Seasonal characterization and dosimetry-assisted risk assessment of indoor particulate matter ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$) collected in different schools

Francisco Sánchez-Soberón[1], Joaquim Rovira[1,2]*, Jordi Sierra[1,3], Montse Mari[1], José L. Domingo[2], Marta Schuhmacher[1]

[1]Universitat Rovira i Virgili, Chemical Engineering Department, Environmental Analysis and Management Group, Av. Països Catalans 26, 43007, Tarragona, Spain

[2] Universitat Rovira i Virgili, School of Medicine, Laboratory of Toxicology and Environmental Health, IISPV, Sant Llorenç 21, 43201 Reus, Catalonia, Spain

[3]Laboratori d'Edafologia, Facultat de Farmacia, Universitat de Barcelona, Av. Joan XXIII s/n, 08028 Barcelona, Catalonia, Spain

*Corresponding author. Postal address: Universitat Rovira i Virgili, Chemical Engineering Department, Environmental Analysis and Management Group, Av. Països Catalans 26, 43007, Tarragona, Spain. email address: joaquim.rovira@urv.cat

Abstract

Inhalation of particulate matter (PM) has been linked to serious adverse health effects, such as asthma, cardiovascular diseases and lung cancer. In the present study, coarse ($PM_{10-2.5}$), accumulation mode ($PM_{2.5-0.25}$), and quasi-ultrafine ($PM_{0.25}$) particulates were collected inside twelve educative centers of Tarragona County (Catalonia, Spain) during two seasons (cold and warm). Chemical characterization of PM, as well as risk assessment were subsequently conducted in order to evaluate respiratory and digestive risks during school time for children. Levels and chemical composition of PM were very different among the 12 centers. Average PM levels were higher during the cold season, as well as the concentrations of most toxic metals. In most schools, PM levels were below the daily PM_{10} threshold established in the regulation (50 $\mu g/m^3$), with the exception of school number 1 during the cold season. On average, and regardless of season, coarse PM was highly influenced by mineral matter, while organic matter and elemental carbon were prevalent in quasi-ultrafine PM. The concentrations of the toxic elements considered by the legislation (As, Cd, Pb, and Ni) were below their correspondent regulatory annual limits. Calculated risks were below the safety thresholds, being fine fractions ($PM_{2.5-0.25}$ and $PM_{0.25}$) the main contributors to both digestive and respiratory risks.

Abbreviations: AC: air conditioning; ADAF: age dependent adjustment factor; AT: averaging time; ATSDR: Agency for Toxic Substances and Disease Registry; BW: body weight; CCI: Consolidated Coatings Inc.; DL: detection limit; ED: exposure duration; EF: exposure frequency; ELCR: excess lifetime cancer risks; HQ: hazard quotient; ICP-MS: inductive coupled plasma-mass spectrometry; ICP-OES: inductive coupled plasma-optical emission spectrometry; IR: inhalation rate; I/O ratio: indoor/outdoor ratio; MAGRAMA: Spanish Ministry of Agriculture, Fishing, and Environment; MECD: Spanish Ministry for Education, Culture, and Sports; MM: mineral matter; NIOSH: National Institute for Occupational Safety and Health; OC: organic carbon; OM+EC: organic matter and elemental carbon; PM: particulate matter; RAIS: Risk Assessment Information System; RfD: reference dose; SF: slope factor; SIA: secondary inorganic aerosols; SOA: secondary organic aerosols; SS: sea spray; ST: school time; TE: trace elements; US EPA: United States Environmental protection Agency; USGS: United States Geological Survey; WHO: World Health Organization

Highlights

- Sources of toxic elements are present inside the classrooms
- Higher PM levels and toxic elements concentrations during cold season
- Risk were below the safety thresholds regardless of season
- Carcinogenic risks were mostly linked to fine fractions ($PM_{2.5-0.25}$ and $PM_{0.25}$)

Keywords: coarse PM; quasi-ultrafine PM; school; indoor; main components; children risk assessment

1. Introduction

Aerosols, or particulate matter (PM) are considered the most harmful air pollutant, responsible of more than 7 million premature annual deaths worldwide (WHO, 2018). PM consists of a mixture of airborne solid particles and liquid droplets, comprising an array of different materials, such as sea spray, soot, pollen or fly ashes (Yue et al., 2006). Since it is complex to define PM attending to its chemical composition, it is usually classified according to its size. Thus, the most extensively studied aerosols are those smaller than 10 μm (PM_{10}) and smaller than 2.5 μm ($PM_{2.5,}$ also known as fine particles) (US EPA, 2016). Along with these two groups, a greater attention has been put during the last years into ultrafine PM. This particles represent those aerosols smaller than 0.1 μm (named as $PM_{0.1}$, or ultrafine particles) (Asuccio et al., 2005). Due to their smaller size, ultrafine PM presents unique features that make them more challenging, such as a higher surface area and their ability to trespass cellular membranes (Geiser et al., 2005).

One of the most vulnerable population groups to PM are children, due their greater inhalation rate per body weight, and their not fully developed immunological system (Thurston, 2000). In addition to the health effects happening after PM inhalation, systematic early exposure to PM could lead to the development of diseases in future stages of the children (Khalili et al., 2018; H.-Y. Liu et al., 2018). In order to evaluate children exposure to PM, outdoor levels are usually used as input for risk assessment (Ghosh et al., 2018; P. Liu et al., 2018). However, most of the children exposure to PM occurs in indoor environments, where children spend around 90% of their time (Matz et al., 2015). A great part of this time is spent inside classrooms, which, in the case of Spain, it means approximately 20% of the children weekday's routine (MECD, 2018). This environment has special characteristics regarding indoor air quality, due the combination of classroom-specific PM sources and the influence from outdoor environments (Mohammadyan et al., 2017).

Nowadays it is possible to find a body of knowledge regarding indoor air quality in schools (Chithra and Shiva Nagendra, 2018). Moreover, the study of number and mass of different sizes of PM inside schools has been extensively developed (Slezakova et al., 2019). However, in order to understand the formation and origin of indoor PM in schools, and assess their plausible risks to children it is necessary to know not only the levels of different PM sizes, but also their chemical composition. In this regard, some efforts have been made for schools located within urban backgrounds (Hochstetler et al., 2011; Pacitto et al., 2018; Viana et al., 2014a, 2014b). Similarly, it is possible to find studies devoted to the chemical characterization of indoor PM in schools located nearby industrial areas, but ultrafine fraction has not been properly addressed so far (Al-Hemoud et al., 2017; Raysoni et al., 2017; Tran et al., 2014, 2012; Wang et al., 2014).

