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

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

3  
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15

16 **Abstract**

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

36 **Keywords**

37 Particle size distributions; Elemental concentrations; Schoolchildren; ISAAC; Asthma  
38 and rhinitis.

39

40

## 41 1. Introduction

42 Industrial areas are often considered major sources of environmental pollution as they  
43 release numerous pollutants such as particulate matter (PM) and gases. Studies carried  
44 out to identify the concentrations, size distributions, chemical composition and temporal  
45 characteristics of PM have reported that atmospheric emissions from industrial activities  
46 may contain iron, carbon and smaller elements such as lead, aluminium, zinc, manganese,  
47 chromium, cadmium, copper, nickel, titanium, vanadium and other trace metals [1–4].  
48 For example, the different sizes of PM released into the atmosphere during smelting vary  
49 depending on several factors, such as the composition of the original ore and the high  
50 melting temperature and/or additives used in the process, so the size distributions,  
51 concentrations, chemical components and toxicological properties can have different  
52 negative impacts on public health [5].

53 Many studies have shown that particle-induced health effects depend on their size and  
54 chemical composition, affecting different age groups unevenly [6,7]. In the case of  
55 children, vulnerability is due to their higher breathing rate, lower body mass, incomplete  
56 metabolic system, immature host defence and outdoor activity patterns [8,9]. The size  
57 distribution and density of particles define the site of deposition in the respiratory tract,  
58 while physiological and anatomical parameters affect the deposition profile [10]. On the  
59 other hand, the elemental composition, although it represents a small percentage of the  
60 total mass of PM, may be a cause of concern due to its toxic properties [11]. PM is an  
61 important transporter of various metals and long-term air pollution can lead to continued  
62 children's exposure to these constituents. Air pollution exposure to some metals can  
63 trigger immune responses in children, as well as disruption of the blood-brain barrier,  
64 resulting in compromised neurological and immunological function in the brain [12].  
65 Furthermore, in a study involving the use of A549 lung adenocarcinoma cells exposed to  
66 high concentrations of particles lower than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) it was concluded that lung  
67 cancer patients from polluted urban areas can develop more aggressive tumour  
68 phenotypes, with enhanced cell proliferation, migration, and chemoresistance [13]. It has  
69 been documented that PM-bound metals are involved in many cellular mechanisms,  
70 affecting different systems and organs [14].

71 There is public concern about the health risks arising from the proximity to petrochemical  
72 industries, since contaminants from these activities have been associated with some  
73 diseases. Liu et al.[15] found that changes in concentrations of industrial pollutants  
74 influence rates of childhood asthma development in small towns. According to the  
75 authors, depending on the industrial emission sources and the chemical composition,  
76  $\text{PM}_{2.5}$  can be more or less toxic, and consequently influence the development of asthma  
77 differently. In fact, the association between asthma and  $\text{PM}_{2.5}$  emitted by metal smelters  
78 was higher compared to that found for the pulp and paper mill sector. In another study  
79 carried out in a region in the Netherlands with a high concentration of industries and low  
80 traffic density, researchers identified that exposure to air pollution was associated with  
81 adverse birth outcomes occurring between 2012 and 2017. Increased exposure to  $\text{PM}_{10}$ ,  
82  $\text{NO}_x$ ,  $\text{SO}_2$ , and volatile organic compounds (by interquartile range of 0.41, 1.16, 0.42 and

83 0.97  $\mu\text{g m}^{-3}$ , respectively), corresponded to an average decrease in birth weight of 21 g to  
84 30 g [16].

85 In Portugal, the small-town of Estarreja account for 20% of the country's chemical  
86 industry [17]. Since 1985, an air quality monitoring station has provided continuous  
87 monitoring of air quality near the Estarreja Chemical Complex (ECC). Some studies have  
88 also been carried out with the aim of evaluating the impact of industrial activity [18]. For  
89 instance, Figueiredo et al. [18] showed that although industrial activities represented  
90 around 80% of the municipality's total emissions between 2001-2009, levels decreased  
91 for almost all pollutants analysed for the same period, but  $\text{PM}_{10}$  and  $\text{O}_3$  consecutively  
92 exceeded the regulated standards. In a more recent study, Alves et al. [19] verified that  
93 the annual average values of  $\text{PM}_{2.5}$  in Estarreja have approached or exceeded the World  
94 Health Organisation (WHO) guideline ( $10 \mu\text{g m}^{-3}$ ) but remained within the acceptable  
95 values set by European legislation ( $< 25 \mu\text{g m}^{-3}$ ). However, in the same study, when  
96 researchers analysed  $\text{PM}_{2.5}$  samples in the vicinity of the industrial chemical hub, they  
97 found many toxic compounds (e.g., aromatic ketones, ethylene glycol) and observed that  
98 the levels of some metals and plasticisers peaked when winds blew from the industrial  
99 area.

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

117

## 118 **2. Methodology**

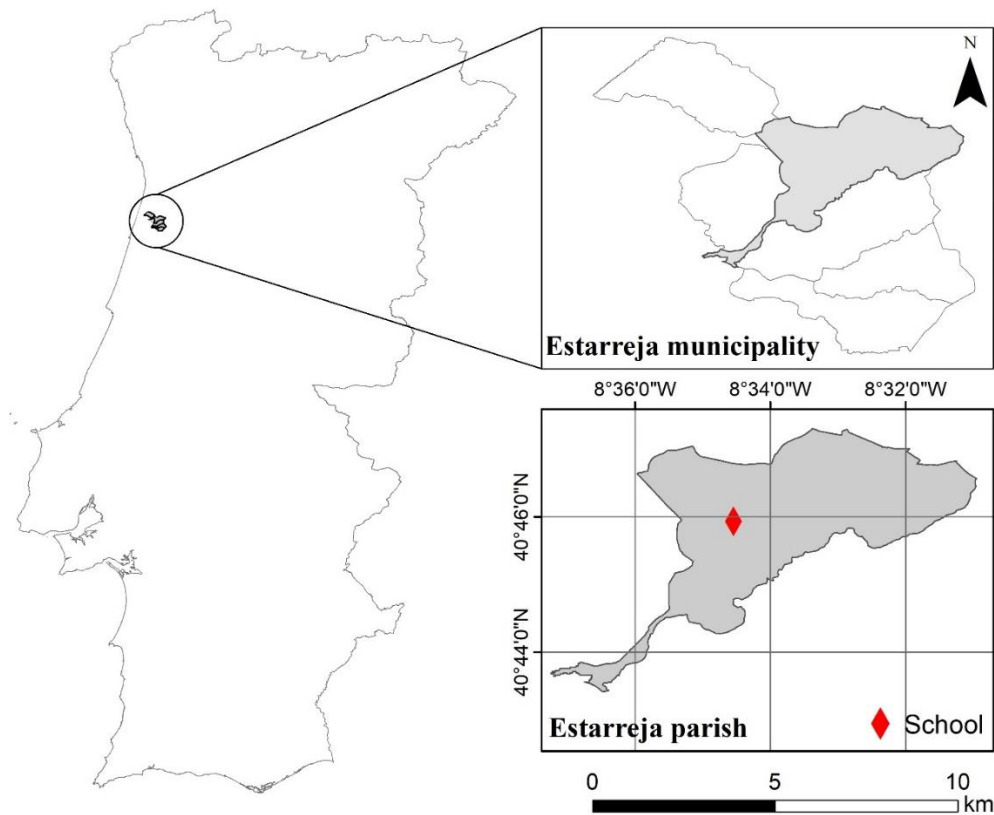
119

### 120 **2.1. Characteristics of the school and study population**

121 The study area covers a school surrounded by low-rise buildings, a small parking lot and  
122 a railway line. The Estarreja Chemical Complex is located approximately 1 km to the  
123 north (**Fig.1**). In the 1930s, several industrial units were installed in Estarreja. The first

124 unit was dedicated to chlorine and caustic soda production [18]. Nowadays the ECC,  
125 located north of the town, covers an area of around 290 ha and is made up of various  
126 industrial, commercial, storage and service activities, which include, among others, the  
127 production of nitric acid, aniline and nitrobenzene, sodium and chlorate compounds,  
128 polyvinyl chloride and polyurethanes [18,19]. The town is also affected by intensive and  
129 extensive farming emissions, as well as road traffic.

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



135

136 **Figure 1.** Study area. The location where data collection was carried out is marked with a red  
137 diamond.  
138

## 139 2.2. Sampling methodology

140 Two Personal Cascade Impactor Samplers (PCIS) operating at 9 L/min were used to  
141 collect simultaneous samples of particulate matter in a classroom (indoor) and in the  
142 schoolyard (outdoor). Sampling was carried out in winter 2022 and spring 2023 for 4  
143 weeks in each season respectively. Sampling periods began on Monday afternoon and  
144 ended on Friday afternoon. At the end of each week, the indoor PCIS was moved to a  
145 classroom in another building. In total, 4 rooms were monitored, one in each school  
146 building (Table 1). The PCIS was used to separate and collect particles in five size ranges

147 ( $\mu\text{m}$ ): 10–2.5 (coarse particles), 1.0-2.5, 0.50-1.0, 0.25-0.50, and  $< 0.25$  quasi-ultrafine  
 148 (q-UFP). Particles above each cut-point were collected on a 25-mm Teflon filter in each  
 149 appropriate stage. Particles lower than the 0.25-micron cut-point were collected on a 37-  
 150 mm PTFE after-filter. After gravimetric determination of mass concentrations for all size  
 151 ranges, the samples were analysed by particle-induced X-ray emission (PIXE) at the  
 152 INFN laboratory (Florence, Italy) to obtain the elemental composition. A detailed  
 153 description of the PIXE technique is provided in Lucarelli et al. [20].

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

160 **Table 1.** Description of sampling in the indoor environment.

Measurement periods*	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	1 <sup>st</sup> cycle, 1 <sup>st</sup> grade; room attended by the same class; age group between 6 and 7 years
Third week Nov - Dec 2022 April – May 2023	Room A; 2 <sup>nd</sup> cycle, 5 <sup>th</sup> and 6 <sup>th</sup> grades; room attended by different classes; age group between 10 and 11 years
Fourth week Dec 2022 May 2023	Room B; 2 <sup>nd</sup> cycle, 5 <sup>th</sup> and 6 <sup>th</sup> grades; room attended by different classes; age group between 10 and 11 years

161 \*Samples taken in 2022 correspond to the winter campaign, while measurements taken in 2023  
 162 correspond to the spring campaign.

