



## Chemical Composition of Quasi-ultrafine Particles and their Sources in Elderly Residences of São Paulo Megacity

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### ABSTRACT

Atmospheric quasi-ultrafine particles (qUFP; PM<sub><0.25</sub>) can cause harmful effects to human health, mainly to elderly people. Although not always considered, these effects can be mostly due to its chemical composition. The scope of this work is (i) to quantify the abundance of ions and trace elements in qUFP in elderly residences, (ii) to identify the sources of these qUFP and (iii) to estimate the respiratory deposition doses (RDD) of qUFP and black carbon (rBC), which is an important component of qUFP, to various parts of the respiratory tract. In order to evaluate the qUFP chemical composition in elderly residences in the Metropolitan Area of São Paulo (MASP), we collected qUFP by using a Personal Cascade Impactor Sampler (PCIS). 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 calculated the RDD through an equation, which use the tidal volume of lung, the typical breath frequency, the deposition fraction and the mass concentration of different size fractions of a PM. We collected 60 samples from 59 residences between May 2014 and July 2015. The major of ions concentrations in qUFP were found to be SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, and the major trace elements were Si and Fe. Some residences have a high concentration of the toxic heavy metals Cu, Ni, Pb and Cr. We found six dominant sources of the indoor qUFP: vehicular emission (57%), secondary inorganic aerosol (21%), soil and construction (7%), wall painting (7%), cooking (5%) and industry (3%). The maximum RDD of qUFP and rBC are in the tracheobronchial part. Our results show that vehicular emissions dominate the indoor qUFP concentrations and uptake in elderly residences in the MASP.

**Keywords:** Indoor air quality; Chemical composition; quasi-ultrafine particulates; Elderly residence; Indoor sources; Respiratory deposition doses

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### INTRODUCTION

Atmospheric aerosol particles in the urban environment are characterized by different sizes, shapes, and chemical composition (Heal *et al.*, 2012; Kumar *et al.*, 2014). Particles smaller than 0.1 µm in diameter, also referred to as ultrafine particles (UFP), typically occur in large number concentrations while their contribution to the mass concentration is marginal (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 µm contribute to over 99% (Kumar *et al.*, 2009, 2010). It is reported that the smaller the particles, the larger their toxic potential. For example, particles with diameters less than 0.25 µm 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 this work, we aim to focus on particles with diameters up to 0.25 µm, which we refer to as quasi-ultrafine particles (qUFP), hereafter. 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). The qUFP is an operational definition. In contrast to

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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 that the high mass concentrations of particles are expected to be in the coarse and accumulation ranges.

In this work, we sampled qUFP in elderly residences in order to analyze trace elements and ions concentrations. We focused on the elderly population because it is fastest growing in worldwide (United Nations, 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). As the elderly population increases, we will have an epidemic of chronic diseases, mainly dementias, cerebrovascular accident, chronic obstructive pulmonary disease, diabetes, heart failure and coronary insufficiency (Mathers *et al.*, 2015). In fact, the elderly are more likely to have multi-morbidities, either by the progressive decrease of the functional reserve related to the senescence process or by the greater exposure to the risk factors. Therefore, they are a risk group for particles of air pollution (Peled, 2011). 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). We also focus on the indoor environment because elderly people spend about 80% of their time indoors (Segalin *et al.*, 2017), which can be most relevant for their health. In the best of our knowledge, this is the first study in elderly residences in a Latin American megacity, such as São Paulo, to study the chemical characteristics of the qUFP.

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). For example, 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). Black carbon (BC) can affect negatively the respiratory system and cognition of elderly people (Jansen *et al.*, 2005; Power *et al.*, 2013). Exposure to silica (Si) has been associated with kidney disease, lung cancer, rheumatoid arthritis, tuberculosis and pneumoconiosis (Steenland *et al.*, 2001; Attfeld and Costello, 2004). Moreover, nickel (Ni) and vanadium (V) together have negative effects on cardiac function and influence in the short-term mortality (Campan *et al.*, 2001). Similarly, BC combined with iron and nickel has been found to affect the cardio regulatory system (Chang *et al.*, 2007). 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 Metropolitan Area of São Paulo (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).

We intend to quantify how large the contribution of vehicular emissions is to indoor air pollution in elderly residences. We also want to identify the other possible sources for qUFP. 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 1). Only one study analysed the source of indoor qUFP based on their chemical composition (Viana *et al.*, 2014; summarized in Table 1). In the best of our knowledge, there are no studies of source attribution for outdoor qUFP and UFP in Brazil, and also no information available about the source of airborne particles in residences in Brazil. There are hardly any studies focusing on elderly residents. Therefore, this is the first study in Brazil with the objectives (i) to quantify ions and trace elements present in qUFP mass concentration inside elderly residences, (ii) to identify the sources of the qUFP indoor elderly residences and (iii) to estimate the respiratory deposition doses (RDD) of the qUFP and its proportion of black carbon (rBC) in different parts of respiratory tract.

