

Indoor/outdoor relationships and mass closure of quasi-ultrafine, accumulation and coarse particles in Barcelona schools

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Abstract

The mass concentration, chemical composition and sources of quasi-ultrafine (quasi-UFP, PM_{0.25}), accumulation (PM_{0.25-2.5}) and coarse mode (PM_{2.5-10}) particles were determined in indoor and outdoor air at 39 schools in Barcelona (Spain). Quasi-UFP mass concentrations measured (25.6 µg/m³ outdoors, 23.4 µg/m³ indoors) are significantly higher than those reported in other studies, and characterised by higher carbonaceous and mineral matter contents and a lower proportion of secondary inorganic ions. Results suggest that quasi-UFPs in Barcelona are affected by local sources in the schools, mainly human activity (e.g. organic material from textiles, etc.; contributing 23-46% to total quasi-UFP mass) and playgrounds (in the form of mineral matter, contributing about 9% to the quasi-UFP mass). The particle size distribution

patterns of toxicologically relevant metals and major aerosol components was characterised, displaying two modes bimodal size distributions for most elements and components, and a unimodal one mode distribution for inorganic salts (ammonium nitrate and sulphate) and elemental carbon (EC). Regarding metals, Ni and Cr were partitioned mainly in quasi-UFPs and could thus be of interest for epidemiological studies, given their high redox properties. Children exposure to quasi-UFP mass and chemical species was assessed by comparing the concentrations measured at urban background and traffic areas schools. Finally, three main indoor sources across all size fractions were identified by assessing indoor/outdoor ratios (I/O) of PM species used as their tracers : human activity (organic material), cleaning products, paints and plastics (Cl⁻ source), and a metallic mixed source (comprising combinations of Cu, Zn, Co, Cd, Pb, As, V and Cr). Our results support the need to enforce targeted legislation to determine a minimum “safe” distance between major roads and newly built schools to reduce exposure to traffic-derived metals in quasi-UFPs.

Keywords: ultrafine particles; metals, children exposure; playground sand; skin cells; lubricant oil; printer; photocopier; schools; urban traffic emissions

1 Introduction

Airborne ultrafine particles (defined as particles with aerodynamic diameters <100-200 nanometres) have been linked to adverse health effects, and more strongly than coarser particles because of the ability of the former to penetrate deeper into the respiratory tract and to translocate to other organs (Oberdorster, 2001; Kreyling et al., 2006; Paur et al., 2011; Strak et al., 2012; WHO, 2012, 2013). Also, the ultrafine particle fraction has a high trace metal content (Sioutas et al., 2005; Daher et al., 2013), especially regarding health-relevant species with a high oxidative stress potential (Cahill et al., 2011a; Cahill et al., 2011b). Despite this, scientific evidence of trace metal contents in ultrafine particles in ambient air is only fairly new but the related literature is growing (Hughes et al., 1998; Smolík et al., 2004; Morawska et al., 2008; Cho et al., 2009; Buonanno et al., 2011; Verma et al., 2009, 2011; Price et al., 2010; Knibbs and Morawska, 2012; Lü et al., 2012; Daher et al., 2013; Keuken, 2013; Kumar et al., 2013; Ozgen, 2013).

Ultrafine particles may be either newly formed in the atmosphere through gas-to-particle conversion processes, or directly released by anthropogenic sources such as vehicular traffic (Sardar et al., 2005; Westerdahl et al., 2005). The ultrafine particle range is generally known to include the two lowest particle size modes, the nucleation and Aitken modes. The smallest particles are mostly formed from gas phase vapours via nucleation (nucleation mode, with aerodynamic diameter <30 nm), although a fraction of soot may also be present in this particle size range. The Aitken mode particles are produced via growth from nucleation mode and/or emitted by a wide variety of anthropogenic sources (aerodynamic diameter between 30 nm and 100 nm (Hinds, 1999). The largest submicron particles are in the accumulation mode, with a major source being growth from Aitken mode by coagulation and condensation processes.