### 163 **2.3. Exposure to environmental factors**

164 A questionnaire based on the International Study of Asthma and Allergy in Children  
 165 (ISAAC) [21] was given to each classroom teacher to be distributed to parents or legal  
 166 guardians who filled out the various fields. Parents were provided with a description of  
 167 the project on the first page of the questionnaire. The main objective of this survey was  
 168 to assess the prevalence of respiratory symptoms in children and characterise  
 169 environmental factors and other possible sources of domestic air pollution (Table S1,  
 170 Supplementary Material). Based on the information provided in the questionnaire, the  
 171 variables related to exposure to environmental factors were classified into three groups:  
 172 personal factors, housing conditions and dietary habits. Personal factors included the

173 child's gender, age and breastfeeding. Factors related to home environment included  
174 frequency of trucks on the street, distance from the industrial complex, living with a  
175 smoker and household pets.

176

## 177 **2.4. Data analysis**

178

### 179 **2.4.1. Logistic regression models**

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

196

## 197 **3. Results and Discussion**

198

### 199 **3.1. Air quality at school**

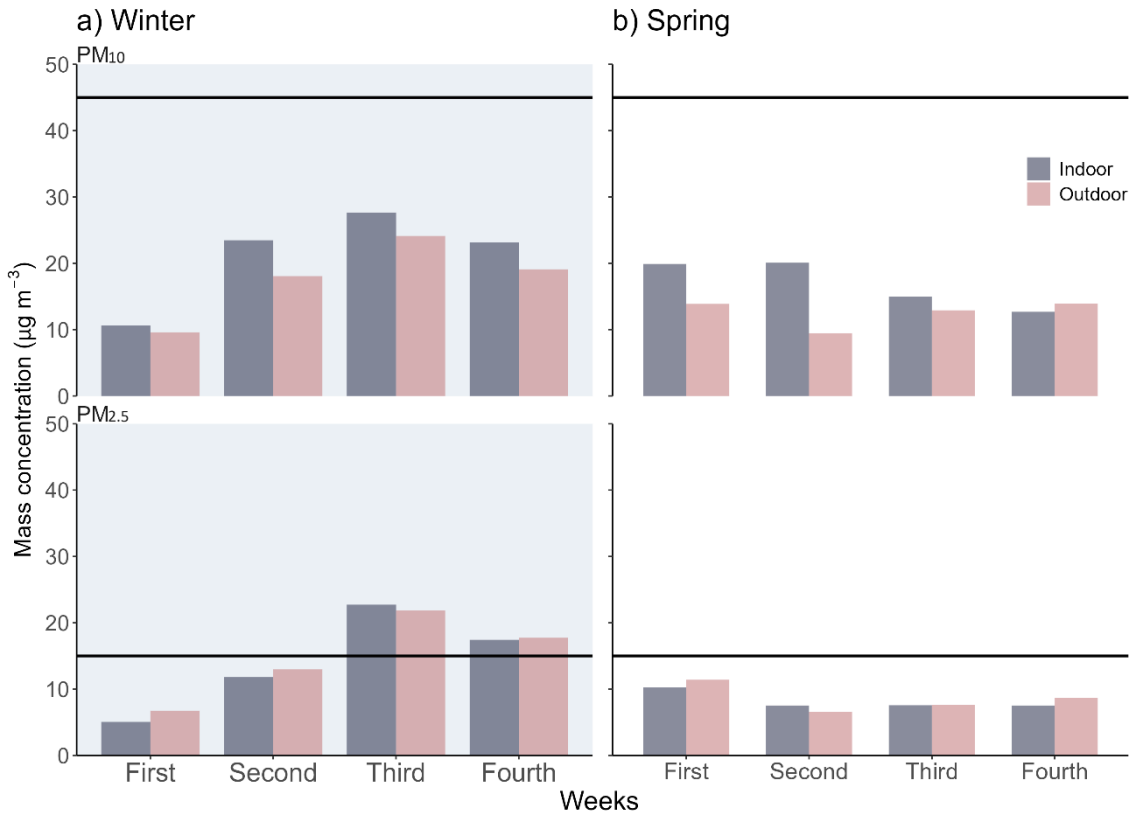
200

#### 201 **3.1.1. Size segregated particulate matter concentrations**

202 **Figure 2** shows the mass concentrations of PM in classrooms and the schoolyard. The  
203 global averages obtained for PM<sub>10</sub> and PM<sub>2.5</sub> in the two campaigns were 19.1 and 11.2  
204  $\mu\text{g m}^{-3}$  in classrooms and 15.1 and 11.7  $\mu\text{g m}^{-3}$  outdoors, respectively. Both indoors and  
205 outdoors, the lowest values were recorded in the first week of winter, coinciding with  
206 intense precipitation that possibly contributed to the washout of particulate pollution.  
207 Except for the first week, winter concentrations were significantly higher in classrooms  
208 and in the schoolyard than those in spring. The highest concentrations of PM<sub>2.5</sub> and PM<sub>10</sub>  
209 in both environments were recorded in the third week of winter, when low wind speeds  
210 and lower precipitation and air temperature values were recorded compared to other  
211 weeks of the same season (**Table S3**, Supplementary Material). More unfavourable  
212 atmospheric dispersion conditions, especially at night, and the intensification of  
213 residential biomass combustion may have contributed to the higher concentrations of PM



214 observed in this period [22]. Although the school samples corresponded to a period longer  
 215 than 24 hours, PM<sub>10</sub> never exceeded the daily WHO guidelines (45 µg m<sup>-3</sup>), while in the  
 216 last two weeks of winter the concentrations of PM<sub>2.5</sub> in the schoolyard and in the  
 217 classrooms were higher than the value recommended by that organisation (25 µg m<sup>-3</sup>).



218  
 219 **Figure 2.** Mass concentrations of PM in a) winter and b) spring. The top panel shows PM<sub>10</sub> and  
 220 the bottom panel PM<sub>2.5</sub>. The black line represents the WHO guidelines for PM<sub>10</sub> and PM<sub>2.5</sub> (45  
 221 and 15 µg m<sup>-3</sup>, respectively) for 24 hours.  
 222

223 The indoor-to-outdoor (I/O) ratio for PM<sub>10</sub> was higher than for PM<sub>2.5</sub> (Table 2), probably  
 224 due to indoor sources previously reported in other school environments in Portugal, such  
 225 as the release of clothing and paper fibres, peeling of the skin and, above all, resuspension  
 226 of mineral dust. It has been shown that these sources, combined with poor ventilation,  
 227 contribute to high levels of coarse material in the indoor air of school microenvironments  
 228 [23,24]. According to Madureira et al. [25], student activities in classrooms affect the I/O  
 229 ratios of PM<sub>2.5</sub>, since a decrease from day to night from 0.83 to 0.64 was observed in the  
 230 42 classrooms studied. It has been argued that a significant mass fraction of PM in the  
 231 outdoor environment is due to fine particles emitted either by primary sources, such as  
 232 road traffic, industry and biomass burning, or formed secondarily by photochemical  
 233 reactions in the atmosphere.

234 **Table 2.** Concentrations (µg m<sup>-3</sup>) and seasonal proportions of PM<sub>2.5</sub> and PM<sub>10</sub> in  
 235 classrooms and the schoolyard.

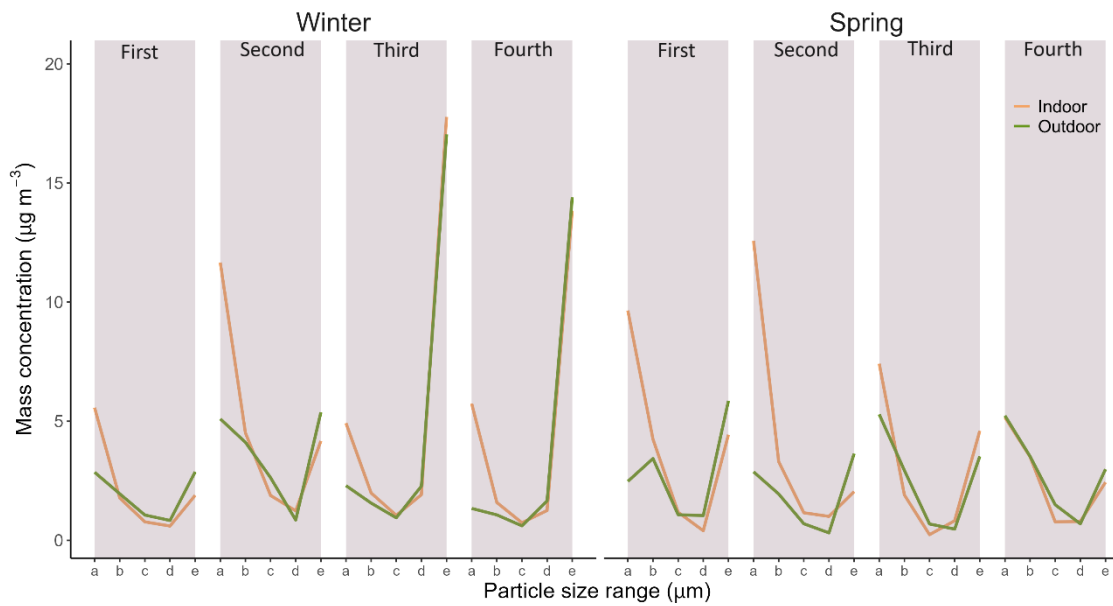
	PM <sub>2.5</sub>		PM <sub>10</sub>		PM <sub>2.5</sub>		PM <sub>10</sub>	
	Winter	I/O	Spring	I/O	Winter	I/O	Spring	I/O
First week	5.05	0.75	10.3	0.90	10.6	1.11	20.0	1.43

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

236

237 The seasonal particle size distributions as a function of mass median aerodynamic  
 238 diameter (MMAD) and geometric standard deviation (GSD) are shown in **Table S4**,  
 239 Supplementary Material. PM presented lower MMAD in the schoolyard than in the  
 240 classrooms and all samples contained polydisperse particles (GSD > 1.2) in both seasons.  
 241 It was evidenced that PM contained a greater proportion of smaller particles in winter  
 242 (MMAD between 0.18 and 1.05) when compared to spring (MMAD between 0.61 and  
 243 1.67). In this study, outdoor PM samples presented an average MMAD of 0.62 and 1.21,  
 244 while for indoor samples the diameters were 1.40 and 2.43 in winter and spring,  
 245 respectively. Şahin et al. [26] collected samples at 7 points in Istanbul over a period of  
 246 two years and found a similar pattern, although with MMAD values higher than those  
 247 estimated in this study. The authors observed a decrease in the fraction of fine PM during  
 248 the summer period, which was attributed to the decrease in the use of fuels for domestic  
 249 heating. This behaviour was clearly identified at the station located in the residential area  
 250 of Rasathane, where the smallest MMAD was observed in winter.