## METHODOLOGY

### *Site Description and Study Design*

There are more than 21 million inhabitants in MASP out of which 12 million reside in São Paulo City (IBGE, 2016; Kumar *et al.*, 2016; Andrade *et al.*, 2017). The study of the elderly in this region is important because over 12% of its population is 60 or older. It is worth highlighting that the elderly population is growing fast, not only in MASP but worldwide (Alessandri and Maeda, 2011; United Nations, 2015; IBGE, 2016). The residences sampled in this study are those with at least one elderly volunteer (aged 60 years or older) that were previously approved for this study. Within

**Table 1.** Review of past relevant studies including indoor qUFP and UFP.

PM types	Environment types	Key conclusions	References
UFP	One 32 m <sup>3</sup> full-scale chamber in Horsholm, Denmark	● From 11 indoor specific sources tested was the combustion of pure wax candles that produce more number of UFP.	Afshari <i>et al.</i> (2005)
UFP	One suburban residence in Virginia, USA	● Complex cooking was the majority source of UFP number, followed by outdoor sources.	Wallace (2006)
UFP	One laboratory in New York, USA	● Out of the seven oil tested, soybean, canola, and safflower oil had the lowest generation of particles	Torkmahalleh <i>et al.</i> (2012)
qUFP	39 Schools in Barcelona, Spain	● 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> .	Viana <i>et al.</i> (2014)
UFP	Two residences in California, USA	● In electric appliances and cooking pans, the sources of UFP were detergent residue and organics sorbed from indoor air.	Wallace <i>et al.</i> (2015)
UFP	One laboratory in Piacenza, Italy	● Burn wood in a manual heaters utensil instead pellet in an automatic produce more UFP with more toxic chemical composition	Ozgen <i>et al.</i> (2017)

the framework of this project, we selected volunteers from the Faculty of Medicine Clinics Hospital at the University of São Paulo. The selection criteria were pre-established by the team of geriatricians *who* selected healthy elderly people without any previous diseases such as diabetes, cardio-respiratory or cancer diseases. All the elderly participants had accomplished at least 4 years of formal education with no neurological or psychiatric illness (Trezza *et al.*, 2015). All of them were submitted to three different tests which are important for evaluating independent living capacity, i.e., (i) the Mini-Mental State Examination (MMSE; Folstein *et al.*, 1975), (ii) the Geriatric Depression Scale (GDS; Sheikh *et al.*, 1991), and (iii) the Short Physical Performance Battery (SPPB; Guralnik *et al.*, 1994). The MMSE is for evaluating any potential presence of a cognitive deficit of the individual. The GDS assesses possible symptoms of depression, while the SPPB checks the balance deficit. Only the elderly that passed all three tests were considered to be in good conditions and thus qualified to be volunteers for this study. In this way, the location of the residences were randomly arranged. All residences were located in the regions with the highest concentration of elderly people within the MASP. We have 59 residences sampled with 60 valid individual samples and referring to 60 approved volunteers. As described by Segalin *et al.* (2017), only one residence had two samples, collected on different days. Most of these residences sampled in the MASP are located in São Paulo, just two in the city of Osasco and one in Embu das Artes (Fig. 1). The measurements started in the morning in accordance with the availability of the elderly volunteers. The instrument was operated in the living room of the elderly residences for a period of 24 hours in each residence. The residences, as described for Segalin *et al.* (2017), are natural ventilated and liquefied petroleum gas from individual bottled and piped natural gas was used as cooking fuel. The elderly spend almost 80% of the 24 hours sampling period inside their residences (Segalin *et al.*, 2017).

### Instrumentation

The PM data came from Segalin *et al.* (2017), who operated

a Personal Cascade Impactor Sampler (PCIS), which separates the PM into five size ranges, i.e., 10–2.5, 2.5–1.0, 1.0–0.5, 0.5–0.25, and < 0.25  $\mu\text{m}$  aerodynamic diameters. The quasi-ultrafine particle fraction (qUFP, aerodynamic diameter < 0.25  $\mu\text{m}$ ) is thus represented by the last stage of the impactor. The PCIS was described in detail by Misra *et al.* (2002) and Sioutas, (2004). The PCIS was combined with a Leland Legacy Sample Pump (SKC Inc., Cat. No. 100–3000) with 9 L min<sup>-1</sup> rate flow, in order to provide reliable results during the entire 24 h sampling periods (Sioutas, 2004). The PCIS was used with a 37 mm Teflon filter for qUFP to avoid any chemical interference with the PM and in chemical analysis (Misra *et al.*, 2002). Although the PCIS is designed as a personal monitor, Segalin *et al.* (2017) deployed them in the living rooms of the elderly residences. The acceptance and willingness of most elderly people to carry the PCIS as a personal monitor was not good enough, mainly because the pump made a continuous noise (Segalin *et al.*, 2017).

### Data Collection and Analysis

We have 60 samples from 59 residences collected between May 2014 and July 2015 (Segalin *et al.*, 2017). The days of measurements were randomly selected and coordinated with the elderly availability. Thirty-one measurements were made in 2014 and 29 in 2015, most of them during the respective southern winter periods (May, June and July). All elderly that had been approved to the tests (Section 2.1) participated in the campaign throughout. There were no drop-outs. We did not conduct outdoor sampling during the same sampling period due difficulty to get permission to install the instruments outside the building.

