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The relationship between indoor and outdoor levels of PM10 and its chemical composition at schools in a coastal region in Spain

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ABSTRACT

PM10 levels and its chemical composition were studied inside and outdoor of seven primary schools (3 in urban environment, 3 in industrial environment, 1 in rural environment) located in the Mediterranean coast in an area with an important industrial nucleus dedicated to the treatment of raw mineral materials. The main objective of this work is a comparison between these levels obtained inside and outside schools and also asses the influence of various natural and anthropogenic emission sources on particles concentrations found inside. The indoor airborne samples were collected using RespiCon TM. In the three outdoor sampling stations was used a minivol air sampler type 3.1 LVS of Derenda. PM10 Chemical composition was obtained by ICP-MS (elements) and ion chromatography The ratio I/O (indoor/outdoor) has been calculated taking into account only the samples taken in the same conditions. In all schools the ratio I/O for PM10 was greater than unity (between 1.3 and 7.8), indicating that existed significant indoor sources of these particles. In the three schools located in the industrial environment were collected PM10 samples inside and outside in non-teaching periods. Comparing the values of I/O when the classrooms were unoccupied with respect to the average value of these same schools when the classrooms are occupied, the behaviour is different depending on the location. On the other hand, a sample in an industrial school was obtained when some infrastructure works were being carried out outside of school. This caused a significant increase in the concentration of particles in the interior (I/O = 19.9). From the levels of As, Ni, Cd, Pb, Al, B, Zn, Mg, Sb, F^-, ClO^{2-}, NO^{3-} and SO_4^{2-} in PM10 inside and outside of each school, also the ratios I/O were calculated. These chemical ratios I/O were higher than unity in all cases and generally higher than those recorded in the case of PM10. Finally, Pearson correlation coefficients (r) between the elements and anions and the PM10, and between the different elements and anions were calculated for the purpose of establishing the existence of common emission sources.

1. Introduction

It is well known by epidemiological researches that there is a strong relationship between air pollution and morbidity and mortality, with air pollution potentiating a wide range of diseases and cardiovascular problems, especially in young, elderly and ill people. According to Xing et al. (2016), adults exposed to ambient air pollution, for example PM10 (particulate matter 10 micrometers or less in diameter) and coarse particulate, have shown increased prevalence of respiratory disease. Such health problems include cardiac arrhythmias, reduced lung function, asthma, chronic bronchitis, and increasing respiratory symptoms such as sinusitis, sore throat, dry and wet cough, and hay fever (Moreno et al., 2004). Recent researches also suggests that these problems can be related to specific components of particulate matter rather than mass (Ghio and Devlin, 2001; Khaniabadi et al., 2017).

Children have certain characteristics that make them more susceptible to air pollution than adults. On the one hand, their breathing rate is higher (Faustman et al., 2000; Landrigan et al., 1999) and on the other hand respiratory systems of children under five are not fully developed and their immune system is not mature (Banerjee, 2000; Boy et al., 2000; Khalequzzaman et al., 2007).

However, people in developed countries are spending the majority of their time (more than 70%) in various indoor environments (Guo et al., 2004). For young people, the school environment is where they spend the

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most considerable portion of the day in, apart from at home (Silvers et al., 1994). Despite this evidence most air pollution studies focus on the general population (considering all age groups) and on the relationship with the pollutant levels outdoors.

Pallarés et al. (2019) establish a catalogue that brings together the morphologic characteristics of the main types of particles found among the indoor airborne fine particles captured in the primary schools in the studied area and to assess the influence of outside emission sources, on the particles found inside of schools with natural ventilation.

It is generally accepted that indoor concentrations of particles derive from two sources: indoor and outdoor. However, the significance of both sources depends on a number of variables, the most important of which are the generation rate of particles indoor, the outdoor particle concentration, air exchange rate, particle penetration efficiency from the outdoor to the indoor environment, and the particle deposition rate in indoor surfaces (Kamens et al., 1991; Thatcher and Layton, 1995).

Ratios between the concentrations of particles and chemical elements found indoor and outdoor a building give an indication of the contribution of indoor sources. It is expected that in the absence of internal sources, the ratios I/O (indoor/outdoor) between the concentrations are less than or equal to 1 (Chao et al., 1998; Jones et al., 2000) and the ratios will be higher unit in the presence of significant indoor sources (Zuraimi et al., 2003; Stranger et al., 2007).

In places where there is no clear source of contamination in the interior, the occupant-related activities may represent the main source of particles. These are usually composed of clothing fibres, hair fragments, soil particles, skin cells, resuspension of particles of different nature due to the movement, and emissions of materials used, as well as paper, spores and fibres, etc. (Branis et al., 2005).

