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Characterization of particles emitted by pizzerias burning wood and briquettes: a case study at Sao Paulo, Brazil

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Abstract

The burning of biomass in pizza ovens can be an important source of air pollution. Fine particulate matter represents one of the most aggressive pollutants to human health, besides the potential to interfere with global radiative balance. A study in real-world condition was performed in three pizzerias in São Paulo city. Two of the pizzerias used eucalyptus timber logs and one used wooden briquettes. The results from the three pizzerias revealed high average concentrations of $PM_{2.5}$: 6,171.2 μg/m^3 at the exit of the chimney and 68.2 μg/m^3 in indoor areas. The burning of briquette revealed lower concentrations of $PM_{2.5}$. BC represented approximately 20% and 30% of the $PM_{2.5}$ mass concentration in indoor and at chimney exhaust, respectively. Among the trace-elements, potassium, chlorine and sulfur were the most prevalent in terms of concentration. Scanning Electron Microscopy (SEM) analysis revealed particles with an individual and spherical morphology, i.e., the conglomeration of spherical particles, flattened particles in the formation of fibres, the overlapping of layers and the clustering of particles with sponge-like qualities. The average emission factors for $PM_{2.5}$ and BC due to the burning of logs were 0.38 g/kg and 0.23 g/kg, respectively. The total emissions of $PM_{2.5}$ and BC were 116.73 t/year and 70.65 t/year, respectively, in the burning of timber logs.

Keywords: Air pollution, $PM_{2.5}$, black carbon, biomass burning, pizzeria, X-ray fluorescence; emission factors

Introduction

Biomass is one of the main sources of energy in the world (WER 2016). However, there are few studies around the world analysing the impact of wood and charcoal use for cooking in metropolitan areas. In Brazil, the biomass represents 25.1% of the energy matrix and is used mainly in residences and in food-related commercial establishments (i.e restaurants, bakeries and pizzerias). In the city of São Paulo, the consumption of pizzas is very important, 1.5 million pizzas are produced daily, being the second city in the world in pizza consumption (BEN 2016). Moreover, biomass burning is also a significant source of air pollutants (Taner et al. 2013; Kliucininkas et al. 2014; Ozgen et al. 2014; Shen et al. 2014): carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), sulphur dioxide (SO_2), nitrogen oxide (NO_x), black carbon (BC) and particulate matter (PM).

PM is one of the most harmful pollutants to human health and may also contribute to climate change. Particles suspended in the atmosphere can influence the amount of solar radiation that reaches the earth's surface through scattering and absorption processes, causing heating or cooling of the atmosphere, depending on the physico-chemical and optical properties of the particles (Artaxo et al. 2009). Seinfeld and Pandis (1998), define $PM_{2.5}$ as a group of solid and liquid particles suspended in the atmosphere with an aerodynamic diameter of ≤ 2.5 µm. International studies have proven the relationship between exposure to $PM_{2.5}$ and respiratory diseases (Polichetti et al. 2009; Peled 2011; Saldiva et al. 2013). In recent years, new studies established the relationship between exposure to $PM_{2.5}$ and the decline in cognition and the rise in diabetes (Krãmer et al. 2010; Weuve et al. 2012).

The most important anthropic sources of PM are industries, vehicle emissions and biomass burning (Jacobson 2002). Among the diverse elements that compose the mass of $PM_{2.5}$ coming from the burning of biomass, BC is normally present in high concentrations due to its smaller size and its chemical nature. BC is related to adverse effects on human health beyond being an important agent in climatic change. While some aerosols have a climate cooling effect, BC particles are associated with warming (IPCC 2013). Moreover, the interaction of BC with snow and ice is the focus of many research studies related to changes in albedo and in the global radiative balance (Bond et al. 2011; Smith and Bond 2013). Besides that, the BC particles can be allocated to the body, including the brain, with adverse effects.

The Metropolitan Area of São Paulo (MASP), where the city of São Paulo is located, is one of the largest megacities in the world, with more than 20 million inhabitants and 8 million vehicles, as well as a major industrial and technological park of Brazil (Fig. 1). The MASP has an extensive air quality monitoring network, which has shown that inhalable particles often exceed the National Air Quality Standards (NAAQS) during the winter season, from June to August (CETESB 2018). Between the winter and summer, the dry and wet seasons, respectively, daily mean temperatures range from 16°C in July to 28°C in February. As mentioned before, Miranda et al. (2012) and Andrade et al. (2012) have demonstrated that aerosol concentrations are higher during the winter and vehicle emissions constitute the main source of urban pollutants in São Paulo.

The burning of biomass in pizzerias constitutes a significant source of BC and $PM_{2.5}$ within the city of São Paulo. More than 7.5 ha of eucalyptus forest is being burned in MASP every month by pizzerias and steakhouses (Vieira-Filho et al. 2013). Moreover, the burning of fuelwood by pizzerias represents approximately 3% of atmospheric emissions at MASP (Kumar et al. 2016). The city has around 8,000 pizzerias and it is estimated that 80% of those pizzerias use eucalyptus hardwood ovens. From this 80%, approximately 2% use softwood briquettes as fuel (Sgarbi et al. 2013). The briquette is formed from compacted wood shavings and is slightly used in Brazil (Gentil 2008). The lack of official standards in the production of briquettes and the different types of chemical additives used to bind them together creates products of varying quality (Sola et al. 2011; Roy and Coscadden 2012; Ozgen et al. 2014).

In Brazil, there are no studies concerning the burning of biomass in pizzerias. Outside of Brazil, there are various studies of microenvironments like restaurants and pizzerias (Brauer et al. 2000; Wallace et al. 2004; Hussein et al. 2006; Branis and Kolomazniková 2010; Buonanno et al. 2010; Taner et al. 2013).

Studies found in the literature were carried out under controlled conditions of flow rate, temperature, use of dilution camera in the obtaining of emission factors (Dash 1982; Gonçalves et al. 2010; Shen et al. 2014; Calvo et al. 2014). This research was conducted in the city of São Paulo, Brazil, and studied indoor and chimney exhaust $PM_{2.5}$ and BC concentrations, morphology and particles chemical composition related to the burning of biomass in three pizzerias. Brazil map highlighting São Paulo State and MASP and the locations of Pizzeria 1 (P1), Pizzeria 2 (P2) and Pizzeria 3 (P3) where the sampling sites are situated are illustrated in figure 1.

Fig.1 Brazil map highlighting São Paulo State and MASP. P1, P2 and P3 are sampling sites, respectively

This study intended to estimate the emissions of $PM_{2.5}$ and BC coming from the burning of fuelwood and briquettes. The measurements were carried out under real operating conditions of the three pizzerias, on weekdays and weekends, inside the pizzeria hall where staff and customers stay and at the chimney exhaust. The estimates of the total emissions were made based on calculated emission factors and considering the annual consumption of wood/briquettes by pizzerias. This is the first study on the contribution of biomass burning in pizzerias performed in Brazil.