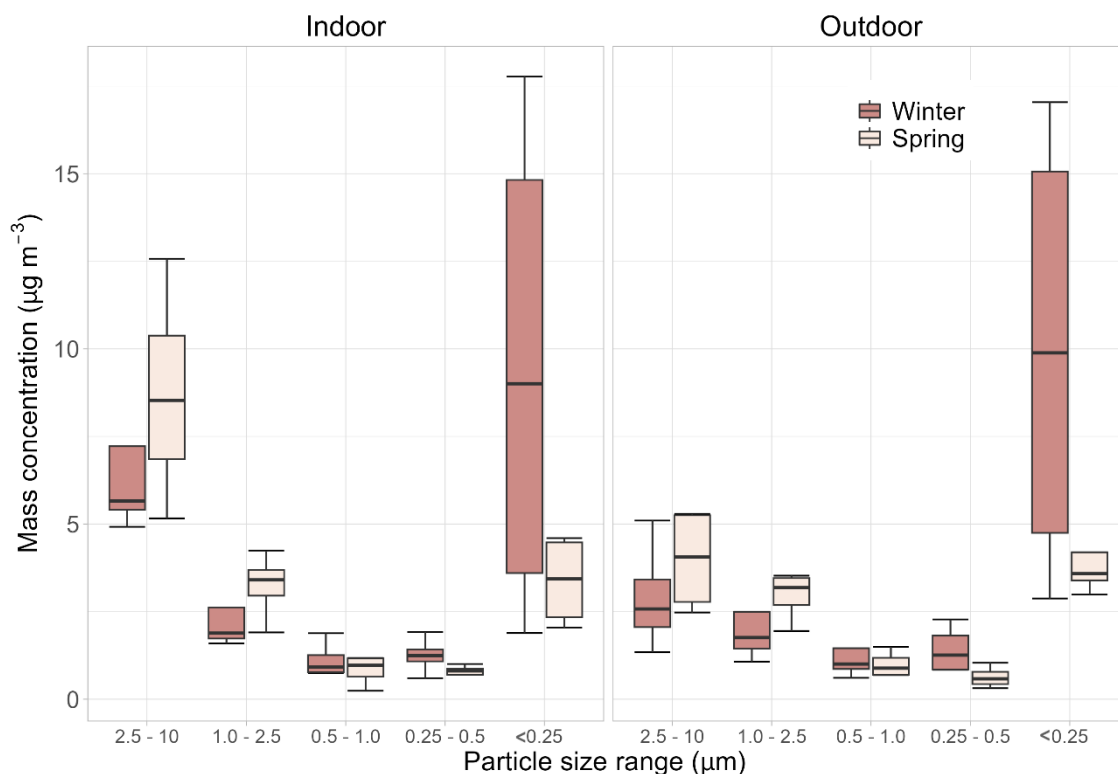
251 The PM size distributions depicted in **Fig. 3** for both winter and spring show a  
 252 comparatively greater variability for coarse fractions and a smaller variability for q-UFP.  
 253 This may be due to the activities carried out in the classrooms, since the I/O for PM<sub>10</sub> was  
 254 higher than 1 in both seasons. This observation is well in line with the study by Viana et  
 255 al. [27], who reported higher mean PM<sub>10</sub> concentrations than the corresponding outdoor  
 256 levels for 39 primary schools across Barcelona (Spain). Whether outdoors or indoors, q-  
 257 UFP displayed higher concentrations compared to other particle size fractions in the last  
 258 two weeks of winter. The average mass concentrations of PM<sub>0.25</sub> in the schoolyard were  
 259 17.0 and 14.4 µg m<sup>-3</sup>, which were 7.4 and 10.7 times higher than the PM<sub>2.5-10</sub> levels. These  
 260 peak concentration values were found when the air temperature was below 14 °C and  
 261 weak wind conditions prevailed, with average speeds below 0.84 m s<sup>-1</sup>. In this period, the  
 262 winds blew from SE, indicating contributions from the residential area of the town.



263  
264  
265  
266  
267  
268  
269

**Figure 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).

270 It was observed that  $PM_{2.0-10}$  concentrations in classrooms were higher in spring, contrary  
271 to what happened with q-UFP (**Fig. 4**). In winter, the concentration of indoor q-UFP  
272 particles was up to 5.7 times higher than in spring. Comparisons with the literature  
273 indicate that the concentrations quantified at the school are lower than the values obtained  
274 in other places around the world. For example, Viana et al. [28] reported that the average  
275 concentration of q-UFP measured in several schools in Barcelona between January and  
276 June was  $25.6 \mu\text{g m}^{-3}$  outdoors and  $23.4 \mu\text{g m}^{-3}$  indoors. Furthermore, when compared to  
277 studies in residential environments, concentrations in this school are largely lower. Braniš  
278 et al. [29] found that the average outdoor q-UFP concentration ( $10.9 \mu\text{g m}^{-3}$ ) measured by  
279 cascade impactors was higher than the indoor value ( $9.90 \mu\text{g m}^{-3}$ ) in an elementary school  
280 gym and an adjacent outdoor location in the central part of Prague between 2005 and  
281 2009. They showed that the correlation coefficient ( $r$ ) between the corresponding sizes of  
282 outdoor and indoor aerosols increased with decreasing aerodynamic diameter of the  
283 collected particles, indicating a higher infiltration rate of almost q-UFP. However, the  
284 outdoor > indoor pattern may be different for other non-school environments, as observed  
285 by Du et al. [30] in India, who documented indoor (kitchen) and outdoor (in the backyard  
286 of each house) concentrations in rural homes that used improved wood stoves of 77 and  
287  $25 \mu\text{g m}^{-3}$ , respectively.



288

289 **Figure 4.** Size segregated particle mass concentrations for all sample sets in both seasons.

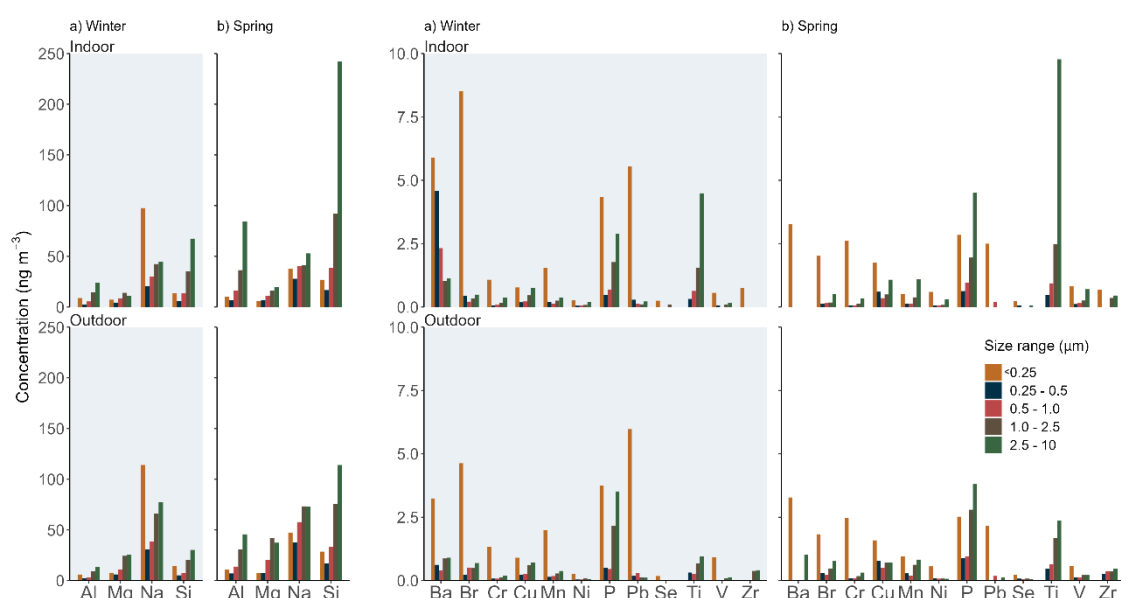
290 A close value between winter and spring was obtained for particles in the aerodynamic  
 291 diameter ranges 0.5-1.0  $\mu\text{m}$  (stage c) and 0.25 -0.5  $\mu\text{m}$  (stage d) both indoors and outdoors  
 292 (**Fig. 4**). However, for the q-UFP range in winter, indoor and outdoor concentrations were  
 293 much higher than those observed in spring. In winter, the indoor (9.4  $\mu\text{g m}^{-3}$ ) and outdoor  
 294 (9.9  $\mu\text{g m}^{-3}$ ) concentrations were, on average, 3.8 and 3.7 times higher than the spring  
 295 levels (I/O ratio for q-UFP = 0.9 in both seasons). This difference points to the prevalence  
 296 of residential biomass burning in winter, whose emissions of mostly ultrafine particles  
 297 have an enormous capacity to infiltrate from outside to inside classrooms. As for coarse  
 298 particles, the differences observed between classrooms and the schoolyard in winter and  
 299 spring may indicate the presence of specific indoor sources, such as dust resuspension  
 300 (I/O ratio for coarse particles > 2.2 in both seasons). Furthermore, while in the schoolyard  
 301 the contribution of coarse particles to the mass of  $\text{PM}_{10}$  increased from winter (1.34  $\mu\text{g}$   
 302  $\text{m}^{-3}$ ) to spring (5.29  $\mu\text{g m}^{-3}$ ), the opposite behaviour was observed with q-UFP particles,  
 303 whose concentration varied from a minimum value of 14.4  $\mu\text{g m}^{-3}$  in winter to just 2.99  
 304  $\mu\text{g m}^{-3}$  in spring (**Fig. S2**, Supplementary Material). Thus, in winter, q-UFP represented a  
 305 substantial fraction of  $\text{PM}_{10}$ , accounting for up to 75% of its mass in the schoolyard and  
 306 up to 64% in the classrooms. The high levels of q-UFP particles in winter suggest the  
 307 impact of specific sources that act in this season, mainly affecting concentrations in the  
 308 outdoor environment. Contrarily, in spring, coarse particles (2.5 – 10  $\mu\text{m}$ ) were the main  
 309 contributor to  $\text{PM}_{10}$  in classrooms, constituting mass fractions between 40% and 62%.

310

311 **3.1.2. Chemical constituents**

312 The concentrations of elements detected in PM are shown in **Table S5**, Supplementary  
 313 Material. The particle size segregated composition of some elements is depicted in **Fig.**  
 314 **5**. High concentrations of Na, S, Cl and K (winter) and K and S (spring) were observed  
 315 in the q-UFP fraction both outdoors and indoors. In turn, high concentrations were  
 316 observed in the PM<sub>2.5-10</sub> fraction for Ca and Cl in winter and Ca, Cl and Si in spring. In  
 317 general, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe were found in all PM sizes in both  
 318 seasons, while other elements such as V, Cr, Ni, Se, Rb, Sr, Y, Zr, Mo, Ba and Pb were  
 319 only detected in some PM granulometries. Ti was detected in all particle samples larger  
 320 than 0.25 µm. The coarse fraction samples (stage a) mainly contained a variety of  
 321 different elements typical of mineral matter (Si, Ca, Mg, Al, Fe). The highest  
 322 concentrations of these elements were observed in both indoor and outdoor samples in  
 323 spring (**Fig. 5**), which can be explained by the increase in dust resuspension from both  
 324 road mobility and agricultural activities in the surroundings, phenomena that are  
 325 enhanced by the scarcity of precipitation in this drier season.

