.25}$  surpassed the WHO recommendation for  $PM_{2.5}$  in 8.3% (5 residences) of the residences (Figure 14); emphasizing that  $PM_{0.25}$  is present inside the  $PM_{2.5}$ . This high concentration of finer particles is extremely dangerous to health, especially to elderly.

The BC is not a regulated and monitored pollutant also, but it can present unhealthy values. The highest concentration of rBC was  $13.1 \mu\text{g m}^{-3}$  (Figure 14, letter a) due to the absence of rains days before sampling, and during the same, low RH and weak winds, besides the residence being near to roads of intense traffic (residence #6, Table 10). About  $26.2 \pm$

12.3% of the  $PM_{0.25}$  in the residences was composed of rBC (Figure 13). Past studies in the MASP showed proportions that can vary from 21 to 38% of rBC in outdoor  $PM_{2.5}$  (Castanho and Artaxo, 2001; Ynoue and Andrade, 2004; Miranda et al., 2012). There is no analysis of rBC in indoor and outdoor  $PM_{0.25}$  in Brazil. In 13.3% of the residences, the rBC present in  $PM_{0.25}$  exceeded 40% of its composition. This occurs because all these residences are located on or near large avenues, with intense and constant vehicular traffic. In one of these residences the percentage of rBC in the sample reached 71.6% of the  $PM_{0.25}$  (Figure 14, letter c).

We chose 10% of samples (six residences) with a higher proportion of rBC in  $PM_{0.25}$  to analyse the meteorological conditions that may have influenced this higher proportion of rBC. These residences are #6, #9, #30, #36, #47 and #52 and they are presented in Table 10 with their respective meteorological data and the name of the great nearby avenues. The wind speed, RH and temperature did not present specific standard for these residences.

**Table 10.** The mean precipitation (P in mm), days without precipitation before the sampling (W/P), relative humidity (RH in %), wind speed (W in  $m.s^{-1}$ ) and air temperature (T in  $^{\circ}C$ ) from the IAG - USP station for the 10% residences with the highest proportion of rBC in  $PM_{0.25}$ .

Residence	Day	rBC	Large avenue	P	W/P	RH	W	T
30	26/11/2014	44	Bandeirantes e Ibirapuera	21.2	0	83.5	52.3	26.2
36	26/03/2015	48	Jaguaré	0	3	74	37	20
6	01/07/2014	49	Marginal	0	4	63.5	31.85	17.9
47	19/05/2015	50	Professor Castro Júnior e Conceição	0	5	87	43.5	24.3
9	26/06/2014	50	Dom Pedro I e Av. do Estado	0.05	0	75	3.5	18.8
52	10/06/2015	72	Brigadeiro Faria Lima e Nações Unidas	0	0	67.5	33.8	16.9

Precipitation occurred only during sampling #9 and #30. Besides the intense precipitation occurred during the sampling in the residence #30 and consequently low mass concentrations of  $PM_{0.25}$  measured, the proportion of rBC in the  $PM_{0.25}$  was high (43.8%). This occurred because the residence is very close to two large avenues with an intense vehicular traffic (Bandeirantes Avenue and Ibirapuera Avenue). The residence #9 presented characteristics similar to #30, although 0.1 mm precipitation occurred, it is also a residence between two avenues of intense vehicular traffic (Avenida Dom Pedro I and Avenida do Estado). In the other residences there was no precipitation and they are close to high vehicular traffic routes, which justify high proportions of rBC observed in  $PM_{0.25}$ .

## 4.5. Ions and trace elements in qUFP

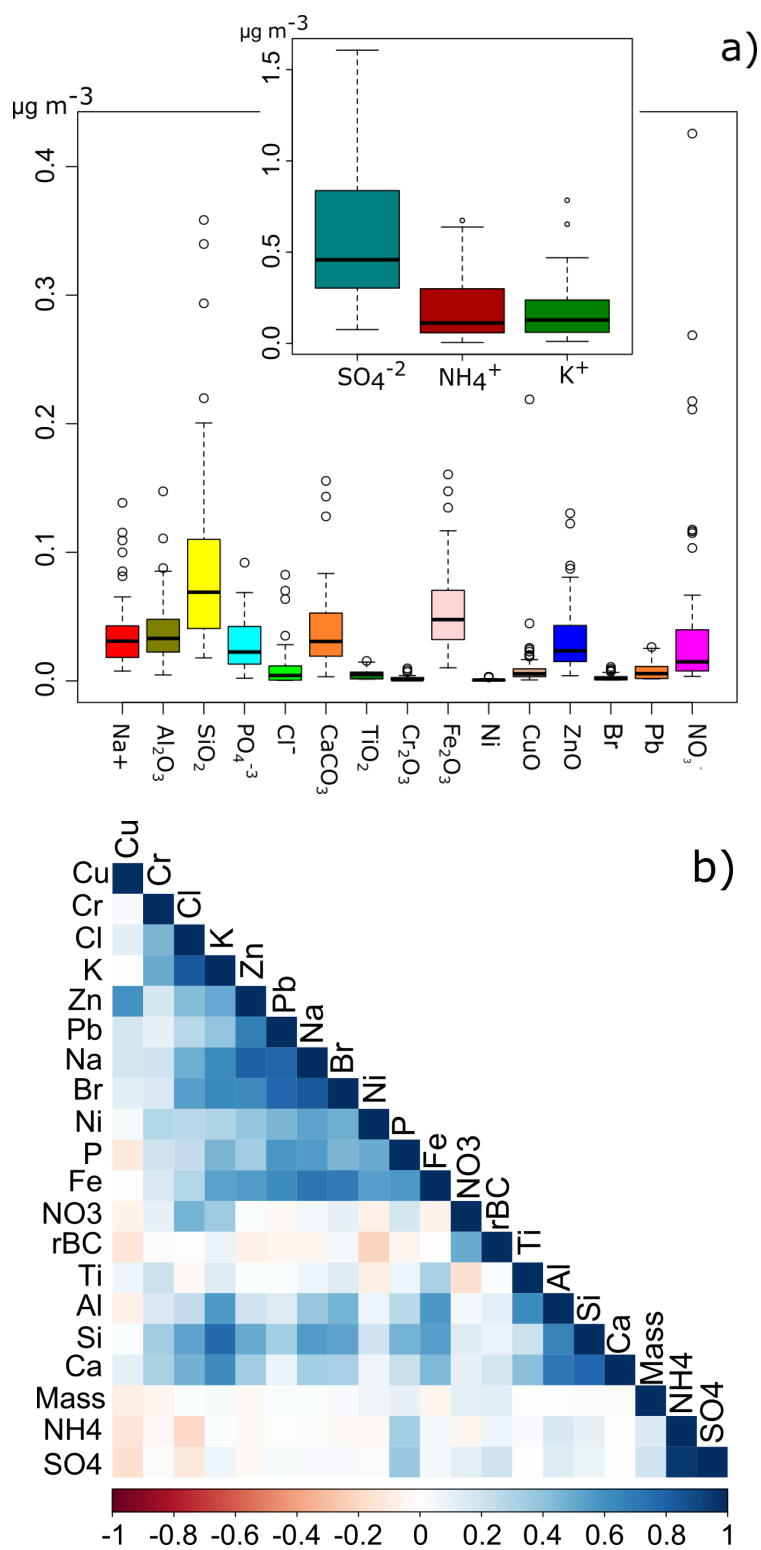
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Figure 16 shows the concentration of ions and trace elements in qUFP and the correlations among them in elderly residences in the MASP. Both ions and trace elements show high variability and non-normal distributions (Figure 16a), as confirmed by the Shapiro-Wilk normality test. The ions and trace elements are positively asymmetrical, except for  $Na^+$  (negatively asymmetrical) and they present high values, except for sulfate ( $SO_4^{2-}$ ). The ions  $SO_4^{2-}$  and  $NH_4^+$  have similar correlation patterns, with high correlations between the two, and without any significant correlation with most other ions and trace elements (Figure 16b). The total mass concentration has no significant correlations with trace elements, just a little anticorrelation with Cu and a positive correlation with P,  $NO_3^-$  and rBC (Figure 16b). There