The present study is aimed at increasing the current knowledge regarding composition and risks of indoor PM in schools located under the influence of different aerosol sources. To accomplish

that, coarse, accumulation mode, and quasi-ultrafine PM ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$, respectively) were collected inside the classrooms of twelve schools located in urban, suburban, and industrial areas. Since characteristics of PM are dependent on weather conditions, we collected samples in two seasons: cold and warm. An analysis of metals, soluble inorganic ions, and total carbon was subsequently performed with the collected particles. Finally, a health risk assessment was conducted to calculate children's exposure and to assess the health risks associated to the inorganic components of PM.

2. Materials and methods

2.1. Site description and PM monitoring

In brief, PM sampling was performed inside classrooms of 12 different schools in Tarragona County (Catalonia, Spain) during two seasons (cold and warm) (Figure 1). This area is characterized by presenting a very heterogenous industrial cluster, comprising several chemical and petrochemical industries. Furthermore, the area is also influenced by the presence of a Municipal Solid Waste (MSW) incinerator and a Hazardous Waste (HW) incinerator (EEA, 2019). Sampled classrooms were very diverse, and the main features of them are summarized in Table 1. Coarse ($PM_{10-2.5}$), accumulation mode ($PM_{2.5-0.25}$), and quasi-ultrafine ($PM_{0.25}$) particles were collected. This last PM fraction was taken as an approximation to ultrafine fraction, since cut-off point of ultrafine PM could be longer than 0.1 μm depending on the physical structure of the particles (Saffari et al., 2013). Two low volume pumps (Leland Legacy, SKC Inc., Eighty Four (PA), USA) attached to two cascade impactors (Sioutas, SKC Inc., Eighty Four (PA), USA) (n=2) were used as collecting devices. To ensure enough amount of data, samplers were working uninterruptedly for 72 h. from Monday to Thursday in every school. Particles were collected onto 25 mm diameter (in the case of coarse and accumulation mode PM) and 37 mm diameter (for quasi-ultrafine PM) quartz fiber filters. Before sampling, clean filters were conditioned at 20 ºC and 40% humidity, and weighted several times till reaching constant mass values. Subsequently, filters were weighted under same conditions of temperature and humidity to elucidate PM mass by weight difference. Further details of site and sampling procedures can be consulted in Supplementary Information.

2.2. Analytical methods and main components determination

Analytical determinations were recently reported (Rovira et al., 2018). In brief, one set of filters were used for elemental determination. Trace elements were analyzed by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS), while macroelements were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after acidic digestion of filters. The second set of filters was divided into two portions. The first portion was used to obtain the levels of soluble inorganic ions by means of ionic chromatography (Cl^-, SO_4^{2-}, NO_2^-, and NO_3^-) and spectrophotometry by means of Berthelot's reagent (NH_4^+). The second portion of the filter was employed for total carbon (TC) determination by pyrolysis at 1000 ºC. A full list of analyzed metals, as well as their limits of detection and further details of analytical procedures can be consulted in Supplementary Information.

Main components determination was performed following previously published procedures (Pérez et al., 2008; Viana et al., 2014b). In brief, the different chemical constituents were classified into five main components attending to its nature: mineral matter (MM), sea spray (SS),

secondary inorganic aerosols (SIA), organic matter and elemental carbon (OM+EC), and trace elements (TE). Full details of main components calculation can be consulted in Supplementary Information.