326



327

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

331

332 In general, the outdoor and indoor environments showed higher elemental concentrations  
 333 in stage b (Dp: 1.0 -2.5 µm) than in the other stages (25 and 27%, respectively). However,  
 334 in spring, stage c (0.5-1.0 µm) in classrooms (78%) and stage d (0.25 -0.5 µm) in the  
 335 schoolyard (68%) were those that presented the highest elemental contribution compared  
 336 to the other particle sizes (**Table S6** Supplementary material). The mineral fraction was  
 337 higher in spring than in winter. Elements such as Al, Ca, Fe, K, Mg, Mn, Na and Ti  
 338 contributed, on average, 20% of the total elemental mass concentrations in PM<sub>0.5</sub> (stage  
 339 c) at the schoolyard, and 30% (stage c) in the indoor environment. In the finest fraction  
 340 (PM<sub>0.25</sub>), the elemental load represented less than 13% of the total mass for this size range

341 in the schoolyard in winter and 33% in spring. However, for  $PM_{0.25}$ , K and S were the  
342 ones that contributed most to the total elemental mass in winter (34% both, at the  
343 schoolyard), while in spring, the most abundant was S (71 and 70%, indoors and outdoors,  
344 respectively). Furthermore, a cluster analysis by particle size showed that both K and S  
345 in the schoolyard belonged to a separate group (Fig. S5, Supplementary material). P, on  
346 the other hand, was detected in both seasons. In winter, the highest values were recorded  
347 in the finest fraction (stage e) in the schoolyard, while in spring, the highest  
348 concentrations were observed in the coarsest fraction (stage a). In winter, no positive  
349 correlations were found between P (stage e) with other elements, but in spring, P (stage  
350 a) correlated well ( $p < 0.05$ ) with Cu, Cr and V. P is carried by dust particles, cloud  
351 droplets and dissolved in rainwater. It may be associated with the use of fertilisers,  
352 cleaning products and other chemicals [31].

353 The contributions of Zn, Fe, Pb, Ni, Cr, Mn and V are typically associated with industrial  
354 activities in the vicinities, such as foundries and metallurgical industries [32]. The  
355 concentrations quantified in this study were lower when compared to their levels reported  
356 in other locations influenced by industries. Elements such as Ba, Br, Cr, Cu, Mn, V and  
357 Ni presented the highest values in the  $PM_{0.25}$  fraction (**Fig. 6**). Pb was detected mainly in  
358 winter, while Se, V and Zr were identified with greater presence in spring. Moreover,  
359 some positive correlations ( $p < 0.05$ ) were observed between these elements, mainly in q-  
360 UFP in winter. Industrial activities carried out close to the school can contribute to the  
361 emission of metal(loid)s, since the industrial park integrates a manufacturing unit  
362 dedicated to the production of metal parts for various sectors, factories producing home  
363 appliances, equipment for clinical, rehabilitation and geriatric health, and a unit dedicated  
364 to the manufacture of fine stoneware products [19]. Elements that are normally associated  
365 with dust resuspension, pavement wear, road traffic, use of antioxidants, vehicle additives  
366 and lubricants and industrial activity, such as V, Al, Fe, Ti, As, K, Pb, Co, Mn, Ca and  
367 Cr [33–35] appeared grouped in the same category in all stages.

368 Particles released from steel wheels and rails can be traced through the Mn/Fe ratio, with  
369 values close to 0.01 confirming this origin [36]. In this study, the Mn/Fe ratio varied, on  
370 average, between 0.01 and 0.04 in winter, and between 0.01 and 0.02 in spring, which is  
371 consistent with a dominant origin in the steel used in wheels, rails and brakes. In both  
372 winter and spring, particles  $> 2.5 \mu\text{m}$  had ratios  $< 0.01$  both indoors and outdoors. A train  
373 line passes through the west side of the school, and less than 2 km away is the nearest  
374 railway station. The highest concentrations of these elements were quantified in the  
375 classroom closest to the train line.

376 According to **Fig. 6**, in both seasons, the highest concentrations of S, K and Zn in q-UFP  
377 were observed in outdoor samples (Fig. 7). The I/O ratio for q-UFP was close to or below  
378 one, especially in winter, except for Zn in the first week of winter. The average  
379 concentration of K in  $PM_{0.25}$  in the indoor and outdoor environments were higher in  
380 winter ( $242 \text{ ng m}^{-3}$  and  $326 \text{ ng m}^{-3}$ , respectively). Potassium is an elemental tracer  
381 commonly used to check whether pollution comes from the burning of biomass,  
382 particularly wood [37]. However, potassium is also emitted from other important sources

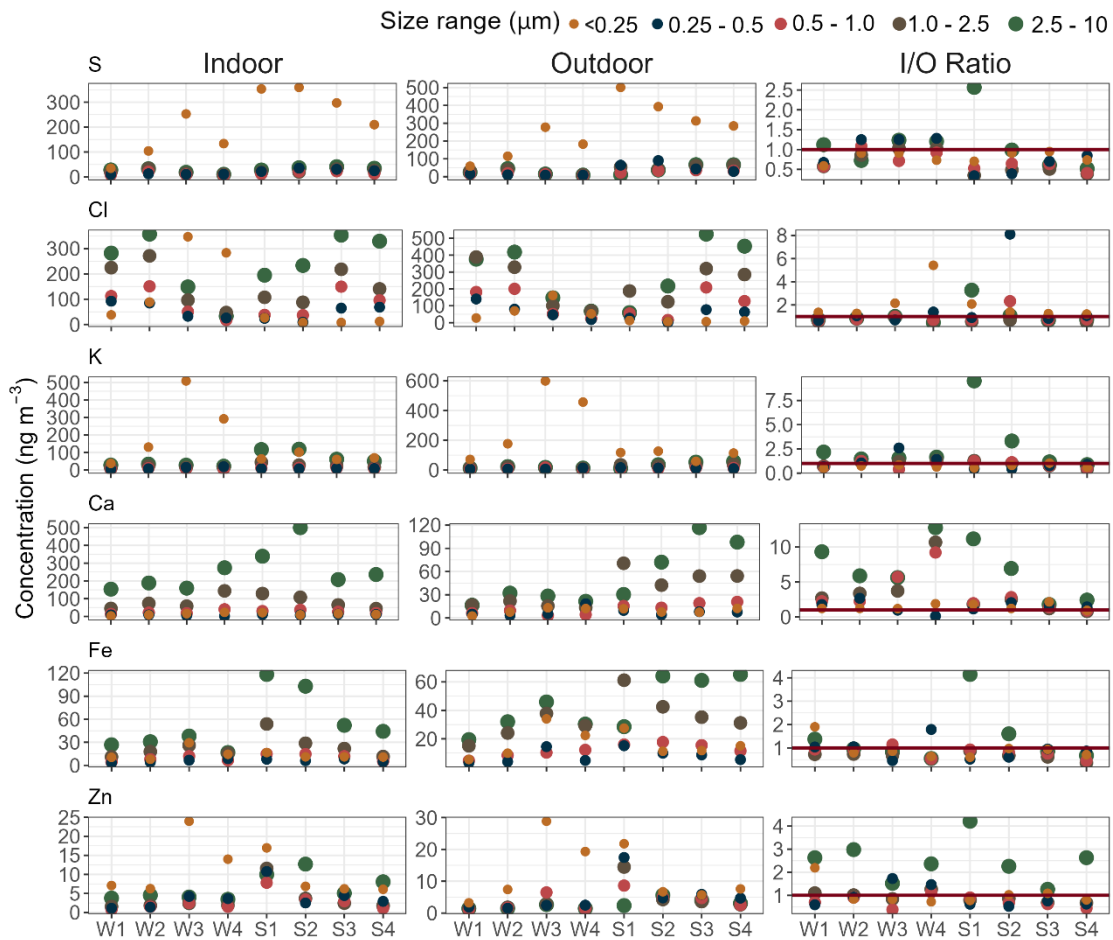
383 and the content of this element in fine particle emissions from biomass burning depends  
384 on biofuels and combustion appliances [38]. According to Niemi et al [39], K from  
385 biomass burning is emitted as KCl (known as young smoke) and then transformed into  
386  $K_2SO_4$  and  $KNO_3$ . The S/K ratio can be used to describe the rate of accumulation of S  
387 compounds in biomass burning aerosols during their transport [40]. The S/K ratio in the  
388  $PM_{0.25}$  fraction observed in winter ( $\sim 0.5$  indoors and outdoors) is close to the values  
389 described in other studies [41] and shows that the biomass burning aerosols detected in  
390 the school were relatively freshly emitted. In contrast, in spring, the average S/K ratio  
391 was 4.1 and 3.5 indoors and outdoors, respectively, indicating that biomass burning  
392 aerosols were aged. Furthermore, K in the finest fraction generally showed positive  
393 correlations with Zn, Pb, S and Mn only in winter (Fig. S4, Supplementary material),  
394 which also suggest that these elements are emitted from biomass burning [42].

395 As previously mentioned, S presented higher concentrations in spring compared to winter  
396 (**Fig. 6**). In spring, S in the finest fraction ( $PM_{0.25}$ ) exhibited a positive correlation ( $p <$   
397  $0.05$ ) with V, Ni, Zn, and Fe, while in winter correlated well ( $p < 0.05$ ) with Br, Zn, Fe,  
398 Mn, Cu, Si, Ca, Pb and K. Sulphur is present in nature as a common constituent of many  
399 minerals. On the other hand, it is possible to find sulphur in natural gas and crude oil.  
400 Sulphur is released into the atmosphere in the form of gas and dust generated by activities  
401 such as oil refining, kraft paper mills, metallurgical processes, smelting gases, copper and  
402 iron extraction and biomass burning [31]. It may be that one of these activities has a  
403 greater influence in spring than in winter, or that due to seasonal weather conditions, the  
404 contribution of S changes from season to season. Long-range atmospheric particle  
405 transport was disregarded since Pearson correlations between S and the major single-  
406 bonded mineral dust elements Al and Si were not significant for both elements, indicating  
407 a weak linear relationship (Fig. S4, Supplementary material). In contrast, the highest  
408 concentrations of Ca and Fe were detected indoors in stage a ( $PM_{2.5-10}$ ), being higher in  
409 the spring samples. However, the I/O ratio of Ca (5.6 - 12.8) in the  $PM_{10-2.5}$  size fraction  
410 obtained in winter was higher than that in spring (1.8 - 11.2), indicating that Ca does not  
411 necessarily infiltrate with PM, but it mainly results from the resuspension of dust  
412 transported into rooms on clothes and especially on the soles of shoes.

