Air quality in schools and children's exposure to particulate pollution in Barcelona

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ABSTRACT

Exposure to air pollutants has been widely linked to negative health effects (leading to an increase in mortality and morbidity rates of the population), and particularly to respiratory and cardiovascular problems. Moreover, impairments on neurodevelopment are suspicious to also be associated with exposure to air pollution. Children constitute a particularly vulnerable population group because of their physiological and behavioural characteristics. They have higher ventilation rates and higher levels of physical activity with the result that they receive much higher doses of air pollutants than adults. Children spend a large part of their time at schools, which is a very particular microenvironment: classrooms are usually crowded rooms which are occupied during long periods.

In the framework of the ERC Advanced Grant BREATHE Project, an extensive sampling campaign in the indoor and outdoor environments of 36 schools in Barcelona and 3 in Sant Cugat del Vallès was carried out during one year to characterise air quality in schools and children's exposure to air pollutants. The schools selected were considered to be representative of the city, since the mean NO_2 levels measured at BREATHE schools was similar to the modelled NO_2 concentrations for rest of schools in Barcelona (data from the ESCAPE project, year 2009). The same pollutants monitored at schools were also measured in an urban background station in Barcelona (UB-PR).

The results from this work evidence that spatial variation of concentrations of equivalent black carbon (EBC; black carbon concentrations corrected by elemental carbon (EC) levels), NO_2 and ultrafine particles (UFP, in number concentration) in schools showed an increasing gradient towards the city centre, following the traffic density in the city. On the other hand, the impact of local school sources prevent particulate matter with an aerodynamic diameter<2.5 μm ($PM_{2.5}$) from being a good indicator of traffic emissions in schools, even though there are some similarities in the distribution of $PM_{2.5}$ across the city.

The range of concentrations and variability for EBC, NO_2 and UFP measured in the 39 schools was higher outdoors, since outdoor environments are influenced to a larger degree than indoors by outdoor emission sources and meteorological factors. Concentrations in the playgrounds across all schools and sampling campaigns were 1.6 times higher than indoors for NO_2 and 1.5 times higher for UFP, while EBC concentrations were similar in both environments. On the contrary, $PM_{2.5}$ had a much higher (1.6 times) concentration indoors than outdoors because organic carbon (OC;

which was the most important contributor to indoor $PM_{2.5}$, and the second in the outdoor environment behind mineral matter), Ca, Sr and Cr were mainly generated indoor. OC was particularly affected by indoor sources, since nearly all the range of its indoor/outdoor (I/O) was above 1 in almost all the schools and days.

NO_2 showed a similar infiltration degree in both the warm and cold seasons (the infiltration factors, F_{inf}, were 0.50 and 0.56, respectively), thus independently of the windows opening or closing. However, rather than a low infiltration, the lower levels found indoors might be explained by indoor consumption of NO_2 in gas-phase reactions with terpenes and other unsaturated hydrocarbons (from furniture, paints, cleaners, photocopiers, among others). Indoor-to-outdoor correlation showed low R^2 and F_{inf} for UFP because of indoor particle sources (the intercepts, corresponding to the indoor generated PM, C_{ig}, were high) or processes that might increase indoor UFP independently of outdoor particles. Actually, schools in Barcelona had higher indoor particle number concentrations during the warm season despite the lower levels found outdoors with respect to the cold one. However, indoor levels are still influenced by the outdoor ones as well as by the ambient temperature and humidity.

A source apportionment analysis by Positive Matrix Factorization (PMF) allowed the identification of eight factors or sources (*mineral*, *traffic*, *road dust*, *secondary sulphate and organics*, *secondary nitrate*, *sea spray*, *heavy oil combustion*, *metallurgy*) which corresponded to well-known sources of PM in the study area, plus a ninth factor which was observed for the first time. This factor was named *organic/textile/chalk*, and it was characterised by the previously mentioned components with very high indoor concentrations: OC, Ca and Sr. It was the largest source of $PM_{2.5}$ in classrooms, contributing to 45% of indoor $PM_{2.5}$. Sources of OC in particularly crowded facilities such as schools could be cotton fibres from clothes, skin flakes, and other organic emissions. Besides, the chalk from blackboards was responsible for Ca, and Sr emissions. In playgrounds, this source was still significant (16% on average), while on the contrary it had a near-zero contribution in the urban background station (UB-PR). This seems to confirm that this was a local source from the schools.

Mineral components of $PM_{2.5}$ showed the broadest I/O ratios, with the median ratio close to or higher than 1 and with the maximum observed during the cold season, because of the accumulation in the classrooms (windows were closed) of these particles and fewer outdoor activities. The *mineral* factor was identified by PMF by the typical crustal species such as Al, Mg, Li, Fe, Ca, Ti and Rb and considered a mixture of several sources, including resuspension from sandy playgrounds. It was the source with the highest variability and especially dependant on the type of playground (sandy: 16

and 9.1 μg·m^{-3}; paved: 2.5 and 3.6 μg·m^{-3}; outdoors and indoors respectively). On the other hand, much lower mineral contributions were found in UB-PR (0.6 μg·m^{-3}), also indicating that this is a mainly local source of schools. *Mineral* and *organic/textile/chalk* sources were responsible for the very high concentrations in the indoor environment (37 μg·m^{-3}) and for almost doubling concentrations in playgrounds (29 μg·m^{-3}) than in UB-PR (17 μg·m^{-3}).

Motor exhaust emissions (OC, EC) and metals from brake wear (Cu, Sb, Sn and Fe) were the main components of the *traffic* factor. Contributions were quite similar at the three studied environments: classrooms (4.8 ± 3.9 μg·m^{-3}), playgrounds (5.5 ± 4.2 μg·m^{-3}) and UB-PR (4.1 ± 2.7 μg·m^{-3}; the last being a 24h average instead of 8h). In many schools, indoor concentrations of traffic-related components were higher than outdoors, probably due to a relatively closer location of the indoor sampler to the street than the outdoor one, to indoor resuspension of PM (including the traffic-related components) and/or precipitation scavenging outdoor pollution. EBC showed one of the highest F_{inf}, with the 92% of indoor EBC coming from the outside during the warm season and 75% during the cold one. The very low intercepts in the indoor-to-outdoor correlation indicate the absence of significant indoor sources of EBC. These results point out the necessity to locate future schools far away from trafficked streets.

The *secondary sulphate and organics* factor (traced by SO_4^{2-} and NH_4^+) showed strong correlations between indoor and outdoor (r^2=0.83), indicating a high agreement between both environments, and no major indoor sources. The *secondary nitrate* (explained mainly by NO_3^-) had a high variability among schools, attributed to the thermal instability of NH_4NO_3 and the different conditions in temperature usually encountered in Barcelona throughout the year. In fact, there was also an important difference between the classroom and playground, with lower concentrations indoors due to the higher temperatures found in this environment that cause the evaporation of NH_4NO_3.

Many trace elements had low or no correlation with EBC and Al_2O_3, what indicates a source other than traffic or crustal emissions, such as the *heavy oil combustion* (mostly from shipping emissions) and the *metallurgy* factor identified by PMF. However, some elements such as As, Co and Pb were quite correlated with mineral matter, suggesting that mineral matter could be polluted by dry and wet deposition of these pollutants on the playground and retained by absorption on crustal elements.

Among trace metals, V and Cd had the highest F_{inf} (≥ 0.70) as well as the lowest concentrations of C_{ig} with respect to the corresponding median indoor concentrations. Pb had a similar F_{inf} than the rest of trace metals (between 46-60%; excluding mineral

elements) but its R^2s were higher, even though C_{ig} for Pb was quite high (>42% of the median) indicating the presence of indoor sources, such as old lead-based paints. Trace metals (except Sb and Cr) had lower F_{inf} during the cold season, thus the entrance of these elements was to some extent hindered by windows. Some of the trace metals were affected by significant indoor sources in a number of schools. Cr should be highlighted, since it had higher levels indoors in both seasons (I/O ratio = 1.46) and, in fact the C_{ig} for Cr accounted for the 95% and 83% of its median indoor concentrations (cold and warm seasons, respectively), indicating a clearly contribution from indoor origin. Further research is required in order to identify indoor sources of these trace metals, some of which are especially relevant due to their toxicity.

Results evidenced that the age of the school building was only significantly (p-value<0.05) associated with indoor levels for Fe and 4 trace elements (Cr, Li, Co, Se) typically related to industrial emissions. Newer buildings tended to have higher concentrations of the previously mentioned elements than the older ones, probably due to higher indoor emissions but further research is needed to identify specific sources in indoor environments. Moreover, the type of window seemed to be importantly associated with higher indoor levels of mineral components (such as Al_2O_3, Fe, Mg) and components with a very high contribution from indoor sources (OC, Ca, Sr) in those schools with aluminium or PVC windows. Therefore, the presence of a more isolating window (such as the Al/PVC framed instead of wood framed) would be an important barrier for the dispersion of mineral components, which might stay resuspended indoors in such a crowed environment. Moreover, also higher indoor levels of Co and As were found in schools with Al/PVC windows, probably due to indoor emissions or because of their possible presence in the school sand. On the other hand, NO_2 infiltration is hindered by Al/PVC windows, since those schools with wood framed windows tend to have an increase of around 8 $\mu g \cdot m^{-3}$ of NO_2 in the indoor environment.

Although personal exposure to air pollutants is generally estimated from a limited number of monitoring stations in the local air quality monitoring network the more precise way to assess it is by personal measurements. With the aim to accurately assess personal exposure, EBC personal measurements of 45 schoolchildren with portable microaethalometers were carried out simultaneously to school measurements. The relationship between personal monitoring and fixed stations at schools (indoor and outdoor) and in UB-PR was evaluated. The highest EBC concentrations were found in personal measurements, which were 20% higher than in fixed stations at schools and 10% higher than in UB-PR. In addition, the range of EBC concentrations was wider for the personal measurements compared to school and UB-PR measurements owing to

peak concentration events that took place mainly during commuting time. In fact the geometric mean of EBC concentrations were significantly higher during commuting time (2.0 $\mu g \cdot m^{-3}$) than during periods when children were in the classroom (1.2 $\mu g \cdot m^{-3}$) or in the school playground (1.0 $\mu g \cdot m^{-3}$). The lowest concentrations were reported when children were at home (0.9 $\mu g.m^{-3}$). Linear mixed-effect models showed low R^2 between personal measurements and fixed stations at schools ($R^2 \leq 0.28$), which increased to $R^2 \geq 0.70$ when only periods when children were at schools were considered. For the UB-PR station, the respective R^2 were 0.18 and 0.45, thus indicating the importance of the distance to the monitoring station when assessing exposure. During the warm season, the fixed stations agreed better with personal measurements than during the cold one. The mean daily-integrated exposure to EBC for the 45 children was 34.6 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$ and it showed a high variability among the children (standard deviation: 13.8 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$). For the daily-integrated dose (a parameter that also takes into account a dosimetry factor), the mean accounted for 18.2 $\mu g \cdot d^{-1}$ (standard deviation: 7.7 $\mu g \cdot d^{-1}$). This variability was a result of the different time-activity patterns of each child, who can carry out very different activities in locations with different EBC concentrations. Exposure and dose could be significantly different even between children attending the same school, and this variability could not be taken into account only with the fixed stations. Children spent 6% of their time on commuting but received 20% of their daily EBC dose, due to co-occurrence with road traffic rush hours and the close proximity to the source. Children received 37% of their daily-integrated EBC dose at school. Indoor environments (classroom and home) were responsible for the 56% EBC dose.

This thesis provides an in-depth analysis of air quality in schools and children's exposure and dose. The results obtained are thought to be valuable for policy makers and urban planners.

RESUM

L'exposició als contaminants atmosfèrics s'ha relacionat àmpliament amb efectes negatius a la salut (donant lloc a un augment de les taxes de morbimortalitat de la població), i especialment amb problemes respiratoris i cardiovasculars. A més, també es sospita de l'associació entre l'exposició als contaminants atmosfèrics i un menor desenvolupament neuronal. Els infants constitueixen un subgrup de la població particularment vulnerable degut a les seves característiques fisiològiques i de comportament. Tenen un major nombre de respiracions per minut i una major activitat física, pel que, per a una igual exposició, reben una major dosi de contaminants atmosfèrics que els adults. Els infants passen gran part del seu temps a les escoles, les quals són un microambient molt singular: les classes es troben normalment abarrotades d'alumnes i són ocupades durant períodes de temps llargs.

Es va dur a terme una intensiva campanya de mostreig durant un any al ambients interior i exterior de 36 escoles a Barcelona i 3 a Sant Cugat del Vallès per caracteritzar la qualitat de l'aire a les escoles i l'exposició dels i de les alumnes als contaminants atmosfèrics. Les escoles seleccionades es consideren representatives de la ciutat, ja que la mitjana de concentració de NO_2 mesurada a les escoles BREATHE va ser similar a la mitjana de les concentracions modelitzades per a la resta d'escoles de Barcelona (dades del projecte ESCAPE). El mateixos contaminants que es mesuraven a les escoles també es van monitoritzar a una estació de fons urbà a Barcelona (UB-PR).

La variació espacial de les concentracions de carboni negre equivalent (EBC; concentracions de carboni negre corregides per les concentracions de carboni elemental, EC), NO_2 i partícules ultrafines (UFP; en concentració en número) va mostrar un gradient ascendent cap al centre de la ciutat, seguint el patró de densitat de trànsit rodat. D'altra banda, tot i que s'observà una certa similitud en la variació espacial a la ciutat per al material particulat amb diàmetre aerodinàmic inferior a 2.5 μm ($PM_{2.5}$), l'impacte de fonts locals de les escoles van impedir que el $PM_{2.5}$ pugui ser considerat un bon indicador d'emissions de trànsit a aquestes.

El rang de concentracions i la variabilitat de l'EBC, NO_2 i UFP mesurats a les 39 escoles que participaren a l'estudi va ser major a l'exterior, ja que els ambients exteriors es troben més influenciats per factors meteorològics que els interiors. Les concentracions mesurades al pati de les escoles van ser 1.6 vegades més altes que les trobades a l'interior de la classe per al NO_2 i 1.5 vegades per a les UFP, mentre que les concentracions d'EBC eren similar als dos ambients. Contràriament, el $PM_{2.5}$ va tenir

concentracions molt més altes (1.6 vegades) a l'interior que a l'exterior, tot i que la majoria dels components del PM van tenir nivells més alts a l'exterior. No obstant, el carboni orgànic (OC; que va ser el component que més va contribuir al $PM_{2.5}$ interior i el segon a l'exterior rere la matèria mineral), el Ca, el Sr i el Cr van ser generats principalment a l'interior. L'OC va ser especialment afectat per fonts interiors, ja que pràcticament tot el seu rang de ràtios interior/exterior (I/E) estava per sobre de 1 a totes les escoles i dies de mostreig.

El NO_2 va mostrar una infiltració similar tant durant l'estació càlida com la freda (els factors d'infiltració, F_{inf}, van ser de 0.50 i 0.56 respectivament), per tant la infiltració és independent de l'obertura de les finestres. No obstant, més que no pas una baixa infiltració, les concentracions més baixes trobades a l'interior podrien ser explicat per un consum interior del NO_2 en reaccions en fase gasosa amb terpens i altres hidrocarburs insaturats (emesos pel mobiliari, pintures, productes de neteja, fotocopiadores, entre d'altres). Correlacions entre les concentracions interiors i exteriors van mostrar baixes R^2 i F_{inf} per les UPF degut a la presència de fonts interiors d'aquestes partícules (els interceptes, corresponent a la concentració generada a l'interior, C_{ig}, eren alts) o de processos que podrien augmentar els nivells d'UFP independentment de les concentracions a l'exterior. De fet, les escoles a Barcelona van tenir concentracions en número d'UFP a les aules més altes durant la estació càlida tot i els nivells més baixos trobats a fora respecte a la temporada freda. No obstant, els nivells a l'interior també es troben influenciats pels exteriors, així com per la temperatura ambient i la humitat.

Una anàlisi de contribució de fonts mitjançant un model de Positive Matrix Factorisation (PMF) va permetre la identificació de vuit factors (*mineral, trànsit, pols de carretera, sulfat secundari i orgànics, nitrat secundari, aerosol marí, combustió de fuel-oil, metal·lúrgia*) que corresponen a fonts de PM ben conegudes de l'àrea d'estudi, més un novè factor que va ser observat per primera vegada. Aquest factor va ser anomenat *orgànic/tèxtil/guix*, i caracteritzat pels components amb altes concentracions a l'interior mencionats anteriorment: OC, Ca i Sr. Aquesta va ser la font més important de $PM_{2.5}$ a les aules, aportant el 45% del $PM_{2.5}$ a l'interior. Possibles fonts d'OC en espais amb molta densitat de persones poden ser fibres orgàniques de la roba, cèl·lules de la pell i altres emissions de caire orgànic. D'altra banda, el guix utilitzat per les pissarres és el responsable de les emissions de Ca i Sr. Als patis, aquesta font també va ser important (16% de mitjana), mentre que, contràriament, pràcticament no va tenir presència a l'estació d'UB-PR. Per tant, es tracta clarament d'una font d'origen local a les escoles.

Els components minerals de $PM_{2.5}$ són els que van tenir un major rang de ràtios I/E, amb la mediana de la ràtio molt propera o superior a 1 i amb el màxim valor observat durant la estació freda per l'acumulació dins les aules (amb finestres tancades) d'aquestes partícules, així com un menor nombre d'activitats al pati. El factor *mineral* va ser identificat mitjançant PMF per les espècies típiques de l'escorça terrestre com el Al, Mg, Li, Fe, Ca, Ti i Rb i va ser considerat una barreja de fonts, incloent-hi la resuspensió de la sorra als patis. Va ser la font amb la major variabilitat i especialment dependent del tipus de pati (de sorra: 16 i 9.1 $\mu g \cdot m^{-3}$; pavimentat: 2.5 i 3.6 $\mu g \cdot m^{-3}$; pati i aula respectivament). D'altra banda, les contribucions de *mineral* a UB-PR (0.6 $\mu g \cdot m^{-3}$) van ser molt més baixes, indicant també un origen local de les escoles. Per tant, les fonts *mineral* i *orgànic/tèxtil/guix* van ser les responsables de que les concentracions de $PM_{2.5}$ fossin molt altes a les aules (37 $\mu g \cdot m^{-3}$) i de que als patis (29 $\mu g \cdot m^{-3}$) fossin quasi el doble de les de UB-PR (17 $\mu g \cdot m^{-3}$).

Les emissions dels tubs d'escapament dels vehicles (OC, EC) i metalls del desgast dels frens (Cu, Sb, Sn i Fe) són els components principals del factor de *trànsit*. Les contribucions van ser similars als tres ambients estudiats: aules (4.8 ± 3.9 $\mu g \cdot m^{-3}$), patis (5.5 ± 4.2 $\mu g \cdot m^{-3}$) i UB-PR (4.1 ± 2.7 $\mu g \cdot m^{-3}$; aquest últim essent una mitjana de 24h en comptes de 8h). A moltes escoles, les concentracions a l'interior dels components del trànsit eren més altes que als patis, probablement degut a una localització més propera de la classe al carrer en relació al punt de mesura del pati, a una major resuspensió del PM (incloent els components emesos pel trànsit) a l'interior de les aules i a un rentat de l'atmosfera per precipitació a l'exterior. L'EBC presentà un dels majors F_{inf}, amb el 92% de la concentració interior d'EBC provinent de l'exterior durant l'estació càlida i el 75% durant la freda. Els baixos interceptes de la correlació interior-exterior van indicar l'absència de fonts interiors importants d'EBC. Aquests resultats ressalten la necessitat de situar futures escoles a localitzacions allunyades de carrers amb molt de trànsit.

El factor de *sulfat secundari i orgànics* (traçat pel SO_4^{2-} i el NH_4^+) va mostrar altes correlacions entre les contribucions interiors i exteriors, indicant una concordança entre els dos ambients, i no se li va atribuir cap font interior important. El *nitrat secundari* (explicat principalment per NO_3^-) va mostrar una gran variabilitat entre les escoles degut a la inestabilitat tèrmica de el NH_4NO_3 i les diferents condicions de temperatura que normalment es troben a Barcelona al voltant de l'any. De fet, també hi havia una important diferència de temperatura entre les aules i el pati, amb menors concentracions a l'interior d'aquest factor degut a les altes temperatures que es troben en aquest ambient i que causen la evaporació del NH_4NO_3.

Varis elements traça van mostrar baixa o nul·la correlació amb EBC i Al_2O_3, el que indica un origen diferent de les emissions de trànsits o mineral, com per exemple la *combustió de fuel-oil* (principalment per emissions dels trànsit de vaixells) i el factor de *metal·lúrgia*, ambdós identificats per PMF. No obstant, alguns elements com el As, Co i Pb presentaven una certa correlació amb la matèria mineral, el que suggereix que aquesta matèria mineral pot haver estat contaminada per deposició seca i humida d'aquests contaminants al pati.

Entre els metalls traça, V i Cd tenen els majors F_{inf} ($\geq$ 0.70) així com les menors concentracions de C_{ig} respecte a la mediana de concentració interior. El Pb va tenir un F_{inf} similar a la resta de metalls (entre el 46-60%, excloent els elements minerals) però la seva R^2 va ser més alta, inclús tenint en compte que el C_{ig} per al Pb va ser bastant alt (>42% de la mediana), indicant la presència de fonts interiors. Els metalls traça (excepte Sb i Cr) van tenir un menor F_{inf} durant la estació freda, pel que la seva entrada es va veure dificultada per les finestres tancades. Alguns dels metalls traça es van veure afectats per fonts interiors importants en algunes escoles. Cal ressaltar el Cr, ja que va tenir concentracions més altes a l'interior a les dues estacions (ràtio I/E = 1.46) i, de fet, el C_{ig} del Cr correspon al 95% i el 83% de la seva concentració mediana (estació freda i càlida, respectivament), indicant una clara contribució originada a l'interior. Es requereix més recerca per tal de poder identificar les possibles fonts d'aquests metalls traça, molts d'ells coneguts a causa de la seva alta toxicitat.

Els resultats van demostrar que l'antiguitat de l'edifici només es troba significativament (p-valor<0.05) associada amb els nivells a l'aula pel Fe i 4 elements traça (Cr, Li, Co, Se) típicament relacionats amb les emissions industrials. Els edificis més nous tendeixen a tenir concentracions més altes d'aquests elements que els més antics, probablement degut a emissions per part dels nous materials però és necessari investigar amb més detall les fonts específiques a l'interior de les escoles. D'altra banda, el tipus de finestra (de marc d'alumini/PVC o fusta) es va relacionar amb unes concentracions a l'aula més altes de components minerals (com el Al_2O_3, Fe, Mg) i d'aquells components amb alta contribució de fonts interiors (OC, Ca, Sr) en aquelles escoles amb finestra d'alumini o PVC. Per tant, la presència d'una finestra més aïllant (la d'alumini/PVC) seria una barrera important per la dispersió de la matèria mineral, que és resuspesa contínuament en una sala amb una alta densitat de persones. A més, les concentracions interiors de Co i As també foren significativament més altes en escoles amb finestres d'alumini/PVC, probablement per emissions interiors o per la seva possible presència a la sorra del pati. D'altra banda, la infiltració del NO_2 es troba dificultada per finestres

d'alumini/PVC, ja que aquelles escoles amb finestres de fusta tendeixen a tenir un augment d'uns 8 $\mu g \cdot m^{-3}$ de NO_2 a les aules.

Encara que l'exposició personal als contaminants atmosfèrics normalment s'estima a partir d'un nombre limitat d'estacions de mesura de la xarxa de vigilància de la qualitat de l'aire, la millor manera d'avaluar-la és a partir de mesures personals. Amb l'objectiu d'avaluar l'exposició personal d'una forma precisa, es van dur a terme mesures personals d'EBC de 45 alumnes amb microetalòmetres portàtils de forma simultània a les mesures a les escoles. A més, va ser avaluada la relació entre les mesures personals i les estacions fixes a les escoles (a l'interior i l'exterior) i a l'UB-PR. Les mesures personals van mostrar les concentracions més altes d'EBC en comparació amb les de l'escola i de l'UB-PR. Addicionalment, el rang de concentracions d'EBC també va ser més ampli per a les mesures personals, degut a pics de concentració que van tenir lloc principalment durant el temps de desplaçament. De fet, la mitjana geomètrica de concentracions d'EBC va ser significativament més alta durant el temps de desplaçament (2.0 $\mu g \cdot m^{-3}$) que durant els períodes en que els infants es trobaven a la classe (1.2 $\mu g \cdot m^{-3}$) o al pati (1.0 $\mu g \cdot m^{-3}$). Les concentracions més baixes es van observar quan els alumnes es trobaven a casa (0.9 $\mu g.m^{-3}$). Models lineals d'efectes mixtes van mostrar R^2 baixes entre les mesures personals i les estacions fixes a les escoles ($R^2 \leq 0.28$), que van augmentar fins a $R^2 \geq 0.70$ si només es consideraven els períodes en que els alumnes es trobaven a l'escola. Per a l'estació de UB-PR, les respectives R^2 van ser 0.18 i 0.45, el que indica la importància de la distància a l'estació de monitoratge quan s'avalua l'exposició. Durant la temporada càlida, les estacions fixes van tenir una major concordança amb les mesures personals que durant la freda. L'exposició diària integrada a EBC dels 45 alumnes va ser de 34.6 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$ i va mostrar molta variabilitat entre els diferents alumnes (desviació estàndard: 13.8 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$). Per a la dosi diària integrada (un paràmetre que també té en compte el factor dosimètric), la mitjana va ser de 18.2 $\mu g \cdot d^{-1}$ (desviació estàndard: 7.7 $\mu g \cdot d^{-1}$). Aquesta variabilitat és el resultat dels diferents patrons de temps-activitat de cada alumne, ja que poden dur a terme activitats molt diferents en localitats amb diferents concentracions d'EBC. L'exposició i la dosi pot ser molt diferent inclús entre alumnes que anaven a la mateixa escola, i aquesta variabilitat no es pot tenir en compte amb les estacions fixes. Els alumnes van passar el 6% del seu temps diari fent desplaçaments en els que rebien el 20% de la seva dosi diària d'EBC, degut a la ocurrència simultània amb les hores punta de trànsit i la proximitat a la font d'emissió. Els infant reberen el 37% de la seva dosi integrada diària d'EBC a les escoles. Els ambients interiors (escola i casa) van ser responsables del 56% de la dosi d'EBC.

Aquesta tesi aporta una anàlisis en profunditat de la qualitat de l'aire a les escoles i de l'exposició i dosi dels infants. Aquesta informació pot ser molt valuosa per als responsables polítics i planificadors urbans.

RESUMEN

La exposición a contaminantes atmosféricos se ha relacionado ampliamente con la aparición de efectos negativos en la salud (dando lugar a un aumento en las tasas de morbimortalidad de la población), y especialmente con problemas respiratorios y cardiovasculares. Además, también se sospecha de la posible asociación entre la exposición a contaminantes atmosféricos y un menor desarrollo neuronal. Los/las niños/as constituyen un subgrupo de la población particularmente vulnerable debido a sus características fisiológicas y de comportamiento. Tienen mayor número de respiraciones por minuto y una mayor actividad física, dando como resultado que, para una misma exposición, reciben una mayor dosis de contaminantes atmosféricos que los adultos. Los niños pasan gran parte de su tiempo en las escuelas, las cuales son un microambiente muy singular: las clases se encuentran normalmente abarrotadas de alumnos y están ocupadas durante periodos de tiempo muy largos.

Se llevó a cabo una intensiva campaña de muestreo de los ambientes interiores y exteriores de 36 escuelas en Barcelona y 3 en Sant Cugat del Vallès durante un año para caracterizar la calidad del aire en las escuelas y la exposición de los alumnos a los contaminantes atmosféricos. Las escuelas seleccionadas se consideran representativas de la ciudad, ya que la media de concentración de NO_2 medida en las escuelas BREATHE fue similar a las concentraciones modelizadas para el resto de escuelas de Barcelona (datos del proyecto ESCAPE). Los mismos contaminantes que se midieron en las escuelas también se monitorizaron en una estación de fondo urbano en Barcelona (UB-PR).

La variación espacial de las concentraciones de carbono negro equivalente (EBC; concentraciones de carbono negro corregidas por las concentraciones de carbono elemental, EC), NO_2 y partículas ultrafinas (UFP; en concentración en número) mostraron un gradiente ascendente hacia el centro de la ciudad, siguiendo el patrón del tráfico rodado. Por otro lado, aunque se observa una cierta similitud en la variación espacial para el material particulado con un diámetro aerodinámico inferor a 2.5 μm ($PM_{2.5}$), el impacto de las fuentes locales de las escuelas impiden que el $PM_{2.5}$ pueda ser considerado un buen indicador de emisiones de tráfico en éstas.

El rango de concentraciones y de variabilidad del EBC, NO_2 y UFP medidos en las 39 escuelas que participaron en el estudio fue mayor en el exterior, ya que los ambientes exteriores se encuentran más influenciados por las principales fuentes de emisión y por factores meteorológicos que los interiores. Las concentraciones medidas en el patio de

las escuelas fueron 1.6 veces más altas que las encontradas en el interior de la clase para el NO_2 y 1.5 veces para las UFP, mientras que las concentraciones de EBC eran similares en los dos ambientes. Contrariamente, el $PM_{2.5}$ tuvo concentraciones mucho más altas (1.6 veces) en el interior que en el exterior, aun cuando la mayoría de componentes del PM tuvieron niveles más altos en el exterior. No obstante, el carbono orgánico (OC; que fue el componente que más contribuyó al $PM_{2.5}$ del interior y el segundo al $PM_{2.5}$ exterior tras la materia mineral), el Ca, el Sr y el Cr fueron generados principalmente en el interior. El OC estuvo especialmente afectado por fuentes interiores, ya que prácticamente todo su rango de ratios interior/exterior (I/E) se encontró por encima de 1 en todas las escuelas y días de muestreo.

El NO_2 mostró una infiltración similar durante la estación cálida y la fría (los factores de infiltración, F_{inf}, fueron de 0.50 y 0.56 respectivamente), por lo tanto la infiltración es independiente de la apertura de ventanas. No obstante, más que por una baja infiltración, los niveles más bajos encontrados en el interior respecto al exterior podrían ser explicados por un consumo interior del NO_2 en reacciones en fase gaseosa con terpenos y otros hidrocarburos insaturados (emitidos por el mobiliario, pinturas, productos de limpieza, fotocopiadoras, entre otros). Las correlaciones entre las concentraciones interiores y exteriores mostraron R^2 y F_{inf} bajos para las UFP debido a la presencia de fuentes interiores (los interceptos, correspondientes a la parte generada en el interior, C_{ig}, eran altos) o de procesos que podrían aumentar los niveles de UFP independientemente de las concentraciones en el exterior. De hecho, las escuelas de Barcelona tuvieron concentraciones en número de UFP más altas durante la estación cálida a pesar de los niveles más bajos encontrados en el exterior durante la temporada fría. No obstante, los niveles en el interior también se encuentran influenciados por los exteriores, así como por la temperatura y la humedad.

Un análisis de contribución de fuentes mediante un modelo de Positive Matrix Factorisation (PMF) permitió la identificación de ocho factores (*mineral, tráfico, polvo de carretera, sulfato secundario y orgánicos, nitrato secundario, aerosol marino, combustión de fuel-oil, metalurgia*) que corresponden a fuentes de PM bien conocidas del área de estudio, más un noveno factor que fue observado por primera vez. Este factor fue llamado *orgánico/textil/tiza*, y caracterizado por los componentes con alta concentración en el interior mencionados anteriormente: OC, Ca y Sr. Esta fue la fuente más importante de $PM_{2.5}$ en las aulas, aportando el 45% del $PM_{2.5}$ interior. Posibles fuentes de OC en espacios con alta densidad de personas pueden ser fibras orgánicas de la ropa, células de la piel y otras emisiones de carácter orgánico. Por otro lado, la tiza utilizada en las pizarras es la responsable de las emisiones de Ca y Sr. En los patios, esta fuente también

fue importante (16% de media) mientras que, contrariamente, prácticamente no tuvo presencia alguna en la estación de UB-PR. Por lo tanto, se concluye que se trata de una fuente de origen local en las escuelas.

Los componentes minerales de $PM_{2.5}$ son los que tuvieron un mayor rango de ratios I/E, con la mediana de la ratio muy cercana o superior a 1 y con el máximo valor observado durante la estación fría por acumulación dentro de las aulas (con ventanas cerradas) de estas partículas, así como por un menor número de actividades en el patio. El factor *mineral* fue identificado mediante PMF por las especies típicas de la corteza terrestre como el Al, Mg, Li, Fe, Ca, Ti y Rb, y fue considerada una mezcla de fuentes, incluyendo la resuspension de la arena en los patios. Fue la fuente con mayor variabilidad y especialmente dependiente del tipo de patio (de arena: 16 y 9.1 $\mu g \cdot m^{-3}$; pavimentado: 2.5 y 3.6 $\mu g \cdot m^{-3}$; valores referentes a patio y aula respectivamente). Por otro lado, las contribuciones de mineral a UB-PR fueron muy bajas (0.6 $\mu g \cdot m^{-3}$), indicando también un origen local de las escuelas. Las fuentes *mineral* y *orgánico/textil/tiza* fueron las responsables de que las concentraciones de $PM_{2.5}$ en las aulas fuesen muy altas (37 $\mu g \cdot m^{-3}$) y de que en los patios fueran el doble que las de UB-PR (17 $\mu g \cdot m^{-3}$).

Las emisiones de los tubos de escape de los vehículos (OC, EC) y metales traza del desgaste de los frenos (Cu, Sb, Sn y Fe) son los componentes principales del factor *tráfico*. Las contribuciones fueron muy similares en los tres ambientes estudiados: aulas (4.8 ± 3.9 $\mu g \cdot m^{-3}$), patios (5.5 ± 4.2 $\mu g \cdot m^{-3}$) y UB-PR (4.1 ± 2.7 $\mu g \cdot m^{-3}$; este último siendo una media de 24h en vez de 8h). En muchas escuelas, las concentraciones de los componentes de tráfico en el interior eran más altos que en los patios, probablemente debido a una localización más cercana de la clase a la calle en relación al punto de medida del patio, una mayor resuspension del PM (incluyendo componentes emitidos por el tráfico) en el interior de las aulas y la limpieza de la atmósfera por precipitación en el exterior. El EBC presentó uno de los mayores F_{inf}, con el 92% de la concentración interior de EBC proveniente del exterior durante la estación cálida y el 75% durante la fría. Los bajos interceptos de la correlación interior-exterior indicaron la ausencia de fuentes interiores importantes de EBC. Estos resultados resaltan la necesidad de situar futuras escuelas en localizaciones alejadas de calles con mucho tráfico.

El factor de *sulfato secundario y orgánicos* (trazado por el SO_4^{2-} i el NH_4^+) mostró altas correlaciones entre las contribuciones interiores y exteriores, indicando una concordancia entre los dos ambientes, y no se le atribuyó ninguna fuente interior importante. El *nitrato secundario* (explicado principalmente por el NO_3^-) mostró una gran variabilidad entre las escuelas debido a la inestabilidad térmica del NH_4NO_3 y de las

diferentes condiciones de temperatura durante el año. De hecho, también hay una importante diferencia de temperatura entre las aulas y el patio, con menores concentraciones de este factor en el interior debido a las altas temperaturas que encontramos en este ambiente y que causan la volatilización del NH_4NO_3.

Varios elementos traza mostraron una baja o nula correlación con EBC y Al_2O_3, lo que indica un origen diferente de las emisiones de tráfico o mineral, como por ejemplo la *combustión de fuel-oil* (principalmente emisiones de tráfico de barcos) y el factor de *metalurgia* identificado por PMF. No obstante, algunos elementos como el As, Co y Pb presentaron una cierta correlación con la materia mineral, lo que sugiere que la materia mineral puede haber estado contaminada por deposición seca y húmeda de estos contaminantes en el patio.

Entre los metales traza, V y Cd tienen el mayor F_{inf} ($\geq$ 0.70) así como la menor concentración de C_{ig} respeto a la mediana de concentración interior. Pb tuvo un F_{inf} similar que el resto de metales (entre el 40-60%, excluyendo los elementos minerales) pero su R^2 fue más alta, incluso teniendo en cuenta que el C_{ig} para el Pb fue alto (>42% de la mediana), indicando la presencia de fuentes interiores. Los metales traza (excepto Sb y Cr) tuvieron un menor F_{inf} durante la estación fría, por lo que su entrada se vio dificultada por las ventanas cerradas. Algunos de los metales traza se vieron afectados por fuentes interiores importantes en algunas escuelas. Cabe resaltar el Cr, ya que tuvo concentraciones más altas en el interior durante las dos estaciones (ratio I/E= 1.46) y, de hecho, el C_{ig} del Cr corresponde al 95% y el 83% de su concentración mediana (estación fría y cálida, respectivamente), indicando una clara contribución de origen interior. Se requiere más investigación para poder identificar las posibles fuentes de estos metales traza, muchos de ellos conocidos por su toxicidad.

Los resultados demostraron que la antigüedad del edificio solo se encuentra significativamente asociada con los niveles del aula para el Fe y 4 elementos traza (Cr, Li, Co, Se; p-valor<0.05), típicamente relacionados con las emisiones industriales. Los edificios más nuevos tienden a tener concentraciones de los elementos mencionados anteriormente más altas que los antiguos, probablemente debido a emisiones por parte de los nuevos materiales, pero también es necesario investigar con mayor detalle la fuente específica en el interior de las escuelas. Por otro lado, el tipo de ventana (de marco de aluminio/PVC o madera) se relacionó con unas concentraciones en el aula más altas de los componentes minerales (como el Al_2O_3, Fe, Mg) y de aquellos componentes con alta contribución de fuentes interiores (OC, Ca, Sr) en aquellas escuelas con ventana de aluminio o PVC. Por lo tanto, la presencia de una ventana más

aislante (como la de aluminio/PVC respecto a las de madera) sería una barrera importante para la dispersión de la materia mineral, que se encuentra en continua resuspensión en los entornos con una alta densidad de personas. Además, las concentraciones interiores de Co y As también fueron significativamente más altas en escuelas con ventanas de aluminio/PVC, probablemente por emisiones interiores o por su posible presencia en la arena del patio. Por otro lado, la infiltración del NO_2 se vio dificultada por las ventanas de aluminio/PVC, ya que aquellas escuelas con ventanas de madera tendieron a tener un aumento de unos 8 $\mu g \cdot m^{-3}$ de NO_2 en las aulas.

Aunque la exposición personal a los contaminantes atmosféricos se estima normalmente a partir de un número limitado de estaciones de la red de calidad del aire, la mejor manera de evaluarla es a partir de las medidas personales. Con el objetivo de evaluar la exposición personal de una forma precisa, se llevaron a cabo medidas personales de concentraciones de EBC de 45 alumnos con microetalómetros portátiles de forma simultánea a las medidas en las escuelas. Además, se evaluó la relación entre las medidas personales i las estaciones fijas en las escuelas i en UB-PR. Las medidas personales mostraron concentraciones más altas de EBC respecto a las de las escuelas y UB-PR. Adicionalmente, el rango de concentraciones también fue más amplio para las medidas personales, debido a picos de concentración que tuvieron lugar principalmente durante el tiempo de desplazamiento. De hecho, la media geométrica de concentración de EBC fue significativamente más alta durante el tiempo de desplazamiento (2.0 $\mu g \cdot m^{-3}$) que durante los períodos en el aula (1.2 $\mu g \cdot m^{-3}$) o en el patio (1.0 $\mu g \cdot m^{-3}$). Las concentraciones más bajas se observaron cuando los alumnos se encontraban en casa (0.9 $\mu g.m^{-3}$). Modelos lineales de efectos mixtos mostraron R^2 bajas entre las medidas personales y las estaciones fijas en las escuelas ($R^2 \leq 0.28$), que aumentaron hasta $R^2 \geq 0.70$ si solo se consideraban los períodos en los que los alumnos estuvieron en la escuela. Para la estación de UB-PR, las respectivas R^2 fueron de 0.18 y 0.45, lo que indica la importancia de la distancia a la estación de medida cuando se evalúa la exposición. Durante la temporada cálida, las estaciones fijas tuvieron una mayor concordancia con las medidas personales que durante la estación fría. La exposición integrada diaria a EBC para los 45 alumnos fue de 34.6 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$ y mostró una gran variabilidad entre los distintos alumnos (desviación estándar: 13.8 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$). La media de la dosis integrada diaria (un parámetro que también tiene en cuenta el factor dosimétrico) fue de 18.2 $\mu g \cdot d^{-1}$ (desviación estándar: 7.7 $\mu g \cdot d^{-1}$). Esta variabilidad es el resultado de diferentes patrones de tiempo-actividad de cada alumno, ya que pueden llevar a cabo actividades muy diversas en ubicaciones con diferentes concentraciones de EBC. La exposición y la dosis pueden ser significativamente diferentes incluso entre alumnos que asistían a la misma escuela, y esta variabilidad no se puede tener en cuenta

con las estaciones fijas. Los alumnos se pasaron el 6% de su tiempo diario desplazándose durante el que recibían el 20% de su dosis diaria de EBC, debido a la ocurrencia simultánea con las horas punta de tráfico y la proximidad a la fuente. Los niños y niñas recibieron el 37% de su dosis integrada diaria de EBC en las escuelas. Los ambientes interiores (escuela y casa) fueron responsables del 56% de la dosis de EBC.

Esta tesis aporta un análisis en profundidad de la calidad del aire en las escuelas y de la exposición y dosis de los niños y niñas. Esta información puede ser muy valiosa para los responsables políticos y planificadores urbanos.

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CHAPTER 1
Introduction

1. INTRODUCTION

The Earth primitive atmosphere consisted of a mixture of carbon dioxide (CO_2), nitrogen (N_2), water vapour (H_2O_v) and a trace amount of hydrogen (H_2; Fegley Jr et al., 1986). Early in the history of mankind the only "pollutants" in the atmosphere were generated because of dust resuspended from the soil; biogenic emissions; seismic, geothermal and volcanic activity; and wildfires. Many years after, with the discovery of fire and the knowledge on how to use and maintain it increased the emissions of CO_2 and other pollutants into the atmosphere. Even though the change in the atmosphere in this period was negligible, the first cases of severe indoor pollution occurred.

It was when the first localities appeared that the outdoor air pollution began to be serious. At the beginning of civilisation, the cities could emit a penetrating stench of rotting flesh, food and manure (McNeill, 2003). Thereafter, the population started using firewood or manure as domestic fuel for heating. In the 3rd Century B.C. an Aristotle student stated that the "smell of burning coal was disagreeable and troublesome" (Eavenson, 1939) and the Roman philosopher, Seneca, already wrote about the heavy air of Rome in 61 A.D. (Stern et al., 1973). The growth of population areas coupled with the switch from wood-burning to coal-burning fires created clouds of smoke and soot over cities as early as the eleventh century. Long before public health researchers documented the association between negative health outcomes and inner-city pollution, an intuitive Maimonides (1138-1204) warned against the health risks that come along to city living: "*Comparing the air of cities to the air of deserts and arid lands is like comparing waters that are befouled and turbid to waters that are fine and pure. In the city, because of the height of its buildings, narrow streets and all that is poured from its inhabitants and their fluids… the air becomes stagnant, turbid, thick, misty, and foggy… If the air is altered slightly, the state of the Psychic Spirit will be altered significantly*".

One of the most remarkable episodes of air pollution in the history occurred in London in 1952. From the early 1780, coal became the main fuel in the Industrial Revolution when the steam engines obtained their energy from coal, with the consequent emissions of sulphur dioxide (SO_2), CO_2 and other pollutants generating unbreathable atmospheres. From the 4th until the 10th of December of 1952 a very cold weather in London pushed its inhabitants to burn huge quantities of coal, creating a dense atmosphere, named *smog* (which comes from the combination of the words smoke and fog) and causing the death of 4,000 people (mainly children, elder people and people with respiratory problems). Four years later, the Clean Air Act, regulated the smoke produced by coal combustions in households. Sulphur emissions were reduced by a 90% from 1962 to 1988 due to fuel change (Brimblecombe, 1987).

Moreover, the Industrial Revolution was the starting point for the release of new chemical elements and compounds into the environment. As an example, the metallurgic industry emitted considerable amounts of copper (Cu) and lead (Pb). And from 1960, vehicle exhaust has been added to the chimneys of the industries and homes. In 1990, traffic was already the main source of air pollution in the world (Walsh, 1990).

Even that nowadays the urban smog is not a widespread problem (partly explained by the domestic coal substitution by cleaner fuels); many cities (especially those characterised by a sunny climate) suffer from *photochemical smog*, being Los Angeles one of the most representative example. The topography and the climate of Los Angeles facilitate the formation of the photochemical smog. It is located in the middle of a plain surrounded by mountains except for the part that faces the sea. This conditions makes the city to suffer often from daytime thermal inversions that hinder the dispersion of pollutants (Edinger, 1973; Tiao et al., 1975). In fact, the sea breeze returns the pollution of the day before. In 1947, the city started to control the state of the atmosphere in order to achieve a cleaner air. Because of that, during the 1970s ozone (O_3) and other photochemical pollutants were nearly halved even that the car fleet had increased. Despite this good news, during the 90's the photochemical smog was a serious health problem and the worst problem of air pollution in the United States (McNeill, 2003).

1.1. AIR QUALITY

In the glossary of the European Environment Agency (http://glossary.eea.europa.eu), air quality is defined as "the degree to which air is polluted" and "the type and maximum concentration of man-produced pollutants that should be permitted in the atmosphere". The type and maximum concentration of each pollutant that may not be exceeded during a specified time is prescribed by regulations and a good air quality management may regulate, plan and work towards the accomplishment of the stated goals and objectives.

1.1.1. Effects of air pollutants on health and the environment

Among the principal subjects in current environmental research there are the effects of air pollutants on the atmosphere, climate, and public health.

The presence of particles in the atmosphere is essential for cloud formation and, therefore, for rain production (IPCC, 2013, 2007; Zhang et al., 2011). However, since the industrial revolution and the intensive consumption of fossil fuel for energy, the natural balance of aerosols and gaseous pollutants in the atmosphere has changed dramatically. Particulate Matter (PM) affects negatively to the ecosystems (Peters, 1973; WBG, 2000); accelerates the construction material deterioration (Alastuey, 1994) reduces visibility and has an important influence on climate change (IPCC, 2013, 2007). In fact, changes in atmospheric aerosol composition can disrupt the radiative balance by changing the amount of solar radiation reaching the earth's surface, owing to the fact that some aerosols have a big capacity in absorbing of solar energy (positive radiative forcing) and others in reflecting solar radiation (negative forcing; IPCC, 2013).

Air pollution has acute and chronic effects on the human health and can affect a number of different systems and organs (Pope III et al., 2002). The exposure to fine (PM with an aerodynamic diameter < 2.5 μm, $PM_{2.5}$) and ultrafine particles (UFP; PM with an aerodynamic diameter < 0.1, $PM_{0.1}$) has been clearly related to adverse health effects (Atkinson et al., 2014; Lim et al., 2012). Its effects include from minor respiratory irritation to chronic respiratory and heart disease, lung cancer, acute respiratory infections in children, chronic bronchitis in adults, or asthmatic attacks (Kampa and Castanas, 2008). Moreover, short and long term exposures have been related to premature mortality and reduced life expectancy (Lim et al., 2012).

Given the complexity of PM components, not only a single cause or mechanism is likely to emerge. Negative effects may be very different depending on particle size and composition (Valavanidis et al., 2008; WHO, 2013). In addition to PM size and composition, the large surface area of ultrafine particles might also play an important role causing more severe health effects (Oberdörster et al., 2005; Stoeger et al., 2006). Most of the processes in the human body take place via the particle surface, which is increasing significantly with decreasing particle size in the nanometre size range for the same amount of mass (Fissan et al., 2007; Maynard and Kuempel, 2005). Wilson et al. (2005) described that PM_{10} (aerodynamic diameter < 10 μm) influences the respiratory tract and can penetrate even into lower respiratory system. Exposure to air pollution increase the cases of chronic bronchitis and asthma (Künzli et al., 2000), the rates of rhinitis (Karakatsani et al., 2010), and a decrease in lung function (Gauderman, 2002); generating premature mortality to subtle sub clinical respiratory symptoms (Brunekreef and Holgate, 2002; Katsouyanni, 2003; Katsouyanni et al., 2001; Samet and Krewski, 2007). In fact, it has been estimated that air pollution is responsible up to an 8% of lung cancer deaths and 3% of respiratory infection deaths (WHO, 2009).

A large number of epidemiological and experimental studies have also identified PM (and especially $PM_{2.5}$ particles, rather than PM_{10}) as an important risk factor for the development and exacerbations of cardiovascular disease (increasing morbidity and mortality; Dockery and Stone, 2007; Dockery et al., 1993; Miller et al., 2007; Pope III et al., 2002; WHO, 2006), acting independently of known risk factors such as smoking, hypertension, hyperlipidaemia and diabetes (Bai et al., 2007). In fact, in the REVIHAAP Report (WHO, 2013), experts concluded that the previous conclusions of the 2005 global update of the World Health Organisation (WHO) air quality guidelines (WHO, 2005) about the evidence for a causal link between $PM_{2.5}$ and adverse health outcomes in human beings were confirmed and strengthened and, therefore, clearly remain valid. More specifically, human exposure to PM has been linked to a number of cardiovascular conditions (Brook et al., 2010; Sun et al., 2010), including myocardial infarction (Peters et al., 2001), hypertension (Ibald-Mulli et al., 2001), atherosclerosis (Allen et al., 2009; Araujo and Nel, 2009; Künzli et al., 2004), hearth rate variability (Cavallari et al., 2008), thrombosis (Baccarelli et al., 2008; Emmerechts et al., 2010; Lucking et al., 2008) and coronary heart disease (Puett et al., 2009).

In the review carried out by the WHO (2012) entitled "*Health Effects of Black Carbon*" they observed that short-term health effects show stronger association with black carbon (BC) than with $PM_{2.5}$ or PM_{10}, what suggest that BC is a better indicator of harmful particulate substances from combustion sources than total and undifferentiated PM mass. Although BC, emitted importantly by diesel engines, may not be a directly toxic component of $PM_{2.5}$, it may operate as a universal carrier of a wide variety of chemical constituents that might be highly toxic to sensitive targets in the human body (WHO, 2012).

$PM_{2.5}$ and $PM_{0.1}$ have the capability to be inhaled deeply into the lungs and be deposited on the alveoli to produce a series of harmful effects (Kampa and Castanas, 2008). In fact, especially UFP, can be translocated from the lung to the blood circulatory system (and arrive to a target organ) or even be taken up directly to the brain through the olfactory epithelium (Chen et al., 2006; Nemmar, 2002; Nemmar et al., 2001; Oberdörster et al., 2004). Although, there is a gap of scientific information about the effects of UFP on brain and neurodevelopment (Guxens and Sunyer, 2012), the recent review on evidence of health aspects of air pollution by WHO (2013) considers that there is emerging evidence that suggests the association between impaired neurodevelopment and a long-term exposure to $PM_{2.5}$.

Therefore, according to their potential effects on human health described in the previous studies, PM, and particularly BC and UFP are of major significance and should be characterised when assessing human exposure to air pollutants.

1.1.2. Atmospheric Particulate Matter

Atmospheric PM is made up of liquid and/or solid particles suspended in the atmosphere (Mészáros, 1999). They range from few nanometres to tenths of micrometres. The term aerosol is generally used as synonym of PM, although it also includes the air mass transporting the particles (Putaud et al., 2004). According to Mészáros (1999), PM pollution is defined by the alteration of the natural composition of the atmosphere as a consequence of the input of suspended particles and, therefore, it could be due to natural or anthropogenic causes.

Origin

PM can be released into the atmosphere by different sources, with both natural and anthropogenic origins. PM is a ubiquitous component on the atmosphere, since it is emitted by several natural sources (soil re-suspension, salt particles formed from sea spray, volcanoes emissions, forest fires...) and can be transported for long distances by the wind (Bozlaker et al., 2013; Kallos et al., 2007; Wagstrom and Pandis, 2011). It is an essential factor for cloud condensation and, thus, rainfall production (IPCC, 2013). Although natural sources are dominant at a global scale (natural sources generate a flux of about 12100 Tg in front of the 300 Tg with an anthropogenic origin; Giere and Querol, 2010; Figure 1.1), human activities contribute to increase locally, regionally and globally the levels of PM. Anthropogenic emissions come from six main sources: transportation (road, shipping, air), burning of fossil fuels for energy generation, domestic and non-domestic heating, industrial processes, non-industrial fugitives sources (agriculture, off road machinery and construction among others) and biomass burning. As said before, PM is considered an atmospheric pollutant (regardless of its origin, anthropogenic or not) since the alteration that causes on the regional atmosphere composition can cause harm or discomfort to humans and damage to the environment (Mészáros, 1999).

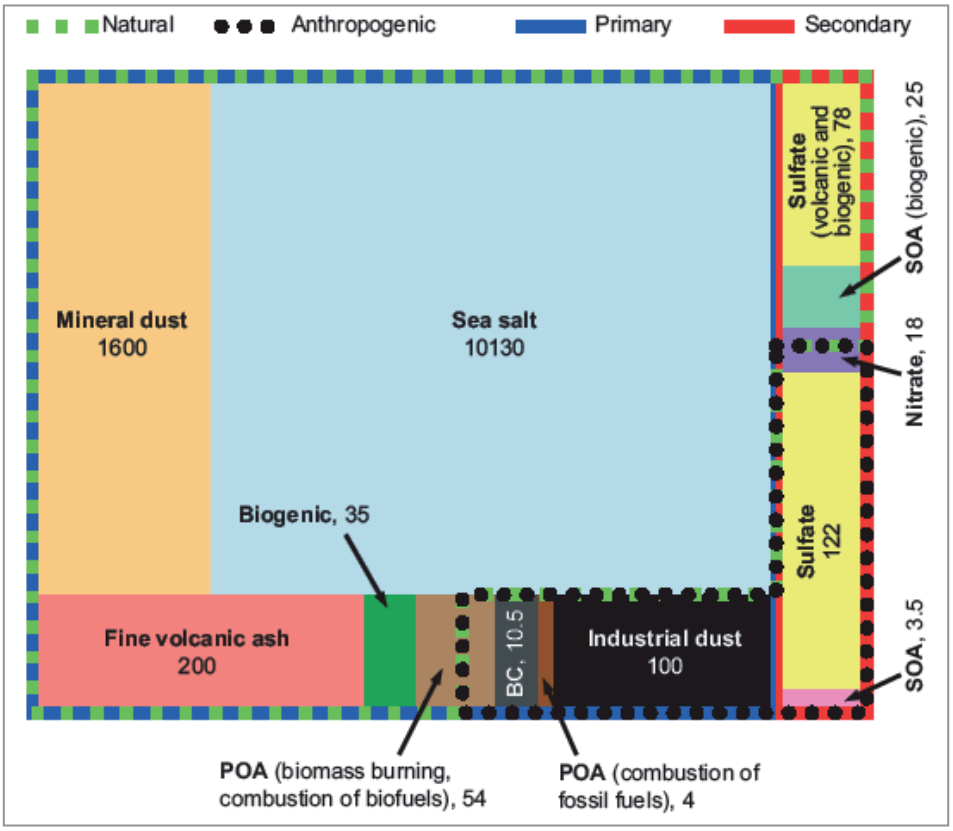

Figure 1.1. Fluxes of primary and secondary atmospheric PM, expressed in teragram per year (Tg=1012g) and shown as a fraction of the area of a rectangle. POA= primary organic aerosol; SOA= secondary organic aerosol; BC=Black carbon. Source: Giere and Querol (2010).

Particles emitted directly into the atmosphere from emission sources are named primary PM while the secondary PM are the ones that come into being in the air by gas-to-particle conversion (Mészáros, 1999). The formation of secondary PM may result from nucleation of gaseous precursors to form new (nano)particles or from condensation of these gases on previously existing particles (Kulmala and Kerminen, 2008). Particles may leave the atmosphere in two ways: by dry deposition (when deposited in the Earth surface) or by wet deposition (when the particle is scavenged by cloud droplets or rainfall during precipitation; Seinfeld and Pandis, 2006).

The wide range of natural and anthropogenic emission sources of many PM and gaseous pollutants and their subsequent transformations causes the PM to consist of a mixture of primary and secondary compounds, of organic and inorganic nature, with different grain size distribution and varied morphological, chemical, physical and thermodynamic properties.

Aerosol size and processes

The aerodynamic diameter is a physical property of a particle in a viscous liquid such as air. It is defined as the diameter of a perfect sphere with unit-density and same terminal settling velocity of the given irregular particle (Hinds, 1999). This property is important for particle transport, removal, collection and respiratory tract deposition. In fact, PM is generally categorised according to its diameter. The most common categories are: (1) Total Suspended Particles (TSP), which include all particles up to 30 μm in diameter; (2) PM_{10}, when the aerodynamic diameter of the particle is less or equal to 10 μm; (3) $PM_{2.5\text{-}10}$ includes the particles with an aerodynamic diameter from 2.5 to 10 μm, the particles included in this range are also called coarse PM; (4) $PM_{2.5}$, also referred to as fine PM in this thesis, comprises the particles up to 2.5 μm in aerodynamic diameter; (5) PM_1, are particles that have a diameter of less than or equal to 1 μm; (6) $PM_{0.1}$ which includes particles with a diameter of less than 0.1 μm (1 to 100 nanometres) known as ultrafine particles (briefly UFP) and (7) nanoparticles with a diameter < 50nm. According to health experts and to particle penetration in the human body, PM is commonly classified as follows (European Committee for Standardization (CEN), 1993): (1) PM_{100} (aerodynamic diameter > 100μm) is referred to as inhalable PM; (2) PM_{10} is the thoracic fraction since it can enter the thoracic airways; (3) particles with a diameter less than 4 μm (PM_4) are known as respirable PM as it could penetrate the conductive airways of the tracheobronchial tree that distributes the inhaled air to the gas-exchange airways in the lungs; and, finally, (4) $PM_{2.5}$ is known as alveolar fraction. (5) UFP ($PM_{0.1}$) could even transfer from pulmonary tissue to blood circulation. This is sketched in Figure 1.2.

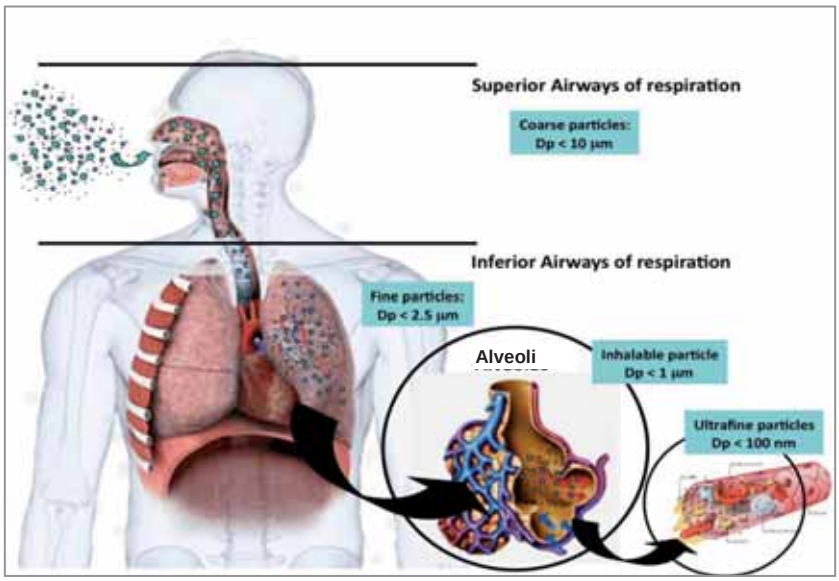

Figure 1.2. Sketch showing how much a particle can enter in the respiratory system according to the aerodynamic diameter of the particle. Source: Guarieiro and Guarieiro (2013).

As a rule, coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$ or PM_1) particles have different sources and formation mechanisms. The use of this dichotomy allow us to generalise the fact that fine particles are dominated by secondary PM (particles formed in the atmosphere from gaseous precursors) while the coarse fraction is mostly primary in origin, as it might be in the case of soil resuspension, road dust resuspension, and sea salt, among others (Pérez et al., 2008).

Nowadays, in air quality, the fractions most commonly monitored are PM_{10} and $PM_{2.5}$; focusing in $PM_{2.5}$ rather than PM_{10} because it has been more directly related with health effects (Wilson and Suh, 1997; Zanobetti and Schwartz, 2009). With the same aim UFP are becoming a new air quality target. In a study carried out in urban environments of Barcelona by Dall'Osto et al. (2012), they concluded that particle size distributions measured across the city tended to show a similar patter dominated by a mode centred on 20-30 nm diameter (emitted by diesel engine exhaust), which justifies the monitoring of the finest particles.

Atmospheric particulate levels are typically reported in terms of the number or mass of particles per unit of air volume (number or mass concentration). The dimension of the number concentration is cm^{-3} (to be precise should be particles per cm^3; $pt \cdot cm^{-3}$ or $\# \cdot cm^{-3}$), while the mass concentration is mainly expressed in $\mu g \cdot m^{-3}$ or $ng \cdot m^{-3}$. Both, number and mass concentration, vary in time and space as a function of emission rates, meteorology, secondary formation of PM and sinks. However, PM levels and composition not only depend on the type and volume of emissions, but also on environmental factors (especially temperature, humidity, solar radiation, rainfall and dispersive atmospheric conditions) and geographical factors (proximity to the coast, topography, soil cover and proximity to arid zones) of a given region (Erisman and Schaap, 2004; Vardoulakis and Kassomenos, 2008; Viana et al., 2005). Hence, once emitted, the evolution of the PM in the environment is affected by the factors suggested above and processes such as dilution, coagulation, condensation and deposition, which influence the mass, the number and the size distribution (Figure 1.3). The factors affecting the number and size distribution of fine and ultrafine aerosols have been studied widely in Northern and Central Europe (Ketzel et al., 2004; Nilsson and Kulmala, 1998; Olivares et al., 2007; Rose et al., 2006; Wehner et al., 2002), but this kind of studies are scarcer in southern Europe, especially in the Mediterranean area (Brines et al., 2015, 2014; Dall'Osto et al., 2012a; Fernández-Camacho et al., 2010; Pey, 2007; Pey et al., 2009; Rodríguez and Cuevas, 2007; Rodríguez et al., 2005; Sorribas et al., 2007; Van Dingenen et al., 2004).

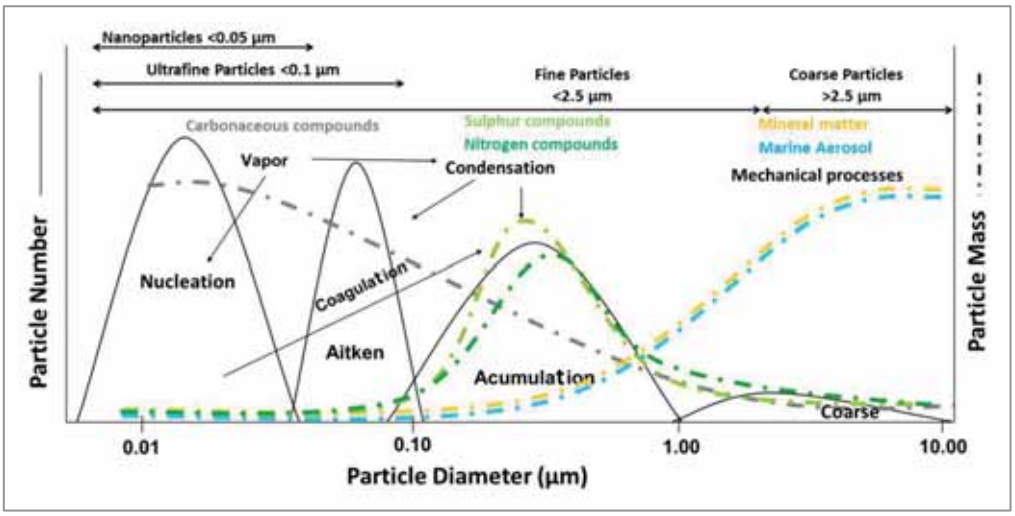

Figure 1.3. Sketch showing the relationship between the particle size, number distribution and mass, and chemical composition as well as some processes affecting their dynamics. Source: Pey, 2007; (elaborated from Harrison and Van Grieken, 1998; Warneck, 1988).

