

Characterization, Source Apportionment and Health Risk Assessment of PM_{2.5} for a Rural Classroom in the Amazon: A Case Study

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Classrooms are microenvironments in which children and teenagers may be exposed to fine particulate matter (PM_{2.5}). Iranduba is a rural city in the Amazon region close to many brick kilns and road with high traffic levels. In this study, indoor and outdoor PM_{2.5} levels were measured in a classroom in Iranduba, and the PM_{2.5} exposure effects on student's health were calculated. High indoor PM_{2.5} concentrations and high indoor-to-outdoor ratio values indicated particle accumulation within the classroom. The high percentage of black carbon (10%) in the dry season revealed the influence of burning processes on PM_{2.5} composition. Se, S, and Pb had an enrichment factor > 5, indicating that there is an important source for these elements in the city. The positive matrix factorization (PMF) model indicated soil resuspension, burning processes and vehicular emissions as the main PM_{2.5} sources. The excess risk shows that our classroom occupants are expected to be 30% more likely to develop lung-cancer than a group exposed to a background level of PM_{2.5}. Therefore, it is important to have an effective ventilation system in order to reduce the accumulation of pollutants within the classroom and also to control/decrease the emission of pollutants in the city.

Keywords: PM_{2.5}, black carbon, trace elements, PMF, health risk assessment

Introduction

An important component of air pollution is the breathable particulate matter with an aerodynamic diameter of less than 2.5 µm (fine particulate matter, PM_{2.5}).¹ PM_{2.5} has been gaining special attention due to its negative effects on health, such as vascular diseases, allergies, asthma, and respiratory inflammations,^{2,3} which mainly affect children and the elderly. Schools are environments where children and adolescents spend most of their time,⁴ thus, the classrooms are microenvironments which are suitable for air quality studies and investigations regarding the effects of the students' exposure to airborne pollutants.⁵ It

is important to note that children are physiologically more susceptible to the negative health effects of air pollution, since they breathe a higher volume of air in relation to their body mass when compared with adults, in addition to their lungs being at a stage of incomplete development.³

Black carbon (BC) makes up a significant proportion of the urban aerosol mass and has a unique and important role in the Earth's climate system since it changes the properties of clouds, and also affects the health of a country's population, as well as the visibility in large cities.⁶ BC is usually a marker of anthropogenic pollution. This can originate mainly from combustion processes, such as the burning of diesel in vehicles or in industrial engines, solid fuels (coal and biomass), burning of fields and forest fires.⁷ Trace elements present in the PM_{2.5} when

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deposited in the environment may potentially be more available to the environment than those normally found in that environmental compartment, and thus impact the ecosystem.⁸ The concentration of elements in the particles is usually a sum of natural and anthropogenic sources.^{9,10} Due to the diversity in the sources of these trace elements, the characterization of PM_{2.5} can be a complex issue. In order to overcome this difficulty, receptor models such as the positive matrix factorization (PMF) have been used in many environmental studies.¹¹

Although many studies have analyzed a vast array of aspects relating to the atmospheric composition of the Amazon region, no studies have investigated the PM_{2.5} composition of rural school environments in the region. Since Iranduba is a rural city that is a major producer of bricks and other ceramic products in the state of Amazonas, and is close to the forest where fires and deliberate burning of land occurs for land clearing, it was chosen as the location of our study. The PM_{2.5} mass concentration, black carbon (BC) levels and trace element concentration measured inside and outside a classroom were evaluated. In addition, possible sources of PM_{2.5} in Iranduba were determined via the PMF, and health and death risks were evaluated as a result of inhalation of these particles.

Experimental

Sampling site and school characteristics

The sampling site was located in the municipality of Iranduba (40,781 inhabitants), in the state of Amazonas (Brazil), 26 km southwest from the capital (Figure 1). Although Iranduba is relatively close to the capital Manaus, it is surrounded by the Amazon forest and is bordered to the south by the Solimões River. It has peculiar characteristics to be considered a rural city such as the very small urbanized area (0.52%)¹² and just 2.9% of appropriate paved roads. Iranduba's economy is based on fish farming, livestock raising, and brick making.¹³ Köppen's climatic classification describes the region as Af (average rainfall of at least 60 mm each month).¹⁴

The Isaias Vasconcelos School (I.V.S.) (60°11'7.24" W, 3°16'59.79" S) is located in downtown in the outskirts of the city, 200 meters of the principal avenue and 12 km far from the access road (Figure 1).¹³ It provides morning and afternoon classes for students from 13 to 18 years-old and has an average of 35 students *per* class. The school is near to evident sources of air pollution, and cases of respiratory diseases among students appear to be common. The



Figure 1. (a) Location of sampling site (yellow circle) in Brazil; (b) municipality of Iranduba in zoom and its urban area; (c) location of the Isaias Vasconcelos School (I.V.S.) in the city of Iranduba.¹⁵

classrooms have polyvinyl chloride (PVC) ceilings and a burnished concrete floor, white walls, whiteboards, natural ventilation, and fans which are turned on very hot days.

PM_{2.5} sampling

PM_{2.5} aerosol samples were collected simultaneously in indoor and outdoor environments using 37 mm polycarbonate filters (Nuclepore®, Amersham, United Kingdom) and a Harvard impactor (Air Diagnostics, Harrison, ME, USA) (10 L min⁻¹). To study possible influences due to rainfall regime, sampling was conducted in two campaigns: in the two months with the highest monthly rainfall (hereinafter called wet season) (March and April) and in the driest months (hereinafter called dry season) (August and September) in 2016. The months of sampling were chosen according to the Climatological Normal of Iranduba.¹⁶ A total of 18 samples pairs (indoor and outdoor) were taken in each period. After sampling, the filters were stored on clean Petri dishes until analysis. A clean filter (called “blank filter”) was separated from every ten samples and analyzed with the same rigor and methodology used for the sampled filters. Blank filters values were used for the correction of any possible pre-existing filter contamination. At both sites the sampling equipment was installed at least 1.5 meters from ground level. At the indoor sampling point, the collector was kept away from doors and windows, and the outdoor sampling collector was placed in an open area within the school grounds. The sampling in both campaigns was conducted during the school period, with the students inside the classroom. The sampling started at the beginning of the classes in the morning (7 a.m.) and finished at the end of afternoon classes (5 p.m.); a total of 10 h of collection *per* day, from Monday to Friday, for five weeks in each season. The relevant meteorological data was acquired from an automatic monitoring station in the experimental field of the Brazilian Agricultural Research Company which

is located in Iranduba. A wind rose chart was created with the WRPlot (Lake Environment®) program.¹⁷ Northeasterly winds (78 degrees, 0.5 m s⁻¹) from the Atlantic Ocean were predominant in the wet season, whereas during the dry season southeasterly winds (143 degrees, 0.4 m s⁻¹) from the central part of Brazil were prevalent (Figure 2).¹⁸

