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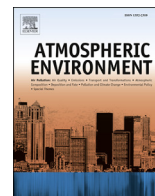
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Road traffic and sandy playground influence on ambient pollutants in schools



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HIGHLIGHTS

- The impact of road traffic on ambient pollutants around schools is higher on weekdays.
- NO_x concentrations decrease with distance to the main road.
- Playground sands are fine enough to be re-suspended and affect ambient PM.
- The sandy playground leads to an increase in PM₁₀ concentrations up to a factor of 57.
- The influence of the sandy playground decreases drastically with distance.

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ABSTRACT

Urban air pollution has a greater impact on children's health compared to adults. In the framework of the BREATHE (BRain dEvelopment and Air polluTion ultrafine particles in sChool childrEn) project, the present work studies the impact of road traffic and the presence of sandy playgrounds on the outdoor air quality around schools. Four schools were selected for intensive campaigns of one month. PM_{2.5} samples were collected daily from 8:00 to 20:00 and chemically analysed. Real time measurements of NO_x, black carbon (BC), PM₁, PM_{2.5} and PM₁₀ concentrations were carried out. Sand samples from five school playgrounds were characterized. The results confirm the representativeness of the general BREATHE project campaigns (eight weekdays measurements at each of the 39 schools). NO_x, BC and PM_x concentrations were higher in the school located nearest to traffic in the city centre with the daily pattern reflecting the traffic rush hours. The NO_x concentrations were found to decrease with distance to the main road. The road traffic influence on ambient pollutants was higher on weekdays than weekends. The PM₁₀ concentrations at one of the schools were mainly driven by the influence of the sandy playground, with peaks up to 25, 57 and 12 times higher than night background concentrations during mid-morning break, lunch break and end of school day, respectively. The airborne mineral matter concentrations registered at this school further confirm this origin. Nevertheless the influence of the re-suspension from the sandy playground was very local and decreased drastically within a short distance. The possible impact of the use of the private car for children's commuting on the outdoor air quality of the schools cannot be quantitatively assessed due to the overlapping with the rush hour of the city.

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1. Introduction

Urban air pollution has a greater impact on children's health compared to adults, with most studies emphasising acute respiratory dysfunction, chronic cardiovascular disease or allergies

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development (Bateson and Schwartz, 2008; Gehring et al., 2010; Hoek et al., 2012). The use of asthma medication among elementary school children was associated with particulate pollution (Gordian and Choudhury, 2003). The breathing of air pollutants has been proved to negatively affect the neurological development of young children (Sunyer, 2008; Guxens and Sunyer, 2012). Several studies exist around the world to better understand the air quality in and around schools (e.g. Wichmann et al., 2010; Crilley et al., 2013; Raysoni et al., 2013). In this context the BREATHE (BRain dEvelopment and Air polluTion ultrafine particles in scHool childrEn) project, funded by the European Union, aims at studying the impact of urban air pollution on the cognitive development of children. As an essential part of the study, an extensive aerosol measurements campaign was carried out at 39 primary schools located in the metropolitan area of Barcelona to characterize the children exposure to air pollutants. The results of this campaign were compiled and analysed by Rivas et al. (2014) and Moreno et al. (2014).

Barcelona is located by the Mediterranean Sea, in the NE of the Iberian Peninsula. It has the Collserola Hills to the W-NW and the Besòs and the Llobregat river valleys in the N and S, respectively. Barcelona city has a high traffic density and a large proportion of diesel vehicles, and therefore its air quality is highly influenced by road traffic (e.g. Querol et al., 2001b; Amato et al., 2009; Pérez et al., 2010). Some studies have also evidenced the within-city variability in air pollutants in Barcelona (Minguillón et al., 2014), which should be accounted when studying human exposure (Kloog et al., 2013). Nevertheless, it is hardly likely to have an urban background without the road traffic influence in the city of Barcelona.

Bearing this in mind, and in the framework of the BREATHE project, the present work was designed to study the impact of road traffic on the outdoor air quality around schools and other possible sources of contamination such as the presence of sandy playgrounds. Four representative schools were selected, one of them easily accessed by public transport, whereas the rest are mainly accessed by private cars. Time and spatial variations in the gaseous and particulate road traffic tracers are studied in detail, as well as the presence of such chemical tracers in the school playground sand.

2. Methodology

2.1. Selection and description of the schools

Four schools were selected for the present study. The selection of the schools was done in the framework of the larger sampling campaign for the BREATHE project, which was designed to perform the sampling at two schools per week, one located in an urban background area and the other one situated near traffic (Rivas et al., 2014). For the present study, we followed the same criteria. According to the privacy guidelines of the BREATHE project, the school names are avoided and instead they are named with SC followed by a number. Measurements were performed at schools SC01, SC04, SC07, and SC17.

Location of the schools is shown in Fig. 1. SC01, SC04 and SC07 were located far from the city centre, but close to a motorway ring road. All three schools are difficultly accessed by public transport and many of the children reach the school in private cars. The percentage of children reaching the school by car was 47%, 85% and 70%, for SC01, SC04 and SC07, respectively, as opposed to only 10% for SC17, where most of the children (76%) commute on foot. SC01 and SC04 were located to W-NW of the aforementioned motorway. SC01 was 400 m far from the motorway, whereas SC04 was less than 100 m away from the motorway, but the motorway is underground in the corresponding section. SC07 was located to the SE

of the motorway, less than 50 m away. Playgrounds from these three schools were mainly paved, although some unpaved areas were used in SC04 and SC01. SC17 was located near the city centre, in a major crossroad and hence highly affected by road traffic from the city. It had a large sandy playground. Characteristics of the schools are summarized in Table 1.