The rBC mass concentration was quantified by optical reflectance measurements with a refractometer (smoke stain reflectometer model 43D; Diffusion Systems Ltd., London, UK) (Segalin *et al.*, 2016). 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 analyzes were carried out by using ionic chromatography and



**Fig. 1.** Localization of (a) São Paulo, Brazil, (b) Metropolitan Area of São Paulo (MASP) and (c) the elderly residences. The different colors in (c) represent the group 1 (red) and 2 (blue) found by clusters analysis in section 3.2. Adapted from Segalin *et al.* (2017), map by Google Maps.

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 2/3 or more samples below detection limits (DL, see Supplementary information, SI, Tables S1–S2; Leal *et al.*, 2004; Arana, 2014) 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 ( $\text{Fe}_2\text{O}_3$ ) (SI, Table S3; Kotz and Purcell, 1987; Hueglin *et al.*, 2005; Beuck *et al.*, 2011).

#### Cluster Analysis

In order to group the elderly residence by mass concentration, trace elements and ions, we choose the *pvcust* 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 *pvcust* 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  $\text{AU} \geq 95\%$  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 (see also Segalin *et al.*, 2017). 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 (Segalin *et al.*, 2017).

#### 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,  $D$ , into two matrices  $W$  and  $H$  (Cichocki et al., 2009):

$$D = WH + \varepsilon \quad (1)$$

where the matrix  $W$  is the matrix with the proportion of each source in each elderly residence, while the matrix  $H$  contains the proportion of each ion and trace element in each source, and  $\varepsilon$  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 ( $S_{ij}$ ) was calculated with Eq. (2) in accordance with Chueinta et al. (2000), using the estimated measurement error (Eq. (4)) from Ogulei et al. (2006b) and the constant  $C = 0.04$ , that produce the best value proximity between the residual sum of squares ( $Q$ ) and the theoretical value (Ogulei et al., 2006a):

$$S_{ij} = \sigma_{ij} + C N_{ij} \quad (2)$$

$$\sigma_{ij} = 0.01 (N_{ij} + \underline{N}_j) \quad (3)$$

where  $\sigma_{ij}$  is the estimated measurement error,  $C$  is a constant,  $N_{ij}$  is the mass concentration a  $\underline{N}_j$  is the arithmetic mean of the  $N_j$  values, in the  $i$  sample in  $j$  variable. An extra modelling uncertainty of 5% was added in PMF model to cover any methodological error (Khan et al., 2016). We categorize 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 1/3 of data below DL (Br, Cr, Ti, Ni and  $\text{NO}_3$ ; Table 2). 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:

$$Q_{expected} = (S \times SS) - ((F \times S) + (F \times SS)) \quad (4)$$

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 (SI Table S4).

#### Respiratory Deposition Doses (RDD)

We calculated the total respiratory deposition doses (RDD) in the respiratory tract of elderly using the Eq. (6) adapted from Hinds (1999) by Azarmi and Kumar (2016) with the same parameter and values used by other studies (Kumar et al., 2017; Segalin et al., 2017; Rivas et al., 2017). The RDD is calculated as:

$$RDD = (VT \times f) \times DF \times PM_i \quad (5)$$

where  $VT$  is a tidal volume ( $\text{m}^3$  per breath),  $f$  is the typical breath frequency (breath per minute),  $DF$  is deposition fraction of qUFP (Hinds, 1999), and  $PM_i$  is the mass concentration of qUPF. The  $DF$  for the head airway, tracheobronchial and alveolar regions were estimated using parameterizations

**Table 2.** Information about mass concentration, trace elements, ions and rBC of qUFP in elderly residences in MASP.

	Below DL*		Average	Stand. Dev.	Max.	Residence number of the max	Min.	Residence number of the min
qUFP <sup>a</sup>	0	$\mu\text{g m}^{-3}$	13.6	25.5	204	27	1.72	56
rBC <sup>b</sup>	0		2.78	2.32	13.1	6	0.2	56
$\text{SO}_4^{2-}$	0		0.61	0.42	1.61	14	0.075	2
$\text{NH}_4^+$	5		0.19	0.18	0.67	40	0.004	2
$\text{K}^+$	0		0.17	0.15	0.78	60	0.011	56
Al	3	$\text{ng m}^{-3}$	20.8	13.8	78	25	2.46	36
Si	0		42.1	33.9	167	60	8.37	17
P	1		12.7	8.9	40.2	13	0.92	56
Ti	22		3	2.1	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	0.7	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	3.3	44
Br	30		2.58	2.28	10.9	5	0.82	36
Pb	18		7.4	5.82	26.3	13	1.64	36
$\text{Na}^+$	13		36.3	27.6	139	13	7.66	36
$\text{Ca}^{2+}$	0		15.7	12.3	62.2	9	1.29	43
$\text{Cl}^-$	17		9.88	16.3	82.5	60	0.55	36
$\text{NO}_3^-$	36		42.1	73.2	426	1	3.58	2

\* Number of residences with concentration data below the detection limit (DL); <sup>a</sup> Data from Segalin et al. (2017); <sup>b</sup> Data from Segalin et al. (2016).

according to Hind, 1999 (SI, Table S6 and Eqs. (S1)–(S5)). Since  $VT$  and  $f$  depend on the physical activity and person gender (Hinds, 1999), we calculated  $RDD$  for male and female elderly and we chose light exercise and seated positions as their physical activities, as more appropriate for elderly inside their residences (Segalin et al., 2017).