Moreover, the type of ventilation used is a very important factor that determines the level of particulate indoor and therefore the values of the ratio I/O (Parker et al., 2008). Numerous studies have compared different types of ventilation and determined its influence. Thompson et al. (1973) in his study found that the ratios I/O of the PST were less than 0.1 in air conditioned buildings with higher filtration systems while were much higher in buildings with natural ventilation where there was also a high movement of people. Similar events were observed by Zuraimi et al. (2007) with the PM2.5 particulate, with values of I/O close to unity with the natural ventilation and recording a significant decrease when using air conditioning systems with filters.

The highest concentration of PM10 and PM2.5 found by Gemenetzis et al. (2006) in Thessalonika indoors were associated with limited ventilation and high outdoor concentrations. The use of a receptor model indicated that emissions from traffic, resuspension of road dust and heating are the main sources of PM10 in the outside (Samara et al., 2003).

The study area is located in the Mediterranean coastal basin, province of Castellón (Spain) with major problems of high concentration of particulate matter in ambient air, and also is located next to an industrial centre based on the treatment of ceramic raw mineral materials as ceramic red clays and silicates (important particulate emissions). It is a strategic zone in the framework of EU pollution control. Around 80% of the European Union ceramic tile and ceramic frit manufacturers are concentrated in two areas, forming the so-called ceramic clusters - in Modena (Italy) and in Castellón (Spain). Based on the studies in the literature (Alastuey et al., 2000) and on the data shown on Internet by the regional authorities derived from the air quality networks in these areas, it can be deduced that metals and other chemical components and PM10 are the two parameters of most concern regarding EU legal requirements (Minguillón et al., 2007).

Winds have a great influence on the dispersion and transport of air pollutants, which makes it important to know the type of wind that is predominant in a sampling area. In coastal areas, the most important air currents are periodic land and sea breezes (Pogosyan, 1965). Previous studies of the system of winds in the province of Castellón (Boix, 1996; Gómez et al., 2001; Álvarez et al., 2004) showed much defined characteristics for these two components of the wind. The direction and speed of these two wind components in one area may vary depending on the topography. A general characteristic of the coastal areas is the low speed of the winds (Querol et al., 2004; Galindo et al., 2018). The change from one component to another depends on the hours of the day, and therefore the beginning and end of each breeze component depend on seasonality.

The main objective of this study is a comparison between the values of PM10 and their chemical composition obtained inside schools (in classrooms of children up to 5 years) and in ambient air. In addition, the work aims to asses the contribution of natural and anthropogenic particles emission sources on indoor concentrations. Finally, if necessary, recommendations will be proposed to reduce particulate levels indoors.

2. Materials and methods

2.1. Site description

This study concentrates on a strip of land in the province of Castellón (Spain) that ranges from its capital, located on the *Plana de Castellón* where there are no natural barriers, passing through the locality of Alcora situated on the slope of a mountain, and ending in the village of Lucena located in the mountainous interior (Fig. 1). These localities (Castellón, Alcora and Lucena) represent three different environments: urban, industrial and rural respectively.

In the city of Castellón (urban area) three schools were selected: S1, S2 and S3. As a fundamental characteristic, all are located near road networks with a high density of traffic. The three sampling sites were situated in different zones of the city, so as to analyse whether, the orientation with regards to the regimes of air flows, and the distinct urban morphologies influence the concentration levels of indoor particles. In addition, an outside sampling station was located on the terrace of a building in the centre of the city to obtain information of PM10 in ambient air.

The three schools in the town of Alcora share as a principle feature, their greater proximity to an important industrial belt. As in the case of the urban schools, three primary schools were chosen: S4, S5 and S6, in different points with differing orientations and surroundings. In addition, an outdoor sampling station was located on the terrace of a building in the centre of the town.

In the municipality of Lucena (rural area), a village with a low density of traffic and a low concentration of industry, the school selected was S7. In this case, outdoor sampling point was located on the terrace of this school.

Table 1 summarizes main characteristics of the seven schools studied. In all schools, a natural ventilation of classrooms is performed.

2.2. Instruments and method

The sampling period spans from one year (July and August excluded). Samples were taken for duration of 5–8 hours depending on the school hours to obtain a monthly sample for each of the schools.

The indoor airborne samples were collected using RespiCon TM. This collector is a multi-stage, virtual impactor that traps airborne particles on three individual collection filters. At a flow rate of 3.11 l/min., the first stage separates out and collects the particles that are smaller than 2.5 μm. The second stage collects particles between 2.5 and 10 μm, while the third stage collects the remaining particles. Quartz fibre filters (37 mm diameter) were used to collect indoor particles.