Ultrafine particles (UFP)

As stated before, UFP are those with an aerodynamic size below 0.1 µm (Figure 1.3). These are present in all the environments but they are especially important in urban environments due to the proximity to anthropogenic sources, such as road traffic (Rose et al., 2006; Wehner et al., 2002; Zhu et al., 2002). These might be very abundant in number concentration, notwithstanding their apportionment to the mass concentration is very low (Harrison et al., 2000; Kumar et al., 2014). UFP are classically divided into two subgroups depending on their size and formation mechanism (Seinfeld and Pandis, 2006):

(1) Nucleation (<20 nm): UFP from this mode are dominated by newly formed particles from gaseous precursors (mainly H_2SO_4, NH_3 and VOCs; Kulmala, 2003). With a very fine size at the beginning (and might be very abundant in number concentration), they quickly tend to join with other particles by coagulation or grow by condensing secondary PM, resulting on coarser particles (Charron and Harrison, 2003; Rodríguez et al., 2005; Wehner et al., 2002; Zhu et al., 2002). Furthermore, a relatively small fraction of primary UFP emitted by anthropogenic sources such as road traffic or other combustion particles may also influence this mode, since the typical prevailing mode of diesel engines in ambient air reaches around 20-30 nm (Dall'Osto et al., 2012b).

(2) Aitken (20 - 100 nm): particles in this mode can be emitted directly or can evolve from the coagulation and condensation on pre-existing particles (Kerminen et al., 2007; Lingard et al., 2006; Wehner et al., 2002). As previously stated, since diesel engines prevailing mode is around 20-30 nm (Dall'Osto et al., 2012b), Aitken particles are particularly important in urban zones with important traffic influence, especially in those where the car fleet has a great proportion of diesel vehicles. In fact, diesel cars used to emit more than 10 times, in terms of mass concentration, and 10^5 times, in terms of particle number concentrations, than gasoline engines (Harris and Maricq, 2001). Owing to improvements in diesel engines, this difference is currently much lower, but diesel cars still may emit higher number of particles than gasoline cars (Ban-Weiss et al., 2010).

Fine particles

Fine particles are those with an aerodynamic diameter below 1 or 2.5 μm (Figure 1.3). These include the UFP and the:

(3) Accumulation mode (100 - 1000 nm): those particles that have been part of coagulation processes among other particles and/or condensation processes of semi-volatile compounds on their surface with a final diameter between 100 - 1000 nm. Primary particles emitted by heavy vehicles are an important fraction of this mode (Rose et al., 2006; Zhu et al., 2002). These particles are not very important in number concentration as those on Aitken mode, however their influence is important when referring to mass concentration (Seinfeld and Pandis, 2006). Residence time of accumulation mode particles in the atmosphere is longer than those in the previous modes, which allow them to be transported for longer distances.

Coarse particles

(4) Coarse particles have an aerodynamic diameter above 2.5 μm (in air quality, usually 2.5-10 μm is considered as coarse, Figure 1.3). These are dominated by a primary origin, such as marine or crustal particles. In a global scale, they are essentially naturally emitted (Giere and Querol, 2010, Figure 1.1). However, in urban and/or industrial areas, the mineral fraction is mainly anthropogenic (Amato et al., 2009a; Querol et al., 2004a, 2001a; Salvador, 2005). On the other hand a relatively reduced fraction of the coarse PM could have a secondary origin, such as some species of nitrate and sulphate that often can influence the coarse fraction (Querol et al., 2001b). In this case, marine or crustal

particles (with a primary origin) react with gaseous molecules and modify their original composition (for example: $NaCl_{(s)} + HNO_{3(g)} \rightarrow NaNO_{3(s)} + HCl_{(g)}$). So that these reactions occur, an enriched calcium carbonate or marine aerosol and acidic gas/particles of anthropic origin are needed.

Composition

As said before mineral particles and marine aerosol dominate the PM on a global scale (IPCC, 2007). At local and regional scales, however, PM levels and composition are governed by local and regional anthropogenic emission sources.

According to the nature of particles, the next compositional groups are established (Seinfeld and Pandis, 2006): mineral dust, sea spray, carbonaceous matter (organic and elemental carbon), sulphate derived particles and nitrate derived particles. The predominance of these chemical components in the different size factions of PM is linked to the prevailing emission sources and the formation mechanisms of the particles.

Mineral dust

Mineral (or crustal) matter emitted from desert areas, is the second main component of the total PM mass present in the global atmosphere (about 14% of global planetary emissions (Giere and Querol, 2010). Generally, these particles are characterised by their coarse grain size in comparison with the rest of PM (Putaud et al., 2004).

Mineral particles originate due to wind action on Earth surface so its composition depends on the geology of the emission region. The principal components are Al, Ca, Si, Fe, Ti, K and Mg (Condie, 1993). Other important but trace elements are Co, Rb, Ba, Sr, Li, Sc, Cs, and rare earth elements (Bonelli et al., 1996; Chester et al., 1996). The major mineral species in PM are quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), clay minerals (especially kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($K(Al,Mg)_3SiAl_{10}(OH)$), smectite ($(Na,Ca)Al_4(Si,Al)_8 \cdot 2H_2O$) and palygorskite ($(Mg,Al)_5(OH)_2[(Si,Al)_4O_{10}]_2 \cdot 8H_2O$)) and feldspars, such as microcline/orthoclase ($KAlSi_3O_8$) or the albite/anorthite ($(Na,Ca)(AlSi)_4O_8$). In minor quantities, calcium sulphate ($CaSO_4 \cdot 2H_2O$) and iron oxides (Fe_2O_3) can also be found in PM (Adedokun et al., 1989; Avila et al., 1997; Caquineau et al., 1998; Glaccum and Prospero, 1980).

At local scale the anthropogenic mineral dust load in PM_{10} and $PM_{2.5}$ can be very relevant. As examples of activities that can emit mineral dust there are road dust, the land-use changes (which modify surface conditions), agricultural or mining activities, production of ceramics and cement, and construction and demolition. In urban areas, road traffic is one of the principal sources of mineral matter which consists mainly of a mixture of mineral particles (pavement abrasion and dust deposited on the pavement) mixed with carbonaceous particles (from traffic emissions deposited on the road) and metals (Fe, Cu, Sb, Ba from brakes; Ti, Rb, Sr from pavement; and Zn from tyres; Amato et al., 2009b). Construction and demolition is also an important source of mineral PM in urban areas (Amato et al., 2009b; Reche et al., 2011b).

Marine aerosol

Marine aerosol (or sea spray) is the most abundant component of PM in a global scale (approximately 80% of terrestrial global emissions (Giere and Querol, 2010; Figure 1.1). However, on a local/regional scale in Europe, out of the coastal Atlantic cities, sea spray rarely exceeds 5% of the PM_{10} ambient air concentration (Pérez, 2010). Sea spray aerosols are emitted directly to the atmosphere generated by two main mechanisms: the rupture of air bubbles from seawater that reach the surface and the waves in coastal areas (Mészáros, 1999). Marine aerosol concentrations at a given region are determined by the geographic area, proximity to the coast and meteorology.

These particles are mainly in the coarse fraction and their chemical composition is defined by oceans and seas composition, mainly Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+} and K^+ (Mészáros, 1999), being NaCl the main component (Warneck, 1988).

Carbonaceous aerosols

Carbonaceous particles represent less than 1% of the global planetary emissions (Giere and Querol, 2010), but on a local/regional scale, carbonaceous aerosols may account up to 20-40% of the ambient PM_{10} and $PM_{2.5}$ mass concentration (Putaud et al., 2004; Querol et al., 2004b, 2004c), becoming one of the most relevant fractions of PM in urban areas.

The carbonaceous fraction of the PM consists of both elemental (EC) and organic carbon (OC). The sum of EC+OC+mineral carbon is the Total Carbon (TC).

EC is graphitic carbon primary emitted due to incomplete combustion processes such as fossil fuel (Seinfeld and Pandis, 2006) and biomass burning (Husain et al., 2007). Also named BC (depending on the analysis method: EC is defined from a thermo-optical criterion while BC is determined by optical properties), it has been clearly

associated to negative health effects (WHO, 2012) and is known by its impact on radiative forcing and global climate change due to its great capacity of absorption of radiation (Boucher et al., 2013; IPCC, 2013, 2007; Sloane et al., 1991). EC has a primary (mostly) anthropogenic origin and is mainly emitted by road traffic (specially diesel engines, Gillies and Gertler, 2000; Matti Maricq, 2007; WHO, 2012) and other important sources such as power generation, specific industrial processes, biomass combustion and residential and domestic emissions. Many studies with the aim to identify possible negative health effects of BC have been carried out, but generally they were based in a very short time exposition to high concentrations of diesel exhaust or pure EC. Sehlstedt et al (2010a) documented an airway and systemic inflammation after the exposure to diesel engine exhaust, including nose and throat inflammation (Sehlstedt et al., 2010b). Other negative effects were found out by Lucking et al. (2008). They found that exposition to diesel exhaust increased thrombogenicity. In fact, a WHO report on the health effects of BC (WHO, 2012) suggest this might not be a directly toxic component of fine PM but may act as a carrier of harmful constituents (such as semi-volatile organic compounds, SVOC) to the target tissue, as adverse responses were only observed for whole diesel engine exhaust but no for EC-free exhaust or EC-only particles (Frampton et al., 2006; Routledge et al., 2006). Thus, because of its role, EC/BC may be a good indicator for combustion-derived and potentially very harmful particles (WHO, 2012).

OC can be emitted as primary aerosol particles or formed as secondary particles from condensation of non-methane volatile organic compounds (NMVOCs). The main emission sources of OC are fossil fuel combustion, biomass burning and agricultural activities but also natural biogenic forest emissions. In urban areas, the anthropogenic volatile hydrocarbons and other NMVOCs are mostly emitted by fugitive emissions of fuel vaporization and fossil fuel and biomass combustion processes. These are important precursors of secondary organic aerosols (SOA). Frequently OC is expressed as Organic Matter (OM) in order to consider the mass of O, N and H, also present in organic compounds.

Moreover, bio-aerosols such as pollen, spores, microorganisms and vegetal or insect debris, among others or biogenic emissions of volatile precursors of SOA can contribute to increase OC levels. However, it is worth noting that in urban and industrial areas the prevailing sources of OC are anthropogenic (Lonati et al., 2005; Rodríguez et al., 2002; M Viana et al., 2006), or biogenic but transformed to SOA due to anthropogenic cause (Hoyle et al., 2011).

An 80% fraction of the carbonaceous species in urban and industrial areas is present in the finer fractions (Harrison and Yin, 2008), usually in the size range <0.1 μm (nucleation and Aitken modes).

Secondary inorganic aerosols (SIA)

Main secondary inorganic compounds in PM are sulphate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+). These are formed in the atmosphere from their precursor gaseous species (sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3); Stockwell et al., 2003). In a general planetary scale, the SIA account for the 2% of the global emissions (Giere and Querol, 2010) but it might represent up to 30-40% in a local/regional scale of the PM_{10} mass concentration (Putaud et al., 2010; Querol et al., 2008).

SO_2 is emitted into the atmosphere by industrial processes, energy generation, shipping, domestic and residential emissions and/or road traffic. Once in the atmosphere its oxidation gives rise to the sulphuric acid (H_2SO_4), which nucleate or condensate to form sulphate (SO_4^{2-}) aerosols (Kulmala, 2003). H_2SO_4 reactions with NH_3 will form particulate ammonium sulphate ($(NH_4)_2SO_4$) and, in a minor proportion, calcium or sodium sulphate ($CaSO_4$, Na_2SO_4) by interaction with calcium carbonate ($CaCO_3$) and sodium chloride (NaCl), respectively. H_2SO_4 and $(NH_4)_2SO_4$ show a fine distribution (<1 μm) while the $CaSO_4$ and Na_2SO_4 are in the coarse fraction (>1 μm, Milford and Davidson, 1987).

NO_x is emitted mainly by traffic in urban areas but also by electricity generation, industrial processes and domestic and residential emissions. These oxides turn into nitric acid (HNO_3) by oxidation. Once the HNO_3 is formed it is neutralised and transformed into ammonium, sodium or calcium nitrate (NH_4NO_3, $NaNO_3$, $Ca(NO_3)_2$, respectively; Mészáros, 1999). The size distribution of particulate nitrate depends on the neutralising agent: NH_4NO_3 is present mainly in the fine range (<1 μm) but $NaNO_3$ and $Ca(NO_3)_2$ species are found mainly in the coarse fraction (>1 μm, Milford and Davidson, 1987). NH_4NO_3 presents instability under warm and dry ambient conditions. Thus, in warm regions of Europe, NO_3^- presents a marked seasonal pattern (Harrison et al., 1994; Querol et al., 2004b, 2004c, 2001b) with higher NO_3^- levels during the winter and an important summer decrease as a consequence of this thermal instability. Gaseous HNO_3 predominates over particulate NO_3^- during this period of the year (Song et al., 2001; Wittig et al., 2004) and $Ca(NO_3)_2$ or $NaNO_3$ formation is observed.

Hydrogen chloride (HCl) is also a precursor for SIA formation. The excess available NH_3 (that has not previously reacted with H_2SO_4 or HNO_3), may react with HCl to

form ammonium chloride (NH_4Cl). As well as for NH_4NO_3, its semi-volatile nature and the existence of the thermodynamic equilibrium between precursor gases and particulate ammonium salts, the formation mechanisms are rather complex (Finlayson-Pitts and Pitts, 1999; Trebs et al., 2004).

Trace elements

Trace elements have a small contribution to the PM mass. However, owing to their high toxicity, they can be a threat to human health at very low concentrations (Valavanidis et al., 2008).

A number of trace elements such as Cu, Sb, Fe, Zn and Ba are typical tracers for vehicle brakes and tyre wear (non-exhaust; Thorpe and Harrison, 2008). On the other hand, industrial emissions (from metallurgical processes, cement and ceramic productions, etc.) can be responsible for high concentration of trace metals, such as Cu, Pb, Ni, Cd and As (Barcan, 2002; Minguillón et al., 2007; Querol et al., 2007), which are toxic components of PM that might have important negative health effects. Urban air quality in coastal cities is also influenced by engine emissions of seagoing and oceangoing vessels, since shipping emissions (mainly V, Ni and SO_4^{2-}) are significant contributors to PM in many coastal cities (Lack et al., 2009; Pandolfi et al., 2011; Yau et al., 2013).

1.2. OUTDOOR AIR QUALITY IN URBAN ENVIRONMENTS

The sources affecting urban ambient PM have been widely characterised (Amato et al., 2011, 2009a; Minguillón et al., 2012b; Pekney et al., 2006; Song et al., 2001). *Road traffic* is the most important source of primary PM, with emissions from road transport arising from both exhaust and non-exhaust sources (Viana et al., 2008). The most significant sources of non-exhaust PM are abrasion of brakes, tyres and components of motor vehicles, and the abrasion of the road surface itself (Amato et al., 2009b). A further non-exhaust source is the resuspension of previously deposited material from the road surface due to vehicle-induced turbulence, tyre shear and turbulent action of the wind (Charron and Harrison, 2005; Harrison et al., 2001; Querol et al., 2001b, 1998). The impact of *industry* emissions (metallurgical processes, cement and ceramic production, among other) is still noticeable on air quality in some urban areas (Minguillón et al., 2012a; Querol et al., 2007). In coastal urban areas, emissions from commercial *shipping* (passenger and cargo) may also constitute a relevant source of PM

(Lack et al., 2009; Pandolfi et al., 2011). *Biomass burning* emissions, residential/domestic, agricultural and from wildfires, can also be a source of PM in urban areas (Aiken et al., 2010; Duan et al., 2004; Reche et al., 2012b; Viana et al., 2013). Other, *domestic and residential* emissions (excluding domestic biomass burning) have generally a small contribution to PM levels in the urban scale, and they are generally included in regional nitrate and sulphate contributions or in traffic contributions. In spite of the relative impact of construction-demolition works emissions on PM_{10} and $PM_{2.5-10}$ levels, the contribution of this source is difficult to estimate, since the related trace metals content is close to typical soil dust or desert dust resuspended (Reche et al., 2011b).

Differences in the impact of the described sources are evident from region to region in Europe, so different national policies and control strategies might be needed to achieve a reduction of atmospheric aerosol levels on a continental scale, and thus standard control parameters must be always under review.

Air quality regulations

The European Commission has developed an extensive body of legislation (Directives 2004/107/EC and 2008/50/EC, transposed to the Spanish legislation as RD 102/2011) that establishes health based standards and objectives for some air pollutants in ambient air (there is no standard for indoor air quality).

The Council Directive 1996/62/EC on ambient air quality assessment and management recognises the necessity of defining common objectives about air quality in the European Community in order to avoid, prevent or reduce damaging effects on human health or on environment as a whole. With this aim, limit and objective values or alert thresholds for atmospheric pollutant concentrations were set. PM_{10}, SO_2, NO_x and Pb limits were defined firstly in the Council Directive 1999/30/EC. This Directive was transposed to the Spanish legislation by the RD 1073/2002 with two limits proposed for the PM_{10} concentrations, one on a daily basis and the other on an annual one. The annual limits ask the arithmetic average of PM_{10} concentrations measured during a year to be below 40 $\mu g \cdot m^{-3}$, while the daily limit requires the 90.4 percentile of PM_{10} measured during a year to be below 50 $\mu g \cdot m^{-3}$. Pb (contained in PM_{10}) annual average concentration in air limit was established to be 500 $ng \cdot m^{-3}$.

Table 1.1. Current standard limits on ambient air quality in Europe

POLLUTANT	AVERAGING PERIOD	EUROPEAN LEGISLATION			WHO GUIDELINES
		LEGAL NATURE	CONCENTRATION	PERMITTED EXCEEDANCES PER YEAR	
PM_{10}	24 h	Limit value entered into force 1/01/2005**	50 $\mu g \cdot m^{-3}$	35 (or percentile 90.4)	
	1 y	Limit value entered into force 1/01/2005**	40 $\mu g \cdot m^{-3}$	-	20 $\mu g \cdot m^{-3}$
$PM_{2.5}$	1 y	Target value entered into force 1/01/2010. Limit value enters into force 1/01/2015	25 $\mu g \cdot m^{-3}$*	-	10 $\mu g \cdot m^{-3}$
Exposure concentration obligation for AEI		Concentration obligation will enter into force in 1/01/2015	20 $\mu g \cdot m^{-3}$	-	
Exposure reduction target for AEI		Target value will enter into force in 1/1/2020	18 $\mu g \cdot m^{-3}$		
Sulphur dioxide (SO_2)	1 h	Limit value entered into force 1/01/2005	350 $\mu g \cdot m^{-3}$	24	
	24 h	Limit value entered into force 1/01/2005	125 $\mu g \cdot m^{-3}$	3	20 $\mu g \cdot m^{-3}$
Nitrogen dioxide (NO_2)	1 h	Limit value entered into force 1/01/2010***	200 $\mu g \cdot m^{-3}$	18	200 $\mu g \cdot m^{-3}$
	1 y	Limit value entered into force 1/01/2010***	40 $\mu g \cdot m^{-3}$	-	40 $\mu g \cdot m^{-3}$
Lead (Pb)	1 y	Limit value entered into force 1/01/2005	0.5 $\mu g \cdot m^{-3}$	-	0.5 $\mu g \cdot m^{-3}$
Carbon monoxide (CO)	8 h	Limit value entered into force 1/01/2005	10 $mg \cdot m^{-3}$	-	10 $mg \cdot m^{-3}$
Benzene	1 y	Limit value entered into force 1/01/2010	5 $mg \cdot m^{-3}$	-	
Ozone (O_3)	8 h	Target value entered into force 1/01/2010	120 $\mu g \cdot m^{-3}$	25 d averaged over 3 y	100 $\mu g \cdot m^{-3}$
Arsenic (As)	1 y	Target value entered into force 1/01/2012****	6 $ng \cdot m^{-3}$	-	
Cadmium (cd)	1 y	Target value entered into force 1/01/2012****	5 $ng \cdot m^{-3}$	-	
Nickel (Ni)	1 y	Target value entered into force 1/01/2012****	20 $ng \cdot m^{-3}$	-	
Polycyclic Aromatic Hydrocarbons (PAH)	1 y	Target value entered into force 1/01/2012****	1 $ng \cdot m^{-3}$ (expressed as Benzo(a)pyrene, BaP)	-	

*Standard introduced by the Directive 2008/50/EC
**Under the Directive 2008/50/EC. Member States can apply for an extension until three years after the date of entry into force of the Directive 2008/50/EC in a specific zone. Request is subject to assessment by the Comission.
***Under the Directive 2008/50/EC. Member States can apply for an extension of up to five years in a specific zone. Request is subject to assessment by the European Commission.
***Under the Directive 2004/107/CE

The second Daughter Directive 1999/30/EC included new target values for CO and benzene. O_3 was added to the third Daughter Directive 2002/3/EC. Moreover, the Directive 2004/107/EC included objectives values for annual averages of Polycyclic Aromatic Hydrocarbons (PAH), Hg, As, Cd and Ni concentrations in PM_{10}. Finally, the new Directive 2008/50/EC on ambient air quality and cleaner air in Europe (known as CAFE, Clean Air for Europe) unifies Directives 1996/62/EC and 1999/30/EC, as well as other standards in this field. As innovative aspects, this Directive introduces different target value for $PM_{2.5}$ concentration that must become a limit value by 2015 (25 $\mu g \cdot m^{-3}$) and by 2020 (20 $\mu g \cdot m^{-3}$) in a second stage. Moreover, it defines the $PM_{2.5}$ Average Exposure Indicator (AEI) for urban background, expressed in $\mu g \cdot m^{-3}$ and based in measurements performed at urban background and agglomerations, as a three-calendar year running annual mean concentration averaged over all sampling points established. The AEI will be used to know if the exposure concentration obligation and the national exposure reduction target established by the Directive are met. The exposure concentration obligation establishes 20 $\mu g \cdot m^{-3}$ as the obligation value for the AEI to be met in 2015. The national exposure reduction target, to be met in 2020, depends on the initial ambient concentration, being between 0% when initial AEI are lower than 8.5 $\mu g \cdot m^{-3}$ and 20% for initial AEI between 18 and 22 $\mu g \cdot m^{-3}$. When levels are higher, additional measures should be taken until the levels reach to 18 $\mu g \cdot m^{-3}$.

Besides the European legislation, based on expert evaluation of current scientific evidence, the WHO published air quality guidelines (WHO, 2005, 2000) that are designed to offer guidance in reducing the health impacts of air pollution. In many cases, the WHO guidelines are much stricter than those limit or target values established in the European Directives. Table 1.1 summarises all the limits above and target values from the European Legislation and the guidelines from the WHO.

1.3. INDOOR AIR QUALITY

It is in indoor environments where people spend most of their time (approximately 90%; Monn, 2001). Nevertheless, this environment has been less studied than the outdoor one (as an example, during the decades from 1991 to 2010, there were fifty times more published papers on chemistry in the outdoor environment than on chemistry in indoor environments; Weschler, 2011). There are no mandatory limit values established by the European Commission but there exist some guidelines from the WHO (WHO, 2010; Table 1.2). The lower number of studies focusing on indoor in

comparison to outdoor air can be attributed to the heterogeneous direct indoor sources as well as the multiplicity of microenvironments (office spaces, industrial facilities, households, among many others; Viana et al., 2011). The most studied topic in indoor air research is indoor chemistry (gas-phase and surface chemistry) were O_3 has a principal role as the starting point of a chain of oxidation reactions (Destaillats et al., 2006; Weschler and Shields, 1999; Weschler et al., 1992). A key distinction between indoor and outdoor chemistry is that photolysis is minimal indoors (Weschler and Shields, 1997; Weschler, 2011).

Table 1.2. WHO indoor air quality guidelines for selected pollutants (WHO, 2010).

POLLUTANT	AVERAGING PERIOD	GUIDELINES
CO	15 m	100 $mg \cdot m^{-3}$
	1 h	35 $mg \cdot m^{-3}$
	8 h	10 $mg \cdot m^{-3}$
	24 h	7 $mg \cdot m^{-3}$
NO_2	1 h	200 $\mu g \cdot m^{-3}$
	1 y	40 $\mu g \cdot m^{-3}$

Indoor PM, some of its components, and specific gaseous pollutants have been studied in different indoor facilities (offices, homes, schools, restaurants, among others) usually concurrently with outdoor measurements to study the degree to which outdoor sources contribute to indoor levels. Therefore, infiltration of air pollutants from the outdoor environment to the indoor air is also a leading subject of study in this field, with many publications (Alzona et al., 1978; Bennett and Koutrakis, 2006; Chao et al., 2003; Kearney et al., 2011; Long and Sarnat, 2004; Long et al., 2001; MacNeill et al., 2012; Viana et al., 2011; Younes et al., 2011). Indoor PM levels and composition are affected by outdoor air concentrations, air exchange rates, penetration factors, as well as deposition and resuspension mechanisms (Chen and Zhao, 2011, and references therein). Although it is obvious that pollutants leak from outdoor air to the indoor environment, there are a far wider range of air pollutants indoors that originate from building materials, consumer products and an extensive list of activities that are carried out indoors (Brimblecombe and Cashmore, 2004). Some indoor activities that may

cause the formation of new particles or resuspension of deposited ones could be cooking, cleaning, walking, candle lighting, and, particularly, smoking (Abdullahi et al., 2013; Arku et al., 2014; Koutrakis et al., 1992; Qian et al., 2014; Singer et al., 2006; Slezakova et al., 2011). Cooking and cleaning affect particularly to UFP number concentration (Abt et al., 2000; He et al., 2004; Kearney et al., 2011; Wallace and Ott, 2010), while the coarser modes of PM are usually more affected by resuspension (by walking and other movements) and its levels are dependent on occupancy of the room (Branis et al., 2005; Custódio et al., 2013; Kopperud et al., 2004; Qian et al., 2014). Indoor levels of OC have also been related to human occupants, just through the simple presence of their bodies (Weschler, 2015).

The interest in the PM elemental composition arises from the potential toxicological effect of elements such as Pb, As, Hg and Cd, as well as the feasibility of using them as source tracers. Inorganic chemical characterisation of indoor PM is still scarce, with some studies determining usually few PM components and even less studies performing source apportionment in indoor environments. Many studies report high contribution from species originated outdoors to the indoor environment (such as SO_4^{2-} and traffic tracers; Arhami et al., 2010; Barraza et al., 2014; Brown et al., 2008; MacNeill et al., 2012; Martuzevicius et al., 2008; Meng et al., 2012). Barraza et al. (2014) performed a source apportionment model to indoor $PM_{2.5}$ chemical composition dataset obtained from 47 households in Santiago (Chile). They identified 6 sources, 3 of them being outdoor contributors (motor vehicles, street dust, and secondary sulphates) and the other 3 being indoor sources (indoor dust, cleaning and cooking, and cooking and environmental tobacco smoke).

The assortment of processes and pollutant sources that can be found in the indoor air makes this environment very complex and further studies are needed to fully characterise it.

1.4. AIR QUALITY IN SCHOOLS: A PARTICULARLY COMPLEX ENVIRONMENT

It is known that children are a particularly vulnerable population group because of their physiological and behavioural characteristics. They have higher ventilation rates and higher levels of physical activity (Trasande and Thurston, 2005). Children spend most of their day in the indoor environment (approximately 90%; Buonanno et al., 2012; US-

EPA, 2008). In the case of Spain, the school year lasts about 180 days and children spend at school an average of 25h per week at primary level (INCA, 2013).

Schools are microenvironments with some particular characteristics: classrooms are usually crowded rooms which are occupied during long periods. Moreover, children tend to be very active, and therefore move around inside the classroom and within the school facilities. Therefore, according to what was mentioned in the Section 1.3, this scenario can be severely affected by indoor PM resuspension (Qian et al., 2014) and organic emissions from children (Weschler, 2015).

Fromme et al. (2007) carried out a study in 64 primary and secondary schools in Munich (Germany) and concluded that children indoor exposure to PM_{10} and $PM_{2.5}$ was very high, especially in rooms with high number of pupils and low level classes because of the more pronounced physical activity of younger children. Moreover, they observed that inadequate ventilation is a major determinant for poor indoor air quality. In another study carried out by Molnár et al. (2007) and Wichmann et al. (2010), indoor and outdoor $PM_{2.5}$ samples were collected and NO_2 was determined with passive samplers in 40 different sites (20 non-smoking homes, 10 preschools and 5 schools) in Stockholm (Sweden). They found strong association between indoor and outdoor BC and NO_2, with lower levels inside the classrooms. On the other hand, $PM_{2.5}$ seemed to intrude less from outdoors, but indoor levels were compensated by indoor sources. They also concluded that the S, Ni, Br, and Pb elements concentrations were significantly lower in indoor environments that outdoors, being only Ti significantly higher indoor (indicating the possible provenance from TiO_2 in painting pigments). In school gyms, Braniš and Šafránek (2011) found that days with physical education in the schedule had the highest I/O ratio, especially for the $PM_{2.5\text{-}10}$ fraction and less pronounced in $PM_{1\text{-}2.5}$. Likewise, Blondeau et al. (2005) observed that resuspension due to children activity in 8 schools in La Rochelle (France) was less influential as particle size decreased as a reflection of the way deposition velocities vary as function of size.

In the Mediterranean region, Dorizas et al. (2015) found that PM (PM_{10}, $PM_{2.5}$, PM_1, $PM_{0.5}$) concentrations in schools in Athens (Greece) were affected by ventilation rates and presence of students, with higher PM concentrations during teaching hours than non-teaching hours. I/O ratios of PM_{10} and $PM_{2.5}$ were generally higher than 1, indicating the high contribution of indoor sources. In 3 primary schools in Lisbon (Portugal), Almeida et al. (2011) also found an agreement between physical activity of the students and high contributions due to resuspension of the previously settled

particles and that the studied schools were inadequately ventilated. On the other hand, Buonanno et al. (2013) studied UFP number concentrations and BC in 3 schools in Cassino (Italy) and concentrations were generally higher in the outdoor than in the indoor environment, since no indoor sources were detected. Besides, BC in the indoor and outdoor environment of the urban schools was 5 times higher than the suburban school. Diapouli et al. (2007) also observed I/O ratios below 1 for UFP in 7 primary schools in Athens (Greece) and identified cleaning as a source of these particles. Although far from the Mediterranean region, Laiman et al. (2014) also identified cleaning as a major source of UFP in classrooms of 25 schools in Brisbane (Australia), as well as printing and heating.

Accordingly, when assessing children exposure to air pollutants, there should be taken into account that schools may have different concentrations that those reported by outdoor air quality monitoring sites and, actually, to those measured in other indoor environments.

1.5. PERSONAL EXPOSURE AND DOSE

Ott (1982) defined the concept of human exposure as "the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time". From this definition, we have, on the one hand, ambient air pollutants which are ubiquitous in the urban atmosphere and subject to high spatial and temporal variability (Adgate et al., 2002; Hoek et al., 2002; Mangia et al., 2013; Minguillón et al., 2014, 2012b). On the other hand, every individual person has their own activity-pattern. Thus, quantifying human exposure to air pollutants is a challenging task for the reason that it is the result of a variety of interactions between environmental and human systems (Steinle et al., 2013). However, there is an evident need for a good characterisation and quantification of exposure to air pollutants (Morawska et al., 2013), since outdoor central sites for air quality monitoring might not accurately reflect people's exposure (Brown et al., 2008; Nerriere et al., 2005; Wallace and Ott, 2010) considering that people spend most of their time in the indoor environment. A more refined exposure assessment might help to obtain stronger results in epidemiological studies in virtue of avoiding the exposure misclassification of the individuals that might derive when estimating exposure with few fixed monitoring sites.

Personal measurements are the most representative measure of people's exposure (Jantunen et al., 2002) and previous studies (carried out in adult populations) showed that personal exposures are often higher than indoor and outdoor levels (Lai et al., 2004; Molnár et al., 2006; Oglesby et al., 2011). Personal measurements might be the most precise methodology to assess personal exposure, but it also requires a laborious, time-consuming and resource intensive fieldwork (Monn, 2001). Besides, personal monitoring requires the collaboration of volunteers and puts a burden on them.

Few studies with personal measurements have been carried out to assess the exposure of child populations (Borgini et al., 2011; Buonanno et al., 2013b, 2012; Janssen et al., 1999; Mazaheri et al., 2014; Van Roosbroeck et al., 2007). Children exposure might differ from adults since their day-to-day activities are different and they spend great amount of time in microenvironments which are not usually attended by adults, such as schools.

1.6. THE BREATHE PROJECT

The BREATHE project (BRain dEvelopment and Air polluTion ultrafine particles in scHool childrEn), funded by the European Community's Seventh Framework Program ERC Advanced Grant, seeks to study whether the traffic-related air pollution (particularly UFP) would affect negatively to brain development increasing cognitive and neurobehavioral disorders.

Air pollution is suspected to act as a developmental neurotoxic (Grandjean and Landrigan, 2014). The influence on the brain is unknown, with some preliminary evidence in animals. In rats, the exposure to diesel exhaust and UFP results in elevated cytokine expression and oxidative stress in the brain (Bos et al., 2012; Gerlofs-Nijland et al., 2010) and in an alteration of their behaviour (Yokota et al., 2011). In children, exposure to traffic-related air pollutants during pregnancy or infancy, a period when the brain neocortex is developing rapidly, has been associated to cognitive delays (Guxens et al., 2012; Suglia et al., 2008).

Air pollution hazards for childhood neurodevelopmental and behavioural disorders represent a new horizon for research of major worldwide impact. BREATHE addresses this issue using unconventional and innovative epidemiological methods interfaced with environmental chemistry and neuroimaging.

The overall objective of the BREATHE project is to detect the neurodevelopmental (cognitive, behavioural, and neurostructural) effects of urban air pollution. To this aim, BREATHE combines epidemiological, psychometric, genetic, neuroimaging and mathematical approaches in six closely linked components (sub-studies) conducted in about 2,900 school age children from the general population in 39 schools (Table 1.3). This present study is carried out in the framework of the study 2 of the BREATHE project on air quality assessment at school and exposure assessment of children in school age.

Table 1.3. Components (studies) of the BREATHE project.

TASK	TITLE	GOAL	POPULATION	METHODS
1	Schoolchildren study	Phenotype characterization in children from high and low traffic schools	7-9 year-old children (n=2900)	Computer tests Teacher/parent questionnaires Oral swaps for study 3
2	Air quality at schools and children's exposure	Create methods for precisely estimating personal air pollution exposure	39 schools 7-9 year-old children (n=80)	Personal air sampling Air quality sampling Statistical modelling
3	Gene-environment interaction	Search for susceptibility and mechanism	The school study 2900 children	Genotyping of SNP/CNV in candidate susceptible genes
4	Neuroimaging	Create methods assessing intermediate structural phenotypes	7-10 year-old children (n=80) with/without ADHD	Magnetic Resonance Imaging
5	Population-based causal modeling	Measure subacute/chronic effects	7-9 year-old children (n=2900)	Mathematical modeling Biostatistical analysis Sensivity analysis Genetic interaction studies
6	Replication study	Replicate previous findings	Children (n=2900) INMA cohorts	Association studies Biostatistical analysis

1.7. OBJECTIVES AND STRUCTURE OF THE THESIS

1.7.1. Gaps

All the studies described above in Sections 1.4 and 1.5 have contributed to characterise children's exposure to air pollutants and indoor and outdoor PM levels and composition in schools. However, significant gaps still remain open and need to be studied. Therefore, this thesis has been designed to contribute to reduce knowledge gaps on the following aspects on children's exposure to air pollutants at schools:

1. PM in school indoor and outdoor spaces has not been yet well characterised.
2. Research on inorganic chemical composition of PM and on levels of UFP and BC at school facilities is very scarce and focused only in few PM components.
3. Processes and sources affecting PM levels and its composition, both in the indoor and outdoor environment in schools are still an open question.
4. Studies about children personal exposure based on personal 24h measurements are still very scarce. For children, they are almost non-existent.

1.7.2. Objectives

The present thesis aims to fill a number of the knowledge gaps previously identified through an exhaustive sampling campaign in 39 schools in Barcelona (36) and Sant Cugat (3) and online personal measurements of BC in 50 children. This study aims to achieve the following objectives:

1. To characterise indoor and outdoor air quality at schools in Barcelona, focusing on $PM_{2.5}$ and its chemical components, BC, UFP and NO_2.

2. To evaluate the variability of air pollutants among the different schools, especially the parameters that are most influenced by traffic emissions.

3. To identify and quantify the main aerosol sources and processes governing concentrations of $PM_{2.5}$ in indoor and outdoor environments in schools.

4. To study the infiltration of ambient air pollutants to indoor air in schools and assess how ventilation, type of windows and building age affects this process.

5. To assess the agreement in BC concentrations between personal measurements, different monitoring stations at schools and a reference urban background

station in Barcelona to determine whether a single station is a good surrogate for individual exposure.

6. To determine children's daily integrated exposure and dose to BC and identify the main activities or locations which contribute to this exposure/dose.

1.7.3. Structure of the thesis

After this introduction, a methodology section will summarise the experimental and statistical techniques used to reach the aforementioned objectives. Results are presented in form of four research articles published in peer-reviewed journals. Taking this into consideration, the following methodology section will focus more on principles of operation for the instruments employed in order to avoid repetition, as the methodology is also described in each publication. A summary discussion of the main findings in each article, and how the findings relate to each other, will be presented, followed by the main conclusions of this thesis. Finally, a brief section will discuss future research directions and implications of the work presented here.

The original articles included in this thesis are briefly described below:

1. Rivas, I., Viana, M., Moreno, T., Pandolfi, M., Amato, F., Reche, C., Bouso, L., Àlvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X., 2014. Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain. *Environment International* 69, 200–212.

   This work describe the results on the concentrations during school hours of NO_2, $PM_{2.5}$ and its chemical components, BC, UFP and Lung Deposited Surface Area (LDSA) from the two sampling campaigns at the 39 BREATHE schools. The spatial variability of NO_2, $PM_{2.5}$, BC and UFP concentration in school across Barcelona is also assessed and some main school-related sources are identified.

2. Amato, F., Rivas, I., Viana, M., Moreno, T., Bouso, L., Reche, C., Alvarez-Pedrerol, M., Alastuey, A., Sunyer, J., Querol, X., 2014. Sources of indoor and outdoor PM2.5 concentrations in primary schools. *Science of the Total Environment* 490, 757–765.

The sources contributing to indoor and outdoor $PM_{2.5}$ at schools and to outdoor $PM_{2.5}$ in the urban background (UB) reference station of Palau Reial (UB-PR) were identified in this work by a constrained Positive Matrix Factorisation (PMF) model for source apportionment. Additionally to the typical PM sources in Barcelona, a school-related source was observed only indoors. The different contribution to the mineral source for sand and paved playground was assessed as well as the main parameters affecting the contribution from traffic source.

3. Rivas, I., Viana, M., Moreno, T., Bouso, L., Pandolfi, M., Àlvarez-Pedrerol, M., Forns, J., Alastuey, A., Sunyer, J., Querol, X., 2015. Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in $PM_{2.5}$ in schools. *Atmospheric Environment* 106, 129–138.

   The infiltration of different outdoor pollutants into the indoor environment at schools was assessed in this article. Some pollutants showed I/O ratios much higher than 1, indicating a significant contribution from indoor sources to indoor concentrations. The effect on the infiltration process of ventilation, building age and type of window frame was evaluated.

4. Rivas, I., Donaire-Gonzalez, D., Bouso, L., Esnaola, M., Pandolfi, M., de Castro, M., Viana, M., Àlvarez-Pedrerol, M., Nieuwenhuijsen, M., Alastuey, A., Sunyer, J., Querol, X. Spatiotemporally resolved Black Carbon concentration, schoolchildren's exposure and dose in Barcelona. *Indoor Air*, *in press*, 2015.

   Using portable microaethalometers and time activity diaries, the children's daily-integrated exposure and dose to BC was quantified. The main activities/locations contributing to the exposure/dose were identified. Moreover, the agreement between BC concentrations from personal measurements, school fixed sites and the UB-PR station was assessed.

CHAPTER 2

Methodology

2. METHODOLOGY

This section describes the methodology and instrumentation used during the air quality campaigns carried out in the schools and for personal measurements of schoolchildren in the framework of the BREATHE study.

2.1. STUDY AREA

The study is carried out in 36 schools in the city of Barcelona and 3 schools located in the municipality of Sant Cugat del Vallès.

The city of Barcelona has 1.62 million inhabitants (IDESCAT 2011), making it the second most populated city in Spain and the tenth within the European Union, with a population density of 15940 inhab·km^{-2}. The city is located in the north-east of the Iberian Peninsula, narrowly constricted between the Mediterranean Sea and the Catalan Coastal Ranges (Figure 2.1). These natural surroundings protect the city from the typically more severe continental weather conditions of inland Catalonia, but also weakens the cleansing effects of advective Atlantic-derived air masses. Along its northern and southern borders, the city is delimited by the Llobregat and Besós river valleys that channel the winds and also contain major industrial activities such as metallurgy. Due to the characteristic geography of the area, transport and dispersion of atmospheric pollutants within Barcelona are mainly controlled by fluctuating coastal winds which typically blow in from the sea during the day (diurnal breeze) and, less strongly, from the land during the night (night breeze). These atmospheric dynamics and the geographic settings have the potential to produce high concentrations of local pollutants within the city (Pérez et al., 2008).

Given not only the geographically confined nature of the city, but the lack of central urban green spaces (Burriel et al., 2004), the urban architecture characterised by square-blocks with narrow streets that reduce the dispersion of pollutants, and the fact that Barcelona has one of the highest vehicle densities in Europe (nearly 5800 vehicles km^{-2} in 2012; Ajuntament de Barcelona, 2012), urban backgrounds levels are considerably high and strongly affected by vehicle emissions (Cyrys et al., 2012; Eeftens et al., 2012; Reche et al., 2011a). In addition to locally sourced air pollution, an extra contribution to ambient PM concentrations in Barcelona is frequently made by the arrival of Saharan dust intrusions, which are dusty air masses from the Sahara and Sahel desert regions of North Africa (Moreno et al., 2006; Pérez et al., 2008; Pey et al., 2008; Rodríguez et al.,

2001). This contribution is estimated as directly adding around 1 - 2 $\mu g \cdot m^{-3}$ to PM_{10} and 0.2 - 1 $\mu g \cdot m^{-3}$ to $PM_{2.5}$ annual averages in the city (Escudero et al., 2007), as well as being responsible for 10 - 20 of the annual exceedances of the PM_{10} daily limit value (23 - 27% of total exceedances). However, most of the airborne mineral particles detected in Barcelona are anthropogenic in origin, resulting from resuspension of the road dust by vehicular traffic, pavement abrasion, construction/demolition works and other human activities (Amato et al., 2009a).

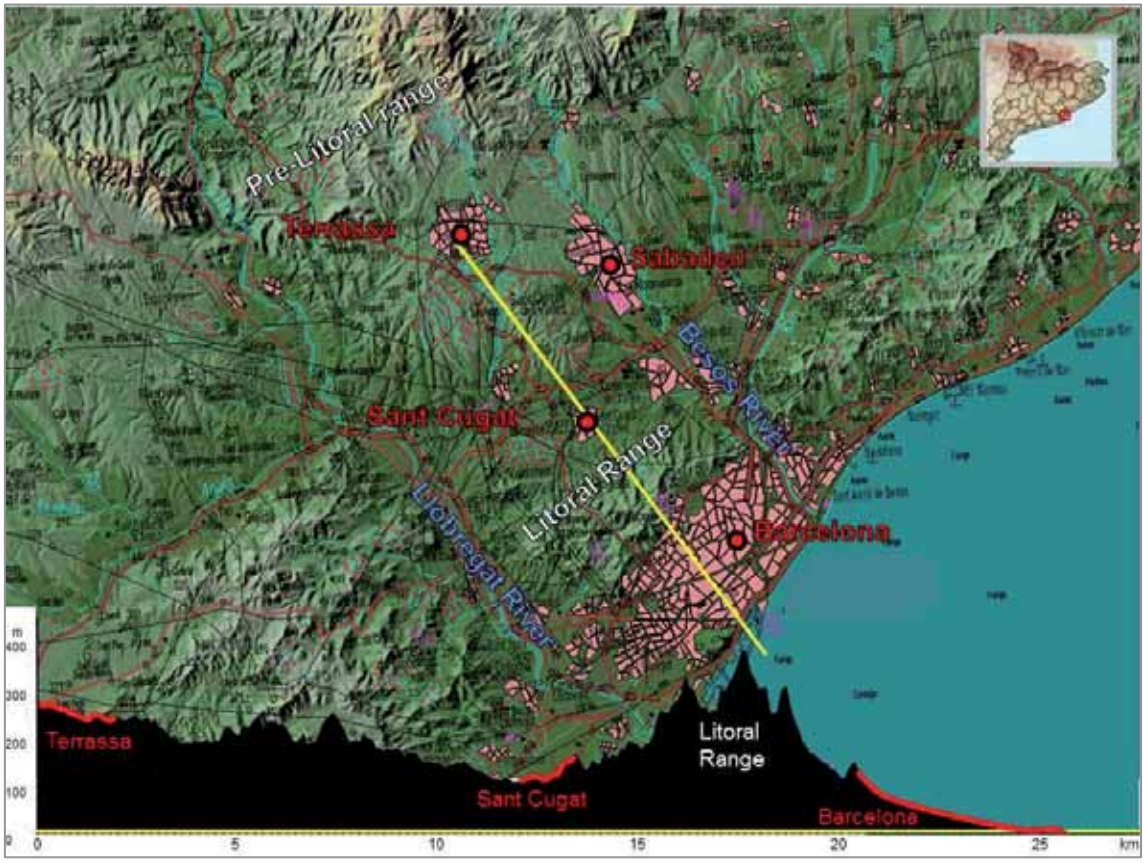

Figure 2.1. Location and topography of Barcelona and Sant Cugat and their surroundings.

A comprehensive description of the mesoscale and local meteorological processes affecting Barcelona can be found in Jorba et al. (2011) and Pey et al. (2010). The general circulation of the atmosphere is influenced by the Azores anticyclone, with a variable position depending on the season. During winter, the anticyclone is settled in the southern latitudes, allowing low pressures above peninsular latitudes and, thus, favouring the renewal of air masses. Since the end of spring until the beginning of autumn, the Azores anticyclone reaches its maximum intensity, avoiding the influence of low pressures from the Atlantic in the Mediterranean basin. These scenarios favour the development of local and mesoscale circulations. During diurnal periods and as a

consequence of high temperatures and the convergence of flow from sea to land, and area of relative low pressure is generated.

The air masses origin in the study area shows a typical seasonality as described in previous studies (Pey, 2007). The transport of air masses from the Atlantic is reported with major frequency during winter, even it can be observed during the whole year. On the other hand, the arrival of dusty air masses from Africa is more commonly observed in summer when it is also typical the local recirculation of polluted air masses. During autumn, the most frequent are the advection episodes from central-Europe, from the southern Mediterranean basin and the anticyclonic scenarios.

Breeze patterns can also be important in the transport of pollutants within the city and even from the urban to the rural sites. In Barcelona, the sea breeze develops around 10:00 UTC (Universal Time Coordinated; arriving later to Sant Cugat due to the Litoral mountain range barrier), whereas the levels of pollutants increase after 18:00 UTC when the mountain breeze starts bringing pollution in from the surrounding industrial valleys and the wider metropolis around the city centre. These temporal patterns are also reinforced by the increase in the boundary layer height during the central hours of the day (that results in the dilution of pollutants) and its decrease starting at approximately 17-18 UTC.

Sant Cugat city is surrounded by the Litoral mountain range in the south-east and the Pre-Litoral mountain range in the north-west. Both geographical accidents protect the city of pollutants intrusions (Figure 2.1). However, the Llobregat valley is an easy entrance to the Vallès Depression (in between the Litoral and Pre-Litoral ranges) for air pollutants carried from the urban and industrial zones that surrounds the river. Once in the Vallès Depression, the pollutants may accumulate due to the bad dispersion conditions.

Whereas air quality in Barcelona improved during the 1980-1990s, mainly due to the reduction in industrial emissions, lately the increasing traffic levels reversed this trend and Pérez (2010) showed how the PM_1 mean annual levels increased from 1999 to 2006, almost parallel to the progressive rise in road traffic flow and especially to the growth of the diesel fleet (DGT, 2011; Pérez et al., 2010). However, in the few past years there have been several effective environmental measures, the synergy of a favourable meteorology for pollutant dispersion and the economic crisis which has consequently end in a reduction of vehicles at traffic rush-hours and the decrease of active industries. This new conditions have reduced notably the PM levels, especially for trace compounds associated with industrial emissions (e.g. OC, EC, Cd, Cu, SO_4^{2-}; Cusack et al., 2012; Querol et al., 2014).

As said before, it is important to highlight that Barcelona has one of the highest vehicle density in Europe (5800 cars·km^2 versus less than 1500 cars·km^2 in north European cities; Ajuntament de Barcelona, 2013). Furthermore, the vehicle fleet is characterized by a high proportion of diesel cars (60% diesel, 39% gasoline), motorbikes (almost 100% gasoline), heavy duty vehicles (79% diesel, 20% gasoline; DGT statistics for September 2014, https://sedeapl.dgt.gob.es/IEST2) and the use of a large proportion of private cars (40%) for the daily mobility of its inhabitants. Furthermore, Barcelona has one of the main harbours in the Mediterranean Basin, with the highest number of cruise ships for tourists in Spain. Shipping emissions (passenger and cargo) may be a significant focus of emission of atmospheric pollutants, and they account for 2-4% of the mean annual PM_{10} levels and for the 14% of $PM_{2.5}$ (Viana et al., 2009).

2.1.1. School monitoring sites

Two one week sampling campaigns were carried out in 36 schools in Barcelona and 3 in Sant Cugat. The first campaign (SC1) took place from 27th January until 22nd June 2012 and the second one (SC2) from 14th September 2012 until 22nd February 2013. In both campaigns, the sampling was performed simultaneously indoors (in a classroom) and outdoors (in the playground). All the schools were monitored during 4 days (from Monday morning to Friday morning) with a minimum of three days (depending on holidays). No data is available for Fridays since it was the day when the monitoring stations were moved from one school to the next one. Each school has an ID number and their location is shown in Figure 2.2.

Two schools were assessed per week and they were paired based on their corresponding modelled NO_2 levels from the ESCAPE project for Barcelona city (Cyrys et al., 2012), so each pair would include a low and high NO_2 school. The participating schools had similar modelled NO_2 concentrations to the remaining schools in Barcelona (51.5 versus 50.9 μg·m^{-3}; Kruskal- Wallis test, p = 0.57).

The indoor monitoring station was always located in a classroom attended by 2nd, 3rd or 4th primary degree pupils, since children aged 7 to 9 years old are the target population of the BREATHE Study. Indoor instruments were located, where possible, next to the opposite wall from the blackboard (to avoid direct exposure to chalk or maker's emission) and from the windows (to avoid direct outdoor levels interference and disturbances resulting from air currents). The outdoor monitoring station was located in the everyday playground where the participating children usually spent their

breaks. The same instrumentation was used in both environments and this indoor-outdoor simultaneity could be observed in Figure 2.3.

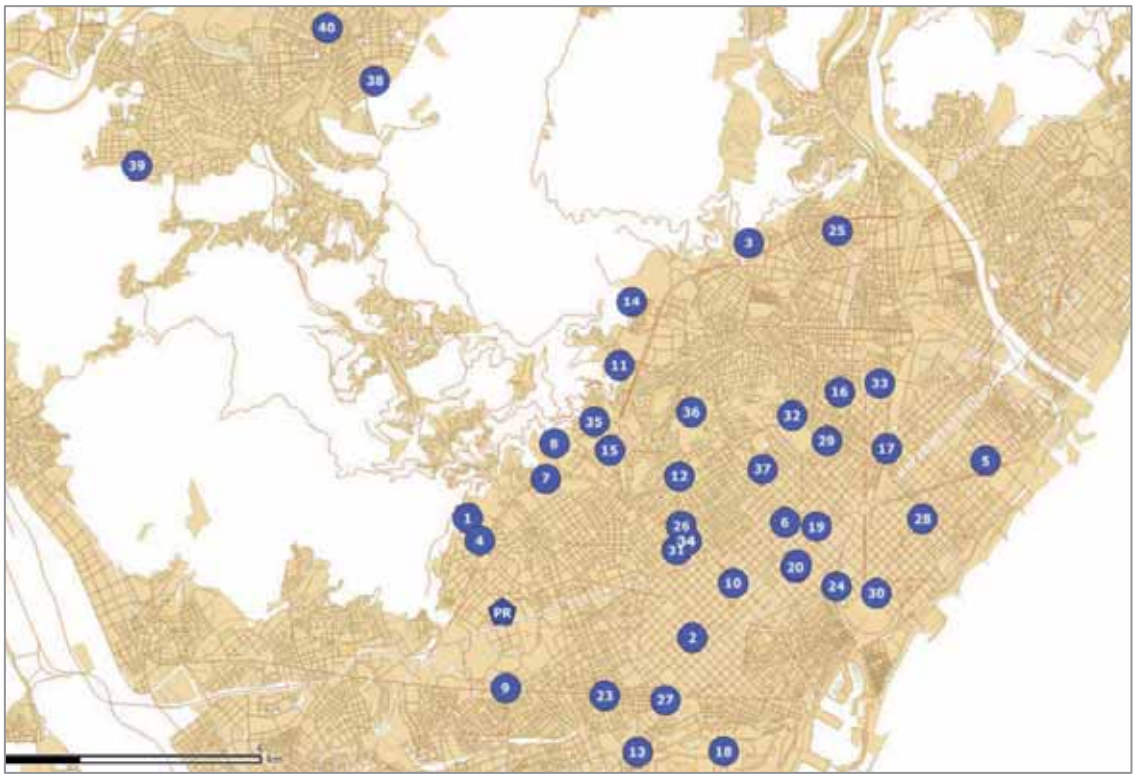

Figure 2.2. Location of the 39 BREATHE schools, and the urban background station of Palau Reial (PR).

Other information was collected regarding schools characteristics during the sampling campaigns, such as orientation and floor of the classroom, type of material of the windows frame, type of playground (paved vs. sand-filled), and type of marker used in the blackboard. Moreover, teachers were asked to write down if the windows were open or closed during the teaching hours (during no teaching hours, windows were always kept closed). Table 2.1 shows the main characteristics of the 39 schools included in the study.

Figure 2.3. Image showing both indoor and outdoor monitoring sites in one of the BREATHE schools.

Table 2.1. Main features of the schools.

School ID	Window material	Building construction year	Playground	Classroom orientation[1]	Playground location[2]	Classroom floor	Playground floor
1	PVC/Al	>1970	paved	Interior	interior	0-1st	1st-2nd
2	Wood (SC1) PVC/Al (SC2)	≤1970	paved	Interior	interior	2nd	ground
3	wood	>1970	paved	Playground	interior	2nd	1st-2nd
4	PVC/Al	≤1970	sand-filled	Playground	street	2nd	ground
5	PVC/Al	>1970	paved	directly street	street	2nd	3-5th
6	wood	≤1970	paved	Interior	street	2nd	1st-2nd
7	wood	≤1970	paved	Playground	street	3-4th	3-5th
8	PVC/Al	>1970	paved	Playground	street	2nd	3-5th
9	PVC/Al	≤1970	paved	Playground	street	3-4th	ground
10	wood	≤1970	paved	directly street	interior	2nd	ground
11	PVC/Al	>1970	paved	Interior	street	0-1st	1st-2nd
12	PVC/Al	>1970	sand-filled	directly street	street	0-1st	1st-2nd
13	PVC/Al	>1970	sand-filled	Interior	interior	0-1st	ground
14	PVC/Al	>1970	sand-filled	Playground	street	2nd	ground
15	wood	≤1970	sand-filled	directly street	street	3-4th	ground
16	PVC/Al	≤1970	paved	Interior	street	2nd	3-5th
17	wood	≤1970	sand-filled	directly street	street	2nd	ground
18	PVC/Al	>1970	sand-filled	Interior	street	0-1st	ground
19	wood	≤1970	paved	Playground	street	0-1st	ground
20	wood	>1970	sand-filled	directly street	street	0-1st	ground
22	PVC/Al	≤1970	paved	directly street	interior	2nd	ground
23	PVC/Al	≤1970	paved	Interior	interior	3-4th	3-5th
24	PVC/Al	≤1970	paved	Playground	street	2nd	1st-2nd
25	wood	>1970	sand-filled	Playground	interior	2nd	ground
26	wood	>1970	paved	Interior	street	3-4th	ground
27	wood	≤1970	paved	directly street	street	3-4th	ground
28	PVC/Al	>1970	sand-filled	directly street	street	2nd	ground
29	PVC/Al	≤1970	paved	Playground	street	2nd	ground
30	wood	>1970	sand-filled	Playground	street	0-1st	ground
31	wood	≤1970	paved	Interior	interior	0-1st	ground
32	wood	>1970	sand-filled	Playground	street	2nd	ground
33	wood	>1970	paved	directly street	interior	0-1st	ground
34	wood	≤1970	paved	directly street	street	2nd	3-5th
35	PVC/Al	>1970	paved	Interior	street	3-4th	3-5th
36	PVC/Al	≤1970	sand-filled	Interior	interior	2nd	ground
37	PVC/Al	>1970	paved	Playground	street	3-4th	ground
38	PVC/Al	>1970	sand-filled	Playground	street	0-1st	1st-2nd
39	PVC/Al	>1970	sand-filled	Interior	interior	0-1st	ground
40	PVC/Al	≤1970	sand-filled	Playground	interior	2nd	ground

[1] *Interior:* classroom windows face to an interior patio, totally surrounded by buildings. *Playground:* classroom windows face a playground which is next to the street. *Directly street:* classroom windows face directly to the street.

[2] *Interior:* the playground is completely surrounded by buildings. *Street:* the playground is partially or totally opened to street.

2.1.2. Reference monitoring station

An urban background reference monitoring station (UB-PR) monitored the same pollutants during all the BREATHE sampling periods, although different instrumentation was used. This station is located in the garden of the IDAEA-CSIC building (41º23'14" N, 02º06'56"E, 78 m.a.s.l.; Figure 2.2) and it is exposed to road traffic emissions from the Diagonal Avenue (approximately 200 m distance), one of the largest avenue in the city. The data collected in the reference station allowed to the seasonal adjustment of the pollutants concentration observed in each school (see Section 2.4.1.), but also to compare levels of pollutants with those representative of the UB of Barcelona.

2.1.3. Personal monitoring

Besides the sampling campaigns at schools, 53 children from 7-10 years old were involved in personal measurements of BC concentrations during 48h each. Sampling was carried out only during weekdays and it took place from 19 March 2012 to 22 February 2013. The children were monitored at the same time that we were sampling at the school they were attending to. The 45 children finally included in the study (with at least 24h of valid data) were attending 25 of the 39 BREATHE schools.

Figure 2.4. Child carrying the belt bag with the MicroAeth AE51. The inlet tube was placed close to the breathing zone.

Children carried the instrument (MicroAeth AE51) in a belt bag with the inlet tube always exposed and placed in the breathing area (Figure 2.4). To minimise annoyance from carrying the instrumentation, children were allowed to leave the device on the table while they were seating in the classrooms; and to leave it on the night stand and charge the batteries during sleeping time.

Besides carrying the instrument, the children were taught to fill in a time-activity diary reporting every time the changed their location, so the microenvironments (ME) where children spent their time were known.

2.2. INSTRUMENTATION

The same instruments were used in all the sampling sites in schools but they differ from the equipment used in the reference station of Palau Reial. These are all listed and described below.

2.2.1. Instrumentation at schools

MicroAeth® (Model AE51)

The MicroAeth AE51 (Figure 2.5.) was used to determine real-time mass concentration of BC. The same instrument was used for personal measurements The instrument draws an air sample at a flow rate between 50 and 150 mL min^{-1} (in this work, it operated at 100 mL min^{-1}) through a 3 mm diameter portion of filter media. As the airflow is drawn through the filter media, the particle sample is collected gradually on the filter medium to create a grey spot of 3 mm of diameter. Optical transmission by a stabilized 880 nm LED light source through this spot is measured by a photodiode detector. The absorbance (light attenuation) of this spot is measured relative to an adjacent portion of the filter (which is the reference) once per timebase period (in our case, 5 minutes). The gradual accumulation of optically-absorbing particles leads to a gradual increase in the attenuation from one period to the next one. The electronics and microprocessor measure and store the data

Figure 2.5. An image of MicroAeth AE51 for BC measurements. Source: (AethLabs, 2011)

each period to determine the increment during each timebase. This is then converted to mass concentration of BC expressed in ng m^{-3} using the already known optical absorbance per unit mass of BC material. After the optical density reaches a certain level, the filter strip (named Ticket Filter) must be replaced to maintain reliable measures (AethLabs, 2011).

DiSCmini (Diffusion Size Classifier Miniature)

The miniature diffusion size classifier (DiSCmini, Figure 2.6) is an instrument for UFP measurement. It gives information about the UFP number concentration, the mean particle size and the LDSA of particles in the size range of 10-700 nm.

Gravimetric and optic methods are rather insensitive for UFP but nanoparticles can easily be charged. Even though DiSCmini is less accurate than traditional aerosol instruments such as CPC (condensation particle counter; from TSI Inc.), it is smaller and easier to carry which are important facts to take into account when the sampling requires to move the instrumentation frequently.

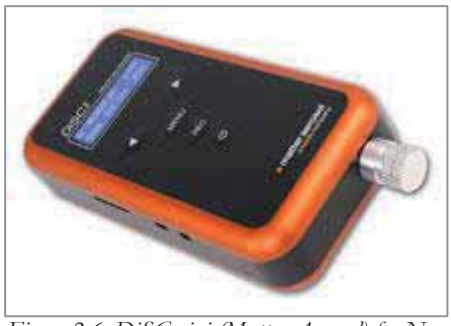

Figure 2.6. DiSCmini (Matter Aerosol) for N, size and LDSA measurements.

This instrument is based on unipolar charging of the particle, followed by detection in two electrometer stages. The theory of operation has been detailed in Fierz et al. (2011). Briefly, firstly the particle is charged in a standard positive unipolar diffusion charger, which provides an average charge on the particles that is approximately proportional to the particle diameter. After charging, excess ions are removed in an ion trap. The charged particles then flow through what is named diffusion stage, which is an electrically insulated stack of stainless steel screens connected to a sensitive electrometer. Some of the particles are captured in this stage and they generate a current ($I_{diffusion}$), while the remaining particles get into a second stage that is equipped with a HEPA filter. Here, all particles are captured, and a current (I_{filter}) is measured with an electrometer. The ratio $R = I_{diffusion}/ I_{filter}$ is a measure of the average particle size, because smaller particles are more likely to be capture in the diffusion stage. The exact relation between R and the particle size is calculated during the instrument calibration. The particle number can be calculated once we know the charge and the size (the diameter). Figure 2.7 is a schematic overview of the theory of operation of DiSCmini.

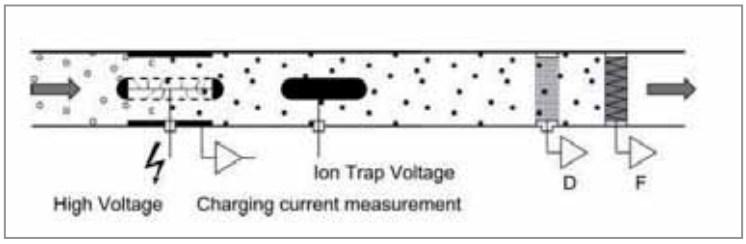

Figure 2.7. Schematic overview of the DiSCmini theory of operation. D = diffusion stage, F = filter stage. Source: (Fierz et al., 2011).