[Aerosol indoor/outdoor \(I/O\) relationships are impacted by particle size distributions, given that infiltration of outdoor particles into indoor air is most efficient for accumulation mode particles, while diffusion losses dominate for the lowest size ranges of ultrafine particles \(<100 nm\) \(Long et al., 2001\).](#)

In urban areas, where the largest fraction of the population in Europe is exposed, particulate matter concentrations (PM₁₀ and PM_{2.5}) are monitored at central outdoor locations in numerous air quality monitoring networks (see AirBase, the European air quality database, www.eea.europa.eu). However, it is estimated that adults spend approximately 60-80% of their time indoors (Klepeis et al., 2001), and in the case of children at least 50% of this time is spent in school. Consequently, indoor exposure in school environments constitutes a significant fraction of total exposure to atmospheric pollutants for children (Buonanno et al., 2013, 2014).

The present work aims to characterise chemical composition, sources and indoor/outdoor (I/O) relationships of the quasi-ultrafine aerosol fraction (quasi-UFP, herein defined as particles with aerodynamic diameter <250 nm), with special attention to trace metal contents and their particle size distribution. In this context, quasi-UFP are characterised per se and also in comparison to larger sized particles (accumulation and coarse mode, PM_{0.25-2.5} and PM_{2.5-10}, respectively), given that the latter may reach different parts of the respiratory tract as a function of lung deposition curves (Asbach et al., 2009). The differences in indoor and outdoor exposure to major species and trace elements as a function of the schools' environments (urban background vs. traffic-oriented) are also discussed. The ultimate goal is to assess children exposure to metals

in ultrafine particles in indoor and outdoor school environments, as part of the ERC Advanced Grant BREATHE (<http://www.creal.cat/projectebreathe>). This work aims to go beyond current state of the art by providing chemically-speciated data of quasi-UFPs impacting child exposure during school hours (indoors), which to the authors' knowledge is currently unavailable in the literature. In addition, this is also the first study which addresses quasi-UFP concentrations and mass closure in outdoor air in Spain, and more specifically with a dense spatial coverage across the city of Barcelona.

2 Experimental Methods

2.1 Sampling sites

Measurements were carried out in 39 schools in Barcelona, representative of 2904 children between ages 8 and 11. The schools were selected in the framework of the Advanced Grant BREATHE, taking into account atmospheric pollution criteria as well as socio-economic and geographic variables. Schools were divided into those representative of the city's urban background pollution levels (with regard to existing NO₂ data, Cyrus et al., 2012) and those representative of high traffic emissions, and were then grouped into pairs (one school of each type) for concurrent sampling. In each school, indoor and outdoor sampling was also carried out simultaneously. For the outdoor location, where possible, sampling was carried out in the playground or on a balcony, in an effort to avoid the direct influence of sand playgrounds. For the indoor location, samplers were placed inside a classroom of children 8-11 years old, close to one of the walls and away from blackboards and windows. In all cases, the teachers were asked to fill in a logbook describing the frequency with which the windows and doors were opened, as well as cleaning activities.

2.2 Sample collection

Filter samples were collected by means of Personal Cascade Impactor Samplers (SioutasTM PCIS, SKC Inc., Eighty Four, PA, USA) (Misra et al., 2002) connected to SKC Leland Legacy pumps, each operating at 9 lpm. Four PCIS were placed simultaneously (2 indoors, 2 outdoors) in each school. As previously stated, samples were collected simultaneously in two schools (one background, one traffic). The PCIS were connected to a timer, by which samples were collected only during school hours

(9:00-17:00 local time, 8 hours). The PCIS stopped at the end of every school day and started the next morning over a period of 4 consecutive days (Monday to Thursday), thus accumulating 32 sampling hours on the same filters (weekly samples). It is important to remember that these were always school (lecture) hours.

Each PCIS collected size-fractionated particles in the following size ranges: <0.25 μm (quasi-UFP), 0.25-2.5 μm (accumulation mode particles), and 2.5-10 μm (coarse PM). The collection substrates were Pall quartz-fibre filters in all cases (Pall Tissuquartz 2500QAT-UP), 25 mm in diameter for the coarse and accumulation stages, and 37 mm for the quasi-UFP.

The sampling campaign took place between January 30 to June 18, 2012,, at a rate of 2 schools per week. To account for the meteorological variability, a second campaign (from summer to winter) was carried out between September 2012 to February 2013. The present work focuses only on the results from the first campaign (from winter to summer).