Methods

Sample sites and pizzerias characteristics

Samples were taken in three pizzerias (P1, P2 and P3) situated in the central region of São Paulo City between October and November of 2013. The surrounding area of each of the pizzerias was similar with an absence of high vegetation, far from industrial areas and located in residential/commercial areas; however, P3 is located on the main thoroughfare while P1 and P2 are located on streets. P1 and P2 used eucalyptus fuelwood while P3 used briquettes. The average daily production during the sampling time was 30, 26 and 38 pizzas in P1, P2 and P3 and the consumption of fuelwood/briquettes was 102.5, 62.6 and 19.8 kg, respectively, during the whole sampling. None of the pizzerias used air conditioning. The chimney diameter was 45 cm and the opening of the indoor oven was 30 cm high and 45 cm wide for all three pizzerias. The main difference between the studied pizzerias was the height of the chimney: 8 m (P1 and P3) and 25 m (P2), as illustrated in figure 2.

Fig. 2 Experimental study arrangement

The samplings of PM were carried out in real operating conditions of the pizzerias in the year of 2013, on weekdays and weekends, inside the pizzeria hall (indoor) where employees and customers normally stay and at the chimney exhaust. Due to the small space and unstable conditions, it was not possible to measure other variables. The sampling duct was positioned in such a way as to limit the external air intake to a maximum, that is, so that only what was coming out of the chimney was measured. The duct was placed parallel to the chimney outside, with the inlet positioned to avoid dilution and cooling. Samplings at P1 occurred from October 11th to 14th, while at P2 and P3 occurred from 18 to 20 October and 02 to 04 November, respectively (Table 1). Meteorological conditions during the sampling days presented no rain, predominantly calm winds, temperatures that varied from 19°C to 31°C and good air quality, in accordance with the local air quality standards.

Table 1. Characteristics of pizzerias, type of biomass used, daily pizza production, sampling period and number of samples

Pizzeria	Biomass type	Sales pizza/day	Sampling periods	Number of samples
P1	Eucalyptus	30	Oct. 11-14	34
P2	Eucalyptus	26	Oct. 18-20	30
P3	Briquette	38	Nov. 02-04	26

Details of equipment and analyses

The Mini-Vol sampler (Airmetrics) was the equipment used in the experimental part of the study to collect $PM_{2.5}$. The Mini Vol operated with a flow of 5 l/min and used filters of polycarbonate, with a diameter of 47 mm and pores of 0.4 µm. The equipment was left in operation, having the readings being checked at the end of the flow time, seeing a possible reduction in the flow rate due to the accumulation of the particulate matter in the filter. Indoor the three pizzerias, the equipment operated from 05:30 PM to 01:00 AM (local time), during the sampling periods of the experiment. Outside the pizzerias, the equipment operated during two periods: from 05:30 to 06:30 PM and from 09:00 to 10:00 PM. The two periods were chosen to distinguish between only biomass burning when the oven is lit and together biomass and pizza burning. In order to avoid filter clogging, the filter was changed every fifteen minutes (900s). A duct was connected to

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the exit of the chimney to concentrate the smoke in the Mini Vol sampler and reduce interference from other sources of pollution (figure 2).

Analysis techniques

After collection, the $PM_{2.5}$ was analysed by different complementary techniques. The mass concentration was determined by the gravimetric method. The measurement consists of weighing the filters before and after the sampling to obtain the weight of the material collected. Gravimetry was used to determine the total mass through an electronic microbalance with a detection limit of 1μg (MX5; Mettler-Toledo, Columbus, OH, USA). In order to avoid weighting errors, filters were stored in a temperature and humidity-controlled environment (22 ± 2°C and 45 ± 3% relative humidity) for 24 h prior to their weighting. Blank concentrations were subtracted from the values obtained for each sample. The black carbon concentrations were determined by optical reflectance with a smoke stain reflectometer (model 43D; Diffusion Systems Ltd, London, UK). For this instrument, the calibration curve to convert reflected light to black carbon concentration was obtained empirically using gravimetric standards. The elemental analysis was performed by EDXRF (Energy Dispersive X-ray Fluorescence) to determine the aerosol elemental composition of each sample using an Epsilon 5, PANalytical B.V. instrument. The X-ray tube anode operates with accelerating voltages of 25–100 kV and currents of 0.5–24 mA, with a maximum power of 600 W. Further details are given by Arana et al. (2014). Each filter was submitted to EDXRF and spectral counting was accumulated for 600 s for elements from Na to K and 300 s for elements from Ca to Pb.

The morphology of the particles was investigated using a SEM (model LEO 440) with energy dispersive X-ray detector attachment, at the Institute of Geosciences, University of São Paulo. Samples were re-covered with carbon. For this analysis, indoor and chimney exhaust samples were chosen from the only burning of fuelwood and briquette and the burning of fuelwood together with pizza, considering the three pizzerias, with the aim of studying the morphological differences of the particles.

Emission factor calculation

Some studies calculated emission factors under controlled conditions like amount of fuel, temperature, dilution and forced ventilation (Gonçalves et al. 2010, Ozgen et al. 2014). In this study, real-world emission factors were calculated based on theoretical data of temperature and flow. These parameters were not monitored due to the complexity of this study, samples taken over the pizzeria roof under real operating conditions. For this purpose, we used data from the experiment carried out by Calvo et al. (2014), since it was not possible to control some variables like temperature and gas flow during the experiment.

This research was carried out mainly in order to have $PM_{2.5}$ mass and chemical characterization,. The city has around 8,000 pizzerias, which can be considered an important source of particles. The equation used to determine emission factors was the same described by Calvo et al. (2014) and applied exclusively to particulate matter.

$$EF_{PM2.5,\Delta t} = \frac{C_{PM2.5}.Q_t.\Delta t}{\Delta m} \quad (1)$$

where:

$EF_{PM2.5,\Delta t}$ emission factor (g/kg) of $PM_{2.5}$ at sampling interval time Δt (900 s) for a filter x;
$C_{PM2.5}$ concentration of $PM_{2.5}$ at time interval (g/m^3);
Q_t gas flow at the chimney exit (m^3/s);
Δm mass consumed during the sampling interval (kg).

Emission factors were calculated only for pizzeria P1, where the mass of wood burned was obtained from the initial weight of the eucalyptus logs. Based on literature (Calvo et al. 2014 and Dasch, 1982) we considered that around 25% of the initial mass of wood was burned every 15 minutes, remaining 5% of the initial mass after 1 hour of combustion. Since the initial mass was weighed, a burning rate was calculated (considering 100% initial and 5% final) to have the wood mass every 15 minutes. Using eucalyptus in a fireplace, Calvo at al. (2014) showed that the temperature at the top of the chimney was around 150°C. Using the Bernoulli equation, exaust velocity (*v*) and gas flow (*Qt*) could be calculated by:

$$v(h) = \sqrt{2gh\,(\frac{T_{smoke}}{T_{air}} - 1)} \qquad (2)$$

$$Qt = v(h).A.t \qquad (3)$$

where

g is 9.8 m/s
h is the height of the chimineys (8 and 25 m)
T_{smoke} is the temperature at the chimney exhaust
T_{air} is the environment temperature
A is the cross section area of the chiminey
t is time in hours

Considering environmental air temperature of 25°C and 150°C for the temperature at the chimney exhaust, the exhaust velocity and gas flow were estimated as 8.1 m/s and 1.3 m^3/s for the 8 meters high chimney and 14.3 m/s and 2.3 m^3/s for 25 meters high chiminey. Exhaust velocity is higher for a higher chimney.