413 The analysis of Cl according to the school environment (indoor and outdoor) revealed  
414 intrinsic characteristics. On one hand, as observed in other studies, cleaning products used  
415 indoors can influence the contribution of Cl [43]. In this study, the highest concentrations  
416 of this element in the  $PM_{0.25}$  fraction were always observed inside classrooms, because  
417 of cleaning work and the use of disinfectants. The I/O ratios for this size fraction were  
418 similar during both seasons, ranging between 0.72 and 2.19 (**Fig. 6**). On the other hand,  
419 Cl originates from sea salt in coastal areas or road salt in continental areas of Europe [44].  
420 The Cl/Na ratio found for seawater (1.8) in coastal aerosols indicates a likely source in  
421 sea salt. In this study, average values of the Cl/Na ratio in all PM sizes at the schoolyard  
422 in winter (0.68 - 3.36) and spring (0.18 - 4.29) were far from the reference value for sea  
423 salt, which denotes the influence of anthropogenic emissions for this element.  
424 Anthropogenic chlorine can be emitted from meat combustion, waste incineration,  
425 industrial emissions, and biomass burning [41]. Furthermore, Cl in  $D_p < 0.25 \mu m$  (stage

426 e) did not correlate with any other element in any season, while coarse Cl (2.5-10  $\mu\text{m}$ )  
 427 correlated positively ( $p < 0.05$ ) with Mg in winter and with K, Si, S, Mg, Al, Ni, Na and  
 428 Ca in spring. However, the groupings by particle size showed that only in the  $\text{PM}_{0.25}$   
 429 fraction was Cl in the same group as Na and S in winter (no significant correlation was  
 430 found with either of the two elements), while in spring, Cl grouped with more than one  
 431 element in  $D_p > 0.5 \mu\text{m}$  (stages c, d and e) (Fig. S5, Supplementary Material). Therefore,  
 432 it was not possible to accurately identify a single emission source, which indicates that  
 433 Cl has multiple origins.

434



435

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

440

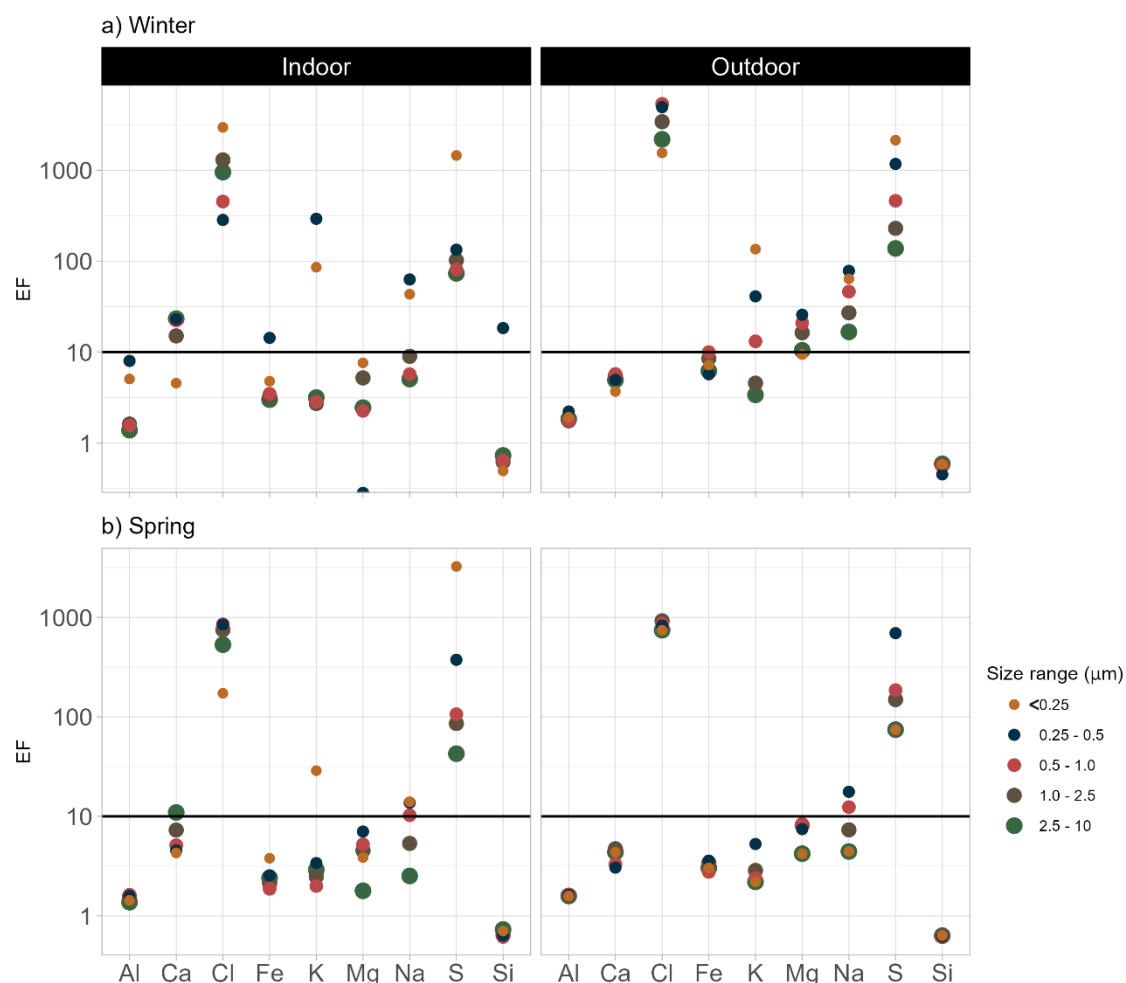
### 441 3.1.3. Enrichment factors

442 Enrichment factors (EFs) were calculated following the methodology described in Zoller  
 443 et al. [45] to assess the contribution of anthropogenic sources to the levels of specific  
 444 elements in PM sampled in classrooms and schoolyard. During the entire sampling  
 445 period, the EF values for Al, Ca, Fe and Si in all stages were relatively low ( $< 10$ ),  
 446 indicating that these elements originate mainly from resuspended soil. Among the



447 elements investigated, in winter, Ca in particles larger than 0.25  $\mu\text{m}$  sampled in  
448 classrooms showed  $FE > 10$ , while in spring only the coarsest fraction (stage a) showed  
449 enrichments greater than 10. In the past, indoor Ca levels were attributed to the use of  
450 chalk or emissions from paper as calcium carbonate [46]. However, as chalk is not used  
451 in the classrooms of the present study, it is possible that Ca was transported stuck to the  
452 soles of pupils' shoes, as observed by Sánchez-Soberón et al. [47] in schools in Spain over  
453 two seasons. Once inside the classroom, it is resuspended, resulting in higher  
454 concentrations in winter because of higher PM levels and reduced ventilation in this  
455 season. Similarly, Molnár et al. [48] and Rivas et al. [49] in school environments, also  
456 found higher Ca levels indoors than outdoors.

457 Elements such as Cl and S presented  $EF > 10$  in all size fractions, both indoors and  
458 outdoors in both seasons. As explained previously, much of the Cl had an anthropogenic  
459 origin, given that not only its ratio with sodium was sometimes higher than that of  
460 seawater, but also because it was highly enriched. In the case of S, the enrichment may  
461 be due to one of the activities mentioned above or to the influence of more than one of  
462 those. K was enriched in particles with  $D_p \leq 0.25 \mu\text{m}$  (stages c and d in classrooms) and  
463 with  $D_p > 0.25 \mu\text{m}$  (stages c, d and e in the schoolyard) in the cold season, while in spring  
464 its enrichment occurred only in the finest fraction ( $D_p < 0.25 \mu\text{m}$ ) in classrooms (**Fig. 7**).  
465 As discussed earlier, K presented I/O ratios lower than 1 for q-UFP in both seasons (mean  
466 = 0.71), possibly associated with biomass burning.



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469  
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471

**Figure 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.

472 The EFs for some chemical constituents detected in the samples pointed to predominantly  
473 non-soil sources. This is the case of Br, Cr, Cu, Ni, Pb and Zn. Their EFs increased with  
474 increasing particle sizes (**Fig. S6**, Supplementary material). Ti showed an opposite trend,  
475 with EFs decreasing as particle size decreased. However, this element presented  
476 concentrations sometimes below the detection limit. Overall, a decrease in the enrichment  
477 factors of Br, Cr, Cu, Mn, Ni, and Pb from winter to spring was registered. The greatest  
478 reduction (from 4285 to 13) was observed in the schoolyard for q-UFP of PM-bound Pb.  
479 Typically, the enrichments of Cu, Pb, Ni, and Cr have been associated with mechanical  
480 abrasion and wear of tyres and brakes [35]. On the other hand, while the EF of Br  
481 decreased 30 times for  $D_p < 0.25 \mu\text{m}$  (stage e) in classrooms, the EF of Cr increased  
482 almost 4 times in the spring (**Fig. S6**, Supplementary material). The variation of EF with  
483 particle size has been previously reported by other researchers. Gao et al. [50] studied soil  
484 dust aerosols to determine whether there is heavy metal selectivity depending on particle  
485 size. The authors indicated that the particle size dependence of heavy metal enrichment  
486 may have important effects on the health impacts of aerosols. In addition, Zhi et al. [51]