Given the distinctive geography of the area, the transport and dispersion of atmospheric pollutants within Barcelona are controlled mainly by fluctuating thermally-driven coastal winds which typically blow in from the sea during the day (sea breeze) and, less strongly, from the land during the night (land breeze). This atmospheric dynamic and the geographic setting have the potential to produce high concentrations of locally derived air pollutants within the city.

2.2. Measurements and schedule

For logistic reasons (availability of instrumentation required), measurements could be carried out at only two schools at a time. Hence, measurements were performed simultaneously at SC04 and SC07 during one-month period (April 2012), and subsequently at SC01 and SC17 during one more month (May 2012). A mobile unit was deployed near the school access, although the exact location depended on logistics. The location of the mobile units in each of the schools and the location of the instrumentation used to measure outdoor during the general BREATHE campaign is shown in Fig. 2. One of the mobile units belongs to IDAEA-CSIC and the other one to Department of Environment of the Autonomous Government of Catalonia. PM_{2.5} samples were collected daily from 8:00 to 20:00 local time by high volume samplers (MCV CAV-A/mb and DIGITEL) on Pallflex quartz fibre filters (QAT 150 UP). Filters were conditioned at 20–25 °C and 50% relative humidity over at least 24 h before and after sampling to determine the PM_{2.5} concentrations gravimetrically.

The mobile units were equipped with real-time NO and NO₂ chemiluminescence analysers to measure hourly concentrations. Additionally, the mobile unit in SC07 and SC17 was equipped with a multiangle absorption photometer (MAAP, model 5012, Thermo), measuring the absorption coefficient with hourly time resolution; and an optical particle counter (GRIMM 1107) measuring PM₁, PM_{2.5} and PM₁₀ hourly concentrations. Equivalent black carbon (BC) concentrations (Petzold et al., 2013) were calculated by the MAAP instrument software by dividing the measured absorption coefficient by the default mass absorption cross section (6.6 m² g⁻¹).

The urban background site Palau Reial (PR, 41°23'14" N, 02°06'56" E, 78 m a.s.l.) was used as a reference as it worked continuously during these campaigns. The site is equipped with a MAAP instrument for the determination of real-time equivalent BC concentrations, an optical particle counter (GRIMM 180) for the determination of real-time PM_x concentrations, and real-time chemiluminescence analysers for NO_x concentrations (the latter belonging to the Department of Environment of the Autonomous Government of Catalonia).

2.3. PM chemical analysis

The PM_{2.5} samples were analysed for major and minor elements, inorganic ions, and EC and OC concentrations. Major and minor elements were analysed following the procedure described by Querol et al. (2001a). Briefly, a quarter of the filter was acid digested (HNO₃:HF:HClO₄), and the resulting solution was analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (ICP-MS). A few mg of the reference material NIST 1633b were added to a fraction of a blank filter to check the accuracy of the analysis of the acidic digestions. Inorganic

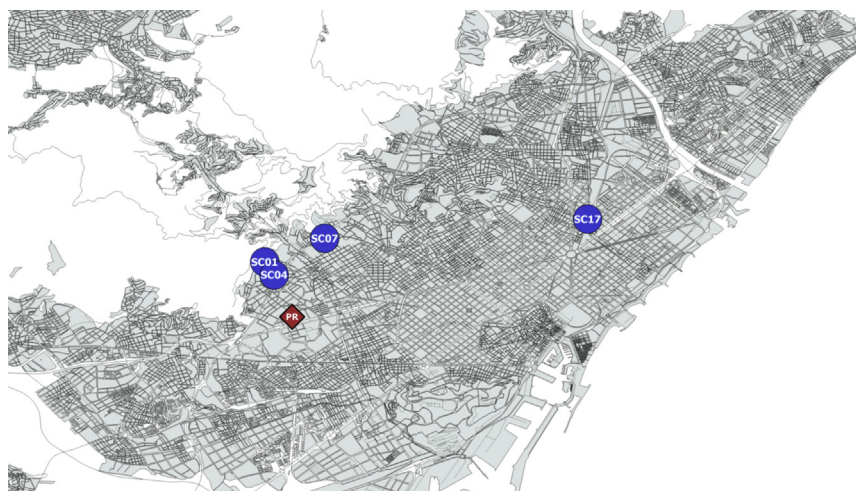


Fig. 1. Location of the reference urban background site (PR) and schools where the sampling took place.

Table 1
Main characteristics of the schools where the sampling took place.

School	Traffic influence	% Children reaching school by car	Distance to motorway	Position with respect to motorway	Playground	# Vehicles in 24 h
SC01	Low	47	400 m	W-NW	Paved + sandy	2894
SC04	Low	85	100 m	W-NW	Paved + sandy	3381
SC07	Moderate	70	50 m	SE	Paved	6992
SC17	High	10	– (city centre)	–	Sandy	10,807

ions were analysed in water extractions of a quarter of the filter by Ion Chromatography (NO_3^- , SO_4^{2-} and Cl^-) and selective electrode (NH_4^+). EC and OC concentrations were determined by thermal-optical methods using a Sunset instrument following the NIOSH protocol (Birch and Cary, 1996). Laboratory blank filters were analysed following the same methodology, and concentrations were subtracted from those found in the samples to calculate the ambient concentrations.