are more high positive correlations between  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Zn}$ ,  $\text{Pb}$ ,  $\text{Na}^+$ ,  $\text{Br}$ ,  $\text{Ni}$ ,  $\text{P}$  and  $\text{Fe}$  (Figure 16b), which indicates that these compounds have similar sources.

The analysed mass concentration of qUFP is dominated by rBC and ions, mainly  $\text{SO}_4^{2-}$  (Table 11). This result is similar to results found in Los Angeles beach harbor, where it was  $\text{SO}_4^{2-}$  that dominated qUFP mass concentration (rBC was not analysed; Hu et al., 2008). The main source of  $\text{SO}_4^{2-}$  in Los Angeles was considered bunker fuel combustion from ships (Arhami et al., 2009). In outdoor environments in MASP,  $\text{SO}_4^{2-}$  is the ion with highest concentration in  $\text{PM}_{2.5}$  (Ynoue and Andrade, 2004; Miranda et al., 2012; Vieira-filho et al., 2016b) and it shows a modal peak of the mass concentration in particles around 0.3  $\mu\text{m}$  diameter (Ynoue and Andrade, 2004; Vieira-filho et al., 2016a).

The residence with the highest concentration of  $\text{SO}_4^{2-}$  is the residence #14. It is located very close to the Rebouças Avenue, a large avenue with intense vehicular traffic. The trace elements contributing mostly to qUFP are Si, followed by Fe and Zn (Table 11). The high concentration of Si in the residence #60 is probably due to nearby construction works happening during the sample collection. This residence also has very large concentrations of  $\text{K}^+$ ,  $\text{Cl}^-$  and Cr. The ions  $\text{K}^+$  and  $\text{Cl}^-$  have a strong positive correlation (Figure 16b) which may indicate biomass burning (Ynoue and Andrade, 2004). In this residence, they are most likely associated with the cooking of fried eggs for lunch. The Cr likely originates from paint (Tan et al., 2013) from both the construction site and the residence itself.



**Figure 16.** Ions and trace elements present in qUFP (a) and the Pearson correlation between them (b) in elderly residences in MASP.

The residence #5, which shows the maximum Fe, also has a maximum in Ni and Br, which can be associated with vehicular emissions: the residence is very close to Consolação Avenue and Júlio de Mesquita Viaduct, both very busy road impacted by buses and passengers cars. The Ni and Cu and were the compounds of indoor qUFP that have a mass concentration (Table 11) similar to found in outdoor  $PM_{2.5}$  in MASP:  $1.0 \pm 1.0$  and  $10 \pm 8$  ng  $m^{-3}$ , respectively (Andrade et al., 2012). For Cu, this occurs basically due to the maximum in residence 56. This residence is far from urbanized area, and the fungicides can be a source for qUFP with high Cu concentration. Other residences, as number #5, #13 and #60, have a high concentration of heavy metals as Ni, Pb, and Cr, respectively (Table 11).



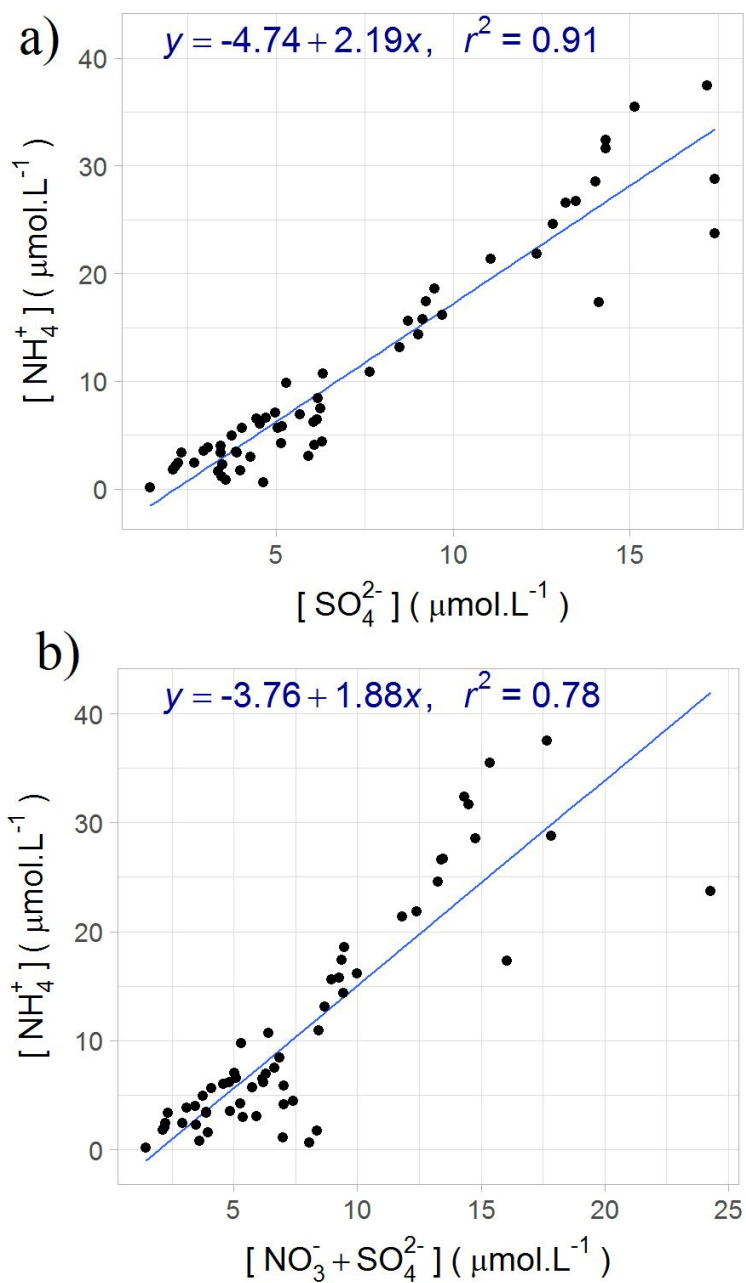
**Table 11.** Information about mass concentration, trace elements, ions and rBC of qUFP in elderly residences in MASP.