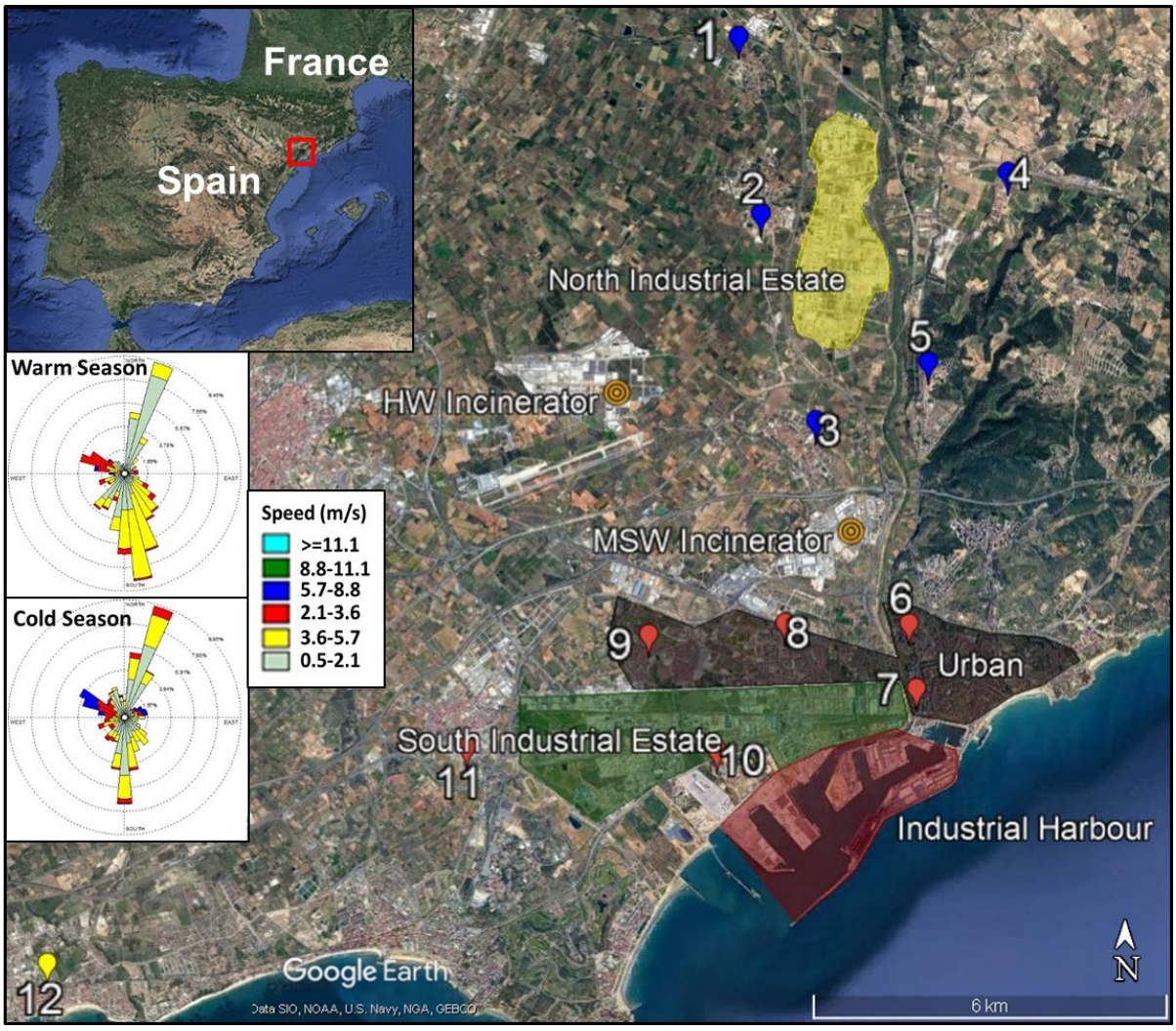

Figure 1: Location of sampled schools and different industrial and urban clusters in the Tarragona County. Blue, red, and yellow location marks represent the influence areas where the schools are located in (north, south, and background, respectively). HW Incinerator: Hazardous Wastes Incinerator; MSW Incinerator: Municipal Solid Waste Incinerator. Base map obtained from Google Earth.

School number	Latitude	Longitude	Floor	Windows surface (m^2)	Type of room	AC (yes/no)	Occupancy (h/day)	Student density (students/m^2)
1	41°12'38.74"N	1°12'11.65"E	First	0.90	Computer lab	no	2	0.42
2	41°11'1.50"N	1°12'27.64"E	Ground	5.60	Computer lab	yes	3	0.34
3	41° 9'7.75"N	1°13'7.55"E	Second	7.50	Computer lab	no	3	0.32
4	41°11'23.79"N	1°15'27.88"E	First	12.00	Computer lab	no	2.5	0.38
5	41° 9'39.98"N	1°14'29.48"E	First	7.70	Computer lab	yes	3.5	0.46
6	41° 7'16.30"N	1°14'15.14"E	Second	8.85	Computer lab	no	2	0.43
7	41° 6'40.67"N	1°14'20.51"E	First	6.44	Computer lab	yes	4	0.55
8	41° 7'16.60"N	1°12'44.89"E	Ground	5.20	Computer lab	no	2.5	0.49
9	41° 7'10.55"N	1°11'5.53"E	Ground	4.48	Computer lab	yes	3	0.51
10	41° 6'6.82"N	1°11'55.13"E	Ground	9.33	Computer lab	no	5	0.40
11	41° 6'9.00"N	1° 8'52.94"E	Ground	1.01	Meeting Room	yes	1	0.37
12	41° 4'10.27"N	1° 3'47.84"E	Second	8.06	Computer lab	no	3	0.42

Table 1: Characteristics of the sampled classrooms

2.3. Exposure and risk model

Human health risks due to the different toxic metals and metalloids present in PM were calculated following the guidelines recommended by the US EPA with slight modifications (RAIS, 2018; US EPA, 2009). Using as inputs the concentrations in toxic metals and metalloids in collected PM, carcinogenic and non-carcinogenic risks during school time were calculated for a 10-years old children, since they represent a middle point in the second and third stages of the primary school (8-12 years old children) (Generalitat de Catalunya, 2016). To have a better approach of potential risks, deposition pattern of PM within the respiratory tract of children were obtained from previous dosimetry modeling exercises performed in the area (Sánchez-Soberón et al., 2018). Afterwards, risks were studied into two different systems: respiratory and digestive. On one hand, the particles retained in the nose and tracheobronchial regions were considered as prone to generate digestive risks since the clearance process in the upper parts of respiratory system propels PM to the digestive tract (Stuart, 1984). On the other hand, those PM retained in the lung were treated as plausible cause of respiratory risks. Therefore, Hazard Quotient (HQ) and Excess Lifetime Cancer Risk (ELCR) were used to assess non-carcinogenic and carcinogenic risks for both systems (i.e. respiratory and digestive) respectively. Full details of calculations can be consulted in Supplementary Information.

2.4. Statistical analyses

Statistical analyses were performed using the package XLSTAT Version 2015.3.01.19349. To elucidate if the data presented a parametric distribution, Levene tests were used. Subsequently, the parametric variables were subjected to Saphiro-Wilk tests to assess if they followed a normal distribution. To study the significance of differences, Student's t-test (in case of parametric, normal distributed data) and Mann-Whitney (in the rest of cases) were used. To study correlations among variables, Pearson correlation tests were applied to the data. Results of statistical tests were considered significant for P values smaller than 0.05 ($p < 0.05$).

3. Results and discussion

3.1. PM levels

The mean PM levels for the different fractions and seasons are summarized in Table 2. Average levels of PM for both periods were below the regulatory limits established for daily and annual PM_{10} (50 and 40 $\mu g/m^3$, respectively), and for annual $PM_{2.5}$ (25 $\mu g/m^3$) (European Commission and EU Parliament, 2008). However, daily regulatory limit value for PM_{10} was exceeded in the cold season in the school number 1 (Tables S2 and S3). This school, along with schools 2 and 6, exceeded the annual values for both PM_{10} and $PM_{2.5}$ during the same period. In the warm season, school 12 was the only center showing PM_{10} values above the yearly regulatory threshold. While the concentrations of PM for all fractions reached higher values in the cold season, $PM_{0.25}$ was the only one showing significant differences between the two seasons. It can be explained taking into account the higher levels of carbonaceous fractions (OM+EC) detected during the cold season, which is explained in more detail in section 3.2.4. No differences were found when comparing the levels of PM in the two different influential areas (North and South) in both seasons. To get an idea of the outdoor influence on indoor environments, PM concentrations obtained in the current study were compared with their outdoor counterpart to be published in a future study (Sierra et al., unpublished data). In relation to this, results were variable: some schools present

higher indoor levels, while other present higher outdoor concentrations (Table 3). Average PM levels for the whole area were similar in both environments for every fraction. However, a significant correlation was not found between outdoor and indoor PM levels. In general terms, those schools using air conditioning (AC) systems during the warm sampling period showed significantly lower levels of indoor $PM_{10-2.5}$ than their outdoor counterpart (Table 1). On the other hand, the centers without AC showed similar $PM_{10-2.5}$ levels in the warm season to those registered outdoors. As previously reported, these results corroborate the influence of AC devices as filtration system of coarse PM, and suggest the opening of windows for ventilation purposes in centers lacking AC (Waring and Siegel, 2008). However, two centers did not follow this pattern. School number 7 registered similar levels in both environments, despite using AC. This trend could be a consequence of its highest levels of student density (>0.5 students/m^2) and occupancy (4 hours per day), leading to a greater dust resuspension (Klinmalee et al., 2009). In turn, school number 10 showed significant lower values of coarse PM indoors in the warm season, in spite of the absence of AC, due to non-occupancy of the room during the warm sampling period.