Chemical analysis

PM_{2.5} mass concentration

PM_{2.5} mass concentration was obtained by weighing the filters, before and after sampling, on a micro-analytical balance with a resolution of 0.1 µg (Sartorius, MAS2.7S-000-DF, Göttingen, Germany). The filters were conditioned for 24 h at 20 °C (± 1 °C) and 50% ($\pm 5\%$) relative humidity before each weighing.^{19,20} The average of at least 3 measurements was used to obtain the PM_{2.5} mass concentration.

Black carbon (BC)

BC determination in PM_{2.5} was carried out using an optical transmissometer (SootScan, OT 21, Magee Scientific Company, Berkeley, USA) with an infrared beam ($\lambda = 880$ nm), for a non-destructive analysis of the filters. The attenuation measurements of the transmitted radiation of each filter (in triplicate), and the value of the absorption coefficient of the filter material were considered in order to determine the BC concentration. The absorption coefficient allows correction of interference from the absorption of radiation by the filter material.

Trace elements

Trace elements (Al, Si, Cr, Cu, Pb, Fe, Co, Ti, Mn, Se, Pt, Sn, S, Sr, Br, P, Na, Cl, K, Mg, Ca and Zn) were measured using energy dispersive X-ray fluorescence (EDXRF) (Minipal 4, PANalytical®, Malvern, United Kingdom). Both the blank and the sampled filters were

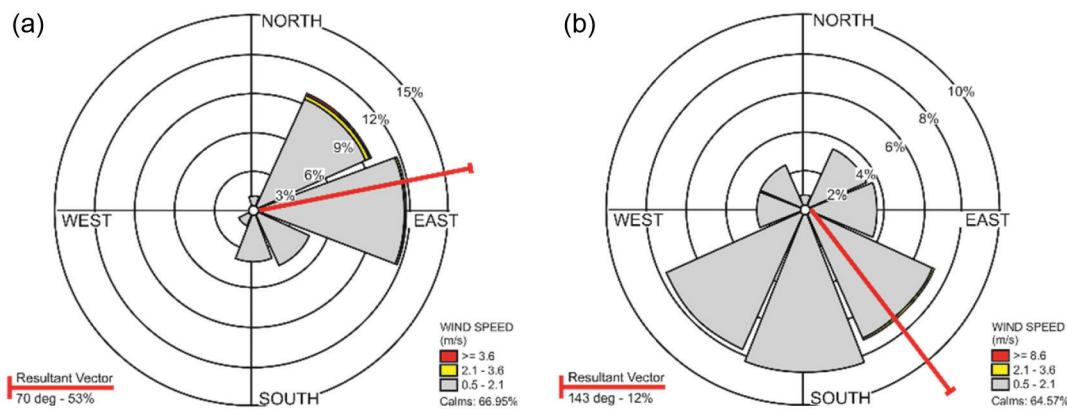


Figure 2. Wind rose charts for the wet season (a) and dry season (b).¹⁸

analyzed in triplicate. The optimum voltage and current for the X-ray source were determined based on reference-standard measurements (Micromatter, Seattle, WA, USA) and validated using a certified standard (NIST-2783 airborne particles in media). The analyzed elements were divided into 2 groups according to optimized voltage and current: (i) 30 kV voltage and 0.3 mA current for Al, Si, Cr, Cu, Pb, Fe, Co, Ti, Mn, Se, Pt, Sn, S, Sr, Br and P, and (ii) 9 kV voltage and current of 1 mA for Na, Cl, K, Mg, Ca and Zn. All measurements were performed in a helium atmosphere with a total of 10 min running time. For all elements, a calibration curve was obtained using standard filters of the same material (polycarbonate) as the sampling filter. All curves were subjected to the same analysis characteristics described previously. The limit of detection (LOD) and the limit of quantitation (LOQ) for each metal were determined.²¹ For both calculations, a mean value from 20 blank filters was obtained.

Data analysis

Statistical data analyses were processed using the Origin Pro® 9.0 program²² at a significance level of $p > 0.05$. The Shapiro-Wilk test was applied to PM_{2.5} mass concentrations, BC levels and trace elements concentration data; the results of which indicated an abnormal behavior of these variables. Thus, non-parametric tests were applied to the data group. In order to reduce data loss, values below the LOQ were replaced by half their value.²³ The Wilcoxon non-parametric test was performed in order to compare the indoor and outdoor groups and the U Test was applied to compare the wet and dry season groups.

Enrichment factor

The enrichment factor (EF) was calculated in order to evaluate the origins of the trace elements of the PM_{2.5} particles, according to the following equation:

$$EF_X = \frac{\left(\frac{C_X}{C_R} \right)_{\text{particles}}}{\left(\frac{C_X}{C_R} \right)_{\text{crustal}}} \quad (1)$$

where C_X is the concentration of the element, and C_R is the reference element concentration (Fe for this study).²⁴ The “particles” and “crustal” indices refer to the C_X and C_R values in the PM_{2.5} and in the soil, respectively. The EF indicates whether the concentration of a given element is higher than that expected from the soil.⁵ EF ≤ 1 values indicate that

soil was the main contributor to PM_{2.5} composition, while values between 1 and 5 imply that the element was derived from sources other than soil, and values above 5 suggest the predominance of anthropogenic sources.⁹

Positive matrix factorization

For source apportionment of indoor and outdoor PM_{2.5}, the U.S. EPA PMF software²⁵ was used. All pollutants determined in PM_{2.5} (PM_{2.5} mass concentrations, BC, and trace elements values) were considered in the model. Details on the application of the PMF model may be found in the literature.^{26,27} The model was set for 20 runs, and the strength of variables selection was based on the signal to noise (S/N) ratio. Variables where S/N < 5 were classified as “weak” and those with S/N > 5 as “strong”. PM_{2.5} was classified as “weak” to limit its influence on the model.²⁸ The lowest possible number of factors were chosen, to which the model parameters were adjusted (normal distribution of residues, with little difference between Q (robust) and Q (true), and a 100% convergence rate).