	Below DL <sup>2</sup>		Average	Stand Dev	Max.	Residence number of the max	Min.	Residence number of the min
qUFP <sup>a</sup>	0	μg m <sup>-3</sup>	13.6	25.7	204	27	1.72	56
rBC <sup>b</sup>	0		2.78	2.32	13.1	6	0.20	56
SO <sub>4</sub> <sup>2-</sup>	0		0.61	0.42	1.61	14	0.075	2
NH <sub>4</sub> <sup>+</sup>	5		0.19	0.18	0.67	40	0.004	2
K <sup>+</sup>	0		0.17	0.15	0.78	60	0.011	56
Al	3	ng m <sup>-3</sup>	20.8	13.8	78.0	25	2.46	36
Si	0		42.1	33.9	167	60	8.37	17
P	1		12.7	8.90	40.2	13	0.92	56
Ti	22		3.00	2.10	9.16	26	0.82	36
Cr	36		1.34	1.22	6.67	60	0.57	18
Fe	0		38.7	23.2	112	5	7.14	44
Ni	23		0.87	0.70	3.28	5	0.27	36
Cu	1		9.46	22.5	175	56	0.62	44
Zn	0		26.7	21.4	105	56	3.30	44
Br	30		2.58	2.28	10.9	5	0.82	36
Pb	18		7.40	5.82	26.3	13	1.64	36
Na <sup>+</sup>	13		36.3	27.6	139	13	7.66	36
Ca <sup>2+</sup>	0		15.7	12.3	62.2	9	1.29	43
Cl <sup>-</sup>	17		9.88	16.3	82.5	60	0.55	36
NO <sub>3</sub> <sup>-</sup>	36		42.1	73.2	426	1	3.58	2

In order to evaluate the acidity of the qUFP, we analysed the stoichiometry between ammonium (NH<sub>4</sub><sup>+</sup>) and on the one hand sulfate (SO<sub>4</sub><sup>2-</sup>) and sulfate plus nitrate (SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>) on the other. Ammonium and sulfate in qUFP have a slope of 2.2 (Figure 17a), indicating a

<sup>2</sup> Number of residences with concentration data below the detection limit (DL)

good neutralization from sulfuric acid by ammonia. However, the ammonia is not quite enough to neutralize both sulfuric and nitric acid (Figure 17b) and to produce the respective ammonium salts. This pattern indicates that less acidity was present in indoor qUFP than found in outdoor PM<sub>1</sub> (< 1 μm; Vieira-filho et al., 2016a). The ammonium linear fit versus sulfate plus nitrate (SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>) has a more consistent determination coefficient in indoor qUFP (R<sup>2</sup> = 0.76) than outdoor PM<sub>1</sub> (R<sup>2</sup> = 0.45; Vieira-filho et al., 2016a). This good relation between ammonium and sulfate and nitrate also indicates that secondary inorganic aerosol mass is produced effectively by the reaction between ammonia and sulphuric acid and nitrate acid from the gas phase.

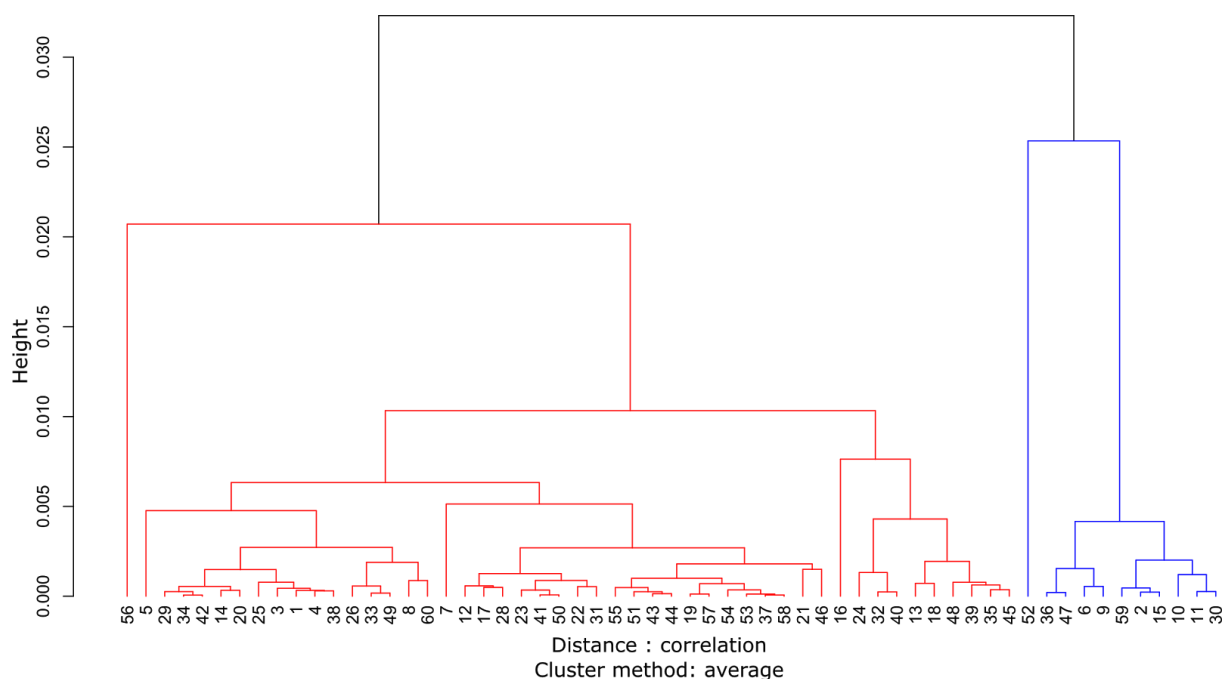


**Figure 17.** Stoichiometry ratios ( $\mu\text{mol L}^{-1}$ ) between ammonium and sulfate (a) and sulfate plus nitrate (b) for qUFP in elderly residences in MASP.

## 4.6. Chemical mass balance and cluster analysis of qUFP

This section will be published on Segalin et al. (2017b).

