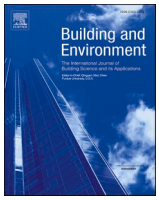
Building and Environment 265 (2024) 111949

Contents lists available at ScienceDirect

Building and Environment

journal homepage: www.elsevier.com/locate/buildenv



Seasonal variations of size-classified aerosol-bound elements in school environments and risk factors for the prevalence of atopic diseases among pupils

Isabella Charres [a,*], Franco Lucarelli [b], Manuel Feliciano [c,d], Leonardo Furst [a], Célia Alves [a]

[a] Department of Environment and Planning, Centre for Environmental and Marine Studies (CESAM), University of Aveiro, 3810-193, Aveiro, Portugal
[b] INFN - Firenze, National Institute for Nuclear Physics - Florence Division, 50019, Sesto Fiorentino, Italy
[c] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253, Bragança, Portugal
[d] Laboratório Associado para a Sustentabilidade e Tecnologia Em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, 5300-253, Bragança, Portugal

ARTICLE INFO

Keywords:
Particle size distributions
Elemental concentrations
Schoolchildren
ISAAC
Asthma and rhinitis

ABSTRACT

Five-stage Sioutas impactors were used to collect particulate matter (PM) in 4 classrooms and the playground of a school with various educational levels near the largest industrial chemical complex in Portugal. Monitoring was carried out over a total period of 8 weeks split equally between winter and spring. Samples were analysed for its elemental composition by PIXE. The prevalence of respiratory symptoms in schoolchildren was assessed by applying the International Study of Asthma and Allergies in Childhood (ISAAC) standardised questionnaire. The mass concentration of quasi-ultrafine particles ($PM_{0.25}$) was higher in winter, but lower than those reported in other studies. Elements accounted for 15.3–17.3 % and 25.6–34.1 % of the total PM_{10} mass in winter and spring, respectively. Elements such as K, S, Zn, Cu and Br presented a dominant mode in $PM_{0.25}$, while Al, Mg, Ca, Fe and Si peaked at 2.5 μm. Throughout the campaign, Cl was the main component of the mass of PM greater than 0.5 μm in the schoolyard, while in classrooms Ca constituted the most abundant element of $PM_{2.5\text{-}10}$. The results indicate that soil dust, cleaning products, biomass burning, traffic, the chemical complex and railway affected PM levels at the school. Taking paracetamol and living near roads with intense traffic of heavy vehicles were found to be statistically significant predictors of asthma symptoms, while the frequent consumption of antibiotics and children exposure to parental smoking during the first year of their life were found to increase the odds of developing symptoms of rhinitis.

1. Introduction

Industrial areas are often considered major sources of environmental pollution as they release numerous pollutants such as particulate matter (PM) and gases. Studies carried out to identify the concentrations, size distributions, chemical composition and temporal characteristics of PM have reported that atmospheric emissions from industrial activities may contain iron, carbon and smaller elements such as lead, aluminium, zinc, manganese, chromium, cadmium, copper, nickel, titanium, vanadium and other trace metals [1–4]. Liu et al. [5] documented that changes in industrial pollutant concentrations influenced childhood asthma development rates in small towns. The authors argued that sources and the composition of particles lower than 2.5 μm ($PM_{2.5}$) may influence health risks differently. In fact, the association between asthma and $PM_{2.5}$ emitted by metal smelters was higher compared to that found for the pulp and paper mill sector. In another study carried out in a region in the Netherlands with a high concentration of industries and low traffic density, exposure to air pollution was associated with adverse birth outcomes between 2012 and 2017 [6].

Several studies have shown that particle-induced health effects depend on their size and chemical composition, affecting different age groups unevenly [7,8]. The size distribution and density of particles define the site of deposition in the respiratory tract, while physiological and anatomical parameters affect the deposition profile [9]. In addition, the elemental composition, although representing a small percentage of the total mass of PM, may be a cause of concern due to its toxic properties [10]. In a study involving the use of A549 lung adenocarcinoma cells exposed to high concentrations of $PM_{2.5}$ it was concluded that lung

* Corresponding author.
E-mail address: isabellacharres@ua.pt (I. Charres).

https://doi.org/10.1016/j.buildenv.2024.111949
Received 10 June 2024; Received in revised form 9 August 2024; Accepted 10 August 2024
Available online 12 August 2024

cancer patients from polluted urban areas can develop more aggressive tumour phenotypes, with enhanced cell proliferation, migration, and chemoresistance [11]. It has also been documented that PM-bound metals are involved in many cellular mechanisms, affecting different systems and organs [12].

Children are particularly vulnerable to the effects of air pollution due to their higher breathing rate, lower body mass, incomplete metabolic system, immature host defence and outdoor activity patterns [13,14]. Long-term air pollution may lead to continued exposure to metals, because PM is a major transporter of several elements, which can trigger immune responses in children, as well as disruption of the blood-brain barrier, resulting in compromised neurological and immunological function in the brain [15].

Considering that children spend a significant part of their day in schools [16,17], where they may inhale high PM concentrations, it is important to manage air quality to reduce exposure while students attend classes. It has been reported that PM concentrations in school hallways can negatively impact classroom air quality [18] and that surrounding school environments also negatively influence PM concentrations and metal loading in classrooms [19]. Children's exposure to air pollution in school settings is known to be associated with adverse health and behavioural outcomes. On the one hand, exposure to particulate matter lower than 10 μm (PM_{10}), dust and some of their elemental constituents such as manganese, lead, and arsenic, in school-aged children has been linked to lung inflammation and respiratory symptoms [20]. On the other hand, pupils' exposure to PM has been associated with poor academic performance [21] and increased absenteeism due to illness [22]. Moreover, one of the factors affecting the level of PM in primary school classrooms is the proximity to industries, as schools with surrounding industrial areas present higher PM concentrations compared to schools not located near industrial complexes [23].

In Portugal, the small-town of Estarreja account for 20 % of the country's chemical industry [24]. Since 1985, an air quality monitoring station has provided continuous monitoring of air quality near the Estarreja Chemical Complex (ECC). Some studies have also been carried out with the aim of evaluating the impact of industrial activity [25]. For instance, Figueiredo et al. [25] showed that although industrial activities represented around 80 % of the municipality's total emissions between 2001 and 2009, levels decreased for almost all pollutants analysed for the same period, but PM_{10} and O_3 consecutively exceeded the regulated standards. In a more recent study, Alves et al. [26] verified that the annual average values of $PM_{2.5}$ in Estarreja have approached or exceeded the World Health Organisation (WHO) guideline (10 $\mu g m^{-3}$) but remained within the acceptable values set by European legislation (<25 $\mu g\ m^{-3}$). However, in the same study, when researchers analysed $PM_{2.5}$ samples in the vicinity of the industrial chemical hub, they found many toxic compounds (e.g., aromatic ketones, ethylene glycol) and observed that the levels of some metals and plasticisers peaked when winds blew from the industrial area.

The industries that make up the ECC have made a great effort to improve processes and adopt the best available technologies to minimise atmospheric emissions in recent decades. Thus, the impact of these measures on the concentrations of PM in the vicinity of the industrial park is a task that needs to be carried out, mainly when most of the student community attends a school that is just 1 km from the chemical complex. Furthermore, atmospheric emissions from industrial activities can even reach residential areas of the town. Taking into account that children represent a vulnerable population and studies in schools characterising the size distribution of particles and their chemical constituents are very scarce, this research aimed to evaluate: i) the mass concentration and chemical composition of size-fractionated particulate matter in the educational establishment closest to the ECC and, ii) the role of personal habits, housing conditions and environmental factors in the prevalence of respiratory symptoms in children attending that school. This research is particularly relevant for the Estarreja school community, but also to infer the influence on the respiratory health of vulnerable groups in the surroundings of other industrial areas. Furthermore, by focusing on the levels, size distributions and chemical composition of the pollutant classified as the most dangerous - particulate matter - it allows information to be gathered about the emission sources.

2. Methodology

2.1. Characteristics of the school and study population

The study area covers a school surrounded by low-rise buildings, a small parking lot and a railway line. The Estarreja Chemical Complex is located approximately 1 km to the north (Fig. 1). In the 1930s, several industrial units were installed in Estarreja. The first unit was dedicated to chlorine and caustic soda production [25]. Nowadays the ECC, located north of the town, covers an area of around 290 ha and is made up of various industrial, commercial, storage and service activities, which include, among others, the production of nitric acid, aniline and nitrobenzene, sodium and chlorate compounds, polyvinyl chloride and polyurethanes [25,26]. The town is also affected by intensive and extensive farming emissions, as well as road traffic.

The classrooms where the study took place have white-painted concrete walls, wooden doors, whiteboard with markers and depend on natural ventilation. The school is attended by around 700 pupils aged 3 to 12, thus integrating pre-school and primary education. The latter is divided into 2 cycles: first cycle (grades 1 to 4) and second cycle (grades 5 and 6). In general, children attend school between 8:00 and 15:00.

2.2. Sampling methodology

Two Personal Cascade Impactor Samplers (PCIS) operating at 9 L/min were used to collect simultaneous samples of particulate matter in a classroom (indoor) and in the schoolyard (outdoor). Sampling was carried out in winter 2022 and spring 2023 for 4 weeks in each season respectively. Sampling periods began on Monday afternoon and ended on Friday afternoon. At the end of each week, the indoor PCIS was moved to a classroom in another building. In total, 4 rooms were monitored, one in each school building (Table 1). The PCIS was used to separate and collect particles in five size ranges (μm): 10–2.5 (coarse particles), 1.0–2.5, 0.50–1.0, 0.25–0.50, and <0.25 quasi-ultrafine (q-UFP). Particles above each cut-point were collected on a 25-mm Teflon filter in each appropriate stage. Particles lower than the 0.25-μm cut-point were collected on a 37-mm PTFE after-filter. After gravimetric determination of mass concentrations for all size ranges, the samples were analysed by particle-induced X-ray emission (PIXE) at the INFN laboratory (Florence, Italy) to obtain the elemental composition. A detailed description of the PIXE technique is provided in Lucarelli et al. [27].

A Davis Vantage Pro2 weather station located in the schoolyard was used to measure meteorological variables such as air temperature (T), relative humidity (RH), precipitation (P), wind speed (WS) and direction (WD) during the two monitoring campaigns. Although, in the calendar, the monitoring period falls in autumn, due to meteorological conditions contrasting with those in spring, throughout the manuscript it will be called the winter period.

2.3. Exposure to environmental factors

A questionnaire based on the International Study of Asthma and Allergy in Children (ISAAC) [28] was given to each classroom teacher to be distributed to parents or legal guardians who filled out the various fields. Parents were provided with a description of the project on the first page of the questionnaire. The main objective of this survey was to assess the prevalence of respiratory symptoms in children and characterise environmental factors and other possible sources of domestic air

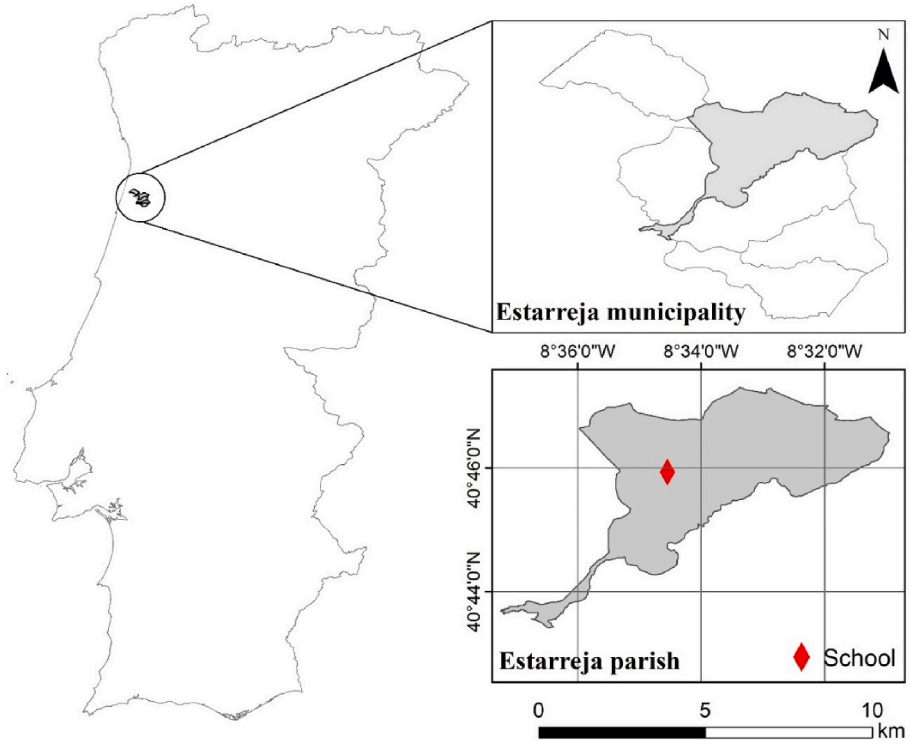


Fig. 1. Study area. The location where data collection was carried out is marked with a red diamond. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Description of sampling in the indoor environment.

Measurement periods[a]	Classroom
First week Nov 2022 April 2023	Kindergarten; room attended by the same class; age group between 3 and 5 years
Second week Nov 2022 April 2023	1st cycle, 1st grade; room attended by the same class; age group between 6 and 7 years
Third week Nov–Dec 2022 April–May 2023	Room A; 2nd cycle, 5th and 6th grades; room attended by different classes; age group between 10 and 11 years
Fourth week Dec 2022 May 2023	Room B; 2nd cycle, 5th and 6th grades; room attended by different classes; age group between 10 and 11 years

[a] Samples taken in 2022 correspond to the winter campaign, while measurements taken in 2023 correspond to the spring campaign.

pollution (Table S1, Supplementary Material). Based on the information provided in the questionnaire, the variables related to exposure to environmental factors were classified into three groups: personal factors, housing conditions and dietary habits. Personal factors included the child's gender, age and breastfeeding. Factors related to home environment included frequency of trucks on the street, distance from the industrial complex, living with a smoker and household pets.