Health risk assessment

The non-carcinogenic health risk assessment for microenvironments (ME) was based on the US EPA²⁹ model and the model created by Chalvatzaki *et al.*,³⁰ considering the inhalation rate and the children’s bodyweight. The non-carcinogenic health risk was calculated considering the hazard quotient (HQ) using the equations below:

$$HQ = \frac{CDI (\text{mg kg}^{-1} \text{ day}^{-1})}{RFD (\text{mg kg}^{-1} \text{ day}^{-1})} \quad (2)$$

$$CDI = \frac{Ca_i \times IR \times ET_i \times EF_i \times ED_i}{AT_i \times BW} \quad (3)$$

$$RFD = RFC \times \frac{IR_d}{BW} \quad (4)$$

where CDI is the chronic daily intake and RFD is the reference dose. HQ = 1 is the maximum level for acceptable (non-carcinogenic) risk, while HQ > 1 indicates that non-carcinogenic diseases are likely. Ca_i is the contaminant concentration in ME_i (mg m⁻³), IR is the inhalation rate (m³ h⁻¹). ET_i is the exposure time in ME_i (h day⁻¹), EF_i is the exposure frequency in ME_i (days year⁻¹), ED_i is exposure duration (years), AT_i is the average time (days), and BW is the body weight (kg). The IR was calculated considering the average values for male and female children (10 and 15 years of age) for sitting and awake

activities as adopted by The International Commission on Radiological Protection (ICRP).³¹ The BW value of 43.25 kg was considered as an average value for male and female children of 10 and 15 years of age.³² The Ca_i is the trace element concentration obtained from indoor PM_{2.5} samples. For the other variables, the school's routine was considered. ET_i represents the daily sampling time (10 h), EF_i corresponds to the minimum school days stipulated by The Brazilian Ministry of Education (200 days year⁻¹), ED_i is the school's time to graduation, considering the sum of elementary and high school years (12 years) and AT_i (AT_i = ED_i multiplied by school days per year) is equal to 2400 days. RFC (mg m⁻³) is the reference concentration provided by US EPA.³³ In this study, only the trace elements (Al, Ti, Se, S, and Pb) which have the RFC values described by US EPA were considered. IR_d is the daily inhalation rate estimated using the ICRP standard.³¹

Excess risk (in percentage) for all-cause mortality (ER₁), for cardiopulmonary or lung cancer diseases (ER₂), and the attributable fraction (AF) calculations are described by the equations 5, 6 and 7, respectively. These parameters are associated with exposure to PM_{2.5} provided by Ostro:³⁴

$$ER_1 = \left\{ \exp[\beta(x - x_0)] \right\} - 1 \quad (5)$$

$$ER_2 = \left\{ \left[\frac{x+1}{x_0-1} \right]^\beta \right\} - 1 \quad (6)$$

$$AF = \frac{ER_i}{(ER_i + 1)} \quad (7)$$

where x is the annual PM_{2.5} mean concentration (μg m⁻³), ER_i is the ER₁ or the ER₂ according to the disease assessment, and β is the risk function coefficient. For ER₁, β = 0.0008 (95% confidence interval (CI): 0.0006-0.0010), and for ER₂: cardiopulmonary mortality β is equal to 0.15515 (95% CI: 0.0562-0.2541) and lung-cancer mortality β corresponds to 0.23218 (95% CI: 0.08563-0.37873). The excess risk estimates the probability of negative health effects on individuals or a population exposed to a PM_{2.5} level higher than the background value (x₀) (3 μg m⁻³). The AF assessments estimate the quantity of deaths that could be avoided as a result of PM_{2.5} concentration reduction to the background level.³⁰

Results and Discussion

PM_{2.5} concentration

The daily levels, average concentrations, standard deviation and other descriptive statistics of indoor and

outdoor PM_{2.5}, measured in the wet and dry seasons in Iranduba are presented in Table 1 and Figure 3. All the values were within the Conselho Nacional do Meio Ambiente (CONAMA, 60 μg m⁻³ over 24 h)³⁵ guideline, as well as less than the World Health Organization (WHO, 25 μg m⁻³ over 24 h)³⁶ guidelines. Indoor PM_{2.5} concentrations during the wet season ranged between 3.6 and 15.2 μg m⁻³, with an average of 9.2 ± 3.3 μg m⁻³, while in the dry season the levels were slightly higher, varying from 8.3 to 25.0 μg m⁻³ and with an average of 14.0 ± 4.6 μg m⁻³. The U Test confirmed that the concentration of indoor PM_{2.5} was significantly different (*p* < 0.05) between the two seasons. This difference may be due to a number of factors, such as changes in wind direction (Figure 2b), since the southeasterly winds may have brought particles from biomass burning from the areas of agricultural production,³⁷ an increase in the frequency of forest fires and the low levels of rainfall, which are all typical of the dry season.

Levels of indoor PM_{2.5} in both seasons were lower when compared with those found inside a rural elementary school (16.18 ± 12.72 μg m⁻³) and a suburban school (17.30 ± 14.23 μg m⁻³) located in Athens, Ohio,³⁸ as well as the values reported for 39 elementary schools in the metropolitan area of Barcelona, Spain (7-105 μg m⁻³).⁸ In contrast, the average concentration of indoor PM_{2.5} in the school in Iranduba during the dry season was 32% higher than the values reported for a public elementary school influenced by vehicular exhausted emissions in Quito (Ecuador),³⁹ and also 205.7% greater than the PM_{2.5} measured for classrooms at a university near avenues with heavy traffic in downtown Fortaleza (Brazil).⁴⁰