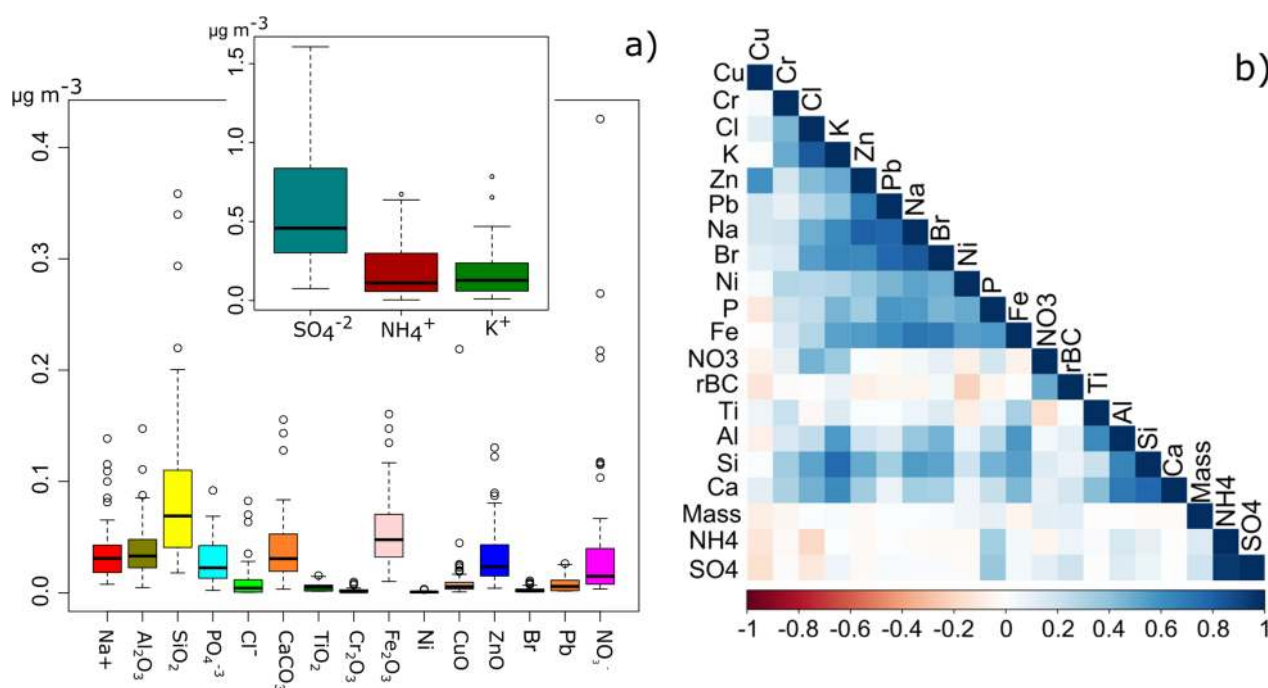
## RESULTS AND DISCUSSION

### Ions and Trace Elements in qUFP

Fig. 2 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 (Fig. 2(a)), as confirmed by the Shapiro-Wilk normality test. The ions and trace elements are positively asymmetrical, except for  $\text{Na}^+$  (negatively asymmetrical) and they present high values, except for sulphate ( $\text{SO}_4^{2-}$ ). The ions  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  correlate highly with each other ( $r = 0.9$ , Fig. 2(b)). They do not correlate significantly with most other ions and trace elements (Fig. 2(b)). The total mass concentration has no significant correlations with trace elements, just a weak negative correlation with Cu ( $r = -0.2$ ) and a positive correlation with P ( $r = 0.2$ ),  $\text{NO}_3^-$  ( $r = 0.2$ ) and rBC ( $r = 0.2$ , Fig. 2(b)). There are more high positive correlations between  $\text{Cl}^-$ ,  $\text{K}^+$ , Zn, Pb,  $\text{Na}^+$ , Br, Ni, P and Fe (Fig. 2(b)), which indicates that these compounds have similar sources.

The analysed mass concentration of qUFP is dominated by rBC ( $2.78 \mu\text{g m}^{-3}$ ) and ions ( $0.97 \mu\text{g m}^{-3}$ ), mainly  $\text{SO}_4^{2-}$  ( $0.61 \mu\text{g m}^{-3}$ , Table 2). 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 2). 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 (Fig. 2(b)) 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. 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 passenger cars. The Ni and Cu and were the compounds of indoor qUFP that have a mass concentration (Table 2) similar to found in outdoor  $\text{PM}_{2.5}$  in MASP:  $1.0 \pm 1.0$  and  $10 \pm 8 \text{ ng m}^{-3}$ , 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 2).



**Fig. 2.** (a) Ions and trace elements present in qUFP and (b) the Pearson correlation between them in elderly residences in MASP.