The different components were grouped as follows: mineral matter, non-sea-salt SO_4^{2-} , NO_3^- , NH_4^+ , EC, OM (organic matter), sea salt, and trace elements. Mineral matter was calculated as the sum of Al_2O_3 , SiO_2 , CO_3^{2-} , non-sea-salt Ca (nss-Ca), Fe, non-sea-salt K, non-sea-salt Mg and mineral Na. Al_2O_3 was calculated stoichiometrically from the Al concentration. SiO_2 concentrations were estimated as $3 \cdot \text{Al}_2\text{O}_3$. CO_3^{2-} concentrations were estimated as 1.5 times the nss-Ca concentration, according to stoichiometry assuming that the nss-Ca is present as carbonates. Mineral Na was calculated as $0.148 \cdot \text{Al}_2\text{O}_3$, according to the mineral composition of the $\text{PM}_{2.5}$ fraction of the analysed school sands (see Section 3.4). OM was estimated as $1.6 \cdot \text{OC}$, assuming an intermediate degree of OC oxidation between primary traffic OC and biomass burning or secondary OC (Aiken et al., 2008), and as previously determined for Barcelona (Minguillón et al., 2011). Sea salt was estimated from the sea-salt Na concentrations (Na_{ss} , resulting from the subtraction of mineral Na from total Na) as $3.235 \cdot \text{Na}_{\text{ss}}$, based on standard sea water composition, including Cl^- , Mg, SO_4^{2-} , Ca and K (Mészáros, 1999). The concentrations of Mg, SO_4^{2-} , Ca and K estimated to be part of the sea salt were subtracted from the total concentrations of these species to calculate the corresponding non-sea-salt concentrations (nss-species name).

2.4. Sand sampling and chemical analysis

Sand samples from five school playgrounds (from four schools)

across the city of Barcelona were collected with a plastic shovel and stored in plastic vessels. One of the samples was taken from a school where the sand had been recently changed with new washed sand and it was used as a reference sample. The sand sampling was designed to investigate the presence of tracers from urban pollution in the sand. The sand samples were dried and sieved to $<63 \mu\text{m}$, and subsequently crushed and milled to obtain powdered samples for analysis. The grain size distribution of $<63 \mu\text{m}$ fraction was determined by means of a laser light-scattering-based particle sizer, MALVERN Hydro 2000MU, with a working range from 0.1 to 1000 μm .

Sand samples were acid-digested in duplicate by using a two-step digestion method devised by Querol et al. (1995). The European Standard leaching test EN-12457 was applied to each of the samples. The content of major and minor elements of the digestions and leachates was determined by ICP-AES and ICP-MS.

Two of the samples were selected for characterization of the different size fractions. Particle size separation was achieved using a cascade impactor Retsch PI-1 without a sampling substrate, allowing separation into seven stages from 0.3 μm to 63 μm in diameter. Soluble and insoluble fractions for each stage were characterized using the same methods described for the $<63 \mu\text{m}$ fraction.

3. Results and discussion

3.1. Gaseous pollutants, BC and PM_x concentrations

Average NO_x concentrations were $25 \mu\text{g m}^{-3}$ and $29 \mu\text{g m}^{-3}$ at SC04 and SC07, respectively, during the first sampling period, and $23 \mu\text{g m}^{-3}$ and $48 \mu\text{g m}^{-3}$ at SC01 and SC17, respectively, during the second sampling period. Note that NO_x concentrations at the reference site PR were lower during the first period ($34 \mu\text{g m}^{-3}$ on average) than during the second one ($46 \mu\text{g m}^{-3}$), which needs to