High-Volume sampler for $PM_{2.5}$ gravimetric samples

Filter $PM_{2.5}$ samples were collected using a MCV CAV-A/mb (MCV S.A; Collbató, Barcelona; Figure 2.8) and a PM1025/UNE inlet (fabricated under European normative, EN12341) used with a specific nozzle plate for $PM_{2.5}$.

It operates with a pump that works with an air flow of 30 m^3 h^{-1} that passes through an inlet with a size-selective plate for $PM_{2.5}$. These particles are retained in a high purity quartz fibre Pallflex filter (Ø150mm), which permits obtaining the gravimetric mass concentration and a complete chemical characterisation of $PM_{2.5}$ (detailed in Section 2.3). All the sampled filters were weighted before and after sampling in order to determine the gravimetric mass concentration of $PM_{2.5}$. This value was afterwards corrected with the chemical results.

Figure 2.8. MCV High-volume sampler with a $PM_{2.5}$ inlet.

One filter per day was sampled from 9h until 17h (local hour). A total of 553 8 h-daily samples were collected during the sampling campaigns (during SC1: 140 indoors, 136 outdoors; during SC2: 143 indoors, 134 outdoors).

Gradko NO_2 Diffusion tubes

The diffusion tubes for NO_2 determination are commercialised by Gradko Environmental (Figure 2.9). They are acrylic tubes fitted with grey and white thermoplastic rubber caps. The grey cap contains the absorbent, which for NO_2 determination is Triethanolamine (TEA), based in the molecular diffusion principle from where there is more concentration to the less concentrated part. Afterwards, in Gradko laboratories, the concentrations of nitrite ions and hence NO_2 chemically adsorbed are quantitatively determined by U.V./Visibe Spectrophotometry with

reference to a calibration curve derived from the analysis of standard nitrite solutions (U.K.A.S. Accredited Methods).

Figure 2.9. A Gradkno diffusion tube in one of the schools.

A dosimeter per school site, both indoor and outdoor sites, was exposed from Monday morning (approximately 8AM local hour) until Friday morning (approximately 8 AM). Simultaneously, a dosimeter was also exposed in Palau Reial reference station for the seasonal adjustment analysis (see Section 2.4.1).

In some selected schools, two passive dosimeters were put side-by-side for quality control of the collected data.

2.2.2. Instrumentation at the reference station

GRIMM model 180

On-line PM_{10}, $PM_{2.5}$, PM_1 levels were continuously monitored by a PM optical counter Grimm Labortechnik GmbH & Co. KG rack mounted environmental dust monitor model 180 (Figure 2.10).

It performs particulate size measurements by 90 degree laser light scattering. The air passes through a flat laser beam produced by a laser diode. As there is no heater at the inlet, even aerosol and semi volatile liquid particles can be identified. Every count from each precisely sized pulse channel is then converted to mass units using a particle density-based equation and the data is then converted to PM_{10}, $PM_{2.5}$ and PM_1 (among others, as it has 15 channels). It has been designed for continuous, unattended automatic operation inside a shelter or container. The main advantage of this version is the possibility to reduce maintenance to only an annual visit while assuring very long and unattended operation.

Figure 2.10. GRIMM monitor (model 180).

High time resolution data of PM_1, $PM_{2.5}$ and PM_{10} 24h/day during all the campaign period was obtained. This data will be used for the seasonal adjustment (Section 2.4.1) of the $PM_{2.5}$ concentrations obtained gravimetrically at school stations.

High-Volume samplers (DIGITEL)

$PM_{2.5}$ gravimetric samples were collected using a high volume sampler (DIGITEL) with the corresponding inlet and the specific nozzle plate for $PM_{2.5}$.

One 24h filter every fourth day was obtained. $PM_{2.5}$ mass concentrations on the filters were determined by standard gravimetric procedures with an uncertainty of 1.5 $\mu g \cdot m^{-3}$ (M. Viana et al., 2006a). The gravimetric data were used to correct the PM measurements obtained with the GRIMM optical counter, following the specifications of the "Guide for Member States for PM_{10} monitoring and inter-comparison with the reference method" (EC Working Group, 2002).

Multiangle Absorption Photometer (MAAP)

BC mass concentrations were continuously monitored by a multi-angle absorption photometer (MAAP, Thermo ESM Andersen Instruments; Fig 2.11) with a PM_{10} inlet operating on a 1-min time resolution.

Figure 2.11. MultiAngle Absorption Photometer (MAAP) for BC measurements.

The MAAP is based in the principle of light attenuation by absorption, scattering and reflection of particles accumulated on a moving filter tape. The instrument measures absorbance (m^{-1}) from particles deposited in the filter using measurements of transmittance and reflectance at different angles. The absorbance is converted to mass concentration of BC ($g \cdot m^{-3}$). The values given by MAAP were corrected by in-situ determination of EC from 24h gravimetric samples by means of the Thermo Optical Transmittance technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC analyser. Reche et al. (2011a) determined the Absorption/EC factor to be 9.2.

The MAAP obtained information on BC mass concentrations 24h/day during all the campaign period operating on a 1-min time resolution. This data will be used for the seasonal adjustment (see Section 2.4.1) of the BC data obtained with MicroAeth AE51 in schools as well as of the traffic source of $PM_{2.5}$ from the source apportionment analysis.

Water-based Condensation Particle Counter (WCPC MODEL 3785)

The Water-based Condensation Particle Counter (WCPC; MODEL 3785; from TSI Inc.; Figure 2.12) gives information about the number of UFP in the size range between 5 and 1000 nm.

Figure 2.12. Water-based condensation particle counter (WCPC). Source: (TSI Inc.)

The WCPC has a laser and optical detector for particles detection. The instrument is based on a condensation technique that deposits a working fluid on the particles to grow or "amplify" their size to a value that can be detected easily with a conventional optical system. The aerosol enters the sample inlet and immediately passes to a region surrounded with wetted media. This results in a supersaturated condition along the radius of the flow stream. Particles in the flow stream act as nuclei for condensation. Water condenses on the particles as they pass up the growth tube and the enlarged particles are then detected by the optical detector.

Five-minute time resolution of ultrafine particles number data was obtained by the WCPC 24h/day during all the school sampling campaign.

Nanoparticle Surface Area Monitor (NSAM MODEL 3550)

The measurements of LDSA parameter were taken as the diffusion charger response of atmospheric particles, measured by means of a Nanoparticle Surface Area Monitor (NSAM MODEL 3550; from TSI Inc.; Figure 2.13).

Figure 2.13. Nanoparticle Surface Area Monitor (NSAM) for measurements of LDSA.

This instrument uses a corona discharge to produce positively charged ions and mixes these ions with particles in a opposed flow mixing chamber. An ion trap is located downstream of this chamber. The particles are deposited on a HEPA filter inside a Faraday cup and the current, induced by the deposited particles, is measured with an electrometer. Between the mixing chamber and particle filter, all excess ions are removed in the ion trap by means of an electric field. Due to the high electric mobility of ions, the voltage can be relatively low. Even though the electric field strength within the ion trap is very low, some charged particles near the electrode of opposite polarity are also removed. Since in the human respiratory tract some particles also get lost before they reach the lung, the ion trap voltage can be adjusted so that the particle

losses in the ion trap match those in certain areas of the human inhalation system. It is found that the response function of NSAM matches the surface area deposited in the tracheobronchial region with an ion trap voltage of 100V, whereas the response function simulates the deposition in the alveolar region with an ion trap voltage of 200V.

Five-minute time resolution data of LDSA parameter (with the settings configured to simulate the deposition in the alveolar region) was collected during the whole sampling period.

2.2.3. Instrumental intercomparison

In order to assure a data compatibility between all monitoring stations, all the instruments employed were inter-compared during a minimum of 48h prior and after each sampling campaign among themselves and the corresponding instrument on the reference station. With the results of these intercomparison exercises, the correct operation of all the devices was checked and, if needed, correction factors were obtained to adjust the measurements of each one.

MicroAeth AE51 intercomparison:

Seven MicroAeth AE51 devices and the MAAP from the reference station were intercompared. The MicroAeths were labelled from BC1 to BC7. At schools, the instruments BC1 to BC4 were used if no substitution of the corresponding device was needed due to bad operation. For personal measurements, BC6 and BC7 were employed.

The coefficient of determination (R^2) from the correlation of BC data among the different MicroAeth employed at schools (BC1-BC5; using the device labelled as BC1 as the reference) were always above 0.95 and the slopes were in the range of 0.9-1.0. The comparison with the MAAP from the reference station showed R^2 generally above 0.80. In the view of the fact that the results among the different MicroAeth employed at schools was very similar, any correction was applied.

However, one of the MicroAeth devices used for personal measurements (BC6) showed considerable differences and the data was corrected to level the concentration to what was measured by the reference MicroAeth (BC1). For the first sampling campaign similar correction factors were found prior and after the sampling. However, during the second campaign, the correction factors prior and after the sampling differ

considerable and a gradual correction factor was applied (the correction factors are presented in Table S1 in Section 3.4). Prior to the second campaign measurements (BC7 was not used during the first one), the correlation between instrument BC1 and BC7 showed a R^2 of 0.93 and the slope was 0.95, so no corrections were applied. No comparison after the second campaign could be done for BC7, since its pump failed during the sampling of the last child and should be sent for servicing.

Besides the intercomparison exercise, in-situ measurements at the schools of EC filter concentrations and BC data obtained with the MicroAeths were correlated. The R^2 was 0.88 and the BC data was then converted to equivalent black carbon (EBC) according to the following equation: $EC = 0.5436 \cdot BC_{AE51}$.

DiSCmini intercomparisons:

Five DiSCmini devices and one 3875 WCPC were intercompared prior and after each sampling campaign. The WCPC measures total particles from 5 to 1000 nm, which differs to the size range measured by DiSCmini (10-700 nm). Therefore, since these devices are not measuring the same parameter, a direct comparison could not be done. Moreover, this is important to bear in mind when looking at UFP at schools and at the reference station of UB-PR. In order to quantify differences in measurements, different intercomparison exercises were conducted (pre and post each campaign), comparing the reference DiSCmini (MD1) and the WCPC. The mean slopes of the linear regression were UFP[DiSCmini]=1.62 · UFP [CPC] for the SC1 (R^2= 0.57) and UFP[DiSCmini] =1.40 · UFP[CPC] for the SC2 (R^2 = 0.69). This difference has to be taken into account when comparing schools and UB-PR levels of UFP.

The R^2 from the correlation of UFP number concentration data among the different DiSCmini employed at schools (using the device labelled as MD1 as the reference) were always above 0.90 and the slopes were generally in the range of 0.9-1.10, although in specific cases it descended to 0.73 and went up to 1.15. Therefore, since the difference among the DiSCmini could be over 20%, all the UFP number concentration data was corrected by a correction factor to level the concentration to the measured by the reference device MD1.

2.3. CHEMICAL ANALYSIS OF $PM_{2.5}$

Once the gravimetric determination of the $PM_{2.5}$ mass concentration was performed, a complete chemical characterisation of the $PM_{2.5}$ sampled in the filters was carried out, following the methodology described by Querol et al. (2001a) with a relative analytical error between 3 and 10% for the elements studied (M. Viana et al., 2006b). All the sampled filters collected during the BREATHE campaigns were chemically analysed. The characterisation of the different elements and components of PM allows the identification of the main emission sources contributing to PM concentrations in the monitoring sites.

Blank and sample conditioning and weighting

$PM_{2.5}$ sampling in filter media was carried out by means of MCV High-Volume samplers using Pallflex quartz micro fibre filters (150 mm diameter).

The filters were firstly heated at 200ºC during a minimum of four hours to eliminate the volatile compounds. Then, they were kept during 3 days in a desiccator for humidity control (25% humidity and 20ºC), being weighted every day. After this process, they were preserved individually in aluminium foil until they were used for sampling. From every fifteen filters, three of them were stored to be used as blanks for the subsequent chemicals analysis.

After sampling, the filter was also preserved in aluminium foil until their conditioning at the above controlled temperature and humidity again in the desiccator during 3 days. The filters were weight again during these three consecutive days. Mean mass concentration was then calculate by weigh difference and by the known volume of air sampled.

Major and trace elements

The complete chemical analysis of the filters used for the mass concentrations determination was obtained following the procedures proposed by Querol et al. (2001a).

From every sample, a quarter was used for acidic digestion to supply solutions for chemical analysis. It consists in a complete dissolution of the sample (even the quartz filter is dissolved) by means of an acid digestion using a mix of HF:HNO_3:$HClO_4$ (5:2.5:2.5 ml) and then kept at 90ºC in a Teflon reactor during 6h driven to dryness. The dry residual is re-dissolved with 2.5 ml HNO_3 to make up a volume of 50 ml with water and to be analysed using Inductively Coupled Plasma Atomic Emission

Spectrometry for the determination of the major elements (ICP-AES: IRIS Advantage TJA Solutions, Thermo) and Mass Spectrometry for the trace elements (ICP-MS: X Series II, Thermo). Bulk levels of major elements (such as Al, Ca, K, Fe, P, Na, Mg, Ti) and trace elements (Sn, Sb, Tl, Cd, Bi, V, Mn, Pb, Sr, Ba, Zn, Cu, Cr, As, P, Ni, Co, La, Ce, Sc, Rb, Zr, Hf, Y, W, Ta, U, Th, among others) were determined in the solution.

To assure the quality of the analytical procedure, a small amount (10 mg) of the Standard Reference Material ® 1633b Coal Fly Ash loaded on a 1/4 quartz micro-fibre filter was also analysed within each acid digestion. The reference material analysis assures the quality of the results permitting the identification of possible analytical or calibration errors.

Water-soluble ion

A quarter of each filter was leached in 30 ml of bidistilled water (Mili-Q) for the extraction of water-soluble ions and subsequent analysis by the following analytical tools:

- ion chromatography (ICHPLC) for SO_4^{2-}, NO_3^- and Cl^-.

- specific electrode for NH_4^+.

Organic and elemental carbon

A section of 1.5 cm^2 was used for OC and EC determination by a thermal-optical transmission technique using a Sunset Laboratory OCEC Analyser with the NIOSH temperature program (Birch and Cary, 1996).

In all cases (major/trace elements, water-soluble ions and OC/EC), laboratory blank concentrations were subtracted in order to consider any impurity or contamination in the filters, before the determinations of final concentrations in ambient air.

Indirect determinations

With the analytical techniques described above it was possible to determine directly up to 45 components in the PM sampled in the filter. Besides, the concentrations of 4 additional components were indirectly determined by means of empirically obtained factors:

(1) $SiO_2 = 3 \cdot Al_2O_3$ and $CO_3^{2-} = 1.5 \cdot Ca$ (Dulac et al., 1992; Molinaroli et al., 1993; Querol et al., 2001a).

(2) The non-mineral carbonaceous compounds were expressed as the sum of organic matter and elemental carbon (OM+EC). The concentration of OM was calculated from the levels of OC multiplied by a factor with the intention of adding the heteroatoms of the organic matter (H, N, O) not analysed with this method. This factor was estimated by various authors to be between 1.2 and 2.1, being higher for remote sites and lower for urban sites with higher traffic density (Putaud et al., 2000; Russell, 2003; Turpin and Lim, 2001). We applied here a factor of 1.6 for both Barcelona and Sant Cugat del Vallès.

$PM_{2.5}$ mass closure

After all the chemical analyses were performed, the components of PM were classified in the following groups:

(1) Crustal or mineral matter: corresponding to the sum of elements which are typically found in rock-forming minerals. Includes Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P.

(2) Sea spray aerosol: the sum of Na^+ and Cl^-.

(3) Carbonaceous compounds: the sum of OC and EC concentrations.

(4) SIA: the sum of SO_4^{2-}, NO_3^- and NH_4^+.

(5) Sum of trace elements.

Approximately 85% of the $PM_{2.5}$ mass was accounted from the addition of the above direct and indirect determinations. The remaining undetermined mass (15%) is attributed to formation, crystallization and moisture water (Querol et al., 2001a) that could not be removed during the sample conditioning.

2.4. DATA PROCESSING

2.4.1. Seasonal adjustment

The seasonal adjustment is necessary to harmonise the daily air pollution variation over time. The variability of air pollution concentrations among different days and season needs to be reduced in order to permit the direct comparison among the different schools (which were monitored in different time periods with different emission and meteorological conditions). This procedure, usually called (back-)extrapolation in time,

is sometimes used in epidemiological studies when past values of pollutant levels is required in order to calculate the exposition of a determined study population usually using Land-Use Regression (Chen et al., 2010; Gehring et al., 2011; Mölter et al., 2010) .

To this end, a ratio method to all pollutants has been applied. In order to apply this method, the reference station data has to cover all the period time and have at least 75% of valid data during this period for every pollutant. The procedure to achieve the seasonal adjustment is summarized in the next steps:

(1) Calculate the average concentration ($\overline{C_i^{PR}}$) for the reference monitoring station (*PR* in this case) covering all the days (k) of the measurement period (SC1 and SC2) for every pollutant *i* (Equation 2.1):

$$\overline{C_i^{PR}} = \frac{\sum_{k=1}^{n}(C_i^{PR})_k}{n} \quad (2.1)$$

(2) Calculate the ratio $(R_i^{PR})_k$ at *PR* per each day *k* of the measurement period for every pollutant *i* according to the following equation (Equation 2.2):

$$(R_i^{PR})_k = \frac{(C_i^{PR})_k}{\overline{C_i^{PR}}} \quad (2.2)$$

(3) Calculate for every day, the final harmonised concentration $(C_i^j)_k^*$ for every pollutant *i* in each of the stations in schools *j* for that day *k* (Equation 2.3):

$$(C_i^j)_k^* = \frac{(C_i^j)_k}{(R_i^{PR})_k} \quad (2.3)$$

2.4.2. Positive Matrix Factorisation (PMF) for source apportionment

Having the knowledge of the amount of source contribution to atmospheric PM is an important task for establishing eventual mitigation or preventive measures. Receptor modelling techniques are tools used to identify and quantify the contributions from the different emission sources to major and trace components levels of ambient particulate

matter. They are based on the mass conservation principle and PM data is described as a function of source profiles and source contributions as in the Equation 2.4:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{ik} \qquad (2.4)$$

i=1,2,…,m j=1,2,…,n

where x_{ij} is the i^{th} concentration of the species j, g_{ik} is the i^{th} contribution of the source k and f_{jk} is the concentration of the species j in source k. Equation 2.4 can be also expressed in matrix form as:

$$X=GF+E \qquad (2.5)$$

where X is the concentration matrix (measured ambient concentrations), G is the source contribution matrix, F is the source profile matrix (elemental abundances in source emissions) and E is the portion of measured elemental concentration that cannot be fit by the model (Hopke et al., 2006, 2003). Different receptor models are available. The difference lies in the knowledge about pollution sources required, the model computation requirements and the final results obtained (Bruinen de Bruin et al., 2006; Schauer et al., 2006). The most widespread models are Principal Component Analysis (PCA, Thurston and Spengler, 1985), Positive Matrix Factorization (PMF, Paatero and Tapper, 1994) and Chemical Mass Balance (CMB, US-EPA, 1987). The main differences among them are that CMB requires a detailed quantitative knowledge on the emission sources chemical profiles (which might be very difficult to obtain) while for PCA and PMF qualitative knowledge is enough. PCA requires only speciation data while PMF also requires uncertainty data.

Accordingly, the question is what information is available to solve Equation 2.4. Based on the premise that the concentrations of a series of chemical species have been measured for a set of PM samples, the x_{ij} values are always known. If the sources that contribute to those samples can be identified and their compositional patterns measured, then only the contributions of the sources to each sample need to be determined. These calculations are generally made using the effective variance least squares approach incorporated into the EPA's CMB model. However, for many locations, the sources are either unknown or the compositions of the local particulate emissions have not been measured. Thus, it is desirable to estimate the number and compositions of the sources as well as their contributions to the measured PM. The multivariate data analysis methods that are used to solve this problem are generally referred to as factor analysis (FA). The purpose of FA is to determine the true

dimensionality of the data and the relationships among the measured variables. The pioneers on incorporating this analysis in aerosol mass apportionment used VARIMAX rotated PCA in order to determine both sources of particulate mass and also their contributions (Henry and Hidy, 1979; Thurston and Spengler, 1985).

The above mentioned FA techniques are based on the Singular Values Decomposition, selecting the eigenvectors which explain the greater part of the variance in the data. With this procedure the factors that minimise the Eucledian length of the residuals of the Equation 2.4 are obtained (Ordinary Least Squares solution). Although in FA the columns of the data matrix are scaled in order to give similar importance to all the variables, this scaling is not optimum because some species can be determined more precisely than others. For this reason, Paatero and Tapper (1993) suggested the use of a Weighted Least Squares scheme with the aim of obtaining a minimum variance solution for Equation 2.4. In particular, they demonstrated that the optimum scaling of the data matrix is achieved when each individual datum is weighted by the corresponding error estimate. However, this weighting causes that the problem cannot be solved by eigenanalysis at all, being necessary to minimize numerically the object function:

$$Q = \sum_{i=1}^{m}\sum_{j=1}^{n}\frac{(x - \sum_{k=1}^{p} g_{ik}f_{ik})^2}{\sigma_{ij}^2} \qquad (2.6)$$

where σ_{ij} is the uncertainty estimate for the species *j* measured at time *i*.

Additionally they proposed to incorporate the basic physical constraint of non-negativity of g_{ik} and f_{jk}, calling their approach Positive Matrix Factorization (Paatero and Tapper, 1994), which can be performed by the program PMF2 released by Paatero (1997). PMF2 is a model which implements a weighted least squares approach to perform positive matrix factorisation of measured data. PMF2 solves the 2-way bilinear model, while a second program, PMF3, has also been developed for the solution of 3-way trilinear models. The programs provide a number of options to control the solutions process which are specific to factor analysis.

However, PMF can also be solved with the Multilinear Engine (ME-2), which is a more recent technique developed by Paatero (1999) for fitting multilinear and quasi-multilinear mathematical expressions or models to two-, three- and many-dimensional data. The main differences of this program are described in Paatero (1999) and briefly listed below:

- The actions of ME-2 are defined in a "script file" written in a special-purpose programming language, allowing incorporating additional tasks such as data processing, etc.
- In ME-2 *a priori* information (e.g. linear constraints) can be included as auxiliary terms of the object function to be minimized. Thus the *a priori* information is incorporated as a target to be approximately accomplished.
- The Gauss Newton scheme is solved in the ME-2 by the Conjugate Gradient algorithm (Hestenes and Stiefel, 1952), taking advantage of the sparse structure of the Jacobian matrix of the multilinear model.
- The non-negativity of g_{jk} and f_{jk} is achieved in ME-2 by inversely preconditioning of the Conjugate Gradient, while in PMF2 logarithmic penalty functions are used (Paatero, 1997).

The abovementioned features of ME-2 make it especially suitable for source apportionment studies where some a priori knowledge (chemical ratios, profiles, mass conservation etc.) of involved sources is available. One of the innovative features of ME-2 (with respect to conventional PMF) is that missing data can be easily handled without influencing heavily on the results of the source apportionment. Other programs such as PMF2 or EPA PMF v3.0 do not accept "empty cells", so only three alternatives are possible: exclude the whole sample, exclude the whole species, or replace by median of the species. Therefore ME-2 does not create the equations for the empty cells, permitting to include species that have not been analysed for the whole period in the analysis.

Briefly, in ME-2 a priori information must be handled in form of equations, termed by Paatero (1999) as auxiliary equations. As indicated, auxiliary equations are included as additional terms Qaux in an enhanced object function Q_{enh}

$$Q_{enh} = Q + Q_{aux} \tag{2.7}$$

One of the simplest forms of auxiliary equation is the "pulling equation?" (Paatero and Hopke. 2009), consisting in pulling a f_{jk} (for instance) toward the specific target value a:

$$Q_{aux} = \frac{(f_{jk} - a)^2}{\sigma_{aux}^2} \tag{2.8}$$

being σ_{aux} the uncertainty connected to the pulling equation, which expresses the confidence of the user on this equation.

CHAPTER 3

Results

3. RESULTS

3.1. Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain

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Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain

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ABSTRACT

Proximity to road traffic involves higher health risks because of atmospheric pollutants. In addition to outdoor air, indoor air quality contributes to overall exposure. In the framework of the BREATHE study, indoor and outdoor air pollution was assessed in 39 schools in Barcelona. The study quantifies indoor and outdoor air quality during school hours of the BREATHE schools. High levels of fine particles ($PM_{2.5}$), nitrogen dioxide (NO_2), equivalent black carbon (EBC), ultrafine particle (UFP) number concentration and road traffic related trace metals were detected in school playgrounds and indoor environments. $PM_{2.5}$ almost doubled (factor of 1.7) the usual urban background (UB) levels reported for Barcelona owing to high school-sourced $PM_{2.5}$ contributions: [1] an indoor-generated source characterised mainly by organic carbon (OC) from organic textile fibres, cooking and other organic emissions, and by calcium and strontium (chalk dust) and; [2] mineral elements from sand-filled playgrounds, detected both indoors and outdoors. The levels of mineral elements are unusually high in $PM_{2.5}$ because of the breakdown of mineral particles during playground activities. Moreover, anthropogenic PM components (such as OC and arsenic) are dry/wet deposited in this mineral matter. Therefore, $PM_{2.5}$ cannot be considered a good tracer of traffic emissions in schools despite being influenced by them. On the other hand, outdoor NO_2, EBC, UFP, and antimony appear to be good indicators of traffic emissions. The concentrations of NO_2 are 1.2 times higher at schools than UB, suggesting the proximity of some schools to road traffic. Indoor levels of these traffic-sourced pollutants are very similar to those detected outdoors, indicating easy penetration of atmospheric pollutants. Spatial variation shows higher levels of EBC, NO_2, UFP and, partially, $PM_{2.5}$ in schools in the centre than in the outskirts of Barcelona, highlighting the influence of traffic emissions. Mean child exposure to pollutants in schools in Barcelona attains intermediate levels between UB and traffic stations.

1. Introduction

Some of the health effects of exposure to air pollution, such as the impact on the respiratory and cardiovascular systems, have been extensively studied. Although it is well-known that exposure to air pollutants leads to an increase in mortality and morbidity rates of the population (e.g. Baccarelli et al., 2008; Künzli et al., 2000, 2004; Pope et al., 2002; WHO, 2005), few studies have focused on the role of air pollution on brain development. Evidence obtained from experimental studies in animals suggests that outdoor air pollution may play a major role in the inflammation of the central nervous system during sensitive periods (such as childhood) and consequently in behaviour and school performance (Block et al., 2012). A growing body of research, albeit limited, from epidemiological studies indicates that exposure to air pollution may be associated with an increased risk of neurodevelopmental disorders and cognitive impairments (Guxens and Sunyer, 2012).

Many epidemiological studies relate $PM_{2.5}$ (particles with and aerodynamic diameter <2.5 μm) to negative health outcomes (Dockery et al., 1993; Jerrett et al., 2005; Krewski et al., 2009; Laden et al., 2006; Lepeule et al., 2012; Pope et al., 2002). However, owing to the small size of ultrafine particles (UFP, particles <100 nm) that can translocate

Abbreviations: UB, urban background; UB-PR, urban background reference station of Palau Reial in Barcelona; SC, sampling campaign; UFP, ultrafine particles; LDSA, lung-deposited surface area; EC, elemental carbon; BC, black carbon; EBC, equivalent black carbon; OC, organic carbon; OM, organic matter.

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from the lung to the blood circulatory system or be taken up directly into the brain through the olfactory epithelium (Chen et al., 2006; Nemmar, 2002; Oberdörster et al., 2004), UFP arise as a potential $PM_{2.5}$ constituent to have large health effects (Knol et al., 2009) even though the evidence is still limited (Rückerl et al., 2011). The negative health effects of the proximity to road traffic might be more related to the exposure to UFP, black carbon (BC) and total PM counts since Zhu et al. (2002) found that they decreased rapidly in the first 150 m away from the traffic line and then levelled off, whereas $PM_{2.5}$ was found to be elevated only moderately.

Mediterranean cities are characterised by high densities of population and motor vehicles: there are about 5800 cars·km^{-2} in Barcelona and about 4500 cars·km^{-2} in Turin and Naples whereas these densities fall to 1000–1500 cars·km^{-2} in northern and central European cities such as Budapest, Amsterdam or Berlin (Ajuntament de Barcelona, 2013). Hence, people living in more densely populated cities are closer to traffic and are more exposed to vehicle exhaust and non-exhaust emissions. In fact, recent studies have shown that cities in southern Europe have higher levels of $PM_{2.5-10}$ than those in northern and central Europe owing to the high vehicle density and drier weather (Eeftens et al., 2012; Querol et al., 2004a). The contribution from road dust (non-exhaust emissions from pavement, tyre and brake wear and re-suspension of the material deposited on the road) to PM levels is also higher in Mediterranean cities (Pant and Harrison, 2013). Some vehicle wear abrasion particles have a mode below $PM_{2.5}$ and another mode above this diameter that would only be present in $PM_{2.5-10}$; e.g. the mass modes of Fe, Cu, Ba and Sb are between 1.2 and 7.2 μm aerodynamic diameter (Gietl et al., 2010); a bimodal structure for Sb has been determined with a mode at 3.6–5.2 μm from brake wear and tear (Ijima et al., 2009).

There is increasing evidence that indoor air quality exposure is also responsible for a rise in mortality and morbidity (Sundell, 2004). However, little is known about air quality in indoor environments, where children spend most of the day (approximately 90%; Buonanno et al., 2012; US-EPA, 2008). Moreover, children constitute a particularly vulnerable population because of their physiological and behavioural characteristics. They have higher ventilation rates and higher levels of physical activity (Trasande and Thurston, 2005) with the result that they are more exposed to air pollutants than adults. Children spend a large part of their time at school both indoors and outdoors. In Spain, the school year lasts about 180 days and an average of 25 h per week at primary level (INCA, 2013). Although the association between air pollution exposure at schools and the impact on health has been the subject of more than 70 epidemiological publications (see Mejía et al., 2011), neurodevelopment has, by contrast, been poorly documented. Newman et al. (2013) found an association between elemental carbon (EC) from traffic and higher hyperactivity scores in children. In a study of one school in a highly polluted area and in another school in an area of low pollution in Quanzhou, China, Wang et al. (2009) found that neuropsychological functions, such as attention, were impaired in the former school with respect to the latter. The mechanisms responsible for the initiation of neuroinflammation in response to air pollution are poorly understood and may be exposure-specific (Block et al., 2012).

At schools, indoor concentrations of particulate matter have been shown to be highly correlated with outdoor levels, suggesting that indoor particles are largely of outdoor origin (Raysoni et al., 2011). However, this indoor penetration of outdoor particles depends not only on the physical barriers of the building and ventilation (natural or mechanical), but also on particle physico-chemical properties (Viana et al., 2011) and size (Tippayawong et al., 2009; Zhu et al., 2002).

It may well be that epidemiological studies are considerably influenced by the methods employed for the collection of air quality data, such as the instrumentation used, the sampling location, the pollutants and parameters monitored and the sampling period (Mejía et al., 2011) since the methodology selected could result in over/under-estimation of exposure. Mejía et al. (2011) have also highlighted the importance of the spatial unit of analysis. In epidemiological studies the nearest air quality monitoring station is generally used to represent the air quality in schools (sometimes using raw data from the station and other times estimating levels at schools). However, measuring in-situ at schools yields more accurate information about the exposure although Buonanno et al. (2013), Janssen et al. (2001) and Salimi et al. (2013) have reported some spatial variation in the concentration of some air pollutants within the school. Therefore, personal exposure monitoring is the most accurate methodology to assess the exposure to air pollutants (Buonanno et al., 2012).

The BREATHE (BRain dEvelopment and Air polluTion ultrafine particles in scHool childrEn) ERC Advanced Grant project seeks to determine whether traffic-related air pollutants have an adverse effect on neuropsychological development, exacerbating cognitive and neurobehavioral disorders. The aim of the present study is to characterise indoor and outdoor air quality and its variability, especially the parameters that are most influenced by traffic emissions at the schools participating in the BREATHE study.

2. Materials and methods

2.1. Study area

The study was carried out in the city of Barcelona (Spain; 15,993 inhabitants·km^{-2}) and in the adjacent municipality of Sant Cugat del Vallès (1761 inhabitants·km^{-2}; IDESCAT, 2012; Fig. 1). Both cities are located in the NE of the Iberian Peninsula and have a Mediterranean climate. Barcelona has one of the highest vehicle densities in Europe (Ajuntament de Barcelona, 2012). The urban traffic fleet is characterised by a large number of cars (60.6%, of which, since 2003, more than 60% of the new car registrations are diesel; DGT, 2011); motorcycles (30.2%), heavy duty vehicles (2.9%). Furthermore, Barcelona is one of the most important ports in the Mediterranean, and receives the highest number of cruise ships in Spain. This constitutes an additional source of atmospheric pollutants that are very often transported across the city by the sea breeze during the day. Owing to the topography of the area, the transport and dispersion of atmospheric pollutants within Barcelona are largely controlled by fluctuating coastal winds which blow in from the sea during the day (diurnal breeze), and, to a lesser extent, by winds from the land at night (night breeze, Jorba et al., 2013). In the city centre, the predominance of narrow streets (street canyons) and a dearth of green areas hinder the dispersion of pollutants. Moreover, the city is not infrequently affected by North African air mass transport (NAF), which contributes significantly to mineral $PM_{2.5}$.

On the other hand, Sant Cugat lies in the Vallès Depression away from the coast and is bounded by the Littoral mountain range to the southeast and by the Pre-Littoral mountain range to the northwest. Although these ranges shield the city from coastal pollutant intrusions (Fig. 1), the Llobregat Valley offers an atmospheric corridor into the Vallès Depression for air pollutants carried from the urban and industrial zones that surround the river. Once in this Depression, the pollutants accumulate due to the poor dispersion conditions.

2.2. Monitoring sites: schools and reference urban background station

Two sampling campaigns were carried out in 36 schools in Barcelona and 3 in Sant Cugat, from 27 January until 22 June 2012 (SC1; sampling campaign 1) and from 14 September 2012 until 22 February 2013 (SC2; sampling campaign 2). Traffic intensity and typology of the fleet around the schools is shown in Table S1. The sampling was performed simultaneously indoors (in a classroom with pupils) and outdoors (in the playground) at two schools per week; of this pair of schools, one was located in an urban background (UB) area, whereas the other one was situated near traffic. Indoor devices were placed where possible next to the wall opposite the blackboard (to avoid direct exposure to chalk or board marker emissions) and away from the windows (to avoid direct

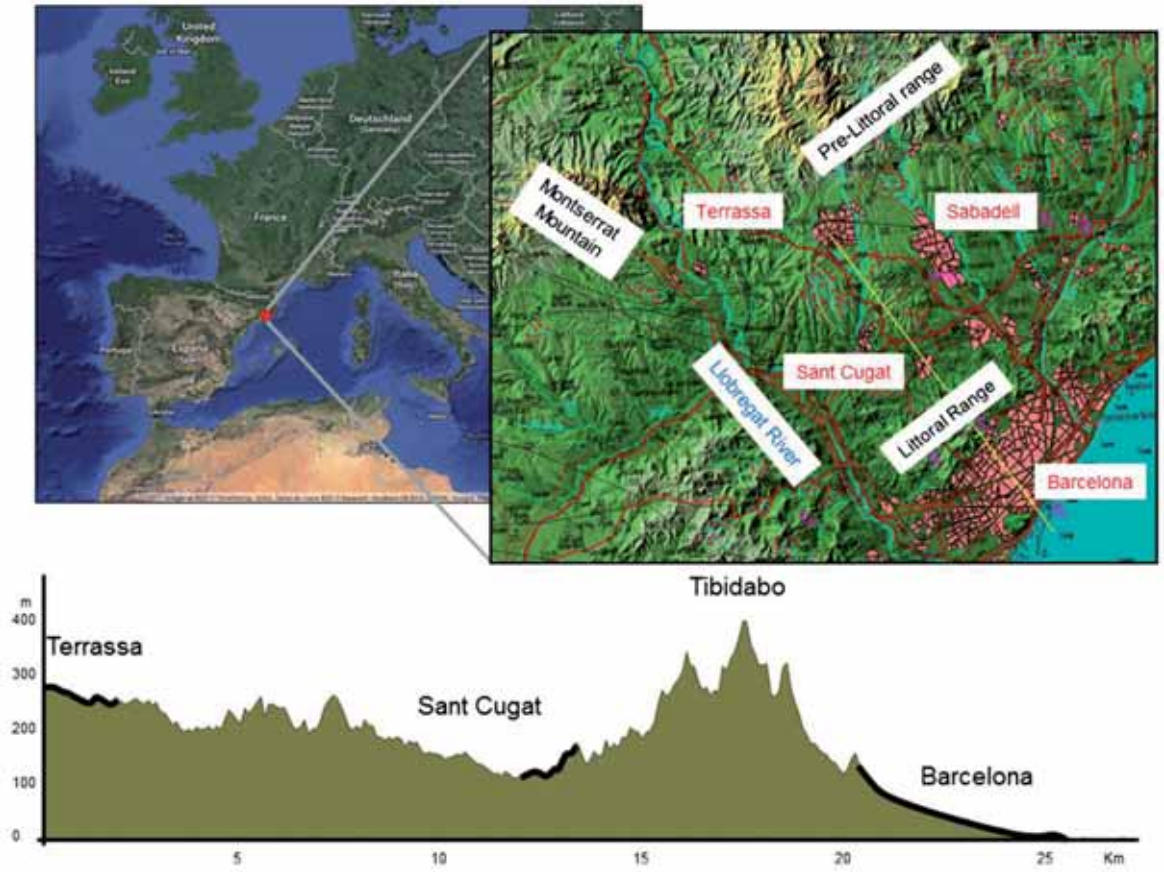

Fig. 1. Location and topographical profile of the study area. The black lines in the topographical profile indicate the location of the cities of Barcelona and Sant Cugat.

influence from outdoor levels and disturbances resulting from air currents). These conditions could not be met in all cases because of concerns for child safety. Air samples were collected at a height between 0.7 and 1.5 m above floor level, which is the height at which the pupils aged 7–9 would usually inhale.

Given that not all the schools were monitored simultaneously, data should be deseasonalised to remove temporal fluctuations when comparing the levels of pollutants between the schools. The data obtained at schools were deseasonalised with reference to the "Palau Reial" UB station (termed UB-PR), where the same pollutants were monitored throughout the sampling period. This station is located in the garden of the IDAEA-CSIC building (41°23′14" N, 02°06′56"E, 78 m.a.s.l) and even though it represents UB conditions, it is exposed to road traffic emissions from the Diagonal Avenue (200 m away), one of the largest thoroughfares in Barcelona (100,000 cars·day^{-1}).

2.3. Sampling and analysis

Air quality in the schools was monitored for four days (from Monday morning to Friday morning), with a minimum of three days. No data are available for Fridays since this was the day when the monitoring instruments were moved from one school to the other. $PM_{2.5}$ samples were obtained by means of a high volume sampler MCV CAV-A/mb (30 m^3·h^{-1}) with an inlet with a specific nozzle plate for $PM_{2.5}$ (MCV). $PM_{2.5}$ was collected on Pallflex quartz fibre filters (PALL 2500 QAT-UP 150 mm) to obtain mass concentration and a complete chemical characterisation, resulting in a total of 553 8 h-daily samples (SC1: 140 indoors, 136 outdoors; SC2: 143 indoors, 134 outdoors). At schools, sampling duration was 8 h per day/filter during school hours (from 9 to 17 h, typical school hours in Barcelona). However, in UB-PR the sampling schedule was a 24 h sample every third day since this sampling is part of a long temporal series programme.

Once the gravimetric determination of the $PM_{2.5}$ mass concentration was performed, a complete chemical characterisation of the PM collected on the filters was carried out following the methodology of Querol et al. (2001) with a relative analytical error between 3 and 10% for the elements under study (Viana et al., 2006). A 1/4 fraction of each filter was bulk acid digested (HNO_3:HF:$HClO_4$) for the determination of the major elements by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; IRIS Advantage TJA Solutions, Thermo) and trace elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; X Series II, Thermo). Another 1/4 fraction of each filter was employed to determine water-soluble ions, SO_4^{2-}, NO_3^- and Cl^- by means of ion chromatography (ICHPLC) and NH_4^+ by means of a selective electrode. A 1.5 cm^2 filter punch was used for organic (OC) and elemental carbon (EC) determination by a thermal–optical transmission technique with a Sunset Laboratory OCEC Analyser with the NIOSH temperature programme (Birch and Cary, 1996). OC was converted into organic matter (OM) by a factor of 1.6, which according to Turpin and Lim (2001) accounts for the heteroatoms (O, H, N) present in the OM. Finally, contents of SiO_2 and CO_3^{2-} were indirectly calculated using well-known experimental equations ($SiO_2 = 3 \cdot Al_2O_3$ and $CO_3^{2-} = 1.5 \cdot Ca$; Dulac et al., 1992; Molinaroli et al., 1993; Querol et al., 2001).

In addition, real-time concentrations of UFP (DiSCmini), mean UFP size (DiSCmini), lung deposited surface area in the alveolar region (LDSA; DiSCmini) and, BC (MicroAeth AE51) were recorded on a 5 or 10 minute basis. Weekly-averaged NO_2 concentrations with Gradko Environmental passive dosimeters were also obtained. All the DiSCmini devices employed were compared and corrected by correlation to a DiSCmini of reference to minimise any measuring differences (prior and post each sampling campaign). DiSCmini measures the number of UFP in the range 10–700 nm (accuracy: $\pm 500\ \#\cdot cm^{-3}$). By contrast, at the UB-PR, the number of UFP was measured with a 3785 TSI CPC, measuring all the particles from 5 to 1000 nm. Therefore we are not comparing exactly the same parameter when measuring UFP at schools and at UB-PR. In fact, the slope and the R^2 of the equations obtained with a pre and post campaign intercomparison between the reference DiSCmini and the CPC were UFP[DiSCmini] = 1.62 · UFP[CPC] for the SC1 ($R^2 = 0.57$) and UFP[DiSCmini] = 1.40 · UFP[CPC] for the SC2 ($R^2 = 0.69$). This measurement difference has to be taken into account when comparing UFP at schools and UB-PR. LDSA in the alveolar region at UB-PR was recorded by a Nanoparticle Surface Area Monitor (3550 TSI NSAM).

The MicroAeth AE51 provides data of BC (in $\mu g\cdot m^{-3}$) derived from absorption values. Eight hour-averages were cross correlated with EC concentrations from filter samples simultaneously collected in situ (at schools; including both campaigns), obtaining the equation $BC_{AE51} = 0.5436 \cdot EC$ ($R^2 = 0.88$). The results were converted to equivalent black carbon (EBC; in $\mu g\cdot m^{-3}$). In the case of UB-PR, absorption values obtained with a Multi Angle Absorption Photometer (MAAP Thermo ESM Andersen Instruments) were converted into EBC in $\mu g\cdot m^{-3}$ by an experimental Absorption/EC factor of 9.2 previously determined by Reche et al. (2011).

For this study, only mean values for school hours from Monday to Thursday were used (for both $PM_{2.5}$ filter samples and real-time measurements of BC and UFP) in order to take into account child exposure to air pollution during the time spent at school. In fact, this time restriction is a major advantage of our research given that PM concentrations (and the other pollutants) would be underestimated if considering 24 h means (Yip et al., 2004). The only exception is NO_2 concentration, which is 4 days averaged and includes the periods when children were not at schools.

2.4. Data deseasonalisation

To compare schools, seasonal adjustment of the daily values was conducted. This procedure, usually called (back-)extrapolation in time, is sometimes used in epidemiological studies when past values of pollutant levels are required to calculate the exposure of a given population using Land-Use Regression (Chen et al., 2010; Gehring et al., 2011; Mölter et al., 2010). Deseasonalised data were only employed for the spatial variation analysis. The remaining results were obtained from the data that were not deseasonalised.

To this end, an adjustment of all pollutant concentrations (both indoor and outdoor) was carried out using data from the UB-PR. The adjusted concentration $(C_i^j)_k^*$ of the *ith* pollutant for the *kth* day at the school *jth* was calculated as shown in Eq. (1):

$$\left(C_i^j\right)_k^* = \left(C_i^j\right)_k / \left[\left(C_i^{PR}\right)_k / \left(\overline{C_i^{PR}}\right)\right] \quad (1)$$

where $(C_i^j)_k$ is the concentration measured at the school, C_i^{PR} and $\left(\overline{C_i^{PR}}\right)$ are the 8 h average corresponding to day *kth* and campaign averages at UB-PR, respectively.

To apply this method, the reference station must cover all the period and have at least 75% of valid data for each pollutant. These two conditions were met for most of the parameters analysed. Nevertheless, missing data of some pollutants were estimated by correlation with existing data of other pollutants at UB-PR.

3. Results

3.1. Levels of air pollutants

Table 1 shows the mean indoor and outdoor concentrations of $PM_{2.5}$, NO_2, UFP, UFP size, LDSA and EBC for BREATHE schools and for the UB-PR site. Averages were calculated for school hours except for NO_2 for which the daily means over 4 days were obtained.

Average outdoor levels are higher than indoors for NO_2, UFP, LDSA and EBC by a factor of 1.6, 1.5, 1.2 and 1.1 respectively (Table 1). Only average $PM_{2.5}$ levels and mean UFP size are higher indoors, with an indoor/outdoor ratio of 1.3 and 1.1 respectively. Mean outdoor concentrations are higher at schools than at UB-PR with school/UB-PR ratios of 1.7, 1.6 and 1.2 for $PM_{2.5}$, UFP and NO_2, respectively. However, levels are similar for EBC and LDSA. Concerning UFP levels it has to be taken into account the different measuring instruments (with different size range) at schools and the UB-PR site. Intercomparison exercises (see Section 2.3) showed that DiSCmini (at schools) measured between 40 and 60% more UFP than CPC (at UB-PR). Therefore, levels of UFP in UB-PR are probably lower than at schools but to a lesser extent than the factor 1.6.

The results obtained in this study are compared in Table 2 with those by Fromme et al. (2007), Molnár et al. (2007), Stranger et al. (2008), Wichmann et al. (2010) and Zwoździak et al. (2013). Other studies (e.g. Crilley et al., 2013; Pegas et al., 2012) are available, but not directly comparable since they focus on other pollutants.

Fig. 2a shows the spatial distribution of average outdoor $PM_{2.5}$, NO_2, EBC and UFP concentrations at the different schools. These maps were made with seasonally adjusted data (see Section 2.4). Two perimeters based on the highest (red) and lowest tercile (green) of EBC outdoor concentrations were drawn in all the maps to facilitate comparison with respect to the other pollutants.

EBC concentrations are markedly lower in the outskirts of Barcelona and Sant Cugat, especially in the area of the Coastal Range (NW of the city, Fig. 2a). These levels display an ascending gradient when approaching the city centre, which is severely affected by high vehicle density and characterised by a street architecture that hinders the dispersion of pollutants. NO_2 concentrations follow a similar spatial pattern: almost all the NO_2 green and red dots fall within the

Table 1
$PM_{2.5}$, NO_2, UFP, and EBC concentrations, UFP size, and LDSA for school hours (except for NO_2) of the 39 schools (indoor and outdoor), and of UB-PR. Highest mean values in bold.

	INDOOR					OUTDOOR					UB-PR				
	Mean	Min	Median	Max	SD	Mean	Min	Median	Max	SD	Mean	Min	Median	Max	SD
$PM_{2.5}$ ($\mu g\cdot m^{-3}$)	**37**	13	33	84	13	29	10	23	111	20	17	10	15	38	7
NO_2 ($\mu g\cdot m^{-3}$)	30	5.1	30	69	12	**47**	14	46	98	17	41	23	38	97	15
UFP ($\#\cdot cm^{-3}$)	15,577	3584	15,376	30,932	6586	**23,396**	9868	20,955	55,804	9986	14,665	6335	13,286	32,654	5452
Size mode (nm)	**42**	30	41	57	5.5	39	27	36	65	7.0					
LDSA ($\mu m^2\cdot cm^{-3}$)	34	8.6	31	71	14	**42**	15	40	83	15	42	21	37	86	14
EBC ($\mu g\cdot m^{-3}$)	1.3	0.39	1.2	2.7	0.56	**1.4**	0.38	1.2	2.6	0.57	1.3	0.55	1.2	2.7	0.6

Table 2
Indoor and outdoor average concentrations of $PM_{2.5}$ ($\mu g \cdot m^{-3}$), UFP (#·cm-3) and EBC ($\mu g \cdot m^{-3}$) for various schools in Europe (w = winter samples; s = summer samples).

Source	Location	N schools	Sampling time	Season	Indoor concentration (BREATHE/other ratio)[a]				Outdoor concentration (BREATHE/other ratio)[a]			
					$PM_{2.5}$	NO_2	UFP	EBC	$PM_{2.5}$	NO_2	UFP	EBC
Wichmann et al. (2010)	Stockholm, Sweden	6	8–16 h		8 (4.5)	17 (1.7)		0.67[b] (1.9)	10 (3.0)	21 (2.3)		1.1[b] (1.2)
Fromme et al. (2007)	Münich, Germany	64	Teaching hours (5 h)	S	22 (1.5)		6509[c] (2.9)					
				W	39 (1.0)							
Zwoździak et al. (2013)	Wroclaw, Poland	1	24 h	S	14 (2.5)				16 (1.8)			
				W	60 (0.6)				49 (0.6)			
Stranger et al. (2008)	Antwerp, Belgium	15 (urban)	8–20 h	S	61 (0.6)	113[d] (0.3)		2.0[e] (0.8)	72 (0.4)	97[d] (0.5)		2.0 (0.8)[e]
				W	57 (0.7)	33[d] (0.9)		1.5[e] (0.8)	53 (0.6)	53[d] (0.9)		2.0 (0.6)[e]
This study	Barcelona, Spain	39	9–17 h		37	30[d]	15,577	1.3	29	47[d]	23,396	1.4
				S	34	32[d]	18,848	1.5	29	48[d]	23,144	1.5
				W	38	29[d]	13,656	1.2	30	47[d]	23,547	1.3

[a] Ratio between the concentration of the considered element in our study (BREATHE) and the concentration found in the study to which it is compared.
[b] Soot.
[c] Different particle size range than BREATHE.
[d] 24 h average.
[e] BS has been converted to EBC.

corresponding EBC perimeter. Only some schools adjacent to the perimeter undergo a change in their category. Spatial patterns for UFP are also similar with one important exception: one school close to the harbour on the coastal side of the Montjuïc headland (S of the city) has high UFP levels albeit with low EBC levels, probably because of the influence from nearby shipping emissions and/or the ring road (Ronda Litoral). The spatial gradient for $PM_{2.5}$ also shows a similar pattern although with several exceptions, with high $PM_{2.5}$ levels in many low EBC schools. However, it should be noted that most of the $PM_{2.5}$ red spots are located close to the city centre. Fig. 2b shows the spatial distribution of indoor concentrations of pollutants under study. Indoor spatial patterns are very similar to those explained for outdoors, which suggests a significant infiltration of outdoor pollutants into indoor environments.

The same maps were created with data that were not seasonally adjusted. Fig. S1a shows how the increasing gradient of EBC and NO_2 outdoor concentrations towards the centre of Barcelona become blurred with respect to the adjusted data. This is why there are green dots in the centre of Barcelona. On the other hand, UFP gradient is more marked than when using deseasonalised data. $PM_{2.5}$ gradient is similar regardless of deseasonalisation. As regards indoor concentrations (Fig. S1b), the distribution of the school terciles is very similar to the scenario without deseasonalisation.

3.2. $PM_{2.5}$ components

The mean indoor and outdoor concentrations for different $PM_{2.5}$ components found at BREATHE schools and at UB-PR station are shown in Table 3. It should be noted that UB-PR concentrations are mean values for 24 h of $PM_{2.5}$ collection, whereas in schools they account for only 8 h. Fig. 3 summarizes the chemical profile of $PM_{2.5}$ at schools in indoor and outdoor environments. Mineral matter was estimated by the sum of the typical mineral compounds (CO_3^{2-}, SiO_2, Al_2O_3, Ca, Mg, Fe, K), and sea salt by Na and Cl.

Data show higher mean concentrations of most of the $PM_{2.5}$ components in outdoor than in indoor environments (Table 3). Exceptions are OC, Ca, CO_3^{2-} and Sr, which attain higher indoor than outdoor concentrations. OC is, moreover, the PM component with the highest contribution to indoor $PM_{2.5}$ mass concentration, 33% of the total indoor $PM_{2.5}$ mass (reaching 44% when considering OM). It accounts for 22% (31% OM) of outdoor $PM_{2.5}$, being the second most important group after mineral compounds (Fig. 3).

A high variability between schools was observed for all the pollutants (high values of standard deviation). In most cases, the range of concentrations and standard deviation is higher in outdoor environments. This is especially true for NO_3^- and mineral components (SiO_2, Al_2O_3, Fe, Ti, Mn, among others) because the levels of crustal elements are very dependent on the presence/absence of sand-filled playgrounds. In fact, the mineral components in schools with sand-filled playgrounds account for 16 $\mu g \cdot m^{-3}$ outdoors and 13 $\mu g \cdot m^{-3}$ indoors whereas in those with paved playgrounds it descends to 4 $\mu g \cdot m^{-3}$ outdoors and 8 $\mu g \cdot m^{-3}$ indoors.

Fig. 4a and b show the relative abundance of EBC, mineral matter and OC (after normalisation of their levels) at each school outdoors and indoors, respectively. This enables us to divide the schools into two groups:

- *Group 1*: schools are defined by high relative normalised ternary proportions of mineral matter (>45%) and low influence of EBC (<25%). These schools are characterised by having sand-filled playgrounds and by being located in the outskirts of Barcelona or in Sant Cugat.
- *Group 2*: schools show low relative normalised abundance of mineral matter (<30%) and high levels of EBC (>35%). These schools are mainly located in the centre of Barcelona and have paved playgrounds.

Note that the indoor range of relative normalised levels of OC is narrower (25–45%) than the outdoor range (15–50%).

Eight hour concentrations (except the 4-day averaged NO_2) of all pollutants measured were plotted versus 8 h means of Al_2O_3 and EBC concentrations as tracers of mineral matter and traffic matter emissions, respectively (Fig. 5a and b, for outdoor and indoor, respectively). Based on this cross correlation analysis of the correlation coefficients (r) and on the PM source apportionment studies performed in the outdoor UB of Barcelona by Amato et al. (2009), specific pollutants of outdoor environments were selected as tracers of the following sources:

- Mineral components (SiO_2, Ca, Fe, K, Mg, Ti, Mn, Sr and rare Earth elements): include elements highly correlated with Al_2O_3 but not with EBC. This group consists of elements of mineral origin and is the most significant in the outdoor environment, and second in importance indoors (Fig. 3). Although $PM_{2.5}$ is outside this group, it is also highly correlated with Al_2O_3, whereas the correlation with EBC is low, especially for the indoor environment ($r = -0.03$ indoors; $r = 0.29$ outdoors, Table S2). Mineral elements have higher levels outdoors with the exception of Ca and Sr (Table 3).
- Traffic-related components (NO_2, Sb, UFP and LDSA): include the elements that correlate highly with EBC (traffic tracer) and do not correlate with Al_2O_3 in either environment. Sb and Cu levels (brake pad abrasion tracers, Sternbeck et al., 2002) are higher in outdoor environments than indoors by a factor of 1.3 and 1.1, respectively.

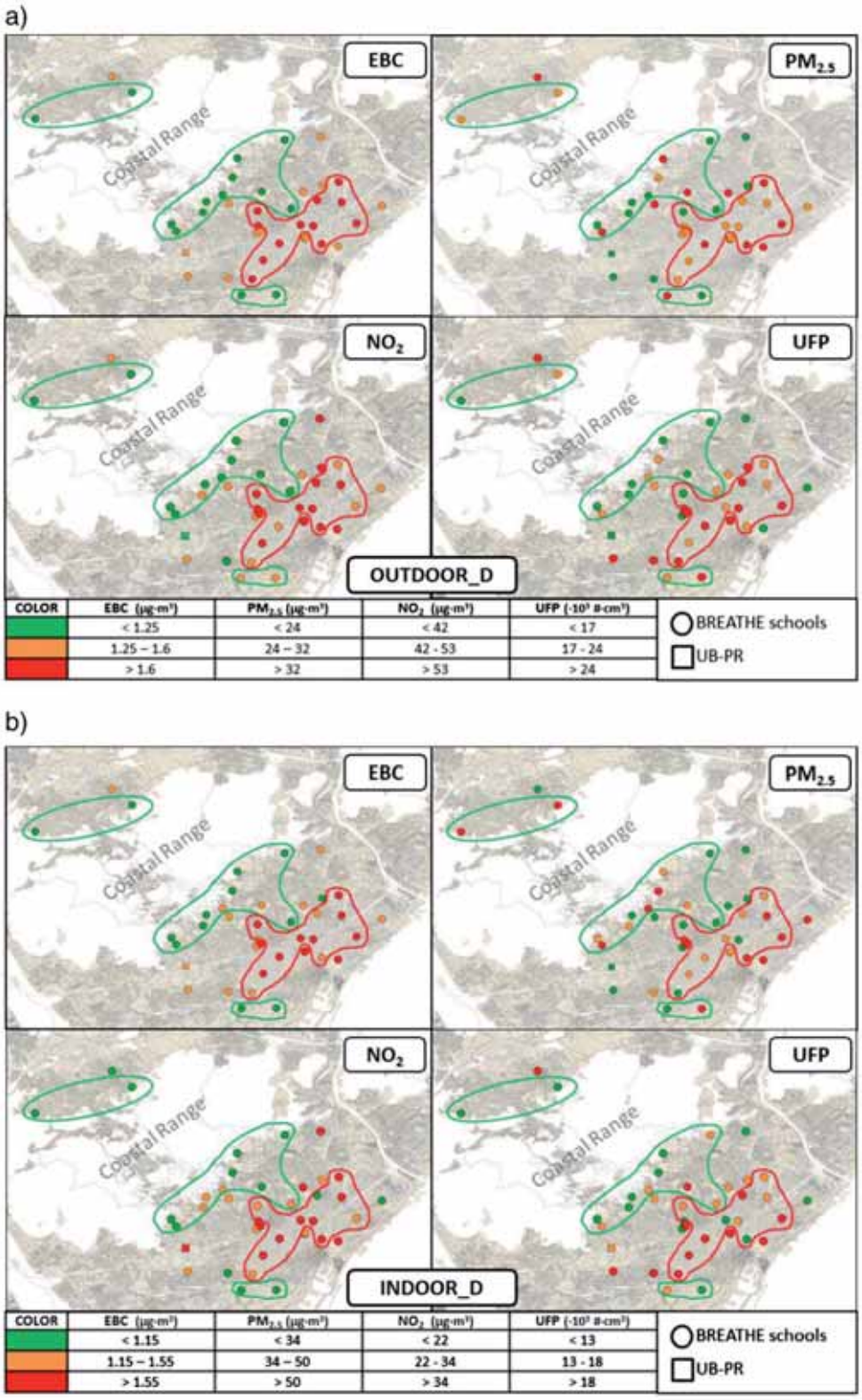

Fig. 2. a. Spatial distribution of seasonally adjusted outdoor levels of NO_2, $PM_{2.5}$, EBC and UFP in the BREATHE school. Perimeters are based on the outdoor EBC highest tercile (red) and the lowest tercile (green). b. Spatial distribution of seasonally adjusted indoor levels of NO_2, $PM_{2.5}$, EBC and UFP in the BREATHE schools. Perimeters are based the on outdoor EBC highest tercile (red) and the lowest tercile (green). UB-PR category refers to outdoor levels.

Table 3
$PM_{2.5}$ components concentrations for the 39 schools (indoor and outdoor) for school hours (8 h) and for the UB-PR (24 h) in Barcelona. Highest mean values in bold. N = number of schools in the first campaign plus schools in the second campaign, (mean of 3.5 samples per school and campaign); n = total number of samples; MM = mineral matter.

	Indoor (N = 77)					Outdoor (N = 75)					UB-PR (n = 26)				
	Mean	Min	Median	Max	SD	Mean	Min	Median	Max	SD	Mean	Min	Median	Max	SD
$(\mu g \cdot m^{-3})$															
OC	10	3.5	9.6	19	3.2	5.5	2.1	4.7	15	2.5	2.1	0.78	1.7	5.4	0.94
EC	1.3	0.25	1.2	2.9	0.64	1.3	0.23	1.3	3.3	0.60	0.94	0.15	0.68	2.2	0.47
CO_3^{2-}	2.3	0.31	2.1	7.6	1.5	1.2	<0.1	0.81	6.3	1.3	0.13	<0.1	<0.1	0.3	0.07
SiO_2	3.7	0.34	2.6	17	3.3	4.4	0.24	1.8	34	6.7	0.32	<0.1	0.21	1.1	0.26
Al_2O_3	1.2	0.11	0.86	5.6	1.1	1.5	<0.1	0.60	11	2.2	0.11	<0.1	<0.1	0.37	0.09
Ca	1.6	0.21	1.4	5.1	0.97	0.82	<0.1	0.54	4.2	0.86	<0.1	<0.1	<0.1	0.19	0.04
Fe	0.42	<0.1	0.29	1.6	0.32	0.58	<0.1	0.28	3.8	0.76	0.14	<0.1	0.10	0.30	0.06
K	0.37	<0.1	0.31	1.2	0.24	0.40	<0.1	0.23	2.2	0.43	0.11	<0.1	<0.1	0.26	0.07
Na	0.34	<0.1	0.28	1.3	0.22	0.34	<0.1	0.25	1.4	0.29	0.18	<0.1	0.20	0.56	0.13
Mg	0.16	<0.1	0.13	0.68	0.12	0.19	<0.1	0.09	1.2	0.26	<0.1	<0.1	<0.1	0.09	0.02
SO_4^{2-}	1.4	<0.1	1.2	4.3	1.1	1.6	0.21	1.2	4.8	1.1	1.9	0.41	1.2	7.3	1.8
NO_3^-	0.72	<0.1	0.61	4.4	0.69	1.8	0.21	1.0	11	2.1	1.0	<0.1	0.41	13	2.1
NH_4^+	0.48	<0.1	0.34	1.8	0.46	0.86	<0.1	0.56	3.7	0.73	0.79	<0.1	0.30	5.7	1.1
MM	10	1.4	7.7	37	7.1	9.1	0.86	4.0	64	12	0.91	0.15	0.65	2.2	0.51
$(ng \cdot m^{-3})$															
Li	0.55	<0.1	0.32	2.2	0.51	0.86	<0.1	0.25	13	1.8	<0.1	<0.1	<0.1	0.34	0.06
Ti	55	5.5	45	233	44	59	2.0	22	502	92	3.8	<0.1	2.7	10	2.9
V	4.8	0.67	3.8	17	3.4	5.9	1.1	4.6	22	4.3	4.2	0.70	2.5	19	5.0
Cr	3.8	<0.1	3.0	14	2.9	3.4	<0.1	2.8	8.6[a]	3.3	1.5	<0.1	0.92	7.0	1.5
Mn	12	2.4	9.4	41	8.2	16	2.1	9.2	85	17	4.3	0.74	3.3	8.8	2.0
Co	0.21	<0.1	0.16	0.81	0.17	0.22	<0.1	0.16	1.3	0.25	<0.1	<0.1	<0.1	0.26	0.06
Ni	2.6	<0.1	2.3	10	1.8	3.3	<0.1	2.8	7.5[b]	3.1	1.8	<0.1	1.0	6.5	1.7
Cu	8.2	3.4	7.6	15	2.7	8.8	3.0	7.9	21	3.9	6.7	1.7	5.3	14	2.7
Zn	52	19	47	147	24	55	14.4	48	181	28	41	5.2	31	92	25
As	0.46	<0.1	0.43	1.4	0.21	0.50	0.19	0.41	2.0	0.27	0.30	<0.1	0.27	0.88	0.17
Se	0.33	<0.1	0.31	1.0	0.22	0.37	<0.1	0.33	0.98	0.22	0.25	<0.1	0.23	0.60	0.16
Sr	4.6	0.59	4.1	15	2.6	2.8	<0.1	1.6	16	3.0	0.48	0.11	0.35	1.3	0.31
Cd	0.14	<0.1	0.12	0.61	0.09	0.17	<0.1	0.14	0.64	0.13	0.11	<0.1	0.11	0.34	0.07
Sn	3.0	0.88	2.5	12	1.8	3.3	0.52	2.6	14	2.3	2.3	0.62	1.6	9.4	1.5
Sb	0.83	0.13	0.83	1.6	0.35	1.1	0.12	1.0	3.6	0.58	1.0	0.28	0.72	3.5	0.63
Ba	19	<0.1	13	133	20	20	<0.1	12	241	31	3.7	<0.1	2.1	37	5.9
La	0.43	<0.1	0.34	1.6	0.32	0.55	<0.1	0.25	3.6	0.72	<0.1	<0.1	<0.1	0.26	0.06
Pb	7.3	1.9	6.9	19	3.1	8.1	3.1	6.9	24	4.3	6.0	0.23	5.6	14	3.7

[a] The highest value after the maximum of 26 $ng \cdot m^{-3}$, which might be considered an outlier due to an extremely polluted week.
[b] The highest value after two maximums of 21 and 17 $ng \cdot m^{-3}$, which might be considered an outlier due to an extremely polluted week.