The average concentration of outdoor PM_{2.5} concentration was half the indoor PM_{2.5}, with an average of 4.7 ± 2.9 μg m⁻³ (1.8-13.6 μg m⁻³) during the wet season and 6.7 ± 3.3 μg m⁻³ (2.0-13.8 μg m⁻³) in the dry season. These values were 47 and 43% lower than outdoor PM_{2.5} concentrations recorded in Manaus in both seasons (8.8 and 11.6 μg m⁻³ in the wet and dry seasons, respectively).⁴¹

The indoor-to-outdoor ratio (I/O) expresses the relationship between indoor and outdoor concentrations. I/O ≤ 1 indicate the contribution of external sources, while I/O > 1 indicate the influence of internal sources and/or particle accumulation inside the classroom.⁹ Results showed the I/O > 1 (Figure 4) for both seasons. The indoor sources of PM_{2.5} could be related to the material used in the manufacture of the classroom furniture, opening and closing of doors and windows, which causes the transfer of outdoor particle into the classroom, the use of brooms, fans, and the occupants' activities that can cause the resuspension of particle already deposited.^{23,42} Therefore, I/O > 1 expresses a need for improvements in classroom

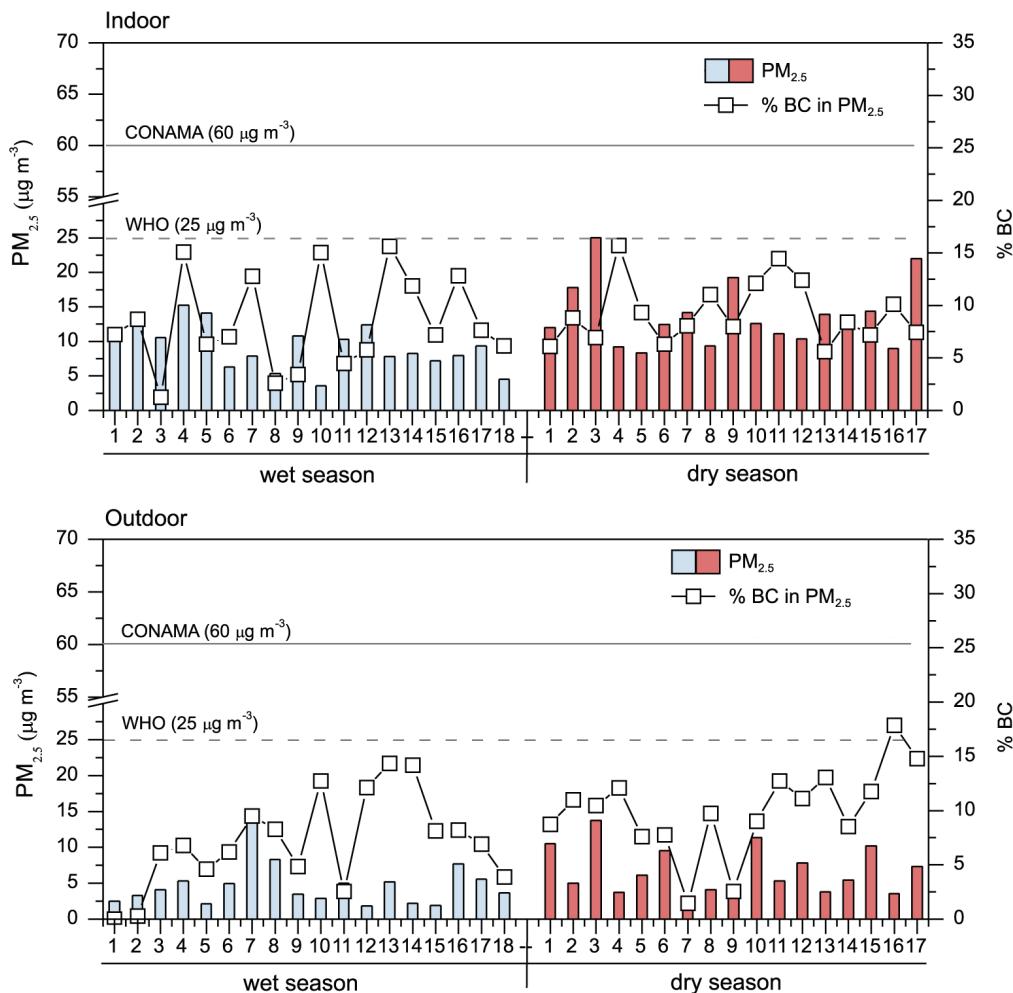


Figure 3. Indoor and outdoor PM_{2.5} daily levels and percentage of BC in PM_{2.5} in both seasons. The solid and dashed line indicate respectively the CONAMA and WHO guideline, both over 24 h.

Table 1. Statistics of indoor and outdoor PM_{2.5} samples in Iranduba and their components

	Indoor						Outdoor					
	w.s.			d.s.			w.s.			d.s.		
	Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max	Avg ± SD	Min	Max
PM _{2.5} / (µg m⁻³)	9.2 ± 3.3	3.6	15.2	14.0 ± 4.6	8.3	25.0	4.7 ± 2.9	1.8	13.6	6.7 ± 3.3	2.0	13.8
BC / (µg m⁻³)	0.8 ± 0.5	0.1	2.3	1.3 ± 0.4	0.7	1.9	0.4 ± 0.3	0.01	1.3	0.7 ± 0.4	0.08	1.4
BC in PM _{2.5} / %	8.4 ± 4.5	1.2	15.6	9.4 ± 2.9	5.6	15.7	7.6 ± 4.0	0.3	14.4	10.0 ± 3.9	1.4	17.9
Al / (ng m⁻³)	488.4 ± 393.7	45.9	1382.1	n.d.	—	—	68.9 ± 106.4	6.4	452.4	n.d.	—	—
Si / (ng m⁻³)	716.3 ± 492.7	135.5	1781.3	n.d.	—	—	188.8 ± 191.6	27.7	892.7	n.d.	—	—
Fe / (ng m⁻³)	426.6 ± 259.2	78.9	967.6	446.3 ± 208.5	205.7	992.3	105.7 ± 91.1	33.5	419.8	93.6 ± 55.5	34.5	241.2
Ti / (ng m⁻³)	65.4 ± 41.4	10.6	155.0	69.0 ± 33.6	26.3	161.4	10.8 ± 12.5	1.5	54.3	10.2 ± 7.7	1.5	29.8
Se / (ng m⁻³)	10.7 ± 5.4	n.d.	22.5	6.0 ± 3.8	n.d.	15.7	3.7 ± 3.6	n.d.	13.3	1.9 ± 2.1	n.d.	6.0
S / (ng m⁻³)	128.9 ± 79.9	n.d.	278.1	233.0 ± 130.1	47.0	528.4	102.6 ± 62.6	n.d.	246.5	108.4 ± 100.0	8.4	333.1
Mg / (ng m⁻³)	114.7 ± 85.2	n.d.	352.9	306.5 ± 275.1	115.6	1135.8	117.9 ± 72.0	n.d.	285.1	257.1 ± 273.6	62.6	988.9
Ca / (ng m⁻³)	156.6 ± 123.8	n.d.	439.2	201.6 ± 107.4	62.2	422.7	20.3 ± 9.4	n.d.	18.7	21.2 ± 14.3	n.d.	45.2
K / (ng m⁻³)	n.d.	—	—	171.9 ± 122.4	5.7	434.9	n.d.	—	—	54.2 ± 65.2	n.d.	239.7
Pb / (ng m⁻³)	n.d.	—	—	7.6 ± 10.4	n.d.	36.1	n.d.	—	—	6.7 ± 10.5	n.d.	35.1