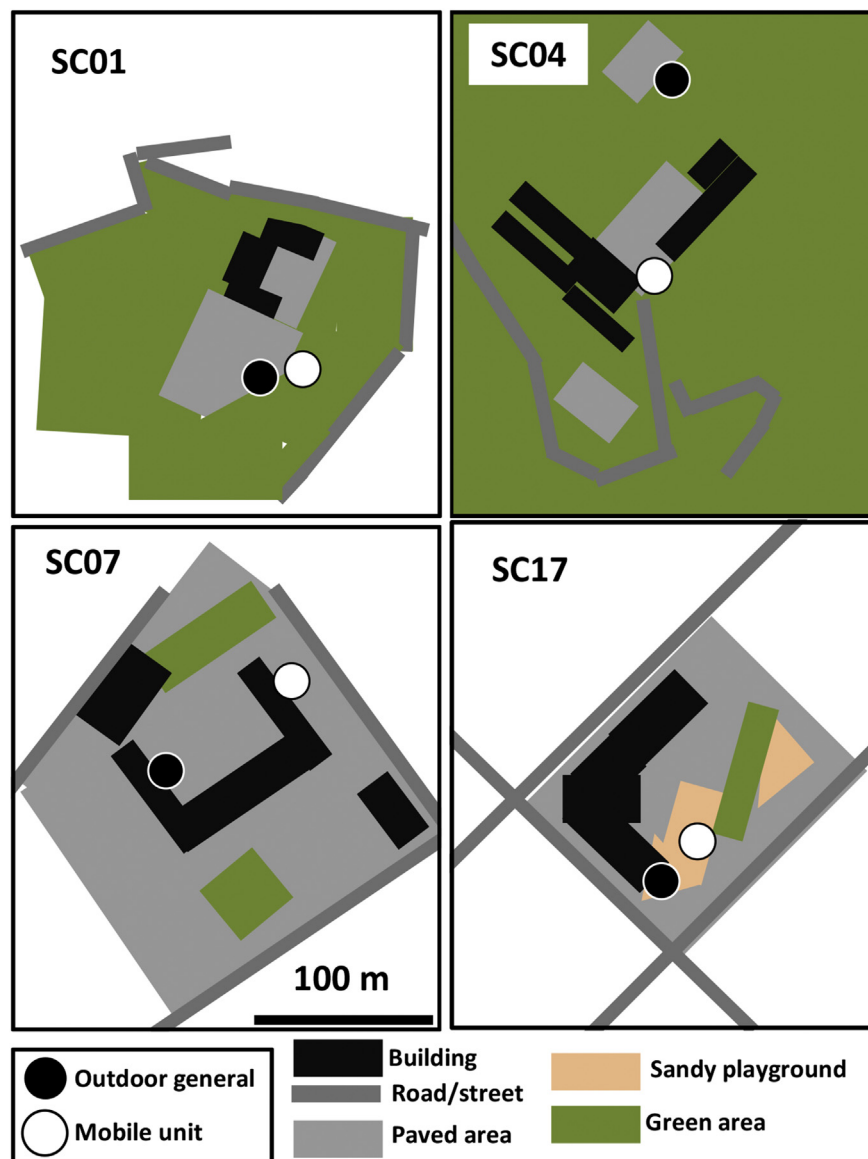


Fig. 2. Detail of the location of the outdoor instrumentation during the general BREATHE campaign and the location of the mobile units during this specific work.

be taken into account when comparing concentrations among schools from different sampling periods. Thus the ratios of the recorded NO_x concentrations respect to those simultaneously recorded at the PR reference site were 0.74 and 0.84 for SC04 and SC07, respectively. This ratio was 0.50 and 1.05 for SC01 and SC17, respectively. Since NO_x is a well-known proxy for road traffic contribution to ambient PM (Minguillón et al., 2012), this indicates that, as expected due to the specific location, the overall influence of road traffic was clearly higher at SC17, compared to the rest of the schools. This was further evidenced by the higher BC concentrations, which were 1.5 times higher at SC17 than at the PR reference site, whereas they were similar at SC07 and PR.

The location at one side or the other of the main motorway does not seem to play a role in the average NO_x concentrations, since they were similar at SC04 and SC07, recorded simultaneously. Nevertheless, the hourly variations will indicate some differences, as explained below. On the other hand, the distance to the motorway may be determinant in the influence of the NO_x emissions, since the school SC01, the most distant from the motorway

among SC01, SC04 and SC07, showed the lowest NO_x concentration ratio with respect to that of the PR reference site.

When examining the hourly variation of the different pollutants registered at the four schools (Fig. 3), a morning increase in NO_x and BC concentrations during weekdays is observed for all the schools, which can be attributed to the rush traffic hours. The influence of children's transport, if any, overlaps with this rush hour impact and hence it cannot be isolated. During lunch break (between 12 h and 15 h in Spanish schools), the same overlap may happen between children's transport and other additional traffic at this time. Therefore, despite the fact that a slight increase during lunch time in NO_x and BC concentrations is registered on weekdays (only not seen for NO_x at SC17), simultaneous measurements at our reference urban background site show the same increase in NO_x concentrations. Nevertheless, this lunch break time increase is not always evident, hence it is very clear in the first sampling period, whereas it is very soft during the second sampling period and it had not been observed in urban background sites in Barcelona in previous studies (Reche et al., 2011). A slight increase at 17–18 h may be