- Secondary inorganic aerosol (SIA: SO_4^{2-}, NO_3^- and NH_4^+): these are urban-regional pollution tracers with the result that they are moderately correlated with EBC but not with Al_2O_3. Together, the secondary inorganic aerosols constitute the third most important group in the two environments (Fig. 3). The levels are similar in both environments but always higher in the playgrounds, and markedly higher outdoors for NO_3^-.
- Industrial elements (Cd) and fuel-oil combustion (Ni, V): these metals have a low correlation (r<0.5) or do not correlate (r<0.2) with EBC and with Al_2O_3. These elements are typically emitted by industrial processes (Cd) and heavy fuel combustion (Ni and V, mostly shipping in Barcelona, Amato et al., 2009). They are also correlated with one another (Table S2). Higher levels of tracers of heavy oil combustion and metallurgical activities (Zn, As, Cd, Cr, Co, Se, V, Ni and Pb, Querol et al., 2007) have been found in playgrounds than in indoor environments.
- OC and other pollutants associated with mineral matter resuspension (as in both environments, Co, Pb): elements which have a moderate correlation (0.2 < r < 0.6) with Al_2O_3 and a low correlation (r < 0.25) indoors or moderate correlation (0.2 < r < 0.6) outdoors with EBC.
- Sea salt (Na): there is no correlation between Na and EBC but Na is moderately correlated with Al_2O_3, suggesting an additional source (mineral) of Na. Its contribution is equal in the two environments.

When comparing outdoor school concentrations of $PM_{2.5}$ components with those measured in UB-PR, outdoor levels at schools are:

- Much higher: almost all the crustal elements (Ti, Al_2O_3, SiO_2, Li, Ca, Sr, La, Ba, Fe, Mn, K) are higher at schools than in UB-PR with a school/UB-PR ratio between 3.6 and 15.4; OC and Cr are 2.6 and 2.2 times higher, respectively (Table 3).
- Higher: Mg is 1.9 times higher in playgrounds than in UB-PR. Na (from sea salt) has a playground/UB-PR ratio of 1.9 and Ni and V (shipping emission tracers) ratios are 1.8 and 1.4, respectively. The different sampling periods (24 h vs 8 h) could play a major role in this component, since sea breezes usually occur at midday. Traffic related components such as Sn (1.5), Cu (1.3) and NO_3^- (1.7) are also higher in playgrounds. The same pattern is observed for industrial elements such as Zn, As, Cd, and Pb (by factors from 1.3 to 1.7).
- Similar: Sb (1.04) and the secondary components NH_4^+ (1.09), and SO_4^{2-} (0.84) have similar levels in the schools and at UB-PR.

4. Discussion

The levels of $PM_{2.5}$, NO_2, and UFP found at schools in Barcelona in both indoor and outdoor environments are higher than expected since $PM_{2.5}$ and NO_2 concentrations are 1.7 and 1.2 times higher than those found in the UB-PR station. Outdoor levels of NO_2 at BREATHE schools can be considered to be representative of all schools in Barcelona considering that they agree with modelled data employing Land Use Regression from the ESCAPE project for all the schools in Barcelona (Cyrys et al., 2012; De Nazelle et al., 2013). The modelled data yielded an average of 50 $\mu g \cdot m^{-3}$, which is practically the same as the value obtained with measurements at the 39 BREATHE schools, and higher than the value at the reference station of UB-PR (41 $\mu g \cdot m^{-3}$).

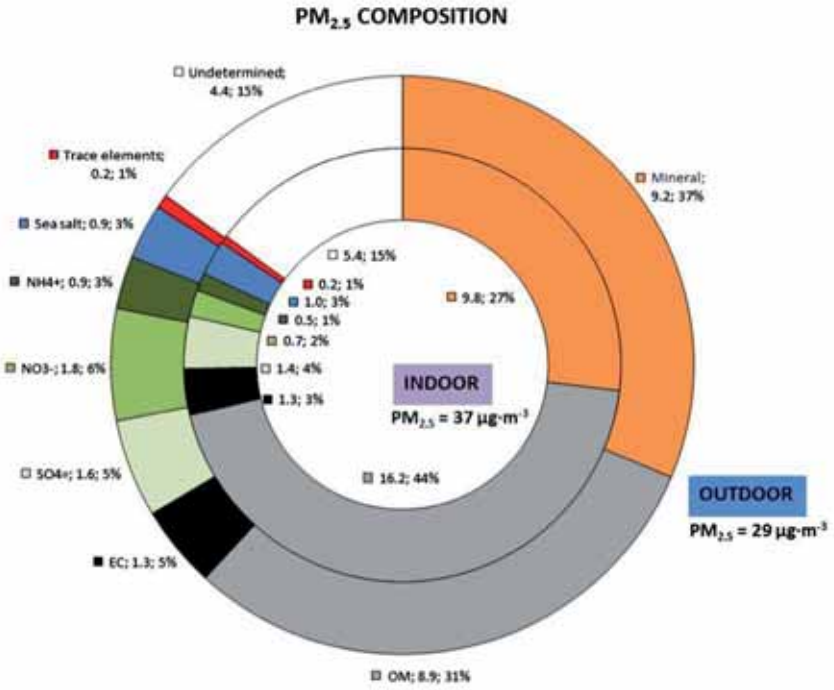

Fig. 3. Average indoor and outdoor $PM_{2.5}$ chemical composition in BREATHE schools.

Outdoor levels are higher than indoors for NO_2 and UFP as expected because the main sources (mostly road traffic) of these pollutants are located outside the buildings (e.g. Dall'Osto et al., 2011; Pey, 2007; Table 1). However, EBC levels are almost the same in both environments, thus indicating a high indoor penetration of this pollutant (in fact, the indoor–outdoor correlation for most of the schools was better for EBC than UFP). Fresh exhaust emissions from traffic are very fine (20–30 nm prevailing mode, Dall'Osto et al., 2011), and this primary UFP may increase their size mode when affected by different processes such as coagulation and condensation that modify their size distribution and, therefore finding slightly finer outdoor particle size with respect to that found indoors. High UFP concentrations combined with a finer particle size leads to higher LDSA values outdoors owing to traffic proximity. By contrast, markedly higher levels of $PM_{2.5}$ are found in classrooms than outdoors, suggesting an important indoor source affecting $PM_{2.5}$ levels.

As expected, most of the $PM_{2.5}$ components have higher concentrations outdoors, except OC (with an important contribution to $PM_{2.5}$), Ca, CO_3^{2-} and Sr. The relatively high indoor levels (close to outdoors in many cases) of externally emitted traffic-related components (NO_2, Sb, UFP and LDSA), SIA, industrial elements (Cd) and elements derived from fuel oil combustion (Ni, V) suggest significant infiltration rates from the outdoor environment. The similarity of the relationship of Sb levels between schools playgrounds and UB-PR agrees with the one discussed for EBC, and, together with the higher levels of Sn, Cu and NO_3^-, corroborates our observation that the schools are exposed to slightly higher traffic emissions than UB in Barcelona. On the other hand, Na (marine in a relevant proportion), Ni and V (mostly from shipping emissions, Amato et al., 2009) have considerable higher levels at schools than at UB-PR, and, apart from the different sampling periods, it should also be noted that the schools are on average closer to the coast than UB-PR. Also higher levels at schools are observed for industrial elements such as Zn, As, Cd, and Pb. This may be attributed to the fact that the trajectories of the air masses from the Vallès Depression (location of industry) do not especially affect the zone where UB-PR is located whereas, some of the schools are directly exposed to industrial metals (Minguillón et al., 2014).

Mineral matter is usually characterised by a coarse grain size owing to its mechanical origin. Thus, in urban areas, levels of mineral matter in $PM_{2.5}$ are lower than 2 $\mu g \cdot m^{-3}$ (in UB-PR, 0.91 $\mu g \cdot m^{-3}$). However, in the present study unusually high levels of mineral matter in $PM_{2.5}$ were found, especially in the schools with sand-filled playgrounds. In fact, mineral matter is the most significant group in the outdoor environment, and second in importance in the indoors (Fig. 3). The activity in the playgrounds probably contributed to the breakdown of mineral particles. These fine mineral particles are continuously resuspended because of the very low precipitation in Barcelona (Querol et al., 2007). In Fig. 5a and b it can be observed that mineral matter correlates with OC and other pollutants such as As, Co and Pb, suggesting that mineral matter was polluted owing to the dry and wet deposition of these elements in the playgrounds and to their possible retention by adsorption on crustal elements. Therefore pollutants are resuspended at the same time as the mineral matter. This seems to be particularly true for As, which is present in both indoor and outdoor groups. It should be noted that outdoors OC is also correlated with EBC, thus suggesting that OC is mostly generated by or at the same time as traffic emissions (Minguillón et al., 2011) whereas in the indoor environment, OC is strongly influenced by local indoor sources since it has no relationship with EBC.

An important source of OC in indoor environments could be cotton fibres from clothes, skin cells, other organic emissions from children (as evidenced in studies at schools, Braniš and Šafránek, 2011; Fromme et al., 2008), cooking emissions (Abdullahi et al., 2013; Brunekreef et al., 2005; Lanki et al., 2007) and also condensation/nucleation of semi-volatile organic compounds (SVOCs, Weschler and Shields, 1999). The chalk for the blackboards might be responsible for the higher levels of Ca, CO_3^{2-} and Sr indoors. X-ray diffraction analysis revealed that it was composed of calcite ($CaCO_3$). Since the atomic radius of Sr is similar to that of Ca, this element often replaces Ca in calcite and gypsum ($CaSO_4 \cdot 2H_2O$), accounting for the higher indoor levels of Sr.

All these elements have also been compared with the Spanish urban concentration ranges defined by Querol et al. (2007, 2008) (Figs. S2a

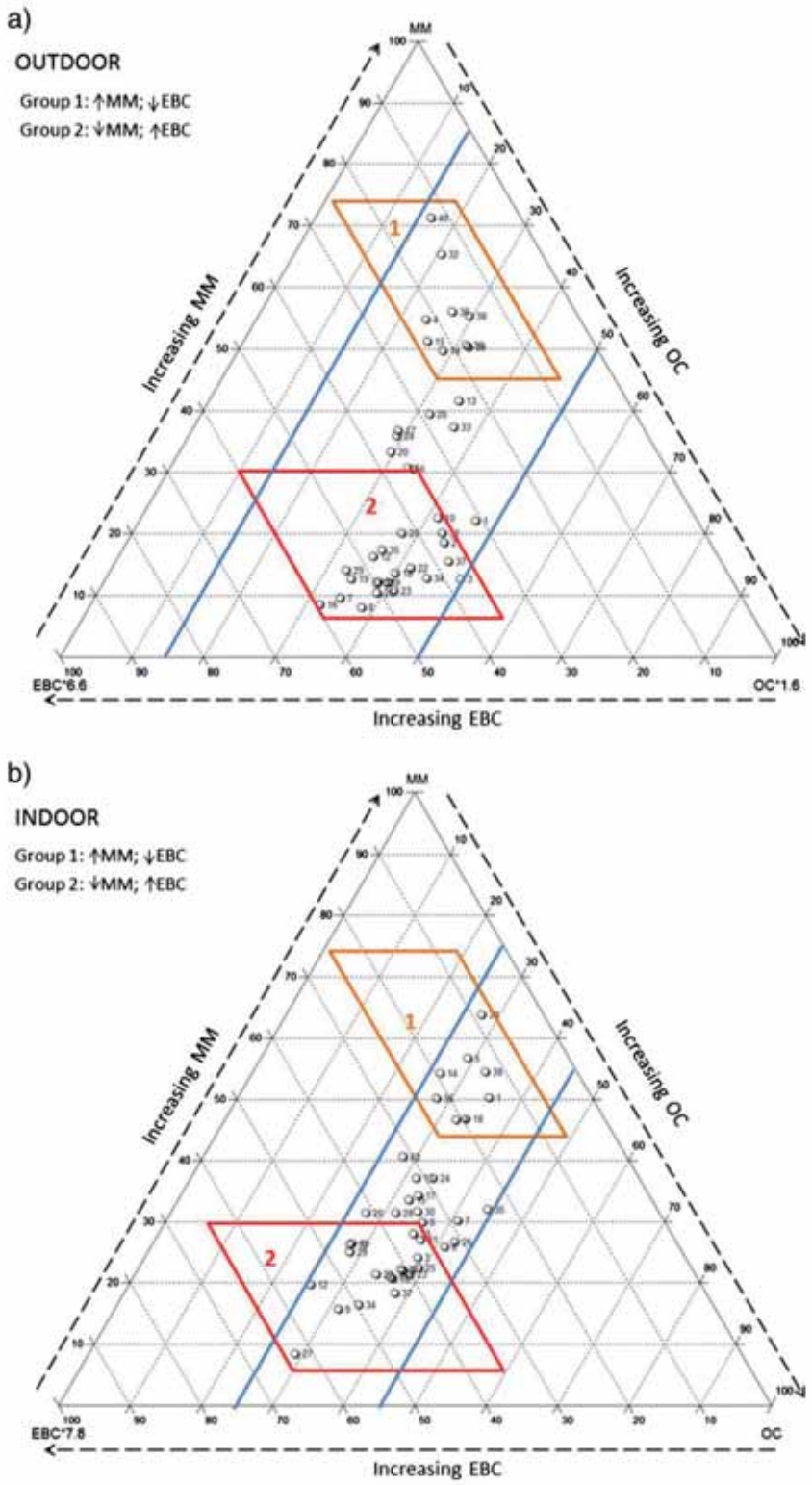

Fig. 4. a. Ternary plot showing the relationship between normalised outdoor EBC, mineral matter and OC for each school. MM = mineral matter. b. Ternary plot showing the relationship between normalised indoor EBC, mineral matter and OC for each school. MM = mineral matter.

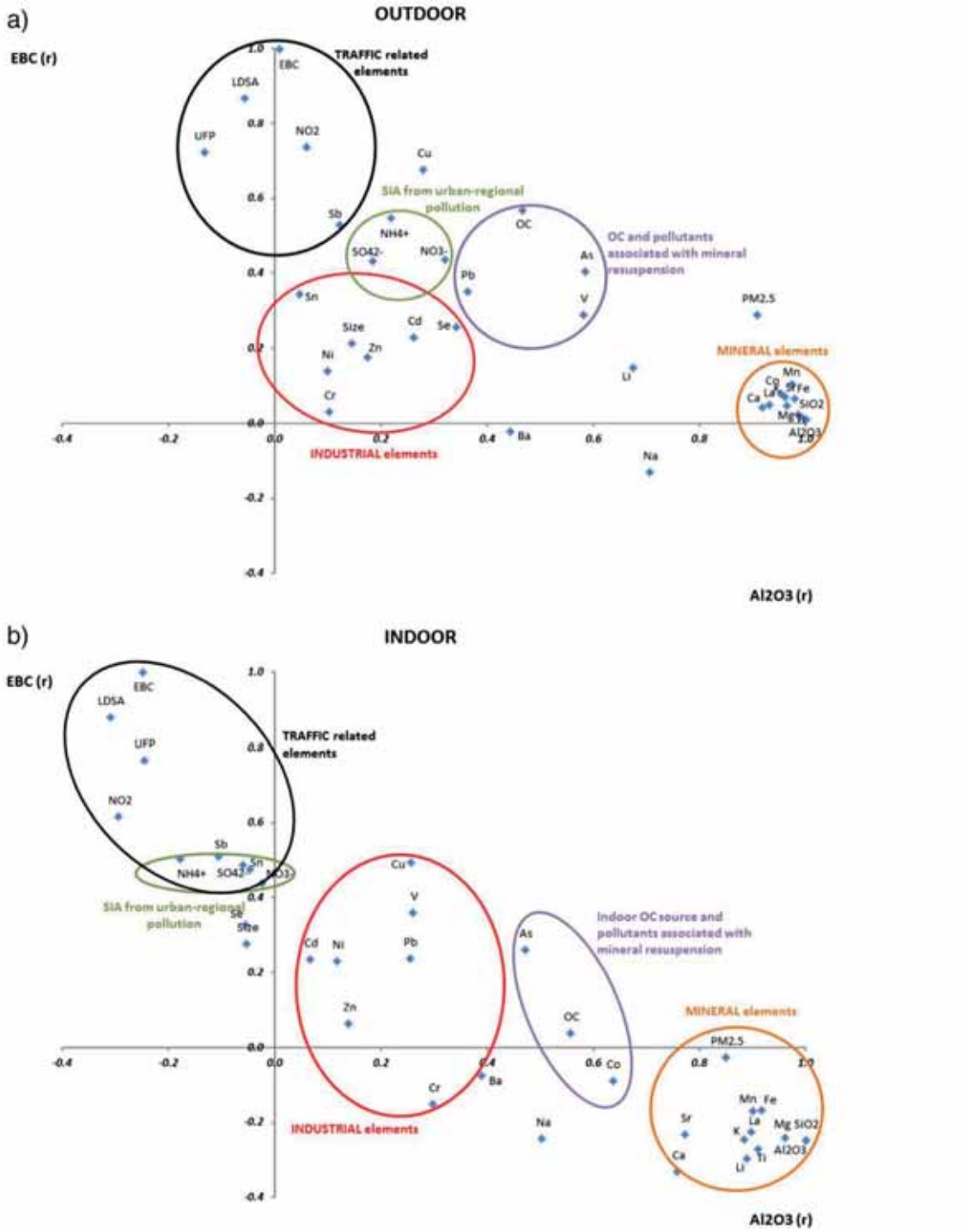

Fig. 5. a. Dispersion plot of the correlation coefficients (r) between EBC and Al_2O_3 and the other pollutants considered for the outdoor environment. b. Dispersion plot of the correlation coefficients (r) between EBC and Al_2O_3 and the other pollutants considered for the indoor environment.

and S2b). OC and mineral components (Ca, Al_2O_3, Fe, K, Sr, Ti, Li, etc.) are the only ones that attain higher concentrations in the school playgrounds than the aforementioned ranges (and are the main reason for the higher $PM_{2.5}$ levels at schools than at UB-PR), whereas the remaining PM components are within these ranges.

High variability among schools is observed for all the pollutants, highlighting the wide range of concentrations children are exposed to. It is especially true for mineral components (related to the presence/absence of sand-filled playgrounds) and for NO_3^-. As regards NO_3^-, the variation between schools could also be due to different environmental conditions (T and RH) throughout the campaign. Harrison et al.

(1994), Wakamatsu et al. (1996) and the references therein reported that NH_4NO_3 (the most common NO_3^--bearing species in PM) is very unstable under typical summer temperatures in Barcelona, resulting in a wide disparity in NO_3^- concentration between colder (February) and warmer months (June and September). This instability is also the cause of the lower levels of NO_3^- found indoors, where the temperature is usually higher than outdoors (in particular during winter). In most cases, the range of concentrations and standard deviations is higher in outdoor environments. This indicates that indoor sources might be similar in schools and that physical barriers (buildings materials, windows, etc.) hinder, albeit slightly, the entry of outdoor pollutants into indoor environments (infiltration rates may vary widely from school to school, Adgate et al., 2003; Dockery and Spengler, 1981). As a representative indoor sourced component, note that the indoor range of relative normalised ternary (OC–MM–EBC) abundance of OC is narrower (25–45%) than the one outdoors (15–50%). By contrast, higher outdoor levels of OC are found in those schools with higher levels of EBC, showing that OC and EBC have a common outdoor source (traffic) as already stated before.

$PM_{2.5}$ levels from BREATHE schools are 4.5 (indoor) and 3.0 (outdoor) times higher to the six schools in Stockholm studied by Wichmann et al. (2010) where only school hours were considered (Table 2). Since $PM_{2.5}$ annual mean levels obtained within the framework of the ESCAPE project in Stockholm County were half those found in Barcelona (8.5 $\mu g \cdot m^{-3}$ vs 16.3 $\mu g \cdot m^{-3}$, respectively; Eeftens et al., 2012), the higher levels in Barcelona are due to a local source of $PM_{2.5}$ at schools (activity of children and the existence of sand-filled playgrounds) plus the higher $PM_{2.5}$ levels usually found in this city. This agrees to what is observed when comparing to Munich schools during summer (1.5 times higher indoor levels in BREATHE schools, Fromme et al., 2007), where the difference at schools cannot be only explained by the typical levels found in both cities (annual $PM_{2.5}$ mean for Munich 14.6 $\mu g \cdot m^{-3}$, similar to the 16.3 $\mu g \cdot m^{-3}$ in Barcelona, Eeftens et al., 2012). Coal for domestic heating in Poland may be the cause for the higher levels of $PM_{2.5}$ found in a school in Wroclaw (on a 24 h average basis in this case, Zwoździak et al., 2013) than in BREATHE schools during winter (BREATHE/Wroclaw ratios of 0.6 for both indoor and outdoor), whereas the opposite is found during summer (being 2.5 and 1.8 times higher in BREATHE, indoor and outdoor respectively). Unexpectedly, mean $PM_{2.5}$ concentrations were higher in five schools in Antwerp (Belgium, Stranger et al., 2008) than in BREATHE (BREATHE/Antwerp ratio of 0.6 for indoor and 0.5 for outdoor). Shifting to NO_2, the annual median concentration in Stockholm County was 14.9 $\mu g \cdot m^{-3}$ whereas in Barcelona it was 54.7 $\mu g \cdot m^{-3}$ (Cyrys et al., 2012), indicating a relationship similar to that of the schools (BREATHE/Stockholm ratio of 1.7 and 2.3 for indoor and outdoor, respectively). In Antwerp, NO_2 concentrations are also higher than in BREATHE (BREATHE/Antwerp ratio of 0.9 for both environments in winter and, 0.3 indoors and 0.5 outdoors in summer). The levels in the Belgian schools are surprisingly high since the ESCAPE annual NO_2 median was 30 $\mu g \cdot m^{-3}$ (Cyrys et al., 2012) which is much lower than the 97 and 53 $\mu g \cdot m^{-3}$ at Antwerp in summer and in winter, respectively. Moreover, EBC (measured in Barcelona) and soot (measured in Stockholm) are not directly comparable. However, higher levels are found in Barcelona (Stockholm vs BREATHE; 0.7 vs 1.3 $\mu g \cdot m^{-3}$ indoors; 1.1 vs 1.4 $\mu g \cdot m^{-3}$ outdoors), especially indoors, probably because of a higher traffic density and a higher diesel vehicle proportion in the fleet. In summer, the levels of UFP in Munich schools are 2.9 times lower than those at BREATHE schools. However, these levels are not comparable because the different particle size cut-off (DiSCmini were employed for this study whereas a SMPS system was used in Munich) for UFP measurement is very important when comparing absolute number concentrations.

Bringing the attention to $PM_{2.5}$ components, the concentrations of K, Ca, Fe, V, Cr, Mn, Ni, Cu, Zn, Pb were compared to those in Stockholm (Molnár et al., 2007, Table S3) with the conclusion that higher levels are found in BREATHE schools. This is particularly evident for mineral tracers owing to higher resuspension rates because of the low rainfall in southern Europe (Querol et al., 2004b). In similarity with our results, Ca levels in Stockholm were also higher in indoors than outdoors. Moreover, Molnár et al. (2007) concluded that the infiltration of outdoor particles during winter was relatively low owing to the tightly insulated buildings in cold climates. No comparison can be made with our study because no seasonally segregated data is shown. However, it may be assumed that buildings in Barcelona are less well insulated since the Cu indoor/outdoor ratio is 0.9 for Barcelona whilst it is 0.5 for schools in Stockholm. When comparing to Wroclaw (Zwoździak et al., 2013), indoor and outdoor levels of K, Ca, Fe, Cr, Ni, Cu, Zn, Pb and As in Barcelona are lower than in Wroclaw with the exception of mineral tracers in summer owing to the previously stated low rainfall and high resuspension in southern Europe (Querol et al., 2004b, Table S3). A similar pattern is found when comparing to Antwerp for K, Ca, Fe, V, Cr, Ni, Cu, Zn and Pb. Therefore, indoor and outdoor pollutants are higher in schools in Barcelona than in schools in Stockholm and Munich, but lower than those in Wroclaw and in Antwerp. Mineral components are an exception because of the higher resuspension rates found in southern Europe (Querol et al., 2004b) and the higher frequency of sand playgrounds in the schools of Barcelona.

Regarding the spatial variation of air pollutants, an increasing gradient of the outdoor concentrations towards the city centre has been observed for EBC, NO_2 and, with one important exception, also UFP (Fig. 2a). Therefore, it may be concluded that the three pollutants have a similar source and spatial dispersion in Barcelona. On the other hand, $PM_{2.5}$ also follows similar patterns although with several exceptions, with high $PM_{2.5}$ levels in many low EBC schools. This again suggests the significance of local school sources of $PM_{2.5}$ in specific cases. However, since most of the schools in the highest tercile of $PM_{2.5}$ concentrations are located close to the city centre, it may also be concluded that despite the school sources that prevent $PM_{2.5}$ from being a good indicator of traffic emissions, road traffic derived particles also contribute to $PM_{2.5}$. The similarities between the patterns of indoor and outdoor suggest a significant infiltration of outdoor pollutants into indoor environments.

The map created with data not seasonally adjusted (Fig. S1) demonstrate that deseasonalisation for EBC and NO_2 is fairly reliable, since the application of this methodology refines the expected ascendant gradient of concentrations towards the center of the city. However, this is unsuitable for UFP since its variability is influenced by complex photochemical processes in addition to road traffic emissions (Dall'Osto et al., 2011; Reche et al., 2011). Deseasonalisation could also be inappropriate for $PM_{2.5}$ because it is influenced by local sources at schools.

Since deseasonalisation was carried out using outdoor levels of the UB-PR station, this technique is probably not suitable for indoor levels. Indoor concentration depends on infiltration of outdoor particles and gaseous pollutants (that might differ in every school because of different building characteristics; Adgate et al., 2003; Dockery and Spengler, 1981) and on indoor-sourced PM (which might also be different in schools depending on the activities that take place; Kopperud et al., 2004; Long et al., 2000). Therefore, owing to the added complexity on the indoor environments, outdoor pollutants concentration should not be used to deseasonalise indoor concentrations.

5. Conclusions

In Barcelona and Sant Cugat, higher levels of air pollutants are found in school playgrounds and classrooms when simultaneously compared with local UB air quality monitoring site. Outdoor $PM_{2.5}$ levels at schools almost double the usual background levels reported for Barcelona, mainly because of the high $PM_{2.5}$ contribution of local school sources of mineral dust and indoor OC (outdoor OC is mainly the sum of local traffic and city-scale traffic emissions). Outdoor levels are higher than indoors for NO_2, UFP, Cu, Sn, among others with typical outdoor sources.

Nevertheless, indoor levels are very close to those found outdoors, indicating a fairly easy penetration of outdoor air pollutants into indoor environments. Moreover, levels of mineral matter components (except Ca) are also higher outdoors and seem to be very dependent on the presence of sand-filled playgrounds (also observed indoors). The unusually high levels of mineral matter found in $PM_{2.5}$ are very significant and suggest the breakdown of mineral particles due to playground activities under the specific Barcelona's climate. Thus, this fine mineral matter is easily resuspended alongside with anthropogenic pollutants (e.g. OC and a few metals) previously deposited in the sand.

By contrast, $PM_{2.5}$ levels are markedly higher indoors, which indicates that a significant fraction of $PM_{2.5}$ mass arises from indoor activities and is characterised mainly by OC (from clothes fibres, organic emissions from children and cooking), but also by Ca, CO_3^{2-} and Sr (from chalk). Since $PM_{2.5}$ is more influenced by indoor sources and mineral matter than traffic emissions or other urban pollutants, $PM_{2.5}$ mass is not a good indicator of traffic pollution in indoor and outdoor environments. However, the levels of $PM_{2.5}$ are also affected by traffic and most of central schools recorded high $PM_{2.5}$ levels. Conversely, levels of EBC, NO_2, UFP and specific metals such as Sb were found to be very good indicators of road traffic emissions in the two environments.

Deseasonalisation of the data based on an UB reference station is feasible for outdoor NO_2 and EBC, but it is unsuitable for outdoor UFP and $PM_{2.5}$, as well as for indoor concentrations.

Since some traffic tracers such as NO_2 are 1.2 times higher in the playgrounds when compared with the local UB reference station, school children in Barcelona are about 20% more exposed to traffic-related pollutants. The levels of pollutants assessed in our study are between those measured at UB and at traffic stations in Barcelona. These stations should, therefore, be considered when characterising child exposure and, possibly, exposure of the general population to air pollutants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2014.04.009.

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Corrigendum

Corrigendum to 'Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain' [Environment International 69C (2014) 200–212]

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The authors regret missing the following correction to the equation. The authors would like to apologise for any inconvenience caused. In the section 'Sampling and Analysis', the paragraph "The MicroAeth AE51 provides… by Reche et al. (2011)", the equation given is "$BC_{AE51} = 0.5436 \cdot EC$."

The correct equation is: $EC = 0.5436 \cdot BC_{AE51}$.

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Child exposure to indoor and outdoor air pollutants in schools in Barcelona, Spain

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SUPPLEMENTARY DATA

Materials and Methods

Since traffic is one of the main source of air pollutants in Barcelona, the urban traffic typology and intensity around each of the BREATHE schools is presented in Table S1. Traffic counts were carried out during 15 minutes (TC15) once or twice per school in the street closer to the monitored classroom (thus, it could happen that this street is not the one with most traffic intensity around the school) at 9:30 local hour. In order to extrapolate this data to a 24h basis, the correlation of the BREATHE 15-minutes counts with the 24h traffic volume (TC24) provided by the Ajuntament de Barcelona (data from 2006) was used ($TC24 = 54.10 \cdot TC15 + 2407$, $R^2=0.82$).

Table S1. Traffic intensity and typology around the BREATHE schools (NA = not available).

School ID	# vehicles in 24h	% light vehicles	% motorbikes	% heavy vehicles
1	2894	79.2	12.5	8.3
2	18206	72.3	24.0	3.8
3	2853	81.8	0.0	18.2
4	3381	75.0	25.0	0.0
5	2935	76.9	0.0	23.1
6	30352	60.9	35.4	3.7
7	6992	82.3	14.2	3.5
8	4071	85.4	9.8	4.9
9	16583	70.2	23.3	6.5
10	11821	68.4	27.0	4.6
11	NA	NA	NA	NA
12	22209	70.6	22.8	6.6
13	4801	76.3	16.9	6.8
14	2813	90.0	10.0	0.0
15	3563	75.4	24.6	0.0
16	3056	54.2	37.5	8.3
17	10807	74.9	16.7	8.4
18	2975	71.4	0.0	28.6
19	25672	67.2	28.1	4.7
20	17286	73.5	20.4	6.2
22	11253	70.6	26.3	3.1
23	17773	61.6	29.9	8.5
24	12903	59.8	30.9	9.3
25	3056	75.0	12.5	12.5
26	30677	60.2	35.8	4.0
27	54522	72.1	16.9	11.0
28	9508	78.9	12.6	8.6
29	12362	65.8	20.7	13.6
30	13269	60.9	33.4	5.7
31	3110	69.2	30.8	0.0
32	5613	65.8	30.4	3.8
33	3279	65.1	25.6	9.3
34	17394	67.5	27.1	5.4
35	3300	95.5	4.5	0.0
36	2630	72.7	27.3	0.0
37	14310	62.7	33.2	4.1
38	3482	96.2	3.8	0.0
39	3097	100.0	0.0	0.0
40	4010	94.9	2.5	2.5

Results

Table S2. Correlation coefficients (r) between the different air pollutants under study (In bold are significant at p <0 .05). Outdoor correlations are in the upper part (blue cells); indoor correlations are in the lower part (grey cells).

	$PM_{2.5}$	NO_2	UFP	Size	LDSA	EBC	OC	SiO_2	Al_2O_3	Ca	Fe	K	Na	Mg	SO_4^{2-}	NO_3^-	NH_4^+	Li	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Sr	Cd	Sn	Sb	Ba	La	Pb
$PM_{2.5}$	1.00	**0.36**	0.05	0.20	0.17	**0.29**	**0.77**	**0.91**	**0.91**	**0.89**	**0.91**	**0.93**	**0.59**	**0.91**	**0.40**	**0.61**	**0.55**	**0.65**	**0.90**	**0.65**	0.13	**0.93**	**0.93**	0.11	**0.49**	**0.24**	**0.76**	**0.45**	**0.90**	**0.42**	0.22	**0.31**	**0.40**	**0.87**	**0.56**
NO_2	-0.09	1.00	**0.52**	**0.24**	**0.68**	**0.74**	**0.61**	0.06	0.06	0.14	0.07	0.11	-0.11	0.06	**0.40**	**0.59**	**0.65**	0.12	0.05	**0.31**	-0.01	0.12	0.15	0.14	**0.61**	0.21	**0.50**	**0.32**	0.12	**0.40**	**0.39**	**0.45**	0.13	0.05	**0.43**
UFP	-0.10	**0.53**	1.00	**-0.24**	**0.90**	**0.72**	**0.28**	-0.13	-0.13	-0.03	-0.07	-0.07	-0.22	-0.11	0.07	**0.31**	0.22	0.03	-0.11	0.00	0.01	-0.03	-0.09	-0.03	**0.49**	0.01	0.08	-0.13	-0.05	-0.09	0.09	**0.53**	-0.08	-0.06	0.05
Size	0.07	0.08	-0.18	1.00	0.04	0.21	0.14	0.15	0.15	0.06	0.12	0.13	-0.01	0.10	**0.28**	**0.29**	**0.35**	0.09	0.15	0.18	-0.10	0.11	0.12	-0.07	0.22	0.06	**0.39**	**0.31**	0.11	**0.34**	0.09	0.23	0.04	0.13	**0.41**
LDSA	-0.12	**0.58**	**0.93**	0.10	1.00	**0.87**	**0.45**	-0.06	-0.06	0.03	0.01	0.00	-0.21	-0.04	0.22	**0.43**	**0.39**	0.15	-0.03	0.14	-0.02	0.03	-0.01	0.05	**0.61**	0.06	**0.29**	0.03	0.02	0.09	0.20	**0.60**	-0.01	0.00	0.23
EBC	-0.03	**0.62**	**0.77**	**0.28**	**0.88**	1.00	**0.57**	0.01	0.01	0.04	0.06	0.07	-0.13	0.02	**0.43**	**0.44**	**0.55**	0.15	0.02	**0.29**	0.03	0.10	0.08	0.14	**0.68**	0.18	**0.40**	**0.26**	0.05	**0.23**	**0.35**	**0.53**	-0.02	0.05	**0.35**
OC	**0.88**	0.04	-0.03	0.06	-0.05	0.04	1.00	**0.47**	**0.47**	**0.54**	**0.50**	**0.57**	**0.24**	**0.49**	**0.51**	**0.70**	**0.74**	**0.39**	**0.47**	**0.48**	0.10	**0.53**	**0.55**	0.10	**0.61**	**0.23**	**0.68**	**0.42**	**0.50**	**0.46**	**0.41**	**0.41**	0.21	**0.48**	**0.61**
SiO_2	**0.85**	**-0.29**	**-0.25**	-0.05	**-0.31**	**-0.25**	**0.56**	1.00	**1.00**	**0.92**	**0.98**	**0.96**	**0.71**	**0.99**	0.18	**0.32**	0.22	**0.67**	**0.99**	**0.58**	0.10	**0.97**	**0.95**	0.10	**0.28**	0.17	**0.58**	**0.34**	**0.96**	**0.26**	0.05	0.12	**0.44**	**0.93**	**0.36**
Al_2O_3	**0.85**	**-0.29**	**-0.24**	-0.05	**-0.31**	**-0.25**	**0.56**	**1.00**	1.00	**0.92**	**0.98**	**0.96**	**0.71**	**0.99**	0.18	**0.32**	0.22	**0.67**	**0.99**	**0.58**	0.10	**0.97**	**0.95**	0.10	**0.28**	0.17	**0.58**	**0.34**	**0.96**	**0.26**	0.05	0.12	**0.44**	**0.93**	**0.36**
Ca	**0.82**	**-0.39**	**-0.37**	-0.01	**-0.42**	**-0.33**	**0.70**	**0.76**	**0.76**	1.00	**0.89**	**0.92**	**0.63**	**0.91**	0.14	**0.38**	0.22	**0.66**	**0.90**	**0.52**	0.14	**0.92**	**0.91**	0.07	**0.33**	0.17	**0.58**	**0.26**	**0.93**	**0.27**	0.05	0.21	**0.41**	**0.87**	**0.36**
Fe	**0.83**	**-0.27**	-0.21	-0.01	**-0.27**	-0.17	**0.57**	**0.92**	**0.92**	**0.79**	1.00	**0.97**	**0.68**	**0.99**	0.19	**0.33**	**0.24**	**0.72**	**0.99**	**0.56**	0.11	**0.98**	**0.94**	0.04	**0.27**	0.15	**0.55**	**0.29**	**0.94**	**0.24**	0.03	0.17	**0.38**	**0.92**	**0.36**
K	**0.86**	**-0.29**	-0.23	-0.05	**-0.28**	**-0.24**	**0.64**	**0.88**	**0.88**	**0.79**	**0.92**	1.00	**0.66**	**0.96**	0.21	**0.44**	**0.30**	**0.71**	**0.96**	**0.55**	0.13	**0.97**	**0.94**	0.00	**0.31**	0.18	**0.60**	**0.30**	**0.94**	**0.33**	0.04	0.22	**0.38**	**0.91**	**0.43**
Na	**0.39**	-0.20	-0.04	**-0.29**	-0.16	**-0.24**	**0.25**	**0.50**	**0.50**	**0.28**	**0.41**	**0.50**	1.00	**0.72**	0.11	0.06	0.06	**0.48**	**0.66**	**0.38**	**0.31**	**0.65**	**0.63**	**0.36**	0.14	**0.27**	**0.33**	**0.38**	**0.68**	0.08	0.22	-0.11	**0.36**	**0.61**	0.20
Mg	**0.85**	**-0.30**	**-0.25**	-0.04	**-0.32**	**-0.24**	**0.59**	**0.96**	**0.96**	**0.80**	**0.93**	**0.88**	**0.51**	1.00	0.19	**0.33**	**0.23**	**0.69**	**0.99**	**0.58**	0.12	**0.98**	**0.95**	0.10	**0.26**	0.18	**0.57**	**0.32**	**0.95**	**0.24**	0.06	0.12	**0.42**	**0.93**	**0.36**
SO_4^{2-}	0.12	**0.36**	**0.45**	**0.31**	**0.52**	**0.48**	0.04	-0.05	-0.05	**-0.29**	-0.09	-0.03	-0.02	-0.08	1.00	**0.25**	**0.72**	0.10	0.17	**0.69**	-0.01	0.17	**0.24**	0.06	**0.33**	0.04	**0.59**	**0.75**	0.16	**0.29**	**0.34**	0.07	-0.07	0.18	**0.47**
NO_3^-	**0.24**	**0.43**	**0.33**	**0.34**	**0.43**	**0.44**	**0.25**	-0.02	-0.02	-0.07	-0.04	0.04	-0.07	-0.04	**0.52**	1.00	**0.80**	**0.29**	**0.33**	**0.31**	0.14	**0.40**	**0.45**	0.00	**0.49**	**0.28**	**0.61**	0.20	**0.33**	**0.50**	**0.23**	**0.55**	**0.23**	**0.35**	**0.59**
NH_4^+	0.04	**0.45**	**0.47**	**0.31**	**0.57**	**0.50**	0.02	-0.18	-0.18	**-0.34**	-0.20	-0.15	-0.02	-0.21	**0.92**	**0.63**	1.00	0.18	0.22	**0.53**	0.06	**0.26**	**0.34**	0.07	**0.48**	0.20	**0.65**	**0.53**	0.20	**0.49**	**0.37**	**0.37**	0.08	**0.23**	**0.61**
Li	**0.77**	**-0.34**	**-0.29**	-0.06	**-0.35**	**-0.30**	**0.51**	**0.89**	**0.89**	**0.76**	**0.96**	**0.91**	**0.45**	**0.89**	-0.14	-0.10	**-0.24**	1.00	**0.71**	**0.31**	0.04	**0.70**	**0.65**	0.03	0.19	0.16	**0.33**	0.08	**0.71**	0.16	-0.03	0.11	**0.27**	**0.65**	**0.36**
Ti	**0.86**	**-0.29**	**-0.31**	-0.01	**-0.38**	**-0.27**	**0.63**	**0.91**	**0.91**	**0.83**	**0.95**	**0.91**	**0.45**	**0.93**	-0.13	-0.04	**-0.23**	**0.94**	1.00	**0.55**	0.09	**0.97**	**0.94**	0.03	**0.25**	0.16	**0.55**	**0.30**	**0.95**	**0.24**	0.01	0.15	**0.40**	**0.94**	**0.36**
V	**0.36**	0.18	**0.38**	0.19	**0.39**	**0.36**	0.17	**0.26**	**0.26**	0.07	**0.24**	**0.27**	0.15	**0.24**	**0.73**	**0.46**	**0.66**	0.19	**0.24**	1.00	0.01	**0.57**	**0.62**	0.17	**0.27**	0.10	**0.66**	**0.76**	**0.52**	0.21	0.21	0.05	0.17	**0.53**	**0.42**
Cr	**0.30**	-0.17	-0.19	-0.03	-0.22	-0.15	0.20	**0.30**	**0.30**	**0.39**	**0.33**	**0.42**	0.09	**0.28**	-0.10	0.01	-0.14	**0.29**	**0.32**	0.06	1.00	0.15	0.19	**0.38**	**0.34**	**0.37**	0.18	0.05	0.13	**0.25**	**0.48**	0.19	0.11	0.13	**0.28**
Mn	**0.81**	**-0.26**	-0.20	0.00	**-0.26**	-0.17	**0.54**	**0.90**	**0.90**	**0.77**	**0.95**	**0.89**	**0.41**	**0.89**	-0.07	-0.01	-0.18	**0.91**	**0.93**	**0.30**	**0.36**	1.00	**0.95**	0.07	**0.35**	0.22	**0.64**	**0.28**	**0.96**	**0.28**	0.06	0.20	**0.41**	**0.93**	**0.43**
Co	**0.67**	-0.13	-0.05	0.09	-0.04	-0.09	**0.54**	**0.64**	**0.64**	**0.58**	**0.70**	**0.71**	**0.29**	**0.64**	0.01	0.11	-0.09	**0.66**	**0.71**	**0.29**	**0.29**	**0.71**	1.00	0.11	**0.35**	0.22	**0.64**	**0.37**	**0.93**	**0.35**	0.12	0.19	**0.47**	**0.91**	**0.45**
Ni	0.12	**0.23**	0.22	0.01	0.21	**0.23**	0.05	0.12	0.12	-0.03	-0.05	-0.08	0.21	0.06	**0.26**	0.15	**0.25**	-0.07	0.02	**0.43**	-0.07	0.05	0.02	1.00	**0.30**	**0.58**	0.16	**0.27**	0.17	0.10	**0.66**	-0.08	**0.59**	0.04	0.11
Cu	**0.39**	**0.27**	**0.31**	0.15	**0.37**	**0.49**	**0.34**	**0.26**	**0.26**	0.20	**0.25**	**0.24**	0.15	0.22	0.21	**0.28**	0.21	0.12	**0.24**	**0.27**	**0.29**	**0.33**	**0.26**	**0.42**	1.00	**0.49**	**0.69**	**0.29**	**0.34**	**0.50**	**0.59**	**0.63**	**0.35**	**0.28**	**0.68**
Zn	**0.27**	0.02	0.03	0.17	0.07	0.06	**0.29**	0.14	0.14	0.22	0.11	0.16	0.09	0.13	0.13	**0.24**	0.15	0.04	0.19	**0.27**	0.20	**0.23**	0.22	**0.35**	**0.38**	1.00	**0.35**	0.14	**0.24**	0.17	**0.54**	**0.23**	**0.63**	0.19	**0.55**
As	**0.56**	0.14	0.15	**0.28**	0.21	**0.26**	**0.36**	**0.47**	**0.47**	**0.27**	**0.42**	**0.45**	0.22	**0.42**	**0.56**	**0.55**	**0.51**	**0.33**	**0.41**	**0.65**	**0.29**	**0.51**	**0.40**	**0.33**	**0.61**	**0.40**	1.00	**0.57**	**0.59**	**0.58**	**0.42**	**0.37**	**0.31**	**0.56**	**0.76**
Se	0.02	**0.26**	**0.35**	**0.24**	**0.37**	**0.33**	-0.08	-0.06	-0.06	**-0.23**	-0.10	-0.04	0.18	-0.08	**0.69**	**0.34**	**0.67**	-0.12	-0.05	**0.75**	-0.02	-0.01	0.09	**0.49**	**0.30**	**0.23**	**0.53**	1.00	**0.31**	0.22	**0.34**	-0.01	0.12	**0.26**	**0.42**
Sr	**0.84**	**-0.23**	**-0.27**	-0.02	**-0.35**	**-0.23**	**0.72**	**0.77**	**0.77**	**0.88**	**0.74**	**0.77**	**0.35**	**0.80**	-0.18	-0.04	**-0.28**	**0.69**	**0.83**	0.15	**0.40**	**0.77**	**0.57**	0.16	**0.38**	**0.32**	**0.40**	-0.04	1.00	**0.28**	0.07	0.15	**0.50**	**0.91**	**0.38**
Cd	**0.24**	**0.24**	0.13	0.23	**0.24**	**0.24**	**0.26**	0.07	0.07	0.06	0.08	0.15	0.01	0.03	**0.31**	**0.37**	**0.33**	0.07	0.13	0.18	0.21	0.16	**0.29**	0.09	**0.61**	**0.23**	**0.56**	**0.34**	0.19	1.00	**0.36**	**0.36**	0.19	**0.31**	**0.56**
Sn	0.12	**0.25**	**0.44**	0.17	**0.54**	**0.49**	0.14	-0.06	-0.06	-0.11	-0.11	-0.08	-0.06	-0.10	**0.52**	**0.26**	**0.48**	-0.17	-0.13	**0.37**	-0.03	-0.10	0.00	**0.38**	**0.53**	**0.26**	**0.45**	**0.38**	0.04	**0.52**	1.00	**0.25**	**0.37**	0.04	**0.49**
Sb	0.03	0.22	**0.29**	**0.42**	**0.43**	**0.51**	0.06	-0.11	-0.11	-0.09	0.00	-0.04	**-0.32**	-0.12	0.10	**0.36**	0.13	-0.10	-0.07	0.16	0.11	0.03	0.02	-0.01	**0.44**	**0.26**	**0.35**	0.05	0.01	**0.38**	**0.42**	1.00	0.17	0.21	**0.47**
Ba	**0.37**	-0.08	-0.10	0.00	-0.11	-0.08	**0.24**	**0.39**	**0.39**	**0.40**	**0.37**	**0.38**	0.15	**0.38**	-0.08	-0.03	-0.12	**0.34**	**0.42**	0.11	**0.32**	**0.38**	**0.31**	**0.30**	**0.42**	**0.44**	**0.30**	0.03	**0.53**	0.19	**0.31**	0.17	1.00	**0.40**	**0.28**
La	**0.79**	**-0.29**	**-0.27**	-0.01	**-0.32**	**-0.22**	**0.51**	**0.90**	**0.90**	**0.74**	**0.91**	**0.86**	**0.40**	**0.86**	-0.05	-0.01	-0.16	**0.90**	**0.91**	**0.26**	**0.35**	**0.93**	**0.67**	0.01	**0.26**	0.16	**0.51**	-0.03	**0.74**	0.20	-0.05	0.01	**0.41**	1.00	**0.41**
Pb	**0.38**	0.17	0.07	**0.31**	0.18	**0.24**	**0.30**	**0.25**	**0.25**	0.17	**0.27**	**0.30**	0.00	0.21	**0.46**	**0.42**	**0.44**	0.19	**0.23**	**0.48**	**0.24**	**0.31**	0.19	**0.23**	**0.52**	**0.49**	**0.73**	**0.38**	**0.26**	**0.52**	**0.43**	**0.44**	0.18	**0.28**	1.00

Table S3. Indoor and outdoor average concentrations for PM2.5 elements for various schools in Europe (w=winter samples; s=summer samples).

Source	Location	Nº schools	Sampling time	Season	Indoor Concentration (BREATHE/other ratio)*									
					K[a]	Ca[a]	Fe[a]	V[b]	Cr[b]	Ni[b]	Cu[b]	Zn[b]	Pb[b]	As[b]
Molnár et al. (2007)	Stockholm, Sweden	5	8-16h		0.14 (2.6)	0.12 (13)	0.14 (3.0)	2.6 (1.9)	1.7 (2.2)	1.1 (2.3)	2.3 (3.6)	17 (3.1)	2.5 (2.9)	
Zwoździak et al. (2013)	Wroclaw, Poland	1	24h	S	0.14 (2.2)	0.26 (4.1)	0.13 (2.7)		2.5 (1.2)	1.3 (2.6)	36 (0.2)	46 (1.2)	34 (0.2)	2.0 (0.3)
				W	0.83 (0.5)	2.2 (0.8)	0.53 (0.9)		6.6 (0.6)	2.4 (0.9)	50 (0.2)	267 (0.2)	85 (0.1)	4.0 (0.1)
Stranger et al. (2008)	Antwerp, Belgium	15 (urban)	8-20h	S	0.55 (0.6)	2.8 (0.4)	0.72 (0.5)	24 (0.3)	13 (0.2)	8.1 (0.4)	30 (0.3)	97 (0.6)	64 (0.1)	
				W	0.36 (1.1)	2.2 (0.8)	0.38 (1.2)	3.8 (1.0)	8.6 (0.5)	3.7 (0.6)	13 (0.6)	54 (1.0)	43 (0.2)	
This study	Barcelona, Spain	39	9-17h		0.37	1.6	0.42	4.9	3.8	2.6	8.2	52	7.3	0.46
				S	0.31	1.1	0.34	6.7	3.0	3.4	8.8	54	7.8	0.53
				W	0.40	1.8	0.47	3.8	4.3	2.1	7.8	52	7.1	0.41
					Outdoor Concentration (BREATHE/other ratio)*									
					K[a]	Ca[a]	Fe[a]	V[b]	Cr[b]	Ni[b]	Cu[b]	Zn[b]	Pb[b]	As[b]
Molnár et al. (2007)	Stockholm, Sweden	5	8-16h		0.09 (4.4)	0.05 (18)	0.14 (4.1)	3.1 (1.9)	1.2 (2.9)	1.5 (2.2)	4.9 (1.8)	19 (2.9)	4.6 (1.8)	
Zwoździak et al. (2013)	Wroclaw, Poland	1	24h	S	0.11 (3.3)	0.09 (7.5)	0.08 (6.8)		1.6 (2.2)	0.70 (6.0)	20 (0.5)	43 (1.3)	27 (0.3)	1.2 (0.5)
				W	0.53 (0.8)	0.16 (5.7)	0.22 (2.8)		4.3 (0.8)	4.0 (0.7)	40 (0.2)	227 (0.2)	81 (0.1)	4.9 (0.1)
Stranger et al. (2008)	Antwerp, Belgium	15 (urban)	8-20h	S	0.52 (0.7)	2.5 (0.3)	1.4 (0.4)	25 (0.3)	13 (0.3)	9.3 (0.5)	27 (0.3)	108 (0.5)	55 (0.1)	
				W	0.20 (2.1)	0.64 (1.4)	0.39 (1.5)	5.3 (0.9)	11 (0.3)	3.5 (0.8)	16 (0.5)	60 (0.9)	51 (0.2)	
This study	Barcelona, Spain	39	9-17h		0.40	0.82	0.58	5.9	3.4	3.3	8.8	55	8.1	0.50
				S	0.36	0.67	0.53	7.6	3.5	4.2	9.2	54	8.1	0.56
				W	0.42	0.90	0.60	5.0	3.4	2.9	8.6	56	8.1	0.47

[a] $\mu g \cdot m^{-3}$ (dimensionless)
[b] $ng \cdot m^{-3}$ (dimensionless)
* Ratio between the concentration of the considered element in this study BREATHE and the concentration found in the study to which it is compared.

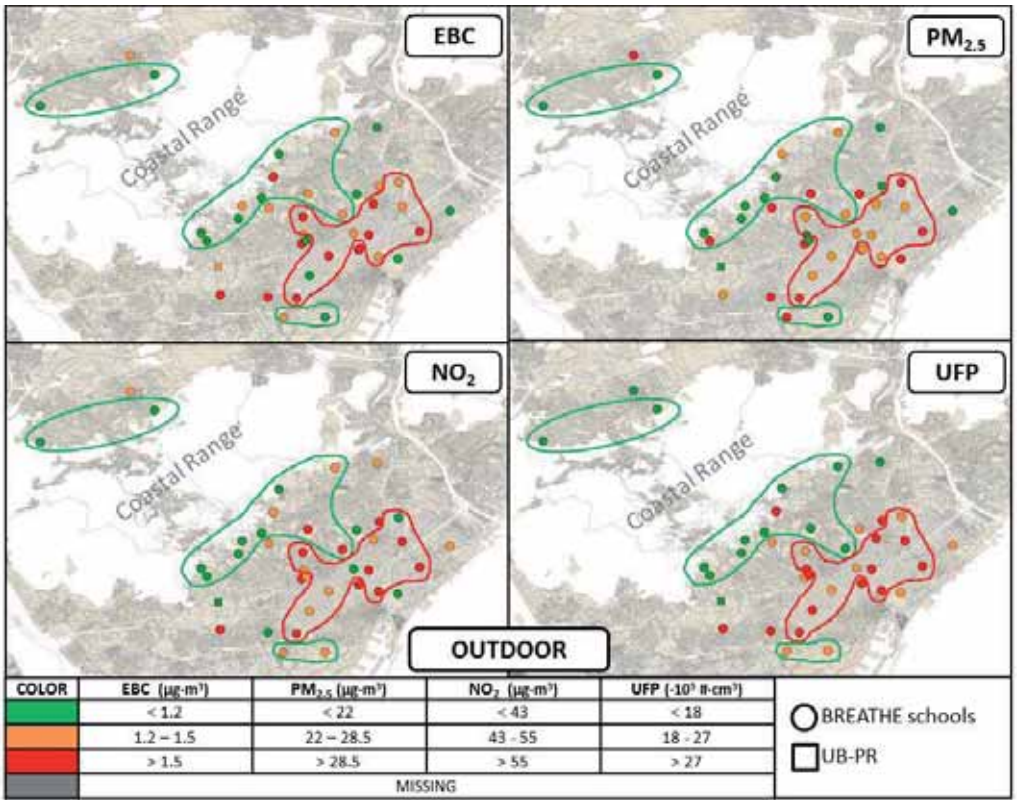

Figure S1a. Spatial distribution of not seasonally adjusted outdoor levels of NO2, PM2.5, EBC and UFP in the BREATHE school. Perimeters are based on deseasonalised outdoor EBC concentration.

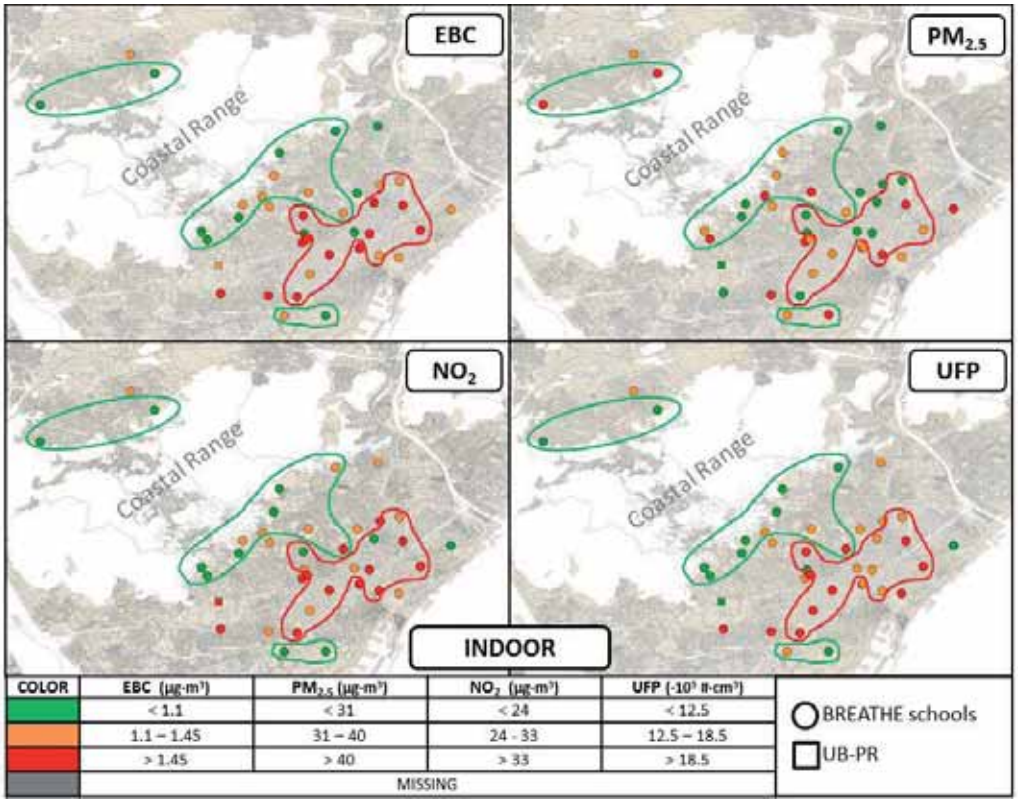

Figure S1b. Spatial distribution of not seasonally adjusted indoor levels of NO2, PM2.5, EBC and UFP in the BREATHE schools. Perimeters are based on deseasonalised outdoor EBC concentration.

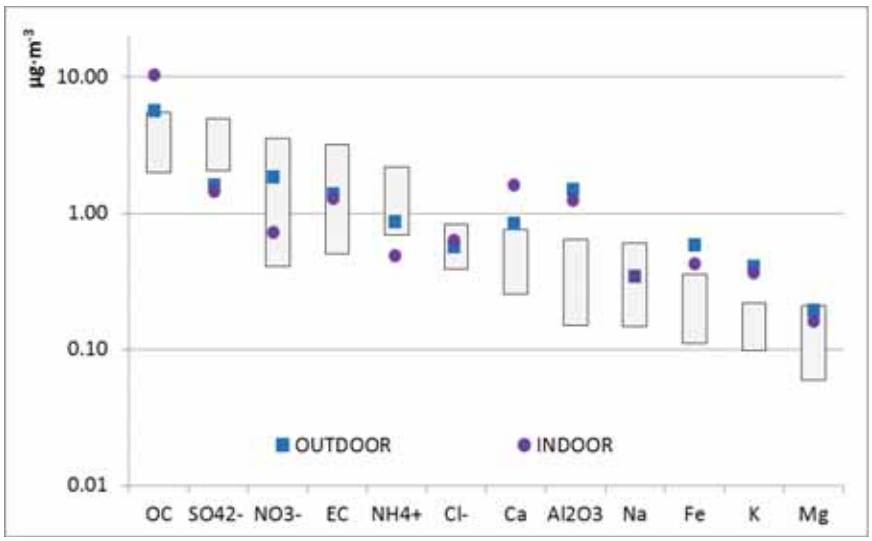

Figure S2a. Bars show the range of annual concentrations of major elements in Spain (Querol et al., 2008). Average indoor and outdoor concentrations at schools are shown.

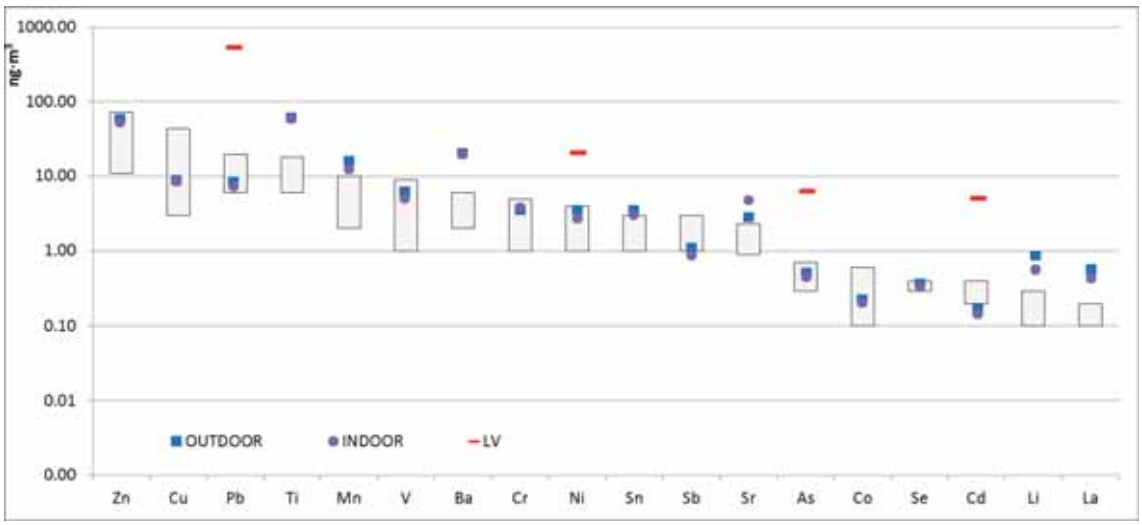

Figure S2b. Bars show the range of annual concentrations of trace elements in Spain (Querol et al., 2007). Average indoor and outdoor concentrations at schools are shown. Red lines indicate the limit or objective value of Directives 2008/50/EC and 2004/107/EC.

3.2. Sources of indoor and outdoor $PM_{2.5}$ concentrations in primary schools

Authors:

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Sources of indoor and outdoor PM2.5 concentrations in primary schools

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HIGHLIGHTS

- We collected PM2.5 samples at indoor and outdoor environments of 39 primary schools.
- Seven outdoor sources and two children-activity-related sources were identified.
- In classrooms, 47% of PM2.5 was indoor generated, mostly organics.
- Unpaved playgrounds increased PM concentrations in classrooms by 5–6 μg/m^3.
- Traffic contributions were higher at classrooms with windows oriented directly to the street.