2.3 Sample analysis

Mass concentrations were gravimetrically determined by pre- and post-weighing the PCIS quartz fibre filter substrates on a Mettler-Toledo Microbalance, after they had equilibrated over 24-hour periods in the weighing room (20-25°C, 25-30% RH). All samples were then analysed for major and trace elements. For each school and week, 2 parallel samples (with 3 filter substrates each) were available: A and B. The filters from PCIS A were acid digested ($\text{HNO}_3\text{:HF:HClO}_4$) to determine major and trace elements by ICP-MS and ICP-OES (Querol et al., 2001). The filters from PCIS B were cut in two halves: one half was leached in deionised water to extract the soluble fraction, which was analysed by ion chromatography and ion selective electrode to determine concentrations of SO_4^{2-} , NO_3^- , Cl^- and NH_4^+ . The remaining half filter was used for determination of OC and EC by thermal-optical transmission (TOT) with a Sunset OCEC Analyzer following the temperature protocol NIOSH. This methodology was applied equally to each of the size ranges (quasi-UFP, accumulation and coarse).

2.4 Data analysis

The major and trace chemical constituents analysed were grouped into four main components: mineral matter (calculated as the sum of Ca, Fe, K, Mg and Al_2O_3 , the

latter obtained from converting Al to Al₂O₃ by a factor of 1/0.53), marine aerosol (sum of Na and Cl), secondary inorganic aerosols (SIA, as the sum of SO₄²⁻, NO₃⁻ and NH₄⁺), organic matter (OM, converted from organic carbon by a factor of 1.8) and elemental carbon (EC). In previous studies focusing on PM₁₀ and PM_{2.5} (Querol et al., 2004; Viana et al., 2013), the contribution from carbonates and SiO₂ were calculated indirectly by applying a factor of 60/40 to Ca in the case of the carbonates and a factor of 3 to Al₂O₃ in the case of SiO₂. This was not done in the present study, given that it is not reasonable to assume the same ratios in ultrafine particles as PM_{2.5}. Furthermore, a recent work (Oeder et al., 2012) evidences that carbonate in indoor environments may originate from handling of paper documents, as it is used as a filler in paper production, thus revealing another source of carbonate indoors. In addition, studies (Lin et al., 2005; Miller et al., 2007; Cernushi et al., 2012) have revealed that anthropogenic sources such as traffic or industry may be major contributors to typically mineral elements such as Al, Si, Ca and Fe in particles <100 nm, and thus the sources of these elements in ultrafine particles should be considered carefully.

3 Results and discussion

3.1. Mass concentrations and mass closure

The basic statistics (mean and standard deviation) of the mass and chemical composition of quasi-UFPs for indoor and outdoor air, along with those of the accumulation and coarse fractions, are summarised in Tables 1a (major species) and 1b (trace elements). For the experimental period (January to June 2012), mean quasi-UF mass concentrations were 25.6 µg/m³ outdoors (±10.7 µg/m³ standard deviation) and 23.4±14.0 µg/m³ indoors, values which are significantly higher compared to those obtained in other regions of the world (e.g., maximum outdoor winter mean concentration of 16.1±2.8 in Los Angeles, Daher et al., 2013; between 7.2 and 11.5 µg/m³ in outdoor air and between 6.0 and 10.3 µg/m³ in indoor air in retirement homes in Los Angeles, Arhami et al., 2010; and 14 µg/m³ in outdoor urban background air in Beirut, Daher et al., 2013b). The standard deviation obtained is also considerably high. The mean concentration values are even higher than the European target set for the year 2020 (18 µg/m³ for PM_{2.5}). It could be argued, given these unexpectedly high