2.4. Data analysis

2.4.1. Logistic regression models

Various combinations of the questions were evaluated in multivariate logistic regression models using backward, forward, and stepwise elimination to select the set of questions that best explained respiratory symptoms and to arrive at a preliminary multivariate model, since the questionnaire has many possible predictors to be included. The backward and stepwise approaches were assumed to work well because they presented the lowest and the same Akaike information criterion (AIC) value in each of the binary health outcome variable models. Thus, they were used to choose the predictors. To ensure selection of the most powerful predictor combinations, the effect of eliminating non-significant variables in a new preliminary multivariate model was evaluated before choosing the final model. This stage was considered because it was observed that by eliminating variables that are insignificant, the performance and the AIC criterion worsen, thus in some cases, even the insignificant variables should be kept. Finally, the most sensitive model (R^2) with the best AIC was selected. The results are presented as odds ratio (OR) and 95 % confidence interval (CI). A p value less than 0.05 was considered statistically significant. The odds ratios were adjusted for gender and age. The statistical analyses were all performed in Rstudio (version 4.2.2).

3. Results and discussion

3.1. Air quality at school

3.1.1. Size segregated particulate matter concentrations

Fig. 2 shows the mass concentrations of PM in classrooms and the schoolyard. The global averages obtained for PM_{10} and $PM_{2.5}$ in the two campaigns were 19.1 and 11.2 μg m^{-3} in classrooms and 15.1 and 11.7 μg m^{-3} outdoors, respectively. Both indoors and outdoors, the lowest values were recorded in the first week of winter, coinciding with intense precipitation that possibly contributed to the washout of particulate pollution. Except for the first week, winter concentrations were significantly higher in classrooms and in the schoolyard than those in spring. The highest concentrations of $PM_{2.5}$ and PM_{10} in both environments were recorded in the third week of winter, when low wind speeds and lower precipitation and air temperature values were recorded compared to other weeks of the same season (Table S3, Supplementary Material). More unfavourable atmospheric dispersion conditions, especially at night, and the intensification of residential biomass combustion may have contributed to the higher concentrations of PM observed in this

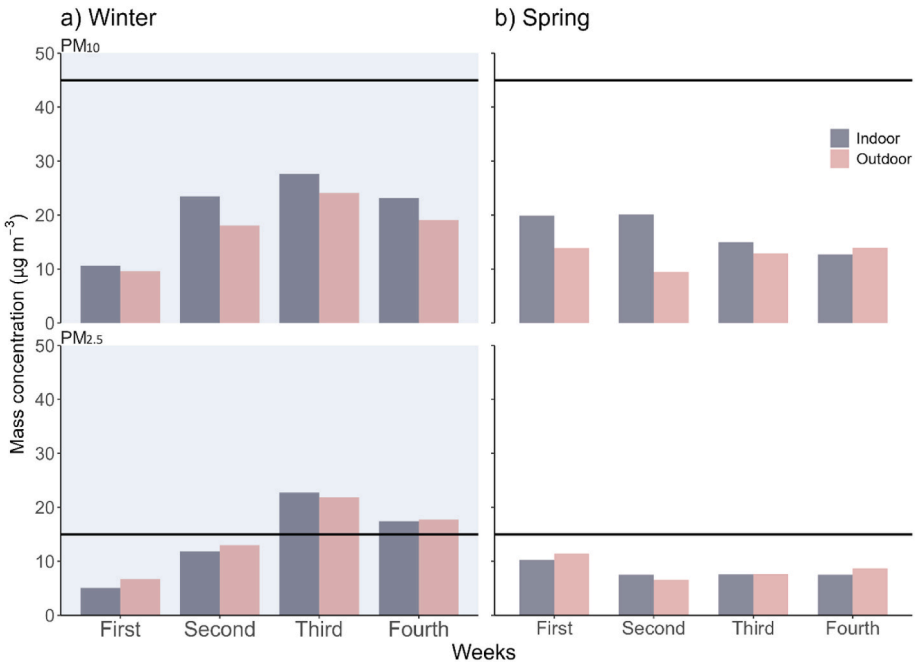


Fig. 2. Mass concentrations of PM in a) winter and b) spring. The top panel shows PM_{10} and the bottom panel $PM_{2.5}$. The black line represents the WHO guidelines for PM_{10} and $PM_{2.5}$ (45 and 15 µg m^{-3}, respectively) for 24 h.

period [29]. Although the school samples corresponded to a period longer than 24 h, PM_{10} never exceeded the daily WHO guidelines (45 µg m^{-3}), while in the last two weeks of winter the concentrations of $PM_{2.5}$ in the schoolyard and in the classrooms were higher than the value recommended by that organisation (25 µg m^{-3}).

The indoor-to-outdoor (I/O) ratio for PM_{10} was higher than for $PM_{2.5}$ (Table 2), probably due to indoor sources previously reported in other school environments in Portugal, such as the release of clothing and paper fibres, peeling of the skin and, above all, resuspension of mineral dust. It has been shown that these sources, combined with poor ventilation, contribute to high levels of coarse material in the indoor air of school microenvironments [30,31]. According to Madureira et al. [32], student activities in classrooms affect the I/O ratios of $PM_{2.5}$, since a decrease from day to night from 0.83 to 0.64 was observed in the 42 classrooms studied. It has been argued that a significant mass fraction of PM in the outdoor environment is due to fine particles emitted either by primary sources, such as road traffic, industry and biomass burning, or formed secondarily by photochemical reactions in the atmosphere.

The seasonal particle size distributions as a function of mass median aerodynamic diameter (MMAD) and geometric standard deviation (GSD) are shown in Table S4, Supplementary Material. PM presented lower MMAD in the schoolyard than in the classrooms and all samples contained polydisperse particles (GSD >1.2) in both seasons. It was evidenced that PM contained a greater proportion of smaller particles in winter (MMAD between 0.18 and 1.05) when compared to spring (MMAD between 0.61 and 1.67). In this study, outdoor PM samples presented an average MMAD of 0.62 and 1.21, while for indoor samples the diameters were 1.40 and 2.43 in winter and spring, respectively. Şahin et al. [33] collected samples at 7 points in Istanbul over a period of two years and found a similar pattern, although with MMAD values higher than those estimated in this study. The authors observed a decrease in the fraction of fine PM during the summer period, which was attributed to the decrease in the use of fuels for domestic heating. This behaviour was clearly identified at the station located in the residential area of Rasathane, where the smallest MMAD was observed in winter.

The PM size distributions depicted in Fig. 3 for both winter and spring show a comparatively greater variability for coarse fractions and a smaller variability for q-UFP. This may be due to the activities carried out in the classrooms, since the I/O for PM_{10} was higher than 1 in both seasons. This observation is well in line with the study by Viana et al. [34], who reported higher mean PM_{10} concentrations than the corresponding outdoor levels for 39 primary schools across Barcelona (Spain). Whether outdoors or indoors, q-UFP displayed higher concentrations compared to other particle size fractions in the last two weeks of winter. The average mass concentrations of $PM_{0.25}$ in the schoolyard were 17.0 and 14.4 µg m^{-3}, which were 7.4 and 10.7 times higher than the $PM_{2.5\text{-}10}$ levels. These peak concentration values were found when the air temperature was below 14 °C and weak wind conditions prevailed, with average speeds below 0.84 m s^{-1}. In this period, the winds blew from SE, indicating contributions from the residential area of the town.

It was observed that $PM_{2.0\text{-}10}$ concentrations in classrooms were higher in spring, contrary to what happened with q-UFP (Fig. 4). In winter, the concentration of indoor q-UFP particles was up to 5.7 times higher than in spring. Comparisons with the literature indicate that the concentrations quantified at the school are lower than the values

Table 2
Concentrations (µg m^{-3}) and seasonal proportions of $PM_{2.5}$ and PM_{10} in classrooms and the schoolyard.

	$PM_{2.5}$				PM_{10}			
	Winter	I/O	Spring	I/O	Winter	I/O	Spring	I/O
First week	5.05	0.75	10.3	0.90	10.6	1.11	20.0	1.43
Second week	11.8	0.91	7.52	1.14	23.5	1.30	20.1	2.12
Third week	22.7	1.04	7.57	0.99	27.7	1.15	15.0	1.16
Fourth week	17.4	0.98	7.52	0.86	23.2	1.21	12.7	0.91

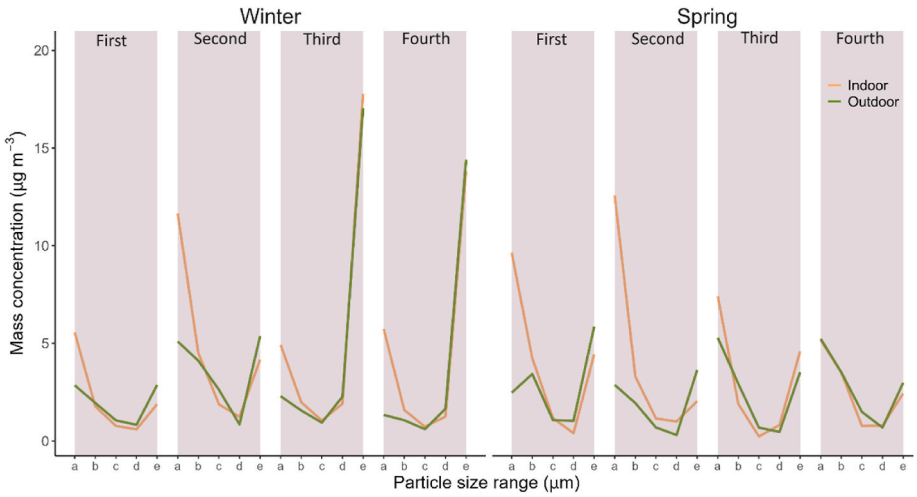


Fig. 3. Size segregated particulate matter concentrations for winter and spring. Impaction stages are referred as: 2.5–10 µm (a), 1.0–2.5 µm (b), 0.5–1.0 µm (c), 0.25–0.5 µm (d) and <0.25 µm (e). The words at the top within the shaded portion indicate the sampling week (For the description and interpretation of the monitoring weeks in this figure, the reader is referred to Table 1 of this article).

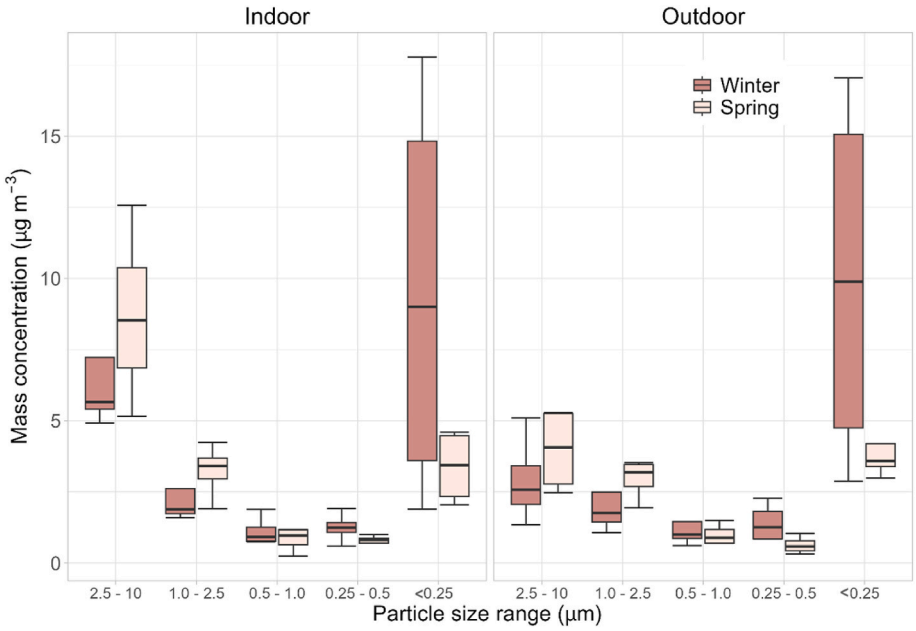


Fig. 4. Size segregated particle mass concentrations for all sample sets in both seasons.

obtained in other places around the world. For example, Viana et al. [35] reported that the average concentration of q-UFP measured in several schools in Barcelona between January and June was 25.6 µg m^{-3} outdoors and 23.4 µg m^{-3} indoors. Furthermore, when compared to studies in residential environments, concentrations in this school are largely lower. Braniš et al. [36] found that the average outdoor q-UFP concentration (10.9 µg m^{-3}) measured by cascade impactors was higher than the indoor value (9.90 µg m^{-3}) in an elementary school gym and an adjacent outdoor location in the central part of Prague between 2005 and 2009. They showed that the correlation coefficient (r) between the corresponding sizes of outdoor and indoor aerosols increased with decreasing aerodynamic diameter of the collected particles, indicating a higher infiltration rate of almost q-UFP. However, the outdoor > indoor pattern may be different for other non-school environments, as observed by Du et al. [37] in India, who documented indoor (kitchen) and outdoor (in the backyard of each house) concentrations in rural homes that used improved wood stoves of 77 and 25 µg m^{-3}, respectively.

A close value between winter and spring was obtained for particles in the aerodynamic diameter ranges 0.5–1.0 µm (stage c) and 0.25–0.5 µm (stage d) both indoors and outdoors (Fig. 4). However, for the q-UFP range in winter, indoor and outdoor concentrations were much higher than those observed in spring. In winter, the indoor (9.4 µg m^{-3}) and outdoor (9.9 µg m^{-3}) concentrations were, on average, 3.8 and 3.7 times higher than the spring levels (I/O ratio for q-UFP = 0.9 in both seasons). This difference points to the prevalence of residential biomass burning in winter, whose emissions of mostly ultrafine particles have an enormous capacity to infiltrate from outside to inside classrooms. As for coarse particles, the differences observed between classrooms and the schoolyard in winter and spring may indicate the presence of specific indoor sources, such as dust resuspension (I/O ratio for coarse particles >2.2 in both seasons). Furthermore, while in the schoolyard the contribution of coarse particles to the mass of PM_{10} increased from winter (1.34 µg m^{-3}) to spring (5.29 µg m^{-3}), the opposite behaviour was observed with q-UFP particles, whose concentration varied from a

minimum value of 14.4 μg m^{-3} in winter to just 2.99 μg m^{-3} in spring (Fig. S2, Supplementary Material). Thus, in winter, q-UFP represented a substantial fraction of PM_{10}, accounting for up to 75 % of its mass in the schoolyard and up to 64 % in the classrooms. The high levels of q-UFP particles in winter suggest the impact of specific sources that act in this season, mainly affecting concentrations in the outdoor environment. Contrarily, in spring, coarse particles (2.5–10 μm) were the main contributor to PM_{10} in classrooms, constituting mass fractions between 40 % and 62 %.