GRAPHICAL ABSTRACT

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ABSTRACT

Children spend a third of their day in the classroom, where air pollution levels may differ substantially from those outdoors due to specific indoor sources. Air pollution exposure assessments based on atmospheric particle mass measured outdoors may therefore have little to do with the daily PM dose received by school children. This study aims to investigate outdoor and indoor sources of PM2.5 measured at 39 primary schools in Barcelona during 2012. On average 47% of indoor PM2.5 measured concentrations was found to be generated indoors due to continuous resuspension of soil particles (13%) and a mixed source (34%) comprising organic (skin flakes, clothes fibers, possible condensation of VOCs) and Ca-rich particles (from chalk and building deterioration). Emissions from seven outdoor sources penetrated easily indoors being responsible for the remaining 53% of measured PM2.5 indoors. Unpaved playgrounds were found to increase mineral contributions in classrooms by 5–6 μg/m^3 on average with respect to schools with paved playgrounds. Weekday traffic contributions varied considerably across Barcelona within ranges of 1–14 μg/m^3 outdoor and 1–10 μg/m^3 indoor. Indoors, traffic contributions were significantly higher (more than twofold) for classrooms with windows oriented directly to the street, rather than to the interior of the block or to playgrounds. This highlights the importance of urban planning in order to reduce children's exposure to traffic emissions.

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1. Introduction

Recently the European Environmental Agency (EEA, 2013) reported that 20–31% of the urban population in the EU region is exposed to PM2.5 concentrations (2009–2011) above the EU reference level (25 μg/m^3) and 91–96% above the WHO PM2.5 guideline (10 μg/m^3). Long-term studies have already shown associations between PM concentrations and population mortality also at levels well below the WHO guideline level for PM2.5, without evidence of a threshold of exposure to PM below which no adverse health effects would be anticipated (WHO, 2006a,b, 2013).

Routine pollutants measurements, which are commonly used in epidemiological studies, may not provide a good characterization of personal exposure (Nerriere et al., 2005; Kornartit et al., 2010). Exposure studies should take into account that adults spend approximately 60–80% of their time indoors (Klepeis et al., 2001), and in the case of children at least a third of their day is spent in the classroom, where PM levels may vary substantially from outdoors due to building insulation, indoor sources and resuspension. In fact, indoor-generated PM may represent a significant fraction of total exposure. Health effects are expected to be much more marked in children, who inhale a higher normalized dose of airborne particles compared to adults, due to both their lung capacity and higher breathing rates for physical activity (Burtscher and Schüepp, 2012; Bateson and Schwartz, 2010; Pinkerton and Joad, 2006; Buonanno et al., 2011, 2012). PM exposures are linked to cognitive deficits, oxidative stress, neuroinflammation and neurodegeneration (Calderón-Garcidueñas et al., 2013). Several individual metals including aluminum, arsenic, cadmium, lead, manganese, and mercury have been demonstrated to affect the neurological system (Pohl et al., 2011), and general accumulation of metal ions in the brain contributes to heightened oxidative stress and neuronal damage (Zatta et al., 2008; Bolognin et al., 2009).

Investigating the levels and sources of atmospheric particulate matter (PM) pollution in primary schools and understanding their role in child health is therefore one of the challenges of our time. Only few studies reported inorganic chemical analysis of PM2.5 indoors and generally are based on few elements and the samples are collected on a few schools (Molnár et al., 2007; Zwoździak et al., 2013; Stranger et al., 2008). To our knowledge there are no studies of source apportionment at indoor and outdoor environment at schools. The BREATHE project (BRain dEvelopment and Air polluTion ultrafine particles in scHool chIdrEn), funded by the European Research Council (ERC Advanced Grant), aims at studying the impact of urban air pollution on the cognitive development of children. The project involves 2904 children attending second, third and fourth grades at 39 primary schools in Barcelona (NE of Spain) which are characterized by contrasting air pollution levels.

In the framework of the BREATHE project, this study aimed to identify major sources of PM2.5 and their contributions based on PM2.5 source apportionment analysis performed indoor (in classrooms with pupils), outdoor (in the playground) and at a reference background station in order to enable source-related studies on children health outcomes. This will supply the source contributions data needed for further epidemiological studies within BREATHE.

2. Methods

PM2.5 filter sampling was carried out over one year (February 2012–February 2013) at 39 primary schools in the Barcelona metropolitan area (identified with numbers from 1 to 40 in Fig. 1, Rivas et al., in press). Thirty-six schools were located in the city of Barcelona (1.6 million inhab.) and 3 in the municipality of Sant Cugat (89,000 inhab.), only 7 km away but separated from Barcelona by the Collserola range (512 m. a.s.l.). The sampling schedule was interrupted during summer school holidays: July and August 2012. The sampling instruments were installed simultaneously at two schools per week, two times during the school year. The indoor and outdoor samplers were always installed in a classroom and in the playground respectively. The orientation (courtyard- or street-facing) and altitude (street level to 4th or 5th storey) of both classroom and playground can also vary. Possible effects on source contributions due to these factors will be explored in this study. In addition 24 h PM2.5 samples were available from a fixed monitoring station (Palau Reial, the only monitoring site of the local network where PM2.5 samples are routinely analyzed) as a reference urban background site, collecting every 4th day during the whole study. Samples were collected onto Pallflex quartz fibre filters (15 cm diameter) by means of high volume (30 m^3/h) MCV samplers four times a week (Monday to Thursday schooldays, plus 10 holiday samples) for 8 h of each day (from 9 am to 5 pm, being children at classroom for about 80% of the time). Before sampling, filters were pre-baked at 205 °C during 5 h and conditioned for 48 h at 20 °C and 50% relative humidity. Weights of blank filters were measured three times every 24 h by means of a Sartorius LA 130 S-F microbalance (1 μg sensitivity). After sampling, filters were brought back to the laboratory to be weighed three more times every 24 h under the same temperature and relative humidity conditions of the first weighing. Once the weights of samples had been determined, filters were subjected to several analytical treatments. A quarter of each filter was acid digested (5 ml HF, 2.5 ml HNO_3, 2.5 ml $HClO_4$) for the determination of major and trace elements and analyzed by inductively coupled plasma mass spectrometry and atomic emission spectrometry, respectively (ICP-MS and ICP-AES) (Querol et al., 2001). A quarter of the filter was leached in 20 ml of bi-distilled water for the extraction of water-soluble ions and subsequent analysis by ion chromatography (IC) for sulfate, nitrate and chloride and by specific electrode for ammonium. Finally, a section of 1.5 cm^2 from the remaining half of the filter was used for the determination of organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyzer with the NIOSH temperature program. Total carbon (TC) was determined as the sum of OC and EC. In every case blank concentrations were subtracted for determining final concentrations in samples.

A constrained Positive Matrix Factorization (PMF) model was used for source apportionment. PMF is a weighted least-squares method so that individual estimates of the uncertainty in each data value are needed. The uncertainty estimates were based on the approach by Amato et al. (2009) and provided a criterion to separate the species which retain a significant signal from the ones dominated by noise. This criterion is based on the signal-to-noise S/N ratio defined by Paatero and Hopke (2003). Species with S/N < 2 are generally defined as weak variables and downweighted by a factor of 3. Nevertheless, since S/N is very sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit was used as complementary criterion. The combination of both criteria permitted the selection of 31 strong species and 2 weak species (Ba and Sn) out of the 61 available species for the PMF analysis. After preliminary tests where PMF was performed separately for indoor and outdoor samples, the best solution was found when gathering indoor and outdoor PM samples from all schools into a single array. Also, the 24-h samples collected at the Palau Reial urban background reference station were included. This data assembling method showed the most satisfactory results for factor profiles since it allowed exploration of a larger area of the N-dimensional source contributions space. The data matrix was uncensored, i.e. negative, zero and below detection limit (BDL) values were included as such in the analyses to avoid a bias in the results (Paatero, 2007). A total of 683 samples were included in the PMF: 577 from schools (47 samples were lost due to power or instrument failures) and 106 from the Palau Reial station. PMF was run by means of the Multilinear Engine program which allowed the handling of *a priori* information such as the source profile of local road dust (average of city centre samples, as reported by Amato et al., 2009) and sea spray (SPECIATE database) in form of targets for pulling equations (Paatero and Hopke, 2009). A bootstrap technique was implemented in the script

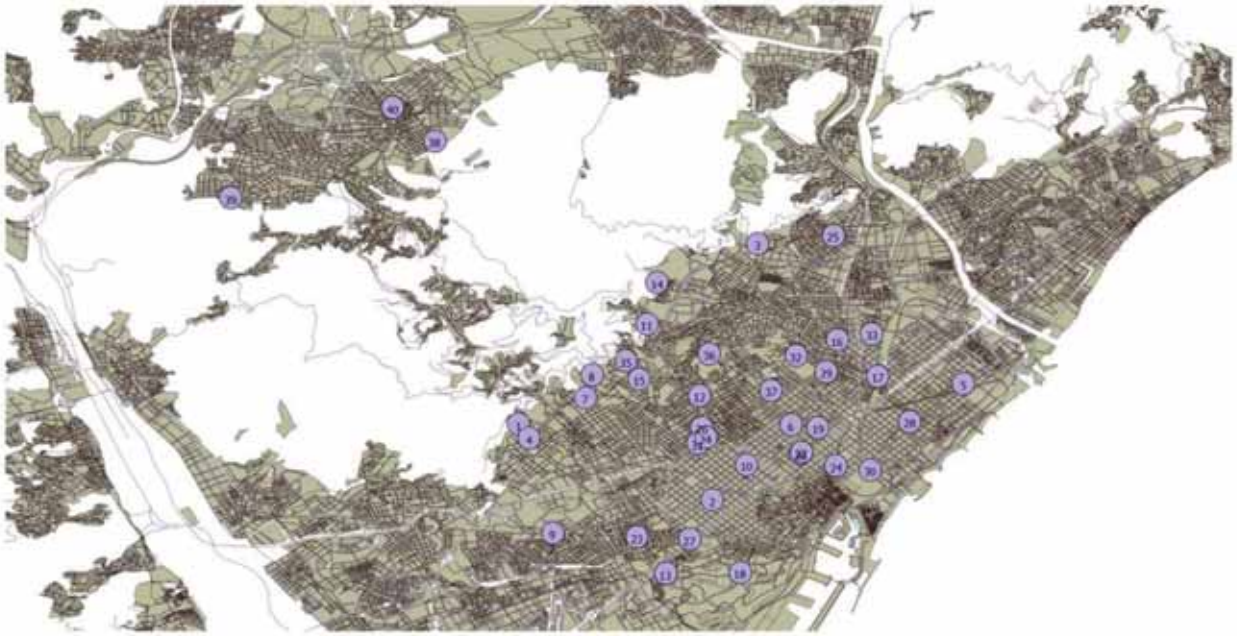

Fig. 1. Map of 39 schools under study, with number identifier.

file of ME-2 in order to estimate the uncertainties of factor profiles, inspired by one of the available techniques from the EPA PMF v3.0 script. It consisted of three different steps: re-sampling, reweighting and random rotational pulling (Tukey, 1958; Efron and Tibshirani, 1986).

3. Results and discussion

During our study PM2.5 concentrations (8-h averages) varied across a range of 1–192 μg/m^3 outdoor and 7–105 μg/m^3 indoor, while the reference background station varied within 6–59 μg/m^3 (average 17 μg/m^3). This manuscript deals principally with PM2.5 source apportionment, the physicochemical variability of PM and other pollutants having already been discussed in Rivas et al. (2014), Viana et al. (2014) and Moreno et al. (2014). The distribution of residuals, G-space plots, F peak values and Q values were explored for solutions with number of factors varying between 3 and 11. The most reliable solution identified 9 main factors/sources responsible for the indoor and outdoor variability of PM2.5 concentrations, showing $r^2 = 0.95$ between observed mass and the sum of source contributions. Eight factors correspond to well-known sources of PM in the study area (Querol et al., 2001, 2004; Amato et al., 2009; Reche et al., 2012a,b), while the ninth factor was identified for the first time and related to children activity, mainly indoor. The nine sources were identified as: Mineral (MIN), Organic/Textile/Chalk (OTC), Traffic (TRA), Secondary Sulfate & Organics (SSO), Secondary Nitrate (SNI), Road Dust (ROD), Metallurgy (MET), Sea Spray (SEA) and Heavy Oil Combustion (HOC) (Figs. 2 and 3 and Fig. S1 in Supporting Information). Some of these sources impact differently depending on children's activities at schools (MIN and OTC), some on the location and characteristics of the school (TRA, ROD and MIN), whereas others reflect the urban background cocktail (SSO, SNI, MET, SEA and HOC) driven primarily by meteorology (sampling periods covered different times of the year for different schools). The analysis of the spatial variability of source contributions is hampered by the meteorology and the questionable deseasonalization of source contributions, since MIN and OTC were mainly influenced by children activity. Therefore we carried out a comparison for school pairs (one school close and the other far from dense traffic roads), given that at each school samplings were performed simultaneously to another school, enabling us to explore the impact of location and orientation of classroom and paved/unpaved playgrounds.

The Mineral factor (MIN) was identified by the typical crustal species such as Al, Mg, Li, Fe, Ca, Ti and Rb (Fig. S2 in Supporting Information), as a mixture of several sources, including suspension from unpaved playgrounds but also dust from urban works and natural soil resuspension. This source showed the largest variability between schools. Schools with a paved playground showed average contributions of 2.5 μg/m^3 and 3.6 μg/m^3 outdoors and indoors respectively, schools with unpaved playground showed values of 16.0 μg/m^3 and 9.1 μg/m^3 respectively. Indoor contributions were, in >50% of days and >50% of schools, higher than those outdoors, regardless of type of playground, due to continuous resuspension of deposited particles indoors. This highlights the importance of cleaning activities in classroom, which should be monitored in future studies. Indoor contributions were also affected by the orientation of the classroom (Fig. 4) relative to the unpaved playground, with maxima daily contributions (41 μg/m^3) in classrooms adjacent to an interior playground; however the median value (7.0–8.1 μg/m^3) was substantially independent of the orientation (Fig. 4). Where playgrounds were paved, MIN contributions predictably demonstrated much lower background mineral dust contributions (daily median within 1.4–2.4 μg/m^3), with higher values indoors, particularly in street-adjacent classrooms. Much lower average contributions (0.6 μg/m^3) were recorded at the urban background site (Fig. 3) for the study period, although this average covers a longer sampling interval (24 h), including night (cleaner) hours. When the two schools simultaneously monitored had paved playgrounds, outdoor and indoor MIN contributions were similar and quite well correlated between school pairs (i.e. 5–24, 3–37, 23–27, 7–34, Fig. S3a in Supporting Information) showing the homogenized nature of urban background contributions. If any of the two school playgrounds was unpaved no correlation was generally found outdoors or indoors, with the exception of sampling during an African dust event which homogenized airborne mineral dust across the city, or where the classroom was located away from the unpaved playground.

The second factor consists of a mixture of organic carbon (OC) from skin flakes, cotton fibers from clothing and other organic material, and a

Ca-rich component from chalk and deterioration of building materials (Fromme et al., 2008). It was therefore labelled as Organic/Textile/Chalk (OTC). This source also explains the high variation in Sr concentrations (Fig. S2), due to its common substitution for Ca atoms in $CaCO_3$ (used for chalk). This is the largest source of PM2.5 in classrooms, contributing on average 16 ± 10 μg/m³ (45% of indoor PM2.5), similar to the annual bulk ambient PM2.5 urban background concentrations in the city of Barcelona, and having rather similar contributions between the different schools (Fig. 5). Outdoor, this source is still significant (16% on average) due to the numerous children activities in the playground (sport, breakfast, playing, etc.). A near-zero contribution from this source was found at the Palau Reial outdoor urban background site. OTC contributions are generally not correlated with any other source, with the exception of the MIN contributions indoor ($r^2 = 0.7$ only for classrooms oriented to an exterior unpaved playground, Fig. S3b in Supporting Information), revealing a possible relation of both sources with the number/activity of children. Another possible explanation is that playground soil is the carrier of organic material as well, suggested also by the higher OTC contributions at schools with unpaved playground than simultaneous contributions at schools with paved playground.

Surprisingly, there are cases of good correlation of OTC contributions between different schools in spite of large discrepancies in absolute terms (μg/m³):

- Simultaneously outdoor and indoor at the school pair sampled during atmospheric stability in coincidence with a Saharan dust intrusion during 18th–22nd October 2012 ($r^2 = 0.54$–0.92, Fig. S3c in Supporting Information), and a pair sampled during an Atlantic advection of air masses ($r^2 = 0.50$–0.92);
- Only indoor at 2 pairs during an Atlantic-European advection ($r^2 = 0.95$) and Atlantic advection and regional recirculation ($r^2 = 0.58$). In both cases indoor contributions were above 15 μg/m³.
- Only outdoor at 5 different pairs, all sampled during March.

The reasons of the unexpected correlations remain unclear.

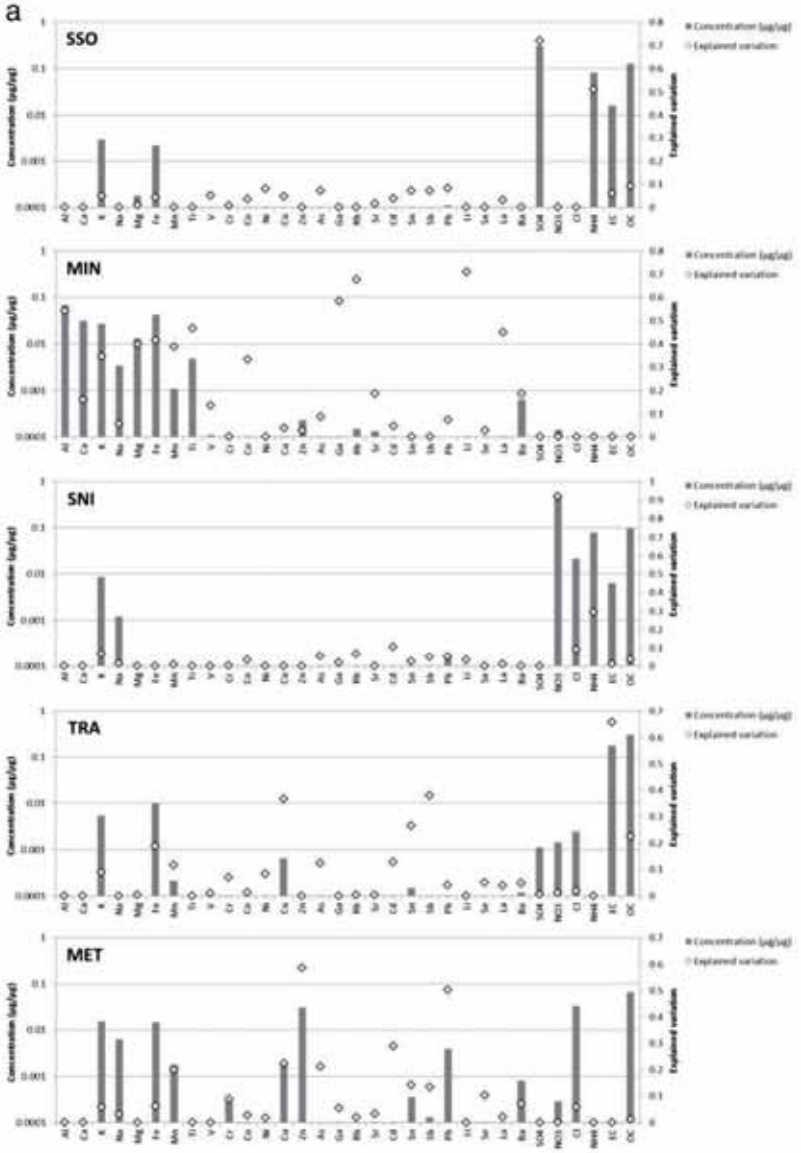

Fig. 2. a: PMF source profiles identified at primary schools in Barcelona.

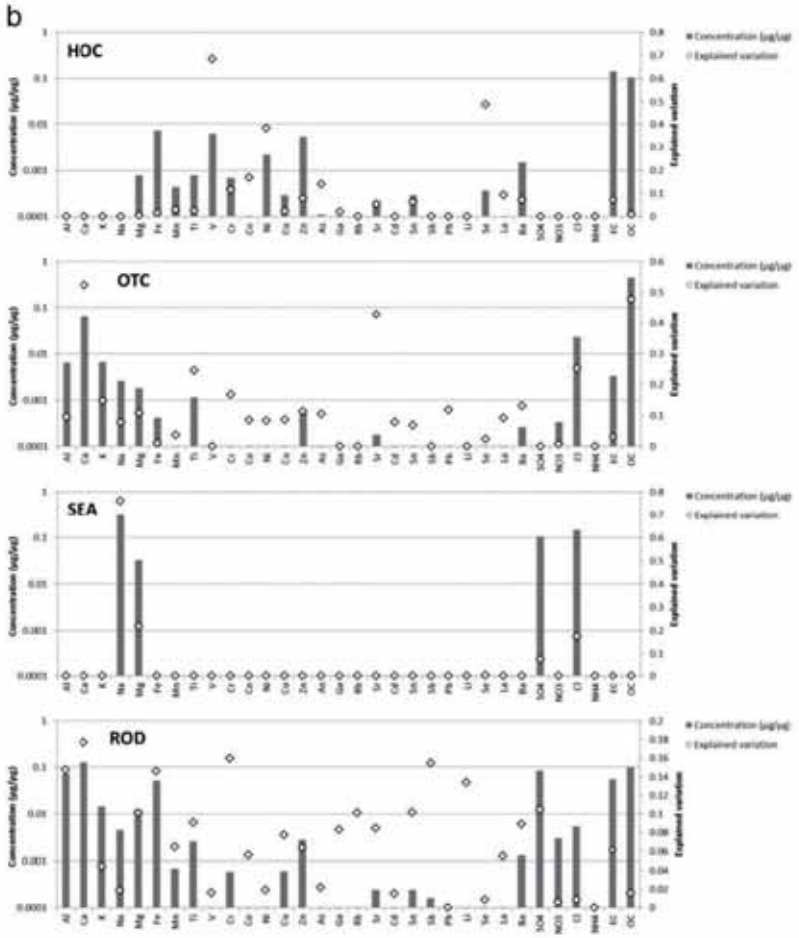

Fig. 2 (*continued*).

The Traffic factor (TRA) comprises organic particles from motor exhaust, as well as elemental carbon (EC) and metals from brake wear (Cu, Sb, Sn and Fe, Fig. 2 and Fig. S2). The ratio OC/EC of 1.7 is typical of traffic monitoring sites, accounting also for secondary organic aerosols (Querol et al., 2013; Turpin and Huntzicker, 1995). Average source contributions were 5.5 ± 4.2 μg/m^3 and 4.8 ± 3.9 μg/m^3 outdoors and indoors, respectively. Similar contributions were estimated at the urban background site 4.1 ± 2.7 μg/m^3 (which is averaged over 24 h). Out of 281 pairs of simultaneous samplings (indoor and outdoor), traffic contributions were higher outdoors in 182 cases. In the rest of the cases, indoor concentrations were higher than those outdoors probably due to:

- The orientation of the classroom directly to the street and the position of the outdoor sampler facing the interior of the block;
- The location of the indoor sampler at a lower floor with respect to the outdoor sampler;
- A combination of the two;
- Indoor resuspension of traffic-related PM;
- Precipitation scavenging outdoor pollution.

However, there were also cases in which outdoor concentrations were higher than indoor with the above conditions.

Thus, TRA contributions were investigated in relation to the orientation of outdoor and indoor samplers. To this end, an adjustment to the indoor and outdoor contributions was carried out using black carbon (BC) data from the Palau Reial urban background site. The adjusted contribution $(C_k^j)^*$ for jth school the kth day at one school was calculated as:

$$\left(C_k^j\right)^* = \left(C_k^j\right) / \left(\left(BC_k^{PR}\right) / \left(\overline{BC^{PR}}\right)\right)$$

where (C_k^j) is the raw TRA contribution at the jth school, BC_k^{PR} and $\left(\overline{BC^{PR}}\right)$ are the 8-h and campaign BC averages at the Palau Reial station, respectively. After adjustment, proximity to street axis increased TRA contributions, as shown in Fig. 6.

The median contribution at outdoor receptors oriented to street (5.6 μg/m^3) was 50% higher than the median at those oriented to the interior of the block (3.7 μg/m^3). This increase was even clearer inside the classroom, with an increasing factor of 2.4 between playground-oriented (2.8 μg/m^3) and street-oriented classroom (6.8 μg/m^3); an intermediate case is represented by classrooms oriented to an exterior playground (3.6 μg/m^3). TRA contributions between school pairs are in general well correlated (Fig. S3d in Supporting Information), although absolute contributions can differ by a factor up to 4 indicating that vehicle exhaust contributions vary similarly across the city, including hotspots. In a few cases, the correlation outdoor was not good due to the uphill position of some schools. Infiltration and classroom orientation may also be responsible for low correlations indoors between some of the school pairs.

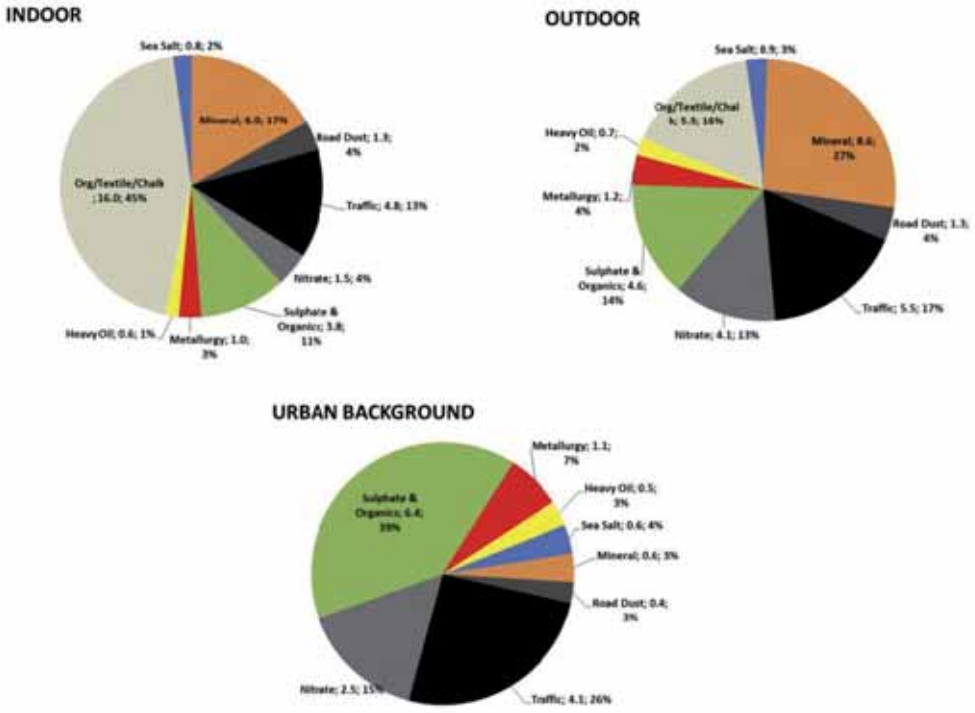

Fig. 3. Average source contributions indoors, outdoors and at the reference background station (different sampling interval).

The Secondary Sulfate & Organics (SSO) factor, traced by SO_4^{2-} and NH_4^+, is the result of the formation of secondary sulfate in the atmosphere from the photochemical oxidation of regionally emitted gaseous sulfur oxides (mostly from shipping and industrial activities in this region) and from long range transport. Condensation of volatile organic compounds is suggested by the high content of OC (13%) in the factor profile and may be responsible for the higher average contribution at the Palau Reial station rather than at outdoor school sites. Source contributions were generally higher outdoors (4.6 ± 4.8 μg/m^3) than indoors (3.8 ± 4.6 μg/m^3) even if a strong correlation was found with indoor concentrations ($r^2 = 0.83$), revealing high infiltration. SSO contributions correlate well outdoor and indoor at the majority of school pairings.

The Secondary Nitrate (SNI) factor explained most of the variance of NO_3^-, as oxidation product of local gaseous NOx emissions (traffic and industrial plants). Previous studies in Barcelona ascribed 70% of SNI to road traffic (Amato et al., 2009) based on the NOx emission inventory. Outdoor (4.1 μg/m^3 on average) and indoor (1.5 μg/m^3 on average) contributions from SNI were less well correlated ($r^2 = 0.55$) than for SSO. When comparing school pairings SNI contributions correlated well outdoors, while indoors ammonium nitrate becomes volatilized more quickly due to higher temperatures (Hidy et al., 2000; Patterson and

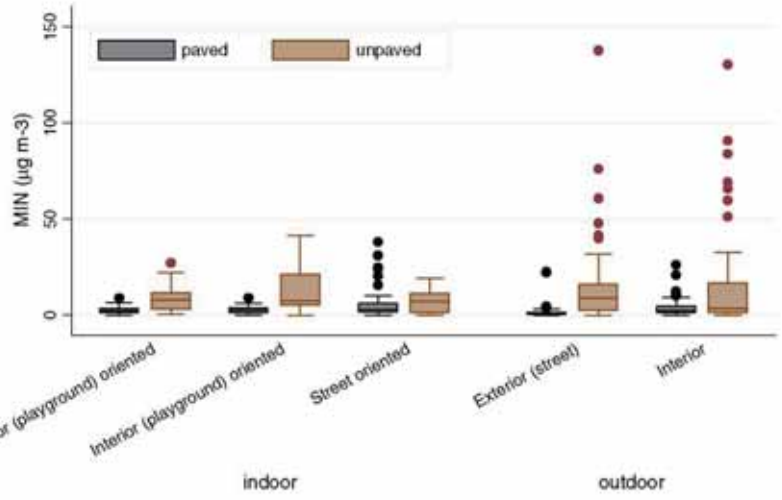

Fig. 4. Indoor and outdoor mineral (MIN) contributions, according to the orientation of classroom and type of playground. Saharan dust days were excluded.

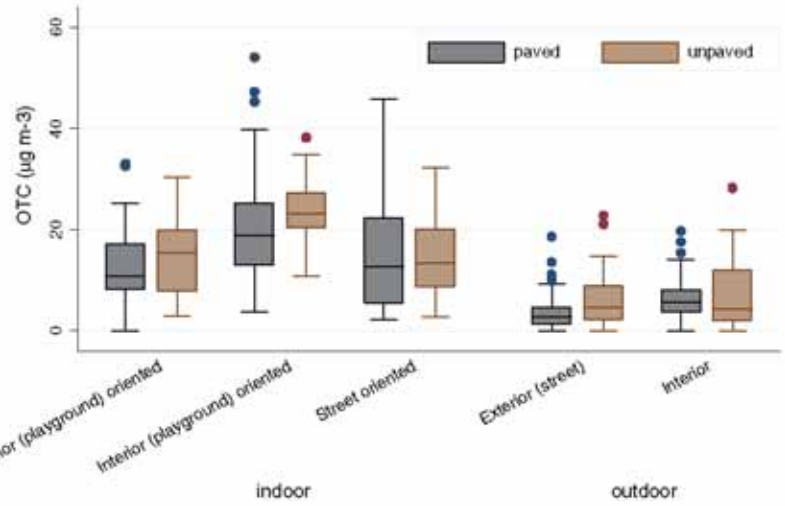

Fig. 5. Indoor and outdoor OTC contributions, according to the orientation of samplers and type of playground.

Eatough, 2000; Lunden et al., 2003; Sarnat et al., 2006) and adheres to room surfaces, reducing the correlation between different school pairs.

The Road Dust source (ROD) is traced by Ca, Fe, Cu and Sb (Fig. 2) and is attributed to particle resuspension from paved roads due to vehicle-generated turbulence and wind. This source was resolved by means of pulling equations, provoking an increase of the Q_{main} and Q_{aux} values by 8% and 83 units respectively (Paatero and Hopke, 2009). Road dust contributions outdoors were uncorrelated with those indoors, but average contributions were both 1.3 µg/m^3 as compared to 0.4 µg/m^3 for the urban background site. Previous studies estimated the annual mean contribution of road dust in Barcelona ambient air at 1.3–2.2 µg PM2.5/m^3 (Amato et al., 2009; Reche et al., 2012a).

The Metallurgy factor (MET) explains most of the variance of Zn and Pb, and to a lesser extent that of Cd, Mn and Cu. This source has been identified in prior studies at the urban background of Barcelona and allocated to the Baix Llobregat industrial basin (SW of Barcelona), with a higher impact on Barcelona during night time due to the land breeze transport (Amato et al., 2011). Mean concentrations during this study were 1.2 µg/m^3 outdoors and 1.0 µg/m^3 indoors, with 0.47 as correlation coefficient. The Sea Spray factor (SEA), traced by Na and Cl^-, is interpreted as fresh sea salt particles and contributed on average 0.9 and 0.8 µg/m^3 respectively for outdoor and indoor samples, which were poorly correlated ($r^2 = 0.43$). The Heavy Oil Combustion (HOC) factor is characterized by high concentrations of EC, OC and traced by V and Ni, reflecting the influence of combustion processes, mostly from shipping and industry in this region. Contributions were highly correlated between indoor and outdoor ($r^2 = 0.79$), similarly to SSO contributions. On average HOC increased outdoor and indoor PM2.5 concentrations by 0.7 and 0.6 µg/m^3, respectively. MET and HOC contributions correlate generally well between pairs of schools except for one pair outdoors and two pairs indoors. On the contrary, coarser particles from SEA and ROD did not show significant correlation in most of cases.

Sources related to urban background emissions showed a marked seasonal variation: SNI, TRA, ROD and MET had maxima in winter months (7.2, 5.4, 2.1 and 1.3 µg/m^3 as respective averages), the outdoor winter/spring ratios being 3.6, 1.3, 2.4 and 1.4 respectively, and 1.7, 0.9, 1.9 and 1.2 indoors. On the other hand SSO, SEA and HOC showed higher contributions in summer (Palau Reial measurements) and spring, with outdoor winter/spring ratios of 0.5, 0.7 and 0.6 respectively.

We estimated at each classroom the indoor-generated PM2.5 (PM_{ig}), considering the two children-related sources subtracted of their infiltration from outdoor air as:

$$PM_{ig} = \left[OTC_i^{wd} - \overline{\left(\frac{OTC_i}{OTC_o}\right)^{we}} \cdot OTC_o^{wd} \right] + \left[MIN_i^{wd} - \overline{\left(\frac{MIN_i}{MIN_o}\right)^{we}} \cdot MIN_o^{wd} \right]$$

where OTC_i^{wd} and OTC_o^{wd} are weekday OTC contributions indoors and outdoors, respectively, while $\overline{\left(\frac{OTC_i}{OTC_o}\right)^{we}}$ is the mean indoors/outdoors ratio of OTC contributions on weekends or holidays. The indoor-generated PM2.5 concentrations were 18.5 µg/m^3 on average, higher than the mean background PM2.5 concentrations in Barcelona, and corresponding to 47% of indoor PM2.5 concentrations. This result is comparable to that found by Fromme et al. (2008) in German classrooms who estimated the proportion of indoor-generated PM as 57% by subtracting the outdoor PM concentrations (corrected with the indoor/outdoor ratio for sulfate) to the indoor measurements.

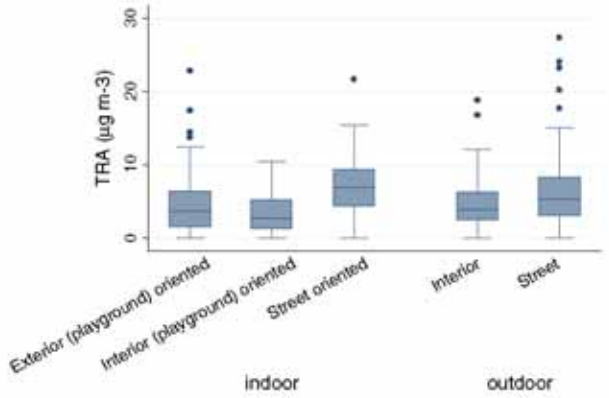

Fig. 6. Adjusted indoor and outdoor TRA contributions, according to the orientation of PM samplers.

4. Conclusions

Seven outdoor and two children-activity-related sources were found to be responsible for the PM2.5 concentrations measured at 39 primary schools in Barcelona. On average, 47% of PM2.5 measured in

classrooms was generated indoors from continuous resuspension of soil particles (13%) and a mixed source (34%) comprising organic (skin flakes, clothes fibers, possible condensation of VOCs) and Ca-rich particles (from chalk and building deterioration). Outdoor sources were responsible on average for the remaining 53% indoor PM concentrations, their absolute contributions (μg/m^3) being only slightly lower than at outdoor receptor locations. The poor building insulation in some schools reduced (although only by 5–21%) the infiltration of traffic emissions, secondary sulfate & organics, metallurgy, sea spray and heavy oil combustion particles, which contributed on average 13%, 11%, 3%, 2% and 1% of indoor PM2.5 concentrations, respectively. Larger reductions indoors were found for the secondary nitrate (1.5 μg/m^3 vs 4.1 μg/m^3 outdoors) due to ammonium nitrate volatilization indoors and for the mineral source at those schools where playgrounds were unpaved (9 μg/m^3 vs 16 μg/m^3 outdoors). Contributions indoors were instead higher for the Organic/Textile/Chalk source (by 67%) and the mineral source at schools with paved playground (by 32%). Thus unpaved playgrounds were found to increase mineral contributions in classrooms by 5–6 μg/m^3 on average with respect to schools with paved playgrounds.

Traffic contributions (4-days average) varied considerably in space within a range of 1–14 μg/m^3 outdoors and 1–10 μg/m^3 indoors. Indoor contributions were significantly higher for classrooms with windows oriented directly to the street, rather than to the interior of the block or to playgrounds. This highlights the importance of urban planning in order to reduce children's exposure to traffic emissions.

In conclusion, our results demonstrate the high exposure of children to PM2.5 due to the high infiltration rate of outdoor urban sources, the proximity to road traffic, the contribution of suspension from unpaved playgrounds, and especially the contribution of the OTC source. These results indicate that exposure assessments based only on total particle mass measured outdoors may bear little relation to the reality of what school children are breathing regularly in their daytime work and play environment.

Conflict of interest

The authors declare that they do not have any actual or potential financial and personal conflict of interest with other people or organizations.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.05.051.

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Sources of indoor and outdoor $PM_{2.5}$ concentrations in primary schools

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SUPPORTING INFORMATION

Quality control

Within each acid digestion of a batch of samples the Standard Reference Material® 1633b Coal Fly Ash was used to calculate the recovery yield of elements analyzed by ICP-MS and ICP-AES, according to the following formula:

$$R_j = \frac{x_j}{x_{cj}} \cdot 100$$

where R_j is the recovery yield (expressed in %), x_i is the fraction mass of j^{th} analyte to the total digested mass and x_{cj} is the certified fraction mass of j^{th} analyte to the total digested mass. The digested mass was fixed to 10 mg and mean recovery yields are presented in Table S1.

Table S1. Elemental recovery yield after Standard Reference Material digestion.

Element	Certified value ($\mu g \cdot g^{-1}$)	SD ($\mu g \cdot g^{-1}$)	Mean value found ($\mu g \cdot g^{-1}$)	SD ($\mu g \cdot g^{-1}$)	R_i (%)
Al	150500	2700	145981	2099	97
Ca	15100	600	15215	785	101
Fe	77800	2300	76495	3491	98
Mg	4820	80	4710	83	98
Na	2010	30	2057	180	102
S	2075	11	1109	839	53
K	19500	300	19133	1001	98
Sc	41.0*		40.6	1.3	99
Ti	7910.0	140.0	8170.0	277.9	103
V	295.7	3.6	310.0	11.3	105
Cr	198.2	4.7	197.3	3.6	100
Mn	131.8	1.7	137.2	6.2	104
Co	50.0*		48.0	1.9	96
Ni	120.6	1.8	110.1	12.9	91
Cu	112.8	2.6	118.2	6.6	105
Zn	210.0*		223.6	16.6	106
As	136.2	2.6	135.3	6.3	99
Se	10.3	0.17	11.0	0.7	107
Rb	140.0*		130.3	7.2	93
Sr	1041.0	14	1053.1	40.8	101
Cd	0.8	0.006	1.3	0.4	171
Sb	6.0*		6.0	0.3	101
Cs	11.0*		10.6	0.9	96
Ba	709.0	27	720.6	35.4	102
La	94.0*		75.8	7.6	81

Element	Certified value (μg·g^{-1})	SD (μg·g^{-1})	Mean value found (μg·g^{-1})	SD (μg·g^{-1})	R_i (%)
Ce	190.0*		189.4	4.8	100
Hf	6.8*		6.7	0.4	98
W	5.6*		17.4	5.6	311
Tl	5.9*		5.8	0.2	98
Pb	68.2	1.1	67.1	1.4	98
Th	25.7	1.3	25.2	0.6	98
U	8.8	0.36	8.9	0.2	102

*only indicative (non-certified values).

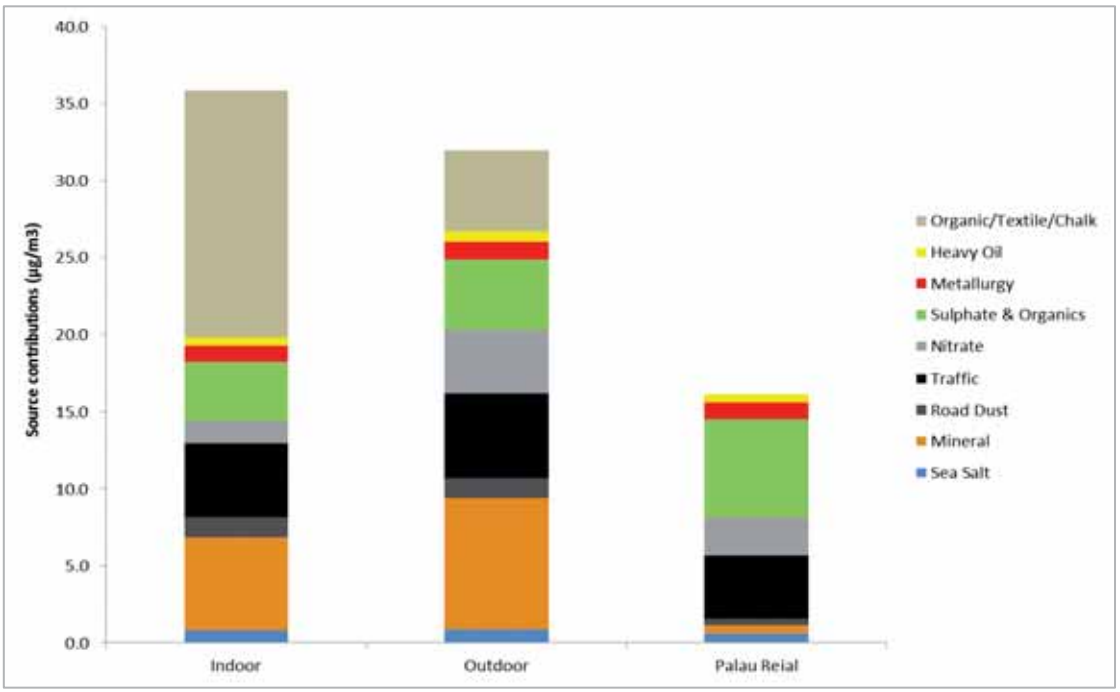

Figure S1. Average absolute contributions of PM2.5 sources outdoors and indoors (8 hour average) and at the urban background station (24 hour average)

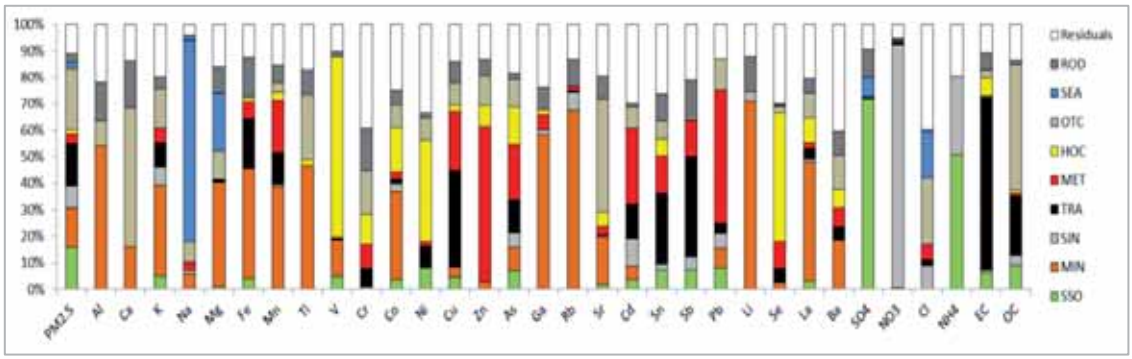

Figure S2. Apportionment of PM components variation among different sources.

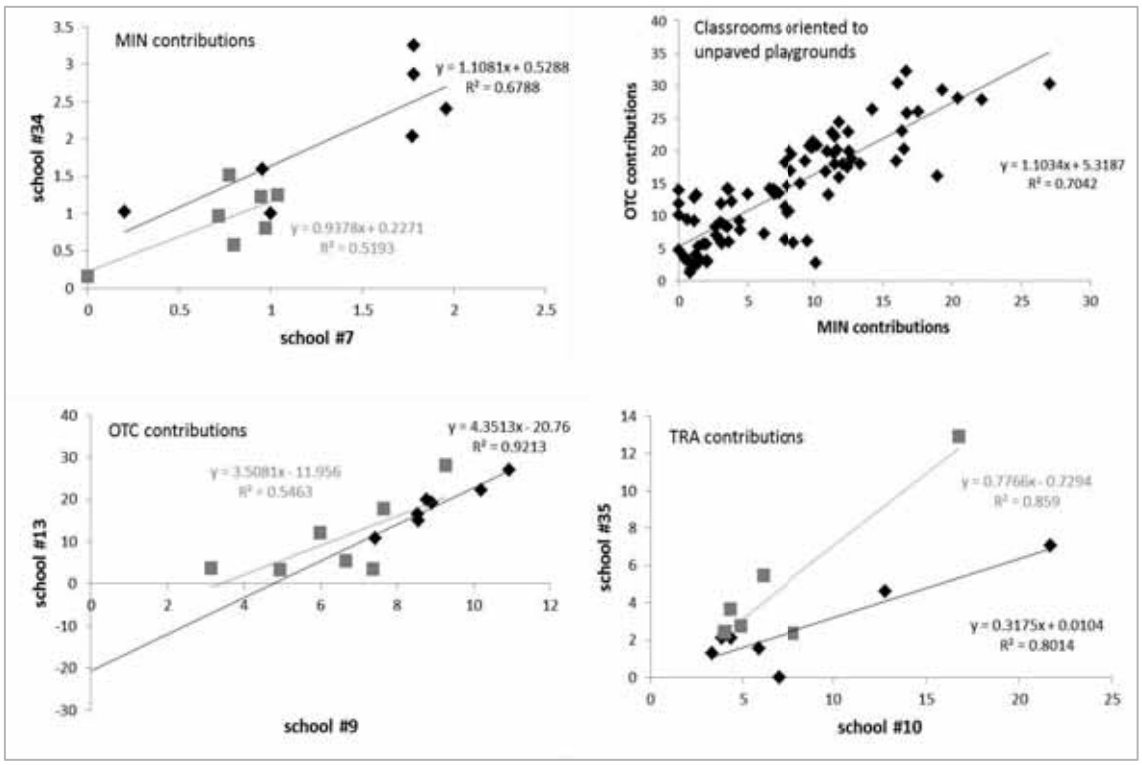

Figure S3. Correlation analysis between source contributions: a) MIN contributions at school pair 7-34; b) correlation between MIN and OTC contributions indoor; c) OTC contributions at school pair 9-13; d) TRA contributions at school pair 10-35.

3.3. Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in $PM_{2.5}$ in schools

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Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in $PM_{2.5}$ in schools

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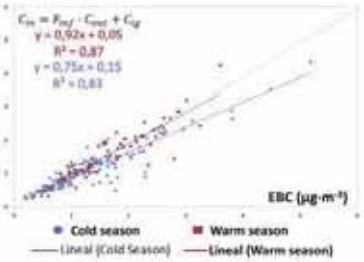
HIGHLIGHTS

- Infiltration of outdoor pollutants into indoor air at schools is assessed.
- Many pollutants have a high infiltration, with maximum reached by EBC and Cd.
- Building age & type of window do not determine infiltration levels.
- Type of window and sandy playground determine indoor mineral levels.

GRAPHICAL ABSTRACT



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ABSTRACT

Infiltration of outdoor-sourced particles into indoor environments in 39 schools in Barcelona was assessed during school hours. Tracers of road traffic emissions (NO_2, Equivalent Black Carbon (EBC), Ultrafine Particles (UFP), Sb), secondary inorganic aerosols (SO_4^{2-}, NO_3^-, NH_4^+) and a number of $PM_{2.5}$ trace elements showed median indoor/outdoor (I/O) ratios $\leq$ 1, indicating that outdoor sources importantly contributed to indoor concentrations. Conversely, OC and mineral components had I/O ratios>1. Different infiltration factors were found for traffic and secondary components (0.31–0.75 and 0.50–0.92, cold and warm season respectively), with maxima corresponding to EBC and Cd. Higher concentrations of indoor-generated particles were observed when closed windows hindered dispersion (cold season). Building age was not a major determinant of indoor levels. Neither were the window's material, except for NO_2 (with an increase of 8 μg m^{-3} for wood framed windows) and the mineral components (also dependent on the presence of sand in a distance <20 m) that reach the indoor environment via soil adhering to footwear with their dispersion being more barred by Aluminium/PVC framed windows than the wooden ones. Enlarged indoor concentrations of some trace elements suggest the presence of indoor sources that should be further investigated in order to achieve a healthier school indoor environment.

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1. Introduction

Since children spend most of their daily time in the indoor environment (around 90%, US-EPA, 2009), indoor air quality must be assessed when calculating child exposure to air pollutants; especially in schools where they spend around 30% of their weekdays (Fromme et al., 2007). Besides, it is important to determine the fraction of outdoor particles that enters the indoor environment and which factors affect this parameter. As a result, there is an increasing interest in this field (El Orch et al., 2014; MacNeill et al., 2012).

Outdoor air pollutants may intrude indoors by two main mechanisms (Chen and Zhao, 2011): through opened windows or doors (natural ventilation) and by infiltration through cracks and leaks in the building envelope (the latter being uncontrolled and having a relatively low exchange rate).

Different parameters may be used to assess the relationship between indoor and outdoor atmospheric particulate matter (PM) concentrations, such as the Indoor-to-Outdoor concentration (I/O) ratio and the Infiltration Factor (F_{inf}, Chen and Zhao, 2011).

The I/O ratio is an extensively used value of the relationship between indoor and outdoor PM concentrations (Abt et al., 2000; Arhami et al., 2010; among many others). However, since it is affected by many factors (mainly indoor particle sources, particle penetration and deposition rate), it is not always useful for understanding indoor–outdoor PM relationships. This might be the reason for inconsistencies among different studies (see Chen and Zhao, 2011). Notwithstanding, if measured for suitably long periods when no particles are generated indoors, the I/O ratio equals the F_{inf} (Long et al., 2001).

The F_{inf} represents the equilibrium of ambient PM that penetrates indoors and remains suspended, avoiding the influence of indoor-sourced PM. In natural ventilated buildings, this can be linearly expressed as (Dockery and Spengler, 1981):

$$C_{in} = F_{inf} \cdot C_{out} + C_{ig} \quad (1)$$

where C_{in} and C_{out} are the indoor and outdoor particle concentrations, respectively, F_{inf} is the infiltration factor and C_{ig} is the average concentration of indoor generated particles.

Outdoor PM may also reach indoor environments via soil adhering to footwear and clothes, and then be resuspended into the indoor air (Layton and Beamer, 2009) with this mechanism being favoured in highly crowded indoor environments, such as schools. Moreover, other processes such as phase change processes (e.g. volatilization of nitrate aerosol; Sangiorgi et al., 2013; Viana et al., 2014), new particle formation (e.g. from the interaction of outdoor O_3 and Volatile Organic Compounds, VOCs; Weschler, 2011 and references therein), and coagulation can influence in some cases the extent to which outdoor particles affect indoor levels (Weschler and Shields, 1999).

In addition to the need for characterising infiltration, assessing actual indoor exposures should also take into account indoor-sourced pollutants, always present in real-world conditions. At school, children participate in a wide variety of activities (e.g. painting, write on the blackboard, dance, move chairs). This results in schools being a very complex microenvironment affected by many different air pollutants (both gaseous or particulate compounds).

The occupancy-associated PM can be an important contributor to PM levels indoors. Although it may originate from the human body itself (skin flakes, hair, and other organic emissions, Fromme et al., 2008; Pegas et al., 2012), higher contributions come from human activities (walking, moving papers, etc.) that resuspend PM previously deposited on indoor surfaces such as floor and furniture (Qian et al., 2014, and references therein). Finally, VOCs are also an important aerosol component in indoor environments being emitted by cooking (Abdullahi et al., 2013 and references therein), building materials, furniture and home complements (Edwards et al., 2001; Uhde and Salthammer, 2007) and by terpene-based cleaning products (Edwards et al., 2001; Singer et al., 2006). VOCs react with ozone (O_3) and nitrogen oxides (NO_x) and lead to gas-phase formation of secondary organic aerosols (SOA, Wang and Waring, 2014; Weschler and Shields, 1999) which are a constituent of Organic Carbon (OC, Turpin and Lim, 2001).

Within the framework of the BREATHE Project, this work focuses in the study of, on one hand, the infiltration of outdoor-sourced particles into indoor school environments (testing the effects of building age and type of window), and, on the other hand, the assessment of the indoor contribution of specific PM components, aiming to achieve an in-depth assessment of indoor air quality in primary schools in Barcelona (Spain).

2. Materials and methods

2.1. Study description and sampling sites

Two one-week sampling campaigns (covering different seasons) were carried out from February 2012 until February 2013 in 36 schools in Barcelona (15,993 inhab·km^{-2}) and 3 schools in the near Sant Cugat del Vallès (1761 inhab/km^2, IDESCAT, 2012), NE Spain (Fig. 1).

Simultaneous indoor (in a classroom with pupils 7–10 years old) and outdoor (in the playground) sampling was carried out concurrently in two schools per week.

School buildings presented a wide range of ages (constructed from 1894 to 2010, information from the Property Tax Account Number, Table S1). All the schools were naturally ventilated by opening and closing windows, which were either Aluminium/PVC or wood framed. The type of windows in each school was reported during the monitoring period. The effect of these three parameters (open/closed windows, building age and type of window) on infiltration rates was evaluated.

2.2. Sampling and analysis

Air pollutants at schools were monitored during four working days (Monday to Thursday) per campaign. $PM_{2.5}$ samples were daily obtained during school hours (9–17 h local time) with a MCV high volume sampler (30 m^3 h^{-1}) on Pallflex quartz fibre filters (150 mm) to obtain mass concentration and a complete chemical characterisation, resulting in a total of 553 8 h-daily samples (283 indoors, 270 outdoors). A 1/4 fraction of each filter was bulk acid digested (HNO_3:HF:$HClO_4$) for the determination of major elements (Al, Ca, Fe, K, Na, Mg) by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sn, Sb, Pb, among others) by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Water-soluble ions (SO_4^{2-}, NO_3^- and Cl^-) were determined in another 1/4 filter by ion chromatography (ICHPLC) and NH_4^+ by a selective electrode. A 1.5 cm^2 filter punch was used for OC and elemental carbon (EC) determination by a thermal-optical transmission technique with a Sunset Laboratory OCEC Analyser with the NIOSH temperature programme (Birch and Cary, 1996). Sampling and analytical procedures are reported in detail by Querol et al. (2001a) and Rivas et al. (2014).

Besides filter samples, 10-min real-time Ultrafine Particles (UFP) number concentration in the range of 10–700 nm, UFP size (DiSCmini, Matter Aerosol) and Black Carbon (BC, MicroAeth AE51, AethLabs) concentrations were monitored, as well as weekly-averaged (including nights) NO_2 concentrations using Gradko

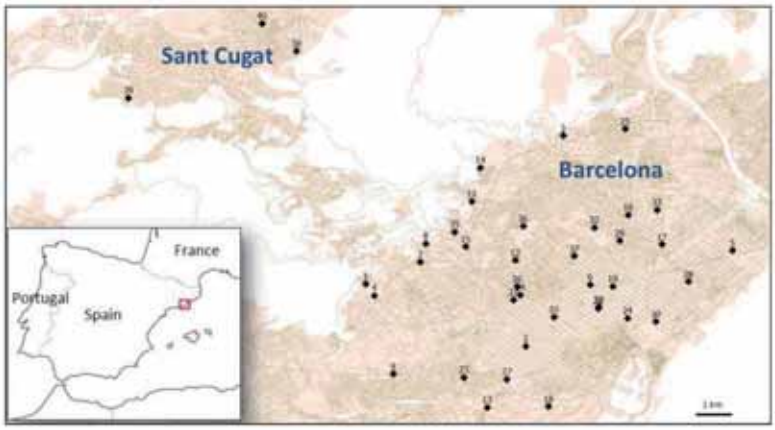

Fig. 1. Location of the schools across Barcelona and Sant Cugat.

Environmental passive dosimeters. All the DiSCmini devices were intercompared and corrected among each other to minimise measuring differences. BC concentrations recorded with the MicroAeth AE51 were converted to Equivalent Black Carbon (EBC) by means of a cross-correlation with in-situ (at schools) collected data of EC on filter samples.

2.3. Data treatment

I/O ratios (section 3.1.) and correlations (section 3.2) were calculated on individual daily basis (sample-by-sample) to avoid the dilution effect of the value when calculating the mean I/O ratio, except for NO_2 (weekly averaged). EBC and UFP real-time concentrations were also daily averaged, taking into account only school hours to coincide with filter data and to tighten the scope to infiltration processes occurring while children are in schools. In order to identify possible similar patterns, air pollutants have been grouped by common origin (some being in more than one group) including: road traffic tracers, components with a very high indoor-sourced fraction, minerals, secondary inorganic aerosols (SIA), marine aerosols, heavy oil combustion tracers, and industrial-sourced metals.

Schools monitored during periods with mean outdoor temperatures below 20 °C were classified into the cold season category and assumed to have the windows closed (59 cases; this is because 20 of the 39 schools were monitored twice, in both campaigns, under cold conditions); inversely, schools with temperatures above 20 °C were considered to be in the warm season and to have opened windows (17 cases). Fewer schools were monitored during the warm season because the longest holidays of the school year take place during summer (including the entire months of July and August). This classification was validated by a questionnaire about window opening filled in by the teachers during the sampling period.

A Linear Mixed-Effects Model (section 3.3.) was carried out with the software STATA 11 to assess the effect on indoor levels of building age, type of window and the presence of sand in the playgrounds. The equation that describes the model is:

$$Y_{it} = \beta_0 + \beta_1(outdoorconcentration)_{it} + \beta_2(typeofwindows:wood)_i + \beta_3(building\,age:\leq 1970)_i + \beta_4(typeofplayground:sand-filled<20\,m)_i + u_i + \varepsilon_{it} \quad (2)$$

where Y_{it} is the indoor concentrations for school i at day t, $t = \{1{-}8\}$, u_i are random effects at school level, assumed normally distributed with mean 0 and variance s^2_u, and ε_{it} are the model residuals assumed normally distributed with mean 0 and variance s^2_ε.

3. Results and discussion

3.1. Indoor/outdoor ratios and coefficients of variation

Descriptive statistics of the I/O ratios and their CV by season are presented in Fig. 2 (air pollutant concentrations are in Table S2). $PM_{2.5}$ showed a median ratio above 1 (1.43 for the cold and 1.39 for the warm season), thus higher levels were found inside the classrooms than in the playground. This is due to important contributions of indoor sources to $PM_{2.5}$ components, discussed in detail below. No significant differences can be observed between seasons.

Tracers of road traffic emissions in Barcelona (NO_2, EBC, UFP, Sn, Sb, Cu, Amato et al., 2009) had median I/O ratios below 1 during the cold season (higher levels outdoors), but very close to 1 for EBC, Cu and Sn. In a few schools Sn, Sb and Cu were an exception in the warm season when slightly higher median levels were found indoors, probably because of the synergies of opened windows and specific indoor emissions of these elements. UFP size median I/O ratio was also >1 since fresh exhaust emissions from traffic are very fine (20–30 as nm prevailing mode, Dall'Osto et al., 2011) but they increase their size by condensation and coagulation processes that might take place indoors. In fact, during the warm season the I/O UFP size ratio was approximately 1, with analogous processes affecting UFP due to similar conditions of temperature and humidity among both environments. In a number of schools, the I/O concentration ratios for EBC, UFP, Sb, Sn and Cu (Fig. 2) were >1, even in the cold season with closed windows. This occurs in schools where the monitored classroom was closer to traffic than the playground site (school characteristics in Table S1). Therefore, since some traffic tracers are very distance-dependent (Gilbert et al., 2003; Zhu et al., 2002), those schools were excluded in the analysis hereafter (16 of 76 cases; only for data of traffic related pollutants). In any case, this evidences the high infiltration rates for traffic related pollutants (MacNeill et al., 2012; Raysoni et al., 2011).

The indoor-sourced fraction of components such as OC (from organic and textile emissions from children and also related to indoor surface emissions), Ca and Sr (from chalk use in blackboards) is known to be higher than outdoor-sourced in schools, as observed in the currently schools under study by means of a PMF receptor model (Amato et al., 2014). The Organic/Textile/Chalk source (mainly explained by OC, Ca and Sr) contributed an average

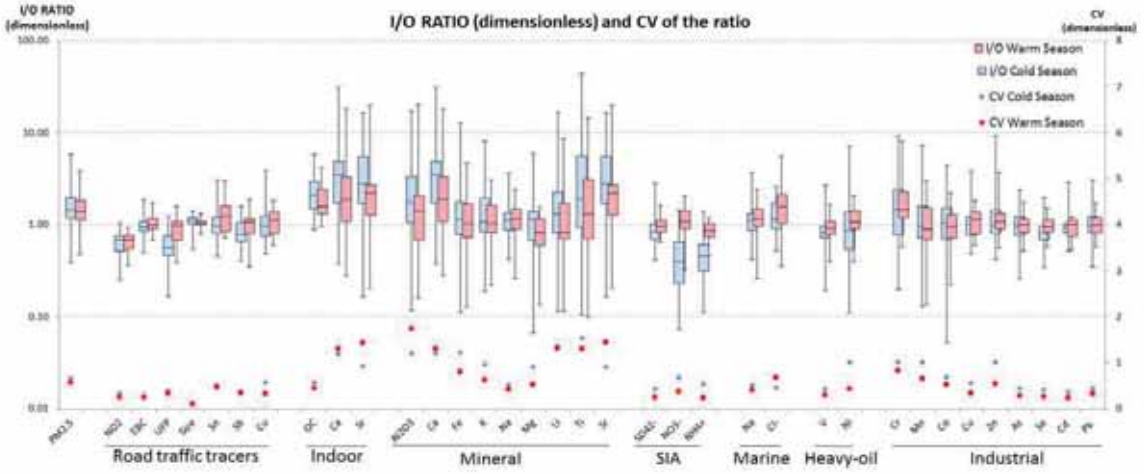

Fig. 2. Boxplot of the I/O ratio for $PM_{2.5}$, NO_2, BC, N, and $PM_{2.5}$ components, main axis. CV of the I/O ratios, secondary axis. Concentrations below the detection limit have been discarded.

of 16.0 μg m^{-3} to indoor levels whereas only 5.3 μg m^{-3} were observed in the playgrounds. Consequently, I/O ratios for these specific $PM_{2.5}$ components were greater than 1 in both seasons, especially during the cold period since the closed windows favour their accumulation. OC was particularly affected by indoor sources, since almost all its I/O ratio range was above 1. On the other hand, the range for I/O ratios was much wider for Ca and Sr because of varying intensities of chalk use and their mineral origin from sandy playgrounds.