w.s.: wet season; d.s.: dry season; Avg: average; SD: standard deviation; Min: minimum; Max: maximum; PM_{2.5}: fine particulate matter; BC: black carbon; n.d.: not detectable.

ventilation using mechanical ventilation, in order to reduce accumulation of pollutants in this environment. A ventilation system equipped with filters capable of retaining particles can decrease the I/O ratio by up to 65% compared to natural ventilation.^{43,44}

It is important to remember that good indoor air quality in the school environments reflects in the occupants' health, as well as in the students' learning and, as a result, their academic performance.⁴⁵

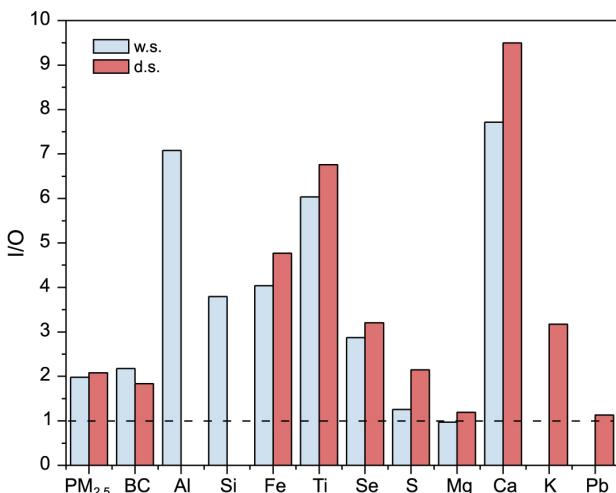


Figure 4. Indoor-to-outdoor ratio (I/O) of PM_{2.5}, BC, and trace elements for wet season (w.s.) and dry season (d.s.).

BC concentration

Indoor BC results indicated that the concentration values were $0.8 \pm 0.5 \mu\text{g m}^{-3}$ ($0.1\text{-}2.3 \mu\text{g m}^{-3}$) in the wet season and $1.3 \pm 0.4 \mu\text{g m}^{-3}$ ($0.7\text{-}1.9 \mu\text{g m}^{-3}$) in the dry season. For BC levels outside the classroom, values of $0.4 \pm 0.3 \mu\text{g m}^{-3}$ ($0.01\text{-}1.3 \mu\text{g m}^{-3}$) and $0.7 \pm 0.4 \mu\text{g m}^{-3}$ ($0.08\text{-}1.4 \mu\text{g m}^{-3}$) were obtained in the wet and dry seasons, respectively (Table 1). The U Test and the Wilcoxon Test showed that BC concentrations were significantly different, both spatially and seasonally ($p < 0.05$). In addition, the I/O ratio (Figure 4) was > 1 for both seasons (2.1 and 1.8 in wet and dry season). BC is usually associated with the incomplete fossil or non-fossil (vegetation) carbon-based fuel burning.⁷ This high I/O value indicates poor ventilation and accumulation of this pollutant inside the classroom, since there were no indoor sources of BC.

BC had significant Spearman correlation with outdoor PM_{2.5} both in the wet (0.68 , p -value: 2.5×10^{-3}) and dry seasons (0.86 , p -value: 1.0×10^{-2}), which represents a possible common source. Figure 3 indicates the BC mass percentage contribution to PM_{2.5} (percentage of BC). There are no significant differences between indoor and outdoor percentage of BC in PM_{2.5}. However, seasonally, there

is a statistical difference between the values of outdoor percentage of BC in PM_{2.5} for the wet and dry season (with the highest values in the dry season) (Table 1), probably due to the accumulation of this pollutant caused by the decrease in rainfall, the increase in BC emissions and the low BC reactivity⁴⁶ indicating that outdoor PM_{2.5} in the dry season was more persistent in the atmosphere.

The percentage of BC in outdoor PM_{2.5} measured in Iranduba (10%) was lower than the percentage of BC measured in Manaus in 2014 (21%)⁴¹ at a site located near an avenue with heavy traffic. In contrast, this value was higher than the percentage of BC in outdoor PM_{2.5} observed in Tangará da Serra (5%), a rural city in Mato Grosso state (Brazil), which was influenced by biomass burning. The authors of this study reported a negative association between exposure to BC and reduction in the peak expiratory flow (PEF) in children.⁴⁶ Therefore, although Iranduba is a rural city in a tropical region, the significant percentage of BC indicates that children and teachers attending the I.V.S., as well as residents of the surrounding area, were possibly subject to a greater risk of major pulmonary and cardiovascular diseases caused by long-term exposure to PM_{2.5}. Thus, caution should be taken when discussing PM_{2.5} in the atmosphere, as discussions based only on the mass value of PM_{2.5} are not complete and the particle's composition must also be taken into account.⁸

Trace elements

To investigate the outdoor environment's influence on the indoor environment, only samples with the same elements in both the indoor and outdoor PM_{2.5} pair were considered for analysis. The results of average concentrations and other descriptive statistics only of trace elements detected above the limit of quantification (LOQ) are presented in Table 1. Earth-crust elements such as Si, Al, and Fe were the most abundant in the indoor PM_{2.5} during the wet season, contributing, respectively, to 34, 23 and 20% of the total mass of the trace elements. During the dry season, the most abundant trace elements were Fe (31%), Mg (21%) and S (16%). In the outdoor PM_{2.5}, during the wet season, the most abundant elements were Si (31%), Mg (19%), and Fe (17%). And, during the dry season, the elements with the greatest contribution to the total mass of the trace elements in the outdoor PM_{2.5} were Mg (46%), S (20%), and Fe (17%).