3.1.2. Chemical constituents

The concentrations of elements detected in PM are shown in Table S5, Supplementary Material. The particle size segregated composition of some elements is depicted in Fig. 5. High concentrations of Na, S, Cl and K (winter) and K and S (spring) were observed in the q-UFP fraction both outdoors and indoors. In turn, high concentrations were observed in the $PM_{2.5\text{-}10}$ fraction for Ca and Cl in winter and Ca, Cl and Si in spring. In general, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe were found in all PM sizes in both seasons, while other elements such as V, Cr, Ni, Se, Rb, Sr, Y, Zr, Mo, Ba and Pb were only detected in some PM granulometries. Ti was detected in all particle samples larger than 0.25 μm. The coarse fraction samples (stage a) mainly contained a variety of different elements typical of mineral matter (Si, Ca, Mg, Al, Fe). The highest concentrations of these elements were observed in both indoor and outdoor samples in spring (Fig. 5), which can be explained by the increase in dust resuspension from both road mobility and agricultural activities in the surroundings, phenomena that are enhanced by the scarcity of precipitation in this drier season.

In general, the outdoor and indoor environments showed higher elemental concentrations in stage b (Dp: 1.0–2.5 μm) than in the other stages (25 and 27 %, respectively). However, in spring, stage c (0.5–1.0 μm) in classrooms (78 %) and stage d (0.25–0.5 μm) in the schoolyard (68 %) were those that presented the highest elemental contribution compared to the other particle sizes (Table S6, Supplementary material). The mineral fraction was higher in spring than in winter. Elements such as Al, Ca, Fe, K, Mg, Mn, Na and Ti contributed, on average, 20 % of the total elemental mass concentrations in $PM_{0.5}$ (stage c) at the schoolyard, and 30 % (stage c) in the indoor environment. In the finest fraction ($PM_{0.25}$), the elemental load represented less than 13 % of the total mass for this size range in the schoolyard in winter and 33 % in spring. However, for $PM_{0.25}$, K and S were the ones that contributed most to the total elemental mass in winter (34 % both, at the schoolyard), while in spring, the most abundant was S (71 and 70 %, indoors and outdoors, respectively). Furthermore, a cluster analysis by particle size showed that both K and S in the schoolyard belonged to a separate group (Fig. S5, Supplementary material). P, on the other hand, was detected in both seasons. In winter, the highest values were recorded in the finest fraction (stage e) in the schoolyard, while in spring, the highest concentrations were observed in the coarsest fraction (stage a). In winter, no positive correlations were found between P (stage e) with other elements, but in spring, P (stage a) correlated well ($p < 0.05$) with Cu, Cr and V. P is carried by dust particles, cloud droplets and dissolved in rainwater. It may be associated with the use of fertilisers, cleaning products and other chemicals [38].

The contributions of Zn, Fe, Pb, Ni, Cr, Mn and V are typically associated with industrial activities in the vicinities, such as foundries and metallurgical industries [39]. The concentrations quantified in this study were lower when compared to their levels reported in other locations influenced by industries. Elements such as Ba, Br, Cr, Cu, Mn, V and Ni presented the highest values in the $PM_{0.25}$ fraction (Fig. 6). Pb was detected mainly in winter, while Se, V and Zr were identified with greater presence in spring. Moreover, some positive correlations ($p < 0.05$) were observed between these elements, mainly in q-UFP in winter. Industrial activities carried out close to the school can contribute to the emission of metal(loid)s, since the industrial park integrates a manufacturing unit dedicated to the production of metal parts for various sectors, factories producing home appliances, equipment for clinical, rehabilitation and geriatric health, and a unit dedicated to the manufacture of fine stoneware products [26]. Elements that are normally associated with dust resuspension, pavement wear, road traffic, use of antioxidants, vehicle additives and lubricants and industrial activity, such as V, Al, Fe, Ti, As, K, Pb, Co, Mn, Ca and Cr [40–42]

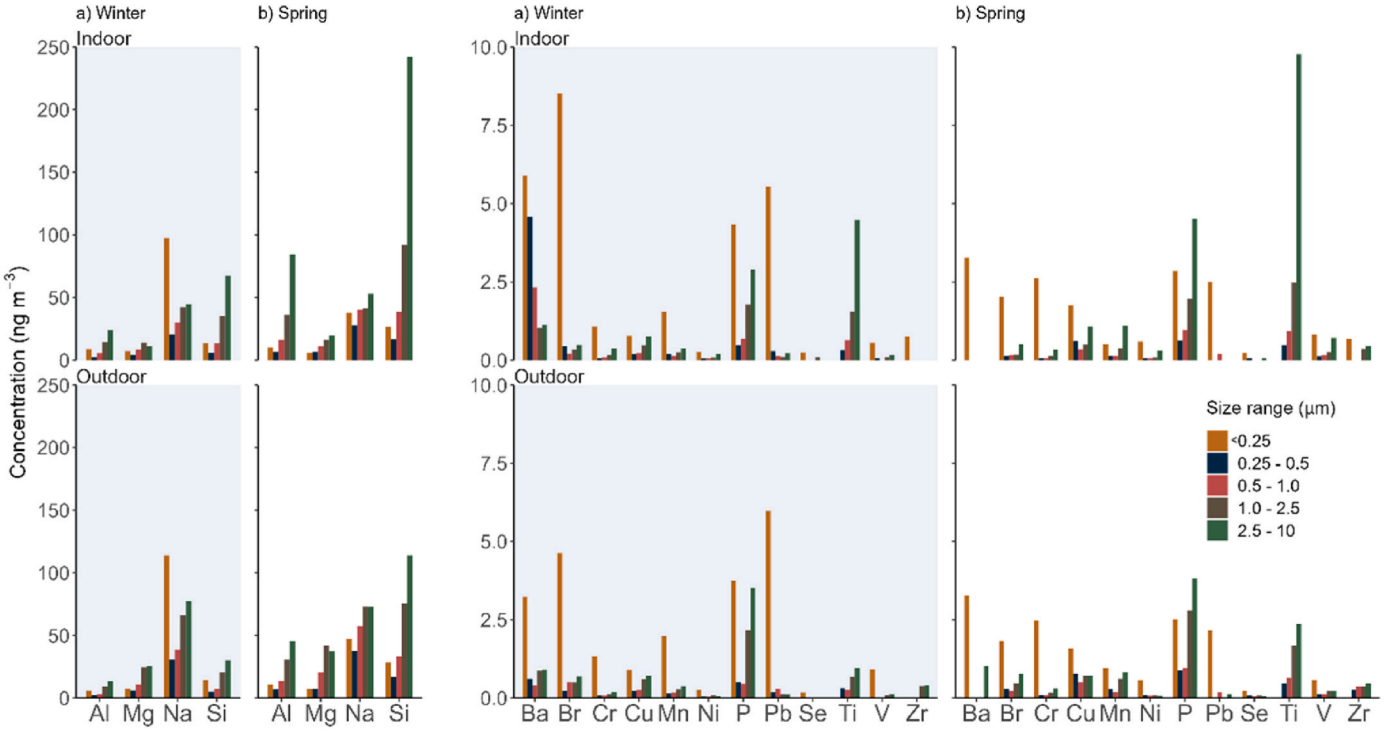


Fig. 5. Average concentration of the main elements in a) winter and b) spring in the classrooms (top) and the schoolyard (bottom). Note the different axis scales adopted to better visualise the concentrations of each element.

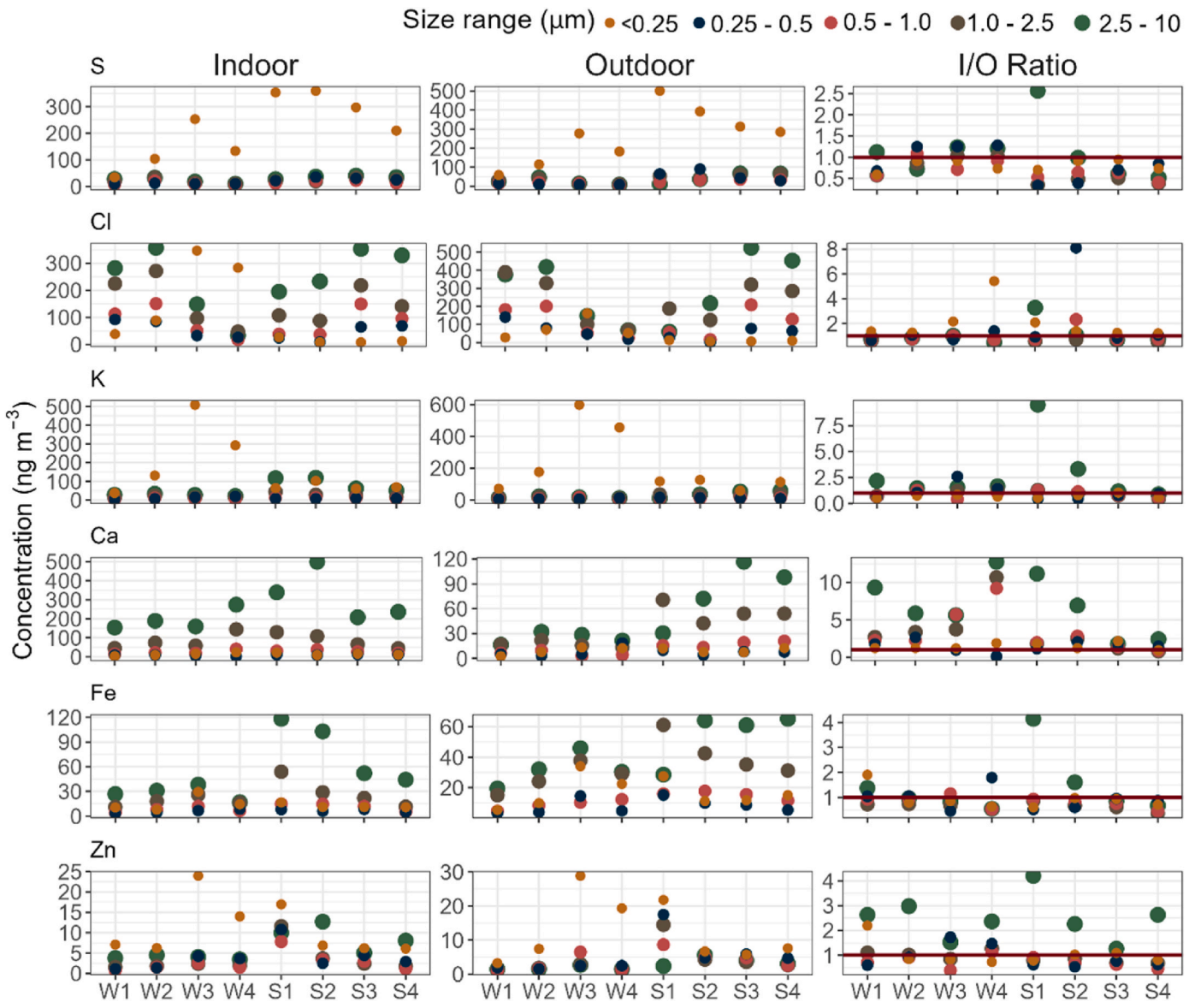


Fig. 6. Concentrations and indoor/outdoor ratios of selected elements in different particle size fractions in winter (W1, W2, W3, W4) and spring (S1, S2, S3, S4). Four monitored classrooms represent the indoor environment, while the schoolyard represents the outdoor environment for the four sampling weeks in each season.

appeared grouped in the same category in all stages.

Particles released from steel wheels and rails can be traced through the Mn/Fe ratio, with values close to 0.01 confirming this origin [43]. In this study, the Mn/Fe ratio varied, on average, between 0.01 and 0.04 in winter, and between 0.01 and 0.02 in spring, which is consistent with a dominant origin in the steel used in wheels, rails and brakes. In both winter and spring, particles >2.5 µm had ratios <0.01 both indoors and outdoors. A train line passes through the west side of the school, and less than 2 km away is the nearest railway station. The highest concentrations of these elements were quantified in the classroom closest to the train line.

According to Fig. 6, in both seasons, the highest concentrations of S, K and Zn in q-UFP were observed in outdoor samples (Fig. 7). The I/O ratio for q-UFP was close to or below one, especially in winter, except for Zn in the first week of winter. The average concentration of K in $PM_{0.25}$ in the indoor and outdoor environments were higher in winter (242 ng m^{-3} and 326 ng m^{-3}, respectively). Potassium is an elemental tracer commonly used to check whether pollution comes from the burning of biomass, particularly wood [44]. However, potassium is also emitted from other important sources and the content of this element in fine particle emissions from biomass burning depends on biofuels and combustion appliances [45]. According to Niemi et al. [46], K from biomass burning is emitted as KCl (known as young smoke) and then transformed into K_2SO_4 and KNO_3. The S/K ratio can be used to describe the rate of accumulation of S compounds in biomass burning aerosols during their transport [47]. The S/K ratio in the $PM_{0.25}$ fraction observed in winter (~0.5 indoors and outdoors) is close to the values described in other studies [48] and shows that the biomass burning aerosols detected in the school were relatively freshly emitted. In contrast, in spring, the average S/K ratio was 4.1 and 3.5 indoors and outdoors, respectively, indicating that biomass burning aerosols were aged. Furthermore, K in the finest fraction generally showed positive correlations with Zn, Pb, S and Mn only in winter (Fig. S4, Supplementary material), which also suggest that these elements are emitted from biomass burning [49].