The EFs were calculated in real conditions and no forced ventilation, for the burning of eucalyptus wood (the most used biomass in pizzerias in São Paulo). The EFs were calculated in the first hour of oven use (05:30 to 06:30 PM) with the controlled fuelwood load. Using Equation (1), emission factor (EF) for $PM_{2.5}$ and BC was calculated considering $PM_{2.5}$ concentration (g/m^3) each 15 minutes and gas flow of the gases.

Emission estimate calculation

After calculating the EF for $PM_{2.5}$ and BC it was possible to estimate the annual contributions of the studied pollutants derived from the burning of fuelwood in the pizzerias of São Paulo. The emissions of $PM_{2.5}$ and BC were estimated and compared with information obtained from fuelwood suppliers and pizzeria owners. It was possible to estimate the emissions of $PM_{2.5}$ and BC of the pizzerias in the city of São Paulo taking into account the quantity of fuelwood sold per year (Bhattacharya et al. 1999, Gianelle et al. 2013 and Majumdar et al. 2013). Particulate material emissions were calculated using the following equation:

$$Emissions_{pollutant} = annual\ consumption\ of\ fuelwood\ (kg) x\ Emission\ Factor_{of\ pollutant} \quad (4)$$

Results

$PM_{2.5}$ and BC concentration

Table 2 presents the measurements and the standard deviations obtained for particulate matter and BC in the three pizzerias at both indoor and at the chimney exhaust. The $PM_{2.5}$ ($\mu g/m^3$) refers to the average of the mass deposited on the filter in each pizzeria; BC ($\mu g/m^3$) refers to the average concentration of BC present in the sample filters. High deviations are due to the large variation in concentration values, especially in the external environment. Chimney exhaust concentrations in are much higher than indoor concentrations.

Table 2 $PM_{2.5}$ and BC concentration averages and standard deviations for indoor and chimney exhaust.

Indoor				
Average concentration (µg/m³) and standard deviations (SD)				
	$PM_{2.5}$		**BC**	
	Average	**SD**	**Average**	**SD**
P1	111.1	46.9	55.5	72.6
P2	40.9	4.0	7.8	1.9
P3	52.7	21.1	12.5	3.9
Chimney exhaust				
Average concentration (µg/m³) and standard deviations (SD)				
	$PM_{2.5}$		**BC**	
	Average	**SD**	**Average**	**SD**
P1	3,424.5	6,401.5	2,068.0	2,969.4
P2	13,660.5	9,704.4	1,505.7	2,180.9
P3	1,428.5	987.9	498.7	671.9

Air Quality Standard (AQs) for $PM_{2.5}$ is 60 µg/m^3 for 24 hs in São Paulo. During the sampling period, the daily average for the pollutant was 20.2, 20.0 and 15.1 µg/m^3 for P1, P2 and P3, respectively. Daily average was below (AQs). As will be seen below, the annual emission of firewood pizzerias may have an influence on air quality in São Paulo. Indoor concentrations were worst for P1.

Figure 3 shows the percentage of BC in the $PM_{2.5}$ composition for the indoor and chimney exhaust environment in the three pizzerias throughout the sampling period. The percentage of BC in the $PM_{2.5}$ composition in P1, P2 and P3 is similar to the results obtained by authors such as Gonçalves et al. (2010). The authors quantified 11-37.1% of elemental carbon in the PM_{10} composition for burning different types of firewood. Fine et al. (2004) concluded that the 2-23% variation was the contribution of elemental carbon in the $PM_{2.5}$ composition from firewood burning. Comparing pizzerias 1, 2 and

3, it can be stated that pizzeria 1 emitted higher concentrations of BC to the environment and pizzeria 2 released lower concentrations.

Indoor concentration

The average concentrations of PM and BC obtained in the internal areas of the three pizzerias during the whole period of sampling was of 68.2 µg/m^3 and 25.2 µg/m^3, respectively. Higher concentrations of PM and BC were measured at P1 (111.1 µg/m^3 and 55.5 µg/m^3). Approximately 50% of the mass composition of the particulate matter at P1 is BC. Comparing P1 and P2 that use eucalyptus wood as fuel, in P2 pizzeria the percentage of BC was lower and also indoor concentrations. One possible explanation is the fact that the pizzeria 2 chimney is taller and also the exhaust velocity of the gases (as mentioned above), this factor may have contributed to less particle emission to the pizzaria hall.

Fig. 3 Indoor and chimney exhaust percentage of BC in the mass of the $PM_{2.5}$ in the three pizzerias.

Chimney exhaust concentration

The chimney exhaust presented higher concentrations compared to the indoor area (table 2). The particulate matter after being ascended was directed through a duct to a single point, the Mini Vol sampler. Figure 4 shows average concentrations and standard deviations for $PM_{2.5}$ and BC obtained at the chimney exhaust, average of the sampling period in each pizzeria These values represent the average concentration at each time interval considering the whole period of the test in the three pizzerias, remembering that membrane filter was changed every 15 minutes. Generally, the mass concentrations are

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greater in the first period of the sampling, from 05:30 to 06:30 PM resulted from the burning of the wood. In this period when the oven is lit, requires a greater amount of energy to reach ideal pizza cooking temperature. From 09:00 PM to 10:00 PM the oven is preheated, a lower quantity of fuelwood is necessary, only enough to ensure the cooking of the pizza, and in this way, lower concentrations of PM and BC are emitted. It was observed that even having used less fuelwood in relation to P1, the concentration of mass for P2 in the chimney exhaust area was greater. P2 presented the differential of having a taller chimney and therefore created greater suction of the indoor air (calculated exaust velocity was 14.3 m/s for 25 m heigh chimney and 8.1 for 8 m heigh chimney) , in this way increasing the concentration of particulate matter collected from the chimney. This could have contributed to the higher concentrations measured at the chimney exhaust. In relation to P3 (the use of briquette), the mass concentration of the chimney area is shown to be less than that of P1 and P2. In relation to the burning of briquettes, works by Johansson et al. (2004) also consider lower emissions coming from the burning of briquettes when compared with the emissions coming from the burning of fuelwood. Roy e Coscadden (2012) complement the affirmation in their conclusion that the concentrations depend on the composition of the materials and type of chemical agglomeration used in the production of the briquettes. The authors compared the emission of the burning of fifteen types of briquette and checked the concentrations of the particulate matter varied from 90 $\mu g/m^3$ to 830 $\mu g/m^3$. In this study we could not affirm if the quality of the briquette used at P3 is good, but authors like Gentil (2008) affirm that in Brazil there is a lack of briquette production standards.

It was observed that the concentration of $PM_{2,5}$ and BC was shown to be variable in the different sampling moments (figure 4), being higher in P2. P1 and P2 use the same type of firewood, eucalyptus. However, the P2 chimney is higher and the state of upkeep furnace is different, which probably influenced the different concentrations, as already presented in the previous section. Comparatively, P3 presented the lowest concentrations. P3 uses briquette.

Fig. 4 Average concentrations of $PM_{2.5}$ and BC of pizzeria 1 (P1), pizzeria 2 (P2) and pizzeria 3 (P3), the chimney exhaust for each time interval of the sampling during the entire period of the campaign. Error bars represent standard deviations.