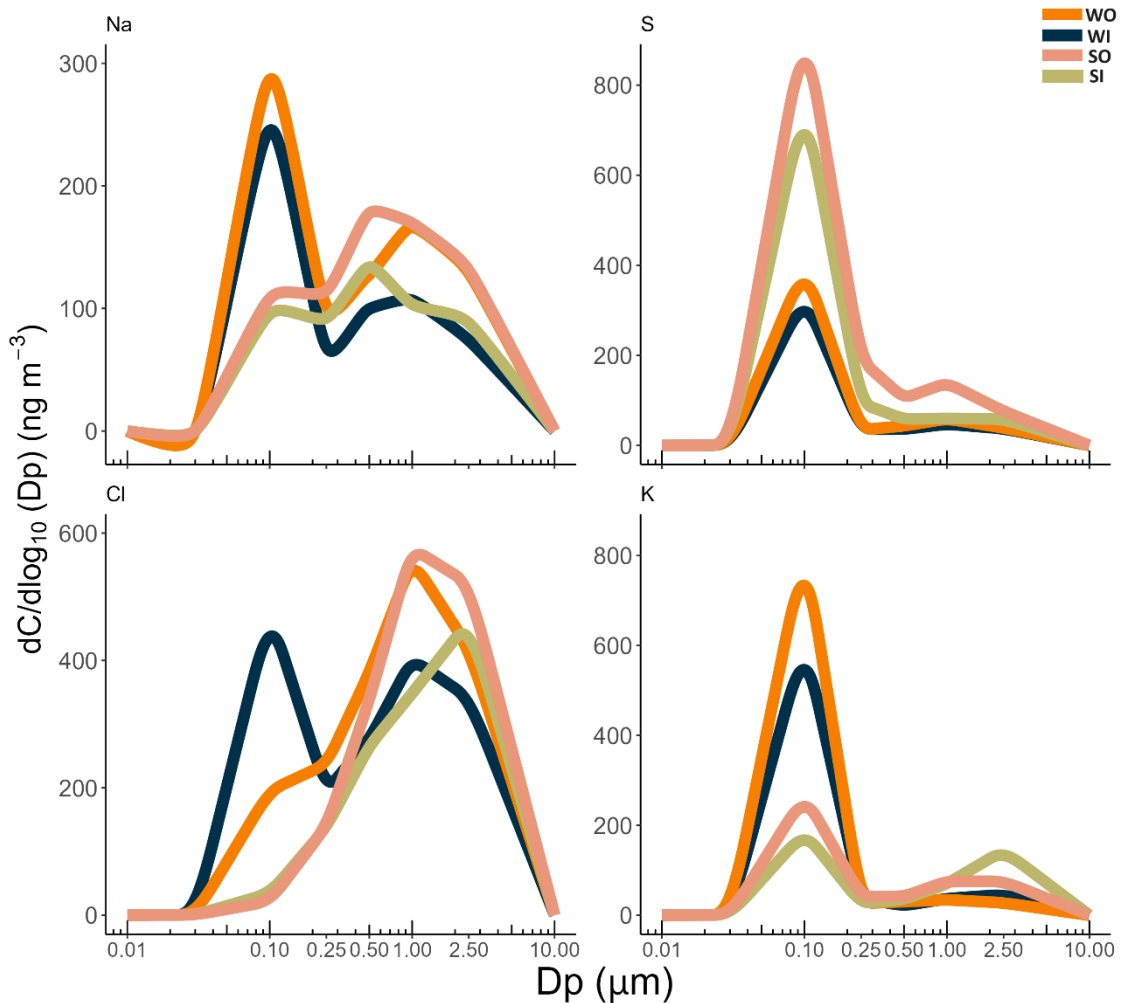
487 suggested that fine particles ( $<2.1 \mu\text{m}$ ) have more active sites around surfaces and  
488 stronger adsorption compared to larger particles ( $>9.0 \mu\text{m}$ ).

489 V and Ni of anthropogenic origin are commonly used as markers of heavy fuels, but in  
490 this study no correlations were found between these two elements. Molybdenum was  
491 found in part of the indoor and outdoor spring samples. Mo has typically been associated  
492 with industrial processes such as steel production [52] and petrochemical plants [1]. The  
493 Mo concentrations can be attributed to the fact that the predominant wind direction (Table  
494 S3 and Fig S3, Supplementary Material) in spring coincides with the location of the  
495 industrial complex, consequently affecting the area where the school is located. In  
496 research carried out near the study area, Alves et al. [19] identified that the highest levels  
497 of Mo were recorded for winds in the WN sector, which suggests an origin mainly in the  
498 industrial complex.

#### 499 **3.1.4. Elemental size distribution**

500 **Figures 8 and 9** depict the size segregated distributions of some elements. In general, the  
501 size distributions of Na, S, Cl, and K were bimodal in both seasons. Except for Cl, the  
502 concentrations of these elements reached peaks for the finest size fraction. K displayed a  
503 bimodal distribution in both campaigns: a dominant peak at  $D_p \sim 0.10 \mu\text{m}$  (stage e) and a  
504 minor peak at  $D_p \sim 1.0 \mu\text{m}$  (stage b). The highest concentrations were recorded in winter  
505 in the schoolyard. In spring, the largest peak also coincided with that determined in  
506 winter, however, a decrease in the mass concentration of K in this very small fraction ( $D_p$   
507  $< 0.25 \mu\text{m}$ ) and a modal shift towards larger particles was observed, particularly in  
508 classrooms. The fine mode of K is most likely related to emissions from residential  
509 biomass combustion, especially in winter, while the coarse mode results from the  
510 resuspension of soil particles.

511 As shown in **Fig. 8**, S revealed a bimodal distribution like that of K with a dominant peak  
512 centred at  $D_p \sim 0.10 \mu\text{m}$ . This peak is much more intense in spring in the outdoor  
513 environment. Sulphur in  $\text{PM}_{0.25}$  in the schoolyard accounted for 40% to 45% in spring  
514 and between 17% and 62% in winter of its total mass concentrations. It can be originated  
515 from coal burning in restaurants and domestic barbecues, fuel oil combustion in  
516 residential boilers and emissions from diesel vehicles.



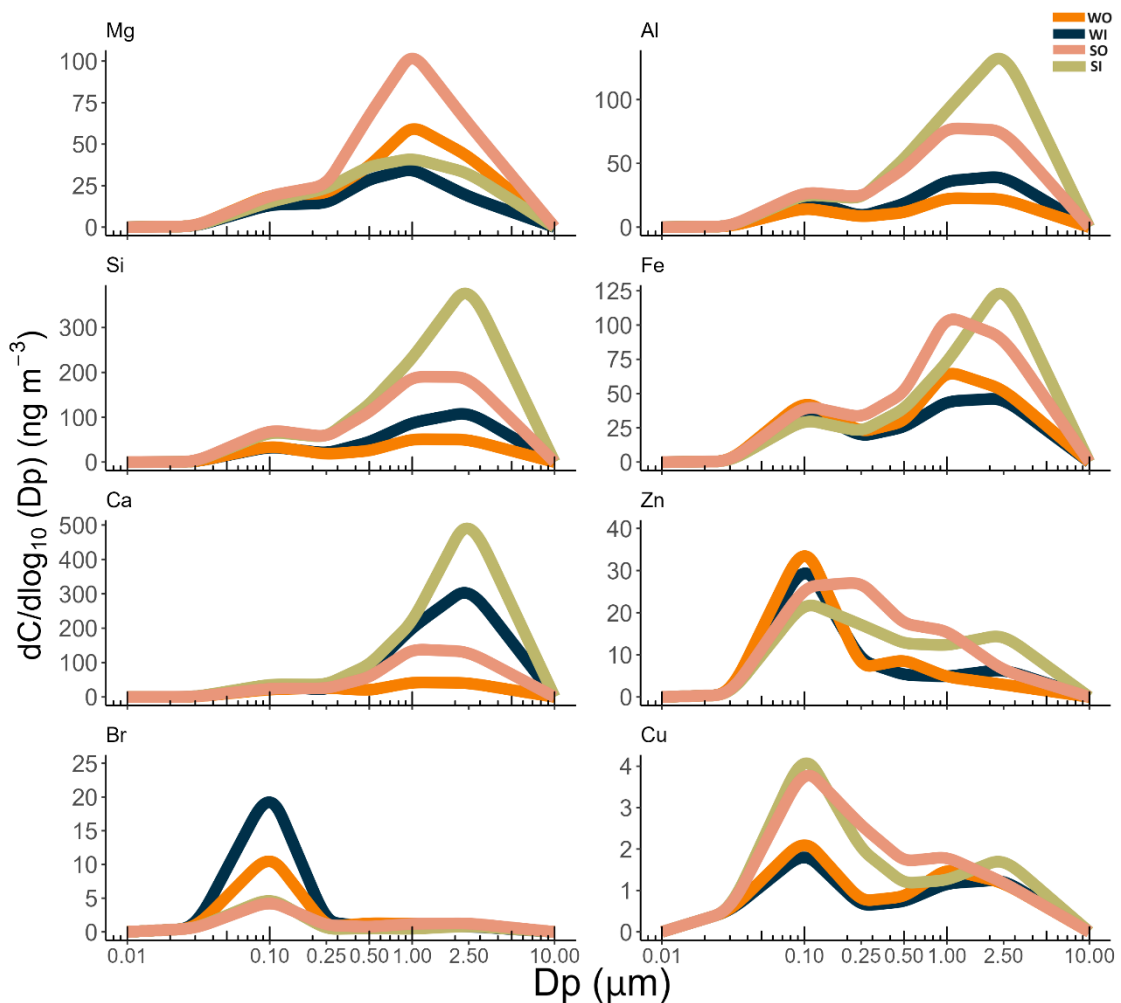
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**Figure 8.** Lognormal mass size distributions of some prevalent elements for winter outdoor (WO), winter indoor (WI), spring outdoor (SO) and spring outdoor (SI).

521 The size distribution of Na in both seasons presented two modes. In winter, the main  
522 mode was found at  $D_p \sim 0.10 \mu\text{m}$ , both outdoors and indoors. In spring, the main mode  
523 was found at  $D_p \sim 0.50 \mu\text{m}$ . Cl and Na showed different patterns. The Cl pattern reflects  
524 an increase in concentrations of coarse sizes, peaking at  $D_p \sim 1 \mu\text{m}$  and  $2.5 \mu\text{m}$ . Unlike  
525 what was observed in classrooms, Cl in winter presented a bimodal distribution, with its  
526 main peak at  $D_p \sim 0.10 \mu\text{m}$ , confirming the influence of the use of chlorinated products  
527 for cleaning and disinfection and the poor ventilation of the rooms in the coldest period.  
528 However, Cl can also originate from other anthropogenic sources, such as burning of  
529 polyvinyl chloride (PVC) and paper [2]. It is worth noting that in the schoolyard Cl  
530 peaked at  $D_p \sim 1.0 \mu\text{m}$  in both winter and spring. The ECC integrates some industries  
531 dedicated to the production of chlorine and caustic soda, as well as synthetic resins,  
532 mainly PVC from vinyl chloride monomer [19], which can emit Cl. Furthermore, as  
533 observed in other studies [4,53], higher Cl concentrations were recorded during the  
534 coldest period (**Fig. S7**). Compared to other places in the world, in winter, the  
535 concentration of Cl in  $\text{PM}_{2.5}$  at the schoolyard was 6.4 times lower than at Nankai  
536 University (Tianjin, China) and 19.2 times lower than that observed in the Indian Institute  
537 of Technology (Delhi). As reported by Wang et al. [4] when analysing the concentration

538 of Cl at Nankai University in the four seasons, in addition to temperature and relative  
 539 humidity, industrial emissions also affect the seasonal differences of this element. In this  
 540 study, the highest Cl values coincide with the northwest wind direction, suggesting the  
 541 contribution from the nearby industrial complex.

542 A completely different behaviour could be observed for Al, which, together with Mg, Si,  
 543 Fe and Ca, is a typical tracer of mineral dust (**Fig. 9**). Al, along with other crustal  
 544 elements, was more abundant in the coarse mode both in the schoolyard and in the  
 545 classrooms, indicating the important role of dust and local soil resuspension processes,  
 546 with higher concentrations during spring. Si and Al showed an equivalent size distribution  
 547 with a relatively similar pattern in the classrooms and schoolyard in both seasons. In the  
 548 schoolyard, the size distribution peaked at  $D_p \sim 1.0 \mu\text{m}$ , while in classrooms, the peak was  
 549 for sizes from 2.5 to 10  $\mu\text{m}$ . The highest Ca concentrations were recorded in the  
 550 classrooms and the main peak was also observed in the range from 2.5 to 10  $\mu\text{m}$  in both  
 551 seasons. As mentioned earlier, indoor Ca likely results from the transport of soil on the  
 552 soles of children's shoes, different from what was reported in previous studies [43,54], in  
 553 which the main source of Ca in classrooms was identified as being chalk.