As previously mentioned, S presented higher concentrations in spring compared to winter (Fig. 6). In spring, S in the finest fraction ($PM_{0.25}$) exhibited a positive correlation ($p < 0.05$) with V, Ni, Zn, and Fe, while in winter correlated well ($p < 0.05$) with Br, Zn, Fe, Mn, Cu, Si, Ca, Pb and K. Sulphur is present in nature as a common constituent of many minerals. On the other hand, it is possible to find sulphur in

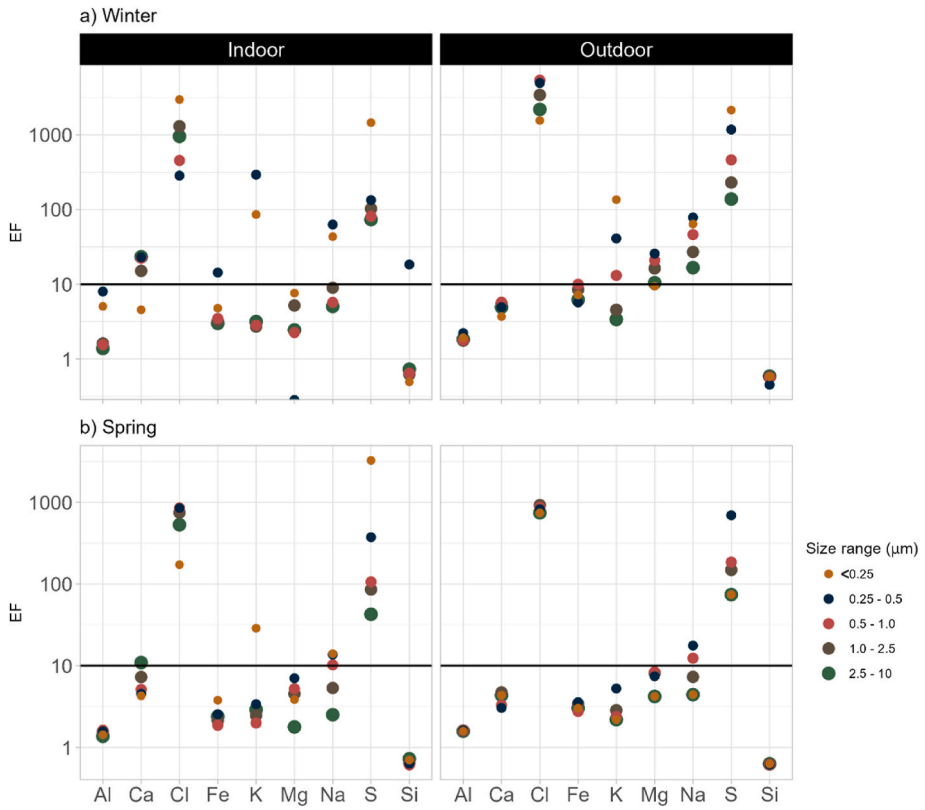


Fig. 7. Average enrichment factors of selected elements in different particle size fractions. EF higher than 10 indicate that the element arises mainly from anthropogenic sources, while for lower EFs the element is of natural origin. Aluminium was considered the reference element.

natural gas and crude oil. Sulphur is released into the atmosphere in the form of gas and dust generated by activities such as oil refining, kraft paper mills, metallurgical processes, smelting gases, copper and iron extraction and biomass burning [38]. It may be that one of these activities has a greater influence in spring than in winter, or that due to seasonal weather conditions, the contribution of S changes from season to season. Long-range atmospheric particle transport was disregarded since Pearson correlations between S and the major single-bonded mineral dust elements Al and Si were not significant for both elements, indicating a weak linear relationship (Fig. S4, Supplementary material). In contrast, the highest concentrations of Ca and Fe were detected indoors in stage a ($PM_{2.5\text{-}10}$), being higher in the spring samples. However, the I/O ratio of Ca (5.6–12.8) in the $PM_{10\text{-}2.5}$ size fraction obtained in winter was higher than that in spring (1.8–11.2), indicating that Ca does not necessarily infiltrate with PM, but it mainly results from the resuspension of dust transported into rooms on clothes and especially on the soles of shoes.

The analysis of Cl according to the school environment (indoor and outdoor) revealed intrinsic characteristics. On one hand, as observed in other studies, cleaning products used indoors can influence the contribution of Cl [50]. In this study, the highest concentrations of this element in the $PM_{0.25}$ fraction were always observed inside classrooms, because of cleaning work and the use of disinfectants. The I/O ratios for this size fraction were similar during both seasons, ranging between 0.72 and 2.19 (Fig. 6). On the other hand, Cl originates from sea salt in coastal areas or road salt in continental areas of Europe [51]. The Cl/Na ratio found for seawater (1.8) in coastal aerosols indicates a likely source in sea salt. In this study, average values of the Cl/Na ratio in all PM sizes at the schoolyard in winter (0.68–3.36) and spring (0.18–4.29) were far from the reference value for sea salt, which denotes the influence of anthropogenic emissions for this element. Anthropogenic chlorine can be emitted from meat combustion, waste incineration, industrial emissions, and biomass burning [48]. Furthermore, Cl in Dp < 0.25 μm (stage e) did not correlate with any other element in any season, while coarse Cl (2.5–10 μm) correlated positively ($p < 0.05$) with Mg in winter and with K, Si, S, Mg, Al, Ni, Na and Ca in spring. However, the groupings by particle size showed that only in the $PM_{0.25}$ fraction was Cl in the same group as Na and S in winter (no significant correlation was found with either of the two elements), while in spring, Cl grouped with more than one element in Dp > 0.5 μm (stages c, d and e) (Fig. S5, Supplementary Material). Therefore, it was not possible to accurately identify a single emission source, which indicates that Cl has multiple origins.

3.1.3. *Enrichment factors*

Enrichment factors (EFs) were calculated following the methodology described in Zoller et al. [52] to assess the contribution of anthropogenic sources to the levels of specific elements in PM sampled in classrooms and schoolyard. During the entire sampling period, the EF values for Al, Ca, Fe and Si in all stages were relatively low (<10), indicating that these elements originate mainly from resuspended soil. Among the elements investigated, in winter, Ca in particles larger than 0.25 μm sampled in classrooms showed FE > 10, while in spring only the coarsest fraction (stage a) showed enrichments greater than 10. In the past, indoor Ca levels were attributed to the use of chalk or emissions from paper as calcium carbonate [53]. However, as chalk is not used in the classrooms of the present study, it is possible that Ca was transported stuck to the soles of pupils' shoes, as observed by Sánchez-Soberón et al. [54] in schools in Spain over two seasons. Once inside the classroom, it is resuspended, resulting in higher concentrations in winter because of higher PM levels and reduced ventilation in this season. Similarly, Molnár et al. [55] and Rivas et al. [56] in school environments, also found higher Ca levels indoors than outdoors.

Elements such as Cl and S presented EF > 10 in all size fractions, both indoors and outdoors in both seasons. As explained previously, much of the Cl had an anthropogenic origin, given that not only its ratio with sodium was sometimes higher than that of seawater, but also because it

was highly enriched. In the case of S, the enrichment may be due to one of the activities mentioned above or to the influence of more than one of those. K was enriched in particles with Dp ≤ 0.25 μm (stages c and d in classrooms) and with Dp > 0.25 μm (stages c, d and e in the schoolyard) in the cold season, while in spring its enrichment occurred only in the finest fraction (Dp < 0.25 μm) in classrooms (Fig. 7). As discussed earlier, K presented I/O ratios lower than 1 for q-UFP in both seasons (mean = 0.71), possibly associated with biomass burning.

The EFs for some chemical constituents detected in the samples pointed to predominantly non-soil sources. This is de case of Br, Cr, Cu, Ni, Pb and Zn. Their EFs increased with increasing particle sizes (Fig. S6, Supplementary material). Ti showed an opposite trend, with EFs decreasing as particle size decreased. However, this element presented concentrations sometimes below the detection limit. Overall, a decrease in the enrichment factors of Br, Cr, Cu, Mn, Ni, and Pb from winter to spring was registered. The greatest reduction (from 4285 to 13) was observed in the schoolyard for q-UFP of PM-bound Pb. Typically, the enrichments of Cu, Pb, Ni, and Cr have been associated with mechanical abrasion and wear of tyres and brakes [42]. On the other hand, while the EF of Br decreased 30 times for Dp < 0.25 μm (stage e) in classrooms, the EF of Cr increased almost 4 times in the spring (Fig. S6, Supplementary material). The variation of EF with particle size has been previously reported by other researchers. Gao et al. [57] studied soil dust aerosols to determine whether there is heavy metal selectivity depending on particle size. The authors indicated that the particle size dependence of heavy metal enrichment may have important effects on the health impacts of aerosols. In addition, Zhi et al. [58] suggested that fine particles (<2.1 μm) have more active sites around surfaces and stronger adsorption compared to larger particles (>9.0 μm).

V and Ni of anthropogenic origin are commonly used as markers of heavy fuels, but in this study no correlations were found between these two elements. Molybdenum was found in part of the indoor and outdoor spring samples. Mo has typically been associated with industrial processes such as steel production [59] and petrochemical plants [1]. The Mo concentrations can be attributed to the fact that the predominant wind direction (Table S3 and Fig. S3, Supplementary Material) in spring coincides with the location of the industrial complex, consequently affecting the area where the school is located. In research carried out near the study area, Alves et al. [26] identified that the highest levels of Mo were recorded for winds in the WN sector, which suggests an origin mainly in the industrial complex.

3.1.4. Elemental size distribution

Figs. 8 and 9 depict the size segregated distributions of some elements. In general, the size distributions of Na, S, Cl, and K were bimodal in both seasons. Except for Cl, the concentrations of these elements reached peaks for the finest size fraction. K displayed a bimodal distribution in both campaigns: a dominant peak at Dp ~0.10 μm (stage e) and a minor peak at Dp ~1.0 μm (stage b). The highest concentrations were recorded in winter in the schoolyard. In spring, the largest peak also coincided with that determined in winter, however, a decrease in the mass concentration of K in this very small fraction (Dp < 0.25 μm) and a modal shift towards larger particles was observed, particularly in classrooms. The fine mode of K is most likely related to emissions from residential biomass combustion, especially in winter, while the coarse mode results from the resuspension of soil particles.

As shown in Fig. 8, S revealed a bimodal distribution like that of K with a dominant peak centred at Dp ~0.10 μm. This peak is much more intense in spring in the outdoor environment. Sulphur in $PM_{0.25}$ in the schoolyard accounted for 40 %–45 % in spring and between 17 % and 62 % in winter of its total mass concentrations. It can be originated from coal burning in restaurants and domestic barbecues, fuel oil combustion in residential boilers and emissions from diesel vehicles.

The size distribution of Na in both seasons presented two modes. In winter, the main mode was found at Dp ~0.10 μm, both outdoors and indoors. In spring, the main mode was found at Dp ~0.50 μm. Cl and Na

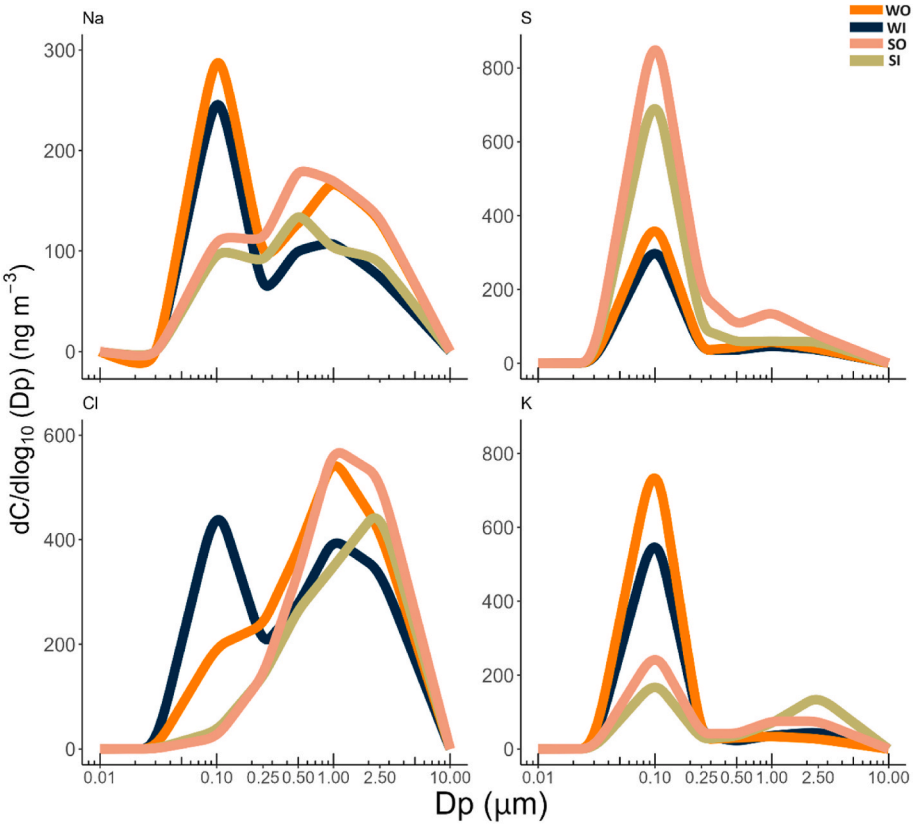


Fig. 8. Lognormal mass size distributions of some prevalent elements for winter outdoor (WO), winter indoor (WI), spring outdoor (SO) and spring outdoor (SI).

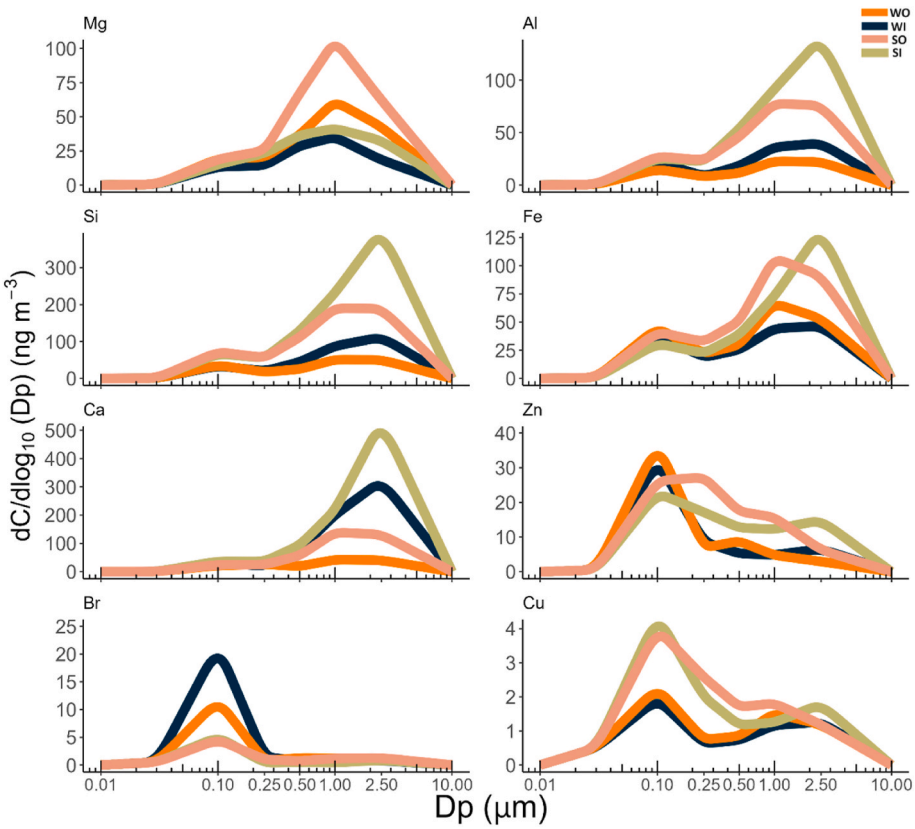


Fig. 9. Lognormal mass size distributions of some crustal elements and some heavy metals for winter outdoor (WO), winter indoor (WI), spring outdoor (SO) and spring outdoor (SI).

showed different patterns. The Cl pattern reflects an increase in concentrations of coarse sizes, peaking at Dp ~1 μm and 2.5 μm. Unlike what was observed in classrooms, Cl in winter presented a bimodal distribution, with its main peak at Dp ~0.10 μm, confirming the influence of the use of chlorinated products for cleaning and disinfection and the poor ventilation of the rooms in the coldest period. However, Cl can also originate from other anthropogenic sources, such as burning of polyvinyl chloride (PVC) and paper [2]. It is worth noting that in the schoolyard Cl peaked at Dp ~1.0 μm in both winter and spring. The ECC integrates some industries dedicated to the production of chlorine and caustic soda, as well as synthetic resins, mainly PVC from vinyl chloride monomer [26], which can emit Cl. Furthermore, as observed in other studies [4,60], higher Cl concentrations were recorded during the coldest period (Fig. S7). Compared to other places in the world, in winter, the concentration of Cl in $PM_{2.5}$ at the schoolyard was 6.4 times lower than at Nankai University (Tianjin, China) and 19.2 times lower than that observed in the Indian Institute of Technology (Delhi). As reported by Wang et al. [4] when analysing the concentration of Cl at Nankai University in the four seasons, in addition to temperature and relative humidity, industrial emissions also affect the seasonal differences of this element. In this study, the highest Cl values coincide with the northwest wind direction, suggesting the contribution from the nearby industrial complex.