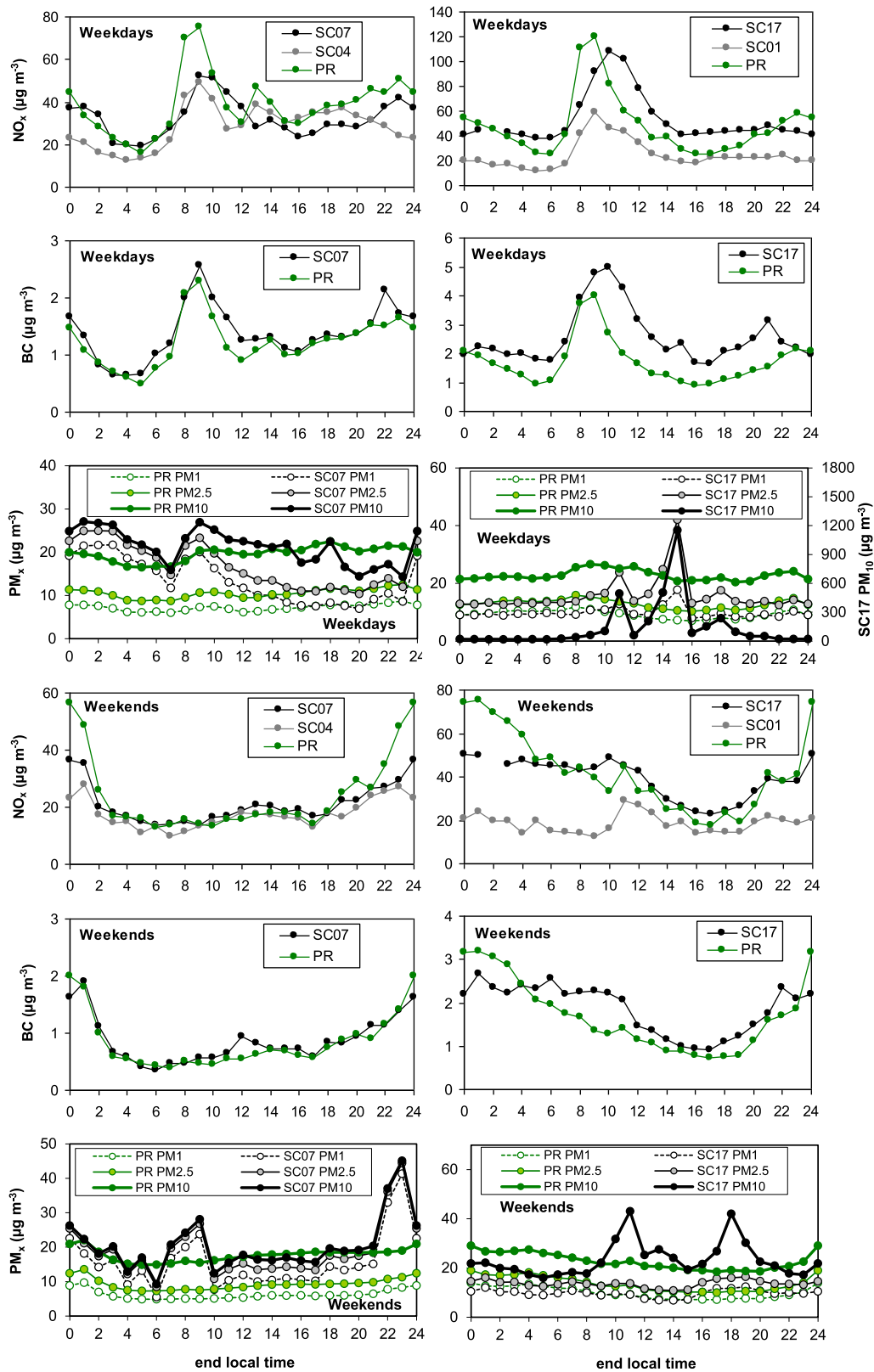


Fig. 3. Average daily pattern for the whole sampling periods for NO_x, BC, PM₁₀, PM_{2.5} and PM₁ concentrations at the four schools, when available. The time corresponds to the end of the hourly time slot. PM₁₀, PM_{2.5} and PM₁ are the raw concentrations as obtained from the instrument. Note the different scale for PM₁₀ concentrations from SC17 for weekdays.

attributed also to the children's transport, coinciding with the ending time of Spanish school day (around 17 h). This afternoon increase is partially masked by the general road traffic influence

from the city and therefore it is not as marked as the lunch one.

The influence of the motorway on NO_x concentrations is clearly seen in the weekend daily patterns. There is an increase during the

late hours of the weekend days in the schools near the motorway, coinciding with the return of people to the city after the weekend activities. Nevertheless, the impact varies with the location of the school with respect to the motorway. Thus, night NO_x concentrations were lower at SC04, located upwind with respect to the motorway, than at SC07, located downwind of the motorway. Likewise, the weekend increase is larger at SC07 than at SC04.

The PM_x concentrations registered at SC07 further confirm the aforementioned patterns. The increase in PM_x concentrations during the morning rush hours during weekdays evidences the road traffic influence, and a slight increase is also observed at 17–18 h. During weekends, there is also an increase during the morning and a huge increase in the late hours of the day, with concentrations reaching values 2.5 times higher than during the daytime hours, revealing the influence of the traffic generated by the people returning to the city at the end of the weekend.

The PM_x concentrations registered at SC17 on weekdays are mainly driven by the influence of the sandy playground, which masks any additional sources. The large increases in PM_{10} concentrations registered at 10–11 h, 13–15 h and 17–18 h coincide with the mid-morning break, lunch break and end of school day, respectively. Hourly PM_{10} concentrations during these periods can be 25, 57 and 12 times higher than the average concentrations during the night (note the different scale for PM_{10} concentrations in Fig. 3). The maximum weekend PM_{10} hourly concentrations only reach values twice as high as during the night. PM_1 concentrations remained relatively low both during weekdays and weekends, which is in agreement with the influence of the sandy playground, affecting mainly the coarse PM fraction.