Both in indoor and outdoor PM_{2.5}, most elements presented higher concentrations in the dry season compared to the wet season. The low levels of rainfall were possibly the main contributor to increase in the PM_{2.5}'s suspension

time in the atmosphere. Another reason may be the higher frequency of opening of windows and doors due to rises in the temperatures, which would increase the infiltration rate as a result of the thermal gradient formed and causes the wind to flow into the classroom.⁴⁷ Some element concentrations inside the classroom in Iranduba were greater than those found in other school environments. Al, Si, and Fe concentrations in Iranduba were twice as high as those described at an elementary school in the city of Curitiba (Brazil).⁴⁸ K and Ti levels in the dry season were 16 and 78% higher than concentrations in classrooms in Wroclaw (Poland).⁴⁹

Pb and Se concentrations in outdoor PM_{2.5} were 19 to 27% and 69 to 83% higher than the values measured in three other cities with different characteristics (industrial and coastal, urban/traffic and rural) located in the Nord-Pas-de-Calais region (France).⁵⁰ Dry season Se concentrations in outdoor PM_{2.5} were four times higher than the values reported in Tehran (Iran) (0.3 ng m⁻³), in a region influenced by intense daily vehicular traffic.⁹ Although Pb and Se in Iranduba had the lowest concentrations compared to other elements, these values were significant and could be harmful. The elements' I/O ratios were all > 1, except for Mg in the wet season (Figure 4). Indoor sources of Pb, for example, could be the use of lead-based paint on the walls, desk and chairs.¹¹ For the other elements, no clear indoor sources were identified in the classroom. Therefore, these I/O > 1 values demonstrated once again accumulation of the pollutants, the influence of the occupant's activities, pollutant infiltration from outside and the transport of these elements into the classroom via students' and teachers' shoes, hair, and clothing.^{11,51}

Source analysis

Enrichment factor and Spearman correlation

Figure 5 shows the EF and the temporal and seasonal concentrations for all trace elements. Despite their high concentration values, Al, Si and Ca presented EF < 1, indicating Earth-crust as the only source. S, Pb, and Se showed significant EF values in both seasons, indicating a strong influence of anthropogenic sources. Although Se had the lowest concentration, it also presented the highest EF value, both in the wet (29,887 and 40,298.4 for indoor and outdoor PM_{2.5}, respectively) and dry seasons (13,957 and 19,823.4 for indoor and outdoor PM_{2.5}, respectively). Se presented a moderate correlation with S (0.56, *p*-value: 1.6×10^{-2}) and Mg (0.54, *p*-value: 2.2×10^{-4}) in the dry season, indicating a possible common sources (burning of diesel, brick kilns, wear of vehicle parts).^{8,52} As there was no seasonal distinction between EF values for Se, its sources for indoor and outdoor PM_{2.5} in Iranduba were probably active and continuous throughout the year, impacting the region's atmosphere.

EF values for K inside the classroom indicate prevalence of Earth-crust source. However, the K values had a high Spearman correlation with the Mg (0.75, *p*-value: 3.2×10^{-4}) measured in outdoor PM_{2.5} during the dry season. Both K and Mg values also had a high Spearman correlation with outdoor BC during this season (0.86, *p*-value: 1.7×10^{-4} , and 0.74, *p*-value: 1.2×10^{-4} , respectively). Together, these high correlations indicate a possible influence of biomass burning on PM_{2.5} composition, considering that Mg is the coordinating metal for chlorophyll and K is a recognized marker of biomass burning.^{47,53} In addition to biomass burning, Mg

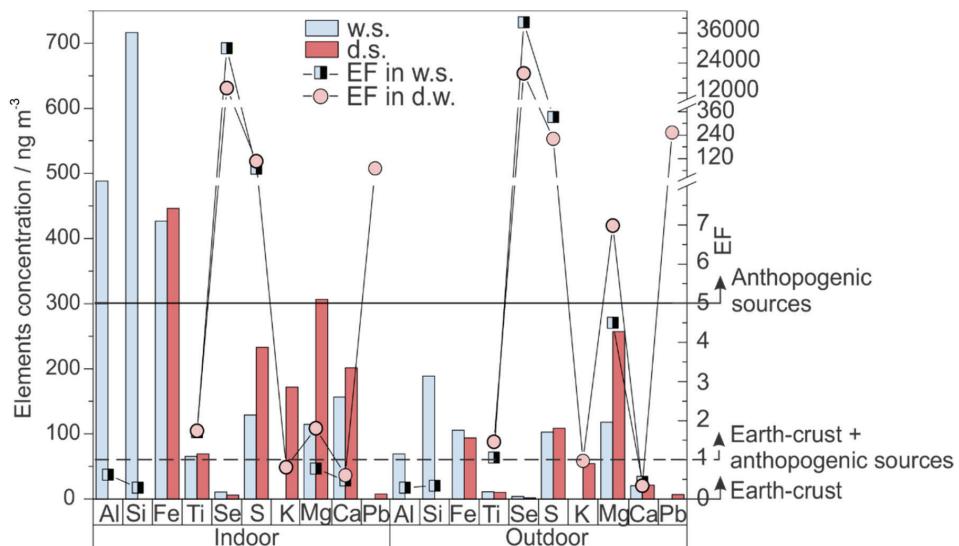


Figure 5. Average trace element concentrations (ng m⁻³) and their enrichment factor (EF) in indoor and outdoor PM_{2.5} during the wet season (w.s.) and the dry season (d.s.).