	Cold Season						**Warm Season**					
	$PM_{10-2.5}$		**$PM_{2.5-0.25}$**		**$PM_{0.25}$**		**$PM_{10-2.5}$**		**$PM_{2.5-0.25}$**		**$PM_{0.25}$**	
µg/m³	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**	**Average**	**SD**
PM	12.08	7.47	7.87	4.31	11.94	7.20	8.11	8.03	5.99	1.83	6.10	2.40
Al	0.43	0.37	0.16	0.17	0.06	0.05	0.23	0.25	0.13	0.21	0.03	0.01
Al_2O_3	0.81	0.70	0.31	0.33	0.12	0.10	0.44	0.47	0.25	0.40	0.06	0.03
SiO_2	2.42	2.09	0.92	0.99	0.35	0.30	1.31	1.40	0.75	1.21	0.19	0.08
Ca	0.97	0.82	0.47	0.39	0.38	0.41	0.46	0.36	0.23	0.26	0.06	0.05
CO_3^{2-}	1.45	1.22	0.71	0.59	0.57	0.61	0.68	0.54	0.35	0.39	0.08	0.08
Mg	0.11	0.06	0.05	0.03	0.05	0.05	0.06	0.04	0.03	0.01	0.03	0.01
Fe	0.18	0.13	0.08	0.05	0.04	0.04	0.03	0.06	0.02	0.05	0.06	0.07
Mn	4E-03	3E-03	4E-03	7E-03	3E-03	5E-03	7E-04	2E-03	5E-05	1E-05	7E-04	4E-04
Ti	0.03	0.03	0.01	0.01	2E-03	3E-03	0.01	0.01	0.01	0.02	3E-04	6E-04
Na	0.55	0.29	ND†		ND		0.59	0.17	ND		ND	
Cl^-	0.17	0.14	0.16	0.20	0.08	0.05	0.10	0.12	0.04	0.05	0.02	0.02
SO_4^{2-}	0.12	0.06	0.40	0.23	0.71	0.35	0.05	0.06	0.43	0.29	0.49	0.32
NH_4^+	4E-03	4E-03	0.01	0.03	0.09	0.07	0.04	0.04	0.11	0.12	0.24	0.09
NO_3^-	0.26	0.08	0.42	0.14	0.28	0.12	0.28	0.37	0.17	0.15	0.19	0.25
NO_2^-	0.06	0.04	0.01	0.03	0.01	0.01	0.04	0.04	0.01	0.01	0.01	0.01
TC‡	2.18	1.12	1.87	1.24	3.16	1.53	1.63	1.38	1.43	0.86	1.90	1.14
§OC+EC	1.89	1.02	1.77	1.19	3.04	1.43	1.52	1.31	1.37	0.86	1.88	1.13
¶OM	2.39	1.29	2.23	1.49	3.84	1.80	1.91	1.65	1.73	1.09	2.37	1.43

Table 2: Average concentrations and standard deviations (SD), expressed in µg/m^3 for the different macro-components of PM.†ND: Non Detected; ‡TC: Total Carbon; §OC+EC: Organic and Elemental Carbon; ¶OM: Organic Matter

		Cold Season		Warm Season	
		$PM_{10-2.5}$	**$PM_{2.5}$**	**$PM_{10-2.5}$**	**$PM_{2.5}$**
PM and macro-components	PM	1.19	0.93	0.86	1.37
	Al, Al_2O_3, and SiO_2	4.68*	0.62	1.74	3.27*
	Ca and CO_3^{2-}	2.04	0.68	0.49	0.32*
	Mg	0.98	0.25*	0.30	0.38*
	Fe	0.98	1.99	0.18**	2.53
	Mn	0.73	3.14	0.01**	0.03**
	Ti	3.46*	1.29	0.61	2.49
	Na	0.09**	NC†	0.12**	NC
	Cl^-	0.27	1.28	0.25	0.50
	Sea Spray	0.29	NC	0.18	NC
	SO_4^{2-}	0.29	1.12	0.37	1.43
	NH_4^+	1.77	1.41	0.26**	0.77
	NO_3^-	0.33*	2.31*	0.42*	1.20
	NO_2^-	7.10	1.87	4.91**	0.59
	TC	2.02*	2.47**	0.78	1.72*
	OC+EC	1.92*	2.77**	0.79	1.88**
	OM	2.15*	2.69**	0.84	1.94**
	OM+EC	2.20*	2.97**	0.87	2.06**
Trace elements	Ba	1.23	0.68	0.02*	0.38
	Cd	NC	0.16	NC	NC
	Co	2.16	1.40	NC	NC
	Cr	0.78	2.35	0.01	1.83
	Cu	0.44	0.32**	0.20	0.20**
	Mo	0.67	0.10**	NC	NC
	Ni	2.57	0.43	NC	NC
	Pb	1.23	1.34	0.27*	0.49*
	Sb	0.51	2.78*	0.56	1.65*
	Sn	0.29*	2.98	3.09	1.58
	Sr	1.20	3.83	0.25	0.71
	U	0.32	0.05**	NC	NC
	V	0.31	0.94	NC	NC
	W	>1	>1	NC	NC
	Zn	0.44	1.25	NC	0.37*
	Zr	14.48	0.53	2.21	0.81**

Table 3: Average Indoor/Outdoor (I/O) ratio of the different macrocomponents and toxic trace elements for the whole sampling area. Outdoor concentrations have been taken from ongoing studies (data pending of publication). I/O values for $PM_{0.25}$ are not depicted, since this fraction

was not collected outdoors. *Significant differences ($p<0.05$) between outdoor and indoor concentrations; **significant differences ($p<0.01$) between outdoor and indoor concentrations; †NC: not calculated

3.2. Main Components

The mean concentrations of PM macrocomponents are shown in Table 2. Also, the contribution to total PM from main components is depicted in Figure 2.