3.2. $\text{PM}_{2.5}$ chemical composition

The concentrations of the different components in $\text{PM}_{2.5}$ varied differently depending on their main sources affecting the schools. Thus, the regional components, such as nss-sulphate and sea salt, were registered in similar concentrations for each pair of schools with simultaneous measurements (Table 2). On the contrary, the mineral matter concentrations were extremely higher at SC17 compared to the other three schools (Table 2 and Fig. 4). This difference is attributed to the contribution of the sandy playground, which is further confirmed by the relatively lower mineral concentrations registered at SC17 during weekends, compared to weekdays although still higher than in the other schools. Nevertheless, as discussed later in detail, the influence of the resuspension from the sandy playground on the ambient concentrations in the schools facilities is very local. EC and OM concentrations, which can be mostly attributed to road traffic in the Barcelona urban environment (Minguillón et al., 2011), were measured in similar concentrations at the first pair of schools, whereas the second pair of schools shows a higher influence of road traffic at SC17 than at SC01. Again, the road traffic origin of these variations is supported by the differences weekday–weekend,

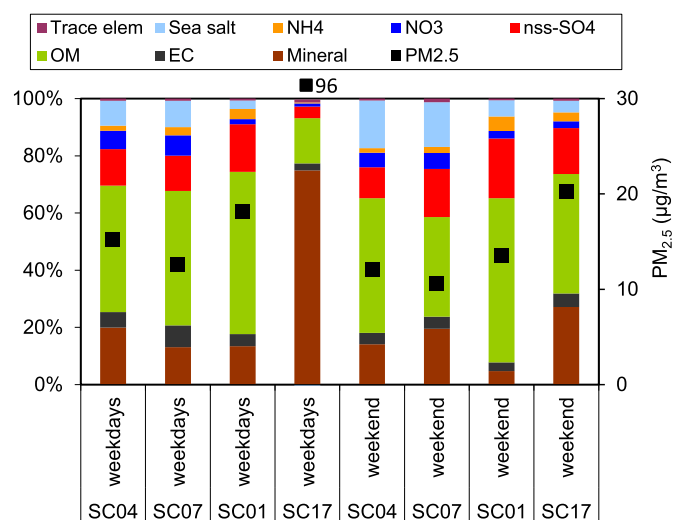


Fig. 4. Average $\text{PM}_{2.5}$ concentration (right axis) and relative chemical composition (left axis) at each of the schools for weekdays and weekends.

which are evident at all four schools. Nitrate, although being a secondary compound, is not originated from long range transport, but formed from traffic precursors (nitrogen oxides) quickly enough to be detected near the precursors' source. Hence, the NO_x concentrations registered at SC17, highly affected by road traffic, were higher than those registered simultaneously at SC01. Moreover, the concentrations were higher during weekdays compared to weekends.

Therefore, the road traffic influence during daytime is higher on weekdays compared to weekends, and higher in the city centre compared to the schools located far from the centre. The influence of the weekend traffic near the motorway is not reflected in this daytime chemical composition, due to the time in which the sampling takes place (8–20 h), as shown by the hourly NO_x data.

The trace elements concentrations recorded at each of the schools are shown in Fig. 5, where they are compared to the usual urban range in Spanish cities as a reference (Querol et al., 2008). For the first pair of schools (SC04 and SC07) the concentrations of most of the elements fall within the usual urban range. When comparing between both schools, relatively small differences are observed, as well as when comparing weekdays vs weekend concentrations. For the second pair of schools (SC01 and SC17) the differences are more evident. The concentrations of Li, Sc, Ti, Cr, Mn, Co, Rb, Sr, Y, Ba, La, Ce, Pr, Nd and W are clearly higher at SC17 than at SC01, and higher than the usual urban background range. These elements are related to the mineral matter, and hence they are linked to the existence of a sandy playground in the school. Moreover, the concentrations during weekdays are higher than those during weekends, which further confirms their origin. Additionally, the concentrations of V, Ni, Cu, Zn, As, Cd, Sn and Sb are also markedly higher at SC17 than at

Table 2
Average $\text{PM}_{2.5}$ chemical composition ($\mu\text{g m}^{-3}$) at each of the schools during weekdays and weekends.

		n	Mineral	EC	OM	Nss-sulphate	Nitrate	Ammonium	Sea salt	Trace elements
SC04	Weekdays	13	2.6	0.7	5.7	1.6	0.8	0.2	1.1	0.1
SC07	Weekdays	14	1.4	0.8	5.0	1.3	0.8	0.3	1.0	0.1
SC01	Weekdays	19	2.1	0.6	8.7	2.6	0.3	0.5	0.5	0.1
SC17	Weekdays	14	61	2.0	13.0	3.2	0.9	0.3	<0.1	0.8
SC04	Weekend	6	1.4	0.4	4.8	1.1	0.5	0.2	1.7	0.1
SC07	Weekend	4	1.8	0.4	3.1	1.5	0.5	0.2	1.4	0.1
SC01	Weekend	8	0.5	0.3	6.6	2.4	0.3	0.6	0.7	0.1
SC17	Weekend	8	4.7	0.8	7.2	2.8	0.4	0.5	0.7	0.1