In P1 the mean hourly concentration was higher in the interval of 05:45 - 06:00 PM, more than 11,000 μg/m³. In this period the oven is colder and requires more wood to reach the maximum temperature. The lowest concentrations were generally obtained in the second part of the sampling, i.e. between 09:00 to 10:00 PM. In relation to BC, the highest concentration was also obtained in the interval of 05:45 to 06:00 PM, with a value of approximately 5,500 μg/m³ . In P2, the behavior was different. The highest concentration of $PM_{2,5}$, 20,000 μg/m³, was measured in the second part of the sample. On the other hand, the highest concentration of BC, 5,000 μg/m³, was obtained in the first sampling period (05:30 to 05:45 PM). The highest and lowest concentrations are not necessarily related to the sampling period, the need or not for more wood, but also to the characteristics of firewood. Although P1 and P2 used eucalyptus wood, any differences in wood log size, moisture and the thickness of the bark certainly influenced the concentrations. Wood properties influence the efficiency of the combustion process, and consequently emit different concentrations of PM and BC, especially during the wood devolatilization period (Calvo et al. 2014). In relation to P3, the temporal variation was similar to P1: higher concentrations were quantified during the first period of sampling. However, with values well below those quantified in P1.

Chemical Composition of $PM_{2.5}$

The results from X-ray fluorescence presented a spectrum of chemical elements with differing characteristics (Table 3). Metallic elements, non-metallic elements and heavy metals are present at differing concentrations in the characterisation of particulate matter.

Table 3 Average element concentrations (μg/m³) and standard deviation obtained indoor and at the three pizzerias

	Average element concentrations (μg/m³) and standard deviations											
	Pizzeria 1				**Pizzeria 2**				**Pizzeria 3**			
	Indoor		**Chim exh***		**Indoor**		**Chim exh***		**Indoor**		**Chim exh***	
	Average	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**
Na	0.65	0.10	8.78	10.70	0.23	0.20	15.04	11.45	0.27	0.12	1.25	1.79
Mg	0.06	0.02	0.43	0.78	0.06	0.04	1.14	1.37	0.18	0.23	0.72	1.38
Fe	0.40	0.09	0.30	7.83	0.25	0.07	0.31	6.42	0.47	0.09	0.49	7.42
Ca	0.13	0.08	1.45	9.70	0.09	0.11	1.04	8.11	0.11	0.13	0.96	1.16
Al	0.19	0.00	5.07	0.49	0.10	0.01	7.36	0.86	0.15	0.02	6.82	0.19
Si	0.37	0.30	4.81	7.93	0.19	0.57	4.39	17.44	0.25	0.82	1.79	1.94
P	0.04	1.21	0.27	259.07	0.02	1.46	0.66	159.30	0.04	0.01	0.15	10.24
S	1.21	3.11	5.52	231.54	0.81	2.35	16.96	171.39	1.55	0.31	3.11	19.95
Cl	1.08	0.05	149.99	3.58	0.94	0.01	175.72	1.28	0.01	0.06	7.90	1.09
K	3.32	0.01	159.88	0.63	1.89	0.00	226.36	0.31	0.74	0.01	21.70	0.25
Ti	0.00	0.00	0.25	0.06	0.00	0.00	0.18	0.05	0.03	0.00	0.30	0.02
V	0.00	0.00	0.03	0.48	0.00	0.01	0.02	0.88	0.00	0.01	0.00	0.11
Mn	0.01	0.09	0.20	0.57	0.00	0.22	0.39	0.72	0.01	0.24	0.20	0.50
Ni	0.00	0.00	0.08	0.07	0.00	0.00	0.08	0.08	0.00	0.00	0.09	0.08
Cu	0.03	0.01	0.22	0.20	0.03	0.03	0.20	0.21	0.02	0.01	0.16	0.12
Zn	0.13	0.03	1.06	1.71	0.07	0.04	2.19	2.15	0.07	0.05	0.26	0.24
Br	0.05	0.06	2.68	4.12	0.01	0.01	3.65	5.17	0.10	0.05	9.23	11.29
Cd	0.07	0.06	1.23	1.24	0.03	0.02	1.12	1.73	0.01	0.02	0.95	0.98
Pb	0.04	0.02	0.11	0.20	0.02	0.02	0.520	0.73	0.03	0.00	0.20	0.29

*Chim exh: Chimney exhaust

The results obtained here are similar to other studies about the burning of biomass in which potassium, chlorine, sulphur, and sodium were the main elements (Sexton et al. 1985; Fine et al. 2004; Gonçalves 2010; Salam et al. 2013; Taner et al. 2013). The potassium is found in high concentrations in the processes that involve the burning of biomass, like the burning of fuelwood in pizzeria ovens. The chlorine and the sodium also presented elevated concentrations. Sodium is generally associated with chlorine to form sodium chloride (NaCl), used as cooking salt (basic ingredient for many fillings used in pizzerias like cheese, smoked sausage, salami and pepperoni). In general, the chlorine is characterised as a trace element of vehicle emissions, sea-salt (Viana et al. 2008), and biomass burning (Santos and Reis 2011). Sulphur is one of the components of fuelwood.

Medium level concentrations were quantified for the elements: aluminium, silicon, iron and calcium. In the study conducted by Gonçalves et al. (2010) about the characterisation of the burning of four types of biomass, including eucalyptus, the authors attributed the concentrations of these elements as being characteristic of the type of ecosystem, seen as the trees can absorb nutrients present in the water in the soil. Another important source of aluminium and calcium could be the composition of some products used in the preparation of the pizzas. The flour and the yeast are of traditional and well-used brands in pizzerias and contain in its composition high concentrations of aluminium (Santos and Reis 2011). Elements such as lead, cadmium, zinc, chromium, copper and lower concentrations of vanadium, arsenic and nickel were quantified, although for elements such as selenium, nickel and titanium the highest concentrations were quantified in P3, see table 3. The results obtained in the elemental characterization of biomass burning performed by Taner et al. (2013) also presented heavy metals in their composition. The results of Alves et al. (2011) and Salam et al. (2013) presented lead, zinc and copper as the most representative heavy metals in terms of concentration. But it also needs to be noted that titanium and nickel are also minority chemical constituents of biomass (Jacobson, 2002) and may contribute to the emissions found.

About indoor element concentrations, low concentrations of elements dangerous to health were measured in the internal areas when compared to the standards established by the Occupational Safety and Health Administration (OSHA), the agency that exclusively legislates working environments. Comparing average concentrations of elements normally highlighted in literature (Cr, Mn, Ni, Cu, Zn and Se) (Gonçalves et al. 2010; Taner et al. 2013; Nordin et al. 2014) with element exposure standards for 8 hours, established by the OSHA, for Z, Cu and Cr the concentrations were high when compared with the values of the reference, 0.005 µg/m³, 0.001 µg/m³ e 0.001 µg/m³, respectively (table 4). Studies conducted by Nordin et al. (2014) and Uski et al. (2015) also revealed high concentrations of these elements when burning fuelwood.