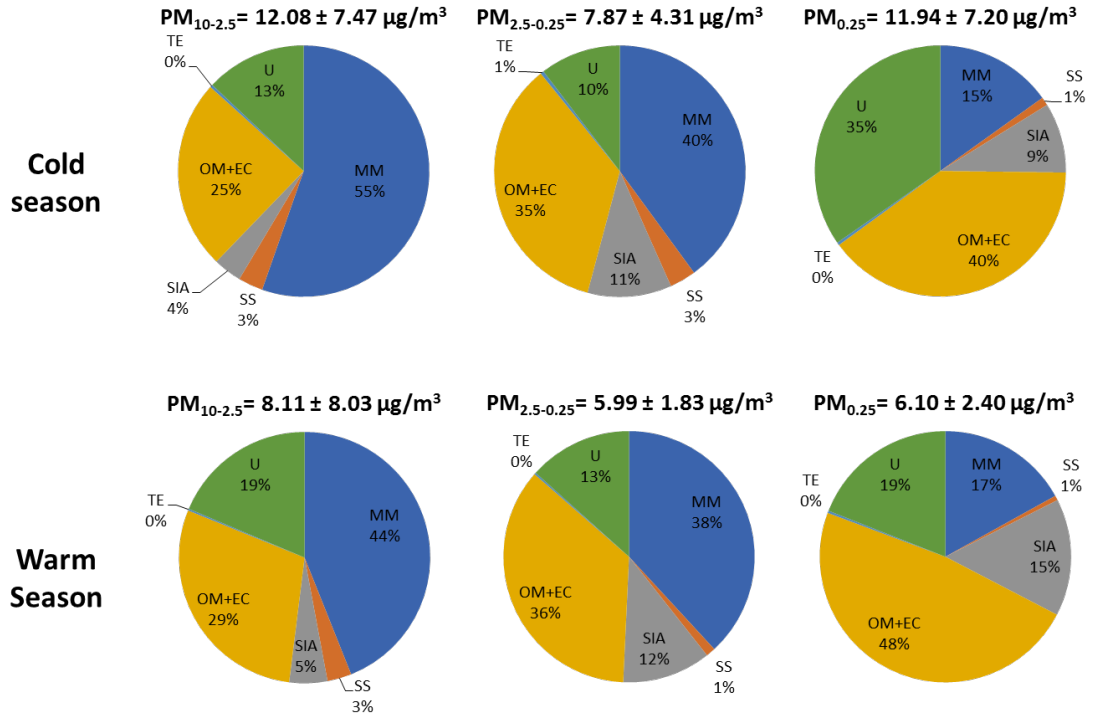

Figure 2: Average main components and their contribution to PM mass for the sampling area as a whole. PM levels are given as mean ± SD. MM: Mineral Matter; SS: Sea Salt; SIA: Secondary Inorganic Aerosols; OM+EC: Organic Matter and Elemental Carbon; TE: Trace Elements; U: Unaccounted.

3.2.1.Mineral matter (MM)

As expected from previous studies, mineral matter was mostly located in the coarse and accumulation mode, regardless season and location (Sánchez-Soberón et al., 2015). Levels of mineral matter and its addends (i.e., Ca, Mg, Fe, Mn, Ti, P, K, CO_3^{2-}, SiO_2, and Al_2O_3) were higher in the colder season, as a consequence of the higher outdoor $PM_{10-2.5}$ levels (unpublished data). Comparing with outdoor levels, Ca, carbonates, and Mg showed a general trend to exhibit I/O ratios below 1, excepting the case of cold season coarse PM, when I/O ratios were close to 1 or higher (Table 3). In the current study, most of the classrooms evaluated were computer labs equipped with whiteboards, discarding the presence of majoritarian sources of indoor Ca, such as chalk or paper filling (Oeder et al., 2012; Rivas et al., 2014). Therefore, the main origin of Ca and carbonates, along with Mg, is found in the outdoor mineral dust. These elements would be transported stuck to the sole of the student's shoes. Once indoors, they would be resuspended, resulting in higher concentrations during cold season (Qian et al., 2014). As in the case of coarse

PM above discussed, the opening of windows would equalize outdoor and indoor levels, while the use of AC system would reduce indoor concentrations, resulting in an overall decrease of average I/O ratios. A similar trend was followed by Mn, with the peculiarity that in School 10 -in the cold season- it was distributed towards fine fractions ($PM_{2.5-0.25}$ and $PM_{0.25}$). The sampling room in this spot is located besides a vocational training workshop, where emissions of fine Mn could be expected as a consequence of welding activities (NIOSH, 2013). Apart from outdoor mineral origin, Al and its derivatives (SiO_2 and Al_2O_3), and Ti exhibited I/O ratios higher than 2 in $PM_{2.5}$ warm season, which suggests the presence of indoor sources of these metals. Previous studies have detected construction materials and paints as contributors to the presence of these elements in indoor environments (Molnár et al., 2007; Rasmussen et al., 2018). Potassium and P were not detected indoor, although outdoor levels were detected (unpublished data). In addition to the exclusive outdoor origin of these elements, our results can be also due to the high limit of detection experienced when analyzing them.

3.2.2.Sea-spray (SS)

In the present investigation, Na was under detection limits in most schools during both seasons. This phenomenon could be explained by the high detection limit (1.06 $\mu g/m^3$) of the ICP-OES. Nevertheless, sea spray levels were estimated from coarse Cl^- content. In spite of the lack of significant differences, average sea spray concentrations were higher in the colder season, as it was observed for outdoor PM (unpublished data). As in the case of mineral-bonded metals, this component is mainly located in the coarse fraction, having its main origin in the sea (Pey et al., 2013). Consequently, the levels of this component are significantly lower in the indoor environment, due to the lower infiltration factor of coarse PM (Diapouli et al., 2013). Sea-spray for fine fractions was not calculated, since fine Cl^- could have its origin in different industrial operations (Wey et al., 2008). In our study, however, accumulation mode and quasi-ultrafine Cl^- seem to be also impacted by indoor sources, such as cleaning products and flame retardants, as can be deduced by I/O ratios > 1 (Kodavanti et al., 2018; Wong et al., 2017).