in urban areas could also be derived from automobile exhaust emissions due to its use as an additive in diesel and engine lubricating oils.^{8,52} Mg concentration in outdoor PM_{2.5} during the dry season ($257.1 \pm 273.6 \text{ ng m}^{-3}$) was higher than that observed in Manaus (132.0 ng m^{-3}),⁴⁰ and the outdoor Mg had a high Spearman correlation with S (0.90, *p*-value: 1.2×10^{-2}), which is usually derived from the primary emission of sulfur dioxide (SO₂) by fossil-fuel burning. Therefore, these results reinforce the possible predominance of the burning process as being a contributing factor to PM_{2.5} emissions in Iranduba, such as the burning of diesel in trucks that are principally used as a means of transporting the bricks produced in the city.³⁸

Positive matrix factorization (PMF)

Since PMF results were similar at both sites, both will be discussed together (Figure 6). In the wet and dry seasons, four and five main factors/sources of PM_{2.5} were identified, respectively. The interpretation of the factors was based on the greatest contribution of markers indicated in the literature, since chemical pollutants determined in particulate matter are usually emitted by specific sources.⁵⁴ For the wet season, the first factor represents soil resuspension, which explained 33% of PM_{2.5} composition, followed by burning processes as the second factor with 31.4%. The third factor was influenced by urban dust resuspension (UDR) (21.3%) and the last one by fossil-fuel combustion (14.3%). For the dry season, the first factor was vehicular emission (27.8%), followed by biomass burning (19.8%), burning processes (19.2%), UDR (16.7%) and fossil-fuel combustion (16.4%).

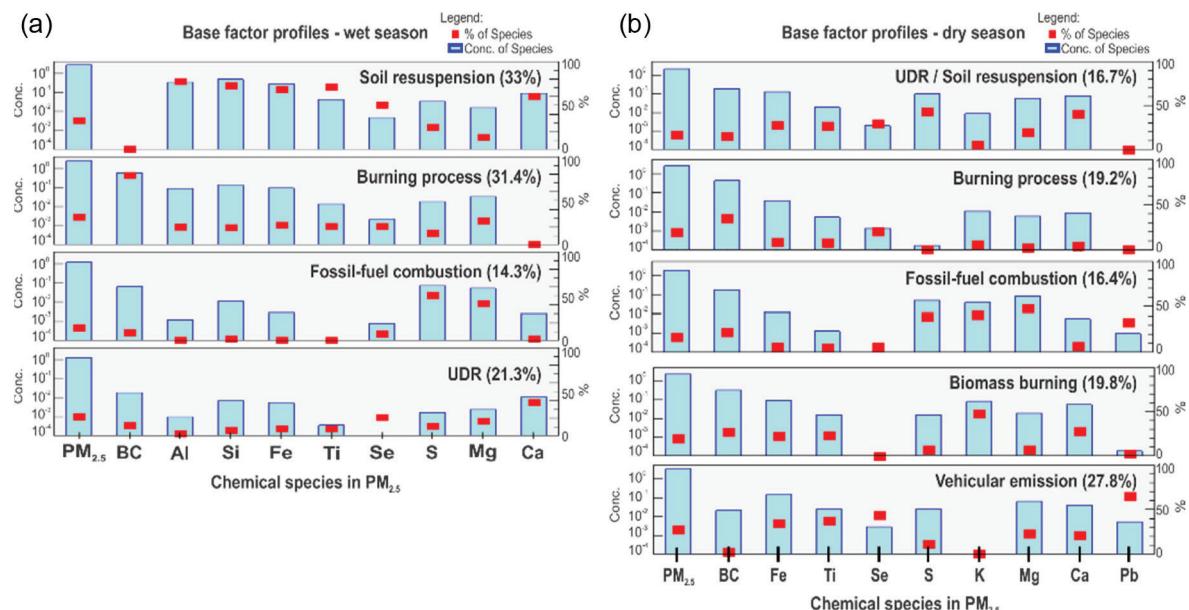


Figure 6. Base factor profiles of chemical species in PM_{2.5} during (a) the wet season and (b) the dry season, where UDR is an acronym for urban dust resuspension.

The soil resuspension factor was characterized by significant contributions of Al, Si, Fe, Ti, and Ca, which are largely associated with natural emission of soil resuspension.^{27,53} The EF values (Figure 5) for these elements confirmed soil resuspension was the major source. Only Ti had EF > 1, which indicates anthropogenic sources, in addition to the natural origin. For the UDR factor, Ca, Se, Mg, Si, Fe, S, and BC contributions were observed. Most of these elements are naturally emitted from the soil (Ca, Se, Mg, Si, and Fe).^{9,28} However, Se, Fe, S, and BC could also originate from accumulated road-particulate matter resuspension due to wear of vehicle parts, traffic, or industrial emissions.^{9,55,56} In the dry season, there was no clear distinction between soil resuspension and the UDR factor, when compared to the wet season.

Both vehicular emission (Fe, Ti, Se, and Pb) and fossil-fuel combustion (S, Mg, Se, K, Pb, and BC) factors usually originate from traffic-related primary emissions. However, vehicular emissions can also derive from non-exhaust emissions including many sources, except tailpipe exhaust emissions.⁵⁷ The main sources are brake and tire wear, wear of the clutch and other vehicle components, and asphalt particle suspension.⁵⁶ In this study, Se and Pb played a major role in contributing to the vehicle emission factor and presented high EF values (Figure 5), thus indicating a predominance of anthropogenic sources. Both are usually related to brake pad wear,^{28,54,57} tire and household waste incineration (common practices in Iranduba and surrounding cities),^{49,58} and from road dust resuspension in industrial regions.⁵⁹ This should be of concern since Se inhalation causes harmful effects, such

as damage to the lungs and cardiovascular system.⁵⁸ Pb can be absorbed by the human body through breathing, food, soil or water contamination. All of which cause damage to the central nervous system.⁶⁰ Therefore, in the dry season, the population of Iranduba was more susceptible to the negative health effects of Se and Pb, since vehicular emission was the main source contributing to the composition of PM_{2.5} in this period. The fossil-fuel combustion factor represents tailpipe exhaust emissions. For this factor, S and Mg showed the highest contributions, followed by K, Pb and BC. These components have been described as markers of fossil-fuel combustion additive in diesel (S, Mg, and Se)^{38,61} and motor oil combustion (BC, Pb).^{49,54}

The biomass burning factor was only identified in the dry season. This was due to the high contribution of K, a marker of biomass burning.^{38,61} The burning process factor was observed, in both the wet and dry seasons, represented by the high relative BC contribution to this factor, especially during the wet season. BC originates from incomplete combustion processes of carbon-based fuels.⁶² Apart from BC, there were no other clear markers with significant values that could clarify the main activity influencing this factor, possibly originating from a mixture of processes involving combustion. This PMF factor showed that there were strong PM_{2.5} sources of BC in Iranduba which also release Earth-crust elements (brick kilns being one of the possible sources due to the use of clay in the production of bricks)^{63,64} and elements of anthropogenic activities.