554  
 555 **Figure 9.** Lognormal mass size distributions of some crustal elements and some heavy metals for  
 556 winter outdoor (WO), winter indoor (WI), spring outdoor (SO) and spring outdoor (SI).  
 557

558 The size distributions of the main elements identified in all samples from the two  
 559 monitoring campaigns are also shown in **Fig. 9**. Zn, Br and Cu exhibited predominance  
 560 in the finest particles ( $D_p < 0.25 \mu\text{m}$ ), with approximately 17% of the total mass of these  
 561 elements within this size, probably because of the presence of anthropogenic sources of  
 562  $\text{CH}_3\text{Br}$  emissions from agricultural pesticides, coal burning, biomass burning, and  
 563 stratospheric transport from halon degradation [55]. Zn and Br presented higher  
 564 concentrations in winter than in spring. The unimodal diameter of Zn was found to be  $D_p$   
 565  $\sim 0.10 \mu\text{m}$ , which coincided with the unimodal diameter of the mass distribution of Br.  
 566 The usual tendency for the size distribution to peak at  $0.10 \mu\text{m}$  indicates that most of the  
 567 production of these elements could be associated with the same source, since a strong  
 568 positive correlation ( $r = 1.00$   $p < 0.05$ ) between them was only found at  $D_p < 0.25 \mu\text{m}$  in  
 569 the schoolyard in winter. Interestingly, these elements showed their highest abundances  
 570 in the q-UFP. In winter, 85% and 72% of the total mass of Br in the indoor and outdoor  
 571 environments, respectively, was within particles of this size. Unlike Zn and Br, Cu  
 572 displayed bimodal size distributions in both seasons. As shown in Fig. S6, Cu enrichment  
 573 factors were in the range from 81 to 1096 at all particle sizes in both classrooms and  
 574 schoolyard over the two seasons. This result shows that Cu does not have a natural origin.  
 575 In contrast, Şahin et al. [3] reported in their study in Istanbul that street dust in Besiktas  
 576 (one of 5 outdoor monitoring sites) contributed substantially to the composition of PM,  
 577 with the elements Mn, Cu and Fe having slightly higher concentrations in the coarse PM.  
 578 According to the authors, the size distribution of the elements depends on the location  
 579 and sources.

### 580 **3.2. Environmental factors and health outcomes**

581

#### 582 **3.2.1. Characteristics of the studied population**

583 Based on the number of students, 677 questionnaires were distributed among  
 584 schoolteachers, of which 334 were returned and 30 were excluded because they were  
 585 incomplete (confidence level (95%) and margin error (4%)). Therefore, for the final  
 586 analysis, 304 questionnaires were considered, which represents 45% of the total  
 587 population. According to the questionnaires, the share of female was just above 50% and  
 588 the median age of children was 9 years, varying between 3 and 12 years (**Table 3**).  
 589 Regarding the family socioeconomic status, only 37% of the mothers completed higher  
 590 education. About 65% of children watched TV between 1 and 3 hours a day and 40% had  
 591 not practiced a breathless physical activity in a week. In relation to some household  
 592 environment factors, 51% of children live less than 5 km from the industrial complex and  
 593 35% live on streets where trucks pass frequently during the week. Furthermore, 34% of  
 594 the schoolchildren were exposed to environmental tobacco smoke at home.

595 **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 hours 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

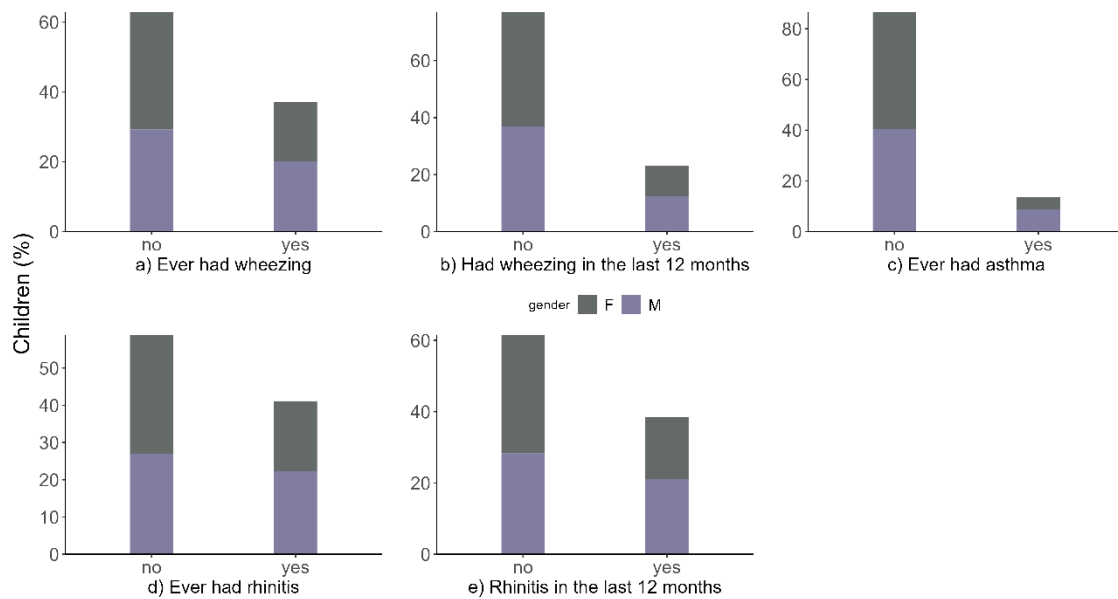
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596

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

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

611



612  
613 **Figure 10.** Summary of questionnaire-based respiratory symptoms.  
614

### 615 3.2.2. Effects of environmental factors on respiratory symptoms

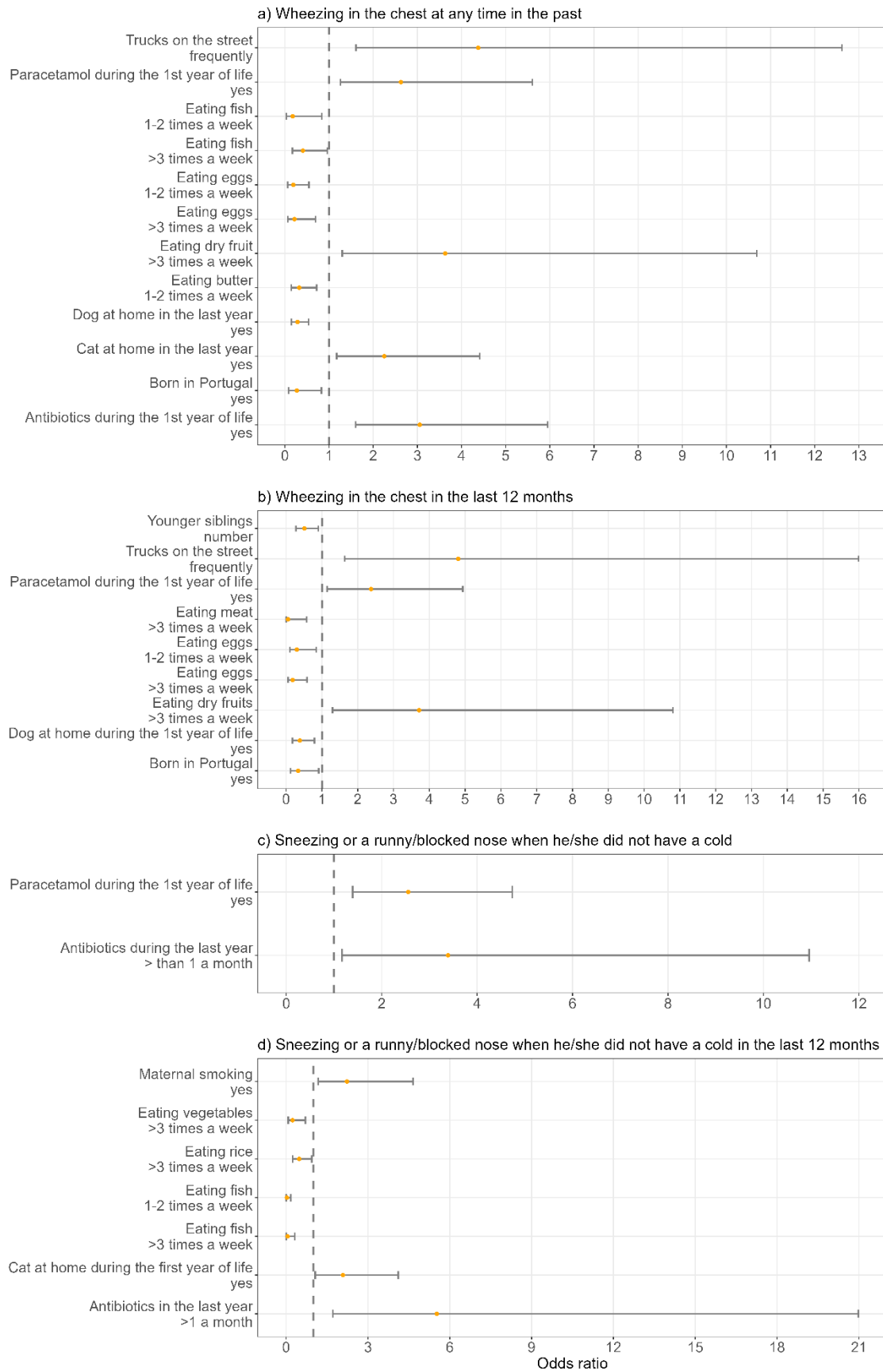
616 For the analysis of the questionnaires, two models for asthma and another two for rhinitis  
617 symptoms were built. Asthma was defined by positive responses to questions about ever  
618 having wheezing/whistling attacks or in the past year (Table S2). The results show that  
619 the model (**Fig. 11**, Panel a) was statistically significantly better than a reference model  
620 in explaining wheezing at any time in the past [ $\chi^2$  (25) = 115.0;  $p < .001$ ], with 78.3%  
621 sensitive. Frequent truck traffic on the streets, having a cat at home, taking paracetamol  
622 and antibiotics were positive and statistically significant predictors of the outcome. When  
623 taking antibiotics during the first year of life, the odds of wheezing increased.