Table 4 Minority concentrations of quantified elements in the indoor environment, compared to OSHA standards

	Element Concentration (indoor) ($\mu g/m^3$)					
	Cr	**Cu**	**Zn**	**Se**	**Mn**	**Ni**
P1	0.023	0.055	0.139	0.009	0.016	0.005
P2	0.002	0.064	0.105	0.010	0.010	0.005
P3	0.018	0.034	0.136	0.012	0.011	0.002
Standards OSHA	**0.001**	**0.001**	**0.005**	**0.0002**	**0.005**	**0.001**

Morphology of $PM_{2.5}$

The morphological characterisation of the particulate material presented different types of forms: spongy appearance, individual morphological spheres, conglomerates of small spherical particles forming "bunches of grapes" and flat shapes forming in layers (Fig. 5). The images analysed represented different conditions (indoor and outdoor, with and without pizza in the oven and in the burning of briquette and in different temperatures, since early on, with no pizza, when the oven is lit, temperature is lower and at the end of sampling is higher), which influenced the morphology of the particles. Lower temperatures in the furnace can generate bigger particles, with rounded or elongated shape (figure 5a). On the other hand, high temperatures generate small particles (figure 5c), usually with a spherical shape.

Fig. 5 Micrographs corresponding to the burning of fuelwood: (a) indoor, (b) chimney exhaust, (c) wood burning (d) wood-burning plus a pizza in the oven (e) briquette burning.

The filter analysed represented the burning of fuelwood at indoor (figure 5a) reveals the formation of smooth spheres accumulating on a larger particle. The predominant elements in the sample were: chlorine, aluminium, silicone, and potassium. In smaller quantities, there was calcium and iron. The filter representing chimney exhaust (figure 5b and 5c) illustrated the particle morphology emitted from the burning fuelwood when the ovens were lit; the moment characterised as having the greatest temperatures and corresponds only with the presence of biomass in the oven. Smaller sizes of particles are found during this phase, predominantly BC particles forming a sponge-like look of the carbonaceous composition. The major elements are potassium and calcium, in smaller quantities are aluminium, chlorine and iron. For the briquette, the most expressive chemical elements in terms of concentration are silicon, aluminium, calcium and iron indoors, and a significant concentration of bromine outdoors. The morphological results obtained by Rosasco (2009) concerning biomass burning showed similar results to those obtained here revealing small particles with sponge shape. They are particles emitted in high-temperature conditions, of which there are particles predominantly of a size smaller than 1 μm and with a chemical composition predominantly of BC, followed by potassium and chlorine elements normally associated with the burning of biomass. (figure 5d) characterised the particle morphology corresponding to the burning of biomass, along with the presence of a pizza in the oven. The main types of morphologies were similar to those found indoors (spherical forms with some adjoining). The other types of morphologies were: particles similar to fibres flat and elongated particles, entangled and others forming a greater structure with a smooth texture (Pooley and Mille 1999; Jacobson 2002; Sachdeva and Attri 2008). Also the presence of microspheres together, this conglomerate was called "a bunch of grapes" by (Pooley and Mille 1999).For the briquette related image (figure 5e) we found the largest differences in terms of morphology compared with the micrographs found in the literature (Sola et al. 2011). This difference owes itself to the substances that make up the briquette (in Brazil there is no standardisation in the production of briquettes). Although this morphology cannot be classified due to the absence of similar micrographs available in the literature, reveals a more pointed form, which represents greater harm to human health (Martins 2010).

Emission Factors and emissions estimates

Table 5 shows $PM_{2.5}$ and BC concentrations and EFs for 4-day sampling at P1, every 15 minutes. We analysed separately each day; no extra wood was added during the first hour of sampling during 10/11/2013. For the other three days, extra wood was added after the oven was lit. fig. 6 shows 15-minute averages and standard deviations for all samplings. EFs grew in the first half-hour, reduced and then surged once more due to the adding of more fuel to the oven. Because of the uncertainty in the concentration of BC on the day 10/12/2013, the value was not considered.

Table 5 Profiles of pollutant concentrations and $PM_{2.5}$ and BC emission factors for pizzeria 1 (P1)

Time (minutes)	Date	$PM_{2.5}$ ($\mu g/m^3$) x1000	BC ($\mu g/m^3$) x1000	EF $PM_{2.5}$ (g/kg)	EF BC (g/kg)
05:30-05:45 PM	**10/11/2013**	6.72	5.53	0.42	0.35
05:45 -06:00 PM	**10/11/2013**	3.12	2.40	0.26	0.20
06:00-06:15 PM	**10/11/2013**	1.45	0.98	0.17	0.12
06:15-06:30 PM	**10/11/2013**	0.79	0.47	0.17	0.10
05:30-05:45 PM	**10/12/2013**	3.87	1.45	0.21	0.80

05:45 -06:00 PM	**10/12/2013**	35.67	11.52	2.57	0.83
06:00-06:15 PM	**10/12/2013**	1.79	1.23	0.19	0.13
06:15-06:30 PM	**10/12/2013**	9.88		1.88	
05:30-05:45 PM	**10/13/2013**	3.33	4.84	0.35	0.51
05:45 -06:00 PM	**10/13/2013**	3.92	4.33	0.54	0.59
06:00-06:15 PM	**10/13/2013**	3.34	0.60	0.66	0.12
06:15-06:30 PM	**10/13/2013**	3.03	0.40	1.10	0.14
05:30-05:45 PM	**10/14/2013**	2.70	2.31	0.25	0.21
05:45 -06:00 PM	**10/14/2013**	3.82	3.56	0.46	0.43
06:00-06:15 PM	**10/14/2013**	0.77	0.68	0.13	0.12
06:15-06:30 PM	**10/14/2013**	0.25	0.14	0.08	0.05

Figure 6 shows the average EFs and error bars for $PM_{2.5}$ and BC in P1 during the sampling time. Error bars are standard deviations (n = 4, corresponding to the 4-days sampling period). In the first time interval of the sampling of 05:30-05:45 PM, the average values of EFs for $PM_{2.5}$ and BC were very close (0.3 g/kg). The adding of extra wood during the interval of 05:45 -06:00 PM increased the EFs and with average values close to $PM_{2.5}$ and BC, 0.42 ± 0.15 g/kg and 0.41 ± 0.20, respectively. In contrast, during the interval 06:00-06:15 PM, the EF decreased, probably due to the no adding of wood. In this period, the average EF for $PM_{2,5}$ and BC was 0.30 ± 0.26 g/kg and 0.13 ± 0.01, respectively (standard deviations are too small for BC) and cannot be shown in figure 6. Behavior were very different when compared to the second sampling interval, for particulate matter. In the last interval, 45-60 minutes the EFs increased again. The adding of more wood increased EFs for $PM_{2,5}$ and BC to 0.50 ± 0.63 g/kg and 0.11 ± 0.05, respectively. Comparing our results with studies which calculated the emission factors for the burning of eucalyptus fuelwood in different oven technologies under controlled conditions (Gonçalves et al. 2010; Roy and Coscadden, 2012; Calvo et al. 2014; Ozgen et al. 2014). Gonçalves et al. (2010) calculated values of EF for particulate matter between 1.12 g/kg and 2.89 g/kg. The values obtained by Calvo et al. (2014)

were higher 7.61 ± 2.46 g/kg, on the other hand, Shen et al. (2012) obtained 0.60 ± 0.58 g/kg, values close to the result obtained from this research.