3.2.3.Secondary Inorganic Aerosols (SIA)

Higher levels of SIA were observed in the colder season for most schools and particle fractions. However, the behavior of its four summands differs. Thus, sulfates experienced an increase in its levels when decreasing PM size, showing higher levels in colder season, while ammonium also showed the highest contribution in the $PM_{0.25}$ fraction, but its levels were higher in the warmer season. This seasonal behavior was also noticed in outdoor ammonium, and could be caused by agricultural activities. The warm season (late summer/early autumn) coincides with the fertilizing period in the area and higher temperatures enhances ammonia volatilization (Zhang et al., 2014). During the warm season, these two secondary compounds were significant correlated (Pearson's r =0.69) in $PM_{0.25}$ for the whole area of study. This correlation explains a higher variability (Pearson's r = 0.82) in the case of the South area. These correlations, together with the relative levels of every compound, suggest the formation of ammonium sulfate from its gaseous precursors (i.e. SO_2 and NH_3) in the ultrafine particle fraction during the warm season (Gong et al., 2013). In turn, nitrates were prevalent in the accumulation mode ($PM_{2.5-0.5}$) during the cold season, regardless of the study area. Cold season indoor levels of nitrates in $PM_{2.5}$ were significantly higher than those found outdoor (Table 3). On the other hand, indoor warm values of nitrates were mainly located in the coarse mode, reaching lower values than their outdoor counterparts. During this season, the coarse nitrates correlated with Ca levels (Pearson's r = 0.95 and 0.81 for North and South areas, respectively), suggesting the formation of calcium nitrate

through uptake of NO_X on mineral dust (Usher et al., 2003). This seasonal pattern has been found in previous studies, and it is explained by different temperature-depending processes leading to the formation of nitrates in particles (Viana et al., 2014b). No significant differences were found in indoor NO_2^- levels among seasons or fraction. Nitrites were mainly located in the coarse fraction, showing I/O ratios higher than 1. Some studies have also observed this phenomenon, suggesting the presence of indoor sources of NO_2^- or its precursors (Balasubramanian and Sheng, 2007; Song et al., 2014).

3.2.4. Carbonaceous Materials (OM +EC)

Higher levels of carbonaceous materials were found in the cold season, regardless of the study area and fraction. These differences were statistically significant for $PM_{0.25}$ fraction. However, their contributions to total PM mass were higher during the warm season, because of lower PM levels and mineral contribution to coarse and accumulation mode fractions in the warm season. Strong correlations ($p<0.01$) were found between outdoor and indoor concentrations of OM+EC $PM_{2.5}$ (Pearson's $r = 0.73$, respectively) in the cold season, while no linear correlations were found in the warm season. These results suggest that cold season levels are more influenced by outdoor OM+EC, while indoor warm season concentrations present a higher influence from indoor sources, such as fragments of furniture, clothes, and skin flakes (Pegas et al., 2012; Rivas et al., 2014). It seems plausible a higher contribution of skin flakes during the warm period, since in this season clothes cover less surface of the children body, retaining thus less death cells than under colder conditions (Butte and Heinzow, 2002). Unlike other studies, increasing indoor contributions of OM+EC were noticed when decreasing the PM size (Mašková et al., 2015; Viana et al., 2014b). In addition to the higher influence of outdoor PM aforementioned, it could be also indicative of a higher formation of indoor secondary organic aerosols (SOA). In the current study, we sampled in computer rooms containing printers and white boards. The presence of these two elements could lead to formation of ozone and volatile organic compounds (VOCs) respectively, which, when reacting in the atmosphere, could form SOA in the ultrafine PM (Morawska et al., 2009). Regarding areas of influence, no significant differences in OM+EC levels were noticed between North and South. However, warm season levels of OM+EC were significantly higher in the background school than in the two other areas, especially in the coarse fraction. As above discussed, these results suggest a higher contribution from coarse OM materials (i.e., skin flakes and clothes fragments), joined to a less intense cleaning schedule during the sampling period.

3.2.5. Trace elements (TE)

Average concentrations of toxic trace elements are shown in Table 4. Detailed school-by-school concentrations are shown in Tables S4 and S5. Indoor levels of Pb, As, Cd, and Ni did not surpass the annual concentration limits established by the European legislation (500, 6, 5, and 20 ng/m^3, respectively) in any of the sampled schools (EU Parliament, 2005; European Commission and EU Parliament, 2008). Trace elements were higher in colder season in every school and PM fraction. Arsenic, Be, Hg, Li, Se and W could not be detected. In contrast, Cu, was among the most prevalent elements. Copper showed a homogeneous distribution among the different fractions, without significant differences among seasons. Regardless of fraction, average Cu I/O ratios were lower than 1, indicating an outdoor origin for this metal (Amato et al., 2014). Average coarse and fine indoor Pb levels were significantly higher during the cold season. In this season, Pb levels in coarse and fine PM were higher in the indoor environment. However, this trend is reverted in warm season, showing I/O ratios significantly lower than 0.5 for coarse and fine fractions. In addition to outdoor Pb sources, indoor levels of this metal could be also related to

indoor sources, such as old paintings and computer solders (ATSDR, 2017). Peeling off of painting is correlated with temperature fluctuation, which could be greater in the cold season due to heating systems use during daytime (CCI, 2014). In turn, Sn was mainly present in the quasi-ultrafine ($PM_{0.25}$) fraction. Levels of indoor Sn in fine particles were significantly related to their outdoor counterparts, albeit the latter exhibited higher concentrations. As for Pb, the extra amount of Sn could have its origin in indoor computer solders (Royal Society of Chemistry, 2018). Distribution pattern (i.e., prevalence in coarse fraction) and I/O ratios of Ba, Sr, and Zr were similar to those found for mineral matter, confirming the crustal origin of these metals (Tran and Alleman, 2009). Higher levels of Sb in coarse PM were registered outdoor for both seasons, while greater levels of this metal were found in indoor $PM_{2.5}$. Antimony is recognized as a minor mineral compound, which had been related previously with road traffic (Mari et al., 2016; USGS, 2014). However, nowadays, it is extensively found in flame retardants, which would explain why Sb is more abundant in the indoor fine PM (Babushok et al., 2017). Zinc and Cr showed I/O ratios higher than 1 for fine fractions. Apart from the outdoor environment, indoor sources of these metals, such as painting, driers, wood stains, and stainless steel coatings, have been previously reported (Canha et al., 2014; Rivas et al., 2015). Molybdenum, U, Co, Ni, V, Cd, and W were only found indoor in the cold season, which coincides with the higher outdoor concentrations for most of them. I/O ratios of Mo are lower than 1 for every fraction. However, this metal showed an indoor prevalence towards the coarse fraction, while outdoor levels showed higher levels in the fine fraction. It could be the result of the influence of bacterial sources of Mo in indoor environments, which have a greater impact indoor during the cold season, and/or are removed in the warm season by AC systems (Frankel et al., 2012; Magalon et al., 2011). Uranium I/O ratios are lower than 1, being present in the coarse fraction, suggesting a mineral origin from outdoors (Gieré et al., 2012). W was only present in six schools, mainly in the coarse fraction. All these schools showed I/O ratios lower than 1 for this metal, except school number 10. As in the case of Mn, W could have been used in welding operations performed besides the sampled classroom of this school (USGS, 2018). Nickel and V showed prevalence in the quasi-ultrafine fraction. Nickel was only present in $PM_{10\text{-}2.5}$ in schools 1 and 3, whose origin could be related with wall dust (Suryawanshi et al., 2016). Apart from that, Ni and V exhibited I/O values below 1 for most fractions. Therefore, their most likely origin are the industrial emissions found outdoors (de Foy et al., 2012). A similar trend was also followed by Cd but having the peculiarity that outdoor levels are prevalent in the coarse fraction. The origin of this metal is related to coarse PM emitted by car's pieces abrasion, which restricts its entrance in indoor environments (Coudon et al., 2018). Similarly to Pb, the presence of these elements in indoor aerosols can be influenced by the greater temperature fluctuation experienced in the cold season. On the other hand, outdoor levels of Co showed a homogeneous distribution along the different PM fractions (unpublished data). However, indoor Co was mainly located in the coarse fraction, showing levels significantly higher than those detected outdoor. According to the current results, this element could have two main origins. Coarse Co showed significant correlation (Pearson's $r = 0.46$) with Fe, suggesting a mineral origin of this metal (British Geological Survey, 2009). As above commented, the resuspension of mineral dust in indoor environments could increase the levels of this element indoor, despite having an outdoor origin. However, quasi-ultrafine Co showed a significant correlation (Pearson's $r = 0.79$) with Ni, corroborating the industrial origin of this metal in finest fractions (Cobalt Institute, 2017).