In the three outdoor sampling stations, the same data capture set was used; it is a minivol air sampler type 3.1 LVS of Derenda. This device is considered as a referent according to the European regulations on the particle sampling PM10 (UNE 12341:1999) and it allows the daily collection of the PM10 particle concentration. This set provides data on the aspirate volume and on the temperature, pressure and average relative humidity of those registered during the 24 hours of the sampling.

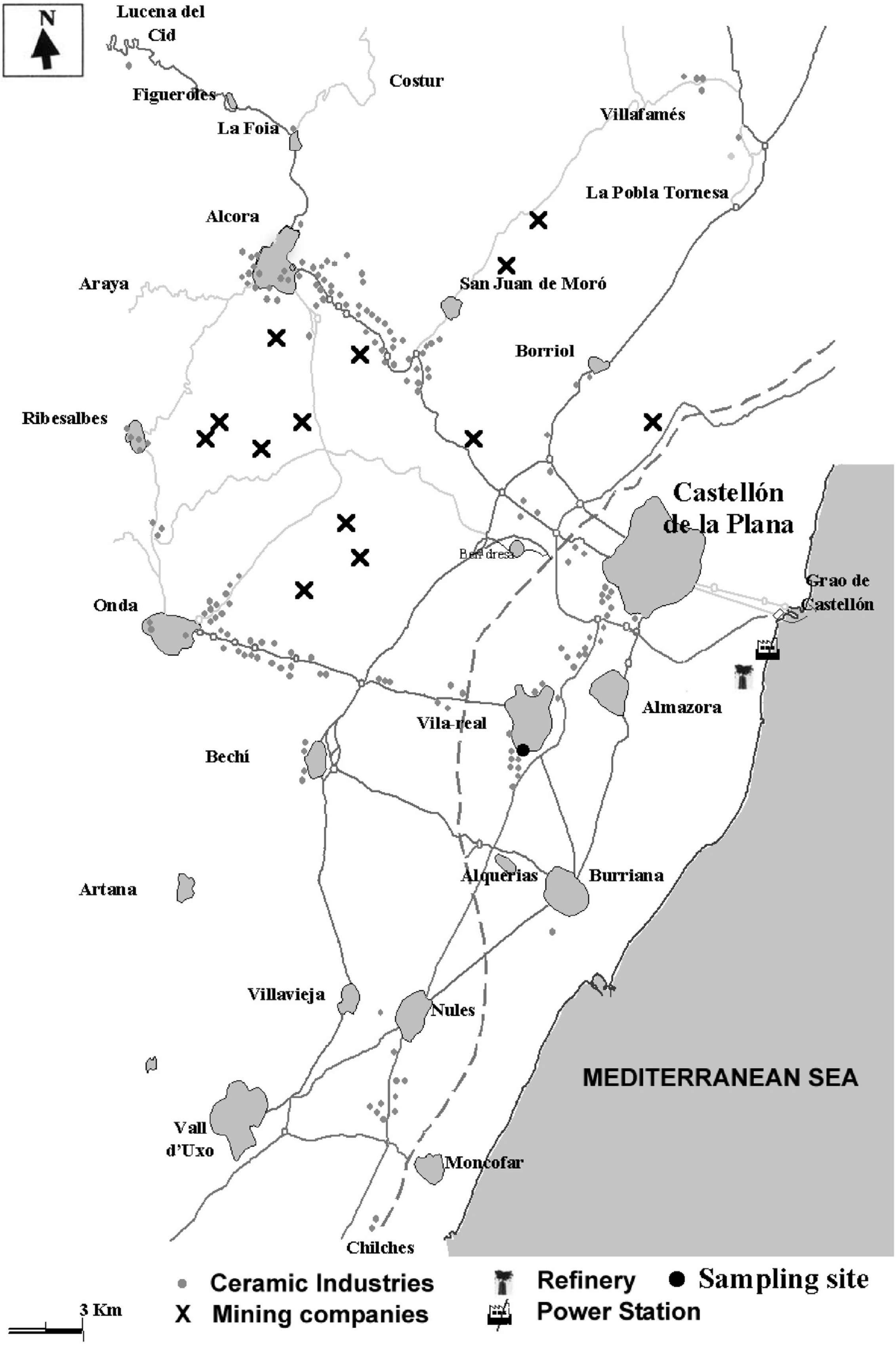

Fig. 1. Location of the studied area.

Table 1
Main characteristics of the schools.

School	Site	City zone	Traffic density	Classroom volume (m^3)	Orientation of windows	Number of students
S1	Urban	E	High	268.03	WNW	40
S2	Urban	NW	Medium	159.56	SSE	21
S3	Urban	W	High	173.49	ESE	20
S4	Industrial	SE	Medium	36.17	WNW	25–30
S5	Industrial	E	Medium	109.09	ENE	26
S6	Industrial	SW	Low-Medium	97.67	SSE	60
S7	Rural	SE	Low	182.60	SE	8–12

The aspirate air (2.3 m^3/h) by using a pump goes through a cutting head which allows under 10 µm particles passing through. The particulate remains in quartz fibre filters with a diameter of 47 mm.