A completely different behaviour could be observed for Al, which, together with Mg, Si, Fe and Ca, is a typical tracer of mineral dust (Fig. 9). Al, along with other crustal elements, was more abundant in the coarse mode both in the schoolyard and in the classrooms, indicating the important role of dust and local soil resuspension processes, with higher concentrations during spring. Si and Al showed an equivalent size distribution with a relatively similar pattern in the classrooms and schoolyard in both seasons. In the schoolyard, the size distribution peaked at Dp ~1.0 μm, while in classrooms, the peak was for sizes from 2.5 to 10 μm. The highest Ca concentrations were recorded in the classrooms and the main peak was also observed in the range from 2.5 to 10 μm in both seasons. As mentioned earlier, indoor Ca likely results from the transport of soil on the soles of children's shoes, different from what was reported in previous studies [50,61], in which the main source of Ca in classrooms was identified as being chalk.

The size distributions of the main elements identified in all samples from the two monitoring campaigns are also shown in Fig. 9. Zn, Br and Cu exhibited predominance in the finest particles (Dp < 0.25 μm), with approximately 17 % of the total mass of these elements within this size, probably because of the presence of anthropogenic sources of CH_3Br emissions from agricultural pesticides, coal burning, biomass burning, and stratospheric transport from halon degradation [62]. Zn and Br presented higher concentrations in winter than in spring. The unimodal diameter of Zn was found to be Dp ~0.10 μm, which coincided with the unimodal diameter of the mass distribution of Br. The usual tendency for the size distribution to peak at 0.10 μm indicates that most of the production of these elements could be associated with the same source, since a strong positive correlation ($r = 1.00$ $p < 0.05$) between them was only found at Dp < 0.25 μm in the schoolyard in winter. Interestingly, these elements showed their highest abundances in the q-UFP. In winter, 85 % and 72 % of the total mass of Br in the indoor and outdoor environments, respectively, was within particles of this size. Unlike Zn and Br, Cu displayed bimodal size distributions in both seasons. As shown in Fig. S6, Cu enrichment factors were in the range from 81 to 1096 at all particle sizes in both classrooms and schoolyard over the two seasons. This result shows that Cu does not have a natural origin. In contrast, Şahin et al. [3] reported in their study in Istanbul that street dust in Besiktas (one of 5 outdoor monitoring sites) contributed substantially to the composition of PM, with the elements Mn, Cu and Fe having slightly higher concentrations in the coarse PM. According to the authors, the size distribution of the elements depends on the location and sources.

3.2. Environmental factors and health outcomes

3.2.1. Characteristics of the studied population

Based on the number of students, 677 questionnaires were distributed among schoolteachers, of which 334 were returned and 30 were excluded because they were incomplete (confidence level (95 %) and margin error (4 %)). Therefore, for the final analysis, 304 questionnaires were considered, which represents 45 % of the total population. According to the questionnaires, the share of female was just above 50 % and the median age of children was 9 years, varying between 3 and 12 years (Table 3). Regarding the family socioeconomic status, only 37 % of the mothers completed higher education. About 65 % of children watched TV between 1 and 3 h a day and 40 % had not practiced a breathless physical activity in a week. In relation to some household environment factors, 51 % of children live less than 5 km from the industrial complex and 35 % live on streets where trucks pass frequently during the week. Furthermore, 34 % of the schoolchildren were exposed to environmental tobacco smoke at home.

Some children live in homes where the use of fuel combinations such as electricity and gas, electricity and coal, gas and coal, are common for cooking activities. Half of the children live in houses where gas is the primary energy source for cooking (Fig. S1, Supplementary material). On the other hand, homes were heated mainly with wood (36 %) and electricity (34 %) in winter. Only 22 pupils declared to live in dwellings where gas is used as heating fuel, while 7 % of homes have no heating system.

Parent-reported rhinitis symptoms were the most common among respiratory manifestations. Overall, 41 % and 38 % of the children had experienced sneezing, a runny nose, or a stuffy nose without cold ever in life and on the previous 12 months, respectively (Fig. 10). Asthma ever in life was reported in 13 % of children. All respiratory symptoms were more frequent in boys than in girls. More boys than girls were in the "yes" category of any of the questions associated with asthma. The boy: girl ratio for the frequency of respiratory symptoms varied in the range from 1.17 to 1.92. The lowest ratio respects to rhinitis symptoms ever in life (Fig. 10).

3.2.2. Effects of environmental factors on respiratory symptoms

For the analysis of the questionnaires, two models for asthma and another two for rhinitis symptoms were built. Asthma was defined by positive responses to questions about ever having wheezing/whistling attacks or in the past year (Table S2). The results show that the model (Fig. 11, Panel a) was statistically significantly better than a reference model in explaining wheezing at any time in the past [χ^2 (25) = 115.0; $p < 0.001$], with 78.3 % sensitive. Frequent truck traffic on the streets, having a cat at home, taking paracetamol and antibiotics were positive and statistically significant predictors of the outcome. When taking antibiotics during the first year of life, the odds of wheezing increased.

In this study, it was found that paracetamol consumption during childhood increases the risk of developing asthma and rhinitis. Paracetamol, given in the first year of life, is associated with greater likelihood of being in the "yes" category of developing asthma symptoms (OD = 2.62 [95 % CI 1.25–5.53]). In addition, belonging to the yes category for taking paracetamol is associated with an increased odds of being in the yes category of having a runny nose when the child did not have a cold at any time in the past (OD = 2.55; IC 95 %: 1.39–4.70). Similarly, a significant association was observed between paracetamol and the occurrence of asthma among children in the study carried out by Beasley et al. [63], which included more than 205 thousand children aged 6–7 years in 31 countries. Multivariate analyses indicated that the use of paracetamol in the first year of life might be a risk factor for the development of asthma in childhood. One of the reasons why paracetamol is commonly associated with increased risk of asthma is because use of this medication decreases antioxidant glutathione levels in the lung, which leads to reduced lung antioxidant defenses [64].

The model showed that living near streets with frequent truck traffic is a predictor for the development of asthma symptoms (Fig. 11 a). Children who live on streets where many trucks pass are 4.38 times more likely to belong to the "yes" category for ever had wheezing than children who live on streets frequented by few vehicles. After finding a positive correlation between the prevalence of wheezing and allergic rhinitis and indicators of traffic density, a study in Bochum, Germany, indicated that truck exhaust emissions resulting from the circulation of heavy vehicles close to home caused or exacerbated asthma symptoms and allergic rhinitis in seventh- and eighth-grade schoolchildren [65]. In a more recent study, Singh et al. [66] found an association between frequent truck traffic close to home and the presence of allergic rhinitis, rhinoconjunctivitis, and eczema among Indian children of two age groups. According to Annesi-Maesano et al. [67], inhaling traffic-related air pollutants, individually or in combination, can improve immune and airway responses to inhaled allergens.

Among the dietary variables, the consumption of vegetables, fish, meat, rice and eggs were statistically significant predictors for some respiratory symptoms. Children who eat vegetables more than 3 times a week reduce the probability of developing rhinitis by 63 % compared to children who never eat vegetables during the week (OD = 0.37; 95 % [CI: 0.12–1.18]). Some researchers found that reduced intake of fruits and vegetables may play a critical role in the development of asthma and allergies. For example, in a systematic review by Hosseini et al. [68] it was reported that most studies found beneficial associations between the consumption of fruits and vegetables and the risk of asthma and/or respiratory function. In fact, the consumption of fruits and vegetables appears to protect against asthma. Similarly, the findings of a study in Greece suggests a beneficial effect of fruits, vegetables and nuts commonly consumed during childhood on the symptoms of asthma and rhinitis. The Mediterranean diet may explain the relative lack of asthma and allergy symptoms in children in the population of this country [69]. In this study, the positive association was not seen with nuts. Contrary to what was documented in the research in Greece, it was observed that the consumption of nuts increases the odds of developing asthma (Fig. 11. Panel a and b). In a previous study, sensitization to peanut and hazelnut storage proteins was associated with higher levels of inflammation markers and food hypersensitivity symptoms in children with asthma [70]. The study concluded by reporting that storage protein sensitization appears to be associated with asthma morbidity. However, according to the researches, the reason for stronger signs of inflammation in asthmatic patients with than without sensitization to nut storage proteins is still unclear.

Having a dog at home in the last 12 months and during the first year of the child's life has shown a protective effect. Belonging to the yes category of having a dog at home reduces the odds by 68 % of belonging to the yes category of developing asthma (OD = 0.32; 95 % CI: 0.19–0.59). The findings of some epidemiological studies on respiratory symptoms have been contradictory. Some demonstrated protective effects, while others showed associations with increased asthma

Table 3
Characteristics of the studied population.

	No. of subjects
Gender	
• Female	154
• Male	150
Age, median	9
Education of mother	
• Primary	48
• Secondary	142
• Higher	114
Sedentary activity (watching television), 1–3 h a day	198
Children living near the industrial complex, <5 km	155
Children living near busy streets	105
Tobacco smoke at home, yes	104
Smoker dad, 10–15 cigarettes a day	29
Smoker mom, 10–15 cigarettes a day	8

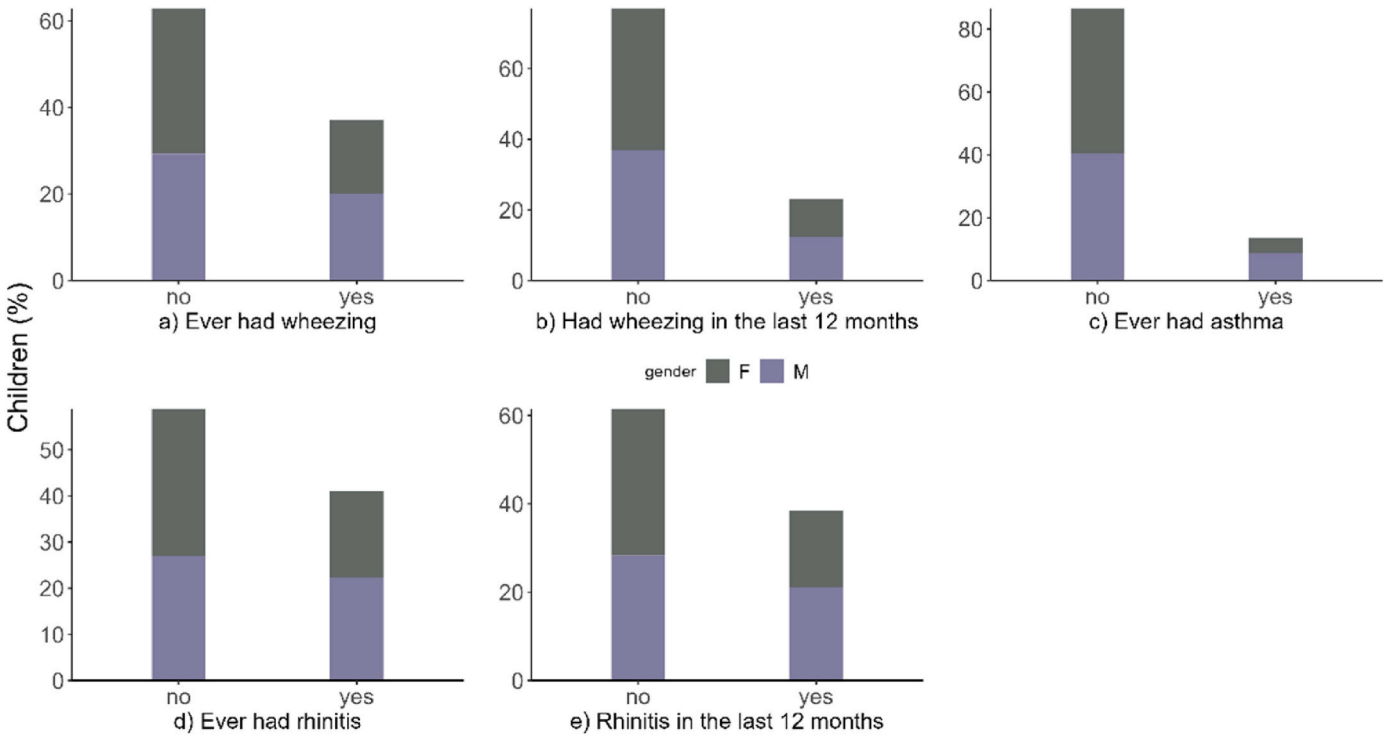


Fig. 10. Summary of questionnaire-based respiratory symptoms.

symptoms in children. On one hand, a study conducted in Japan evaluated 410 newborns who owned dogs/cats at home and their history of wheezing and asthma through five follow-up questionnaires, up to the age of 6. After an adjusted logistic generalized estimation analysis, the model showed no significant associations of the interaction between dog and/or cat ownership and follow-up time with the risks of wheeze and asthma. However, the findings suggest that owning dogs and cats from a young age does not increase the risks of wheezing and asthma compared with Japanese children who never owned them [71]. On the other hand, Brunekreef et al. [72] did not find that combined exposure to dogs and cats was more strongly associated with symptoms in children aged 6–7 years than exposure to cats or dogs alone. The strongest relationship in the youngest age group was found between exposure to cats and wheezing, independent of exposure to dogs. According to the authors, it may be that the associations change with age and that combined exposure to cats and dogs only becomes more important in adolescence. On the other hand, another common predictor was antibiotic use. Frequent intake (more than once per month) of antibiotics was associated with a higher risk of having rhinitis, whereas antibiotic intake during the child's first year of life was associated with asthma symptoms. Other studies have also suggested that antibiotics are associated with various symptoms of allergy and asthma [66]. In a birth cohort study in Japan, Yamamoto-Hanada et al. [73] examined the signs of asthma and allergic diseases in children and found that exposure to antibiotics at younger than 3 years increased the risk of developing allergic diseases at 5 years. Any antibiotic and cephem use within the first 2 years of life was associated with current asthma at 5 years.