The acidity of aerosol particles is a parameter obtained not by direct pH measurements, but by proxies based on ion balances and molar ratios of ions, involving the equilibrium relationships of the major ions present in the water-soluble fraction (Vieira-Filho *et al.*, 2016; Weber *et al.*, 2016; Shi *et al.*, 2017; Ding *et al.*, 2019). The importance of aerosol acidity is directly related to its effects on human health (Wyzga and Folinsbee, 1995; Raizenne *et al.*, 1996; Rohr and Wyzga, 2012), as well as being a parameter affecting fundamental atmospheric physical-chemical processes in the formation of secondary aerosol and also in the formation and growth of cloud condensation nuclei. Aerosol acidity affects both the gas-aerosol partition of semi-volatile and volatile species as well as thermodynamic and kinetic parameters of acid-catalysed reactions (Vieira-Filho *et al.*, 2016; Shi *et al.*, 2017; Ding *et al.*, 2019). In order to evaluate the acidity of the qUFP, we analysed the stoichiometry between ammonium ( $\text{NH}_4^+$ ) and on the one hand sulphate ( $\text{SO}_4^{2-}$ ) and sulphate plus nitrate ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) on the other. Ammonium and sulphate in qUFP have a slope of 2.2 (Fig. 3(a)), indicating a good neutralization from sulfuric acid by ammonia. However, the ammonia is not quite enough to neutralize both sulfuric and nitric acid (Fig. 3(b)) and to produce the respective ammonium salts. This pattern indicates that less acidity was present in indoor qUFP than found in outdoor  $\text{PM}_{10}$  ( $< 1 \mu\text{m}$ ; Vieira-filho *et al.*, 2016a). The ammonium linear fit versus sulphate plus nitrate ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ) has a more consistent determination coefficient in indoor qUFP ( $R^2 = 0.76$ ) than outdoor  $\text{PM}_{10}$  ( $R^2 = 0.45$ ; Vieira-filho *et al.*, 2016a). This good relation between ammonium and sulphate 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.

#### Chemical Mass Balance and Cluster Analysis of qUFP

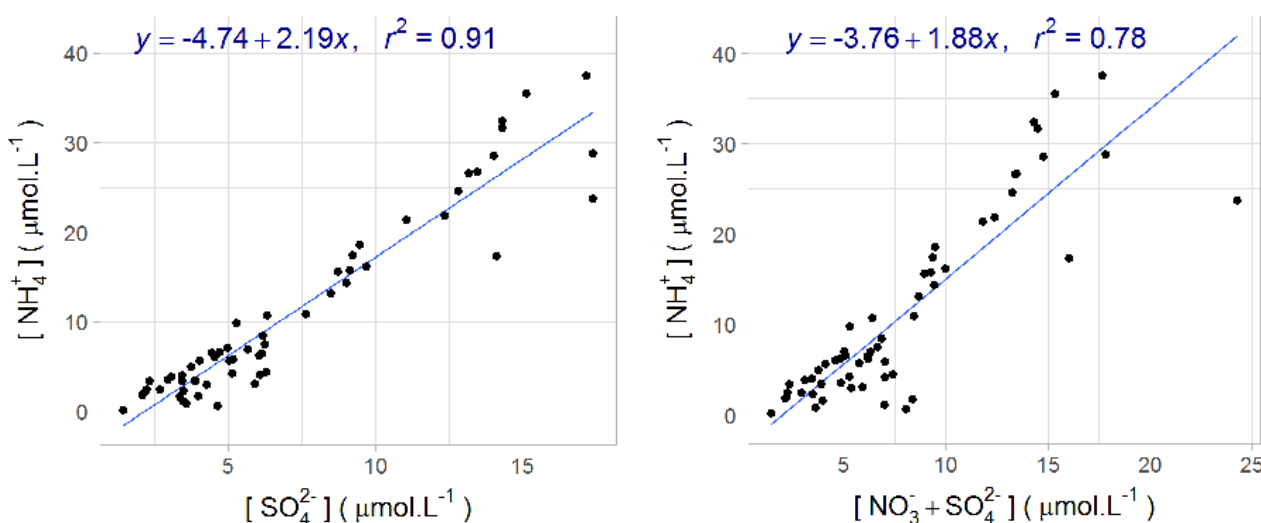
We use cluster analyses to classify the elderly residences by trace elements, ions and mass concentrations. The best fit of the cluster analyses grouped the residences into 2 groups

framed in red and blue in Fig. 4, respectively. The location of the residences is presented in Fig. 1, where the red and blue colours 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 (Fig. 5). 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 2) are in the Group 1 (Fig. 4). 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 (Fig. 5).