Indoor and outdoor samples from all locations were subjected to gravimetric analysis to determine the mass of PM10 collected. Before the sampling and after being collected, the filters must be kept under conditions of a temperature of 20 ± 1 °C and controlled humidity (50 ± 5) % for 48 hours, before being weighted. Filters were weighed pre- and post-collection on analytical balance with a precision of 10 µg. The PM concentrations are shown in µg of pollutant per cubic meter of aspirate air.

A portion of quartz filter (1/2 of filter) was used to obtain the concentration of As, Cd, Ni, Pb, Al, B, Zn, Mg and Sb in PM10. The samples were separated for their subsequent chemical analysis with acid digestion. Later on, it was necessary to determine its elemental contribution in the chemical analysis. In this study there was an attempt to follow the recommendations exposed in the European regulations on determination of heavy metals in samples of particle pollutants. HNO_3 and H_2O_2 were used as reactants (Pallarés et al., 2007; Jordán et al., 2009). The Inductively coupled plasma mass spectrometry (ICP-MS) allowed the determinations. This is one of the methods specified in the European Council Directive 2004/107/CE. For this purpose, a Hewlett Packard set, model 4500, was used. The median filter blanks concentration ($n = 10$) was: As (0.01), Ni (0.09), Cd (0.30), Pb (0.82), Al (0.05), Sb (0.04) and median LOD concentration ($n = 10$) was: As (0.02), Ni (0.05), Cd (0.40), Pb (1.42), Al (0.08), Sb (0.09).

In the other half of the filter made the analysis of the levels of fluoride, chlorite, chloride, nitrite and sulphate in the PM10. For this purpose, soluble fraction of the samples was extracted with ultrapure water and the samples were analyzed by ion chromatography, by means an ion chromatograph Dionex DX-120. The limit of detection (LOD) was 0.5 µg m^{-3} for sulphate, fluoride, chlorite and chloride. LOD was 0.25 µg m^{-3} for nitrate.

2.3. Statistical analysis

The software SPSS 17.0 was used for Statistic analysis of the data. Pearson correlation coefficients were initially calculated between chemical composition (elements and anions analyzed) and the PM10. And then Pearson coefficients were calculated between the different chemical elements and anions. Pearson's correlation coefficient (ranging from -1 to +1) is a measure of the strength of the association between the two variables. A value of +1 is the result of a perfect positive relationship between these variables. In the case of concentrations of two chemicals, a high positive relationship is associated with the existence of common emission sources.

Table 2
Average of PM10 concentrations obtained and I/O ratios.

School	Site	Indoor PM10 conc. calculated (µg/m^3) [min-max]	Outdoor PM10 conc. (µg/m^3) [min-max]	I/O ratio	I/O ratio$_{\text{unoccupied}}$
S1	Urban	132 [98–161]	53 [36–77]	2.6	—
S2	Urban	114 [65–140]	54 [36–79]	2.3	—
S3	Urban	141 [94–186]	59 [31–100]	2.6	—
S4	Industrial	69 [21–102]	53 [37–73]	1.3	3.4
S5	Industrial	261 [205–322]	36 [19–53]	7.8	1.9
S6	Industrial	145 [97–183]	45 [37–65]	3.5	2.3
S7	Rural	71 [16–169]	36 [16–55]	2.1	—

3. Results and discussion

3.1. Average concentrations and ratios I/O of PM10

A study of equivalence between the two samplers was carried out using in the measurements (TM Respicon inside and IND-LVS, outside), and were estimated the PM10 levels within the equivalence function that relates the values obtained both cases (UNE 12341:1999).

The averages of the ratios I/O obtained in each school were calculated (Table 2), for this purpose had not been taken into account the samples that had not been captured in the same conditions, as those which were collected in non-teaching periods and the sample that was taken during the construction works outside the classroom.

Table 2 shows that in all schools the ratio I/O for PM10 was greater than unity, indicating that there were significant indoor sources of these particles (Zhu et al., 2005). However, this ratio needs to be investigated further. The ratio I/O could be greater then unity also for a transport event from outside towards inside environment and not only for particle indoor sources.

The lowest ratio I/O was obtained for the S4 school. This ratio close to 1 is because the location is constantly exchanging air from outside, which causes the concentrations obtained are similar inside and outside. If a window is open the ratio I/O is close to 1 for all particle sizes (Zhu et al., 2005). Perhaps, the fact that school facilities are situated on the first floor makes the access to the class is not straight from the street and thus the number of particles introduced by shoes is less. And finally it should be noted that this is a nursery school (not all children walk and do not present the same activity as students of an infant school) and thus the effect of resuspension of particles is minimized at this location.