Moreover, maternal smoking during the first year of life only showed a clear relationship with the development of rhinitis symptoms (Fig. 11 panel d). As reported in other studies, environmental tobacco smoke harms children's respiratory health. Lin et al. [74] suggested that exposure to environmental tobacco smoke in the first 2 years of life may increase the incidence of wheezing, rhinitis and eczema and decrease the remission of these symptoms in preschool children (aged 3–8 years old). In this study, maternal smoking was negatively associated with active rhinitis. Children exposed to cigarette smoke during their first year of life are twice as likely to develop rhinitis as children who have never been exposed (OD = 2.23; 95 % CI: 1.13–4.41). Finally, children born in Portugal have a decreased risk of developing asthma compared to schoolchildren born in other countries (OD = 0.51; 95 % CI: 0.28–0.91). This result was different to that observed by Migliore et al. [75], in which migrant children had a lower prevalence of asthma symptoms than children born in Italy. The researchers found that the prevalence increased with the number of years of life in Italy, indicating that exposure to environmental factors may play an important role in the development of asthma in childhood. Lower risks for lifetime asthma (OR = 0.39; 95 % CI: 0.23–0.66) and current wheeze were found for children who had lived in Italy for 5 years or less, while children born in Italy had risks higher than aboard children.

4. Study strengths and limitations

Unlike much of the work on monitoring particulate matter in schools, this study did not only consider the fractions specified in air quality guidelines (PM_{10} or $PM_{2.5}$), but rather size-segregated samples obtained simultaneously in several classrooms and outdoor air. On the other hand, carrying out sampling campaigns in two distinct periods, followed by the PM elemental speciation, makes it possible to evaluate some seasonal variability in the contribution of emission sources and atmospheric processes dependent on meteorology. Despite these strengths, some limitations should be pointed out to this research. Since it was necessary to accumulate sufficient mass to allow the determination above detection limits of several PM-bound elements, weekly samplings over two months were carried out. However, this sampling scheme prevents comparison with regulated or recommended values and the capture of daily variability in emissions from some sources. To increase representativeness, in future studies, more classrooms and other periods of the year should be included. This can help to evaluate variations in PM concentration distribution patterns, its chemical composition and respective sources, and to identify occasional events that require intervention. On the other hand, the present study does not allow for an integrated assessment of exposure, given that time spent and

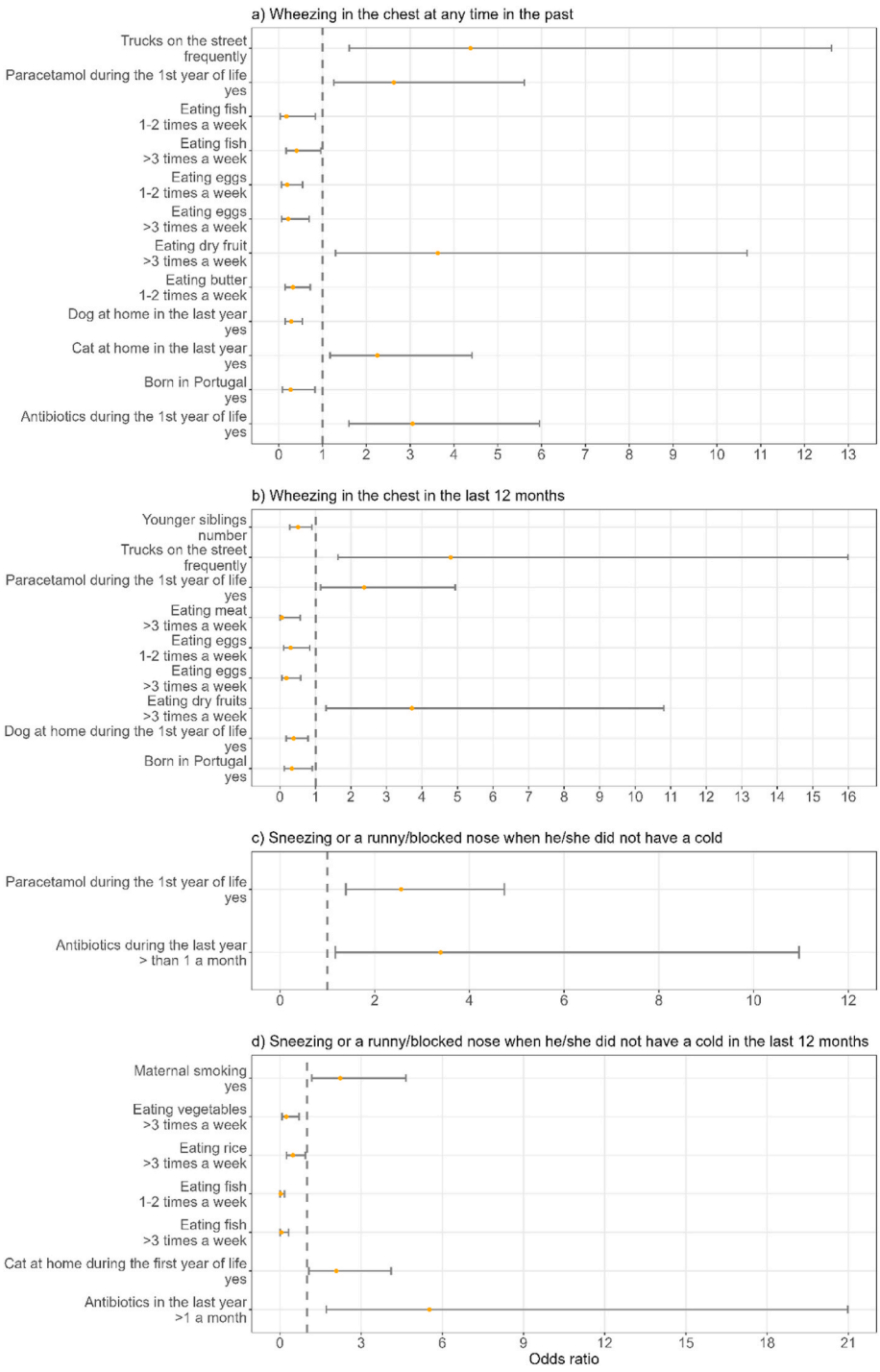


Fig. 11. Panels (a, b, c and d) summarise the results of the logistic regression models, which include only the significant factors with $p < 0.05$. Panels a and b are for asthma, while c and d are for rhinitis. Odds ratio (OR) with 95 % confidence interval (CI). The full questions corresponding to the factors presented in the graph are highlighted in bold in Table S1 of the Supplementary Material.

concentrations in other microenvironments, such as housing, were not monitored. Thus, it is recommended to consider time-activity patterns and measurements in the different microenvironments frequented by children. Another limitation of the present study is related to the methodological design which, by including measurements in only 4 rooms, limited the use of PM concentrations in statistical models. Although the results corroborate those observed in other studies, the associations found in logistic regression must be analysed with caution because the participation rate was 45 % and the only action to avoid selection bias was an explanation to parents and teachers on how to interpret and fill out the questionnaires. Previous studies have expressed that responses may be prone to misclassification [76,77], as parents of children with any respiratory symptoms may be more likely to report symptoms than parents of children without symptoms. In addition, due to the cross-sectional design of the study, the results do not allow establishing causal relationships between environmental factors and health outcomes.

5. Conclusion

This study investigated, characterised and compared indoor and outdoor particulate matter over two seasons in a Portuguese school close to the largest chemical industrial complex in Portugal, in addition to applying a standardised questionnaire to obtain additional information related to respiratory allergies, children's lifestyle, home and environment conditions. The elemental composition of the size-segregated particulate matter samples suggests that multiple sources contribute to pollutant levels in classrooms: work materials, cleaning products, dirt on the soles of shoes, infiltration of emissions from residential wood combustion, agricultural activities, exhaust and non-exhaust emissions from road traffic, chemical complex and railway. The largest mass fraction of PM outdoors was observed for particles with Dp $<$ 0.25 μm, accounting 75.5 % to PM_{10} in winter, while indoors the coarser fraction (2.5–10 μm) encompassed the highest contribution to the total PM_{10} in spring (62.5 %). The elemental content was higher in spring, representing approximately 22 % and 28 % of the total mass of the coarsest fraction (2.5–10 μm) in classrooms and the schoolyard, respectively, while the corresponding contribution to the total mass of the finest fraction (q-UFP) was 35 % and 33 %. In winter, K was the prevalent element in particles with Dp $<$ 0.25 μm (34 % in terms of total mass of $PM_{0.25}$), while in spring S dominated the chemical composition of $PM_{0.25}$ both indoors and outdoors, with concentrations ranging from 209 to 359 ng m^{-3} and 284–501 ng m^{-3}, respectively. The most notable finding was that Cl contributed most to the total mass of Dp $>$ 0.25 μm outdoors in both seasons. Although this element may be of natural origin, it is likely that industrial activity close to the school could be an important emission source of Cl. From the results of the ISAAC questionnaire, it was concluded that the use of paracetamol, the intake of vegetables and living near streets with heavy truck traffic are some of the influential factors on respiratory symptoms among children who attend school. The results of the present study demonstrate the need to promote ventilation in classrooms and to continue with research aimed at characterising whether the range of PM concentrations in and around the school changes significantly throughout the year, which is necessary to identify the sources of the particles, formulate mitigation measures and determine possible adverse effects on students.

Founding sources

This research was conducted in the context of the STEP project - Schools Tackling Estarreja's Air Pollution – funded by the LabEx-DRIIHM-OHM programme (CNRS – INEE, France), which provided funding for this study.

CRediT authorship contribution statement

Isabella Charres: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Franco Lucarelli:** Resources, Investigation. **Manuel Feliciano:** Writing – review & editing, Supervision. **Leonardo Furst:** Methodology. **Célia Alves:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Celia Alves reports financial support was provided by LabEx-DRIIHM-OHM. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The research for this article was supported by Portuguese Foundation for Science and Technology (FCT), through national funds to PhD I. Charres (SFRH/BD/2022.12142). The financial support to CESAM by FCT/MCTES (UIDP/50017/2020 + UIDB/50017/2020 + LA/P/0094/2020), through national funds, is also acknowledged. The authors would especially like to thank the school principal, teachers, parents and pupils who have willingly participated in this study. Special thanks to Prof. Teresa Nunes, from the Department of Environment at the University of Aveiro, for his support and expertise in carrying out both monitoring campaigns. Yago Cipoli from University of Aveiro is acknowledged for their valuable comments during the writing of the paper. Finally, the authors would also like to thank Professor Sonia Gouveia from the Information Systems and Processing group (University of Aveiro) for the support provided in the analysis of part of the data used in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.buildenv.2024.111949.

References

[1] S. Abbasi, B. Keshavarzi, F. Moore, M.R. Mahmoudi, Fractionation, source identification and risk assessment of potentially toxic elements in street dust of the most important center for petrochemical products, Asaluyeh County, Iran, Environ. Earth Sci. 77 (2018), https://doi.org/10.1007/s12665-018-7854-z.

[2] R.C. Moffet, Y. Desyaterik, R.J. Hopkins, A.V. Tivanski, M.K. Gilles, Y. Wang, V. Shutthanandan, L.T. Molina, R.G. Abraham, K.S. Johnson, V. Mugica, M. J. Molina, A. Laskin, K.A. Prather, Characterization of aerosols containing Zn, Pb, and Cl from an industrial region of Mexico City, Environ. Sci. Tech. 42 (2008), https://doi.org/10.1021/es7030483.

[3] Ü.A. Şahin, G. Polat, B. Onat, Mass size distribution and source identification of particulate matter metal components at four urban sites and a background site of Istanbul, Environ. Sci. Pollut. Res. 23 (2016), https://doi.org/10.1007/s11356-016-6323-z.

[4] X. Wang, X. Bi, H. Li, W. Zhang, Q. Dai, L. Song, L. Li, J. Wu, Y. Zhang, Y. Feng, The role of sources and meteorology in driving $PM_{2.5}$-bound chlorine, J. Hazard Mater. 441 (2023), https://doi.org/10.1016/j.jhazmat.2022.129910.

[5] Y. Liu, X. Geng, A. Smargiassi, M. Fournier, S.M. Gamage, J. Zalzal, S. Yamanouchi, S. Torbatian, L. Minet, M. Hatzopoulou, S. Buteau, E.A. Laouan-Sidi, L. Liu, Changes in industrial air pollution and the onset of childhood asthma in Quebec, Canada, Environ. Res. 243 (2024), https://doi.org/10.1016/j.envres.2023.117831.

[6] A.D. Bergstra, B. Brunekreef, A. Burdorf, The influence of industry-related air pollution on birth outcomes in an industrialized area, Environ. Pollut. 269 (2021), https://doi.org/10.1016/j.envpol.2020.115741.

[7] C. Men, R. Liu, Y. Wang, L. Cao, L. Jiao, L. Li, Y. Wang, Impact of particle sizes on health risks and source-specific health risks for heavy metals in road dust, Environ. Sci. Pollut. Res. 29 (2022), https://doi.org/10.1007/s11356-022-21060-w.