We use cluster analyses to classify the elderly residences by trace elements, ions and mass concentrations. The best fit of the cluster analyses grouped the residences into 2 groups framed in red and blue in Figure 18, respectively. The location of the residences is presented in Figure 19, where the red and blue colors represent the residences of the Groups 1 and 2, respectively. We also calculated the mass balances for all the residences and for both groups in order to understand the differences between these groups (Figure 20). The mass balance shows a predominance of rBC in the Group 2, which indicates a stronger relationship between indoor qUFP and outdoor sources than in Group 1 because rBc is usually associated with vehicular emissions (Sánchez-Ccoyllo et al., 2009, Andrade et al., 2012). All the residences with a maximum in trace elements (Table 11) are in the Group 1 (Figure 18). The mass concentration of the ions  $\text{NH}_4^+$  and  $\text{SO}_4^{-2}$  and of the  $\text{K}^+$  is higher in the Group 1 than Group 2 (Figure 20).



**Figure 18.** Clusters dendrogram of the residences in accordance with their mass concentration, ions and trace elements composition. The two clusters were determined with an approximately unbiased  $p$ -value of 0.95.

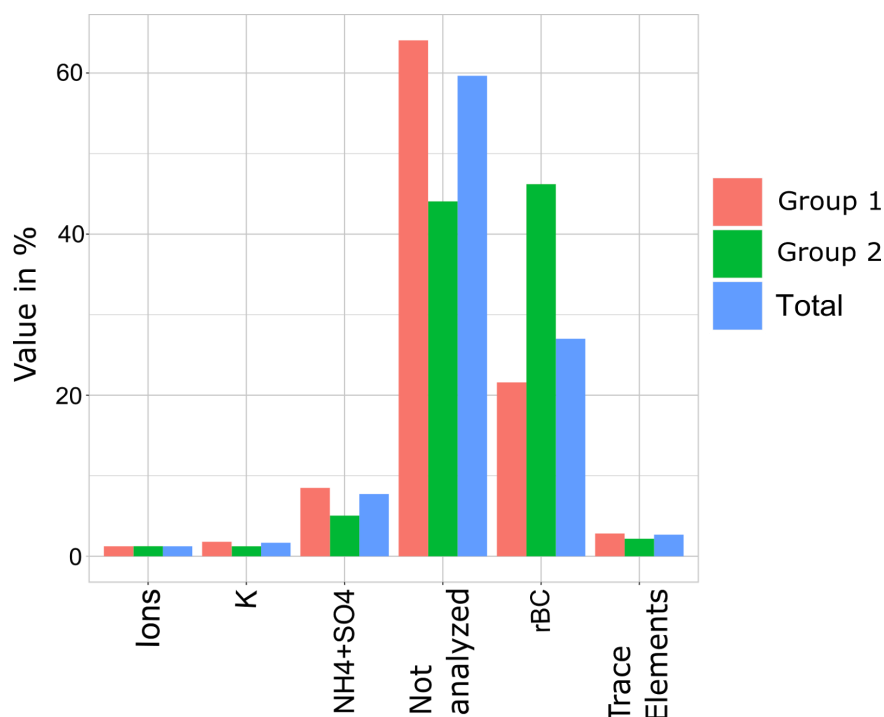


**Figure 19.** Localization of the elderly residences in the MASP in the group 1 (red) and 2 (blue) found by clusters analysis in the Figure 18. Map by Google Maps.

Group 2 has a higher mass concentration ( $12.2 \mu\text{g m}^{-3}$ ) than Group 1 ( $9.9 \mu\text{g m}^{-3}$ ). The Group 2 also present higher average of outdoor temperature, relative humidity, wind speed and, in particular, the precipitation than in Group 1 (Table 12). More precipitation during the measurements should cause a drop in the mass concentration in Group 2. However, it is the group with more mass concentration and with a predominance of rBC (Figure 20). In this context and due to the outdoor sources, we can assume that the localization of the residences can have a stronger influence in the mass concentration and composition of indoor qUFP than the weather conditions during the measurements. This is more evident for the residences in Group 2.

**Table 12.** Average of the meteorological variables from IAG station in days of measurement in residences of elderly for the two groups in Figure 18, classified by cluster analysis.

	Precipitation (mm)	Days without precipitation before measurements	Relative Humidity (%)	Wind Speed (m s <sup>-1</sup> )	Temperature (°C)
Grupo 1	0.6	1.6	76.5	4.7	17.9
Grupo 2	2.6	2.3	80.3	5.6	18.7



**Figure 20.** Mass balance of qUFP with the proportions of ions (separated in 3 parts: K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>+SO<sub>4</sub><sup>2-</sup> and others ions (Ca<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>)), trace elements, black carbon (rBC) and compound not analysed in this work, for all the residences (Total) and for the two groups generated for cluster analysis in Figure 18.

## 4.7. Sources of qUFP

This section will be published on Segalin et al. (2017b).

Through the PMF we identified 6 factors that represent 7, 21, 7, 57, 5 and 3% of the analysed mass concentration of qUFP, respectively (Figure 21). The first factor has high contributions of Na, Zn, Cu, and Pb, elements which are positively correlated to each other (Figure 16b). Although Zn and Cu are typical vehicular source markers (Andrade et al., 2012), they also have indoor sources for qUFP, usually wall paints (Viana et al., 2014). Pb is also a component of wall paint, mostly in old residences (Beauchemin et al., 2011). Factor 2 is considered as secondary inorganic aerosol because of the high concentrations of ions  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , which indicate a large contribution of secondary inorganic aerosol production to qUFP, as described in Section 4.5.