On the other hand, must be stated that S5 school had the highest rate I/O for PM10 of all locations. These high concentrations were associated with school characteristics, such as the orientation and morphology of the streets surrounding it. This school is located next to an unpaved park that all students of children entering the centre have to cross, which significantly increases the contribution of particles due to transport through the shoes and clothing (Molnár et al., 2007). Then these particles are resuspended and an increase of the concentration is produced. Yang et al. (2009) in their study in different schools in Korea obtained average ratios I/O of 2.06 for PM_{10} in classrooms and Stranger et al. (2008), found ratios of up to 8.8 for $PM_{2.5}$. The results are explained in both cases by the student activities that cause resuspension of particles. In S5 school also produces a large accumulation. In the study area there is a large effect of particle accumulation indoor and in ambient air mainly due to climatic characteristics (Hrsak et al., 2001; Gómez et al., 2005). There are not many days during the year in which the wind speed is significant, i.e. days in which there is an effective exchange of indoor air by natural ventilation (type of ventilation used by all schools). The dominant regimes of winds in the study area are breezes which are insufficient at the

Table 3
Ratios PM2.5/PM10 and PM2.5-10/PM10 (%).

School	$PM_{2.5}/PM_{10}$ occupied	$PM_{2.5\text{-}10}/PM_{10}$ occupied	$PM_{2.5}/PM_{10}$ unoccupied	$PM_{2.5\text{-}10}/PM_{10}$ unoccupied
S4	59	41	69	31
S5	40	60	62	38
S6	53	47	56	44

time for renewing the air inside a building.

The other schools had ratios I/O of PM_{10} from 2.1 (rural environment) and 3.5 (industrial environment, S6). In all three schools situated in Castellón (urban environment) similar ratios were obtained, but in the school S2 was slightly lower because this location is less influenced by traffic.

In some studies conducted in urban areas has been demonstrated the influence the orientation, location and configuration of the streets with respect to emission sources on the vertical dispersion of pollutants (Ruwin et al., 1996). In confined spaces, a greater vertical drop in large-sized particles is produced which causes a progressive enrichment in fine particles (Zhu et al., 2005). In open spaces there is a greater variation in vertical profiles and concentration of particles and their distribution is highly influenced by winds as sea breezes, and the distance and intensity of anthropogenic activities (Ruwin et al., 1996; Zhu et al., 2005).

3.2. Ratio I/O of PM10 unoccupied classroom

In the three schools located in the industrial environment (S4, S5 and S6) were collected PM10 samples inside and outside in non-teaching periods. The ratios I/O for PM10 collected in schools S4, S5 and S6 under these conditions were 3.4, 1.9 and 2.3 respectively.

Comparing the values of I/O when the classrooms were unoccupied with respect to the average value of these same schools when the classrooms were occupied (Table 2), a decrease in the ratio I/O was observed when there are not children in S5 and S6 schools, especially in S5. This highlights the importance of the activities of the occupants in indoor ambient. In various studies (Blondeau et al., 2005; Poupard et al., 2005) was found that concentrations of particles inside showed peak in the hours that rooms were occupied due to particle generation by occupants themselves, both by the contribution from the outside, caused by the activities of the school (such as dust from the blackboard) or by the resuspension of previously deposited particles.

However, in S4 school, the ratio I/O obtained in non-teaching periods was greater than the overall average obtained when the classrooms are occupied (Table 2). This is due to an important change in conditions, since in this case windows are completely closed, so there is no air exchange as occurs in other samples, resulting in an accumulation in the interior that causes an increase in the ratio I/O.

Table 3 contains the values $PM_{2.5\text{-}10}/PM_{10}$ and $PM_{2.5}/PM_{10}$ ratios, expressed in % of the cases cited above, schools S4, S5 and S6 when are occupied and not, with the objective of discern whether any changes occur in this samples regarding the proportion of fine and coarse particles.

In the case of S4 school, Table 3 shows that the ratio I/O increases when is unoccupied. This fact can be associated to an increase in the proportion of fine particles (passing to represent 59%–69%) that can be introduced through the cracks of the windows and doors, while the coarse not. This confirms that the increase of I/O ratio is due to the change in ventilation, as windows are closed when not occupied.

Moreover, the decrease of levels I/O at S5 school during classrooms are unoccupied is associated with decreased quite significantly of coarse particles, passing from 60% to 38% of PM10. This finding corroborates the importance of the occupants in the generation, transport and resuspension of the particulate fraction of between 2.5 and 10 μm in this location.

At S6 school, as indicated above, also decreases the value of I/O when the school is not occupied, although in this case the reduction does not reflect any substantial increase in the fine fraction or in the coarse one, compared to the values obtained during school days.