concentrations, that the particle mass was overestimated during weighing of the filters, which would seem supported by the relatively large percentage of undetermined mass in the quasi-UFP fraction (Figure 1). However, the sum of the quasi-UFP and accumulation mode mass ($PM_{0.25} + PM_{0.25-2.5}$, which should be equivalent to $PM_{2.5}$) was compared with the mean $PM_{2.5}$ concentrations obtained with EU reference high-volume samplers (operating concurrently for a simultaneous study within BREATHE), and comparable results were obtained (indoor $PM_{0.25} + PM_{0.25-2.5} = 39.9 \mu\text{g}/\text{m}^3$ vs. indoor $PM_{2.5} = 49.3 \mu\text{g}/\text{m}^3$; outdoor $PM_{0.25} + PM_{0.25-2.5} = 41.1 \mu\text{g}/\text{m}^3$ vs. outdoor $PM_{2.5} = 38.9 \mu\text{g}/\text{m}^3$). Therefore, the quasi-UFP mass concentrations obtained seem quite reliable estimations. It is important however to note that the high concentrations registered are not representative of urban background concentrations in the city, given that the schools are not located in urban background areas (at least 50% of them are located at traffic locations). In fact, results from this study are close to those reported by Daher et al., 2013b, for a traffic area in Beirut, $36.1 \mu\text{g}/\text{m}^3$. This result would suggest that actual population exposure in the city of Barcelona is higher than what is represented by urban background concentrations, given that the population lives and works close to traffic ways and not at urban background locations. Moreover, Rivas et al. (2013) demonstrate that these high $PM_{2.5}$ concentrations in schools are partly due to local emission sources within the schools, such as textiles and organic matter (emitted from human activity) and mineral dust (from playgrounds), given that the $PM_{2.5}$ concentrations measured in the schools are even higher than at traffic and kerbside monitoring stations across Barcelona.

Figure 1 depicts the mean mass closure for quasi-UFP in the 39 schools under study. It is evident that, on average, organic matter is the major contributor to quasi-UFP mass, representing 43% of the mass ($7.3 \mu\text{g}/\text{m}^3$) in indoor air and 26% ($6.7 \mu\text{g}/\text{m}^3$) outdoors. Levels of organic matter are higher indoors probably because of the contribution from skin flakes and organic fibres, among others, from the children (Rivas et al., 2013). When compared with recent studies carried out in outdoor air in the Los Angeles basin (Hughes et al., 1998; Daher et al., 2013), outdoor organic matter levels were also the major contributor with >50% of quasi-UFP mass in ambient air, and similar in terms of mass ($5.2-6.3 \mu\text{g}/\text{cm}^3$ in Los Angeles vs. $6.7 \mu\text{g}/\text{cm}^3$ in Barcelona) even though in relative terms the contribution of OM in Barcelona was lower (26%). Despite its usually large grain size distribution, mineral matter is the second major

constituent in quasi-UFP in Barcelona schools, accounting for 9% ($1.6 \mu\text{g}/\text{m}^3$) of the mass indoors and 9% (2.1) outdoors. It should be taken into account that anthropogenic sources such as combustion, lubricant oils or industry may also contribute to these element in this size fraction (Lin et al., 2005; Miller et al., 2007; Cernushi et al., 2012).

These results are comparable to the Los Angeles data in relative terms (9% in Los Angeles) but much higher in terms of actual mass ($0.7\text{-}0.6 \mu\text{g}/\text{cm}^2$ in Los Angeles vs. $2.1 \mu\text{g}/\text{cm}^3$ in Barcelona). Levels of mineral matter in $\text{PM}_{2.5}$ and PM_1 in outdoor traffic stations in Barcelona are also lower than the values recorded in the schools (Rivas et al., 2013), reinforcing the conclusion that the high mineral matter contents originate from playground dust. Aside from playground dust re-suspension and entrainment towards the classrooms by children, one additional source of mineral matter is suggested in indoor air by the slightly higher ratio $\text{Ca}/\text{Al}_2\text{O}_3$ (0.76) obtained in comparison to outdoors (0.65), even if the difference may not be statistically significant. This might suggest the presence of an additional source of Ca in indoor air, which could be related to the use of chalk on blackboards (still rather frequent in Spanish schools). A similar situation is observed for sulphate ($\text{SO}_4^{2-}/\text{NO}_3^- = 3.35$ indoors vs. 1.25 outdoors), which would support this interpretation given the chemical composition of chalk (Ca sulphate or Ca carbonate), although in the case of nitrate other types of processes such as particle evaporation may be affecting the concentrations and ratios of this species (Lunden et al., 2003a; Smolík et al., 2004; Hering et al., 2007). The contribution from EC, SIA and marine aerosol is relatively small both in indoor and ambient air (between 3-6% of the quasi-UFP mass, around $1\text{-}1.5 \mu\text{g}/\text{m}^3$ each). As expected, EC contributions are highest in the quasi-UFP fraction, as opposed to the accumulation and coarse particle mass. EC concentrations are higher than the results published for Los Angeles in terms of mass ($0.8 \mu\text{g}/\text{m}^3$ in Barcelona vs. $0.4\text{-}0.5 \mu\text{g}/\text{m}^3$ in LA; in both cases lower than those reported for Beirut by Daher et al., 2013b, $1.2 \mu\text{g}/\text{m}^3$) but not as percentage (3% in Barcelona vs. 5% in LA). The sum of secondary inorganic ions in Barcelona is similar to the LA data in absolute terms ($0.7\text{-}1.4 \mu\text{g}/\text{m}^3$ vs. $1.3\text{-}1.5 \mu\text{g}/\text{m}^3$, respectively) but lower in relative terms (4% vs. 14%). ~~Once again, this is a reflection of the higher total quasi-UFP mass in Barcelona.~~ The undetermined fraction averages 53% in ambient air and 32% in indoor air. These undetermined fractions likely include water uptake by the filter substrates, heteroatoms linked to carbonaceous aerosols (mainly in OC), and could be at least in part related to the fact that mineral components such as carbonates or silica are not estimated, as described above. This implies that the estimation of the mineral