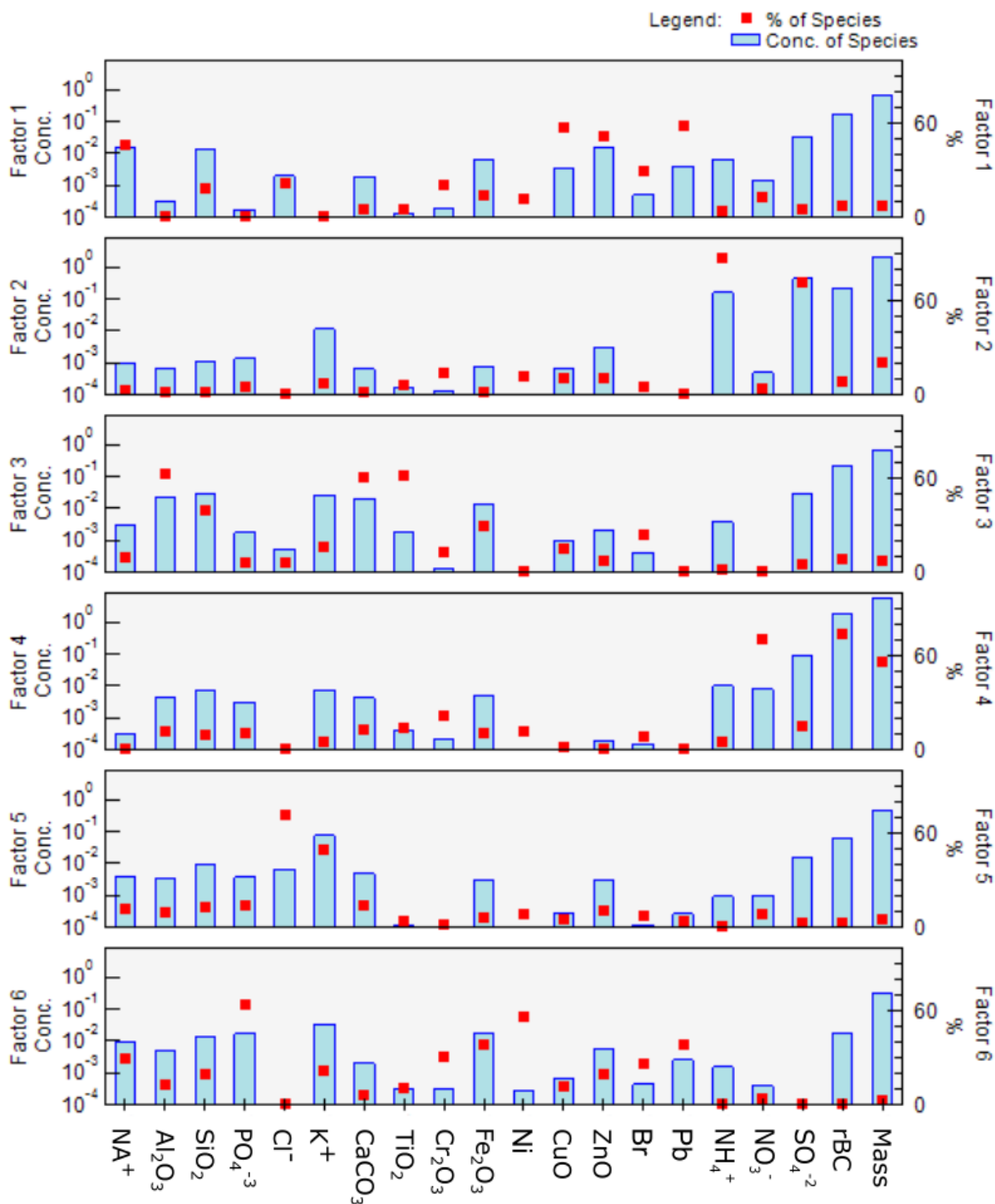
Measurements in tunnels in MASP showed higher concentrations of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  in fine particles within the tunnels than outside, indicating a vehicular contribution to the production of sulfate and ammonium particles in urbanized areas (Vieira-filho et al., 2016b). In the outdoor air in MASP,  $\text{SO}_4^{2-}$  presented a modal peak of the mass concentration distribution around 0.3  $\mu\text{m}$  diameter and its source was  $\text{SO}_2$  from fuel burning by vehicles (Ynoue and Andrade, 2004; Vieira-filho et al., 2016a). Also in outdoor Los Angeles atmosphere, the  $\text{SO}_4^{2-}$  in qUFP was considered originating from fuel combustion (Arhami et al., 2009).

Factor 3 is predominantly Al,  $\text{Ca}^{2+}$ , Si, Fe and Ti, indicating a soil- and construction-related factor (Andrade et al., 2012). Factor 4 is from vehicular emissions since it is dominated by rBC and nitrate (Sánchez-Ccoyllo et al., 2009, Andrade et al., 2012). Factor 5 is predominantly  $\text{K}^+$  and  $\text{Cl}^-$ . These ions indicate biomass burning (Ynoue and Andrade, 2004); as  $\text{Cl}^-$  is also considered to be an indoor source for qUFP (Viana et al., 2014), this factor likely indicates the cooking process. In factor 6, there are high percentages of the P, Ni, Fe and Pb.

In the MASP air, Ni, Fe, and Pb in fine particles are associated with industrial emissions (Castanho and Artaxo, 2001).

According to this analysis, the qUFP in elderly residence originated from 2 indoor sources (Factors 1 and 5) and 4 outdoor sources (Factors 2, 3, 4 and 6; Figure 22). The major mass concentration (88%) of qUFP is associated with outdoor sources, mainly vehicular emission (57%, Factor 4). In the MASP, the major source of outdoor fine particles is attributable to vehicular emission due to more than 8.5 million vehicles (CETESB, 2016; DETRAN, 2017). The vehicular emission in the MASP contributes directly to 37% of the  $PM_{2.5}$  concentration. Further, there is an indirect contribution to the production of secondary aerosol mass (51% of  $PM_{2.5}$ , CETESB, 2016). Outdoor rBC is produced by vehicles predominantly as UFP (Ynoue and Andrade, 2004) and these particles are small enough to penetrate easily into indoor environments (Abt et al., 2000) and so contribute to the mass concentration of qUFP particles in elderly residences (26%).





**Figure 21.** The result of PMF analysis (6 factors) of mass concentrations of trace elements and ions of qUFP sampled in elderly residences in MASP. Blue bars indicate the mass concentrations and red dots the relative contributions to the total mass.