On the other hand, one of the S5 school samples was obtained when some works were being carried out outside of school. This caused a significant increase in the concentration of particles in the interior (I/O = 19.9). However, the PM2.5/PM10 ratio in this case was 0.38, practically the same as the average ratio (0.40) at this school when the classroom was occupied (Table 3). So the works performed outside equally affect the values of fine and coarse particles collected inside.

3.3. Average concentrations and indoor to outdoor ratios of PM_{10} chemical composition

Table 4 shows the descriptive statistics of the concentration values of the chemical elements and anions, analyzed in PM10, that were obtained inside the seven schools (S1, S2, S3, S4, S5, S6 and S7) and outdoor of the three types of location (urban, industrial and rural).

As for the concentration values obtained outside the locations, the highest outside levels of B were obtained in the rural location, and the higher Pb concentrations in industrial one. The urban station reported the highest concentrations of Ni, Zn, Mg, Sb, ClO_2^- and Cl^-. The rest of elements and anions analyzed showed similar values in at least two types of location. Similar Cd concentrations were obtained in the rural and urban environment, of Al and NO_3^- in the industrial and urban areas and similar levels of As, F^- and SO_4^{2-} in three types of location. However, the concentrations recorded inside the schools did not follow the same trend than those obtained outdoor.

The values of ratio I/O obtained for each of the elements and anions (analyzed in PM10) of the seven schools are shown in Table 5. The levels found in the interior were higher in all cases. The ratios I/O allow to have

Table 4
Average indoor and outdoor concentrations of PM10 composition. Elements levels in ng/m3 and anions levels in μg/m3.

	S1	S2	S3	S4	S5	S6	S7	Urban outdoor	Industrial outdoor	Rural outdoor
As	6.79	10.63	6.32	4.28	6.86	3.61	6.09	1.38	1.41	1.41
Ni	48.20	60.92	52.59	44.19	64.95	44.15	51.02	4.52	4.07	3.70
Cd	117.67	104.23	82.21	55.09	67.32	73.18	71.87	0.48	0.29	0.43
Pb	937.59	815.67	485.59	422.06	535.22	568.70	808.32	40.32	78.63	44.68
Al	7432.70	12542.06	9979.29	9773.49	11013.64	6231.75	7119.66	883.19	885.28	717.89
B	18155.15	13945.06	16704.42	13272.33	15915.41	12746.92	16201.46	112.52	109.82	119.43
Zn	1584.09	1468.07	1748.90	1610.77	1512.89	1235.81	1395.56	148.04	121.92	145.16
Mg	1685.75	2045.88	2103.94	1848.68	3295.22	1213.44	1332.33	397.80	280.67	222.29
Sb	48.49	56.15	43.95	57.99	39.03	41.54	44.67	26.18	11.72	14.66
Fluoride (F^-)	5.10	5.12	5.15	4.82	5.48	5.40	5.44	0.26	0.26	0.24
Chlorite (ClO_2^-)	5.78	6.86	6.15	5.34	7.41	7.23	5.98	0.25	0.11	0.12
Chloride (Cl^-)	6.57	11.89	7.89	8.21	9.66	11.14	10.13	0.79	0.57	0.23
Nitrate (NO_3^-)	24.12	32.92	23.84	24.03	43.38	38.84	28.22	3.55	3.87	2.03
Sulphate (SO_4^{2-})	12.14	21.87	17.49	19.33	29.36	29.14	18.14	2.59	2.54	2.04

Table 5
Ratios I/O of PM10 composition.

	Ratio I/O						
	S1	S2	S3	S4	S5	S6	S7
As	4.9	7.7	4.6	3.0	4.9	2.6	4.3
Ni	10.7	13.5	11.6	10.9	16.0	10.8	13.8
Cd	245.1	217.1	171.3	190.0	232.1	252.3	167.1
Pb	23.3	20.2	12.0	5.4	6.8	7.2	18.1
Al	8.4	14.2	11.3	11.0	12.4	7.0	9.9
B	161.4	123.9	148.5	120.9	144.9	116.1	135.7
Zn	10.7	9.9	11.8	13.2	12.4	10.1	9.6
Mg	4.2	5.1	5.3	6.6	11.7	4.3	6.0
Sb	1.9	2.1	1.7	4.9	3.3	3.5	3.0
Fluoride (F^-)	19.6	19.8	19.7	18.5	21.1	20.8	21.7
Chlorite (ClO_2)	23.1	24.6	27.4	48.5	67.4	65.7	49.8
Chloride (Cl^-)	8.3	10.0	15.1	14.4	16.9	19.5	22.0
Nitrate (NO_3^-)	6.8	6.7	9.3	6.2	11.2	10.0	13.9
Sulphate (SO_4^{2-})	4.7	6.8	8.4	7.6	11.6	11.5	8.9

an idea of enrichment due to both processes of accumulation as generation by indoor sources.