Mineral components had the broadest range of I/O ratios, with a median ratio close to or higher than 1. Their levels were affected especially by the presence/absence of sandy playgrounds. The lowest I/O ratio for mineral elements was observed in schools with sandy playgrounds where outdoor samplers registered very high levels of mineral matter due to resuspension during children playground activities, and showing lower levels in classrooms (although they can also be considered high, since mineral particles were carried into the classroom by pupils; Layton and Beamer, 2009; Rivas et al., 2014). On the other hand, the maximum I/O ratios were found during the cold season because of the accumulation of indoor resuspended mineral particles and a lower resuspension in the playgrounds due to fewer outdoor activities during this colder period.

Regarding the SIA, the I/O ratios were clearly lower during the cold season, when median I/O values are below 1. This was especially evident in the case of NO_3^- (median I/O ratio: 0.39) and NH_4^+ (median I/O ratio: 0.45), probably caused by the relatively high temperatures found indoors during the cold season, that led to a higher evaporation rate of the NH_4NO_3 (into $HNO_3 + NH_3$) and thus, a more important transition of the NO_3^- and NH_4^+ from the PM to the gaseous phase (Harrison et al., 1994; Seinfeld and Pandis, 2006). During the warm season, I/O median values became very close to 1, due to windows opening and the fact that both indoor and outdoor temperatures were high enough to cause NH_4NO_3 evaporation (Querol et al., 2001b).

In spite of marine aerosols having an outdoor source, Na and Cl^- usually had higher levels indoors, especially during the warm season (Fig. 2). Probably because of Na also having a partial mineral origin in highly dusty environments (Amato et al., 2014; Viana et al., 2014) and Cl^- being emitted in indoor environments (by cleaning products, among others, Koistinen et al., 2004).

Focussing on trace elements, median I/O ratios for V and Ni (mostly arising from shipping emissions in Barcelona, Amato et al., 2009) during the cold period were 0.82 for V and 0.86 for Ni, which increased to 0.91 and 1.07, respectively, during the warm season because the opened windows facilitated their entrance indoors. Regarding other trace metals related to industrial processes in Barcelona (Amato et al., 2009), we evidenced that Cr had clearly higher levels indoors in both seasons (I/O ratio = 1.46), with an indoor origin attributed to the abrasion of metallic components of chairs and tables (Cr is an important alloying element in stainless steel, with a minimum of 10.5 wt% required for the surface protective layer for corrosion prevention, Bettini, 2007). Moreover, Cr is also present as chromated copper arsenate (CCA), a preservative for furniture and wood building materials against insect, bacterial, and fungal decline (Patch et al., 2009). The rest of trace metals had median I/O ratios~1, some with (a) similar median I/O ratio during both periods: As and Pb; (b) others whose median I/O ratio was slightly higher during summer: Cu, Zn, Se and Cd, because of free entry through opened windows, and (c) those with slightly lower I/O ratio during summer: Mn and Co. In specific schools (6 of 39) both winter and summer I/O ratios were markedly high for elements such as Cr, Cu and As, this probably pointing to the above mentioned emissions from indoor materials or material-treatments that may be relevant for children exposure.

Based on these I/O ratios, both highly indoor-sourced components and mineral components were barred from the analyses in section 3.2 owing to important indoor sources of these components. Other elements might be partly indoor-sourced (Bruinen de Bruin et al., 2006), but outdoor sources were considered predominant and therefore NO_2, EBC, UFP, Sb, SO_4^{2-}, NO_3^-, NH_4^+, V, Ni, Cr (although having high indoor contribution), Cu, As, Se and Pb, were included in the analyses in section 3.2.

Previous studies have reported I/O ratios at schools. Regarding $PM_{2.5}$, Zwoździak et al. (2013) obtained a mean I/O ratio of 2.0 during winter and 4.1 during summer in a school in Wroclaw (Poland), and Stranger et al. (2008) of 1.3 and 2.3 during winter and summer respectively. During winter, our mean I/O ratio (1.86) is between those found by Zwoździak et al. (2013) and Stranger et al. (2008), but in summer they found mean I/O ratio much higher than ours (1.59). For UFP number concentrations, Diapouli et al. (2007) reported I/O ratios between 0.55 and 0.85 in seven primary schools in Athens (Greece), Mullen et al. (2011) between 0.48 and 0.77 in six schools in northern California (USA) and Buonanno et al.

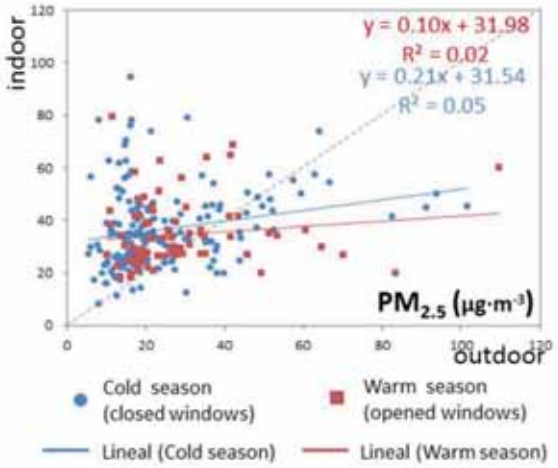

Fig. 3. Scatterplot showing the indoor–outdoor correlation for $PM_{2.5}$, distinguishing by ventilation variable (determined by window's configuration).

(2013) between 0.63 and 0.74 in three schools in Cassino (Italy), all of them during school hours. The median I/O value for UFP in our study (0.66) is within the range of the abovementioned studies; however our I/O range is clearly wider (from 0.17 to 1.62). Pegas et al. (2011) obtained an I/O ratio range for NO_2 of 0.36–0.95 in 14 schools in Lisbon (Portugal), similar to ours (0.25–1.05). Our mean I/O ratio for NO_2 is 0.65, the same that Stranger et al. (2008) found during winter (0.6) but lower to what they found during summer (1.2) in 27 schools in Antwerp (Belgium).

The CV is a normalised measure of dispersion corresponding to the ratio of the standard deviation to the mean and permits the comparison of data with very different means. CV of UFP number concentration was used to quantify spatial variation in microscale environments among 25 schools in Brisbane (Australia), 12 of them showing the presence of spatial variation of UFP (Salimi et al., 2013). In the present work, CV is used to analyse the variation on I/O ratios among schools (Fig. 2). Pollutants related to road traffic emissions had a very low CV (below 0.50, except Cu during the cold season whose CV = 0.55) as well as the SIA (except NO_3^- during the cold season, due to evaporation) and some trace metals (As, Se, Cd and Pb). This indicates that the indoor-to-outdoor relationship of these pollutants was quite similar for all schools and seasons (especially those sourced by traffic). For SIA and trace elements (except Ni and Cd), lower CVs were found during the warm season, probably related to the windows being opened and their free entrance independently of windows and building leaks.

On the other hand, mineral components had CV close to or above 1, with a high variability of the I/O ratio among the schools, especially during the cold season. This might be derived from two causes: (1) the presence/absence of sand playgrounds that specially affect outdoor levels and can make the I/O ratio to strongly diminish, and (2) indoor levels being influenced by the number of pupils and by their activity intensity, resulting in a wide range of I/O ratios.

General trends can be summarised in OC, Ca, Sr, Na, Cl^- and many mineral components (Al_2O_3, Li, Ti, Fe) having I/O ratios >1 and more markedly during the cold season, because of their accumulation indoors due to the closed windows. On the other hand, traffic tracers (NO_2, EBC, UFP, Sn, Sb, Cu), SO_4^{2-} and the trace elements Ni and V were characterised by having I/O ratios <1 (more pronounced during the cold season), because of their source being

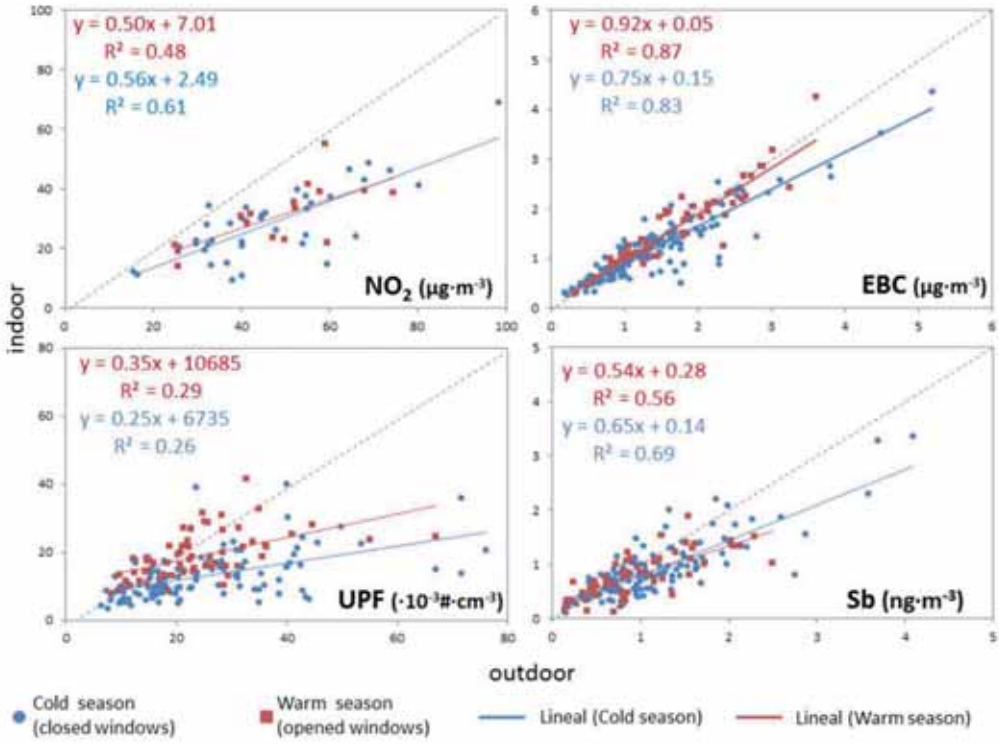

Fig. 4. Scatterplots showing indoor–outdoor correlations for selected traffic-related pollutants, distinguishing by ventilation variable (determined by window's configuration). Some schools have been excluded due to monitored classroom being closer to street than playground (see text for details).

located outdoors. UFP size, as well as some mineral elements (K, Mg), have I/O ratios close to 1.

3.2. Infiltration factors and indoor generated particle concentrations

The effect of windows opening on the F_{inf} and C_{ig} was evaluated (windows were closed during the cold season and opened during the warm one). Indoor versus outdoor daily levels (weekly levels for NO_2) for different air pollutants are presented in Figs. 3 and 4 and S1–S7. Linear regression lines correspond to Eq (1), and, therefore, the slope stands for the F_{inf}, and the intercept for the C_{ig}. A similar assessment was carried out by Sangiorgi et al. (2013) in 4 offices in Milan.

The indoor–outdoor correlation for $PM_{2.5}$ (Fig. 3) shows a zero coefficient of determination (R^2) for both warm and cold season. The flat slopes (0.10 for the warm and 0.21 for the cold season) are due to the very high intercepts obtained (31.98 for the warm and 31.54 for the cold season). These intercepts indicate a very high contribution of indoor sources to $PM_{2.5}$ and when important indoor sources are present, the slope does not correspond to the F_{inf}. This is the reason why in the previous section those components with significant indoor sources were excluded from this analysis (although they are presented in italics in Table S3 and some scatterplots are shown as examples in Fig. S1). These components have an $R^2 < 0.3$ (Table S3), which can be regarded as the lowest threshold to consider the F_{inf} as a reasonable one.

Schools having I/O ratios above 1.2 for traffic-sourced pollutants (generally because of the classroom being closer to the street than the playground) were not considered for the analysis of the components related to traffic owing to their distance-dependence stated previously. NO_2 showed a higher R^2 during the cold season ($R^2_c = 0.61$) than during the warm one ($R^2_w = 0.48$), but similar F_{inf} for both seasons ($F_{inf,c} = 0.56$ and $F_{inf,w} = 0.50$, cold and warm respectively) indicating similar infiltration independently of the windows opening (Fig. 4). Even for schools with classrooms closer to the street than the playground (not included in the correlation), the I/O ratios were below 1. This might be explained by the indoor consumption of NO_2 in gas-phase reactions with terpenes and other unsaturated hydrocarbons (Uhde and Salthammer, 2007; Weschler and Shields, 1999).

In the case of EBC (Fig. 4), very good correlations were found in both seasons ($R^2_w = 0.87$; $R^2_c = 0.83$). Based on the F_{inf}, 92% of indoor EBC comes from outside during the warm season and 75% during the cold one, being the second pollutant with the highest F_{inf} in the cold season (after Cd) and the first in the warm period. This indicates that closing the windows scarcely prevent the infiltration of outdoor EBC particles. For Sb, high R^2 were also found ($R^2_w = 0.56$ and $R^2_c = 0.69$), but the F_{inf} was lower than for EBC ($F_{inf,w} = 0.54$; $F_{inf,c} = 0.65$). NO_2, EBC and Sb have very low intercepts, indicating the absence of significant indoor sources for these pollutants.

Low correlation and F_{inf} for UFP ($F_{inf,w} = 0.35$, $R^2_w = 0.29$; $F_{inf,c} = 0.25$, $R^2_c = 0.26$) were found (Fig. 4), because of indoor particle sources ($C_{ig,w} = 10{,}685$ and $C_{ig,c} = 6{,}735$) that might increase indoor UFP independently of outdoor particles (Reche et al., 2014), and because of coagulation and condensation processes that might affect UFP indoors. In fact, Kearney et al. (2011) found that in 65% of the homes they studied, the indoor-generated UFP were higher than the UFP that infiltrated from outdoors. Actually, schools in Barcelona had higher indoor particle number concentrations during warm season despite the lower levels found outdoors during the same period (Fig. 4, Table S2). This might not only be explained by opened windows but also by the interactions of infiltrated outdoor O_3 with surfaces and household products that may generate new particles in the UFP range (Weschler, 2011). Further research is necessary in this field.

As regard for the infiltration of SIA (Fig. S2), we can observe very different patterns. Infiltration was high for SO_4^{2-}, with outdoor sources contributing 79% ($R^2_w = 0.85$) during the period with opened windows and 71% ($R^2_c = 0.77$) during the cold season. We are not aware of major indoor sources of fine SO_4^{2-} (in fact, C_{ig} is very low in both seasons) and thus this PM component is often used for the determination of infiltration rates as it can be considered a relatively inert tracer (Harrison et al., 1994). NO_3^- and NH_4^+ had a similar behaviour during the cold season ($F_{inf,c} = 0.31$, $R^2_c = 0.66$ for NO_3^-; $F_{inf,c} = 0.41$, $R^2_c = 0.69$ for SO_4^{2-}) since the most common NO_3^- bearing species in PM is NH_4NO_3 (Seinfeld and Pandis, 2006). These low F_{inf} are affected by two conditions: the barrier from building shell and windows, but also the evaporation of NH_4NO_3 indoors. Similar results were obtained in offices in Milan (Sangiorgi et al., 2013). Very low concentrations of NO_3^- during the warm season led to a low $R^2_w = 0.36$. On the other hand, since NH_4^+ can also combine with SO_4^{2-}, (Ottley and Harrison, 1992) a $F_{inf,w} = 0.86$ ($R^2_w = 0.88$) is obtained, similarly to SO_4^{2-}.

Contrary to expectations, for some specific trace elements and in certain schools, higher levels were detected indoors than outdoors, what means that important indoor sources were present for these PM components. Among trace metals, V and Cd had the highest F_{inf} ($F_{inf,c} = 0.71$ and $F_{inf,w} = 0.75$ for V; $F_{inf,c} = 0.79$ and $F_{inf,w} = 0.70$ for

Table 1
Adjusted infiltration factor (F'_{inf}), adjusted concentration of indoor generated particles (C'_{ig}) and fraction of C'_{ig} from the median indoor concentration of each component (C'_{ig} intensity) after adjusting by type of windows, building age and presence of sand in playgrounds (cold season only). In bold, $F'_{inf} > 0.5$ and C_{ig} intensities >50%.

	F'_{inf}	C'_{ig}	C'_{ig} intensity
		(pt cm^{-3})	(% indoor median)$^+$
UFP$^{\alpha}$	0.25**	8692**	**73.7**
		(μg m^{-3})	
$PM_{2.5}$	0.31**	33.46**	**97.1**
NO_2^{α}	0.46**	2.12	7.6
EBC$^{\alpha}$	**0.77****	0.19**	18.7
SO_4^{2-}	**0.70****	0.19*	26.5
NO_3^-	0.31**	−0.06	−13.3
NH_4^+	0.41**	0.03	10.0
OC	0.43**	8.93**	**90.0**
Ca	−0.07	2.24**	**150.8**
Sr	0.06	5.37**	**117.9**
Al_2O_3	0.17**	1.42**	**168.4**
Fe	0.09**	0.50**	**163.4**
K	0.23**	0.39**	**120.7**
Na	**0.50****	0.19**	**75.4**
Cl	**0.55****	0.36**	**59.2**
Mg	0.13**	0.19**	**156.5**
		(ng m^{-3})	
Li	0.05**	0.74**	**203.6**
Ti	0.08	64.88**	**151.2**
Sb$^{\alpha}$	**0.65****	0.23**	30.3
V	**0.72****	0.58**	23.6
Ni	**0.52****	0.82*	42.9
Cr	0.38**	4.76**	**138.6**
Mn	**0.14****	13.37**	**148.9**
Co	**0.19***	0.26**	**174.7**
Cu$^{\alpha}$	0.43**	4.41**	**61.2**
Sn$^{\alpha}$	**0.59****	0.95**	44.3
Zn	**0.63****	24.41**	**54.7**
As	**0.56****	0.21**	**55.7**
Se	0.46**	0.15**	**61.9**
Cd	**0.81****	0.02	13.3
Pb	**0.57****	2.93**	46.7

$^{\alpha}$ Schools having I/O ratios above 1.2 for traffic-related pollutants have not been considered.
* Statistically significant at p-value < 0.05.
** Statistically significant at p-value < 0.01.
$^{+}$ Median of the indoor concentrations during the cold period.

Table 2
Coefficients (difference in concentration) and fraction of the coefficient from the median indoor concentration for building age, type of windows, and type of playgrounds, after adjusting for outdoor concentrations (cold season only).

	Building construction year: <1970 (Ref: >1970)		Type of window: Wood (Ref: Al/PVC)		Playground: Sand-filled <20 m (Ref: Paved/Sand >20m)	
	Coeff	% Indoor median^{+}	Coeff	% Indoor median^{+}	Coeff	% Indoor median^{+}
	(pt cm ^{3})		(pt cm ^{3})		(pt cm ^{3})	
UFP$^{\alpha}$	−2366	−20.1	−2781	−23.6	954	8.09
	(μg m ^{3})		(μg m ^{3})		(μg m ^{3})	
$PM_{2.5}$	−2.30	103.63	−10.75**	−31.20	8.89**	25.81
NO_2^{α}	2.55	9.12	8.06**	28.78	0.69	2.47
EBC$^{\alpha}$	−0.07	−7.10	−0.14	−13.21	0.11	11.11
SO_4^{2}	−0.10	−13.56	−0.05	−6.57	−0.05	−6.64
NO_3	0.06	11.67	0.21	4.33	−0.10	−20.81
NH_4^{+}	−0.09	−30.68	0.11	38.44	−0.08	−26.54
OC	−0.01	−0.08	−2.25*	−22.65	1.23	12.38
Ca	−0.21	−13.94	−1.01**	−68.12	0.67	44.89
Sr	0.12	2.71	−1.80*	−39.48	1.08	23.63
Al_2O_3	−0.46	−54.63	−0.70**	−82.79	1.07**	127.78
Fe	−0.15*	−49.30	−0.23**	−72.12	0.41**	133.56
K	−0.09	−28.06	−0.17**	−53.11	0.39**	120.73
Na	−0.02	−8.30	−0.07**	−26.24	0.03	13.93
Cl	−0.05	−8.36	−0.07	−11.66	0.17*	28.20
Mg	−0.04	−30.57	−0.07**	−58.41	0.10**	84.84
	(ng m ^{3})		(ng m ^{3})		(ng m ^{3})	
Li	−0.27*	−73.19	−0.37*	−10.24	0.65**	179.33
Ti	−15.85	−36.93	−27.19*	−63.35	53.00**	123.49
Sb$^{\alpha}$	−0.15	−19.63	−0.08	−10.34	0.22	28.52
V	0.01	0.36	−0.68*	−27.63	1.04*	41.96
Ni	0.02	0.85	0.06	2.91	0.12	6.01
Cr	−1.95*	−56.94	−1.25	−36.28	0.87	25.49
Mn	−3.93	−43.75	−6.25**	−69.59	10.10**	112.41
Co	−0.09*	−62.41	−0.10*	−66.23	0.09	63.38
Cu$^{\alpha}$	−0.10	−1.33	−0.66	−9.15	0.00	0.03
Sn$^{\alpha}$	−0.36	−16.98	0.05	2.39	−0.05	−2.42
Zn	−6.22	−13.93	−7.32	−16.40	3.13	7.01
As	−0.02	−6.54	−0.09*	−25.29	0.11*	30.44
Se	−0.05*	−18.99	0.02	6.61	−0.03	−12.84
Cd	0.01	4.79	0.01	4.84	−0.02	−15.60
Pb	−0.16	−2.57	−0.86	−13.73	1.18	18.75

$^{\alpha}$ Schools having I/O ratios above 1.2 for traffic-related pollutants have not been considered.
*Statistically significant at p-value < 0.05.
**Statistically significant at p-value < 0.01.
$^{+}$Median of the indoor concentrations during the cold period.

Cd; Fig. S3) and lowest C_{ig} with respect to the median, (being the C_{ig} the 21.9 and 11.1% of the median for V; and 16.5 and 37.4% (the latter not being low) for Cd, cold and warm season respectively, Table S3). Pb had a similar F_{inf} ($F_{inf,c} = 0.55$ and $F_{inf,w} = 0.61$), but with higher R^2, than the rest of trace metals (excluding mineral components). For Pb, C_{ig} represents 46% (cold) and 42% (warm) of the median indoor concentrations, also indicating the presence of indoor sources such as old lead-based paints (Clark et al., 1991). However, no differences can be observed when considering building age, as will be described in section 3.3, so there might be other indoor sources that importantly contribute to Pb.

Trace metals (except Sb and Cr) had lower F_{inf} during the cold season, thus the entrance of these elements was to some extent hindered by windows (Table S3). However, for Ni, As, Cu, and Se the R^2 are not very high (the highest being 0.49 for As during warm season) because the impact of indoor sources might differ in each school. In fact, the abovementioned, and especially Cr, were affected by significant indoor sources in a number of schools (Fig. S3, Table S3). The C_{ig} represents 47% and 42% of the Ni median concentration, 59% and 52% of Cu, 51% and 39% of As, and 52% and 31% of Se, cold and warm seasons respectively. Cr should be highlighted, with the intercept accounting for 95% and 83% of its median indoor concentrations (cold and warm seasons, respectively). Therefore, the F_{inf} of Cr should not be determined by this analysis. Further research is required in order to identify indoor sources of these trace metals, some being well-known because of their toxicity. With the exception of Sb, all trace elements had similar or higher C_{ig} during the cold than the warm season, due to the dispersion of the indoor generated PM to outdoors being hindered by the closed windows.

In summary, for many components the F_{inf} was similar across warm and cold seasons (generally with a slightly higher infiltration during the warm season) with the exception of EBC, SO_4^{2} and Se, which had significantly higher infiltration rates during the period when the windows were opened.

3.3. *Effect of building age, type of windows and type of playground in the F_{inf}, C_{ig} and indoor concentrations*

Building age might have an effect on infiltration, and consequently on indoor pollutant concentrations, since older buildings might have more cracks on the building shell due to deterioration or to less isolating building materials and techniques. Walls are responsible for 18–50% of the infiltration air leakage in a building, and windows and doors (when closed) for 6–22% (Dickerhoff et al., 1982; Harrje and Born, 1982). The type and features of the windows (aluminium or PVC (Al/PVC) *vs* wood framed windows in this study) may also play an important role on the air leakage of this

building component (Younes et al., 2011). Moreover, the presence/absence of sand-filled playgrounds at schools have an influence on both indoor and outdoor levels of mineral components.

In BREATHE schools, the type of window was not related to building age (Pearson $\chi^2 = 0.61$, $p = 0.43$; Table S4). Indeed, a higher proportion of Al/PVC framed windows was present in the older buildings (65%) than in the newer ones (53%), probably due to recent renovation works. We performed linear mixed-effects models (LMM) including school as random effects. Multilevel modelling takes into account the hierarchical structure of the present data (measures grouped within schools). Table 1 shows the adjusted F_{inf} (F'_{inf}) and C_{ig} (C'_{ig}) for the pollutants under study during the cold season (closed windows) obtained by LMM. Only the cold season has been studied in this section to avoid the effect of higher infiltration during the warm season due to opened windows and, thus, focus on the effect of type of windows and building age. Moreover, since the mineral components have also been evaluated with this model, the variable type of playground (sand presence at < 20 m) has also been included. The objective is to highlight that the effect of outdoor concentrations in indoor concentrations (and therefore, for those components which are outdoor sourced, their infiltration) is isolated from the effect of the type of window, building age and type of playground. Except for NO_2, the F'_{inf} (Table 1) for the cold season has not substantially changed when compared to the non adjusted factors presented in the previous section (Table S3). As stated before, Cd and EBC are clearly the pollutants with the highest F'_{inf} (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-}, Sb, Zn, Sn, Pb, Cl^-, Ni, and Na, all of them with a $F'_{inf} > 0.50$.

The C'_{ig} was generally higher than the non-adjusted. The proportion of the median that the C'_{ig} represents is also shown in Table 1. From the pollutants assessed, those with the highest impact of C'_{ig} were (excluding mineral components, all of them with very high C'_{ig}): Cr > OC > Na > UFP > Se > Cu > Cl^- > As > Zn, all of them having >50% of the median indoor concentrations from indoor origin (in bold in Table 1).

Table 2 shows the coefficients for each of the pollutants of the categorical variables (2 categories) "Building Age", "Type of windows" and "Playground" The coefficient indicates the increase in concentration (in the corresponding units) in case of having an older building (constructed ≤ 1970) with respect to a newer one (constructed >1970; which is the reference format) for the "Building age" variable, a wood framed windows with respect to Al/PVC framed windows ("Type of windows" variable); and the presence of sand in the playgrounds at a distance <20 m (with respect to paved playgrounds or playgrounds with sands at >20 m, which is the reference state). Correlations by building age and type of windows are shown in the Supplementary material (Figs. S4–S7).

Results evidence that the age of the school building was significantly (p-value<0.05) associated with indoor levels for Fe and 4 trace elements, most of them typically related to industrial emissions (Table 2). Negative coefficients indicate that newer buildings tend to have around 0.15 μg m^{-3} more of Fe, 1.95 ng m^{-3} of Cr, 0.27 ng m^{-3} of Li, 0.09 ng m^{-3} of Co, and 0.05 ng m^{-3} of Se than the older ones, probably due to higher indoor emissions of these elements by new materials but further research is needed to identify specific sources in indoor environments. The lack of association with indoor levels for most of the pollutants under study is in accordance with previous studies (which included newly constructed schools) that did not find any correlation between airtightness and building age (Sherman and Chan, 2004). Moreover, the type of window seems to be importantly associated with higher levels of mineral components (such as Al_2O_3, Fe, Mg) and the components with a very high contribution from indoor sources (OC, Ca, Sr) in those schools with Al/PVC windows. Mineral components may reach indoor environments more importantly via soil adhering to footwear and clothes than by infiltration. Therefore, the presence of a more isolating window (such as the Al/PVC framed instead of wood framed) would be a much important barrier for the dispersion of mineral components, which might keep resuspended indoors in such a crowed environment. Moreover, also higher indoor levels of Co and As were found in schools with Al/PVC windows, probably due to indoor emissions or because of their possible presence on the school sand. On the other hand, NO_2 infiltration was hindered by Al/PVC windows, since those schools with wood framed windows tend to have an increase of around 8 μg m^{-3} of NO_2. The presence of sand-filled playgrounds had an impact also on indoor concentrations. Schools with sandy playgrounds at <20 m showed a substantial increase of mineral components in indoor concentrations with respect to those with paved playgrounds or sand at >20 m.

4. Conclusions

Infiltration of outdoor-sourced particles into indoor school environments and the identification of indoor sources of PM (including metals) were assessed in 39 schools in Barcelona with the aim to evaluate the infiltration of outdoor-sourced particles into indoor school environments (testing the effects of building age and type of window in this process), and, on the other hand, the indoor contribution of specific PM components.

I/O ratios trends can be summarised in OC, Ca, Sr, Na, Cl^- and many mineral components (Al_2O_3, Li, Ti, Fe) having I/O ratios >1 and more markedly during the cold season, because of their accumulation indoors due to the closed windows. On the other hand, traffic tracers (NO_2, EBC, UFP, Sn, Sb, Cu), SO_4^{2-} and the trace elements Ni and V were characterised by having I/O ratios ≤1 (more pronounced during the cold season), because of their source being located outdoors.

Indoor-outdoor correlations permit to obtain the infiltration factor (F_{inf}, only when $R^2 > 0.3$) and the indoor-generated concentration (C_{ig}). For many components the F_{inf} was similar across warm and cold seasons (generally with a slightly higher infiltration during the warm season when windows are opened). Cd and EBC were clearly the pollutants with the highest F_{inf} in the cold season (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-}, Sb, Zn, Sn, Pb, Cl^-, Ni, and Na, all with a $F_{inf} > 0.50$. Some metals may have higher indoor levels in newer buildings (constructed after 1970) due to specific indoor materials or treatments. Window's frame material affects more importantly to mineral components, hindering their dispersion and leading to higher indoor concentration in schools with Al/PVC window (those mineral components easily reach the indoor environment by soil adhering to footwear). Moreover, higher indoor concentrations of mineral components in schools were related with the presence of sand-filled playgrounds.

Schools are characterised by having a crowded indoor environment where many different activities take place. These characteristics lead to a complex mixture of emissions of different air pollutants that should be characterised when dealing with exposure to indoor PM_x. The characterisation of specific indoor sources is a key topic that should be furthered investigated in order to achieve a healthier school indoor environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.01.055.

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Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in $PM_{2.5}$ in schools

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SUPPLEMENTARY INFORMATION

Table S1. Main features of the schools.

School ID	Window material	Building construction year	Playground	Classroom orientation[1]	Playground location[2]	Classroom floor	Playground floor
1	PVC/Al	>1970	paved/sand>20m	Interior	interior	0-1st	1st-2nd
2	Wood (warm) PVC/Al (cold)	≤1970	paved/sand>20m	Interior	interior	2nd	ground
3	wood	>1970	paved/sand>20m	playground	interior	2nd	1st-2nd
4	PVC/Al	≤1970	sand <20m	playground	street	2nd	ground
5	PVC/Al	>1970	paved/sand>20m	directly street	street	2nd	3-5th
6	wood	≤1970	paved/sand>20m	Interior	street	2nd	1st-2nd
7	wood	≤1970	paved/sand>20m	playground	street	3-4th	3-5th
8	PVC/Al	>1970	paved/sand>20m	playground	street	2nd	3-5th
9	PVC/Al	≤1970	paved/sand>20m	playground	street	3-4th	ground
10	wood	≤1970	paved/sand>20m	directly street	interior	2nd	ground
11	PVC/Al	>1970	paved/sand>20m	Interior	street	0-1st	1st-2nd
12	PVC/Al	>1970	paved/sand>20m	directly street	street	0-1st	1st-2nd
13	PVC/Al	>1970	paved/sand>20m	Interior	interior	0-1st	ground
14	PVC/Al	>1970	paved/sand>20m	playground	street	2nd	ground
15	wood	≤1970	paved/sand>20m	directly street	street	3-4th	ground
16	PVC/Al	≤1970	paved/sand>20m	Interior	street	2nd	3-5th
17	wood	≤1970	sand<20m	directly street	street	2nd	ground
18	PVC/Al	>1970	paved/sand>20m	Interior	street	0-1st	ground
19	wood	≤1970	paved/sand>20m	playground	street	0-1st	ground
20	wood	>1970	sand<20m	directly street	street	0-1st	ground
22	PVC/Al	≤1970	paved/sand>20m	directly street	interior	2nd	ground
23	PVC/Al	≤1970	paved/sand>20m	Interior	interior	3-4th	3-5th
24	PVC/Al	≤1970	paved/sand>20m	playground	street	2nd	1st-2nd
25	wood	>1970	paved/sand>20m	playground	interior	2nd	ground
26	wood	>1970	paved/sand>20m	Interior	street	3-4th	ground
27	wood	≤1970	paved/sand>20m	directly street	street	3-4th	ground
28	PVC/Al	>1970	paved/sand>20m	directly street	street	2nd	ground
29	PVC/Al	≤1970	paved/sand>20m	playground	street	2nd	ground
30	wood	>1970	paved/sand>20m	playground	street	0-1st	ground
31	wood	≤1970	paved/sand>20m	Interior	interior	0-1st	ground
32	wood	>1970	sand<20m	playground	street	2nd	ground
33	wood	>1970	paved/sand>20m	directly street	interior	0-1st	ground
34	wood	≤1970	paved/sand>20m	directly street	street	2nd	3-5th
35	PVC/Al	>1970	paved/sand>20m	Interior	street	3-4th	3-5th
36	PVC/Al	≤1970	sand<20m	Interior	interior	2nd	ground
37	PVC/Al	>1970	paved/sand>20m	playground	street	3-4th	ground
38	PVC/Al	>1970	sand<20m	playground	street	0-1st	1st-2nd
39	PVC/Al	>1970	sand<20m	Interior	interior	0-1st	ground
40	PVC/Al	≤1970	sand<20m	playground	interior	2nd	ground

[1] Interior: classroom windows face to an interior patio, totally surrounded by buildings. Playground: classroom windows face a playground which is next to the street. Directly street: classroom windows face directly to the street.

[2] Interior: the playground is completely surrounded by buildings. Street: the playground is partially or totally opened to street.

Table S2. Descriptive statistics for indoor and outdoor air pollutant concentrations per each season (cold and warm).

	INDOOR												OUTDOOR											
	COLD						WARM						COLD						WARM					
	N	MIN	MEDIAN	MAX	MEAN	SD	N	MIN	MEDIAN	MAX	MEAN	SD	N	MIN	MEDIAN	MAX	MEAN	SD	N	MIN	MEDIAN	MAX	MEAN	SD
UFP ($pt \cdot cm^{-3}$)	180	3233	12653	40014	13860	7161	79	7635	17922	41407	19241	7240	167	6481	20249	76113	23587	12747	76	8181	22188	67095	23531	10322
Size (nm)	180	19	41	56	41	6.8	79	22	41	70	42	8.1	167	20	35	76	38	9.0	76	22	39	55	40	7.0
($\mu g \cdot m^{-3}$)																								
NO_2	51	5.1	28	69	29	13	21	9.6	32	55	31	12	49	15	42	98	46	17	21	14	49	74	47	15
$PM_{2.5}$	189	8.3	34	95	37	15	80	18	30	79	35	13	180	5.5	19	101	25	16	76	10	23	110	29	17
OC	188	0.29	9.9	29	10	3.9	80	3.5	8.6	19	9.1	2.9	179	1.09	4.3	22	5.3	3.2	75	2.1	4.8	11	5.5	2.1
EBC	188	0.14	1.1	5.4	1.2	0.83	80	0.12	1.3	4.2	1.4	0.84	179	0.12	1.2	7.2	1.3	0.86	75	0.10	1.2	3.7	1.4	0.84
Al_2O_3	188	0.10	0.84	6.3	1.2	1.1	80	0.10	0.73	12	1.2	1.5	179	0.10	0.43	8.0	0.91	1.3	75	0.10	0.63	12	1.5	2.1
Ca	188	0.10	1.5	7.1	1.7	1.2	80	0.13	0.85	3.1	1.1	0.81	179	0.10	0.41	4.5	0.68	0.75	75	0.10	0.41	4.9	0.72	0.82
Fe	188	0.10	0.31	2.3	0.43	0.36	80	0.10	0.29	1.6	0.37	0.28	179	0.10	0.22	3.7	0.40	0.50	75	0.10	0.25	4.1	0.57	0.73
K	188	0.10	0.33	1.4	0.37	0.24	80	0.10	0.25	1.5	0.34	0.25	179	0.10	0.20	2.2	0.31	0.30	75	0.10	0.21	2.2	0.38	0.40
Na	188	0.10	0.25	1.4	0.29	0.18	80	0.10	0.32	1.7	0.48	0.40	179	0.10	0.17	1.1	0.25	0.20	75	0.10	0.31	2.2	0.47	0.42
Mg	188	0.10	0.12	0.80	0.17	0.12	80	0.10	0.11	0.93	0.16	0.13	179	0.10	0.10	1.1	0.16	0.16	75	0.10	0.10	1.3	0.21	0.22
SO_4^{2-}	173	0.11	0.73	4.9	1.0	0.87	79	0.53	1.8	6.0	2.3	1.5	172	0.11	0.97	5.5	1.3	1.1	74	0.42	1.9	7.8	2.4	1.6
NO_3^-	161	0.10	0.48	9.2	0.77	1.0	76	0.11	0.67	3.2	0.82	0.64	176	0.11	1.00	17	2.1	2.5	71	0.13	0.61	2.9	0.70	0.44
Cl	188	0.10	0.61	3.0	0.64	0.41	80	0.10	0.46	1.9	0.54	0.35	178	0.10	0.48	1.9	0.56	0.40	75	0.10	0.39	1.6	0.46	0.36
NH_4^+	126	0.11	0.29	3.8	0.47	0.53	74	0.12	0.64	2.8	0.84	0.65	165	0.11	0.56	6.4	0.88	0.98	72	0.11	0.68	3.0	0.89	0.67
(ng-m-3)																								
Li	188	0.10	0.36	2.8	0.57	0.56	80	0.10	0.26	2.7	0.44	0.48	179	0.10	0.22	20	0.60	1.6	75	0.10	0.23	5.3	0.69	0.99
Ti	188	4.1	43	272	57	48	80	3.0	33	189	44.3	38	179	0.10	16	406	38	57	75	3.1	21	402	56	80
V	187	0.18	2.5	20.83	3.5	3.0	80	1.3	5.8	26	7.7	5.5	178	0.28	2.9	22	4.2	3.6	75	0.75	6.8	27	8.7	6.1
Cr	176	0.20	3.4	19.1	4.5	3.6	72	0.16	3.0	10	3.3	2.0	167	0.23	2.8	18	3.4	2.8	64	0.17	2.3	8.9	2.7	1.9
Mn	188	1.8	9.0	50	12	9.3	80	1.3	9.0	39	10.4	6.6	179	0.50	8.4	84	11.7	12	75	1.8	8.7	81	15	15
Co	188	0.10	0.15	1.6	0.21	0.17	80	0.10	0.18	1.6	0.23	0.21	179	0.10	0.11	1.0	0.19	0.15	75	0.10	0.17	1.0	0.23	0.20
Ni	169	0.13	1.9	29	2.5	2.6	78	0.18	3.2	8.4	3.5	2.1	162	0.21	2.3	9.4	2.8	1.8	72	0.28	3.4	9.1	3.6	2.1
Cu	188	1.3	7.5	22	8.0	3.4	80	2.0	7.3	21	8.5	4.3	179	1.6	7.4	24	8.3	4.6	75	2.0	7.1	27	8.6	5.3
Zn	188	10.0	45	304	52	36	80	0.10	41	278	52	41	179	3.6	44	271	54	42	75	8.1	39	188	50	33
As	188	0.10	0.37	1.6	0.42	0.22	80	0.15	0.49	1.4	0.53	0.23	179	0.10	0.39	1.9	0.44	0.26	75	0.12	0.47	1.4	0.54	0.26
Se	141	0.11	0.25	1.2	0.30	0.18	78	0.17	0.52	1.4	0.58	0.28	142	0.11	0.28	1.3	0.35	0.22	73	0.18	0.53	1.3	0.58	0.22
Sr	188	0.43	4.6	16	4.9	2.8	80	0.10	3.1	9.8	3.7	2.4	179	0.10	1.3	17	2.1	2.2	75	0.10	1.9	16	2.7	2.9
Cd	188	0.10	0.12	1.5	0.16	0.13	80	0.10	0.11	0.52	0.16	0.10	179	0.10	0.12	0.97	0.18	0.14	75	0.10	0.11	0.60	0.16	0.09
Sn	188	0.48	2.1	19	2.7	2.2	80	0.43	2.5	23	3.7	3.3	179	0.28	2.1	22	3.1	3.0	75	0.34	2.4	11	3.2	2.5
Sb	186	0.12	0.78	3.4	0.87	0.52	76	0.11	0.78	2.1	0.84	0.47	177	0.15	0.94	6.8	1.1	0.83	71	0.12	0.80	2.5	0.91	0.57
Pb	188	1.4	6.3	30	7.1	3.8	80	1.2	6.1	36	8.0	5.9	179	1.4	6.0	36	7.7	5.6	75	1.2	6.1	40	8.1	6.7

Table S3. I/O ratios, CV of the I/O ratios, Finf, Cig, percentage of the Cig from the corresponding indoor median concentration, and R2. In italics, those components whose Finf cannot be assess due to R2<0.3 because of very high contribution of indoor sources.

	COLD SEASON (closed windows)						WARM SEASON (opened windows)					
	I/O ratio		Linear Regression				I/O ratio		Linear Regression			
	median	CV	F_{inf}	C_{ig}	C_{ig} (% indoor cold median)	R^2	median	CV	F_{inf}	C_{ig}	C_{ig} (% indoor warm median)	R^2
				pt·cm⁻³						*pt·cm⁻³*		
UFP¤	0.57	0.38	0.25	6735	55.1	0.26	0.97	0.32	0.35	10685	60.8	0.29
Size	1.12	0.14	-	-		-	1.03	0.10	-	-		
				µg·m⁻³						*µg·m⁻³*		
$PM_{2.5}$	1.43	0.64	*0.21*	*31.54*	*91.6*	*0.05*	1.39	0.57	*0.10*	*31.98*	*107.1*	*0.02*
NO_2¤	0.68	0.31	0.56	2.49	12.1	0.61	0.68	0.24	0.50	7.01	22.4	0.48
EBC¤	0.94	0.28	0.75	0.15	14.0	0.83	0.98	0.25	0.92	0.05	3.7	0.87
SO_4^{2-}	0.84	0.43	0.71	0.11	15.0	0.77	0.96	0.24	0.79	0.36	20.1	0.85
NO_3^-	0.39	0.68	0.31	0.05	10.4	0.66	1.09	0.37	0.77	0.24	36.0	0.36
NH_4^+	0.45	0.54	0.41	0.02	6.8	0.69	0.86	0.24	0.86	0.00	0.0	0.88
OC	2.09	0.56	*0.26*	*9.05*	*91.2*	*0.05*	1.59	0.43	*0.27*	*7.59*	*88.3*	*0.04*
Ca	3.53	1.19	*0.01*	*1.73*	*116.3*	*<0.01*	1.87	1.30	*0.12*	*1.04*	*123.2*	*0.01*
Al_2O_3	1.75	1.21	*0.21*	*1.03*	*122.5*	*0.06*	1.43	1.73	*0.14*	*1.01*	*137.5*	*0.03*
Fe	1.14	1.21	*0.16*	*0.37*	*121.3*	*0.05*	1.04	0.80	*0.12*	*0.32*	*111.7*	*0.09*
K	1.06	0.96	*0.22*	*0.30*	*92.1*	*0.08*	1.03	0.61	*0.23*	*0.26*	*105.6*	*0.13*
Na	1.11	0.50	*0.46*	*0.17*	*68.1*	*0.30*	1.15	0.41	0.66	0.19	*60.1*	0.47
Mg	1.14	0.91	*0.19*	*0.15*	*126.6*	*0.07*	0.82	0.51	*0.09*	*0.15*	*142.5*	*0.03*
Cl	1.13	0.45	0.56	0.33	54.4	0.32	1.56	0.67	*0.37*	*0.38*	*83.0*	*0.14*
				ng·m⁻³						*ng·m⁻³*		
Li	1.33	1.35	*0.21*	*0.47*	*129.7*	*0.07*	0.84	1.31	*0.18*	*0.33*	*128.6*	*0.14*
Ti	1.91	1.53	*0.14*	*51.79*	*120.7*	*0.03*	1.31	1.30	*0.13*	*37.54*	*113.6*	*0.07*
Sr	2.75	0.91	*0.13*	*4.62*	*101.4*	*0.01*	2.22	1.43	*0.04*	*3.54*	*115.1*	*<0.01*
Sb¤	0.77	0.32	0.65	0.14	17.6	0.69	1.07	0.34	0.54	0.28	35.8	0.56
V	0.82	0.43	0.71	0.54	21.9	0.73	0.91	0.29	0.75	0.65	11.1	0.83
Ni	0.86	1.02	0.52	0.90	46.8	0.33	1.07	0.42	0.57	1.34	41.7	0.34
Cr	1.45	1.01	*0.37*	*3.26*	*95.0*	*0.08*	1.47	0.82	*0.33*	*2.46*	*82.6*	*0.09*
Mn	0.97	1.01	*0.17*	*9.93*	*110.5*	*0.05*	0.89	0.65	*0.12*	*8.46*	*110.5*	*0.08*
Co	1.04	0.69	*0.23*	*0.17*	*113.9*	*0.04*	0.96	0.51	*0.07*	*0.21*	*95.5*	*0.01*
Cu¤	0.99	0.54	0.49	3.80	59.65	0.42	1.14	0.33	0.50	3.82	49.75	0.42
Sn¤	0.97	0.46	0.68	0.60	28.0	0.78	1.24	0.46	0.89	0.83	30.4	0.41
Zn	0.96	1.01	0.63	17.95	40.2	0.54	1.09	0.53	0.69	13.25	32.0	0.55
As	0.97	0.44	0.53	0.19	50.7	0.38	1.01	0.27	0.58	0.19	38.8	0.49
Se	0.80	0.41	0.46	0.13	52.0	0.43	0.94	0.25	0.64	0.16	30.9	0.41
Cd	0.92	0.36	0.79	0.02	16.5	0.67	1.01	0.23	0.70	0.04	37.4	0.58
Pb	0.96	0.43	0.55	2.88	45.8	0.67	0.98	0.31	0.61	2.58	42.1	0.67

¤ For the linear regression, schools having I/O ratios above 1.2 for traffic-related pollutants have not been considered.

Table S4. Cross tabulation of schools by type of windows and building construction year.

Building construction year	Type of windows		Total
	Al/PVC	Wood	
≤1970	13 (65%)	7 (35%)	20
>1970	10 (53%)	9 (47%)	19

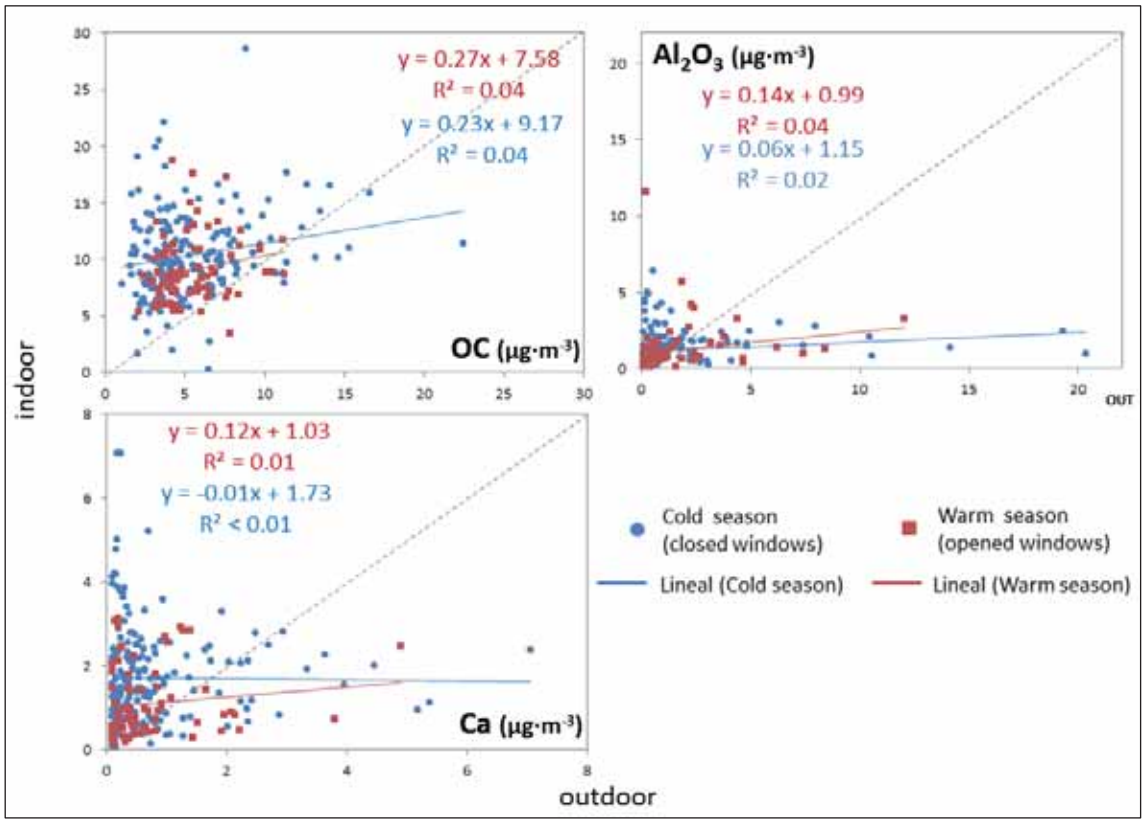

Figure S1. Scatterplots showing indoor-outdoor correlations for different air pollutants which are mainly indoor-generated, distinguishing by ventilation variable (determined by window's configuration). Concentrations below the detection limit have been discarded.

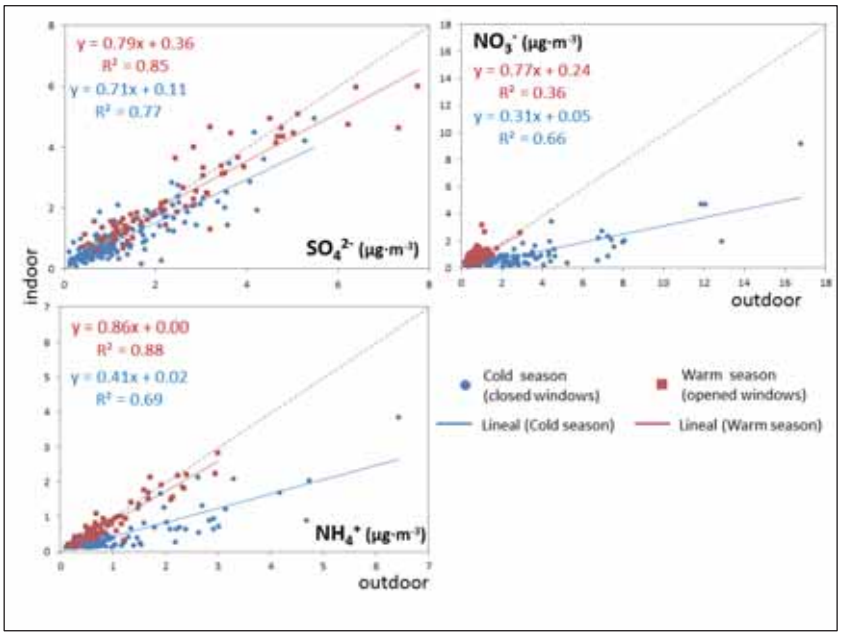

Figure S2. Scatterplots showing indoor-outdoor correlations for SO42-, NO3- and NH4+, distinguishing by ventilation variable (determined by window's configuration).

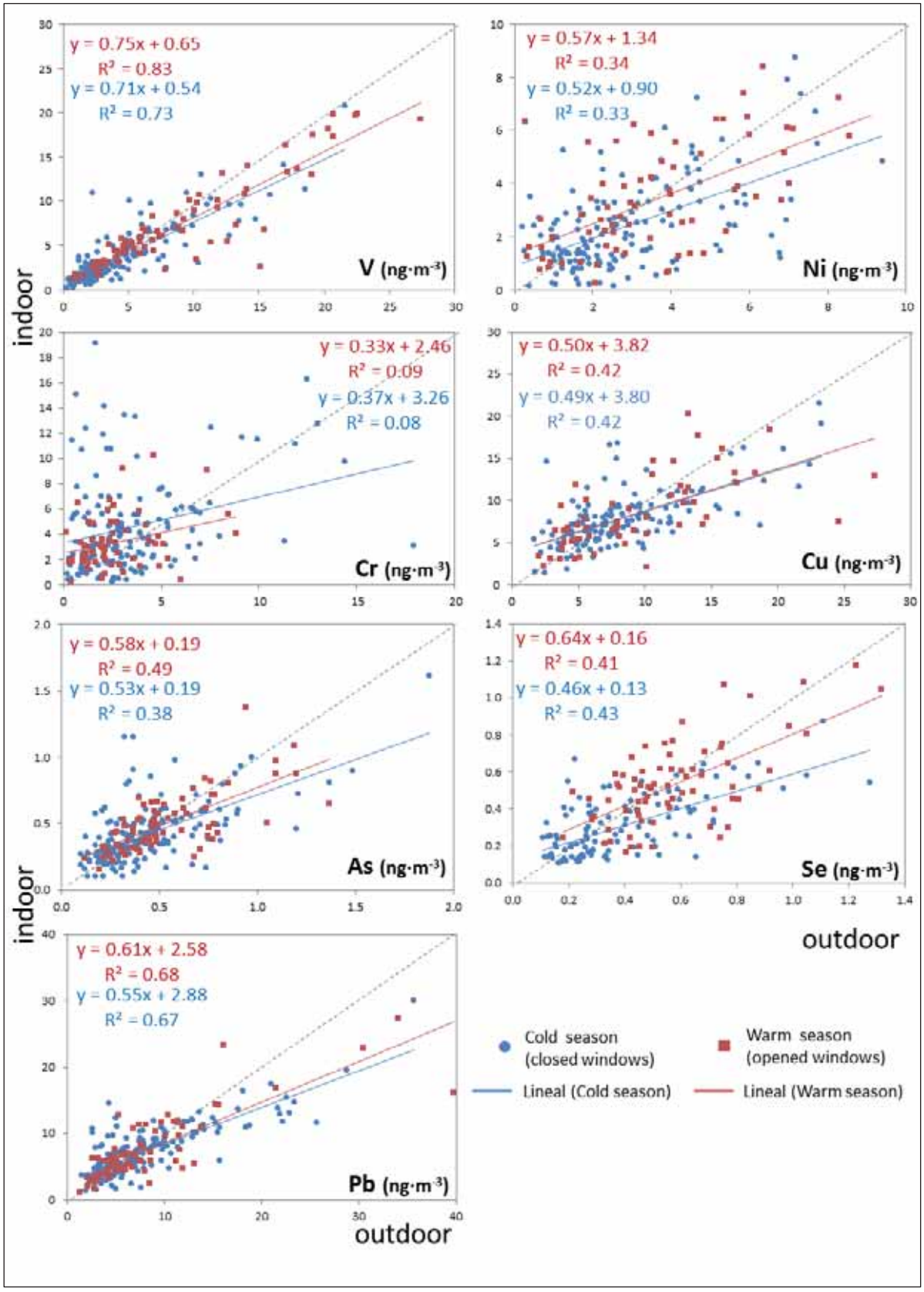

Figure S3. Scatterplots showing indoor-outdoor correlations for trace elements, distinguishing by ventilation variable (determined by window's configuration). Concentrations below the detection limit have been discarded

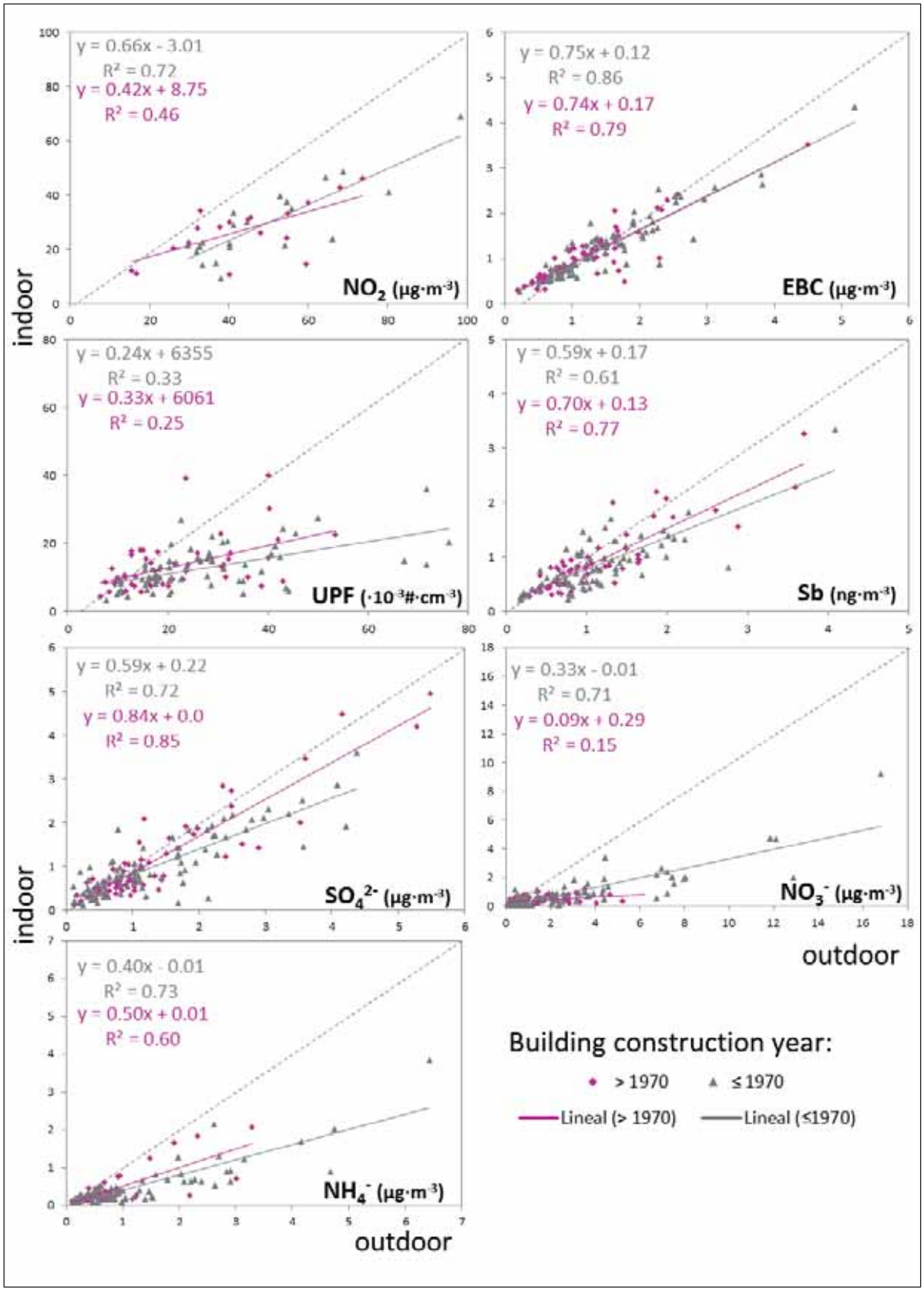

Figure S4. Scatterplots showing indoor-outdoor correlations for different air pollutants, distinguishing by building age variable. Concentrations below the detection limit have been discarded.

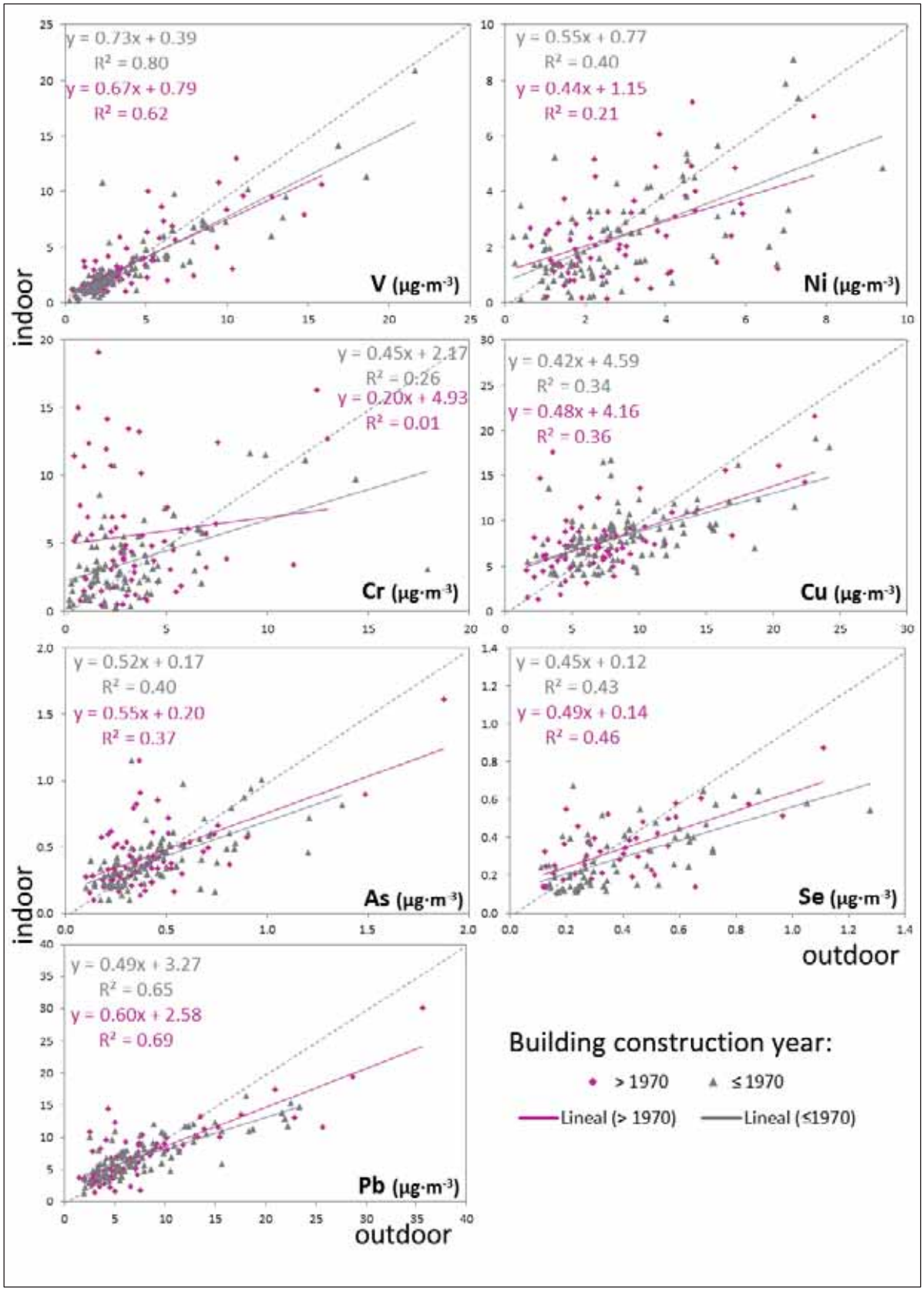

Figure S5. Scatterplots showing indoor-outdoor correlations for different air pollutants, distinguishing by building age variable. Concentrations below the detection limit have been discarded.