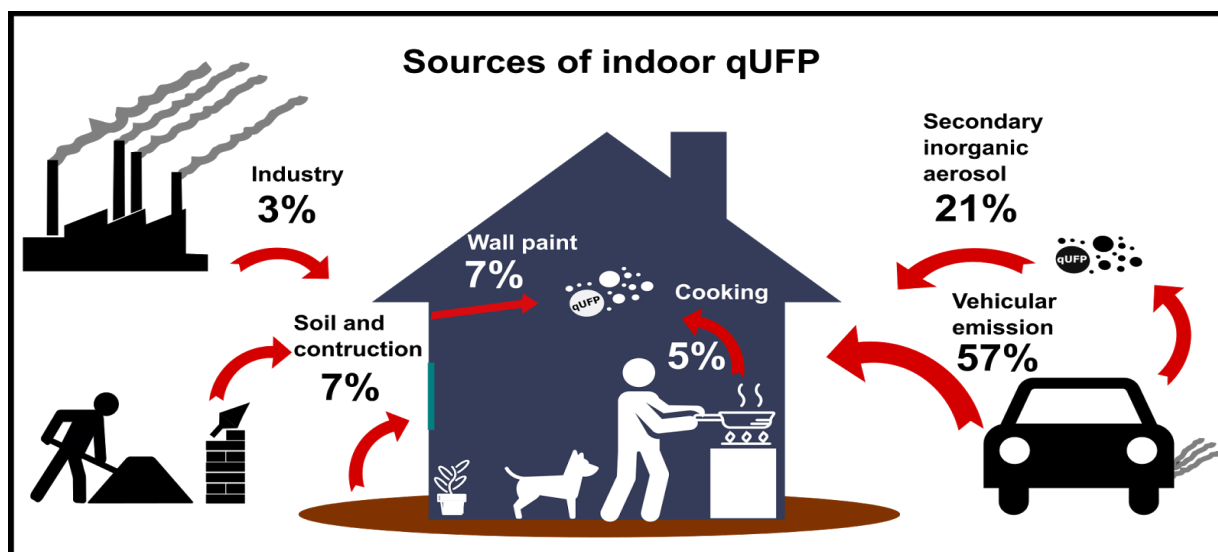
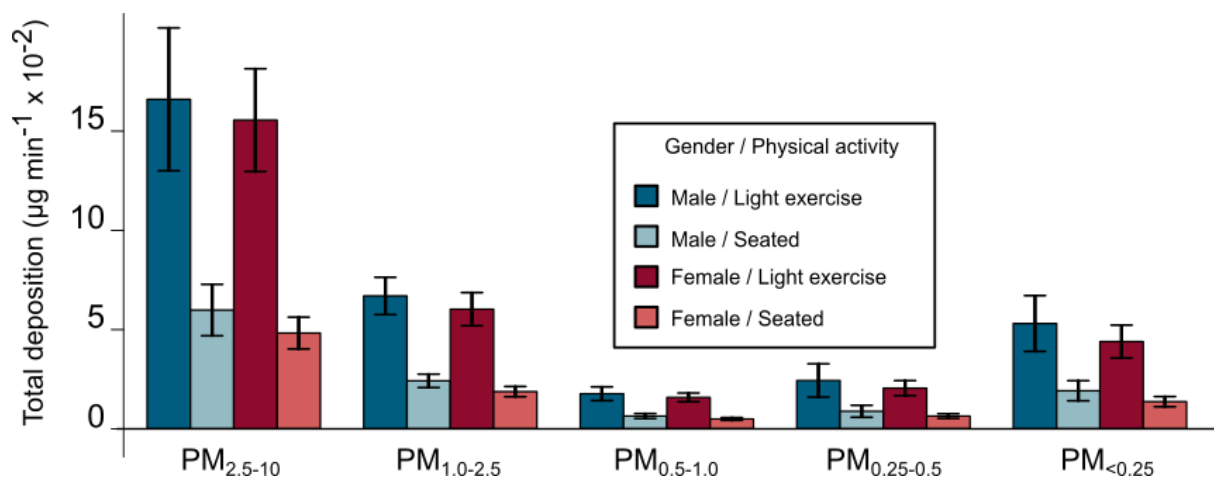


Figure 22. Sources of qUFP indoor elderly residence in MASP.

#### 4.8. Respiratory deposition doses (RDD)

Part of this section was published on Segalin et al. (2017a) and the other part was submitted as Segalin et al. (2017b).

The estimation of RDD for PM size-segregated is important to better understand the deposition of PM in the respiratory tract. We calculated the RDD for elderly male and female during a light exercise and a seated position (Figure 23). Elderly usually do not carry out heavy exercise in their residences and thereby justify our choice of physical activity. We found higher RDD in male than female for the same physical activity (Figure 23). This result was expected because male intakes larger tidal volume than females and hence inhale more PM (Hinds, 1999; Azarmi and Kumar, 2016). This intakes difference is because males have larger bodies than females; for example, the elderly males in our study were 10 cm taller and 5 kg heavier than the females.



**Figure 23.** Respiratory deposition doses (RDD) throughout the respiratory tract of elderly male and female subjects during sitting and light exercises positions for size-resolved particles, without the sample #27.

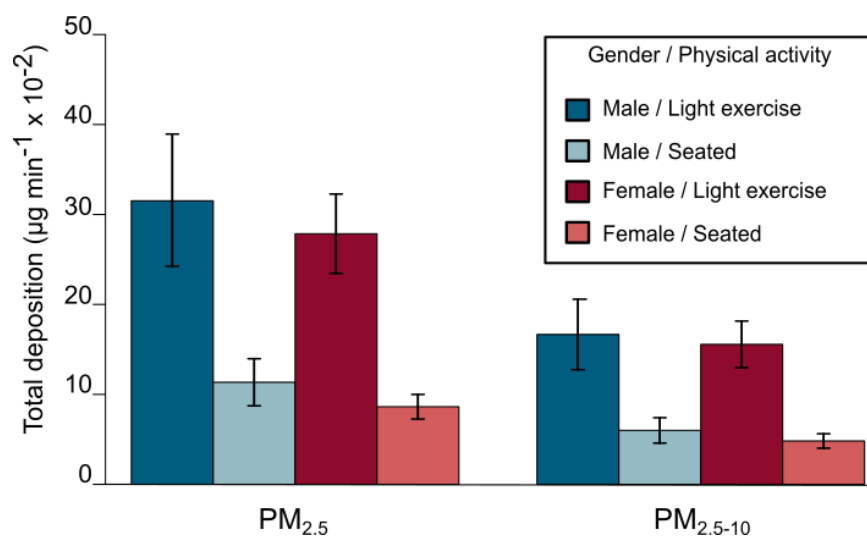
The RDD is higher during the light activity than in seated position (Figure 23). It is because the light activity increases the frequency of breath and hence increases the deposition of PM in the respiratory tract (Hinds, 1999). Table 13 shows the mean proportion of differences between RDD in male and female, using the RDD for males as a reference. The higher difference between RDD in male and female is in seated position. For example, fine particles RDD (sum of RDD in PM<sub>1.0-2.5</sub>, PM<sub>0.5-1.0</sub>, PM<sub>0.25-0.5</sub> and PM<sub>0.25</sub>) are 20% and 6% higher in males for seated and light exercise positions, respectively. The highest RDD difference was found in PM<sub>0.25</sub> which represented almost 29% and 17.2% higher deposition in males for seated and light exercise positions, respectively. This finding is concerning since these smaller particles show harmful effects on the human health compared with more coarse particles (Heal et al., 2012; Kumar et al., 2014; Han et al., 2016) and can favour deposition of endotoxin in pulmonary alveoli (Padhi et al., 2016).

**Table 13.** Mean–difference (%) in RDD between the male and female elderly while sitting or during light exercises considering different PM size stages. The mean–difference value of RDD is calculated considering male elderly RDD 100%.