	Cold Season						Warm Season					
	$PM_{10-2.5}$		$PM_{2.5-0.25}$		$PM_{0.25}$		$PM_{10-2.5}$		$PM_{2.5-0.25}$		$PM_{0.25}$	
ng/m³	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
Ba	4.45	3.76	1.75	1.95	1.35	0.82	0.11	1.33	0.27	2.25	1.04	1.49
Cd	ND†		ND		0.03	0.02	ND		ND		ND	
Co	0.11	0.10	0.04	0.04	0.04	0.02	ND		ND		ND	
Cr	1.48	0.60	1.03	0.79	1.42	1.10	1.02	0.36	1.01	0.37	4.92	4.77
Cu	2.02	1.04	2.00	1.71	1.60	2.17	1.81	1.33	2.39	2.25	1.43	1.49
Mo	1.87	1.18	1.37	0.90	0.32	0.17	ND		ND		ND	
Ni	0.97	1.26	0.58	0.36	1.19	1.47	ND		ND		ND	
Pb	1.15	1.21	0.91	0.83	1.72	1.28	0.26	0.71	0.05	0.01	0.35	0.35
Sb	0.20	0.18	0.31	0.67	0.41	0.29	0.13	0.17	0.06	0.02	0.19	0.15
Sn	0.10	0.03	0.19	0.32	1.16	2.14	0.67	2.07	0.12	0.19	0.19	0.09
Sr	1.91	2.52	1.47	2.21	1.69	2.78	0.56	0.75	0.58	1.26	0.23	0.28
U	0.02	0.02	0.01	0.02	0.01	0.02	ND		ND		ND	
V	0.51	0.42	0.52	0.43	0.91	0.83	ND		ND		ND	
W	0.10	0.16	0.05	0.02	0.06	0.03	ND		ND		ND	
Zn	4.22	7.32	3.88	7.36	13.8	20.0	ND		ND		11.4	3.32
Zr	4.86	8.42	1.07	1.22	0.20	0.16	1.06	1.83	0.40	0.26	ND	

Table 4: Average concentrations and standard deviations (SD) expressed in ng/m³ for the different toxic trace elements of PM. †ND: Non Detected

3.2.6. Unaccounted (U)

The origin of unaccounted materials is diverse. In the present case, it seems plausible to be originated as a consequence of an underestimation on the content of mineral matter or OM+EC. As in previous studies using the same sampling devices, we found the highest content of unaccounted materials in the quasi-ultrafine fraction, which can be explained by the difference in collection method experienced by this fraction (Viana et al., 2014b).

3.3. Exposure and risks

Average deposition masses in the different parts of the respiratory tract for a 5 hours period in classroom are depicted in Figure 3. According to our calculations using previously depicted deposition rates, coarse particles are mostly retained in the upper part (nasopharynx) of the respiratory tract, while accumulation mode and quasi-ultrafine particles are mainly retained in lungs (Sánchez-Soberón et al., 2018). More than 96% of inhaled coarse PM will be able to generate digestive disorders (i.e., mass retained in the nasopharynx and tracheobronchial region). This high percentage is reduced to 34% and 24% for accumulation and quasi-ultrafine particles. At equal concentrations, accumulation model particles are the most prone to generate problems in lungs despite the smaller size of quasi-ultrafine particles. As explained in previous studies, this is a consequence of the Brownian motion followed by particles smaller than 0.5 μm (Bakand et al., 2012). Exposure is directly related to PM concentrations. Consequently, those schools registering higher levels of coarse PM will elicit more effect on digestive system, while those

enriched in accumulation and quasi-ultrafine PM will have a greater effect on potential lung diseases. In this study, school 1 showed the highest values in cold season, while school 12, showed the maximum exposure values for the warm season.

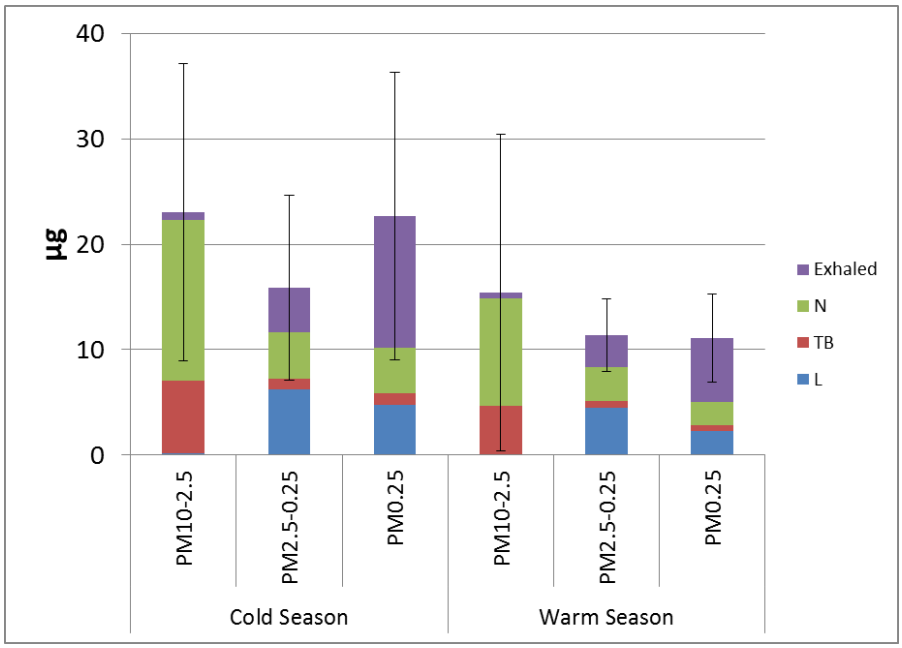

Figure 3: Average daily deposited masses (µg) for the sampling area as a whole retained in the nasopharynx (N), tracheobronchial region (TB), and lungs (L) during school routine. Exhaled depicts the mass of PM inhaled but not retained in the respiratory tract. Bars depict the standard deviation of total inhaled masses