Besides, Table 5 shows that the ratios I/O calculated for the chemical elements and anions, analyzed in the PM10, were higher than unity and generally higher than those recorded in the case of PM10 (Table 2). PM10 particles generally have high concentrations of some trace elements, however, some emissions sources are highly enriched in toxic metals without causing thereby an increase in the levels of PM10 (Bilos et al., 2001). The ratios I/O of metals and anions were varied, but highlighted the high values obtained in the case of two of the elements, Cd and B. The metal concentrations in the interior are often greater than the outside due to selective enrichment of metal-rich fine particles during cleaning processes or due to an internal source (Paustenbach et al., 1997). In their work, Rasmussen et al. (2001) found that concentrations of Pb varied with the type of heating. These results suggest that the method of home heating has an effect of accumulation of metals in the particulate, possibly because of differences in air circulation and the use of particulate filters.

Table 5 shows that the ratios I/O of Zn and fluoride were similar in the seven schools studied. In the S7 school, located in rural area, were registered the highest ratios of chloride and nitrate anions. In S5 and S6 schools (industrial area) were obtained the highest ratios I/O for chlorite and sulphate and only in S5 the highest of Ni and Mg. Moreover, the highest ratio I/O of Sb was obtained in the third school situated in the industrial town (S4). Finally, the ratios I/O calculated for concentrations of As, Pb and B were generally higher for the three schools in the urban environment (S1, S2 and S3).

3.4. *Correlations of PM10 and their chemical composition*

Pearson correlation coefficients (r) were calculated with the aim of studying the relationship of chemical elements and anions analyzed in the PM_{10} captured within schools with this fraction of particulate matter.

Only four of the chemical elements have a significant correlation with PM_{10}: As ($r = 0.66$), Ni ($r = 0.60$), Al ($r = 0.70$) and Mg ($r = 0.85$). These strong relationships indicate the existence of common emission sources of this fraction of particulate matter and As, Ni, Al and Mg inside of schools. A very important factor that affects PM10 indoor is the resuspension of previously deposited particulate. These come from the activities of the occupants inside (Raunemaa et al., 1989; Branis et al., 2005) or from outside, as dust carried by shoes and clothing (Janssen et al., 1999). Thus, the high correlations of these chemicals with PM10 indicate that these activities are possibly the most important sources of these four elements.

In addition, Pearson correlation coefficients were calculated between the different elements and anions analyzed in the PM10 captured within schools in order to determine the possible relationships between them. Moreover, Pearson correlation coefficients were calculated for these same elements and anions obtained in outside locations to see if they have the same behaviour that inside of schools. Table 6 presents a summary of the results obtained from applying this correlation coefficient for concentrations of elements and anions analyzed in the PM10 captured inside and outside schools.

The highest correlations obtained inside schools correspond to those recorded between the concentrations of Cd and Pb ($r = 0.88$), Mg and Al ($r = 0.89$) and those of chloride and sulphate ($r = 0.72$). These high and positive correlations indicate the existence of common emission sources among them, which are of great importance in the concentration levels obtained indoor.

The Pearson correlation coefficients were calculated for the concentrations of Cd and Pb, and of chloride and sulphate registered outside schools. The values obtained were 0.02 and 0.09 respectively. These indicated that the levels of these elements and anions registered in ambient air were not related, i.e. do not exhibit the same behaviour. Therefore, the high correlation that is registered inside the schools is because the most important sources of these elements and anions are indoor sources.

A potential source of cadmium and lead in the interior is the gas or coal heating (Meyer et al., 1999; Komarnicki, 2005), although these elements can be part of painting in old buildings (Meyer et al., 1999), and other classroom materials. The origin of chloride and sulphate within schools is mainly associated with the cleanup of the classroom, as these anions are part of the composition of some of the cleaning products used in these tasks.

On the other hand, Pearson correlation coefficient obtained between the Mg and Al in outdoor locations was 0.79 (Table 6). This showed that both inside and outside are related positively and have a common emission source of importance. Mg and Al have a mineral origin, both natural and anthropogenic. These are all part of the composition of mineral raw materials used in the ceramic industry, such as clays and dolomites (Gómez et al., 2001; Sanfeliu et al., 2002) but in turn have a natural origin in the study area as part of the soil that may be resuspended by wind or other factors such as vehicle traffic.

In addition, the As showed significant correlations ($r > 0.60$) with the Ni, Al and Mg, and Ni also showed it with Al. Good correlations between these elements were also obtained outdoor. This is due to these elements, although are parts of the composition of different type of raw materials, are all used in the ceramics sector, and therefore have a common origin. Also, as previously said in this subsection, these elements were those with a higher correlation with PM_{10}, indicating the existence of potential sources of common importance among these elements. Their origin (elements and PM_{10}) was associated atmospheric particulate emissions related to the use of raw materials ceramics.