Ranges	% of difference in RDD during seated	% of difference in RDD during light exercise
PM <sub>2.5–10</sub>	19.6	6.6
PM <sub>1.0–2.5</sub>	22.4	9.8
PM <sub>0.5–1.0</sub>	18.0	4.7
PM <sub>0.25–0.5</sub>	19.3	6.2
PM <sub>0.25</sub>	28.8	17.2
PM <sub>2.5–10</sub>	20	6
PM <sub>2.5</sub>	24.6	11.4

Among the studied size bins, the largest RDD was found to be for the coarse particles (PM<sub>2.5–10</sub>), followed by PM<sub>1.0–2.5</sub> and PM<sub>0.25</sub> (Figure 23). We summed the RDD in all stages, except in PM<sub>2.5–10</sub>, in order to estimate the RDD to fine particles for comparison purposes (Table 14). The RDD for coarse particles were observed to be up to 5% and 10% higher than those for fine particles during both the light exercise and seated positions for female and male elderly, respectively (Table 14). However, when we calculated the RDD directly based on the PM<sub>2.5</sub> mass concentration an opposite trend was seen, i.e., the RDD of fine particles was greater than those for coarse particles (Figure 24). This change occurred because the *DF* is dependent on the mean particles diameter which was taken as 1.25  $\mu\text{m}$  for PM<sub>2.5</sub>, rather than the mean diameters taken as 1.75, 0.75, 0.38 and 0.13  $\mu\text{m}$  for PM<sub>1.0–2.5</sub>, PM<sub>0.5–1.0</sub>, PM<sub>0.25–0.5</sub> and PM<sub>0.25</sub>, respectively, to estimate the *DF*. These results suggest that the knowledge of

size-segregated diameter is necessary for estimating the accurate deposition fraction (see Section 3.7) that has a direct influence on the RDD outcome.



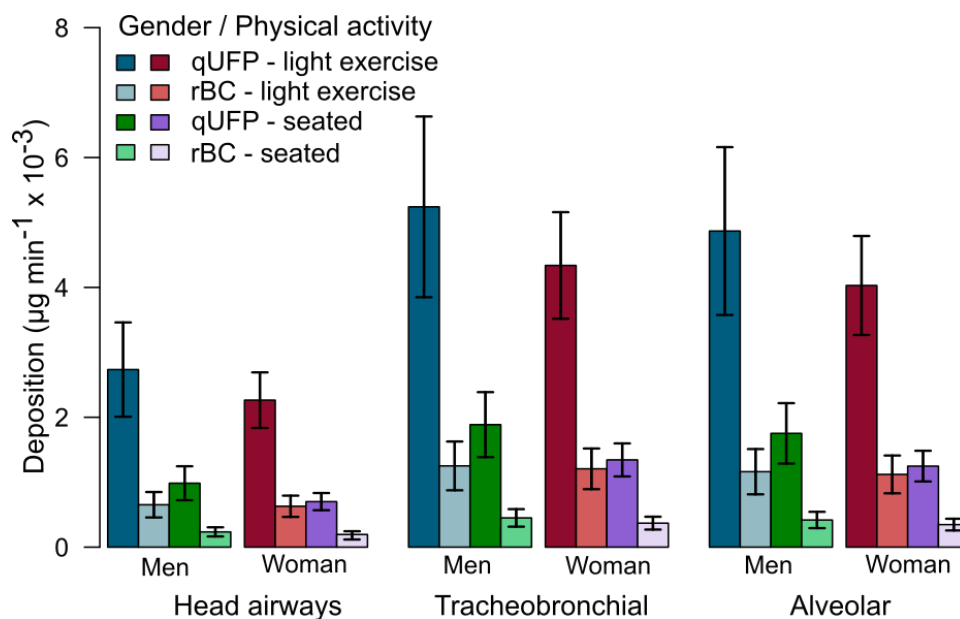
**Figure 24.** Respiratory deposition doses (RDD) throughout the respiratory tract of elderly male and female subjects during sitting and light exercises positions for fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particles, without the sample #27.

**Table 14.** Mean of RDD (µg min<sup>-1</sup>) in male and female, during light exercise and seated position for coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub> – sum of RDD in PM<sub>1.0-2.5</sub>, PM<sub>0.5-1.0</sub>, PM<sub>0.25-0.5</sub> and PM<sub>0.25</sub> size ranges) particles, without sample #27.

	Male/ Light exercise	Male / Seated	Female/ Light exercise	Female/ Seated
PM <sub>2.5-10</sub>	16.6×10 <sup>-2</sup>	6×10 <sup>-2</sup>	15.6×10 <sup>-2</sup>	4.8×10 <sup>-2</sup>
PM <sub>2.5</sub>	15.8×10 <sup>-2</sup>	5.7×10 <sup>-2</sup>	14×10 <sup>-2</sup>	4.3×10 <sup>-2</sup>

Figure 25 shows the RDD of qUFP and rBC for 24 hours in head airways,

tracheobronchial and alveolar regions, for men and women during light exercises and seated position. The RDD of qUFP and rBC in tracheobronchial and alveolar regions are similar for both male and female and light exercise and seated positions, with a little more RDD in the tracheobronchial region than in the alveolar region. The maximum RDD occurs in men during light exercise and in the tracheobronchial region. The RDD total is higher for coarse particles than for qUFP, however, the RDD of qUFP is higher in tracheobronchial and alveolar parts than in the head. The latter poses a larger health risk because these particles can translocate from the alveoli to the bloodstream and eventually cause damage to other parts of the body such brain and heart (Elder et al., 2006; Heal et al., 2012).



**Figure 25.** Rates deposition doses (RDD) of qUFP and its proportion of black carbon (rBC - present in qUFP) in different regions of the respiratory tract for men and women during light exercises and seated position during 24 hours.

## 5. Conclusions

We measured the indoor mass concentration of size-segregated particles in the 0.25–10  $\mu\text{m}$  size range in 5 size bins using a PCIS from 59 elderly residences in the MASP. The aims were to characterise size-segregated PM mass concentration in elderly residences, assess the impact of the meteorological parameters on the behaviour of indoor PM concentrations, evaluate the PM mass concentration indoor and outdoor relationship, characterise the chemical composition and the source of qUFP and estimate the RDD of the size-segregated PM mass concentration. We evaluated the mass concentration of these particles by gravimetric method and compared to  $\text{PM}_{10}$  (sum of all sizes) and  $\text{PM}_{2.5}$  (sum of all sizes, except  $\text{PM}_{10-2.5}$ ) daily guidelines recommended by the WHO and CETESB. We clustered the samples into five groups in order to understand the PM indoor behaviour and evaluate the impact of the meteorological factors. We compared indoor measurements with outdoor measurements from fixed CETESB stations. We analysed ions by chromatography and trace elements by Energy Dispersive X-Ray Fluorescence. We identified the sources of qUFP by applying Positive Matrix Factorization. We also calculated the size-segregated PM and BC deposition fraction in the respiratory tract for female and male elderly seated and light exercise positions.

Our results show that the mean value of measured  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  in elderly residences in MASP are 35.2 and 27.4  $\mu\text{g m}^{-3}$ , respectively. Both the  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  inside the elderly residences exceeded the WHO's guidelines in 13% and 43% of residences, respectively. About 78% of  $\text{PM}_{10}$  is composed by  $\text{PM}_{2.5}$  and 38.5% is composed by  $\text{PM}_{0.25}$ .