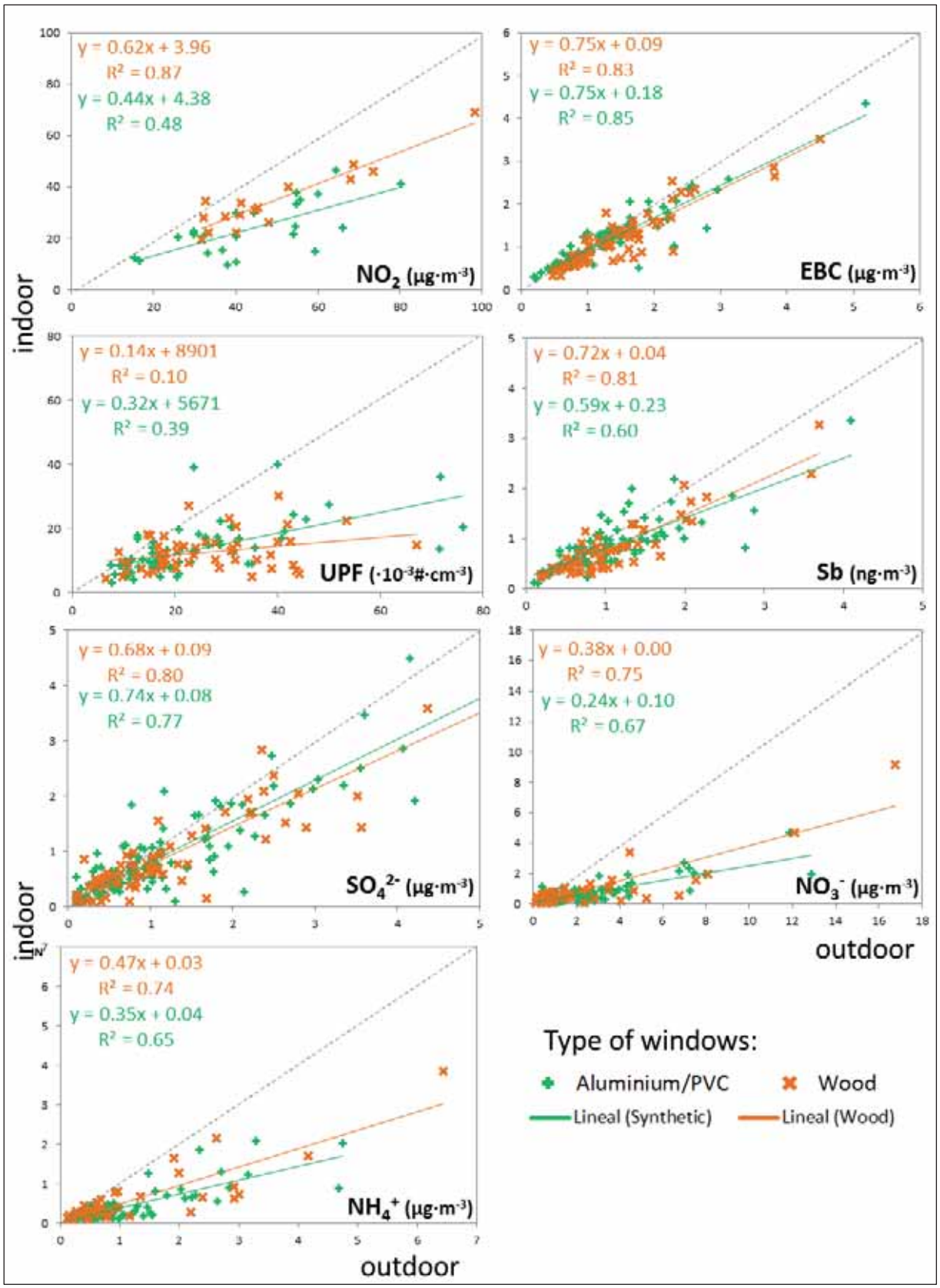

Figure S6. Scatterplots showing indoor-outdoor correlations for different air pollutants, distinguishing by type of window. Concentrations below the detection limit have been discarded.

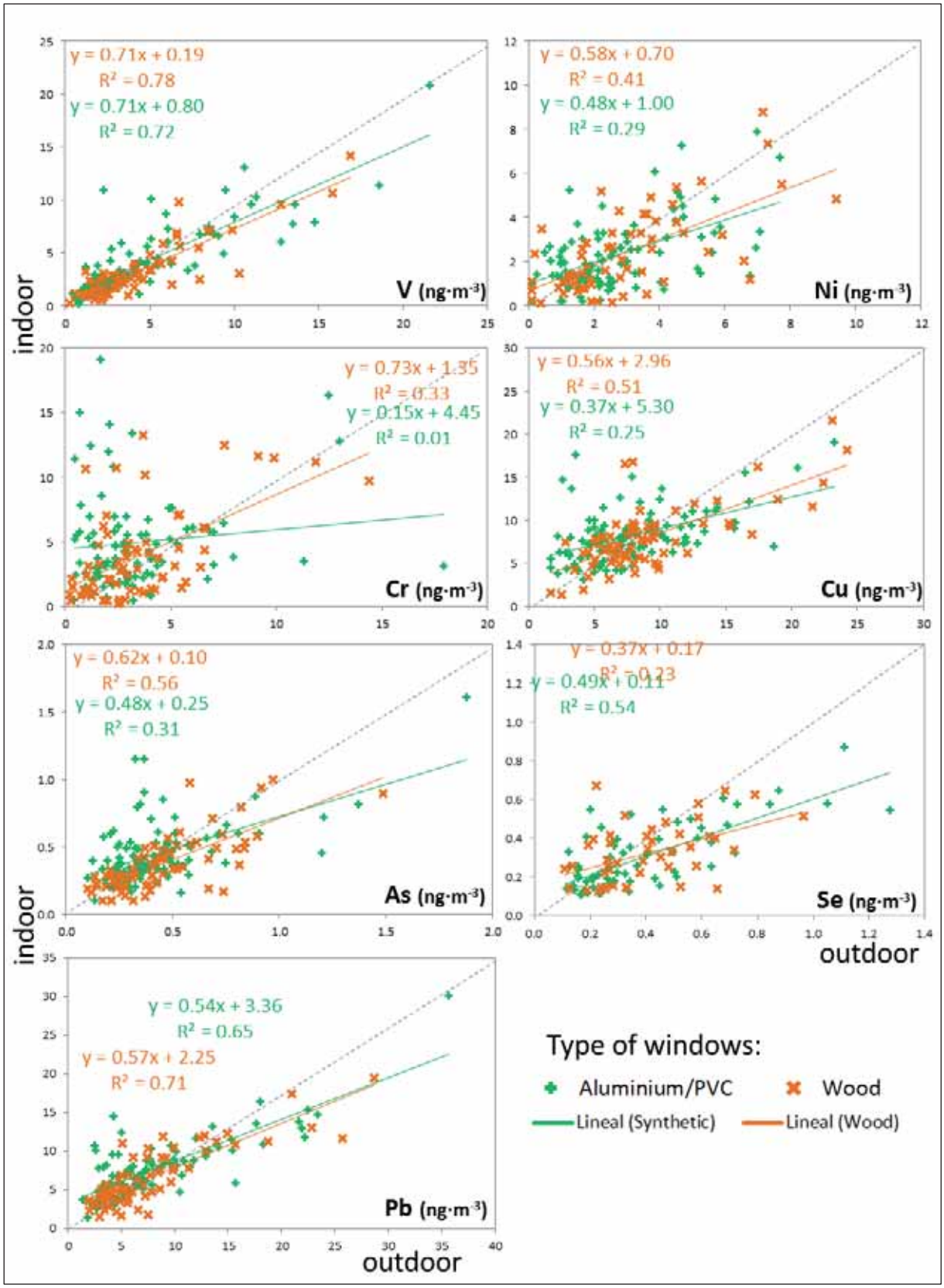

Figure S7. Scatterplots showing indoor-outdoor correlations for different air pollutants, by type of window. Concentrations below the detection limit have been discarded.

3.4. Spatio-temporally resolved black carbon concentration, schoolchildren's exposure and dose in Barcelona

Authors:

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Spatiotemporally resolved black carbon concentration, schoolchildren's exposure and dose in Barcelona

Abstract At city level, personal monitoring is the best way to assess people's exposure. However, it is usually estimated from a few monitoring stations. Our aim was to determine the exposure to black carbon (BC) and BC dose for 45 schoolchildren with portable microaethalometers and to evaluate the relationship between personal monitoring and fixed stations at schools (indoor and outdoor) and in an urban background (UB) site. Personal BC concentrations were 20% higher than in fixed stations at schools. Linear mixed-effect models showed low R^2 between personal measurements and fixed stations at schools ($R^2 \leq 0.28$), increasing to $R^2 \geq 0.70$ if considering only periods when children were at schools. For the UB station, the respective R^2 were 0.18 and 0.45, indicating the importance of the distance to the monitoring station when assessing exposure. During the warm season, the fixed stations agreed better with personal measurements than during the cold one. Children spent 6% of their time on commuting but received 20% of their daily BC dose, due to co-occurrence with road traffic rush hours and the close proximity to the source. Children received 37% of their daily-integrated BC dose at school. Indoor environments (classroom and home) were responsible for the 56% BC dose.

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Practical Implications
This study provides valuable information on the BC dose that schoolchildren receive during weekdays. Owing to the time spent in indoor microenvironments (considering classroom and home, 82%), children receive around half of their BC dose (56%) there. School (classroom and playground) contributes to a third of schoolchildren's daily dose. However, the highest dose:time intensity (3.5:1) is found during commuting activities. Policies focusing on reducing traffic intensities around schools should be enhanced.

Introduction

Many epidemiological studies demonstrate that exposure to atmospheric pollutants, specially particulate matter (PM), has important and varied adverse effects on human health (Beelen et al., 2014; Raaschou-Nielsen et al., 2013; WHO, 2013).

Human exposure was defined by Ott (1982) as 'the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time'. Traditionally, urban population exposure to air pollutants has been assessed based on data from air quality monitoring sites, which usually provide data of a wide variety of pollutants, albeit for few points in a city (Steinle et al., 2013) that might not be representative for all the population. Although outdoor air pollution estimates have been associated with health, a more refined exposure assessment may be needed to reduce exposure misclassification and find stronger associations with health outcomes. Therefore, for an accurate personal exposure assessment the different places in which time is spent (Ashmore and Dimitroulopoulou, 2009) should be considered, as, in fact, people spend around 90% of their time indoors (Buonanno et al., 2012; US-EPA, 2008). Therefore, direct personal exposure measurements are the most representative of people's exposure (Jantunen et al., 2002). However, these personal assessments raise new uncertainties such as how many personal measurements might be taken to be representative of a population or a conurbation, how should be the subjects distributed within city to control for spatial variability or which personal characteristics need to be controlled in order to characterize all existent time–activity patterns within a population. Finally, personal monitoring also puts a burden on people and is labor and resource intensive.

It is important to investigate the relationship between personal exposure and outdoor background concentrations from fixed monitored stations. Previous studies evaluating this relationship for $PM_{2.5}$ came to different conclusions: some of them finding relatively low correlation between exposure from personal and fixed air quality monitoring station (Adgate et al., 2002; Borgini et al., 2011; Brown et al., 2008; Crist et al., 2008) and some others showing high correlations (Janssen et al., 1999; Montagne et al., 2014b). Although Montagne et al. (2014b) found generally high correlation between temporal variation of the outdoor concentration and personal monitoring for different $PM_{2.5}$ components, Montagne et al. (2014a) found that the Land-Use Regression Models did not predict the spatial variation of the same components. Hence, using only the outdoor air component of exposure might not be enough to characterize human exposure to air pollutants (Steinle et al., 2013).

Adults have been the main target of personal monitoring, but less is known about children's personal exposure (Borgini et al., 2011; Buonanno et al., 2013; Crist et al., 2008; Van Roosbroeck et al., 2007). Children are more susceptible than young adults to air pollutants (Kulkarni and Grigg, 2008); therefore, their exposure is a major health concern (Mejía et al., 2011). Differences between adults and children can be summarized in the day-to-day activities which are in conjunction with being in different microenvironments (ME) depending on the activity, and the substantial difference in breathing heights that makes children closer to some pollution sources such as road traffic (HEI Panel on the Health Effects of Traffic-Related Air Pollution, 2010; Reche et al., 2011).

Black carbon (BC) personal measurement studies (Adams et al., 2002; Buonanno et al., 2013; Dons et al., 2011, 2012, 2013) are scarce in the literature, even though it is a good tracer of traffic emissions (especially from diesel engines), a source of major concern in urban environments. Although BC may not be toxic itself, it may have and indirect key role in toxicity as it is supposed to operate as a universal carrier of a wide variety of chemical components, such as semi-volatile organics and other compounds co-released in combustion processes (WHO, 2012). Therefore, a reduction in the exposure to BC should lead to a reduction in negative health outcomes derived from these toxic constituents.

In addition, Morawska et al. (2013) identified two important gaps in literature which are covered in the present work: the relationship between ambient concentration and personal monitoring, and the contribution of school exposure to a child's daily exposure and dose with respect to other MEs.

Framed within the ERC-Advanced Grant (FP7) BREATHE Project, this work's aim was to evaluate (i) the relationship between personal BC exposure of school children assessed by portable microaethalometers and (a) school BC concentrations, obtained by the same instrument at an indoor and outdoor fixed stations at the schools and (b) ambient BC concentration in a reference Urban Background (UB) site; and (ii) the daily-integrated exposure and dose of schoolchildren in Barcelona. In a previous study, we evaluated the relationship between spatial models and personal exposure (Nieuwenhuijsen et al., 2015), while the focus here is on in-depth analyses of the commuting data, and spatiotemporal relationships between ambient and personal BC and dose.

Materials and methods

Instrumentation and calibration

Both personal and fixed stations at schools (indoor and outdoor) were monitored using a MicroAeth AE51 (AethLabs, USA). It is a small (117 × 66 × 38 mm), light (0.28 kg), and battery-powered device which

can be easily carried in a belt bag, reducing wearer nuisance. A Multi Angle Absorption Photometer (MAAP Thermo ESM Andersen Instruments) was employed at a UB site which was monitoring BC during the whole sampling period.

The MicroAeth provides data on BC concentrations derived from absorption values. The factor applied to convert the absorption values into mass concentrations ($\mu g/m^3$) varies in every region, and therefore, the MicroAeths placed on the fixed stations at schools were cross-correlated with offline measurements of EC in gravimetric samples by thermal–optical transmission (Sunset Laboratory OCEC Analyser) collected *in situ* during the sampling campaigns. The site-specific calibration factor applied to convert the BC measured by the MicroAeths to equivalent black carbon (EBC) concentrations was 0.54 (EBC = 0.54·BC, R^2 = 0.88, Figure S1). Moreover, prior and after the two monitoring campaigns, all the MicroAeth were compared between them, and the corresponding correction factor with respect to the reference one was applied to the data of each individual instrument (see Supplementary Material for further information). BC concentrations measured with the MAAP in the background site were converted into EBC by an experimental Absorption/EC factor of 9.2 previously determined versus *in situ* thermo-optical EC filter data by Reche et al. (2011).

The effect of filter loading on BC measurements was kept to a minimum by replacing the filter strips every 24 h and setting a flowrate of 100 ml/min. The time-base was set to 5 minutes to minimize the noise in the measurements due to the sensitivity of MicroAeths to vibration, as well as to extend battery life.

EBC monitoring

Fifty-three children (7–10 years old) were initially involved in the personal measurements during 48 h each, which took place from 19 March 2012 to 22 February 2013. Sampling was carried out only during weekdays. Data from 8 children were discarded because of measuring errors recorded by the MicroAeth and other operational problems, resulting in 45 children being finally included in the study (with at least 24 h of valid data). Children carried the instrument in a belt bag, with the inlet tube always exposed and placed in the breathing zone. To minimize any annoyance derived from wearing the instrument, pupils were allowed to leave the device on the table or hang it from their chair during teaching hours and to leave it on the night stand (and carry the batteries) during sleeping time. It was stressed that it was important to wear the instrument every time they changed location (even between school classrooms), went to the playground or commute.

The children were also instructed to fill in a time–activity diary reporting every time they changed location and activity. The personal measurements sampled by the MicroAeth were classified based on the location (or MEs) of the children as 'classroom' (if the child was inside the school building regardless if it was specifically a classroom), 'school playground', 'home', 'commuting', and 'other' (this category includes MEs of many kind such as public library, swimming pool, shop, ...) according to the information registered in the time–activity diaries. Some commuting time might be misclassified into the 'other' category, as some trips were not clearly specified in the diaries.

The 45 children were attending 25 different schools, which were part of the BREATHE Project. The schools were located in the city of Barcelona (16 000 inhabitants/km^2, IDESCAT, 2012), except two, which were in Sant Cugat del Vallès (1800 inhabitants/km^2, IDESCAT, 2012, Figure 1). At the same time as personal monitoring, online BC concentrations with the MicroAeth device were simultaneously monitored at

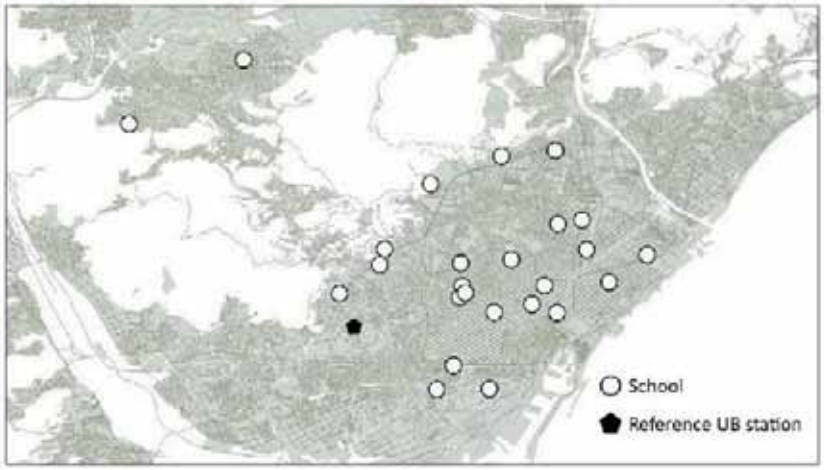

Fig. 1 Location of the reference urban background station and the schools that the children were attending to

schools, both indoors (in a classroom with pupils from 7–10 years old) and outdoors (in the playground or in a balcony) throughout 24 h a day at a height between 0.7 and 1.5 (children's breathing height). Moreover, BC concentrations were also monitored in the reference UB station of Palau Reial, located in the garden of the IDAEA-CSIC building (41°23′14″ N, 02°06′56″ E, 78 m.a.s.l). Therefore, we measured BC concentration across three different spatial units of analysis: personal, school, and city scale (Mejia et al., 2011; Morawska et al., 2013).

Further information about the data collection and air quality assessment at fixed stations at schools can be found elsewhere (Rivas et al., 2014).

Data analysis

Negative measurements were not removed from the analyses (McBean and Rovers, 1998), as the MicroAeth detects the change in optical absorption, and small shifts in the light beam or the filter ticket can cause a temporary decrease in measured absorption. The aethalometer computes the difference with the previous measurement, and therefore, negative measurements are considered offsets in the next observations. On the other hand, negative values in MicroAeth can also be due to sharp changes in relative humidity (i.e., when moving from the indoor to the outdoor environment), as demonstrated by Cai et al. (2014). Although negatives values have been included into the analyses, the 1st percentile has been considered as the minimum when reporting the range in the results section as negative concentrations have no physical meaning.

When comparing data between the different monitoring stations, only data for which simultaneous measurements were available were used (casewise deletion). To assess the relationship between EBC personal measurements and EBC measurements at fixed stations, we carried out linear mixed-effects models (LMMs) with school and student as random effect to account for the repetitive measurement and assessed the proportion of variance that explains the fixed part of the model (R^2).

All the statistical analyses (data management, descriptive statistics, time series and LMMs) were performed with the 10 min averaged values with the R statistical software (v 3.1.0., R Core Team, 2014) and the packages *openair* (Carslaw and Ropkins, 2012) and *lme4* (Bates et al., 2014), among others.

Results and discussion

EBC concentrations

The EBC concentrations measured in the different monitoring sites as well as in personal measurements during the overall experimental campaign are shown in Figure 2 and Table S2. Similar EBC levels were

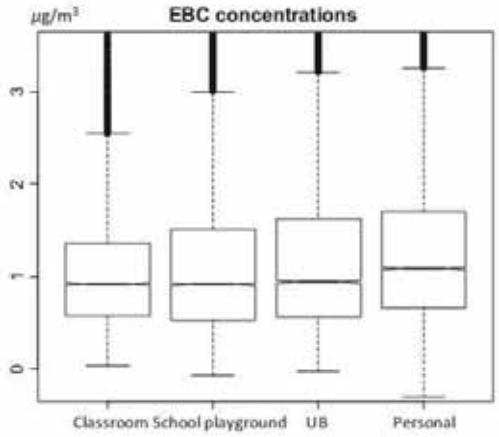

Fig. 2 Boxplot showing EBC concentrations ($\mu g/m^3$, 10-minute time resolution) measured at different monitoring stations (at indoor school classrooms, school playgrounds, urban background, and personal monitoring). Boxes represent the interquantile range (IQR, 25–75 percentile), the line shows the median of the data. The whiskers add and subtract 1.5 the IQR to 75 and 25 percentiles, respectively. The notch displays the confidence interval around the median

obtained in all the stations. The geometric mean (GM) EBC concentration in the fixed stations (schools playgrounds, classrooms, and UB was 0.9 $\mu g/m^3$). The similarities between indoor and outdoor environments could be explained by the relative location of the sampling sites within schools, whereby in some schools, the classroom was relatively closer to outdoor traffic than the outdoors and EBC easily infiltrates from the outdoor to the indoor environment (Rivas et al., 2015). Schools were distributed among high- and low-trafficked areas of the city, which results in mean concentrations similar to the UB site. The increasing variability from the classroom toward the UB site (Figure 2) was interpreted as resulting from the fact that the outdoor environments (school playground and UB) are influenced to a larger degree than the classroom by meteorological factors, which impact EBC levels by diluting or concentrating this pollutant as a function of atmospheric dispersion. The highest GM EBC concentration was obtained for personal measurements (1.0 $\mu g/m^3$; 20% higher than at the school fixed stations, 10% higher than at UB). The range of 10-min EBC concentrations from personal measurements was the widest one (0.1–53.3 $\mu g/m^3$) when compared to the fixed school and UB sites and, and the highest values were due to peak concentration events that took place mainly during commuting time and will be discussed later. There are only few publications reporting personal measurements of BC data on children. Buonanno et al. (2013) monitored 103 children during 48 h (8–11 years old) in Cassino (Italy) and obtained an average of 5.1 $\mu g/m^3$ (range 0.1–521 $\mu g/m^3$) which is much

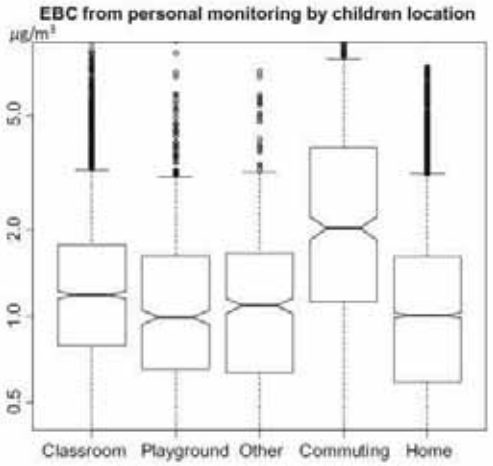

Fig. 3 EBC concentration ($\mu g/m^3$, logscale, 10-minute time resolution) ranges from personal monitoring by time periods corresponding to the ME where children reported to be in the diary. Boxes represent the IQR, the line shows the median of the data. The whiskers add and subtract 1.5 the IQR to 75 and 25 percentiles, respectively. The notch displays the confidence interval around the median

higher than ours (arithmetic mean, AM=1.5 $\mu g/m^3$ EBC, 2.7 $\mu g/m^3$ of uncorrected BC; Table S2).

In Figure 3, we split the concentrations measured by personal monitoring by the ME where children reported to be in the diary each time period (the equivalent figures for the fixed stations are presented in Figure S2). The highest EBC levels from personal monitoring were measured during commuting times (GM=2.0 $\mu g/m^3$, which were significantly higher than in the rest of ME; Figure 3, Table S2), followed by the concentrations to what children were exposed when being in the classroom (1.2 $\mu g/m^3$) and in the school playground (1.0 $\mu g/m^3$). The lowest concentrations were obtained during periods when children were at home or at other ME (0.9 $\mu g/m^3$ in both ME). The previous results were expected, as children (and citizens in general) are very close to traffic when commuting, while the lowest EBC levels are expected during nights, when children are at home. For epidemiological studies with large populations, knowing the amount of time that the subjects spend in commuting (i.e., through questionnaires) may be used as a qualitative indicator of the degree by which personal exposure is higher than fixed monitor EBC concentrations.

The impact of each transport mode used by children for commuting was evaluated and the results are shown in Table 1. Children were asked to write down in the time–activity diary the mode of transport that they used for commuting, but in the 45% of the trips (103 of 229 of identified trips) the transport mode was unknown. For those cases in which we have information, the lowest concentrations were measured for the car mode (GM=1.7 $\mu g/m^3$, AM=2.3 $\mu g/m^3$, probably

Table 1 Mean EBC concentrations from the personal measurements for the different means of transports (reported in the time–activity diary)

Parameter	On foot	Bus	Metro	Car	Mixed	Unknown
N (trips)	75	12	9	21	9	103
Mean trip duration (min)	26	40	39	37	50	20
EBC, GM ($\mu g/m^3$)	1.9	3.9	3.8	1.7	3.6	1.8

GM, geometric mean.

influenced by air recirculation; Hudda et al., 2012; Knibbs et al., 2010) followed by the levels found when commuting on foot (GM=1.9 $\mu g/m^3$, AM=2.4 $\mu g/m^3$). Children commuting by metro were facing a GM EBC concentration of 3.8 $\mu g/m^3$ (AM=4.0 $\mu g/m^3$) with the highest concentrations observed for the bus mode (GM=3.9 $\mu g/m^3$, AM=5.0 $\mu g/m^3$). These results agree to what Dons et al. (2012) observed for 62 adults in Belgium, where bus transportation was the one with the highest BC levels (6.6 $\mu g/m^3$ for bus passengers). However, in their study car was the second highest transportation mode with BC concentrations of 6.4 $\mu g/m^3$ for car drivers and 5.6 $\mu g/m^3$ for car passengers, which in our case showed the lowest mean concentrations (which may be due to differences in air recirculation settings, but this information is not available and cannot be assessed).

EBC Time series

The analysis of the EBC concentration time series allows the identification of peak concentration events and relation to specific activities (when identified in the diary). Moreover, we can evaluate how EBC concentrations monitored in different ME by the different fixed monitoring sites relate to concentrations measured by personal monitoring.

As an example, Figure 4 shows the time series of EBC concentration measured by personal monitoring of 4 children from 2 different schools. EBC concentrations measured by the fixed monitoring stations are also shown. Although the schools were located in different areas of Barcelona, with different traffic intensities (Rivas et al., 2014), most of them showed the morning and afternoon road traffic rush hour, which were not only identified in outdoor monitoring stations but also inside the schools owing to a high EBC infiltration (Rivas et al., 2015). The morning rush hour coincided with children commuting to school. In fact, most of the commuting periods were clearly evident in the personal measurements because of (extremely) high EBC peaks (Figure 4), which were an average of 2.9 times higher than mean concentrations measured at home. The ratio $EBC_{commuting}/EBC_{home}$ ranged between 0.8 and 26.7 (median = 2.5). The 26.7 was an extreme case of a child exposed to very high concentrations during commuting but having very low concentrations while being at home. In fact, the second maximum of this ratio drops

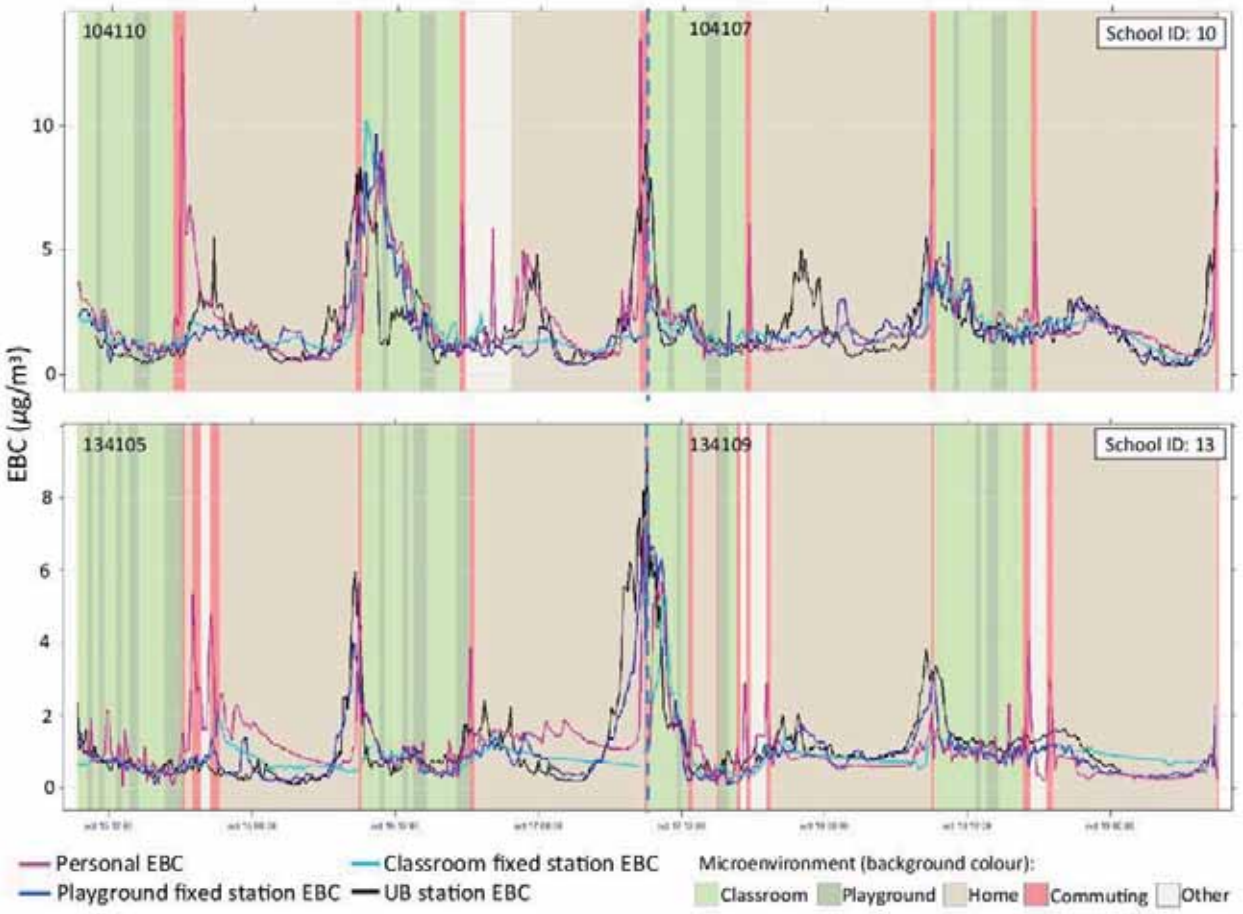

Fig. 4 Time series corresponding to 4 different children (from 2 schools). Lines indicating EBC concentrations (ng/m^3) measured in the personal monitor (pink), school classroom (light blue), school playground (blue), and in the urban background (black) are shown. Background shadow indicates in which microenvironment were children located at each time step

drastically to 5.2. The three cases with the highest ratios are presented in Figure S3.

Although monitored children were not always attending the same classroom where the air quality monitoring was carried out, during school hours, the majority of EBC concentration from personal measurements followed approximately the same levels and trends as the ones measured by indoor school monitoring stations. Generally, indoor and outdoor school levels also followed the UB trends, confirming the previously observed infiltration and the influence of traffic emissions. However, levels at school might be higher or lower than at UB, depending on traffic conditions in the specific streets surrounding the school. Therefore, this makes the estimation of the personal exposure based on a simple (or few) fixed stations difficult, as a more local-scale characterization is needed. In addition, sometimes a lag time between the morning EBC peak in the UB station and in schools can be seen, mainly because the UB station is located near one of the main access roads to the city. This lag time is usually longer when referring to indoor environments, since extra time should be added to account for EBC transport and infiltration from outdoor to indoor air. There is a great variability among each child's time series, probably associated to the living area location (school and home, principally), which might be influenced by different traffic intensities and, thus, different EBC concentrations. In accordance with what Dons et al. (2011) concluded, differences in EBC concentrations to what children are exposed are due to differences between their time–activity pattern and the corresponding location visited.

Agreement between personal measurements and different monitoring sites

Assuming personal monitoring as the most representative measure for exposure (Jantunen et al., 2002), we performed LMMs to test the agreement between personal measurements and those recorded by fixed stations in different locations. The regression coefficients

(RC, which is the equivalent to the slope in a simple linear regression), intercepts, and R^2 (defined here as the proportion of the variance explained by the fixed effect) are shown in Table 2 for all the data and separately by warm and cold season. Low R^2 between personal measurements and fixed stations at schools were found ($R^2 = 0.28$ and $R^2 = 0.26$, classroom and playground, respectively), being the R^2 much higher during the warm (mean temperature >20 °C) than the cold season (especially for the school fixed stations). The coefficients are also higher (closer to 1) for the warm season period, indicating a better prediction from the fixed station (especially the indoor stations at schools, with a RC = 1 and $R^2 = 0.52$) during this season. Studying the agreement between personal measurements and fixed stations in the different microenvironments allows us to have a deeper understanding about which are the microenvironments of which the fixed stations fail to be representative.

Focusing only in the periods when children were at the classroom microenvironment we can observe an important increase of the R^2 (being 0.79 for the classroom and 0.75 for the playground station) when compared to the whole day, indicating the importance of the spatial unit of analysis when assessing human exposure. During the warm season, the coefficients are much closer to 1 than during the cold season, and this worse prediction from the outdoor fixed stations is due to closed windows during colder periods that partially hinder EBC infiltration into the indoor environment. On the other hand, it should be highlighted that during both seasons, the coefficients for the classroom station are close to 1 during classroom and home time (although lower R^2 are found when the children were at home), what indicates that these two indoor environments followed not only similar patterns but also similar levels. Considering the important amount of time spent in the indoor environments, these results suggest the necessity to characterize indoor school environments for an accurate assessment of exposure to EBC of schoolchildren.

The relationship between personal EBC concentrations when children were at school and concentrations at UB fixed station was also assessed by LMM, obtaining an $R^2 = 0.45$ in both classroom and playground times (R^2 between UB and schools are 0.37 for the indoor station and 0.39 for the outdoor one), which was much higher than the R^2 obtained when

Table 2 Regression coefficients (RC), intercept, and R^2 from the linear mixed-effects models performed for EBC concentration from personal measurements as the outcome and fixed stations (in different locations) as fixed-effect predictor. Models were performed for the complete day (including all microenvironments) and only considering the time spent in each of the microenvironment separately

	All seasons			Cold season			Warm season		
Fixed-effect predictor (μg/m³)	RC	intercept (μg/m³)	R^2	RC	intercept (μg/m³)	R^2	RC	intercept (μg/m³)	R^2
All day									
EBC classroom fixed	0.95*	0.4*	0.28	0.85*	0.5*	0.17	1.00*	0.3*	0.52
EBC playground fixed	0.65*	0.6*	0.26	0.53*	0.7*	0.15	0.72*	0.5*	0.50
EBC UB fixed									
Unadjusted	0.39*	0.9*	0.18	0.28*	0.9*	0.14	0.49*	0.9*	0.29
Adjusted*	0.39*	0.9*	0.18	0.28*	1.2*	0.14	0.49*	0.3	0.29
Classroom time									
EBC classroom fixed	0.94*	0.3*	0.79	0.81*	0.4*	0.68	0.99*	0.2	0.79
EBC playground fixed	0.73*	0.5*	0.72	0.46*	0.7*	0.57	0.80*	0.5*	0.73
EBC UB fixed	0.49*	0.9*	0.45	0.11*	1.1*	0.41	0.61*	1.0*	0.40
Playground time									
EBC classroom fixed	1.00*	0.1	0.73	0.87*	0.2*	0.49	0.99*	0.1	0.87
EBC playground fixed	1.02*	0.1	0.75	0.87*	0.2*	0.48	1.01*	0.1	0.89
EBC UB fixed	0.53*	0.8*	0.45	0.18*	0.9*	0.31	0.64*	0.9*	0.47
Home time									
EBC classroom fixed	1.00*	0.3*	0.48	0.92*	0.4*	0.46	1.09*	0.2	0.41
EBC playground fixed	0.48*	0.7*	0.47	0.50*	0.7*	0.46	0.49*	0.7*	0.40
EBC UB fixed	0.31*	0.9*	0.43	0.38*	0.7*	0.46	0.34*	0.9*	0.34
Commuting time									
EBC classroom fixed	0.93*	1.9*	0.30	0.63	2.3*	0.29	1.12*	1.0*	0.43
EBC playground fixed	0.76*	2.0*	0.32	0.43	2.5*	0.29	0.85*	1.3*	0.56
EBC UB fixed	0.53*	2.2*	0.30	0.18	2.7*	0.29	0.65*	1.5*	0.41
Other time									
EBC classroom fixed	−0.01	1.6*	0.37	−0.19	2.2*	0.38	0.13	1.1*	0.18
EBC playground fixed	0.00	1.5*	0.37	0.11	1.9*	0.37	0.14	1.1*	0.18
EBC UB fixed	0.10	1.4*	0.37	0.14	1.7*	0.39	0.15	1.1*	0.19

*Adjusted by distance between school and UB and by traffic density at school.
*P-value <0.05.

considering the whole day (R^2 = 0.18, Table 2). This lower coefficient of determination when compared to the fixed sites in schools is due to specific characteristics of each ME where the children spend their time but also to the spatial variability among the city for this pollutant observed during BREATHE campaigns.

When children were commuting, the corresponding R^2 was around 0.30 in all stations with higher R^2 during the warm season. The high intercepts indicate that children receive a contribution of around 2 $\mu g/m^3$ of EBC that is not accounted by the fixed stations. The low R^2 for commuting periods (≤0.32) can be explained by the proximity of children to the main source of EBC, traffic, and also because their breathing height is very close to exhaust pipes (Mott et al., 1997).

As shown in Table 2, the R^2 for the 'other' microenvironments is also low and the coefficients are not significant. This may be due to the fact that this single category includes very different microenvironments with different characteristics.

In addition to season, distance from school to the UB station and traffic density (traffic counts were performed during 15 min twice per week in each school) were also included in the model as possible predictors of personal EBC concentrations (adjusted model for UB in Table 2). These two variables did not contribute to improve significantly the model. Moreover, distance to school was further studied (Figure S4) and the correlation coefficient between personal EBC measurements and EBC concentrations at UB for each child showed no linear relationship with distance. Other possible influential variables (e.g., architectural features, wind speed, and direction) that were not assessed in this study may have an important role.

Moreover, correlations between five pairs of children (from three different schools) that were monitored simultaneously resulted in a coefficient of determination of 0.08 when correlating the EBC concentration between them. Again, the low relationship between the concentrations these children were exposed to seems to be explained by the distance to road traffic in each specific moment. The fact that the correlation between exposure measurements for different children is low illustrates the difficulties to obtain representative exposure data at individual level.

Children's daily-integrated exposure and dose to EBC

Exposure is often confused with concentration (Morawska et al., 2013), the latter being the most frequently quantified. The concept of exposure incorporates the duration of the contact to a certain concentration by integrating over time (Duan, 1982; Ott, 1982). Determining the dose is a step further than the exposure, and it corresponds to the product of the exposure by a dosimetry factor (Morawska et al., 2013). In our case,

Table 3 Inhalation rates (m^3/h) for children (6–10 years) as a function of the activities usually carried out in each of the microenvironments considered

Microenvironment	Activity associated	Inhalation Rate[a] (m^3/h) (age group: 6–10 years)
School indoor	School/studying/eating	0.42
School outdoor	Playing outdoor	1.27
Commuting	Transportation	0.91[b]
Home (non sleeping time)	Sedentary activities/eating	0.42
Home (sleeping time)	Sleeping and resting	0.31
Others	Entertainment indoor and outdoor	0.91

[a]Inhalation rates obtained from Buonanno et al. (2011).
[b]The original inhalation rate from Buonanno et al. (2011) was 0.58 m^3/h.

the dosimetry factor is the inhalation rate and the ones being employed are presented in Table 3 and were obtained from Buonanno et al. (2011), which were adapted from Adams (1993) and US-EPA (2009). The dosimetry factor for transportation was originally 0.58 m^3/h. However, for the present work, the inhalation rate for a non-sedentary job was considered as the most appropriate for commuting activities, as they might include active transportation that may involve some increment on inhalation rates. To accurately determine the dose, for this section the 'home' has been split into two, considering if the children were sleeping (the activity with the lowest inhalation rate) or doing other sedentary activities. In this study, only working days were considered. The exposure and dose received during weekends may vary considerably from weekdays.

The mean daily-integrated exposure to EBC for the 45 children was 34.6 $\mu g/m^3/h/day$, and it showed a high variability among the children (standard deviation: 13.8 $\mu g/m^3/h/day$, range: 12.8–72.9 $\mu g/m^3/h/day$, Figure S5). For the daily-integrated dose, the mean accounted for 18.2 $\mu g/day$ (standard deviation: 7.7 $\mu g/day$, range: 6.5–40.8 $\mu g/day$, Figure 5) and the variability observed within the exposure was maintained for the dose. This variability was a result of the different time–activity–geography patterns of each child, who can carry out very different activities in locations with different EBC concentrations. Exposure and dose could be significantly different even between children attending the same school, and this variability could not be taken into account only with the fixed stations. Mullen et al. (2011) also observed a high variability in ultrafine particle number concentration among 13 occupants of 4 apartments. This highlights the usefulness of personal monitoring for a precise estimation of the exposure/dose of each subject.

Home was the ME with the lowest EBC concentration. Notwithstanding, from the total daily-integrated exposure, children received the 50% while being at home (30% during sleeping time), where they spent around 58% of their daily time (Figure 6, Figure S6). Children received the highest exposure at

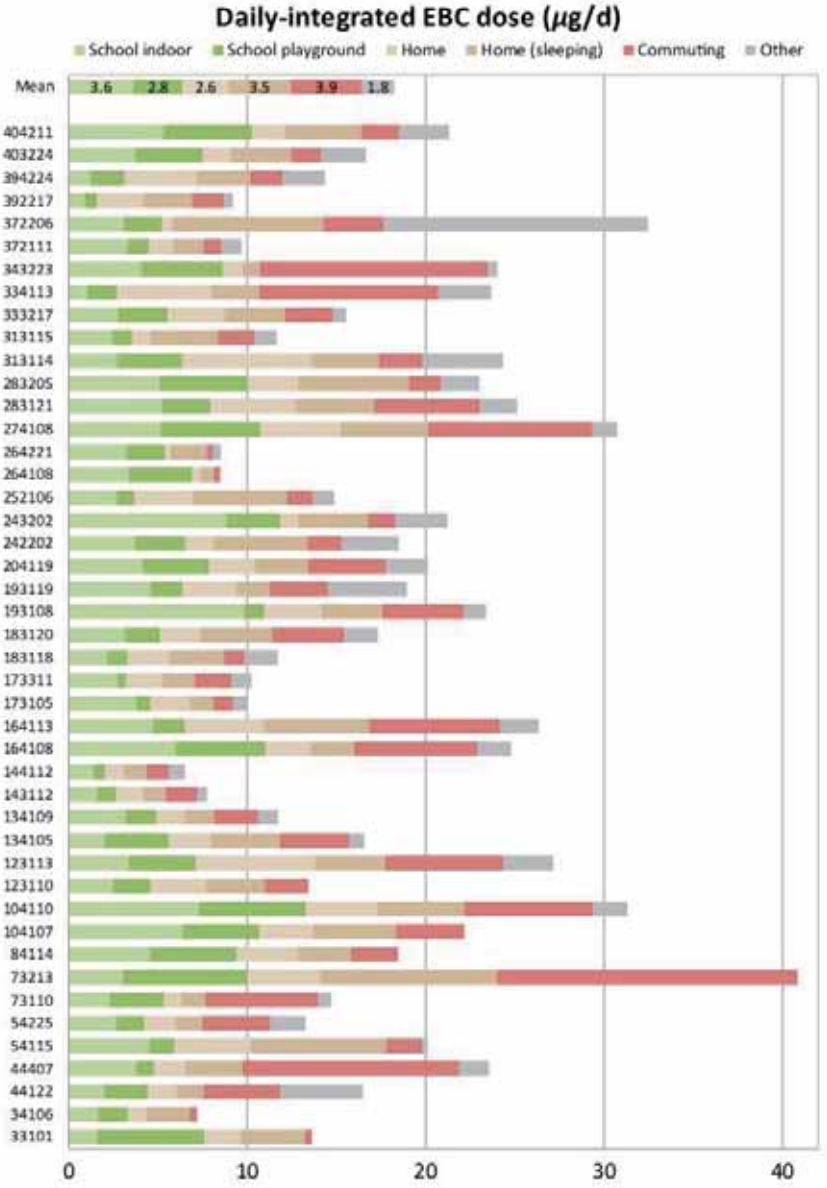

Fig. 5 Estimated daily integrated EBC dose ($\mu g/m^3$) for the 45 children and their mean (for %, refer to Figure S4). The integrated dose represents the product of the exposure in each of the microenvironments ($ng/m^3/h/day$) by the inhalation rate (m^3/h)

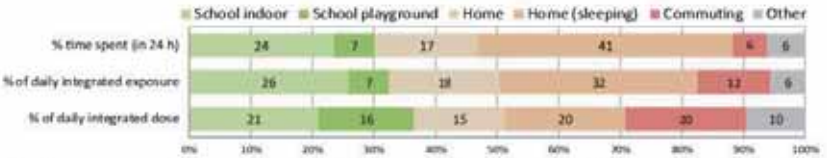

Fig. 6 Mean % of the daytime spent and percentage of daily integrated exposure and dose corresponding to each microenvironment for the 45 children

home because of the large time spent there, since it accounts for the night period. However, since the activities usually carried out at home during week-days are not very active, the home contribution to the daily-integrated dose decreased to only 35% (20% corresponds to sleeping time). Actually, the

lowest ratio of exposure and dose with respect to the time spent was observed at home during sleeping time (ratio exposure:time = 0.77:1, dose:time = 0.47:1). Children spent 31% of their weekday at schools, where they received 33% of their daily-integrated exposure to EBC (26% in the classrooms and 7% at playgrounds) and 37% of the daily-integrated dose (21% and 16%, classroom and playground, respectively). Indoor environments (classroom + home) accounted for the 82% of the daily time of schoolchildren during weekdays. The corresponding daily-integrated exposure and dose received in the indoor environments was 76% and 56%, respectively. Therefore, children received more than half of the dose in the indoor environment. Although the dose received at home is higher, policies for the reduction of EBC emissions around schools would benefit a large number of children given that they spend a considerable portion of their weekdays in a shared location (school).

However, the highest ratio of exposure and dose with respect to the time spent was observed during commuting. It was responsible for 12% of the daily exposure and around 20% of the daily dose whilst it only accounted for the 6% of the time, so a relation 2.1:1 (3.5:1) of exposure:time (dose:time) is observed. The high exposure was explained by the high concentrations found during commuting, and the dose is a combination of the former and the moderate physical activity intensity usually involved in commuting. In fact, the inhalation rate factor employed for commuting may vary considerably according to the mode of transport, being considerably higher in the case of active travel (De Nazelle et al., 2012). However, as 35% of the commuting modes were not reported by children, the same inhalation rate has been used for this activity regardless of the transport mode. Buonanno et al. (2013) obtained a similar percentage of time spent in the different ME for 103 children in Cassino (64% at home, 24% at school, and 4% in transport versus 58%, 30%, and 6% in our study) and also a similar distribution of the exposure contribution (60% at home, 20% at school, and 11% in transport versus 50%, 32%, and 12% in our study), although with a much higher dose (39.2 μg/day versus 18.2 μg/day in our study). On the other hand, Dons et al. (2012) obtained a higher exposure:time and dose:time relationship in transport for 62 adults in Belgium (3.3:1 versus our 2.1:1 of exposure:time; 4.8:1 versus our 3.5:1 for dose:time), with people spending around 6% of their days commuting and receiving the 21% of their daily-integrated exposure and 30% of their dose. In the case of the exposure, it might be due to differences in activities schedule between children and adults (or between regions) and, in the case of the dose, it should also be considered that inhalation rates depend on the person age (increases with age).

Policies to reduce EBC levels should be enhanced throughout the urban area. As more than a third of the daily-integrated dose takes place at schools and commuting has the highest dose:time relationship, specific policies focused on reducing traffic intensities around schools should be implemented. These school targeted actions will favor the abatement of the exposure of a wide fraction of the population, which are also one of the most vulnerable to air pollutants threats.

Conclusions

The present work aimed to contribute to the current knowledge on spatial and temporal monitoring of EBC, specifically when assessing personal exposure of schoolchildren. To accomplish this objective, continuous personal monitoring of EBC was carried out with microaethalometers for 45 schoolchildren (aged 7–10), and fixed monitoring stations were located in indoor and outdoor school microenvironments and at an urban background site. The highest (geometric) mean EBC concentrations corresponded to personal monitoring (20% higher than at the school fixed stations, 10% higher than in the urban background) owing to peak concentration events during commuting times. This was due to two reasons: the co-occurrence of children commuting times and road traffic rush hours, and the closest proximity to the source (road traffic) while commuting. In fact, children spend only the 6% of their daily time in commuting, while based on our estimations, they received around 20% of their total daily EBC dose during this activity. This estimate will vary as a function of breathing rates, especially in transport microenvironments for which their variability is expected to be large. High R^2 from LMM correlations ($R^2 \geq 0.70$) were found between EBC from personal monitors and school fixed sites (both in classroom and playground) when considering only the time periods when children were in each of the microenvironments. On the other hand, the LMM relating personal measurements with the urban background station was weaker ($R^2 = 0.45$) for the same period, thus indicating the importance of the spatial unit of analysis when assessing human exposure. Due to opened windows that facilitate the entrance of outdoor pollutants to indoor environment, during the warm season, the outdoor fixed stations were more representative (higher R^2 and coefficients closer to 1) of the personal exposures than during the cold one. Children spent 82% of their time in indoor environments (classroom and home), where they received 76% and 56% of their daily-integrated exposure and dose, respectively. Considering the important amount of time spent in the indoor environments, it is important to characterize indoor environments for an accurate exposure assessment to EBC. The contribution from schools (including classroom and

playground) to the total daily-integrated EBC dose was the 37%, and the highest dose:time intensity was observed during commuting times. Reducing traffic intensities around schools should be enhanced to minimize the exposure of a wide fraction of the population who spend a large portion of their weekdays in a shared location.

Acknowledgements

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Supporting Information

Additional Supporting Information may be found in the online version of this article:
Appendix S1. Instrumentation calibration and supplementary data.

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Spatio-temporally resolved Black Carbon concentration, schoolchildren's exposure and dose in Barcelona

I.Rivas, D.Donaire-Gonzalez[b], L.Bouso, M. Esnaola, M.Pandolfi, M.de Castro, M.Viana, M. Àlvarez-Pedrerol, M. Nieuwenhuijsen, A. Alastuey, J. Sunyer, X. Querol

SUPPLEMENTARY MATERIAL

Instrumentation calibration

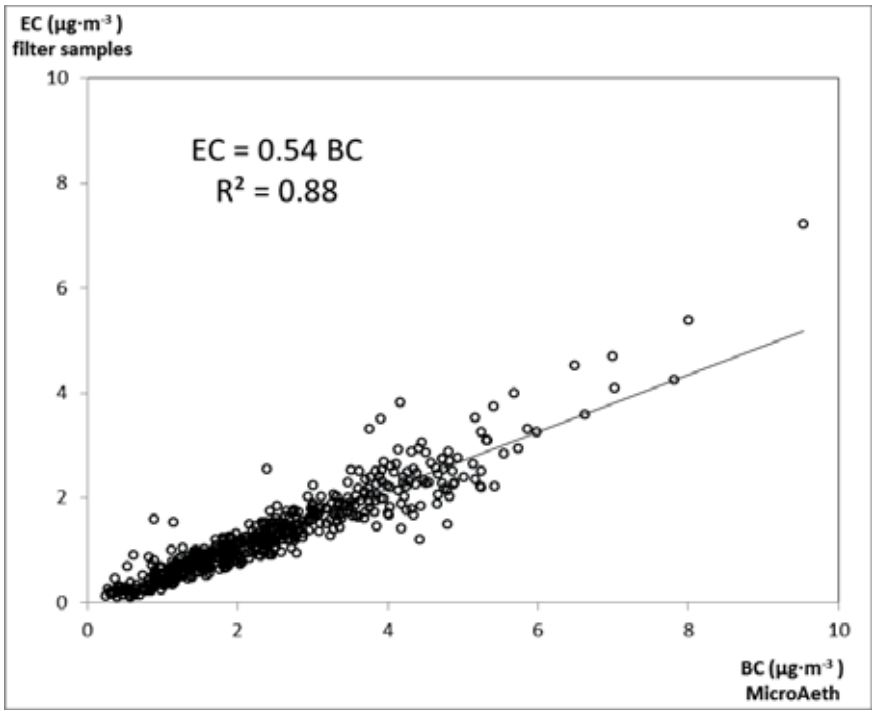

Figure S1. Correlation of BC (measured by MicroAeth) and EC (measured by thermo-optical transmission in 8h filter samples). The slope of the linear regression corresponds to the conversion factor form BC to EBC.

Prior and after each sampling campaign all the MicroAeths employed were intercompared among each other. The MicroAeth with the ID BC1 was considered the reference device. The fixed devices located at indoor (BC2 and BC4) and outdoor (BC1 and BC3) environments at schools do not need any correction, since the four devices were measuring similarly and correlations were good when compared to the MAAP used in the urban background station of Palau Reial. However, those MicroAeth employed for the personal measurements show considerable differences and should be corrected to level the concentration to those measured by BC1. The equation applied is the following:

$$BC1 = CF \cdot BC\_personal \quad (1)$$

where CF is the correction factor, BC1 is the BC concentration measured with the reference MicroAeth (BC1) and BC_personal is the concentration measured with the MicroAeth used for personal measurements (BC6 or BC7).

For the first sampling campaign (SC1) similar correction factors were found prior and after the sampling for BC6. However, during the second campaign (SC2), the correction factors prior and after the sampling differ considerable and a gradual correction factor was applied (Table S1).

Table S1. Correction factor applied to each MicroAeth device used for personal monitoring.

ID SCHOOL	DATE (1st day)	ID DEVICE	CORRECTION FACTOR
SC1			
5	19/03/12	BC6	0.820
7	16/04/12	BC6	0.820
4	23/04/12	BC6	0.820
16	07/05/12	BC6	0.820
33	14/05/12	BC6	0.820
SC2			
8	17/09/12	BC6	0.830
19	24/09/12	BC6	0.819
28	01/10/12	BC6	0.807
27	08/10/12	BC6	0.796
10	22/10/12	BC6	0.784
31	29/10/12	BC6	0.773
24	05/11/12	BC6	0.761
37	12/11/12	BC6	0.750
34	26/11/12	BC6	0.739
17	21/01/13	BC6	0.727
12	28/01/13	BC6	0.716
39	04/02/13	BC6	0.704
25	11/02/13	BC6	0.693
40	18/02/13	BC6	0.670
20	17/09/12	BC7	No correction needed
18	01/10/12	BC7	No correction needed
13	15/10/12	BC7	No correction needed
3	12/11/12	BC7	No correction needed
14	19/11/12	BC7	No correction needed
		BC1	No correction needed
26	03/12/12	BC7	No correction needed

Results

Table S2. EBC concentration measured by each monitoring site (including personal monitoring) by children location (based on the time-activity diary. AM = Arithmetic mean; GM = Geometric Mean.

		EBC concentration (ng·m^{-3})									BC* (ng·m^{-3})
	N	MIN	1%ile	25 %ile	50 %ile	GM	AE	75 %ile	99 %ile	MAX	MEAN
Personal monitoring											
All data	9782	-0.31	0.09	0.7	1.1	1.0	1.5	1.7	7.1	53.3	2.7
School classroom	2320	-0.17	0.17	0.8	1.2	1.2	1.5	1.8	7.2	12.1	2.8
School playground	662	-0.31	0.05	0.7	1.0	1.0	1.4	1.6	6.3	25.4	2.5
Home	5658	-0.06	0.10	0.6	1.0	0.9	1.3	1.6	5.3	12.1	2.3
Commuting	531	-0.06	0.17	1.1	2.0	2.0	3.3	3.9	20.4	53.3	6.1
Other	611	-0.21	0.05	0.6	1.1	0.9	1.4	1.7	6.7	20.1	2.5
School classroom monitor											
All data	9782	0.04	0.11	0.6	0.9	0.9	1.1	1.4	4.5	10.2	2.0
School classroom	2320	0.04	0.26	0.7	1.0	1.0	1.3	1.5	6.6	10.2	2.4
School playground	662	0.14	0.23	0.6	0.9	1.0	1.2	1.5	4.8	8.4	2.3
Home	5658	0.04	0.10	0.5	0.8	0.8	1.0	1.3	2.7	6.8	1.8
Commuting	531	0.09	0.19	0.6	1.0	1.0	1.3	1.5	6.1	7.5	2.3
Other	611	0.25	0.34	0.8	1.1	1.0	1.1	1.3	2.9	4.0	2.1
School playground monitor											
All data	9782	-0.07	0.09	0.5	0.9	0.9	1.2	1.5	5.6	13.2	2.2
School classroom	2320	0.05	0.17	0.6	1.0	1.0	1.4	1.6	7.5	11.2	2.5
School playground	662	0.15	0.19	0.6	0.9	0.9	1.1	1.4	4.9	8.3	2.1
Home	5658	-0.07	0.07	0.4	0.9	0.8	1.1	1.5	5.0	13.2	2.1
Commuting	531	0.12	0.17	0.7	1.0	1.0	1.4	1.4	9.0	13.1	2.6
Other	611	0.14	0.24	0.7	1.0	1.0	1.2	1.5	4.3	4.8	2.3
Urban background monitor											
All data	9782	-0.02	0.10	0.6	0.9	0.9	1.3	1.6	6.6	9.3	2.5
School classroom	2320	0.00	0.24	0.7	1.0	1.0	1.3	1.5	6.6	9.0	2.4
School playground	662	0.19	0.24	0.6	0.9	1.0	1.2	1.4	4.3	8.4	2.2
Home	5658	-0.02	0.08	0.5	0.9	0.8	1.3	1.6	6.5	9.0	2.4
Commuting	531	0.19	0.25	0.8	1.1	1.2	1.7	1.8	7.9	9.3	3.1
Other	611	0.19	0.24	0.9	1.3	1.3	1.8	2.3	6.4	7.0	3.2

*BC not corrected by EC.

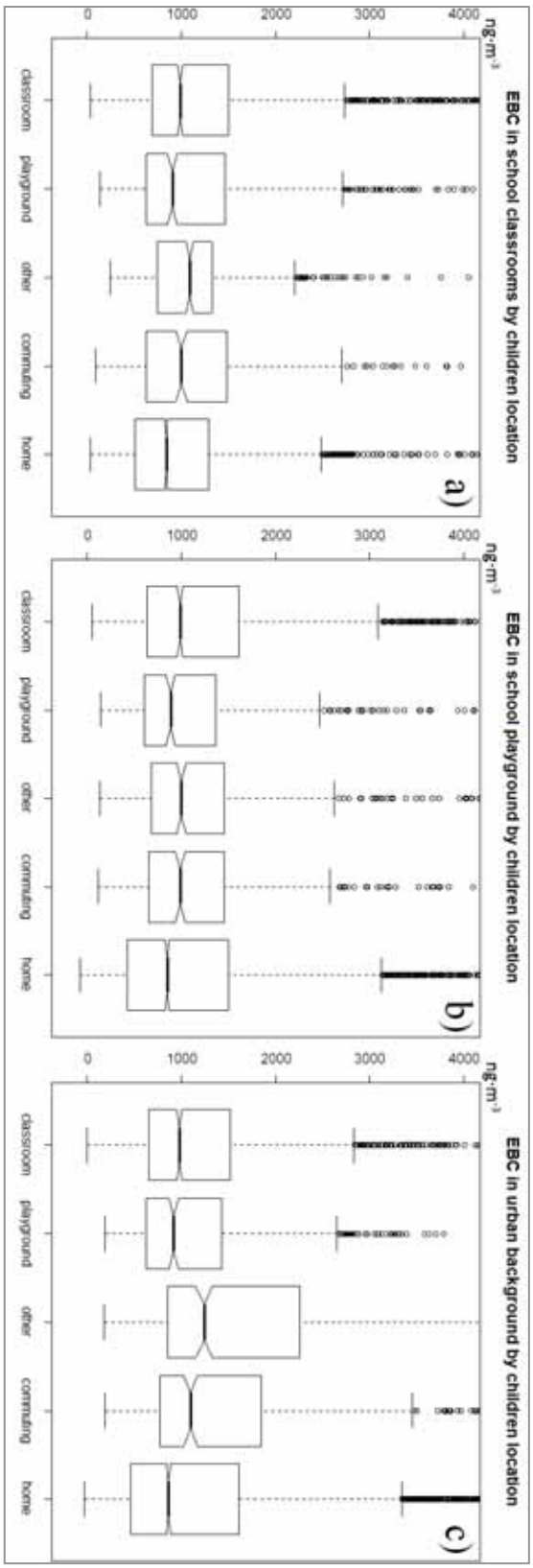

Figure S2. EBC concentration ($ng \cdot m^{-3}$) ranges in different monitoring sites: a) school classroom, b) school playground and c) UB-PR by time-periods corresponding to the microenvironment where children reported to be in the diary. Boxes represent the interquantile range (IQR, 25-75 percentile), the line shows the median of the data. The whiskers add and substract 1.5 the IQR to 75 and 25 percentiles, respectively. The notch displays the confidence interval around the median.

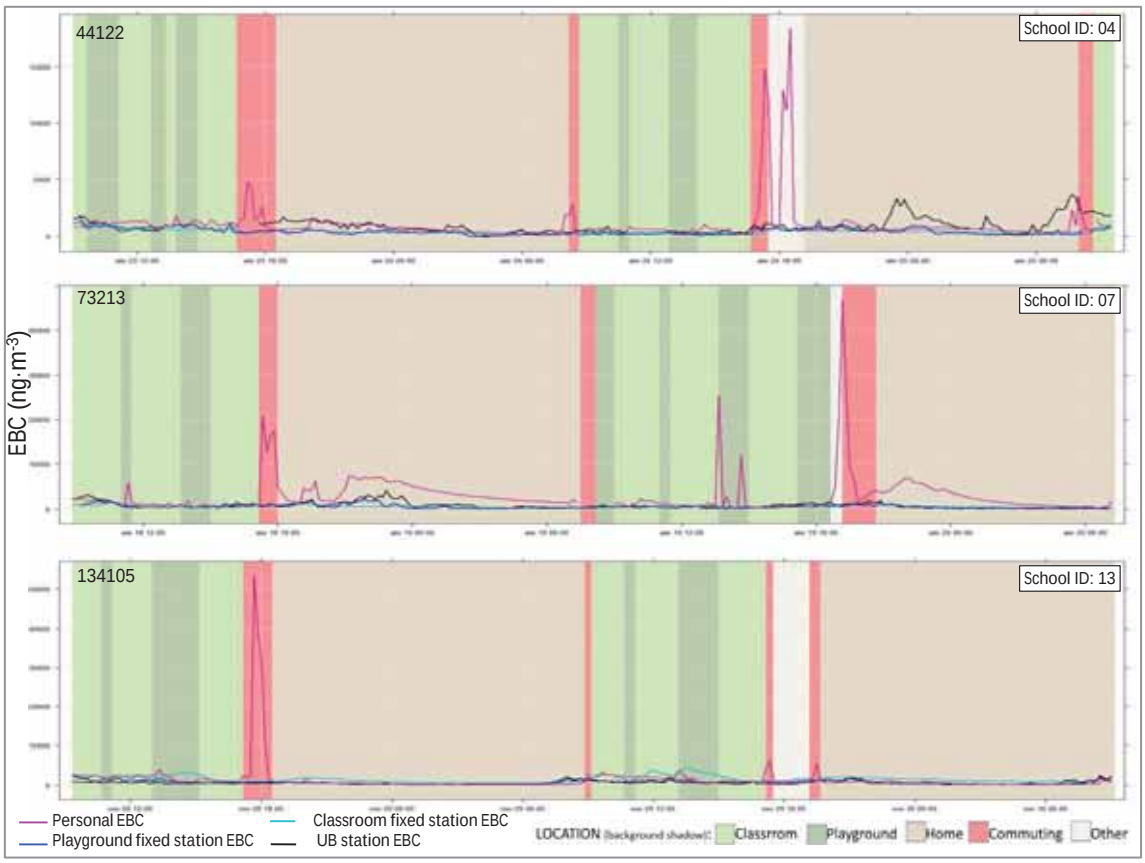

Figure S3. Time-series of to the 3 children with the highest EBCcommuting/EBChome ratio. Lines indicating EBC concentrations measured in the personal monitor, school classroom, school playground and in the urban background are shown. Background shadow indicates in which microenvironment where children located for each time-step. Children number 44122 has a probably non-identified commuting by the time-activity diary, so it is considered in the "other" category.