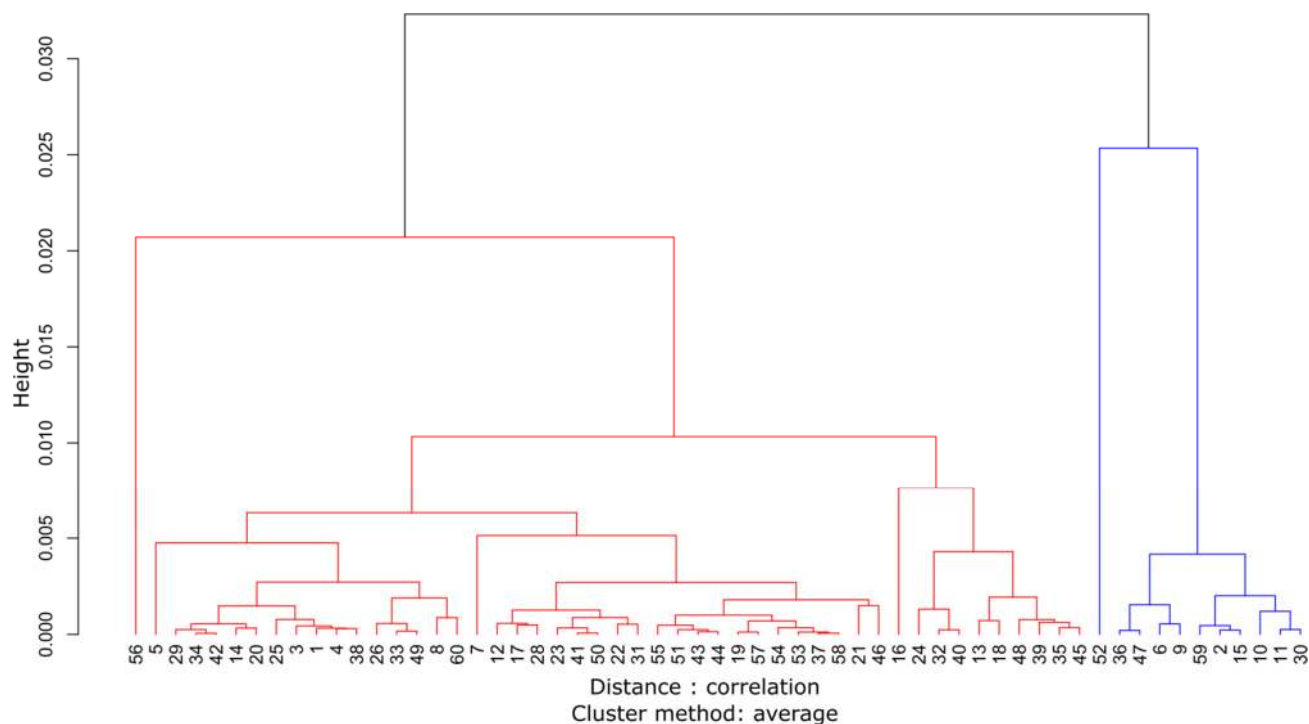
The mass concentration of the groups is an average of the mass concentration of all residences in that group. The difference of mass concentration between the groups is  $2.3 \mu\text{g m}^{-3}$ , Group 2 has 18.9% higher mass concentration ( $12.2 \mu\text{g m}^{-3}$ ) than Group 1 ( $9.9 \mu\text{g m}^{-3}$ ), however is a non-significant difference (p-value over 0.36). The Group 2 also present higher average of outdoor temperature, relative humidity, wind speed and, in particular, the precipitation than in Group 1 (SI Table S5). 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 (Fig. 5). 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.

#### Sources of qUFP

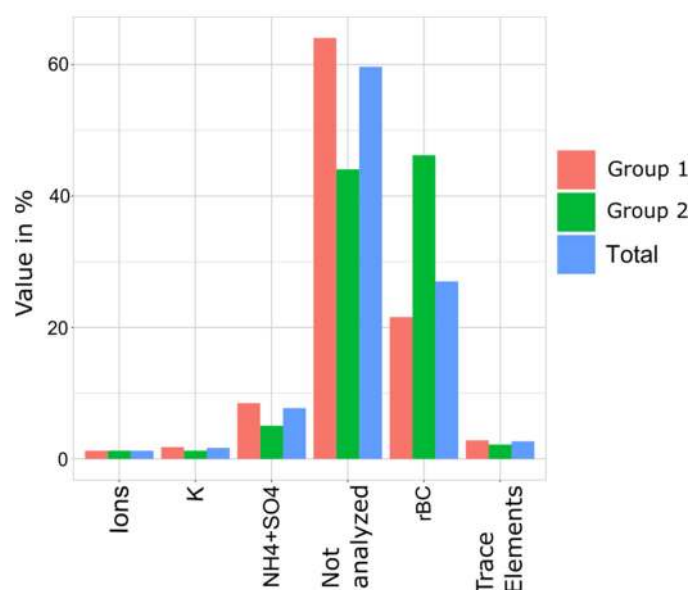
Through the PMF we identified 6 factors that represent 7, 21, 7, 57, 5 and 3% of the analysed mass concentration of qUFP, respectively (Fig. 6). The first factor has high contributions of Na, Zn, Cu, and Pb, elements which are positively correlated to each other (Fig. 2(b)). Although Zn and Cu are typical



**Fig. 3.** Stoichiometry ratios ( $\mu\text{mol L}^{-1}$ ) between (a) ammonium and sulfate and (b) sulfate plus nitrate for qUFP in elderly residences in MASP.



**Fig. 4.** 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.



**Fig. 5.** Mass balance of qUFP with the proportions of ions (separated in 3 parts:  $K^+$ ,  $NH_4^+$  +  $SO_4^{2-}$  and others ions ( $Ca^{2+}$ ,  $Na^+$ ,  $Cl^-$ ,  $NO_3^-$ )), trace elements, black carbon (rBC - from Segalin *et al.*, 2016) and compound not analyzed in this work, for all the residences (Total) and for the two groups generated for cluster analysis in Fig. 4.