624 In this study, it was found that paracetamol consumption during childhood increases the  
625 risk of developing asthma and rhinitis. Paracetamol, given in the first year of life, is  
626 associated with greater likelihood of being in the "yes" category of developing asthma  
627 symptoms (OD = 2.62 [95% CI 1.25 – 5.53]). In addition, belonging to the yes category  
628 for taking paracetamol is associated with an increased odds of being in the yes category  
629 of having a runny nose when the child did not have a cold at any time in the past (OD =  
630 2.55; IC 95%: 1.39– 4.70). Similarly, a significant association was observed between  
631 paracetamol and the occurrence of asthma among children in the study carried out by  
632 Beasley et al. [56], which included more than 205 thousand children aged 6 to 7 years in  
633 31 countries. Multivariate analyses indicated that the use of paracetamol in the first year  
634 of life might be a risk factor for the development of asthma in childhood. One of the  
635 reasons why paracetamol is commonly associated with increased risk of asthma is  
636 because use of this medication decreases antioxidant glutathione levels in the lung, which  
637 leads to reduced lung antioxidant defenses [57].

638 The model showed that living near streets with frequent truck traffic is a predictor for the  
639 development of asthma symptoms (**Fig. 11. a**). Children who live on streets where many  
640 trucks pass are 4.38 times more likely to belong to the "yes" category for ever had  
641 wheezing than children who live on streets frequented by few vehicles. After finding a



642 positive correlation between the prevalence of wheezing and allergic rhinitis and  
643 indicators of traffic density, a study in Bochum, Germany, indicated that truck exhaust  
644 emissions resulting from the circulation of heavy vehicles close to home caused or  
645 exacerbated asthma symptoms and allergic rhinitis in seventh- and eighth-grade  
646 schoolchildren [58]. In a more recent study, Singh et al. [59] found an association between  
647 frequent truck traffic close to home and the presence of allergic rhinitis,  
648 rhinoconjunctivitis, and eczema among Indian children of two age groups. According to  
649 Annesi-Maesano et al.[60], inhaling traffic-related air pollutants, individually or in  
650 combination, can improve immune and airway responses to inhaled allergens.



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**Figure 2.** 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

655 for rhinitis. Odds ratio (OR) with 95% confidence interval (CI). The full questions corresponding  
656 to the factors presented in the graph are highlighted in bold in Table S1 of the Supplementary  
657 Material.

658

659 Among the dietary variables, the consumption of vegetables, fish, meat, rice and eggs  
660 were statistically significant predictors for some respiratory symptoms. Children who eat  
661 vegetables more than 3 times a week reduce the probability of developing rhinitis by 63%  
662 compared to children who never eat vegetables during the week (OD = 0.37; 95% [CI:  
663 0.12 – 1.18]). Some researchers found that reduced intake of fruits and vegetables may  
664 play a critical role in the development of asthma and allergies. For example, in a  
665 systematic review by Hosseini et al. [61] it was reported that most studies found beneficial  
666 associations between the consumption of fruits and vegetables and the risk of asthma  
667 and/or respiratory function. In fact, the consumption of fruits and vegetables appears to  
668 protect against asthma. Similarly, the findings of a study in Greece suggests a beneficial  
669 effect of fruits, vegetables and nuts commonly consumed during childhood on the  
670 symptoms of asthma and rhinitis. The Mediterranean diet may explain the relative lack  
671 of asthma and allergy symptoms in children in the population of this country [62]. In this  
672 study, the positive association was not seen with nuts. Contrary to what was documented  
673 in the research in Greece, it was observed that the consumption of nuts increases the odds  
674 of developing asthma (**Fig. 11**. Panel a and b). In a previous study, sensitization to peanut  
675 and hazelnut storage proteins was associated with higher levels of inflammation markers  
676 and food hypersensitivity symptoms in children with asthma [63]. The study concluded  
677 by reporting that storage protein sensitization appears to be associated with asthma  
678 morbidity. However, according to the researches, the reason for stronger signs of  
679 inflammation in asthmatic patients with than without sensitization to nut storage proteins  
680 is still unclear.

681 Having a dog at home in the last 12 months and during the first year of the child's life has  
682 shown a protective effect. Belonging to the yes category of having a dog at home reduces  
683 the odds by 68% of belonging to the yes category of developing asthma (OD = 0.32; 95%  
684 CI: 0.19 – 0.59). The findings of some epidemiological studies on respiratory symptoms  
685 have been contradictory. Some demonstrated protective effects, while others showed  
686 associations with increased asthma symptoms in children. On one hand, a study  
687 conducted in Japan evaluated 410 newborns who owned dogs/cats at home and their  
688 history of wheezing and asthma through five follow-up questionnaires, up to the age of  
689 6. After an adjusted logistic generalized estimation analysis, the model showed no  
690 significant associations of the interaction between dog and/or cat ownership and follow-  
691 up time with the risks of wheeze and asthma. However, the findings suggest that owning  
692 dogs and cats from a young age does not increase the risks of wheezing and asthma  
693 compared with Japanese children who never owned them [64]. On the other hand,  
694 Brunekreef et al.[65] did not find that combined exposure to dogs and cats was more  
695 strongly associated with symptoms in children aged 6 to 7 years than exposure to cats or  
696 dogs alone. The strongest relationship in the youngest age group was found between  
697 exposure to cats and wheezing, independent of exposure to dogs. According to the  
698 authors, it may be that the associations change with age and that combined exposure to  
699 cats and dogs only becomes more important in adolescence. On the other hand, another  
700 common predictor was antibiotic use. Frequent intake (more than once per month) of

701 antibiotics was associated with a higher risk of having rhinitis, whereas antibiotic intake  
702 during the child's first year of life was associated with asthma symptoms. Other studies  
703 have also suggested that antibiotics are associated with various symptoms of allergy and  
704 asthma [59]. In a birth cohort study in Japan, Yamamoto-Hanada et al. [66] examined the  
705 signs of asthma and allergic diseases in children and found that exposure to antibiotics at  
706 younger than 3 years increased the risk of developing allergic diseases at 5 years. Any  
707 antibiotic and cephem use within the first 2 years of life was associated with current  
708 asthma at 5 years.

709 Moreover, maternal smoking during the first year of life only showed a clear relationship  
710 with the development of rhinitis symptoms (**Fig. 11** panel d). As reported in other studies,  
711 environmental tobacco smoke harms children's respiratory health. Lin et al. [67]  
712 suggested that exposure to environmental tobacco smoke in the first 2 years of life may  
713 increase the incidence of wheezing, rhinitis and eczema and decrease the remission of  
714 these symptoms in preschool children (aged 3–8 years old). In this study, maternal  
715 smoking was negatively associated with active rhinitis. Children exposed to cigarette  
716 smoke during their first year of life are twice as likely to develop rhinitis as children who  
717 have never been exposed (OD = 2.23; 95% CI: 1.13 – 4.41). Finally, children born in  
718 Portugal have a decreased risk of developing asthma compared to schoolchildren born in  
719 other countries (OD = 0.51; 95% CI: 0.28– 0.91). This result was different to that  
720 observed by Migliore et al. [68], in which migrant children had a lower prevalence of  
721 asthma symptoms than children born in Italy. The researchers found that the prevalence  
722 increased with the number of years of life in Italy, indicating that exposure to  
723 environmental factors may play an important role in the development of asthma in  
724 childhood. Lower risks for lifetime asthma (OR=0.39; 95% CI: 0.23–0.66) and current  
725 wheeze were found for children who had lived in Italy for 5 years or less, while children  
726 born in Italy had risks higher than abroad children.

727

#### 728 **4. Study strengths and limitations**

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

744 allow for an integrated assessment of exposure, given that time spent and concentrations  
745 in other microenvironments, such as housing, were not monitored. Thus, it is  
746 recommended to consider time-activity patterns and measurements in the different  
747 microenvironments frequented by children. Another limitation of the present study is  
748 related to the methodological design which, by including measurements in only 4 rooms,  
749 limited the use of PM concentrations in statistical models. Although the results  
750 corroborate those observed in other studies, the associations found in logistic regression  
751 must be analysed with caution because the participation rate was 45% and the only action  
752 to avoid selection bias was an explanation to parents and teachers on how to interpret and  
753 fill out the questionnaires. Previous studies have expressed that responses may be prone  
754 to misclassification [69,70], as parents of children with any respiratory symptoms may be  
755 more likely to report symptoms than parents of children without symptoms. In addition,  
756 due to the cross-sectional design of the study, the results do not allow establishing causal  
757 relationships between environmental factors and health outcomes.

758

## 759 **5. Conclusion**

760

761 This study investigated, characterised and compared indoor and outdoor particulate  
762 matter over two seasons in a Portuguese school close to the largest chemical industrial  
763 complex in Portugal, in addition to applying a standardised questionnaire to obtain  
764 additional information related to respiratory allergies, children's lifestyle, home and  
765 environment conditions. The elemental composition of the size-segregated particulate  
766 matter samples suggests that multiple sources contribute to pollutant levels in classrooms:  
767 work materials, cleaning products, dirt on the soles of shoes, infiltration of emissions  
768 from residential wood combustion, agricultural activities, exhaust and non-exhaust  
769 emissions from road traffic, chemical complex and railway. The largest mass fraction of  
770 PM outdoors was observed for particles with  $D_p < 0.25 \mu\text{m}$ , accounting 75.5% to  $\text{PM}_{10}$   
771 in winter, while indoors the coarser fraction (2.5–10  $\mu\text{m}$ ) encompassed the highest  
772 contribution to the total  $\text{PM}_{10}$  in spring (62.5%). The elemental content was higher in  
773 spring, representing approximately 22% and 28% of the total mass of the coarsest fraction  
774 (2.5 – 10  $\mu\text{m}$ ) in classrooms and the schoolyard, respectively, while the corresponding  
775 contribution to the total mass of the finest fraction (q-UFP) was 35% and 33%. In winter,  
776 K was the prevalent element in particles with  $D_p < 0.25 \mu\text{m}$  (34% in terms of total mass  
777 of  $\text{PM}_{0.25}$ ), while in spring S dominated the chemical composition of  $\text{PM}_{0.25}$  both indoors  
778 and outdoors, with concentrations ranging from 209 to 359  $\text{ng m}^{-3}$  and 284 to 501  $\text{ng m}^{-3}$ ,  
779 respectively. The most notable finding was that Cl contributed most to the total mass  
780 of  $D_p > 0.25 \mu\text{m}$  outdoors in both seasons. Although this element may be of natural origin,  
781 it is likely that industrial activity close to the school could be an important emission source  
782 of Cl. From the results of the ISAAC questionnaire, it was concluded that the use of  
783 paracetamol, the intake of vegetables and living near streets with heavy truck traffic are  
784 some of the influential factors on respiratory symptoms among children who attend  
785 school. The results of the present study demonstrate the need to promote ventilation in  
786 classrooms and to continue with research aimed at characterising whether the range of

787 PM concentrations in and around the school changes significantly throughout the year,  
788 which is necessary to identify the sources of the particles, formulate mitigation measures  
789 and determine possible adverse effects on students.

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803

804

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809

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812

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