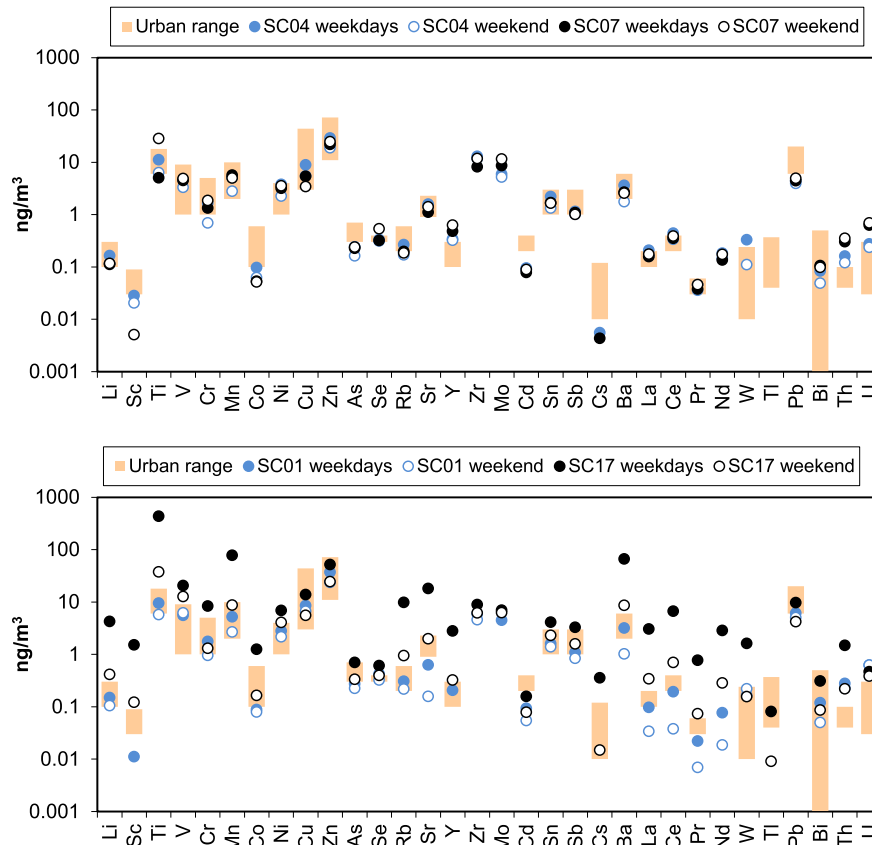


Fig. 5. Average $PM_{2.5}$ trace elements concentrations at each of the schools for weekdays and weekends, and usual urban range (Querol et al., 2008).

SC01 and higher during the weekdays. The origin of these relatively high concentrations may be related to the higher direct emissions from road traffic during weekdays (for Cu, Zn, Sn and Sb), but also to the enrichment of the playground sand in these elements due to accumulated deposition by scavenging of urban particulate matter (for all the mentioned elements), hence resulting in higher ambient concentrations when this sand is re-suspended. In the Section 3.4 we present the characterization of the playground sand from different schools.

3.3. Representativeness of the general BREATHE campaigns

The comparison of the results found in the present study with those from the general BREATHE campaigns (8 weekdays per school divided in two periods of 4 days each, from 9 h to 17 h) (Moreno et al., 2014) can give us valuable information (Table 3). These campaigns will be named general campaigns to differentiate them from the specific campaigns studied in the present work. The ratio between the average weekday chemical composition of $PM_{2.5}$ from the present study with respect to the average chemical composition measured during the general BREATHE campaigns

serves as an indicator of how representative the general campaigns were. These ratios were between 0.8 and 1.3 for EC and between 1.0 and 1.6 for OM, and hence the EC and OM concentrations registered during the general campaigns may be considered quite representative of the general conditions. Nss-sulphate has relatively high ratios for the second pair of schools, which is attributed to the seasonal variability of this compound, higher in summer than in winter, leading to higher concentrations during the present study (May 2012) compared to the times of the year when the general campaigns took place (May 2012 and January 2013). Nitrate and ammonium ratios ranged between 0.7–1.0 and 0.4–2.3. The relatively high variability of ammonium can also be attributed to the different times of the year of the different campaigns.

Mineral ratios differ significantly from the unity for two of the schools (0.2 and 5.9 at SC04 and SC17, respectively). At SC04, mineral concentrations from the present study were much lower than those during the general campaigns. This difference is attributed to the different location of the sampling point, i.e. while it was only 10 m away from a non-paved area during the general campaigns, the mobile unit in the present study was located in a

Table 3
Ratio of the average weekday $PM_{2.5}$ chemical composition from the present study with respect to the average chemical composition measured during the general BREATHE campaigns (8 weekdays per school divided in two periods of 4 days each) at the four schools.

Mineral	EC	OM	Nss-sulphate	Nitrate	Ammonium	Sea salt	Trace elements
SC04	0.2	1.0	1.2	0.7	0.4	2.8	0.5
SC07	1.3	1.3	1.8	1.0	0.8	4.2	0.8
SC01	0.8	1.6	3.5	0.8	2.3	1.3	0.6
SC17	5.9	1.6	3.5	1.7	1.1	0.4	4.4

paved location by the school access to better characterise the traffic influence. This difference in mineral concentrations reflects the very local influence that the soil re-suspension has on the ambient pollutants. At SC17, the situation was reverse, the mineral matter measured during the present study was 5.9 times higher compared to that measured during the general campaigns. The difference is again attributed to the exact location of the samplers, which were in a small sandy playground with a paved section and lower children activity during the general campaigns and in a large sandy playground with intense children activity during the present study. Nevertheless, for SC17, the children exposure may be more similar to that of the present study, since the mobile unit was located in the same playground where the children are.