Human health risks assessment

The hazard quotient (HQ) and hazard index (HI) were obtained for the sum of indoor PM_{2.5} concentrations

measured in both the wet and dry seasons. The health risks were calculated only for inhalation exposure. The highest HQ values were obtained for Ti (0.27) and Pb (0.26). However, the HQ for each element and the HI were all below the limit value of 1, indicating there was no significant risk from inhalation of these trace elements.²⁹ Chalvatzaki *et al.*³⁰ calculated the HQ for children in a metropolitan area of Athens (Greece) and reported a lower Pb HQ value (2.31×10^{-2}) when compared to Iranduba.

The results of hazard quotient (HQ) and hazard index (HI) (sum of all elements) values for non-carcinogenic health risks, and the excess risk (ER) and the attributable fractions (AF) for all-cause mortality for PM_{2.5} samples are presented in Table 2.

Excess risk (ER) and attributable factor (AF) for all-cause, cardiopulmonary and lung-cancer mortality were also calculated for the indoor and outdoor PM_{2.5} (Table 2). The ER percentages for indoor (outdoor) PM_{2.5} were estimated as 0.69% (0.21%), 19% (8.3%) and 30% (13%) for all-cause, cardiopulmonary and lung-cancer mortality, respectively. The ER values for cardiopulmonary and lung-cancer mortality in indoor PM_{2.5} in Iranduba were higher than the ER reported in Kuopio (Finland) (9.5 and 15% for cardiopulmonary and lung-cancer mortality, respectively).³⁰ Nevertheless, both the indoor and outdoor PM_{2.5} samples presented significant ER values, meaning that the population of Iranduba was more liable to develop diseases than individuals exposed to a background PM_{2.5} concentrations ($3 \mu\text{g m}^{-3}$). The AF for indoor (outdoor) PM_{2.5} was 0.68% (0.21%), 16% (7.6%) and 23% (11%) for all-cause, cardiopulmonary and lung-cancer mortality, respectively. Therefore, the reduction in PM_{2.5} accumulation inside the classroom is critical to prevent probable deaths, mainly related to lung-cancer.

Table 2. Hazard quotient (HQ) and hazard index (HI) of trace elements measured in indoor PM_{2.5}, percentage of excess risks (ER), and attributable fractions (AF) of indoor and outdoor PM_{2.5}

Trace element	HQ	HRA for PM _{2.5}				
		Indoor		Outdoor		
		All-cause mortality				
Al	4.07×10^{-2}	ER (95% CI) / %	0.69	(0.52-0.86)	0.21	
		AF (95% CI) / %	0.68	(0.51-0.85)	(0.16-0.27)	
Ti	2.73×10^{-1}	Cardiopulmonary mortality				
Se	1.74×10^{-4}	ER (95% CI) / %	19	(6.7-33.8)	8.3	
		AF (95% CI) / %	16	(6.2-25.3)	(2.9-13.9)	
Pb	2.63×10^{-1}	Lung cancer mortality				
S	7.54×10^{-2}	ER (95% CI) / %	30	(10-54)	7.6	
		AF (95% CI) / %	23	(9.3-35.2)	(2.8-12.2)	
$\Sigma \text{HQ} = \text{HI}$		ER (95% CI) / %				
6.52×10^{-1}		30	(10-54)	13	(4.5-21.4)	
		AF (95% CI) / %	23	(9.3-35.2)	11	
HRA: human health assessment; CI: confidence interval.						

Conclusions

In this study, the indoor and outdoor PM_{2.5} levels were analyzed in a classroom in Iranduba, a rural city in the Amazon region. Results showed the influence of outdoor sources on the composition of indoor PM_{2.5}. In addition, internal sources, such as the cleaning process, footwear, and poor ventilation, contributed to PM_{2.5}, BC, and trace element accumulation, leading to higher concentrations inside the classroom in both the wet and the dry seasons. Earth-crust elements were the most abundant in the wet season, while in the dry season traffic-related elements were the greatest. S, Pb, and Se presented high EF values in both seasons, indicating the influence of important anthropogenic sources for these elements in Iranduba throughout the year.

PMF indicated that soil resuspension, burning processes, and vehicular emissions were the key contributing sources in the composition of PM_{2.5}. Indoor PM_{2.5} levels were detrimental to the health, with significant risk values for cardiopulmonary and lung-cancer mortality. These indicate that the occupants of the classrooms in Iranduba were more susceptible to develop these diseases when compared to students exposed to a background PM concentration. The results of this study reveal the importance of indoor PM_{2.5} measurement in order to evaluate health risks to the students even in small and rural cities such as Iranduba. Although the school selected for this study has natural ventilation, the airflow through the windows was inefficient in removing pollutants and may have contributed to increased indoor PM_{2.5} concentrations.

The poor air quality in classrooms will affect not only the students' ability to learn and school attendance, but also their health and that of other classroom occupants such as teachers and school staff. This study also reveals the need to improve environmental policies on air pollution, both in outdoor and indoor environments, especially in school environment, which establish new and lower maximum levels of pollutants to reduce indoor air pollution.

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Author Contributions

Karenn S. Fernandes was responsible for writing of original draft, data curation, formal analysis; Erickson O. dos Santos for data curation, writing review and editing; Ricardo H. M. Godoi for methodology, resources, writing review and editing; Carlos I. Yamamoto for resources; Cybelli G. G. Barbosa for methodology, investigation, writing review and editing; Rodrigo A. F. Souza for methodology, resources, writing review and editing; Cristine M. D. Machado for conceptualization, writing review and editing, supervision, project administration.

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