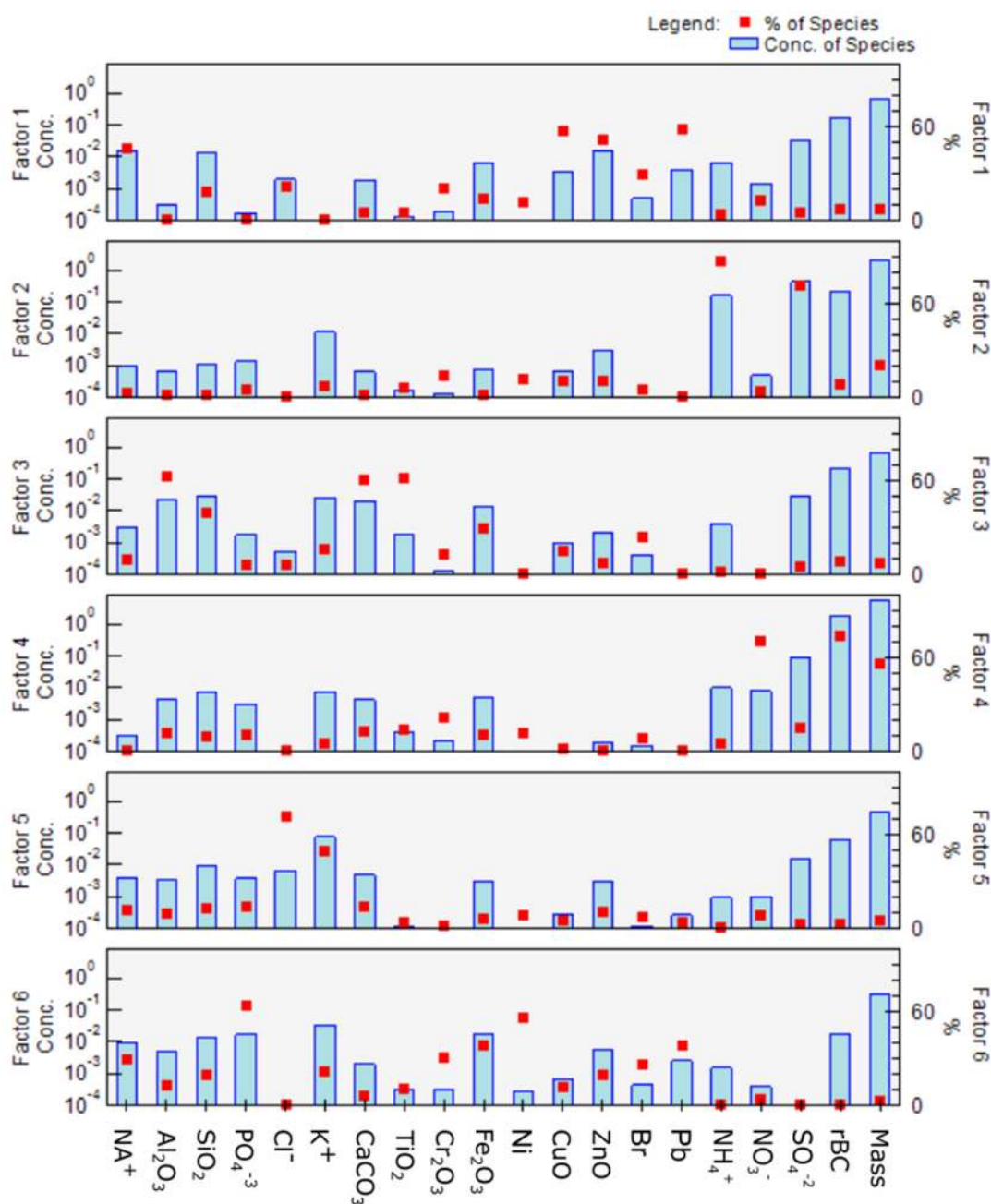
vehicular source markers (Andrade *et al.*, 2012), they also have indoor sources for qUFP, usually wall paints (Viana *et al.*, 2014), and Pb is also a component of wall paint, mostly in old residences (Beauchemin *et al.*, 2011), then for this study Factor 1 is wall paint. Factor 2 is considered as secondary inorganic aerosol because of the high concentrations of ions  $NH_4^+$  and  $SO_4^{2-}$ , which indicate a large contribution of secondary inorganic aerosol production to qUFP, as

described in Section 3.1. Measurements in tunnels in MASP showed higher concentrations of  $NH_4^+$  and  $SO_4^{2-}$  in fine particles within the tunnels than outside, indicating a vehicular contribution to the production of sulphate and ammonium particles in urbanized areas (Vieira-filho *et al.*, 2016b). In the outdoor air in MASP,  $SO_4^{2-}$  presented a modal peak of the mass concentration distribution around  $0.3 \mu m$  diameter and its source was  $SO_2$  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  $\text{Cl}^-$  (Fig. 6). These ions indicate biomass burning (Ynoue and Andrade, 2004) and  $\text{Cl}^-$  is also considered to be an indoor source for qUFP (Viana *et al.*, 2014), this factor likely indicates indoor biomass burning. Based on this, Factor 5 is considered cooking process source of qUFP. 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). Factor 6 is probably representing the qUFP produced in industrial process that penetrates into the residences. The particles inside the residences can be produced there or may come from outside through the windows or doors. In Brazil, the windows are generally always open due to the heat in the summer and the rather mild winters. Factor 1 is a wall paint source, therefore a source of indoor origin. Factor 2 is a secondary inorganic aerosol, Factor 3 is a soil and construction source, Factor 4 is vehicular emissions, all of which are sources of outdoor origin. Factor 5 is cooking (source of