[8] E.S. Galvão, J.M. Santos, E.V. Goulart, N.C.R. Junior, Health risk assessment of inorganic and organic constituents of the coarse and fine PM in an industrialized region of Brazil, Sci. Total Environ. 865 (2023), https://doi.org/10.1016/j.scitotenv.2022.161042.

[9] M. Lazaridis, Modelling approaches to particle deposition and clearance in the human respiratory tract, Air Qual. Atmos. Health. 16 (2023), https://doi.org/10.1007/s11869-023-01386-1.

[10] S.P. Wu, X. Li, S.H. Xiao, J. Zhang, J.J. Schwab, Solubility of aerosol minor and trace elements in Xiamen Island, Southeast China: size distribution, health risk and dry deposition, Sci. Total Environ. 844 (2022), https://doi.org/10.1016/j.scitotenv.2022.157100.

[11] Z. Colin-Val, G. Flores-Navarro, L. Rocha-Zavaleta, D.X. Robledo-Cadena, R. O. Quintana-Belmares, R. López-Marure, Fine particulate matter ($PM_{2.5}$) promotes chemoresistance and aggressive phenotype of A549 lung cancer cells, Toxicol. Appl. Pharmacol. 487 (2024) 116955, https://doi.org/10.1016/j.taap.2024.116955.

[12] M. Kampa, E. Castanas, Human health effects of air pollution, Environ. Pollut. 151 (2008), https://doi.org/10.1016/j.envpol.2007.06.012.

[13] S.S. Aithal, I. Sachdeva, O.P. Kurmi, Air quality and respiratory health in children, Breathe 19 (2023), https://doi.org/10.1183/20734735.0040-2023.

[14] Z. Yu, S.K. Merid, T. Bellander, A. Bergström, K. Eneroth, A. Georgelis, J. Hallberg, I. Kull, P. Ljungman, S. Klevebro, M. Stafoggia, G. Wang, G. Pershagen, O. Gruzieva, E. Melén, Associations of improved air quality with lung function

growth from childhood to adulthood: the BAMSE study, Eur. J. Respir. Med. 61 (2023), https://doi.org/10.1183/13993003.01783-2022.
[15] K. Zheng, Z. Zeng, Q. Tian, J. Huang, Q. Zhong, X. Huo, Epidemiological evidence for the effect of environmental heavy metal exposure on the immune system in children, Sci. Total Environ. 868 (2023), https://doi.org/10.1016/j.scitotenv.2023.161691.
[16] M. Oliveira, K. Slezakova, C. Delerue-Matos, M.C. Pereira, S. Morais, Children environmental exposure to particulate matter and polycyclic aromatic hydrocarbons and biomonitoring in school environments: a review on indoor and outdoor exposure levels, major sources and health impacts, Environ. Int. 124 (2019), https://doi.org/10.1016/j.envint.2018.12.052.
[17] T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis, S.M. Almeida, Children's exposure and dose assessment to particulate matter in Lisbon, Build. Environ. 171 (2020), https://doi.org/10.1016/j.buildenv.2020.106666.
[18] S. Kim, K. Kang, D. Park, T. Kim, Assessment of $PM_{2.5}$ penetration based on airflow paths in Korean classrooms, Build. Environ. 248 (2024), https://doi.org/10.1016/j.buildenv.2023.111103.
[19] S. Dubey, R. John, M. Singh, P. Khare, A. Taneja, Seasonal variation in metals concentration associated with settled dust and their risk assessment in school children of Agra (India), Environ. Adv. 15 (2024), https://doi.org/10.1016/j.envadv.2023.100480.
[20] Z. Hashim, S.B. Shamsudin, N.H.M. Hamizul, S.R.M. Fuad, N. Ali, T.T. Song, J. Sieman, M.A. Ma'pol, J.H. Hashim, Indoor air parameters, heavy metals in school indoor air Particulate matter and dust: relationship with respiratory symptoms and lung Iinflammation among students in Kota Kinabalu, Sabah, Mal. J. Med. Health Sci. 20 (4) (2024) 169–177. https://doi:10.47836/mjmhs20.4.21.
[21] J. Xu, H. Zhao, Y. Zhang, W. Yang, X. Wang, C. Geng, Y. Li, Y. Guo, B. Han, Z. Bai, S. Vedal, J. Marshall, Reducing indoor particulate air pollution improves student test scores: a randomized double-blind crossover study, Environ. Sci. Technol. 58 (2024) 8207–8214, https://doi.org/10.1021/acs.est.3c10372.
[22] S. Deng, J. Lau, Z. Wang, P. Wargocki, Associations between illness-related absences and ventilation and indoor $PM_{2.5}$ in elementary schools of the Midwestern United States, Environ. Int. 176 (2023), https://doi.org/10.1016/j.envint.2023.107944.
[23] Y.S. Son, A review on indoor and outdoor factors affecting the level of particulate matter in classrooms of elementary schools, J. Build. Eng. 75 (2023), https://doi.org/10.1016/j.jobe.2023.106957.
[24] T. Nunes, C. Poceiro, M. Evtyugina, M. Duarte, C. Borrego, M. Lopes, Mapping anthropogenic and natural volatile organic compounds around Estarreja chemical industrial complex, WIT Trans. Ecol. Environ. 174 (2013), https://doi.org/10.2495/AIR130051.
[25] M.L. Figueiredo, A. Monteiro, M. Lopes, J. Ferreira, C. Borrego, Air quality assessment of Estarreja, an urban industrialized area, in a coastal region of Portugal, Environ. Monit. Assess. 185 (2013), https://doi.org/10.1007/s10661-012-2989-y.
[26] C. Alves, M. Evtyugina, E. Vicente, A. Vicente, I.C. Rienda, A.S. de la Campa, M. Tomé, I. Duarte, $PM_{2.5}$ chemical composition and health risks by inhalation near a chemical complex, J. Environ. Sci. 124 (2023), https://doi.org/10.1016/j.jes.2022.02.013.
[27] F. Lucarelli, G. Calzolai, M. Chiari, M. Giannoni, D. Mochi, S. Nava, L. Carraresi, The upgraded external-beam PIXE/PIGE set-up at LABEC for very fast measurements on aerosol samples, Nucl. Instrum. Meth. Phys. Res. B. 318 (2014), https://doi.org/10.1016/j.nimb.2013.05.099.
[28] M.I. Asher, Worldwide variations in the prevalence of asthma symptoms: the international study of asthma and allergies in childhood (ISAAC), Eur. J. Respir. Med. 12 (1998), https://doi.org/10.1183/09031936.98.12020315.
[29] P. Krecl, J. Ström, C. Johansson, Diurnal variation of atmospheric aerosol during the wood combustion season in Northern Sweden, Atmos. Environ. 42 (2008), https://doi.org/10.1016/j.atmosenv.2008.01.026.
[30] J. Madureira, I. Paciência, J. Rufo, M. Severo, E. Ramos, H. Barros, E. de Oliveira Fernandes, Source apportionment of CO_2, PM_{10} and VOCs levels and health risk assessment in naturally ventilated primary schools in Porto, Portugal, Build. Environ. 96 (2016), https://doi.org/10.1016/j.buildenv.2015.11.031.
[31] M. Fonseca Gabriel, I. Paciência, F. Felgueiras, J. Cavaleiro Rufo, F. Castro Mendes, M. Farraia, Z. Mourão, A. Moreira, E. de Oliveira Fernandes, Environmental quality in primary schools and related health effects in children. An overview of assessments conducted in the Northern Portugal, Energy Build. 250 (2021), https://doi.org/10.1016/j.enbuild.2021.111305.
[32] J. Madureira, I. Paciência, E. De Oliveira Fernandes, Levels and indoor-outdoor relationships of size-specific particulate matter in naturally ventilated Portuguese schools, J. Environ. Sci. Health, Part A (2012), https://doi.org/10.1080/15287394.2012.721177.
[33] Ü.A. Şahin, K. Scherbakova, B. Onat, Size distribution and seasonal variation of airborne particulate matter in five areas in Istanbul, Turkey, Environ. Sci. Pollut. Res. 19 (2012), https://doi.org/10.1007/s11356-011-0634-x.
[34] M. Viana, I. Rivas, X. Querol, A. Alastuey, M. Álvarez-Pedrerol, L. Bouso, C. Sioutas, J. Sunyer, Partitioning of trace elements and metals between quasi-ultrafine, accumulation and coarse aerosols in indoor and outdoor air in schools, Atmos. Environ. 106 (2015), https://doi.org/10.1016/j.atmosenv.2014.07.027.
[35] M. Viana, I. Rivas, X. Querol, A. Alastuey, J. Sunyer, M. Álvarez-Pedrerol, L. Bouso, C. Sioutas, Indoor/outdoor relationships and mass closure of quasi-ultrafine, accumulation and coarse particles in Barcelona schools, Atmos. Chem. Phys. 14 (2014), https://doi.org/10.5194/acp-14-4459-2014.
[36] M. Braniš, J. Šafránek, A. Hytychová, Indoor and outdoor sources of size-resolved mass concentration of particulate matter in a school gym-implications for exposure of exercising children, Environ. Sci. Pollut. Res. 18 (2011), https://doi.org/10.1007/s11356-010-0405-0.
[37] W. Du, G. Shen, Y. Chen, X. Zhu, S. Zhuo, Q. Zhong, M. Qi, C. Xue, G. Liu, E. Zeng, B. Xing, S. Tao, Comparison of air pollutant emissions and household air quality in rural homes using improved wood and coal stoves, Atmos. Environ. 166 (2017), https://doi.org/10.1016/j.atmosenv.2017.07.029.
[38] F.S. Do Nascimento, R. Losno, J.L. Colin, W.Z. De Mello, H.E. Da Silva, Atmospheric total suspended particulate trace element identification by XRF at Ilha Grande, State of Rio de Janeiro, Brazil, Water, Air, Soil Pollut 214 (2011), https://doi.org/10.1007/s11270-010-0443-8.
[39] W. Wang, J. Yu, Y. Cui, J. He, P. Xue, W. Cao, H. Ying, W. Gao, Y. Yan, B. Hu, J. Xin, L. Wang, Z. Liu, Y. Sun, D. Ji, Y. Wang, Characteristics of fine particulate matter and its sources in an industrialized coastal city, Ningbo, Yangtze River Delta, China, Atmos. Res. 203 (2018), https://doi.org/10.1016/j.atmosres.2017.11.033.
[40] F. Amato, O. Favez, M. Pandolfi, A. Alastuey, X. Querol, S. Moukhtar, B. Bruge, S. Verlhac, J.A.G. Orza, N. Bonnaire, T. Le Priol, J.F. Petit, J. Sciare, Traffic induced particle resuspension in Paris: Emission factors and source contributions, Atmos. Environ. 129 (2016), https://doi.org/10.1016/j.atmosenv.2016.01.022.
[41] I.G. Hetem, M. de Fatima Andrade, Characterization of fine particulate matter emitted from the resuspension of road and pavement dust in the Metropolitan Area of São Paulo, Brazil, Atmosphere 7 (2016), https://doi.org/10.3390/atmos7030031.
[42] S. Vanegas, E.M. Trejos, B.H. Aristizábal, G.M. Pereira, J.M. Hernández, J. H. Murillo, O. Ramírez, F. Amato, L.F.O. Silva, N.Y. Rojas, C. Zafra, J.E. Pachón, Spatial distribution and chemical composition of road dust in two high-altitude Latin american cities, Atmosphere 12 (2021), https://doi.org/10.3390/atmos12091109.
[43] T. Moreno, V. Martins, X. Querol, T. Jones, K. BéruBé, M.C. Minguillón, F. Amato, M. Capdevila, E. de Miguel, S. Centelles, W. Gibbons, A new look at inhalable metalliferous airborne particles on rail subway platforms, Sci. Total Environ. 505 (2015), https://doi.org/10.1016/j.scitotenv.2014.10.013.
[44] M.A.K. Khalil, R.A. Rasmussen, Tracers of wood smoke, Atmos. Environ. 37 (2003), https://doi.org/10.1016/S1352-2310(02)01014-2.
[45] C. Alves, C. Gonçalves, A.P. Fernandes, L. Tarelho, C. Pio, Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types, Atmos. Res. 101 (2011), https://doi.org/10.1016/j.atmosres.2011.04.015.
[46] J.V. Niemi, H. Tervahattu, H. Vehkamäki, M. Kulmala, T. Koskentalo, M. Sillanpää, M. Rantamäki, Characterization and source identification of a fine particle episode in Finland, Atmos. Environ. 38 (2004), https://doi.org/10.1016/j.atmosenv.2004.06.023.
[47] M. Viana, C. Reche, F. Amato, A. Alastuey, X. Querol, T. Moreno, F. Lucarelli, S. Nava, G. Calzolai, M. Chiari, M. Rico, Evidence of biomass burning aerosols in the Barcelona urban environment during winter time, Atmos. Environ. 72 (2013), https://doi.org/10.1016/j.atmosenv.2013.02.031.
[48] M. Manousakas, M. Furger, K.R. Daellenbach, F. Canonaco, G. Chen, A. Tobler, P. Rai, L. Qi, A.H. Tremper, D. Green, C. Hueglin, J.G. Slowik, I. El Haddad, A.S. H. Prevot, Source identification of the elemental fraction of particulate matter using size segregated, highly time-resolved data and an optimized source apportionment approach, Atmos. Environ. X (2022) 14, https://doi.org/10.1016/j.aeaoa.2022.100165.
[49] O. Sippula, K. Hytönen, J. Tissari, T. Raunemaa, J. Jokiniemi, Effect of wood fuel on the emissions from a top-feed pellet stove, Energy Fuel. 21 (2007), https://doi.org/10.1021/ef060286e.
[50] V. Martins, T. Faria, E. Diapouli, M.I. Manousakas, K. Eleftheriadis, M. Viana, S. M. Almeida, Relationship between indoor and outdoor size-fractionated particulate matter in urban microenvironments: levels, chemical composition and sources, Environ. Res. 183 (2020), https://doi.org/10.1016/j.envres.2020.109203.
[51] C.A. Belis, F. Karagulian, B.R. Larsen, P.K. Hopke, Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe, Atmos. Environ. 69 (2013), https://doi.org/10.1016/j.atmosenv.2012.11.009.
[52] W.H. Zoller, E.S. Gladney, R.A. Duce, Atmospheric concentrations and sources of trace metals at the South Pole, Science 183 (1974) (1979) 198–200, https://doi.org/10.1126/science.183.4121.19.
[53] S. Oeder, S. Dietrich, I. Weichenmeier, W. Schober, G. Pusch, R.A. Jörres, R. Schierl, D. Nowak, H. Fromme, H. Behrendt, J.T.M. Buters, Toxicity and elemental composition of particulate matter from outdoor and indoor air of elementary schools in Munich, Germany, Indoor Air 22 (2012), https://doi.org/10.1111/j.1600-0668.2011.00743.x.
[54] F. Sánchez-Soberón, J. Rovira, J. Sierra, M. Mari, J.L. Domingo, M. Schuhmacher, Seasonal characterization and dosimetry-assisted risk assessment of indoor particulate matter ($PM_{10\text{-}2.5}$, $PM_{2.5\text{-}0.25}$, and $PM_{0.25}$) collected in different schools, Environ. Res. 175 (2019), https://doi.org/10.1016/j.envres.2019.05.035.
[55] P. Molnár, T. Bellander, G. Sällsten, J. Boman, Indoor and outdoor concentrations of $PM_{2.5}$trace elements at homes, preschools and schools in Stockholm, Sweden, J. Environ. Monit. 9 (2007), https://doi.org/10.1039/b616858b.
[56] I. Rivas, M. Viana, T. Moreno, M. Pandolfi, F. Amato, C. Reche, L. Bouso, M. Àlvarez-Pedrerol, A. Alastuey, J. Sunyer, X. Querol, Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain, Environ. Int. 69 (2014), https://doi.org/10.1016/j.envint.2014.04.009.
[57] Q. Gao, S. Zhu, K. Zhou, J. Zhai, S. Chen, Q. Wang, S. Wang, J. Han, X. Lu, H. Chen, others, High enrichment of heavy metals in fine particulate matter through dust aerosol generation, Atmos. Chem. Phys. 23 (2023) 13049–13060, https://doi.org/10.5194/acp-23-13049-2023.