On the other hand, a significant correlation between the anions nitrate and sulphate was detected, both inside and outside locations. This relationship is associated with an important common origin, combustion processes of fossil fuels, such as traffic and natural gas combustion in industrial skills or heating. In this case these anions are not related to concentrations of PM10 in the interior.

4. Conclusions

PM10 concentrations and the levels of the chemical elements and anions analyzed in this fraction of particulate were greater in all cases inside schools than outside. This indicates the presence of indoor emission sources of importance.

Chemical elements and anions, in general, were more enriched in the interior of the buildings than the PM10 fraction. This is associated with selective increase of metal-rich fine particles during the cleaning process or due to an internal source and the existence of some emissions sources that have highly enriched in toxic metals without causing thereby an increase in the levels of PM_{10}.

The calculation of Pearson correlation coefficients between the

Table 6

Correlations (Pearson coefficient) between the concentrations of elements and anions analyzed in the PM10 captured indoor and outdoor.

		Indoor Correlations													
		As	Ni	Cd	Pb	Al	B	Zn	Mg	Sb	Fluoride	Chlorite	Chloride	Nitrate	Sulphate
Outdoor Correlations	As		0.68**	-0.18	-0.25	0.64**	-0.14	0.17	0.66**	0.13	0.20	0.20	0.34**	0.15	0.18
	Ni	0.52**		-0.37	-0.37**	0.63**	-0.50**	-0.02	0.55**	-0.07	0.29*	0.34*	0.22	0.27*	0.17
	Cd	0.29	0.12		0.88**	-0.27*	0.52**	0.25	-0.18	0.04	0.14	0.26	0.09	-0.17	-0.07
	Pb	0.53**	0.23*	0.02		-0.29*	0.47**	0.19	-0.19	0.05	0.05	0.19	0.05	-0.21	-0.14
	Al	0.36**	0.37**	0.14	0.23*		-0.30*	0.36**	0.89**	-0.28**	-0.06	0.20	0.07	-0.05	-0.21
	B	0.27*	0.01	0.22	0.20	0.46**		0.53**	-0.18	0.36**	0.20	-0.15	0.17	-0.12	0.10
	Zn	0.66**	0.25*	0.44**	0.24*	0.29*	0.59**		0.35**	0.08	0.19	0.09	0.08	-0.29*	-0.18
	Mg	0.45**	0.36**	0.45**	0.20	0.79**	0.29*	0.44**		-0.25*	-0.08	0.26	0.09	-0.10	-0.11
	Sb	0.32**	0.18	0.04	0.12	0.12	0.07	0.34**	0.27*		0.36**	-0.14	0.41**	0.07	0.33*
	Fluoride	0.43**	0.30**	0.22	0.40**	0.43**	0.15	0.26*	0.40**	0.19		0.54**	0.59**	0.31*	0.58**
	Chlorite	0.29*	0.15	0.28	-0.02	0.04	-0.03	0.21	0.36**	0.26*	0.47**		0.33*	0.28*	0.32**
	Chloride	0.12	0.24*	0.36*	0.14	0.02	-0.31**	-0.11	0.37**	0.04	0.36**	0.41**		0.47**	0.72**
	Nitrate	0.04	0.18	-0.06	—	0.02	-0.06	-0.02	0.07	0.01	0.18	-0.17	0.15		0.66**
	Sulphate	0.32*	0.45**	0.10	0.19	0.11	-0.02	0.22	0.23*	0.03	0.24*	-0.12	0.09	0.52**	

* Significative correlation; ** Good correlation.

different elements and their chemical and PM10 was useful in assessing the existence of common emission sources.

The differences in the ratios I/O of PM_{10} and those of their composition in the schools studied show that in most cases, the building characteristics (ventilation, orientation, morphology the streets, cleaning, number of students, etc.) are more important than the type of environment where the building is located (urban, industrial or rural).

The use of natural ventilation favours, in general, the reduction of particles in indoor environments. However, there may be cases in which the orientation of the school encourages the penetration of particles within the wind-aided. In these cases, it is advisable to ventilate certain times when the sea breezes and prevailing winds do not favour the entry of particles.

The use of low-emitting materials in the composition of structures and furnishings of the building entails a significant reduction of pollutants. In addition, a substantial improvement in indoor air quality can be achieved by acting at two levels: the air filtration and cleaning.

Declarations

Author contribution statement

S. Pallarés: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Eva Gómez: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Africa Martínez: Conceived and designed the experiments; Wrote the paper.

Manuel Jordán: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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