matter content presented above (possibly including anthropogenic sources) could be conservative, i.e., that the reported high mineral matter could be even higher in quasi-UFPs in Barcelona. It should be remembered that Ca, Fe, Al or Si in quasi-UFPs may also source from combustion processes (Lin et al., 2005). The factor used to convert OC to OM (1.8, Turpin and Lim, 2001) could introduce an additional source of uncertainty, as OM is the major contributor to indoor and outdoor particle mass in all size fractions. The higher outdoor undetermined mass is probably linked to the higher outdoor relative humidity and the consequently higher water uptake by the outdoor filters. It is interesting to observe that the undetermined fraction is always highest for the quasi-UFP when compared with the coarse and accumulation samples. This may be attributed to the fact that coarse and accumulation particles are collected by impaction, which virtually precludes the possibility of gas phase adsorption (including water vapours) on the substrate, as opposed to quasi-UFPs (collected by filtration and thus favouring adsorption of gaseous species) (Chang et al., 2000 and references therein)

When analyzing the mass closure and chemical composition for accumulation and coarse particles, the percent fractions of major constituents are quite similar to those in quasi-UFPs. Organic matter is still the dominant constituent of accumulation and coarse particles, accounting for 45-77% of the mass, followed by SIA in the accumulation fraction (10% of the mass outdoors) and mineral matter in the coarse fraction (11-16% of the mass). The highest contributions of SIA in outdoor accumulation mode particles and of mineral matter in coarse particles follow our expectations. The relatively low SIA contributions in the accumulation mode in indoor air ($0.6 \mu\text{g}/\text{m}^3$, 4%) may seem unexpected given that these species are mostly present in this size fraction (Seinfeld and Pandis, 1998), and that infiltration is most efficient for particles in the accumulation mode (Long et al., 2001). However, particle evaporation (especially regarding ammonium nitrate) is frequent during infiltration processes (Hering et al., 2007), which may result in a lower indoor SIA mass concentration as suggested by the reduction in accumulation mode nitrate concentration from outdoor to indoor air by a factor of 4.1 (compared to a factor of 2.1 in the case of sulphate). The increasing SIA concentration with decreasing particle size range (from coarse to accumulation mode) was also observed in prior studies (Hassanvand et al., 2013). In addition, SIA contributions are low in relative terms as a consequence of the high mass concentrations resulting from the high mineral and organic matter contributions. As

anticipated, EC contributions decrease with increasing particle size (2% to 1% in indoor and outdoor air, for accumulation and coarse particles, respectively, vs. 3% in quasi-UFP). Finally, the marine aerosol contribution remains rather constant (4-6%) across size fractions, however with different sources: whereas coarse outdoor Na and Cl⁻ containing particles originate from sea spray with a Na/Cl ratio close to that of seawater (0.43 vs. 0.55; Mészáros, 1999), the ratio for indoor accumulation and quasi-UFP particles is lower (<0.2) and Cl⁻ concentrations are higher than those of Na, suggesting the influence of an indoor source of fine Cl⁻ particles such as cleaning products.