[58] M. Zhi, X. Zhang, K. Zhang, S.J. Ussher, W. Lv, J. Li, J. Gao, Y. Luo, F. Meng, The characteristics of atmospheric particles and metal elements during winter in Beijing: Size distribution, source analysis, and environmental risk assessment, Ecotoxicol. Environ. Saf. 211 (2021), https://doi.org/10.1016/j.ecoenv.2021.111937.

[59] X. Querol, M. Viana, A. Alastuey, F. Amato, T. Moreno, S. Castillo, J. Pey, J. de la Rosa, A. Sánchez de la Campa, B. Artíñano, P. Salvador, S. García Dos Santos, R. Fernández-Patier, S. Moreno-Grau, L. Negral, M.C. Minguillón, E. Monfort, J. I. Gil, A. Inza, L.A. Ortega, J.M. Santamaría, J. Zabalza, Source origin of trace elements in PM from regional background, urban and industrial sites of Spain, Atmos. Environ. 41 (2007), https://doi.org/10.1016/j.atmosenv.2007.05.022.

[60] C. Manchanda, M. Kumar, V. Singh, Meteorology governs the variation of Delhi's high particulate-bound chloride levels, Chemosphere 291 (2022), https://doi.org/10.1016/j.chemosphere.2021.132879.

[61] D.T. Tran, L.Y. Alleman, P. Coddeville, J.C. Galloo, Elemental characterization and source identification of size resolved atmospheric particles in French classrooms, Atmos. Environ. 54 (2012), https://doi.org/10.1016/j.atmosenv.2012.02.021.

[62] S. Zhai, J.R. McConnell, N. Chellman, M. Legrand, T. Opel, H. Meyer, L. Jaeglé, K. Confer, K. Fujita, X. Wang, B. Alexander, Anthropogenic influence on tropospheric reactive bromine since the pre-industrial: implications for Arctic ice-core bromine trends, Geophys. Res. Lett. 51 (2024), https://doi.org/10.1029/2023GL107733.

[63] R. Beasley, T. Clayton, J. Crane, E. von Mutius, C.K.W. Lai, S. Montefort, A. W. Stewart, N. Aït-Khaled, H.R. Anderson, M.I. Asher, B. Björkstén, B. Brunekreef, P. Ellwood, L. García-Marcos, S. Foliaki, U. Keil, J. Mallol, C.F. Robertson, E. A. Mitchell, J. Odhiambo, N. Pearce, J. Shah, D. Strachan, S.K. Weiland, G. Weinmayr, H. Williams, G. Wong, M.E. Howitt, J. Weyler, L. de Freitas Souza, D. Rennie, L. Amarales, P. Aguilar, A.M. Cepeda, G. Aristizábal, G.A. Ordoñez, M. A. Riikjärv, G. Zsigmond, S. Rego, P.S. Suresh Babu, V. Singh, K.C. Jain, T. U. Sukumaran, S. Awasthi, M.K. Joshi, A.V. Pherwani, S.N. Mantri, S. Salvi, S. K. Sharma, N.M. Hanumante, S. Bhave, C.B. Kartasasmita, M.R. Masjedi, A. Steriu, H. Odajima, C. Imanalieva, J. Kudzyte, K.H. Teh, B.S. Quah, B.E. Del-Río-Navarro, M. Barragán-Meijueiro, R. García-Almaraz, M. Baeza-Bacab, J.V. Merida-Palacio, S. N. González-Díaz, F.J. Linares-Zapién, S. Romero-Tapia, C. Moyes, P. Pattemore, R. MacKay, B.O. Onadeko, G. Cukier, G. Lis, A. Brêborowicz, R. Câmara, J. E. Rosado Pinto, C. Nunes, J.M. Lopes dos Santos, D.Y.T. Goh, H.B. Lee, A. López-Silvarrey Varela, I. Carvajal-Uruëa, R.M. Busquets, C. González Díaz, G. Garcia-Hernández, M.M.M. Suárez-Varela, O. Al-Rawas, Y. Mohammad, S. Mohammad, J. L. Huang, C.C. Kao, P. Vichyanond, M. Trakultivakorn, M.C. Lapides, O. Aldrey, Association between paracetamol use in infancy and childhood, and risk of asthma, rhinoconjunctivitis, and eczema in children aged 6-7 years: analysis from Phase Three of the ISAAC programme, Lancet 372 (2008), https://doi.org/10.1016/S0140-6736(08)61445-2.

[64] H. Farquhar, A. Stewart, E. Mitchell, J. Crane, S. Eyers, M. Weatherall, R. Beasley, The role of paracetamol in the pathogenesis of asthma, Clin. Exp. Allergy 40 (2010), https://doi.org/10.1111/j.1365-2222.2009.03378.x.

[65] S.K. Weiland, K.A. Mundt, A. Rückmann, U. Keil, Self-reported wheezing and allergic rhinitis in children and traffic density on street of residence, Ann. Epidemiol. 4 (1994), https://doi.org/10.1016/1047-2797(94)90103-1.

[66] S. Singh, B.B. Sharma, S. Salvi, J. Chhatwal, K.C. Jain, L. Kumar, M.K. Joshi, S. B. Pandramajal, S. Awasthi, S. Bhave, S. Rego, T.U. Sukumaran, V.A. Khatav, V. Singh, S.K. Sharma, M. Sabir, Allergic rhinitis, rhinoconjunctivitis, and eczema: prevalence and associated factors in children, Clin. Respir. J. 12 (2018), https://doi.org/10.1111/crj.12561.

[67] I. Annesi-Maesano, D. Moreau, D. Caillaud, F. Lavaud, Y. Le Moullec, A. Taytard, G. Pauli, D. Charpin, Residential proximity fine particles related to allergic sensitisation and asthma in primary school children, Respir. Med. 101 (2007), https://doi.org/10.1016/j.rmed.2007.02.022.

[68] B. Hosseini, B.S. Berthon, P. Wark, L.G. Wood, Effects of fruit and vegetable consumption on risk of asthma, wheezing and immune responses: a systematic review and meta-analysis, Nutrients 9 (2017), https://doi.org/10.3390/nu9040341.

[69] L. Chatzi, G. Apostolaki, I. Bibakis, I. Skypala, V. Bibaki-Liakou, N. Tzanakis, M. Kogevinas, P. Cullinan, Protective effect of fruits, vegetables and the Mediterranean diet on asthma and allergies among children in Crete, Thorax 62 (2007), https://doi.org/10.1136/thx.2006.069419.

[70] J. Johnson, A. Malinovschi, J. Lidholm, C.J. Petersson, L. Nordvall, C. Janson, K. Alving, M.P. Borres, Sensitization to storage proteins in peanut and hazelnut is associated with higher levels of inflammatory markers in asthma, Clin. Mol. Allergy 18 (2020), https://doi.org/10.1186/s12948-020-00126-5.

[71] Y. Taniguchi, S. Yamazaki, T. Michikawa, S.F. Nakayama, M. Sekiyama, H. Nitta, H. Mezawa, M. Saito-Abe, M. Oda, H. Mitsubuchi, M. Sanefuji, S. Ohga, N. Mise, A. Ikegami, M. Shimono, R. Suga, Associations of dog and cat ownership with wheezing and asthma in children: pilot study of the Japan Environment and children's study, PLoS One 15 (2020), https://doi.org/10.1371/journal.pone.0232604.

[72] B. Brunekreef, E. Von Mutius, G. Wong, J. Odhiambo, L. García-Marcos, S. Foliaki, Exposure to cats and dogs, and symptoms of asthma, rhinoconjunctivitis, and eczema, Epidemiology 23 (2012), https://doi.org/10.1097/EDE.0b013e318261f040.

[73] K. Yamamoto-Hanada, L. Yang, M. Narita, H. Saito, Y. Ohya, Influence of antibiotic use in early childhood on asthma and allergic diseases at age 5, Ann. Allergy Asthma Immunol. 119 (2017), https://doi.org/10.1016/j.anai.2017.05.013.

[74] Z. Lin, D. Norback, T. Wang, X. Zhang, J. Shi, H. Kan, Z. Zhao, The first 2-year home environment in relation to the new onset and remission of asthmatic and allergic symptoms in 4246 preschool children, Sci. Total Environ. 553 (2016), https://doi.org/10.1016/j.scitotenv.2016.02.040.

[75] E. Migliore, N. Pearce, M. Bugiani, G. Galletti, A. Biggeri, L. Bisanti, N. Caranci, V. Dell'Orco, M. De Sario, P. Sestini, S. Piffer, G. Viegi, F. Forastiere, C. Galassi, G. Ciccone, D. Mirabelli, G. Berti, E. Cadum, P. Piccioni, A. Russo, F. Rusconi, M. Bellasio, V. Gianelle, L. Battisti, D. Kaisermann, M. Gentilini, G. Giannella, F. Talassi, G. Frasca, M. Biocca, E. De Munari, E. Chellini, E. Lombardi, C. Gabellini, D. Grechi, M.G. Petronio, M. Simoni, N. Agabiti, R. Pistelli, G. Corbo, E. Bonci, L. Indinnimeo, L. Armenio, L. Brunetti, M. Cavone, M.L. Lospalluti, M. Massagli, G. Polieri, D. Rizzi, F.R. Rana, M. Rana, S. La Grutta, Prevalence of respiratory symptoms in migrant children to Italy: the results of SIDRIA-2 study, Allergy: euro, J. Allergy Clin. Immunol. 62 (2007), https://doi.org/10.1111/j.1398-9995.2007.01238.x.

[76] C.E. Rutter, R.J. Silverwood, H.C. Williams, P. Ellwood, I. Asher, L. Garcia-Marcos, D.P. Strachan, N. Pearce, S.M. Langan, N. Aït-Khaled, H.R. Anderson, M.I. Asher, R. Beasley, B. Björkstén, B. Brunekreef, J. Crane, C. Flohr, S. Foliaki, F. Forastiere, U. Keil, C.K.W. Lai, J. Mallol, E.A. Mitchell, S. Montefort, J. Odhiambo, C. F. Robertson, A.W. Stewart, E. von Mutius, S.K. Weiland, G. Weinmayr, G. Wong, T. O. Clayton, E. Ellwood, C.E. Baena-Cagnani, M. Gómez, M.E. Howitt, J. Weyler, R. Pinto-Vargas, C. Petrolera de Salud, A.J.D.A. Cunha, L. de Freitas Souza, C. Kuaban, A. Ferguson, D. Rennie, P. Standring, P. Aguilar, L. Amarales, L. A. Benavides, A. Contreras, Y.Z. Chen, O. Kunii, Q.L. Pan, N.S. Zhong, G. Aristizábal, A.M. Cepeda, G.A. Ordoñez, C. Bustos, M.A. Riikjärv, K. Melaku, R. Sa'aga-Banuve, J. Pekkanen, I.E. Hypolite, Z. Novák, G. Zsigmond, S. Awasthi, S. Bhave, N.M. Hanumante, K.C. Jain, M.K. Joshi, S.N. Mantri, A.V. Pherwani, S. Rego, M. Sabir, S. Salvi, G. Setty, S.K. Sharma, V. Singh, T. Sukumaran, P. S. Suresh Babu, C.B. Kartasasmita, P. Konthen, W. Suprihati, M.R. Masjedi, A. Steriu, B.N. Koffi, H. Odajima, J.A. al-Momen, C. Imanalieva, J. Kudzyte, B. S. Quah, K.H. Teh, M. Baeza-Bacab, M. Barragán-Meijueiro, B.E. Del-Río-Navarro, R. García-Almaráz, S.N. González-Díaz, F.J. Linares-Zapién, J.V. Merida-Palacio, N. Ramírez-Chanona, S. Romero-Tapia, I. Romieu, Z. Bouayad, R. MacKay, C. Moyes, P. Pattemore, B.O. Onadeko, G. Cukier, P. Chiarella, F. Cua-Lim, A. Brêborowicz, D. Solé, M. Sears, V. Aguirre, S. Barba, J. Shah, K. Baratawidjaja, S. Nishima, J. de Bruyne, N. Tuuau-Potoi, B.W. Lee, A. El Sony, Are environmental factors for atopic eczema in ISAAC phase three due to reverse causation? J. Investig. Dermatol. 139 (2019) https://doi.org/10.1016/j.jid.2018.08.035.

[77] J. Madureira, I. Paciência, J. Rufo, E. Ramos, H. Barros, J.P. Teixeira, E. de Oliveira Fernandes, Indoor air quality in schools and its relationship with children's respiratory symptoms, Atmos. Environ. 118 (2015), https://doi.org/10.1016/j.atmosenv.2015.07.028.