After calculating the EF, it was possible to estimate the total emissions of $PM_{2.5}$ and BC coming from the pizza ovens in the city of São Paulo. The annual emissions of $PM_{2.5}$ and BC in pizzerias the city of São Paulo were estimated (Table 6). Based on the considerations raised in methodology and on the EF calculated in the previous session, the emission of $PM_{2.5}$ and BC provided by the burning of fuelwood in pizza ovens are presented. 8,000 is the number of pizzerias in the city of São Paulo and 80% (6,400) use wood as fuel in their pizza ovens. The average consumption of wood in each pizzeria is 8 m³ per month (96 m³ per year). Gentil (2008) indicated that 1m³ of wood is approximately equal to 500 kg considering 30% humidity of the wood. Therefore, 96 m³ of wood (annual consumption) corresponded to 48 t/year of wood consumed in each pizzeria in São Paulo.

Table 6 Emission factors and the annual emissions of $PM_{2.5}$ and BC

	EF (g/kg)	**Total (t/year)**
$PM_{2.5}$	0.38	116.74
BC	0.23	70.65

The amount of particulate matter emitted by pizzerias in São Paulo were 116.74 t of $PM_{2.5}$/year (319 kg/day) and 70.65 t of BC /year (194 kg/day). These emissions were not included in the official inventory of the State. In 2017, 7% of $PM_{2.5}$ emissions in the city of São Paulo were derived from the combustion of biomass but do not consider pizzerias in its inventory. If the State is considered as a whole, emissions are even more representative, making up and an important source of stationary air pollution. The emissions obtained can be compared with other studies. The studies of Bhattacharya et al. (2000) estimated the emissions of the burning biomass in some activities that cause contamination in regions of Asia, China, India and Nepal. Each country made use of

6,700 kt (China), 3,500 kt (India) and 51 kt (Nepal) of wood. The annual emissions of Total Suspended Particles (TSP) coming from the use of wood in commerce were of 50 kt, 15 kt and 0.77 kt, respectively. In India, Majumdar et al. (2013) estimated the TSP and BC in two cities, Nagpur and Raipur, arising from the burning of wood in restaurants. The consumption of wood in each city was of 8.1 t and 23 t. In Nagpur, the TSP and BC emissions were 17,039 kg/year and 333 kg/year, and in Raipur the corresponding values were 48,397 kg/year and 945 kg/year, respectively. Finally, Gianelle et al. (2013) inventoried the benzo(a)pyrene and PM_{10} in three regions of Italy. The authors concluded that in the region of Milan, in Via Pascal, the main sources of the referred two pollutants were vehicle emissions, the use of wood in fireplaces and the burning of wood in pizzerias. The total emission of PM_{10} was 850 t/year, however, they did not specify the emission just from pizzerias.

Conclusions

The practice of burning wood in pizzerias represents a potential source of air pollution especially in large urban centres like the city of São Paulo because the city has an elevated number of pizzerias and the related fuelwood consumption emits elevated quantities of particulate matter.

All the pizzerias studied here exceed the German standards of 25 $\mu g/m^3$ (seen as there are no indoor Brazilian standards) for exposure to $PM_{2.5}$ indoors (P1-111.1 $\mu g/m^3$ P2-40.9 $\mu g/m^3$ and P3-52.7 $\mu g/m^3$). High indoors concentrations are a danger to human health.

The most significant elements in terms of concentrations were potassium, chlorine, sulphur, sodium, aluminium, silicon, magnesium, calcium and iron. Concentrations of trace elements like titanium, nickel, selenium, cadmium, strontium were elevated and high concentrations of bromine 9.23 µg/m^3 stand out. Moreover, the concentrations of trace elements like chrome, manganese, nickel, selenium and mainly copper and zinc exceed the indoor values established by the OSHA.

In terms of morphology, the micrographs from the burning of fuelwood presented particles with an individual and spherical morphology, conglomerated spherical particles, flattened particles in the form of fibres and sponge-like particles that formed in layers. The micrographs from the burning of briquettes revealed in their morphology a more pointed look, which in thesis represent greater harm to the respiratory tract.

The emissions coming from the burning of fuelwood in pizzerias in the city of São Paulo were 116.75 t/year of $PM_{2.5}$ and 70.65 t/year of BC. These values give the dimension of the polluting potential that pizzerias represent the air quality of the city, and flag the necessity to think of alternative ways to produce cleaner pizzerias. It is a point of concern that the emissions occur after the sunset when the atmospheric boundary layer starts to become more stable preventing the dispersion of pollutants to high levels of the atmosphere. Moreover, the emissions of $PM_{2.5}$ and BC in pizzerias are significant and should not be excluded from air quality inventories for the city of São Paulo. Perhaps to group the food production activities, most parts of them use eucalyptus wood as a fuel, pizzerias, bakeries and restaurants, and establish a contribution from this area of activity for the emissions of pollutants.

Future work under real operating conditions, such as the one performed here, could attempt to measure other important variables such as exhaust velocity and exhaust gas temperature, furnace internal temperature, as well as other pollutants, not just particulate matter. Other chemical elements are known to be present in the particles, but are not measured by X-ray fluorescence. Other analysis techniques should be employed. In this work it was also observed that a higher chimney may have led to higher suction and lower concentrations within the pizza parlor. This could contribute to the health of employees and customers. But more studies need to be done.

Beyond this, the results presented here, collaborate with the idea that the activities on a smaller scale also harbour a potential impact on the cause of damage to the environment.