**Fig. 6.** 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.

indoor origin) and Factor 6 is an industrial source (source of outdoor origin). According to this analysis, the qUFP in elderly residence originated from 2 sources of indoor origin (Factors 1 and 5) and 4 sources of outdoor origin (Factors 2, 3, 4 and 6). Since the factors represent 7, 21, 7, 57, 5 and 3% of the analysed mass concentration of qUFP, 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 8.39 million vehicles (CETESB, 2016; DETRAN, 2017). The vehicular emission in the MASP contributes directly to 37% of the PM<sub>2.5</sub> concentration. Further, there is an indirect contribution to the production of secondary aerosol mass (51% of PM<sub>2.5</sub>, 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%, Segalin *et al.*, 2016).

#### **Respiratory Deposition Doses (RDD) of qUFP and rBC Mass Concentrations**

Fig. 7 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 is higher for men than for women and higher during light exercise than in a seated position of the persons. The same pattern occurs for RDD in the total respiratory tract because the tidal volume is bigger for men than for women, and it is bigger during light exercises (Hinds, 1999; Azarmi *et al.*, 2016; Segalin *et al.*, 2017). 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

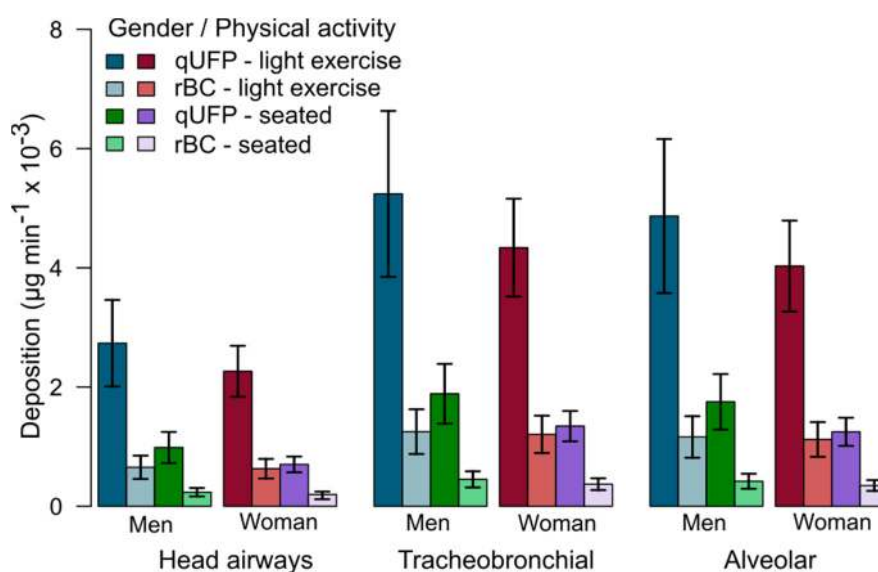
in men during light exercise and in the tracheobronchial region. The RDD total is higher for coarse particles than for qUFP (Segalin, *et al.*, 2017), however, the RDD of qUFP is higher in tracheobronchial and alveolar parts than in the head. The latter poses a larger health risk because these particles 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).

#### **SUMMARY AND CONCLUSIONS**

The goal of this project was to characterize the ion and trace elements concentrations in qUFP, to identify the sources of the qUFP inside elderly residences and to estimate of RDD of the qUFP and the rBC in different parts of the respiratory tract. In the best of our knowledge, this is the first research to study the chemical characteristics of the qUFP in elderly residences in a Latin American megacity. We measured qUFP in 59 residences of elderly with the PCIS in the MASP. The measurements were made during 24 hours, once in each residence, during different days, except in one residence where 2 samples were taken because 2 elderly live there. Overall, a total of 60 samples were analysed.

The predominant ions in indoor qUFP were SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> and the major trace elements 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 sufficient 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. The mass balance of these groups shows a predominance of rBC in Group 2 and of NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and K<sup>+</sup>



**Fig. 7.** Rates deposition doses (RDD) of qUFP and its proportion of black carbon (rBC - present in qUFP from Segalin *et al.*, 2016) in different regions of the respiratory tract for men and women during light exercises and seated position during 24 hours.

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 18.8% higher in Group 2 than in Group 1. We conclude that the location of the residences within the MASP plays a larger role in the mass concentration and chemical balance of indoor qUFP in elderly residence than the weather conditions.

We found 2 indoor sources of qUFP inside the elderly residences, wall painting (7%) and cooking (5%), but the main contribution to the mass concentration of qUFP was associated with the outdoor sources, oil and construction (7%), industry (3%), secondary inorganic aerosol (21%) and mainly vehicular emission (57%).

The RDD of qUFP and rBC were higher in men than in women, higher during light exercise than in the seated position, and 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 deposition in the head.

The above finding confirms that elderly is breathing the air with abundance of qUFPs and a very high mass concentration of toxic metals in some residences, which is mainly due to the high number of outdoor vehicles on roads around their residences. The necessity of a better traffic-related emission control in MASP has been already discussed by many authors. Since the elderly spend most of their daily time inside their residences and considering that demographic projections suggest an increase in their numbers in future, further efforts are needed to improve indoor air quality.

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#### SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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