These findings suggest that the elderly people in the MASP have disproportionately high concentrations of fine particles indoor where they spend almost 80% of their total daily time.

The majority of the residences (67.8%) showed the maximum concentration in the  $PM_{0.25}$ . This suggests that there is a significant production or infiltration of finer size particles in the majority of the elderly residences. The cluster analysis suggested increased concentrations of fine particles in the elderly residences, which were in the close proximity of the heavy road traffic during the days of no precipitation. The unfavourable (stable) weather conditions limiting the dispersion of PM and can favour the increase of the indoor  $PM_{10}$  and  $PM_{2.5}$ . The effect of the construction site was evident on  $PM_{0.25}$  mass concentration through a residence that was next to an active construction site. Smoking cigarettes is another factor that could have contributed to increase  $PM_{0.25}$  mass concentration inside the elderly residences.

The *I/O* ratio for  $PM_{10}$  was found to be 1.06; 40% of residences showed higher indoor  $PM_{10}$  than those outdoors. The *I/O* for  $PM_{2.5}$  was found to be 1.89; about 77% of elderly residences showed higher indoor  $PM_{2.5}$  than those outdoors. This means that the production of fine particles indoor can be very high in the majority of the residences.

The qUFP exceeded the WHO recommendation for  $PM_{2.5}$  in 8.3% (5 residences) of the residences of the elderly. This high concentration of finer particles is extremely dangerous to health, especially the elderly. The rBC also presented unhealthy values, making on average 26.2% of the qUFP mass concentration. In 13.3% of residences, rBC was more than 40% of the qUFP composition, due the proximity of these residences with large avenues with intense and constant vehicular traffic, including buses and trucks.

The predominant ions in indoor qUFP were  $SO_4^{2-}$  and  $NH_4^+$  and the major trace elements, among that measured, were Si and Fe. Some residences had a high concentration of



heavy metals such as Cu, Pb, Ni and Cr that pose a significant health risk. There was a good neutralization of sulfuric acid by ammonia producing secondary inorganic aerosols that form qUFP. However, the ammonia was not enough to neutralize both sulfuric and nitric acids and to produce respective amounts of ammonium salts.

Since our measurements were made in different locations and days, we classified the residences in 2 groups by cluster analyses with the help of the mass concentrations of qUFP and the mass concentration of ions, trace elements and rBC. The mass balance of these groups shows a predominance of rBC in Group 2 and of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{K}^+$  in Group 1. The precipitation and the number of days with precipitation were higher in the residences in the Group 2 than Group 1. However, the mass concentration was higher in Group 2 ( $12.2 \mu\text{g m}^{-3}$ ) than in Group 1 ( $9.9 \mu\text{g m}^{-3}$ ). In this context, we can assume that the localization of the residences, due the outdoor sources, play a larger role in the mass concentration and chemical balance of indoor qUFP in elderly residence than the weather conditions.

We found six sources of qUFP inside the elderly residences. Four of them came from outdoors as soil and construction (7%), industry (3%), secondary inorganic aerosol (21%) and vehicular emission (57%). The indoor sources were wall painting (7%) and cooking (5%). Therefore, the main contribution to the mass concentration of indoor qUFP was associated with the outdoor sources, mainly vehicular emission directly (57%) and indirectly as secondary inorganic aerosols (21%).

The RDD of all size-segregated PM were found to be higher for males than for females during the light exercise and seated positions, mainly because the respiratory rate is higher in male than female during both the physical activity conditions. The highest RDD was found to be higher for the coarse particles, followed by  $\text{PM}_{1.0-2.5}$  and  $\text{PM}_{0.25}$ . The sum of the

RDD for fine particles, based on the size-segregated PM, was found to be lower than those for coarse particles during both activities. Although the coarse particles showed higher RDD the deposition rates the harmful effects are higher for the fine particles which were found in appreciable quantities. The RDD of qUFP and rBC were higher in men than in women, and higher during light exercise than in the seated position. Further, qUFP deposition was higher in the tracheobronchial region than in alveolar and head regions. Higher RDD on the deeper part of respiratory tract causes more damage to the health than in the head, worse situation for elderly people.

The above finding confirms that elderly are breathing the air with abundance of particles, mainly qUFPs. The chemical analysis of qUFP shows a very high mass concentration of toxic metals in some residences and with high percentage of BC, suggesting that the air quality inside these residences is contaminated by such substances and is contributed partly by the high number of vehicles plying on roads around their residences. The necessity of a better traffic-related emission control in MASP has been already discussed by many authors.

Our findings suggest a necessity for routine indoor air quality monitoring and design targeted legislation and control measures to limit exposure to PM in different size ranges in the elderly residences of the MASP. Also, they provide a solid basis for designing remediation actions for indoor PM concentrations in the elderly residences and consequently mitigate their adverse effect on human health. Such actions are important because the population is ageing faster in the MASP, and in general worldwide, this population group is relatively more sensitive to air pollution impacts, and they spend most part of their daily time inside their residences. Further research efforts are warranted to understand and deploy indoor air quality

improvement measures. We suggest to use rBC as an official indicator of air quality in the evaluation of local actions that aim to reduce exposure to the particles generated by combustion, mainly from vehicles, a predominant source of air pollution in the MASP. For the general population, especially for the elderly, we recommend the windows closing as well as doors during peak traffic hours in order to reduce the particles penetration from vehicular source.

## 6. Perspectives

For further studies we suggest analyses on chemical composition of size-segregated PM in asylums in MASP to assess the specific sources of PM in such places, considering that there are many elderly living in the same place. We recommended measurements from indoor and outdoor with the same instruments for more precise comparison. Measurements of the indoor ventilation will be useful. There is also needed for the development of lighter and noiseless personal instruments than the PCIS, enabling personal exposure measurements of this fragile population for longer periods.

During the FAPESP thematic project (2010/10189-5), named as "Human biometeorology: analysis of the effects of environmental variables (meteorological, thermal comfort and atmospheric pollution) and climate change in the geriatric population of the city of São Paulo", were made cognition and equilibrium tests on the elderly in a climatic camera, with temperatures ranging from 16 °C (winter condition) to 24 °C (comfort condition), and from 24 °C to 32 °C (summer/spring condition), with relative humidity around 50%, this tests were made 24 hours after the measurements with PCIS in the elderly residences. In this

context, we recommend for further studies analysis of the relationship between the temperature, relative humidity, size-segregated PM and its chemical composition (from this research) with the cognition and equilibrium of the elderly in MASP.

Additionally, regardless to this thematic project, we recommend a comparison to the above described and tests with RH variations (30% and 70%, already performed) based on RH effects on cognition according to Trezza et al., (2015). Moreover, PM data can be included on further analyses. Thermal comfort indices can be as well very important to the research, since the climate change perspectives present a thermal discomfort in the future on MASP according to Batista et al., (2016).

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