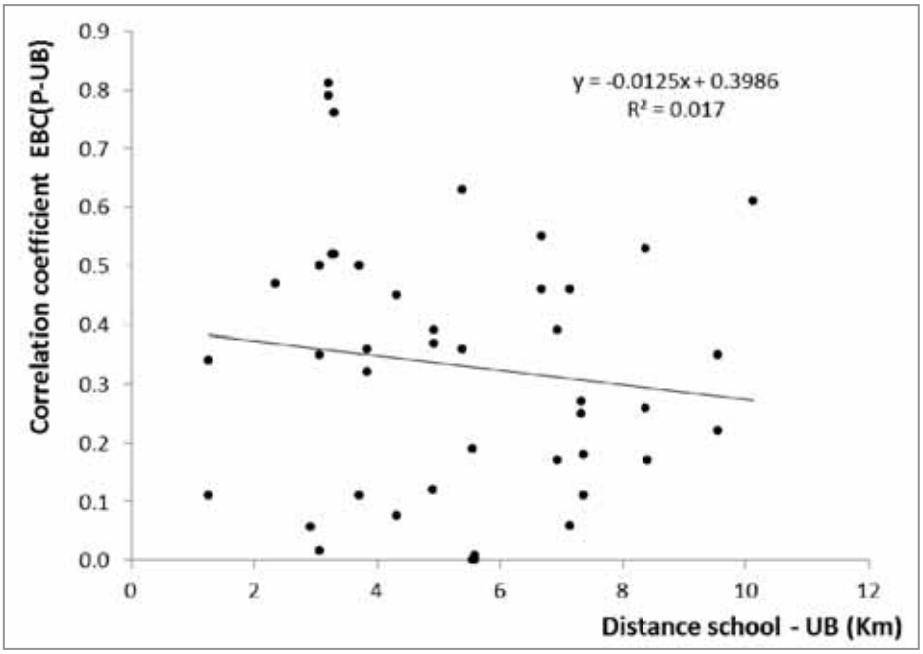

Figure S4. Linear regression between (1) the correlation coefficient obtained when linearly relating EBC form personal measurements and from the UB station and (2) the corresponding distance between schools and the UB station.

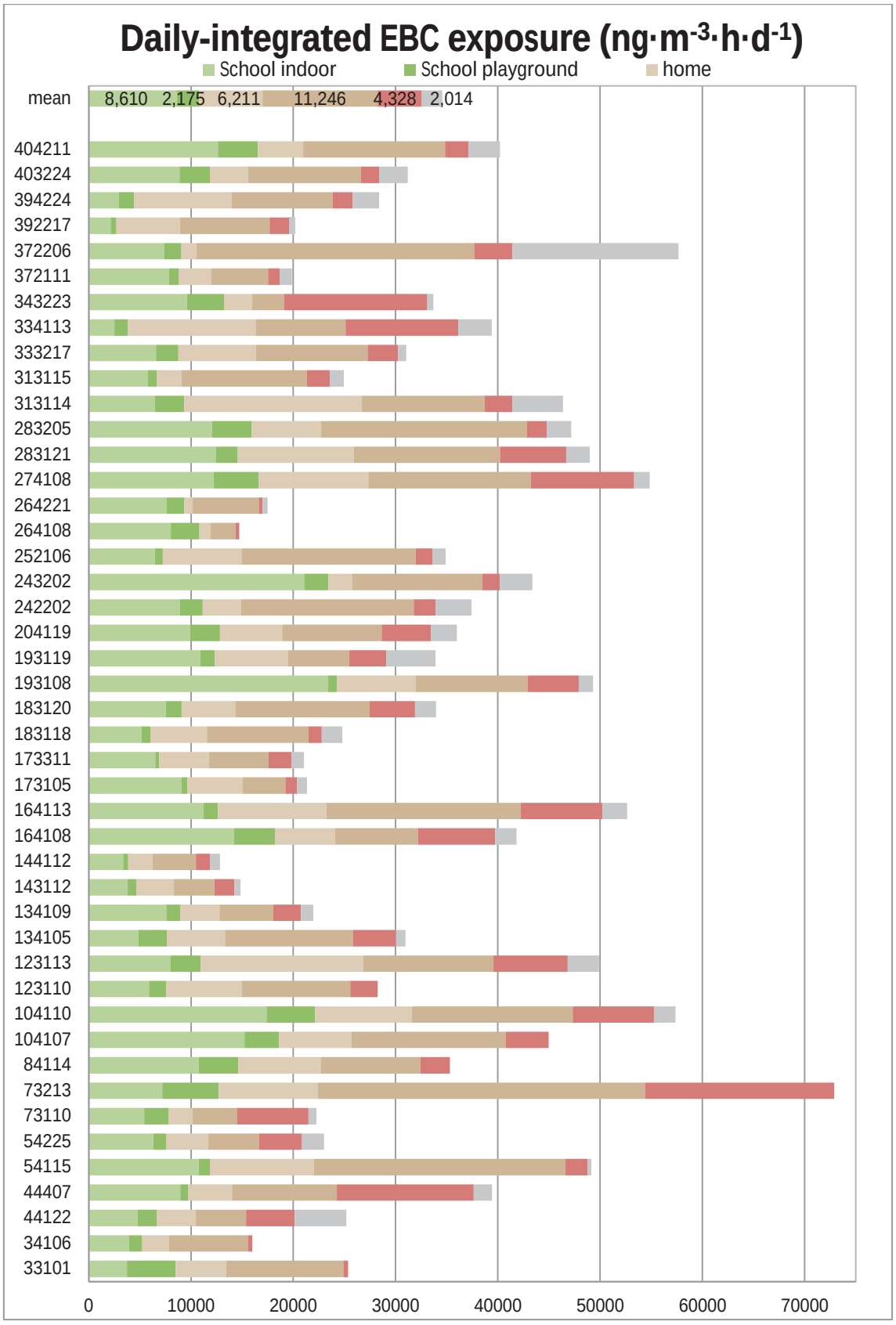

Figure S5. Estimated daily-integrated EBC exposure (ng·m-3·h·d-1) of the 45 children and their mean. The integrated exposure represents the product of the average concentration during occupancy in each of the microenvironments (ng m-3) by the daily average duration of occupancy (h·d-1).

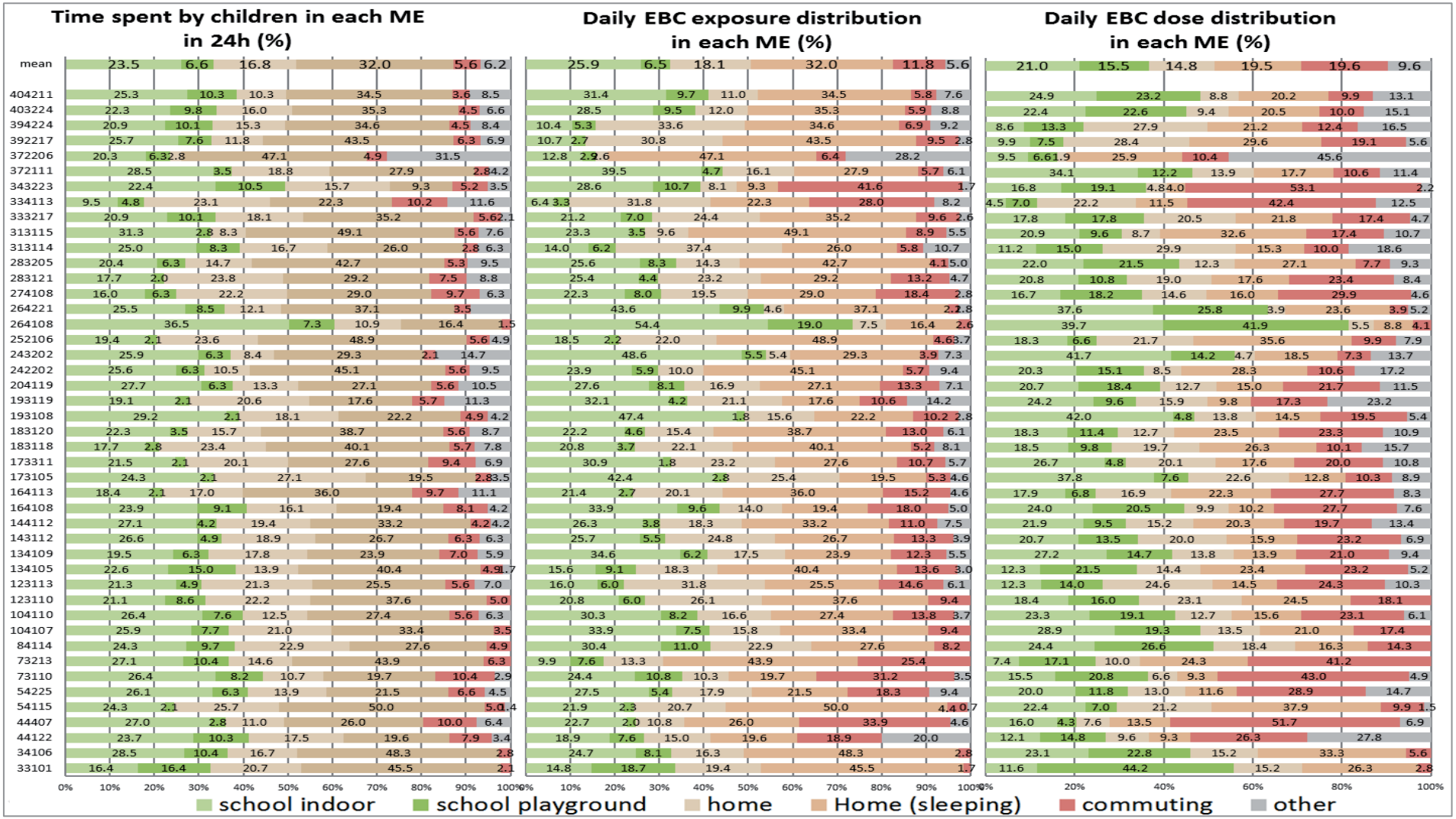

Figure S6. Time spent in each ME during one day (%) and the daily-integrated exposure corresponding to each ME (%) per each of the 45 children (also the mean is shown).

CHAPTER 4

Summarised results and discussion

4. SUMMARISED RESULTS AND DISCUSSION

This thesis aims to characterise indoor and outdoor air quality in schools and children's exposure to air pollutants. To this end, an extensive and intensive sampling campaign was carried out in the indoor and outdoor environment of 36 schools in Barcelona and 3 in Sant Cugat del Vallès. Different instrumentation for air pollutant monitoring was used: a) 8h daily filter $PM_{2.5}$ samples (high volume MCV); b) real-time concentrations of BC (MicroAeth); c) real-time number concentrations of UFP, mean particle size and LDSA (DiSCmini); d) NO_2 concentrations by passive dosimeters (Gradko). Moreover, personal exposure to BC of 53 children (7-9 years old) was also assessed by MicroAeths. The results obtained at schools were compared with those simultaneously measured in the reference UB-PR station. This thesis provides an in-depth analysis of air quality in schools and children's exposure and dose, and this information is thought to be valuable for policy makers and urban planners.

The main results of this study are shown in four scientific publications presented in Section 3. Major findings from the aforementioned articles will be summarized and jointly discussed below. Moreover, results from other publications in the BREATHE schools have also been included in the discussion.

Results evidence that BREATHE schools can be considered representative of the schools of Barcelona, since the mean NO_2 levels measured at BREATHE schools was similar to the rest of schools in Barcelona (according to modelled data from the ESCAPE project (Cyrys et al., 2012; de Nazelle et al., 2013)).

The concentrations and standard deviation (variability) for Equivalent Black Carbon (EBC, BC corrected by EC), NO_2 and UFP measured in the 39 schools participating in the study was higher outdoors (resulting from the fact that the outdoor environments are influenced to a larger degree than the classrooms by outdoor emission sources and meteorological factors). In the case of $PM_{2.5}$, the highest levels were found in classrooms, but the highest variability was again observed outdoors.

Regarding spatial variation, an increasing gradient towards the city centre has been observed for EBC, NO_2 and UFP (the last, with one school as an important exception). Therefore, the three pollutants have a similar source (mainly traffic emissions) and spatial distribution in Barcelona. As opposed to these pollutants, even though there are some similarities in the distribution of $PM_{2.5}$ across the city, the impact of local school sources on $PM_{2.5}$ (which will be discussed in detail below) prevent $PM_{2.5}$ from being a good indicator of traffic emissions in schools.

NO_2

The concentration of NO_2 in the playgrounds across all schools and sampling campaigns (47 $\mu g.m^{-3}$) was 1.6 times higher than indoors (30 $\mu g \cdot m^{-3}$) and also higher than in UB-PR (41 $\mu g \cdot m^{-3}$). This pollutant followed the spatial distribution of higher concentration in the city centre and lower in the outskirts, mimicking traffic. After excluding those schools with weekly averaged I/O ratios above 1.2 for EBC (as a proxy for traffic-related pollutants) to avoid the influence of a relatively shorter distance from the classroom to the street than from the playground, NO_2 showed a similar infiltration in both the warm and cold season (the F_{inf} were 0.50 and 0.56, respectively) indicating similar infiltration independently of the windows being open or closed. However, rather than a low infiltration, the lower levels found indoors are possibly explained by indoor consumption of NO_2 in gas-phase reactions with terpenes and other unsaturated hydrocarbons (Uhde and Salthammer, 2007; Weschler and Shields, 1999), the latter being emitted by wood flooring and furnishings, paints, cleaners, photocopiers, among others (Weschler and Shields, 1997).

$PM_{2.5}$

$PM_{2.5}$ showed much higher concentrations indoors than outdoors (1.6 times higher) and no significant differences in the I/O ratios were observed between seasons. The higher concentrations indoors were due to the important contribution of OC to $PM_{2.5}$ mass. $PM_{2.5}$ at UB-PR was much lower than at the schools (17 $\mu g \cdot m^{-3}$).

The correlation between outdoor $PM_{2.5}$ and Al_2O_3 ($r=0.91$), as tracer for mineral origin, was much higher than between $PM_{2.5}$ and EBC ($r=0.29$), what suggests a stronger influence of mineral components than traffic emissions (this was also observed indoors). Additionally, unusually high levels of mineral matter (characterised by a coarser size) are found in $PM_{2.5}$. However, the intense use of the playground for different children activities might have resulted in the breakdown of mineral particles and their continuous resuspension. Mineral matter shows a high variability among schools, due to the differences in schools according to the presence/absence of sandy playgrounds. Furthermore, $PM_{2.5}$ did not follow the expected spatial distribution of highest levels in the city centre, even if traffic influence on $PM_{2.5}$ levels might still be important in some schools. There are many exceptions, but generally, in schools located in the outskirts (with lower levels of EBC) having a sandy playground is more frequent

(higher levels of mineral matter). This is why $PM_{2.5}$ spatial distribution is not directly related to traffic, as might be expected in air quality monitoring stations, and, actually, it exemplifies the limitation of considering only PM mass values and ignoring the chemistry and potential toxicity of the particles being inhaled.

$PM_{2.5}$ components and source contributions

Most of the $PM_{2.5}$ components had higher concentrations in the outdoor than in the indoor environments, with the exception of OC (the highest contributor to indoor PM, and the second in the outdoor environment behind mineral matter), Ca, Sr and Cr which were attributed to indoor sources. OC was particularly affected by indoor sources, since almost I/O ratios were above 1 in almost all the schools and days. For Ca and Sr, attributed to chalk use in the classrooms (also observed by Canha et al., 2014 and Fromme et al., 2008 in schools from Lisbon and Munich, respectively) the 25th percentile of their I/O ratio was also above 1, with a larger variability than OC owing to the varying intensities of chalk use as well as the mineral origin of these elements from sandy playgrounds.

Concentrations of crustal elements, OC and Cr observed in schools were much higher than in UB-PR (ratio between 3.6 - 15.4), although it should be kept in mind that UB concentrations are based on 24h sampling, instead of the 8h sampling at schools. The concentrations were also higher for some traffic related components (Sn, Ba), and for Ni and V (for the last two, sampling period might be influential here, due to the sea breeze during the day). Levels were similar for Sb, NH_4^+ and SO_4^{2-}, the first from brake wear (Amato et al., 2009b; Thorpe and Harrison, 2008), the last two typically from regional background pollution (Harrison and Pio, 1983).

A source apportionment analysis by PMF identified eight factors which corresponded to well-known sources of PM in the study area (Amato et al., 2009a; Querol et al., 2007, 2001b; Reche et al., 2012a, 2012b), but also a ninth factor was for the first time identified. This factor was named Organic/Textile/Chalk, OTC, and it was characterised by OC, Ca and Sr. This was the largest source of $PM_{2.5}$ in classrooms, contributing to 45% of indoor $PM_{2.5}$. Sources of OC in particularly crowded facilities such as schools could be cotton fibres from clothes, skin cells (identified in filter samples under scanning electron microscopy, SEM; Figure 4.1; Braniš and Šafránek, 2011; Fromme et al., 2008), and other organic emissions from children, cooking emissions (Abdullahi et al., 2013; Brunekreef et al., 2005; Lanki et al., 2007) as well as condensation/nucleation of SVOCs (Weschler and Shields, 1999). The chalk from

blackboards was responsible for Ca, Sr and CO_3^{2-} emissions, as X-ray diffraction analysis revealed that chalk was composed of calcite ($CaCO_3$; the Ca frequently being replaced by Sr). In playgrounds, this OTC source was still significant (16% on average), while on the contrary it had a near-zero contribution in UB-PR. Therefore, it clearly was a local source from the schools. This factor was well correlated (R^2=0.7) with the mineral one (MIN) indoors in those schools with the classroom oriented to a sandy playground, thus suggesting a possible relationship between both sources with the number or activity of children. Another possible explanation is that playground soil is the carrier of organic material as well, suggested also by the higher OTC contributions at schools with sandy playgrounds than simultaneous contributions at schools with paved playground.

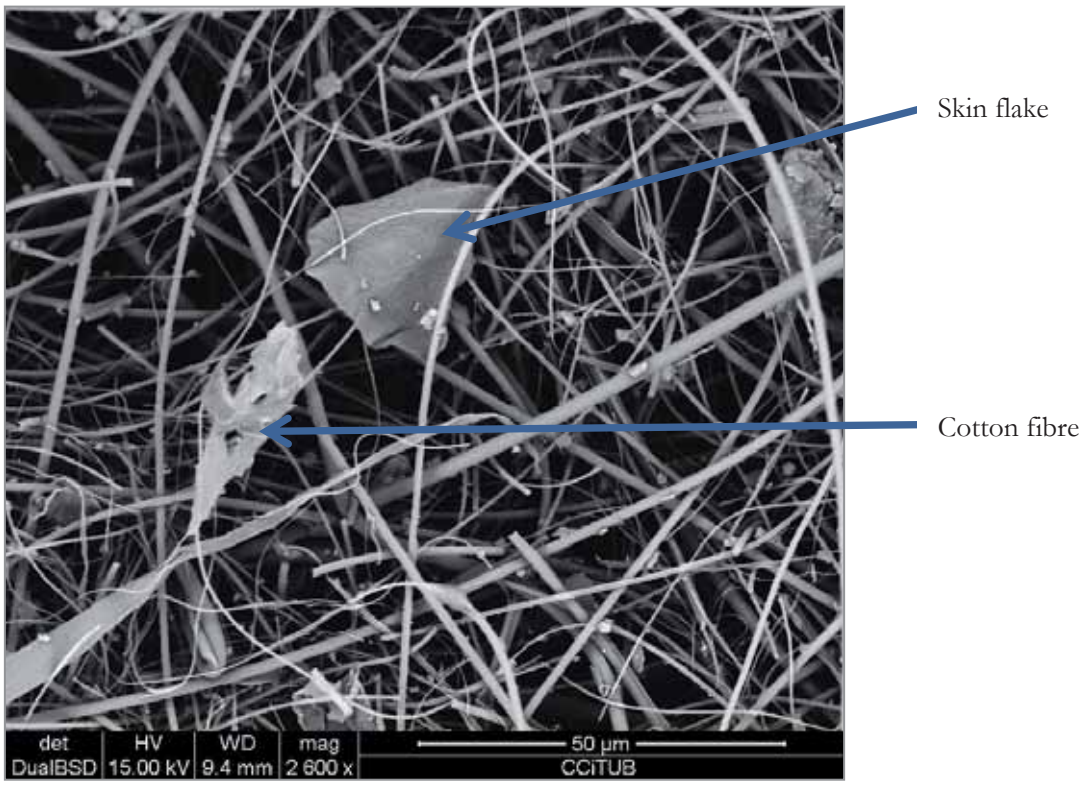

Figure 4.1. Scanning Electron Microscopy photography of a $PM_{2.5}$ filter from a classroom of one of the BREATHE schools.

Mineral components of $PM_{2.5}$ showe the broadest I/O ratios, with the median ratio close to or higher than 1. The maximum I/O ratios were observed during the cold season, when windows were closed, because of the accumulation in the classrooms of these particles and fewer outdoor activities. The MIN factor was identified by typical crustal species such as Al, Mg, Li, Fe, Ca, Ti and Rb and considered of a mixture of several sources, including resuspension from sandy playgrounds but also dust from urban works and natural soil resuspension. It was the source with the highest variability and especially dependant on the type of playground (sandy/unpaved: 16 and 9.1 $\mu g \cdot m^{-3}$; paved: 2.5 and 3.6 $\mu g \cdot m^{-3}$; outdoors and indoors respectively). Moreno et al. (2014)

quantified a reduction of 80% on outdoor Al_2O_3 concentrations between schools that had a sandy playground at less than 20m and those with paved playgrounds. In addition, when two simultaneous schools with paved playgrounds were monitored, MIN contributions were well correlated between schools in both environments, showing the influence in schools of city dust. On the other hand, much lower MIN contributions were found in UB-PR (0.6 $\mu g \cdot m^{-3}$). In more than 50% of the days and 50% of the schools and regardless of type of playground, indoor contributions were higher than those outdoors, due to continuous resuspension of particles deposited indoors. Specifically, classrooms oriented to sandy playgrounds had higher indoor levels than those oriented to paved playgrounds. This highlights the importance of cleaning activities in classrooms, which should be monitored in future studies.

Based on these two sources dependant on children and their activities (by resuspension: MIN, and emission: OTC) the estimated indoor-generated PM was of 18.5 $\mu g \cdot m^{-3}$ (47% of the indoor concentrations; 13% from mineral resuspension, 34% due to organic emissions and Ca-rich particles from chalk) which is similar to what Fromme et al. (2008) found in German classrooms (57%). The importance of these two sources can be also observed when comparing with the Spanish urban concentration ranges defined by Querol et al. (2007, 2008), since outdoor OC and mineral components were higher in this work than the literature values.

Motor exhaust emissions (OC, EC) and metals from brake wear (Cu, Sb, Sn and Fe) are the main components of the Traffic factor (TRA). Contributions were quite similar at the three studied environments: classrooms (4.8 $\pm$ 3.9 $\mu g \cdot m^{-3}$), playgrounds (5.5 $\pm$ 4.2 $\mu g \cdot m^{-3}$) and UB-PR (4.1 $\pm$ 2.7 $\mu g \cdot m^{-3}$; the last being a 24h average instead of 8h). In many cases, indoor concentrations of traffic-related components were higher than outdoors, probably due to the school configuration (such as the orientation of the classroom directly to the main street whereas the playground was in an interior patio or the location of the indoor sampler in a lower floor with respect to the outdoor), to indoor resuspension of PM (including the traffic-related components) and to precipitation scavenging outdoor pollution. The proximity to streets increased the TRA contributions, with playgrounds oriented to streets showing 50% higher TRA contributions than those playgrounds oriented to the interior of the building. For classrooms, those oriented to street had 2.4 times higher contribution than those oriented to interior playgrounds. These results point out the necessity to locate future schools far away from trafficked streets. In already built schools, the children should be preferably located in the classrooms which are further from the busiest street around the school facilities.

The Road Dust source (ROD) is attributed to particle resuspension from paved roads due to vehicle-generated turbulence and wind and characterised by Ca, Fe, Cu and Sb. This source was resolved in form of targets for pulling equations based on a priori information of the source profile of local road dust (Amato et al., 2009a). Contributions were equal in the indoor and outdoor environments (1.3 $\mu g \cdot m^{-3}$), and higher than in the UB-PR (0.4 $\mu g \cdot m^{-3}$).

The Secondary Sulphate & Organics (SSO) factor was traced by SO_4^{2-} and NH_4^+, as the result of the formation of secondary sulphate in the atmosphere from the photochemical oxidation of gaseous sulphur oxides (mostly from shipping and industrial activities in this region) and from long range transport. Condensation of VOCs was suggested by the high content of OC (13%) in the factor profile. SSO contributions were generally higher in the playgrounds (4.6 $\mu g \cdot m^{-3}$) than in the classrooms (3.8 $\mu g \cdot m^{-3}$), but the highest levels were found in UB-PR (6.4 $\mu g \cdot m^{-3}$). Strong correlations for this source were found between indoor and outdoor (r^2=0.83), indicating a high infiltration rate. In fact, infiltration of SO_4^{2-} was high during both seasons (F_{inf} of 0.79 and 0.71, warm and cold respectively) and no major indoor sources were attributed to this component. As explored by Moreno et al. (2014), SO_4^{2-} showed little difference between paired schools, and higher levels in the warmer months due to increasing oxidative photochemical reactions, and no obvious enhancement in schools exposed to higher traffic.

Lower levels were found in UB-PR (2.5 $\mu g \cdot m^{-3}$) than in playgrounds (4.1 $\mu g \cdot m^{-3}$) for the Secondary Nitrate (SNI) factor. This factor was mainly explained by the NO_3^- as oxidation product from local gaseous NO_2 emissions from traffic and industrial plants. NO_3^- had also a high variability among schools, but it was probably due to the different temperatures observed across the year (Querol et al., 2001b), which affect concentrations due to its thermal instability (Harrison et al., 1994; Wakamatsu et al., 1996). In fact, there was also an important difference between the classroom and playground (1.5 and 4.1 $\mu g \cdot m^{-3}$, respectively), with lower concentrations indoors due to the higher temperatures found in this environment. However, during the warm season, when indoor and outdoor temperatures came closer and in both environments were high enough to cause NH_4NO_3 evaporation (the most common NO_3^- bearing species is NH_4NO_3; Seinfeld and Pandis, 2006), the I/O ratios become very close to 1. Although NH_4^+ mimicked both SO_4^{2-} and NO_3^- spikes during the campaigns (Moreno et al., 2014), the infiltration of NH_4^+ and NO_3^- could not be successfully assessed due to their evaporation when reaching the indoor environment. Similar results were obtained by Sangiorgi et al. (2013) in offices in Milan.

Marine aerosol components, Na and Cl^-, are the tracers for the Sea Spray (SEA) factor. However, Na also has a partial mineral origin and, as said before, schools are particularly dusty environments; Cl^- might be also emitted by cleaning products, among others (Koistinen et al., 2004). As a result, the SEA source had typically higher levels indoors, thus suggesting significant indoor sources in many schools.

Many trace elements had low or no correlation with EBC and Al_2O_3, what indicates a different source than traffic or crustal emissions, such as the Heavy Oil Combustion (HOC) and the Metallurgy (MET) factor identified by PMF. However, some elements such as As, Co and Pb were quite correlated with mineral matter. These results suggest that mineral matter could be polluted by dry and wet deposition of these pollutants on the playground and retained by absorption on crustal elements. In fact, Minguillón et al. (2015) analysed 5 sands from 4 different BREATHE schools and observed that sand samples were enriched in those elements (among others) with respect to a recently-changed sand sample. This was particularly true for As (up to 2.6) but also significant for Co (1.5-1.7) and Pb (1.7-2.4). These enrichment factors point to a major anthropogenic origin from these elements.

Ni and V (tracers of the HOC factor, along with high concentrations of EC and OC) reflect the influence of combustion processes, mostly from shipping and also from the industry in this region. Ni and V had lower I/O ratios during the cold season (0.86 and 0.82, respectively) which increased to 1.07 and 0.91 during the warm period because of the open windows that facilitate their entrance indoors.

Among trace metals, V and Cd had the highest F_{inf} (0.71 and 0.75 for V; 0.79 and 0.70 for Cd, cold and warm season respectively) as well as the lowest C_{ig} with respect to the median. Pb had a similar F_{inf} than the rest of the trace metals (between 46-60%; excluding mineral elements) but its R^2s were higher, even though C_{ig} for Pb was quite high (46% and 42% of the median indoor concentrations, cold and warm respectively) indicating the presence of possible indoor sources. Trace metals (except Sb and Cr) had lower F_{inf} during the cold season, thus the entrance of these elements was to some extent hindered by windows. However, for Ni, As, Cu, and Se the R^2 were not very high (the highest being 0.49 for As during warm season) because the impact of indoor sources might differ in each school. In fact, some the above-mentioned elements (As, Cu, Se, and Cr) were affected by significant indoor sources in a number of schools. Cr should be highlighted, since it had higher levels indoor in both seasons (I/O ratio = 1.46) and, in fact the intercept of the indoor-to-outdoor correlation for Cr accounted for the 95% and 83% of its median indoor concentrations (cold and warm seasons, respectively), indicating a clearly contribution from indoor origin. Possible sources can

be the abrasion of metallic components of chairs and tables (Cr is an important alloying element in stainless steel) and emissions from a preservative against insect, bacterial and fungal decline (chromated cooper arsenate, CCA, Patch et al., 2009). In fact, in specific schools (6 of 39) both winter and summer I/O ratios were markedly high for Cr, Cu and As simultaneously. These contributions from indoor materials or material-treatments may be relevant for children exposure.

Therefore, the F_{inf} of Cr should not be determined by this analysis. Further research is required in order to identify indoor sources of these trace metals, some being well-known because of their toxicity. With the exception of Sb, all trace elements have similar or higher C_{ig} during the cold than the warm season, due to the dispersion of the indoor generated PM to outdoors being hindered by the closed windows.

In order to determine the effect on infiltration of the type of windows (Al/PVC vs. wood) and the influence of building age, linear mixed-effects model were applied, including school as random effect. Only the cold season was studied in this section to avoid the effect of higher infiltration during the warm season due to open windows and, thus, to focus on the effect of type of windows and building age. Moreover, since the mineral components have also been evaluated with this model, the variable type of playground (sand presence at < 20m) was also included.

In the model including type of windows, building age and type of playground, the adjusted F_{inf} (F'_{inf}) is still highest for Cd and EBC (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-}, Sb, Zn, Sn, Pb, Cl^-, Ni, and Na, all of them with a F'_{inf} >0.50. From the pollutants assessed, those with the highest impact of C'_{ig} are (excluding mineral components, all of them with very high C'_{ig}): Cr>OC>Na>UFP>Se>Cu>Cl->As>Zn>, all of them having >50% of the median indoor concentrations from indoor origin.

Results evidence that the age of the school building was only significantly (p-value<0.05) associated with indoor levels for Fe and 4 trace elements, most of them typically related to industrial emissions. The coefficients indicate that newer buildings tend to have around 0.15 $\mu g \cdot m^{-3}$ more of Fe, 1.95 $ng \cdot m^{-3}$ of Cr, 0.27 $ng \cdot m^{-3}$ of Li, 0.09 $ng \cdot m^{-3}$ of Co, and 0.05 $ng \cdot m^{-3}$ of Se than the older ones, probably due to higher indoor emissions of these elements by new materials but further research is needed to identify specific sources in indoor environments. This lack of association for most of the pollutants under study is in accordance with previous studies (which included newly constructed schools) that did not find any correlation between airtightness and building age (Sherman and Chan, 2004). Moreover, the type of window seemed to be importantly associated with higher indoor levels of mineral components (such as Al_2O_3,

Fe, Mg) and the components with a very high contribution from indoor sources (OC, Ca, Sr) in those schools with Al/PVC windows. Therefore, the presence of more isolating windows (such as the Al/PVC framed instead of wood framed) would be a much important barrier for the dispersion of mineral components, which might keep resuspended indoors in such a crowed environment. Moreover, also higher indoor levels of Co and As were found in schools with Al/PVC windows, probably due to indoor emissions or because of their possible presence on the school sand. On the other hand, NO_2 infiltration was hindered by Al/PVC windows, since those schools with wood framed windows tended to have an increase of around 8 $\mu g \cdot m^{-3}$ of NO_2. The presence of sand-filled playgrounds had an impact also on indoor concentrations. Schools with sandy playgrounds at <20m showed a substantial increase of mineral components in indoor concentrations with respect to those with paved playgrounds or sand at >20m.

Briefly, the sources characterised impact differently on air quality depending on children's activities at schools (MIN and OTC), on the location and characteristics of the schools (TRA, ROD and MIN), and finally some sources reflect the urban background cocktail (SSO, SNI, MET, SEA and HOC) which is driven primarily by meteorology.

EBC

Similar EBC concentrations were found in classrooms and playgrounds of the 39 BREATHE schools (1.3 vs 1.4 $\mu g \cdot m^{-3}$, respectively), while for UFP and NO_2, the highest concentrations were found outdoors. The good indoor-to-outdoor correlation indicates an easy infiltration of EBC (R^2=0.83 and 0.87, cold and warm season, respectively). In some cases, I/O ratios for EBC as well as for UFP, Sb, Sn and Cu were >1, even in the cold season with closed windows. This occurs in schools with the monitored classroom relatively closer to the street than the playground site. This was also observed for the traffic factor (TRA) identified by PMF at the schools. Therefore these schools were excluded from the subsequent analysis on infiltration of EBC. After excluding those schools, and based on the F_{inf}, results showed that 92% of indoor EBC came from outdoor air during the warm season and 75% during the cold one (becoming the second pollutant with highest infiltration after Cd in the cold season, and the first in the warm one). The very low intercepts in the indoor-to-outdoor correlation indicate the absence of significant indoor sources of EBC. A clear spatial distribution that followed the traffic pattern in the city was also evidenced (and this

distribution of EBC concentrations became clearer when data were deseasonalised, this is, adjusted by meteorological factors).

Besides school campaigns, EBC personal measurements of 45 children (from 25 schools) were also carried out. The highest EBC concentrations were found in personal measurements when comparing the geometric mean (GM) with indoor and outdoor stations in schools (20% higher) and UB-PR station (10% higher). Nevertheless, Buonanno et al. (2013b) obtained an average of 5.1 $\mu g \cdot m^{-3}$ of BC (range 0.1 – 521 $\mu g \cdot m^{-3}$) after monitoring 103 children (8-11 years old) during 48h in Cassino (Italy) which is much higher than the one obtained in this work (arithmetic mean, AM=1.5 $\mu g \cdot m^{-3}$ EBC, 2.7 $\mu g \cdot m^{-3}$ of uncorrected BC).

In addition, the range of EBC concentrations was wider for the personal measurements compared to school and UB-PR measurements owing to peak concentration events that took place mainly during commuting time. In fact the GM of EBC concentrations were significantly higher during commuting time (GM=2.0 $\mu g \cdot m^{-3}$) than during periods when children were in the classrooms (1.2 $\mu g \cdot m^{-3}$) or in the school playgrounds (1.0 $\mu g \cdot m^{-3}$). The lowest concentrations were reported when children were at home (0.9 $\mu g.m^{-3}$). These results are expected since citizens, and especially children, are very close to traffic while commuting and lower levels are expected to happen at night, when people are usually at home. Although the schools were located in different areas of Barcelona (affected by a different traffic density), most of them showed the morning and afternoon road traffic rush hour (sometimes with a lag time between the school and the UB-PR), which were not only identified in outdoor monitoring stations but also inside the schools owing to a high EBC infiltration. The morning rush hour coincided with children commuting to school. In fact, most of the commuting periods were clearly evident in the personal measurements because of high EBC peaks. Thus the ratio $EBC_{commuting}/EBC_{home}$ ranged between 0.8 and 26.7 (median=2.5), with the ratio of 26.7 being an extreme case of a child exposed to very high concentrations during commuting but having very low home concentrations. Actually, the second maximum of this ratio drops importantly to 5.2.

The concept of exposure incorporates the duration of the contact to a certain concentration by integrating over time (Duan, 1982; Ott, 1982) and the dose corresponds to the product of the exposure by a dosimetry factor, which in our case is the inhalation rate and depends on the age and the intensity of the activity (the ones employed here were adapted from Buonanno et al., 2011). The mean daily-integrated exposure to EBC for the 45 children was 34.6 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$ and it showed a high variability among the children (standard deviation: 13.8 $\mu g \cdot m^{-3} \cdot h \cdot d^{-1}$). For the daily-

integrated dose, the mean accounted for 18.2 $\mu g \cdot d^{-1}$ (standard deviation: 7.7 $\mu g \cdot d^{-1}$). This variability was a result of the different time-activity patterns of each child, who can carry out very different activities in locations with different EBC concentrations. Exposure and dose could be significantly different even between children attending the same school, and this variability could not be taken into account only with the fixed stations. In fact, Mullen et al. (2011) also observed a high variability in ultrafine particle number concentration among 13 occupants of 4 apartments. This highlights the usefulness of personal monitoring for a precise estimation of the exposure/dose of each subject. Children received the highest exposure while being at home (50%; 30% of the total corresponds to sleeping time) because of the large time spent there (58% of the day). However, since the activities usually carried out at home during weekdays are not very intense, the home contribution to the daily-integrated dose decreased to only 35% (20% corresponds to sleeping time). Actually, the lowest ratio of % exposure and dose with respect to the % time spent was observed at home during sleeping time (ratio exposure:time = 0.77:1, dose:time = 0.47:1). Children spent 31% of their weekday at schools, where they received 33% of their daily-integrated exposure to EBC (26% in the classrooms and 7% at playgrounds) and 37% of the daily-integrated dose (21% and 16%, classroom and playground respectively). Indoor environments (classroom + home) accounted for the 82% of the daily time of schoolchildren during weekdays. The corresponding daily-integrated exposure and dose received in the indoor environments was 76% and 56%, respectively. Therefore, children received more than half of the dose in the indoor environment. Although the dose received at home is higher, policies for the reduction of EBC emissions around schools would benefit a larger number of children given that they spend a considerable portion of their weekdays in a shared location (school).

The highest ratio of exposure and dose with respect to the time spent was observed during commuting. This activity was responsible for 12% of the daily exposure and around 20% of the daily dose whilst it only accounted for the 6% of the time, so a relation 2.1:1 (3.5:1) of exposure:time (dose:time) is observed. The high exposure was explained by the high concentrations found during commuting, and the dose is a combination of the former and the moderate physical activity intensity usually involved in commuting. In fact, the inhalation rate factor employed for commuting may vary considerably according to the mode of transport, being considerably higher in the case of active travel (de Nazelle et al., 2012). However, since 35% of the commuting modes were not reported by children, the same inhalation rate has been used for this activity regardless of the transport mode. Buonanno et al. (2013b) obtained a similar percentage of time spent in the different microenvironments for 103 children in Cassino (64% at

home, 24% at school and 4% in transport versus 58%, 30% and 6% in this work) and also a similar distribution of the exposure contribution (60% at home, 20% at school and 11% in transport versus 50%, 32% and 12% in this work), although with a much higher dose (39.2 $\mu g \cdot d^{-1}$ versus 18.2 $\mu g \cdot d^{-1}$ in this work). On the other hand, Dons et al. (2012) obtained a higher exposure:time and dose:time relationship in transport for 62 adults in Belgium (3.3:1 versus our 2.1:1 of exposure:time; 4.8:1 versus our 3.5:1 for dose:time), with people spending around 6% of their days commuting and receiving the 21% of their daily-integrated exposure and 30% of their dose. In the case of the exposure, it might be due to differences in activities schedule between children and adults (or between regions) and, in the case of the dose, it should also be considered that inhalation rates depend on the person age (increases with age).

These results allowed us to conclude that policies to reduce EBC levels should be enhanced throughout the urban area. Since more than one third of the daily-integrated dose takes place at schools and commuting has the highest dose:time relationship, specific policies focused on reducing traffic intensities around schools should be implemented. These school targeted actions would favour the abatement of the exposure of a wide fraction of the population, which are also one of the most vulnerable to air pollutants threats.

Knowing how well a single fixed station can be used as a proxy for personal exposure assessment is of a major importance. By means of linear mixed-effects models, we tested the agreement between EBC personal measurements and the fixed station in schools (indoor and outdoor) and in the UB-PR. Low R^2 (defined in this analysis as the proportion of the variance explained by the fixed effect) between personal measurements and fixed stations were found (R^2=0.28 and R^2=0.26, classroom and playground respectively), being the R^2 much higher during the warm (R^2<0.17), than the cold season (R^2>0.50). The regression coefficients (corresponding to the slope) were also higher (closer to 1) for the warm season period, indicating a better prediction from the fixed stations during this period. The importance of the distance of the measurement point to the subject when assessing personal exposure was highlighted by the sharp increase of the R^2 when only periods when the children were in the corresponding microenvironment were considered. For the classroom microenvironment, the R^2 for the whole day is 0.28 and increased to 0.79 when limiting the data to the periods when the children is in this microenvironment (0.26 and 0.75 are the equivalent for the playground). For the classroom and playground periods, the agreement between personal measurements and UB-PR is lower (R^2=0.45), but higher than when considering the whole day (R^2=0.18). This lower R^2 when compared to the fixed sites in schools is due to specific characteristics of each microenvironment where

the children spend their time but also to the spatial variability among the city for this pollutant observed during BREATHE campaigns. When children were commuting, the corresponding R^2 was around 0.30 in all stations, having a better agreement during the warm season. The high intercepts indicate that children receive a contribution of around 2 $\mu g \cdot m^{-3}$ of EBC that is not accounted for by the fixed stations.

On the other hand, it should be highlighted that during both seasons, the slopes for personal measurements versus the classroom station were close to 1 during classroom and home time (although lower R^2 are found when the children were at home), what indicates that concentration on these two indoor environments followed not only similar patterns but also similar levels. Considering the important amount of time spent in the indoor environments, these results suggest the necessity to characterise indoor school environments for an accurate assessment of exposure to EBC of schoolchildren.

In addition to season, distance from school to the UB station and traffic density were also included in the model as possible predictors of personal EBC concentrations. These two variables did not contribute to improve significantly the model. Other possible influential variables (e.g. architectural features, wind speed and direction) that were not assessed in this study may have an important role. Moreover, correlations between 5 pairs of children (from 3 different schools) that were monitored simultaneously resulted in a R^2 of 0.08 when correlating the EBC concentration between them. Again, the low relationship between the concentrations these children were exposed to seems to be explained by the distance to road traffic in each specific moment. The fact that the correlation between exposure measurements for different children is low illustrates the difficulties to generalise exposure data from exposure measurements carried out at individual level.

UFP

Outdoor mean concentration of UPF (10-700 nm) number concentration across all schools and sampling campaigns (23,396 $\#\cdot cm^{-3}$) is 1.5 times higher than indoors (15,577 $\#\cdot cm^{-3}$). During the cold period, UFP mean size was larger indoors (41.3 and 37.7 nm classroom and playground, respectively), since fresh exhaust emissions from traffic are very fine (23-30 nm as prevailing mode, Dall'Osto et al., 2011) but increase their size by condensation and coagulation processes that might take place indoors. Reche et al. (2014), found in BREATHE schools that 24h mean UFP number concentration was always lower than school-hours mean, thus, if non-class periods are included, children's exposure to UFP could be underestimated. Outdoor UFP were not

correlated with the measurements in UB-PR, indicating a major local origin for this parameter (traffic), which results in a large spatial variability across the city. In fact, linear correlations of 10-min outdoor UFP between the paired schools showed R^2 coefficients ranging from 0.003 to 0.47 (0.20 on average) during SC1 and 0.001 to 0.55 (0.29 on average) during SC2. In both campaigns, levels between paired schools could differ by up to 70%. A significant correlation was obtained between outdoor UFP and a traffic classification index calculated for each school (based on deseasonalised data of NO_2 and EC), being the R^2 coefficient 0.29 and 0.63, SC1 and SC2, respectively. Levels were usually higher in schools with a higher traffic influence (by an average of 40% in both environments), hence showing the important role of traffic emissions on UFP levels at primary schools across Barcelona. Actually, UFP number concentrations generally decreased as schools are located farther from the city centre as well as from the coastal area (where SO_2 from harbour activities and shipping is a key factor for secondary particle formation by nucleation processes). In several of the schools, an increase (by 15-70%) in UFP at midday was observed, while EBC concentrations showed a decrease, in both the warm and cold season. Previous studies in the urban environment of Barcelona (Brines et al., 2014; Dall'Osto et al., 2013; Pérez et al., 2010; Pey et al., 2008; Reche et al., 2011a) related this midday increase to nucleation processes mediated by photochemistry (when the solar intensity is at its highest). The fact that this midday peak is also detected at the UB-PR site prompts to new particle formation as the most probable origin.

Since UFP could not be deseasonalised (owing to this local characteristic of UFP levels), the variability of outdoors UFP did not seem to strongly depend on school configuration, although higher levels were found in the schools with the playground oriented to the street and in those playgrounds located closer to ground level than in their paired schools with playgrounds oriented to the interior and located in higher levels.

Low R^2 and F_{inf} were found for UFP because of indoor particle sources such as new particle formation from the interaction of O_3 with household products (the intercepts, corresponding to the C_{ig}, were high) or processes that might increase indoor UFP independently of outdoor particles. However, indoor levels are still influenced by the outdoors ones as well as the ambient temperature and humidity (Reche et al., 2014). Actually, schools in Barcelona had higher indoor particle number concentrations during the warm season despite the lower levels found outdoors with respect to the cold one. This is in accordance to Kearney et al. (2011), who found that in 65% of the homes they studied the indoor-generated UFP were higher than the UFP infiltrated from outdoors.

Which are the implications for public policymakers, schools and families?

From the previous discussion some measures can be suggested to urban planners and public policymakers, as well as to schools and families.

- Future schools should be located away from trafficked roads, since the exposure to traffic-related pollutants is dependent on distance to road traffic.
- New schools should be designed with an air uptake for ventilation of the classrooms taking either filtered air or fresh air away from the road traffic.
- Road traffic density should be lessened around existing schools to diminish children's exposure to air pollutants. Moreover, the classrooms where children spend most of their time should not be facing the busiest road, but facing an interior patio or the calmest street around the school.
- Greening the school may help to abate exposure, but also increasing the green and pedestrian spaces in the surrounding area would result in diminishing the proportion of the area used by cars and consequently would yield to lower levels of pollution.
- Parents and children could decide the best way to get to the school. Therefore, avoiding major roads (in terms of traffic density) for commuting and walking in the most exterior part of the pavement (which is the one further away from traffic) should be advised.
- Pedestrian school pathways should be implemented and designed to go through low traffic streets, or at a distance of the kerbside of roads, in order to increase security and minimise children's exposure to air pollutants.
- The use of public transport for commuting would yield on the reduction of the number of cars around the school and consequently emissions would be abated.
- It is convenient to replace sand from the playgrounds periodically (every one or two years) because atmospheric scavenging of pollutants results in the accumulation of those in the playground sand. Also children activity in the playground results in the size finning of the mineral dust that is highly affecting $PM_{2.5}$ levels.
- Cleaning activities might help to reduce mineral matter resuspension in the indoor environments. However, since the cleaning products that are usually employed react with O_3 to form new particles (in the range of the UFP), cleaning works are recommended to be carried out in the afternoon after school hours to avoid children being exposed to additional concentrations of UFP.

- High levels of textile, chalk and organic particles measured in $PM_{2.5}$ are due to high children density. Therefore ventilation is advised, but only in cases when the classroom is not directly oriented to a major road. If the latter is the case, ventilation should be done during few minutes when children are not present in the classroom and avoiding traffic peak hour.

CHAPTER 5

Conclusions

5. CONCLUSIONS

The main conclusions that can be drawn from the work presented in this thesis are summarised as follows:

- Mean levels of air pollutants in BREATHE schools are high compared to the typical levels recorded at the urban background station (UB-PR) for Barcelona.
    - Since some traffic tracers such as NO_2 are 1.2 times higher in the playgrounds when compared to UB-PR, school children in Barcelona are about 20% more exposed to traffic-related pollutants. The levels of pollutants assessed in this work are between those measured at urban background and at traffic stations in Barcelona.
    - $PM_{2.5}$ at schools cannot be considered a good tracer for traffic emissions owing to local contributions. However, $PM_{2.5}$ is still influenced by traffic contributions since most of central schools recorded higher $PM_{2.5}$ concentrations.
- Regarding spatial variation, an increasing gradient towards city centre has been observed for EBC, NO_2 and UFP. This gradient was blurred for $PM_{2.5}$ owing to the influence of local sources.
    - A major local origin for UFP was observed, resulting in a large spatial variability across the city.
- Seven outdoor (traffic, secondary sulphate & organics, secondary nitrate, road dust, metallurgy, sea spray, and heavy oil combustion) and 2 children-activity-related (organic/textile/chalk and mineral) sources were found to be responsible for the $PM_{2.5}$ concentrations.
    - Outdoor $PM_{2.5}$ concentrations almost doubled those found in UB-PR, mainly due to local (school) sources of mineral matter and indoor OC.
    - $PM_{2.5}$ concentrations are markedly higher indoors, indicating important contributions from indoor sources to $PM_{2.5}$. OC is the main component of this source, but also Ca, Sr, and CO_3^{2-}.
    - 47% of indoor $PM_{2.5}$ is generated indoors (13% from mineral resuspension and 34% from a source that comprises organic – skin flakes, clothes fibres, possible condensation of VOCs – and Ca-rich particles). 53% of indoor $PM_{2.5}$ is from outdoor origin and its absolute contribution to indoor $PM_{2.5}$ ($\mu g \cdot m^{-3}$) is slightly lower than in the outdoor receptor locations.

- Schools with sand-filled playground were found to unusually increase $PM_{2.5}$ mineral contributions (since usually mineral matter affects mainly $PM_{2.5-10}$ and less to $PM_{2.5}$) in classrooms by 5-6 $\mu g \cdot m^{-3}$ and in playgrounds by 13-14 $\mu g \cdot m^{-3}$ on average with respect to schools with paved playgrounds. In fact, an assessment by linear mixed-effect models indicated an association between presence of sand-filled playgrounds at < 20m and a substantial and significant increase of mineral components in indoor environments.
- Unusually high levels of mineral matter in $PM_{2.5}$ suggest the breakdown of these particles due to playground activities and the easy resuspension due to the typical Barcelona dry climate.
- Indoor contributions from traffic emissions were significantly higher for classrooms with windows oriented directly to the street, rather than to the interior of the blocks or to the playgrounds. Thus, urban planning is important in order to reduce children's exposure to air pollutants from outdoor origin.

- Regarding infiltration, outdoor levels of typical traffic sourced pollutants such as NO_2, UFP, Cu, Sn among others are usually higher outdoors, but in many cases indoor levels are very close to the ones found outdoors. This indicates an easy penetration of outdoor air pollutants.
  - I/O ratios for traffic tracers (NO_2, EBC, UFP, Sn, Sb, Cu), SO_4^{2-} and the trace elements Ni and V were characterised by I/O ratios ≤ 1, lower during the cold season because of hindering by closed windows of outdoor sourced particles.
  - Indoor levels of UFP are influenced by outdoor levels, but indoor particle sources and/or processes increased indoor UFP independently of outdoor particles.
  - I/O ratios trends for $PM_{2.5}$ components can be summarised in OC, Ca, Sr, Na, Cl^- and many mineral matter tracers (Al_2O_3, Li, Ti, Fe) having I/O ratios >1, and more markedly in the cold season.
  - Window frame material affects more importantly to mineral components, hindering their dispersion and leading to higher indoor concentration in schools with Al/PVC window (those mineral components easily reach the indoor environment by soil adhering to footwear).
  - Cd and EBC are clearly the pollutants with the highest F_{inf} in the cold season (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-}, Sb, Zn, Sn, Pb, Cl^-, Ni, and Na, all with a F_{inf} >0.50.

- Some trace metals may have higher indoor levels in newer buildings (constructed after 1970) due to specific indoor materials or material's treatments.

- EBC concentrations were higher in the personal measurements than in fixed stations in schools (20% higher) and in the UB-PR (10%) owing to peak concentrations events during commuting times. This was because of two reasons: the co-occurrence of children commuting times with road traffic rush hours, and the closest proximity to the source while commuting.
  - High R^2 from linear mixed effect models ($R^2 \geq 0.70$) were found between EBC from personal monitors and school fixed sites (both in classroom and playground) when considering only the time periods when children were in each of the microenvironments. On the other hand, the linear mixed-effect model relating personal measurements with the urban background station was weaker ($R^2=0.45$) for the same period, thus indicating the importance of the spatial unit of analysis when assessing human exposure.
  - During the warm season, and due to opened windows, the outdoor fixed stations in schools were more representative of the personal exposure (higher R^2 and coefficients closer to 1) than during the cold one.
- Children spent 82% of their time in indoor environments (classroom and home), where they received 76% and 56% of their daily-integrated exposure and dose, respectively. Considering the important amount of time spent in the indoor environments, it is important to characterise indoor environments for an accurate exposure assessment to EBC.
  - The contribution from schools (including classroom and playground) to the total daily-integrated EBC dose was the 37%. Reducing traffic intensities around schools should be enhanced to minimize the exposure of a wide fraction of the population who spend a large portion of their weekdays in a shared location.
  - Children spend only the 6% of their daily time in commuting while received the 12% of their daily-integrated EBC exposure and around 20% of their dose (having the highest exposure:time relation: 2.1:1).

CHAPTER 6

Future research and open questions

6. FUTURE RESEARCH AND OPEN QUESTIONS

The research carried out in this study highlights the peculiarities in air pollutants and sources in indoor and outdoor environments of schools as well as the personal exposure and dose of schoolchildren, and leads to further open questions and gaps in knowledge that future research will hopefully shed some light on

- Further studies should assess the effect of the application of measures for air quality improvement, such as distancing schools from trafficked roads (e.g. introducing the superblocks in big cities with schools oriented to roads with limited road traffic), *greening* the schools and surrounding area, a decrease in the children density in school classrooms for a better indoor air quality and comfort, the use of air filtering devices in classrooms as well as measures to avoid or reduce sand resuspension in unpaved playgrounds.

- Indoor sources of air pollutants should be further investigated. Especially the sources related to ultrafine particles and the trace metals that have been identified in this thesis to have an important indoor contribution (Cr, As, Ni, Cu, Se).

- Organic carbon contributions were the most important in the indoor environment, as very important as well in the playgrounds. Knowing the specific composition of the organic compounds is a main gap that should be filled in further research in order to determine their origin and recommend measures to reduce their concentrations.

- Although there are many studies focused on the interaction of O_3 with volatile organic compounds in the indoor environments, this has not yet been studied in schools. Schools have an important contribution of organic compounds because of the crowded classrooms as well as the presence of many pieces of furniture. In this case, schools from regions with very high levels of O_3 should be studied, since the gaseous and UFP and PM composition might differ considerably if compared to those schools relatively close to significant traffic emissions.

- Personal measurements are a suitable methodology in order to accurately assess exposure. More studies in children will verify the results obtained in this thesis and might help to identify the activities, environments, routes, among other parameters that contribute the most to the personal exposure and dose of

children and, consequently, avoid them or reduce concentrations on these specific sites.

CHAPTER 7.

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ANNEXES

ANNEX I. MY CONTRIBUTION TO THE BREATHE PROJECT

My contribution to the BREATHE project is summarised in the following list:

- I participated and carried out the instrument testing before sampling campaigns.
- I participated in the pilot study carried out in one school before staring the sampling campaigns.
- I led the sampling campaigns and was in charge of the logistics, carrying out the field work for 50% of the schools (including noise measurements).
- I was responsible for data collection for >50% of the instruments, and of data treatment for the entire pollutant database, and compiled the final data in the air pollution database.
- I also weighted the sampled filters and performed the chemical analysis of a selected number of filters prior to their overall analysis.
- I performed the statistical analysis and wrote the scientific articles in which I am the main author.
- I had an active collaboration in the scientific articles in which I am a co-author, involving mainly providing and analysing data and reviewing the final drafts of the manuscripts.

ANNEX II. PRESENTATIONS IN SCIENTIFIC MEETINGS

- M. Viana, I. Rivas, J. Sunyer, L. Bouso, C. Sioutas, A. Alastuey, X. Querol. Indoor and outdoor ultrafine particle characterisation in primary schools in Barcelona. Poster presentation. *European Aerosol Conference*, 2-7 September 2012, Granada (Spain).
- I. Rivas, T. Moreno, M. Viana, L. Bouso, M. Àlvarez, A. Alastuey, J. Sunyer, X. Querol. Indoor and outdoor ultrafine particles levels in primary schools in Barcelona. Oral communication. *4th EFCA Ultrafine Particles International Symposium*, 16-17 May 2013, Brussels (Belgium).
- I. Rivas, M. Viana, T. Moreno, M. Pandolfi, L. Bouso, M. Àlvarez, A. Alastuey, J. Sunyer, X. Querol. Indoor and outdoor levels and composition of air pollutants in primary schools in Barcelona. Poster presentation. *14th EuCheMS International Conference on Chemistry and the Environment (ICCE)*, 25-28 June 2013, Barcelona (Spain).
- I. Rivas, J. Sunyer, T. Moreno, M.Viana, M. Àlvarez-Pedrerol, A. Alastuey, X. Querol. School traffic air pollution in the BREATHE Project. Poster presentation. *25th Environment and Health – Bridging South, North, East and West (ISEE, ISIAQ, ISES)*, 19-23 August 2013, Basel (Switzerland).
- J. Sunyer, M. Àlvarez-Pedrerol, J. Forns, I. Rivas, M. López-Vicente, M. Nieuwenhuijsen, X. Querol. Brain and school traffic air pollution: the BREATHE Project, ecological association. Oral communication. *25th Environment and Health – Bridging South, North, East and West (ISEE, ISIAQ, ISES)*, 19-23 August 2013, Basel (Switzerland).
- M. Viana, I. Rivas, J. Sunyer, L. Bouso, M. Àlvarez, C. Sioutas, X. Querol, A. Alastuey. Exposure to ultrafine particles in indoor and outdoor school environments across Barcelona (Spain). Oral communication. *European Aerosol Conference*, 1-6 September 2013, Prague (Czech Republic).
- I. Rivas, M. Viana, T. Moreno, M. Pandolfi, F. Amato, L. Bouso, M. Àlvarez, A. Alastuey, J. Sunyer, X. Querol. Levels and geochemistry of indoor and outdoor aerosols in primary schools in Barcelona. Oral communication. *8th Asian Aerosol Conference*, 2-5 December 2013, Sidney (Australia).
- M.C. Minguillón, M. Cusack, C. Reche, I. Rivas, M. Viana, X. Querol. Air quality in Spanish cities. First steps in smart sensors validation. Oral communication. COST Action TD1105 EuNetAir, *2nd International Workshop on New Sensing Technologies for Indoor and Outdoor Air Quality Control*, 25-26 March 2014, Brindisi (Italy).

- I.Rivas, L.Bouso, D.Donaire, M.Pandolfi, M.de Castro, M.Viana, M.Àlvarez-Pedrerol, M.Nieuwenhuijsen, J.Sunyer, X.Querol. Spatio-temporally resolved children Black Carbon exposure in Barcelona. Poster presentation. *34th International Technical Meeting on Air Pollution Modelling and its Application*, 4-8 May 2015, Montpellier (France).

ANNEX III. RELATED PUBLICATIONS

Numerous publications have been produced from results obtained during this thesis.

1. M. Viana, I. Rivas, X. Querol, A. Alastuey, J. Sunyer, M. Àlvarez-Pedrerol, L. Bouso, C. Sioutas. Indoor/outdoor relationships of quasi-ultrafine, accumulation and coarse mode particles in school environments in Barcelona: chemical composition and sources. Atmos. Chem. Phys., 2014, 14, 4459-4472. doi:10.5194/acp-14-4459-2014.
2. T. Moreno, I. Rivas, L. Bouso, M. Viana, T. Jones, M. Àlvarez-Pedrerol, A. Alastuey, J. Sunyer, X. Querol. Variations in school playground and classroom atmospheric particulate chemistry. Atmos. Environ. 2014, 91, 162-171. doi: 10.1016/j.atmosenv.2014.03.066.
3. C. Reche, M. Viana, I. Rivas, M. Àlvarez-Pedrerol, A. Alastuey, J. Sunyer, X. Querol. Outdoor and Indoor UFP in primary schools across Barcelona. Science of the Total Environment, 2014, 493, 2014, 943-953. doi: 10.1016/j.scitotenv.2014.06.072
4. M. Viana, I. Rivas, X. Querol, A. Alastuey, M. Álvarez-Pedrerol, L. Bouso, C. Sioutas, J. Sunyer. Partitioning of trace elements and metals between quasi-ultrafine, accumulation and coarse aerosols in indoor and outdoor air in schools. Atmospheric Environment, 2015, 106, 392-401. doi:10.1016/j.atmosenv.2014.07.027.
5. J. Sunyer, M. Esnaola, M. Àlvarez-Pedrerol, J. Forns, I. Rivas, M. López-Vicente, M. Foraster, R. Garcia-Esteban, X. Basagaña, M. Viana, M. Cirach, T. Moreno, A. Alastuey, N. Sebastian, M. Nieuwenhuijsen, X. Querol. Traffic-related air pollution in schools impairs cognitive development in primary school children. PLoS Medicine, 2015, 12(3), e1001792. doi: 10.1371/journal.pmed.1001792.
6. M. Nieuwenhuijsen, D. Donaire-Gonzalez , I. Rivas, M. de Castro (1-4), M. Cirach, G. Hoek, E. Seto, M. Jerrett, J. Sunyer. Variability in and agreement between modelled and personal continuously measured Black Carbon levels using novel Smartphone sensor technologies. Environmental Science & Technology, 2015, 49, 2977-2982. doi: 10.1021/es505362x
7. P. Dadvand, I. Rivas, X. Basagaña, M. Alvarez-Pedrerol, J. Su, M. De Castro Pascual, F. Amato, M. Jerret, X. Querol, J. Sunyer, M. Nieuwenhuijsen. The association between greenness and traffic-related air pollution at schools. Science of the Total Environment, 2015, 523, 59–63. doi:10.1016/j.scitotenv.2015.03.103

8. M.C. Minguillón, I. Rivas, T. Moreno, A. Alastuey, O.Font, P. Córdoba, M. Álvarez-Pedrerol, J. Sunyer, X. Querol. Road traffic and Sandy playground influence on ambient pollutants in schools. Atmospheric Environment, 2015, 111, 94-102. doi: 10.1016/j.atmosenv.2015.04.011

9. P. Dadvand, M. Nieuwenhuijsen, M. Esnaola, J. Forns, X. Basagaña, M. Alvarez-Pedrerol, I. Rivas, M. López-Vicente, M. de Castro Pascual, J. Su, M. Jerrett, X. Querol, J.Sunyer. Greenness and Cognitive Development in Primary Schoolchildren; A Prospective Study. Proceedings of the National Academy of Sciences, 2015. doi: 10.1073/pnas.1503402112

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