For risk assessment purposes, those metals that were non detected in any fraction of any school were discarded. Therefore, all toxic metals were assessed for cold season while Cd, Co, Mo, Ni, U, V, and W were excluded for warm season. To overpass the limitations imposed by low Cr recoveries (≥ 30%; see SI) an uncertainty factor of 10/3 was applied to Cr concentrations for risks calculation purposes.

Non-carcinogenic risks for every school and toxicant assessed were below the safety limits (Hazard Quotient (HQ) <1) for either potentially affected system (i.e., respiratory or digestive) and season (i.e., cold or warm) (Tables S6 and S7). For the digestive system, maximum cold season value was reached in school number 8 (HQ $=1.32 \cdot 10^{-2}$), while in the warm season, the maximum value corresponded to school number 2 (HQ $=3.09 \cdot 10^{-3}$). In both cases, these risks were provoked by Zr, since this element exhibits the lowest oral reference dose (RfD $= 8 \cdot 10^{-5}$ mg/(kg·day)). Coarse levels of this metal were the prevalent contributors (>95%) to its associated risks. With respect to inhalatory non-carcinogenic risks, maximum cold season value was reached for Mn in school 10 (HQ $=3.51 \cdot 10^{-2}$), while the maximum warm season value was found in school number 9, corresponding to Al (HQ $=6.50 \cdot 10^{-3}$). In both scenarios, the maximum contributors to those risks were generated by fraction $PM_{2.5\text{-}0.25}$.

Carcinogenic risks for every school, season, and fraction were also below the safety threshold of 1 case of cancer per 100000 inhabitants (10^{-5}), established in the Spanish regulation (MAGRAMA, 2007). Maximum digestive carcinogenic risk in cold season was reached as consequence of the inhalation Pb in school number 2 with an ELCR number of $1.62 \cdot 10^{-9}$. Most of this risk (98%) was elicited by $PM_{2.5\text{-}0.25}$. On the other hand, the maximum digestive

carcinogenic risks in warm season corresponded to Cr (VI) (ELCR = $4.22 \cdot 10^{-9}$) in school 3. Almost two thirds (64%) of this risk were caused by inhalation of $PM_{0.25}$. It is interesting to note that $PM_{2.5-0.25}$ and $PM_{0.25}$ are the fractions provoking most of the carcinogenic risk in the digestive system despite their deposition rates in nasopharyngeal and tracheobronchial regions are much lower than deposition rates for $PM_{10-2.5}$. This result highlights how higher concentrations of toxic metals in fine fractions ($PM_{2.5-0.25}$ and $PM_{0.25}$) can overpass the limitations set by deposition ratios to elicit gastrointestinal risks. Chromium (VI) was also responsible for maximum respiratory carcinogenic risk in both seasons. School number 3 reached the maximum levels in cold and warm seasons ($7.26 \cdot 10^{-7}$ and $1.65 \cdot 10^{-6}$ respectively). Most of the risk in cold season was due to the accumulation mode fraction (86%), while warm season risk was mostly a consequence of quasi-ultrafine levels (83%). Carcinogenic risks were highly affected by the fact that both Pb and Cr (VI) are mutagenic. Therefore, their carcinogenic risks have been multiplied by an age-dependent adjustment factor (ADAF) of 3. It is important to remark the role of PM deposition pattern within the respiratory tract. In the cold season, maximum indoor concentrations of Cr (VI) were reached in coarse PM. However, this fraction is mostly retained in the upper parts of the breathing system, and consequently, their lung carcinogenic potential is negligible.

In the current study, the risks were below safety thresholds. However, it is important to note that our assessment was done taking into account only 20% of children daily routine, during 175 days a year. Therefore, assessing the exposure in other environments and exposure routes (i.e., dermal and ingestion) could increase the chances of experiencing risks. Another aspect to take into consideration is the effect of mixtures. In the present investigation, we evaluated the digestive and respiratory risks in a one-metal-at-a-time fashion. Following this approach, we did not consider the plausible interaction among the different metals, which could affect the overall health effects (Heys et al., 2016). Finally, it would be needed to acknowledge the effect of occupancy. To ensure a sufficient amount of sample, PM was collected for 72 h. However, children were present in classrooms for period of 4 daily hours at most, during which the chemical composition and levels of PM can be impacted through resuspension (Tran et al., 2014). A more time extensive sampling strategy focused on occupancy hours will help to obtain a more accurate risk values in future studies.

4. Conclusions

In the present study, we collected three fractions of PM inside twelve classrooms influenced by different urban, industrial, and natural sources during two different seasons (cold and warm). A subsequent chemical characterization of these PM was performed to know their origin and to evaluate their toxic potential. Mean levels of PM were higher during the colder season, with most of schools showing PM levels below regulatory thresholds. Coarse particles dominated the mass of PM in both seasons. The two prevalent contributors to PM mass were mineral matter and carbonaceous materials, with decreasing and increasing contributions, respectively, when diminishing the PM size. Indoor concentrations and composition of some PM compounds (such as sea spray, mineral matter, Cu, Pb, Al, NO_3^-) varied significantly with respect to their outdoor counterpart, highlighting the importance of indoor processes in the air quality of this environment. Children exposure to PM is mainly located in the upper part of the respiratory tract (nasopharyngeal and tracheobronchial regions). Finally, the carcinogenic and non-carcinogenic risks were below their respective safety thresholds for both, digestive and respiratory systems.

Acknowledgements

Financial support for this study was provided by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (ERDF) as part of the project CTM2015-65303-P. J. Rovira received funds from the Health Department of the Generalitat de Catalunya, Catalonia, Spain through "Pla Estratègic de Recerca i Innovació en Salut" (PERIS 2016–2020) fellowship (SLT002/ 16/00094).Authors want to thank the Directive Boards of the twelve educative centers involved in the present study for their kind cooperation.

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