3.4. Playground sands characterization

The size distribution of the studied playground sands (<63 μm) reveals that they contain a non-negligible amount of fine particles, hence they comprise 5–7% of particles <2.5 μm , 11–15% of particles <5 μm , and 19–26% of particles <10 μm in mass (Fig. 6). The lowest limit of the range corresponds to the recently-changed sand. Hence, the relatively fine size distribution of the sands may be a result of the children's activity, stepping on the sand and acting as a mill or crusher. The deposition of fine particles from anthropogenic activities may also influence the size distribution of the playground sand. The finer fraction of the sand can be re-suspended owing to the children's activity and/or wind effect.

The comparison of the concentrations of the sand samples with the reference sand sample reveals that sand samples are enriched in Zn (by a factor of 2.0–2.6), As (up to 2.6), Cu (1.4–2.1), Ni (1.6–2.4), Co (1.5–1.7), Cr (1.5–2.0), Pb (1.7–2.4), and depleted in Sb (0.3–0.4) and Mo (0.5–0.9). These enrichment factors point to a major anthropogenic origin for these elements.

Most of the elements enriched with respect to the reference sand sample (As, Zn, and Pb) and other species such as Ca, Mg, S, Cr, Co, Ni, Cu, water soluble Cl, and water soluble NH_4^+ were clearly present in the fractions <10 μm and <5 μm . Hence, As, Zn, Co, Ca and Pb contents in the fraction <10 μm were between 24 and 37% those in the fraction <63 μm . This proportion was more variable for S, Mg, water soluble Cl, and water soluble NH_4^+ , ranging from 7 to 97%.

According to the occurrence of carbonate (mainly calcite) and sulphate (mainly gypsum) in the sand samples, Ca, S, K, Na, Mg, Sr

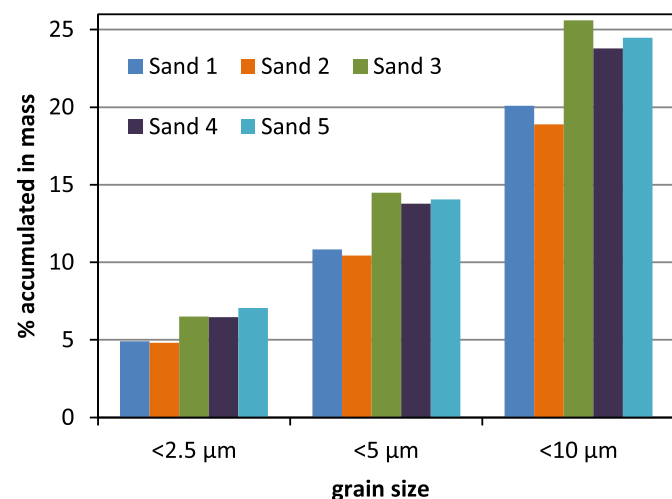


Fig. 6. Percentage in mass of particles <2.5 μm , 5 μm and 10 μm (with respect to the <63 μm fraction) in the playground sands.

and Ba showed the highest solubility. On the other hand, As, Sb, Mo, Zn, and Co showed low but non-negligible solubility in the <63 μm fraction, and it was higher in the finest fractions (especially in the fraction <2.5 μm). Most of these elements are most probably present in the oxy-anionic form, soluble at the slightly alkaline pH (7.6–8) of the playground sands.

The results of the composition and solubility of specific elements in the playground sands indicate that their composition is influenced by deposited material by scavenging of anthropogenic ambient pollutants. Therefore the re-suspension of this playground sands may have an effect on the air quality of the schools beyond the mineral matter concentrations.

4. Conclusions

It is impossible to avoid the road traffic influence on the air quality in the modern European cities although differences can be observed depending on some factors. Thus, during school hours, this influence is higher during the weekdays compared to the weekends, and higher in the city centre compared to the schools located in the surrounding areas. The distance to motorways or major roads may also be determinant in the influence of the NO_x emissions. This should be considered by city planners when designing new areas as expansion of the existing towns.

The concentrations and chemical composition of PM registered during the general BREATHE project campaigns may be considered quite representative of the general conditions. Therefore this study further validates the extensive results obtained from the aforementioned project.

There may be an impact of the use of the private car for children's commuting on the outdoor air quality of the schools, although due to the overlapping of this effect in time with the rush hour of the city it cannot be quantified.

The presence of sandy playgrounds leads to higher ambient $\text{PM}_{2.5}$ and PM_{10} concentrations, especially at the time of children activity, i.e. entrance and exit school times, and during lunch and mid-morning breaks. Hourly PM_{10} concentrations during these periods can be up to 57 times higher than the average concentrations during the night. The mineral major and trace elements concentrations are also much higher at schools with sandy playgrounds. Although this influence within the outdoor school area is local and decreases significantly with distance to the sandy playground, the BREATHE study showed that mineral particles are carried by children into the classrooms leading to increase ambient concentrations indoors.

The playground sands have a considerable fraction of particles below 10 μm , which may be easily re-suspended by children activity. The enrichment in some trace elements found in the playground sands caused by the accumulated rain scavenging of ambient particulate matter may result in higher ambient concentrations of these elements when this sand is re-suspended, beyond the mineral matter concentration, although more studies are needed on this issue. To avoid such effect, the playground sand could be systematically renewed by clean, less-crushed sand.

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