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Figures

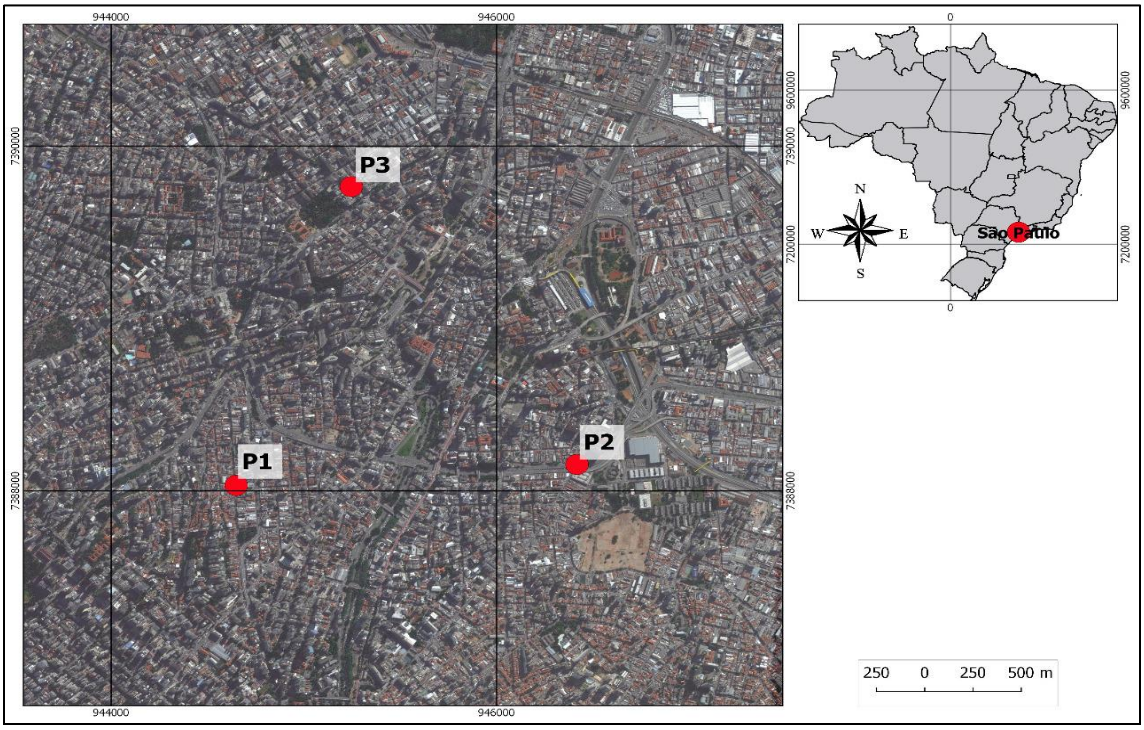
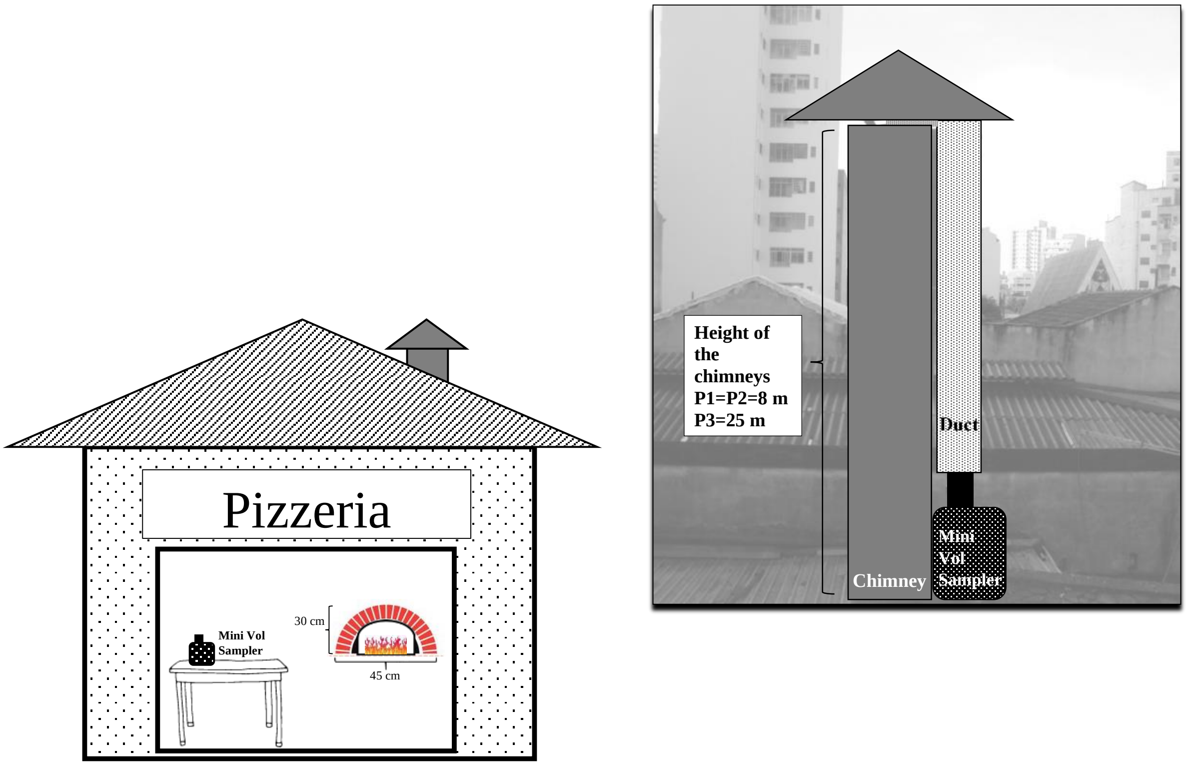


Fig.1 Brazil map highlighting São Paulo State and MASP. P1, P2 and P3 are sampling sites, respectively, pizzeria 1, pizzeria 2 and pizzeria 3.



a b

Fig. 2 Experimental study arrangement a) indoor in the pizza hall and b) chimney exhaust sampling on the roof of the pizzeria

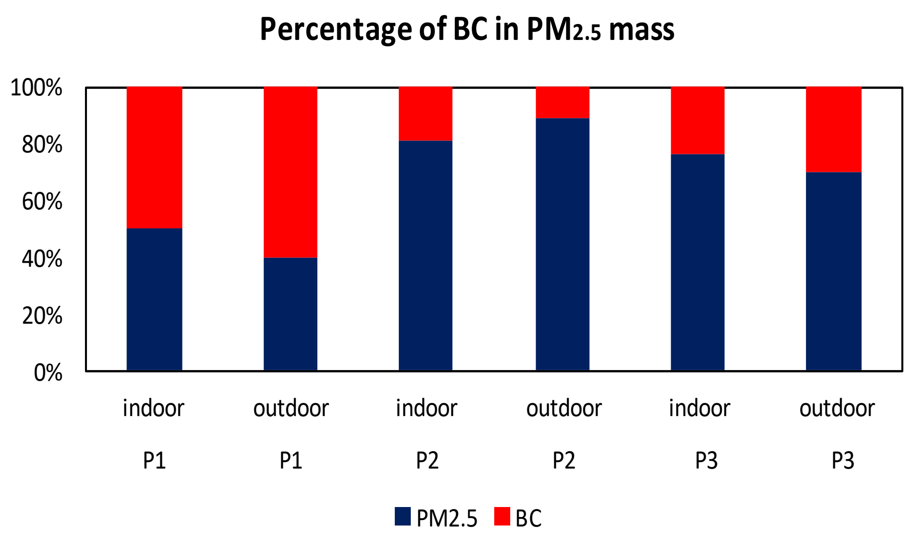
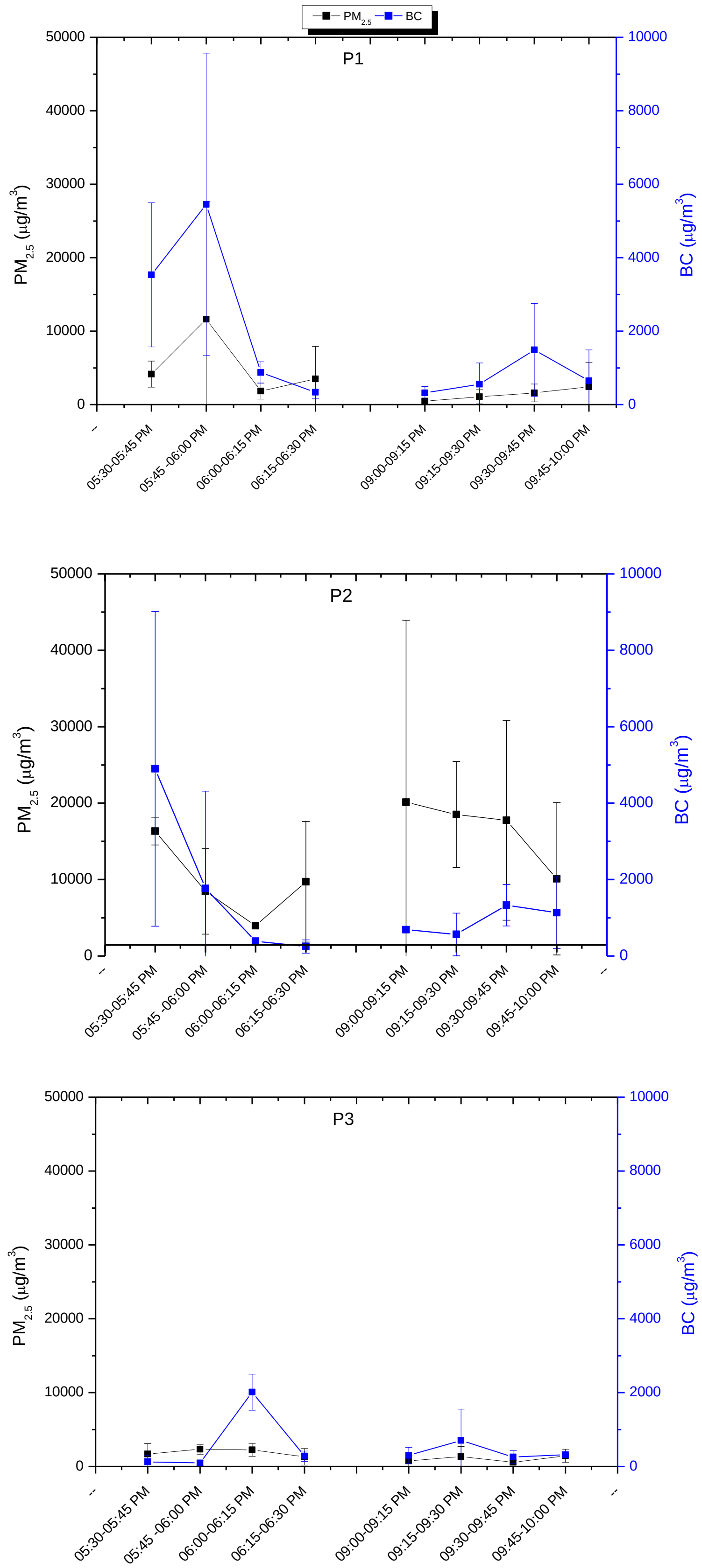


Fig. 3 Indoor and chimney exhaust percentage of BC in the mass of the $PM_{2.5}$ in the three pizzerias.



791 **Fig. 4** Average concentrations of $PM_{2.5}$ and BC of pizzeria 1 (P1), pizzeria 2 (P2) and pizzeria 3 (P3), exit
792 of chimney for each time interval of the sampling during the entire period of the campaign. Error bars
793 represents standard deviations.

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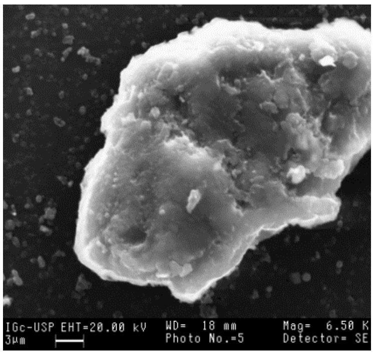
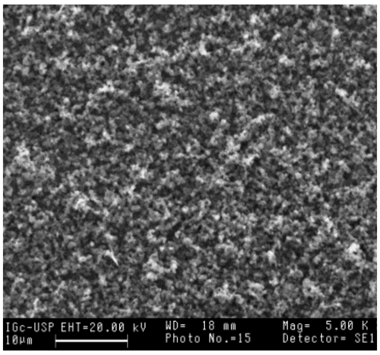


a



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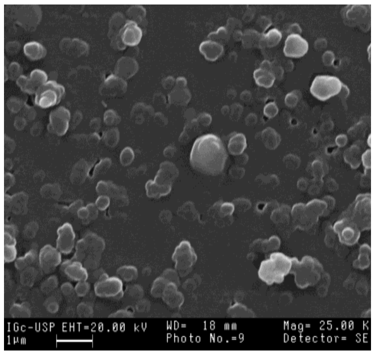
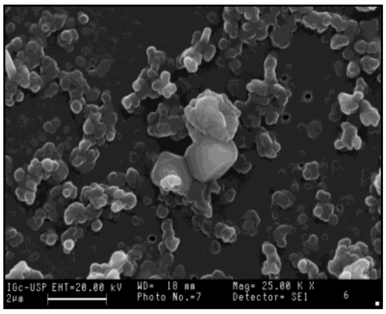


c



d

e

Fig. 5 Micrographs corresponding to the burning of fuelwood: (a) indoor, (b) outdoor, (c) wood burning (d) wood burning plus a pizza in the oven (e) briquette burning.

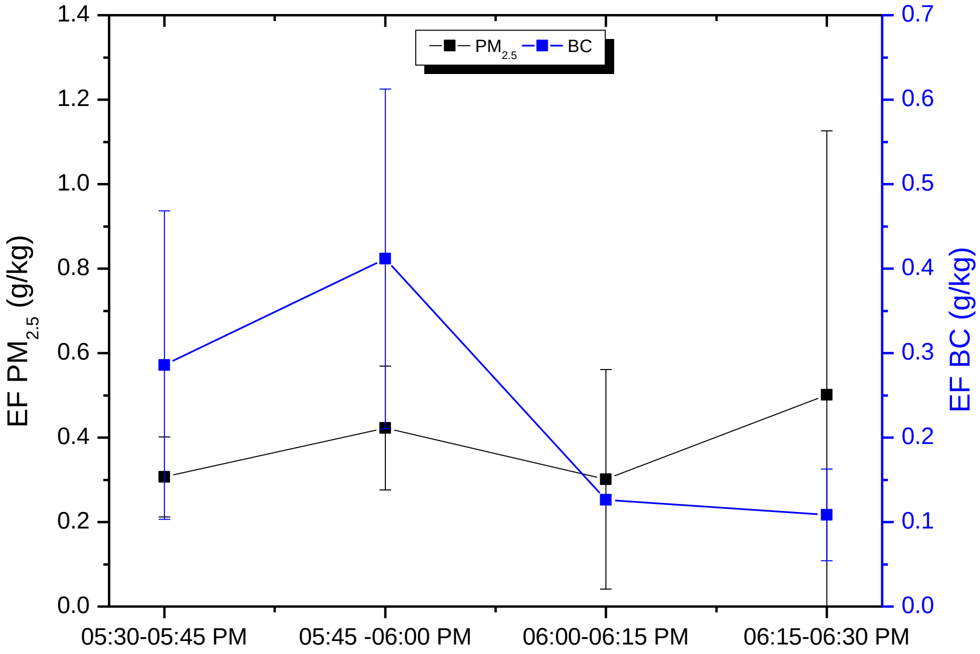


Fig. 6 Average EFs and error bars for $PM_{2.5}$ and BC in P1 during the sampling time. Error bars are standard deviations (n = 4, corresponding to the 4-days sampling period)