The relationship between indoor and outdoor concentrations for the major components in each of the size fractions under study is assessed in Figure 2. Results show that, on average for all schools, the quasi-UFP mass is higher in outdoor air, as a result of the influence of traffic emissions in the ultrafine particle range, whereas the indoor particle mass increases with increasing particle size, possibly due to the presence of indoor sources mostly of organic and mineral matter and to the losses by diffusion of UFPs in indoor air. The same trend is observed for mineral matter. Secondary inorganic aerosol concentrations are higher outdoors across all size fractions, because their sources are mostly of outdoor origin, and due to evaporation losses during nitrate infiltration—~~(mostly concerning nitrate)~~. Conversely, despite the major outdoor contribution to organic matter from vehicular and biological sources, indoor OM concentrations are always higher or equal to outdoor levels, and this is attributable to the major influence of indoor sources. Finally, EC and marine aerosol concentrations originate from outdoor major sources (vehicular traffic and the sea breeze), and their indoor concentrations reflect the degree of infiltration from outdoors. However, while sea spray particle levels remain rather constant across size fractions and between indoor and outdoor air, EC concentrations are higher outdoors in quasi-UFPs because in this size range (dominant in terms of mass for EC) infiltration processes are affected by depositional and/or diffusion losses (Chao et al., 2003). In addition, the behaviour of traffic-derived metals (Sn, Sb and Cu, used as traffic tracers by Rivas et al., 2013) was also assessed, showing how the influence of these traffic tracers in indoor air increases from the coarse to the quasi-ultrafine fraction, where their contribution (summed up) is mostly equal in indoor and outdoor air.

3.2. Trace metals in quasi-UF particles

As described above, ultrafine particles have the potential to translocate to other organs outside the respiratory tract (Strak et al., 2012). For this reason, it is essential to characterise the particle size distribution of toxicologically relevant species such as Cu, Cr, Mn, Zn, As, V, Ni, Cd and Sb (Becker et al., 2005; Loxham et al., 2013). ~~The~~ ~~mean size distribution~~ ~~patterns~~ among the 3 size fractions ~~studied-available~~ of major and trace elements in indoor and outdoor air are shown in Figures 3a and 3b (and Table S1 in Supporting Information). Our results demonstrate three markedly different size distribution ~~patterns~~ for major components, and two distinct size distributions for trace elements, which were common for indoor and outdoor air.

In the case of major PM components (Figure 3a and Table S1), most of them showed ~~two modes a bimodal mass distribution~~, with prevalence in the coarse size range, followed by the quasi-UFP range, for indoor and outdoor air. Examples of these are components of mineral, ~~and~~ marine ~~and organic~~ origin such as K, Ca, Fe, Mg, Na, Al₂O₃, ~~and~~ Cl⁻, ~~and also~~ OM and the total PM mass. ~~Cl⁻ may originate from marine but also anthropogenic sources, as described above.~~ The second most frequent size ~~distribution pattern~~ was observed for EC in indoor and outdoor air, showing ~~a unimodal distribution one mode~~ with a clear prevalence for quasi-UFPs (56% of the mass indoors, 68% outdoors) and with decreasing mass in the accumulation and coarse modes. The same distribution was observed for sulphate and ammonium in indoor air, although not in outdoor air where the accumulation mode prevails for these species (>40% in mass). The reduction in accumulation mode sulphate and ammonium particles from outdoor to indoor air (>50% reduction) could be related to infiltration losses linked to particle size, which would affect ammonium sulphate particles. However, this effect was not observed for nitrate particles, which maintain a unimodal ~~size distribution pattern~~ (prevailing in the accumulation mode) in indoor and outdoor air.

The opposite trend is observed for mineral components Al₂O₃ and K: whereas in indoor air their size distribution ~~pattern~~ is ~~characterised by one mode (unimodal and mainly in coarse mode (61% and 54% in mass, respectively),~~ in outdoor air they show ~~two modes a bimodal distribution~~ with similar % of mass in the quasi-UFP and coarse modes (47% of the K mass in coarse particles and 47% in quasi-UFP; 48% in each in the case of Al₂O₃). This could be explained by the contribution of outdoor sources to these components in the quasi-UFP mode, including for example traffic emissions,

given that these elements are also ingredients of lubricant oil additives ([Miller et al., 2007](#); Saffari et al., 2013) Also, previous studies (Sanders et al., 2003) have demonstrated that brake wear particles can be found in UFPs, produced to a lesser extent by abrasion processes, but mainly from vaporisation of metals due to the high temperatures reached during the braking process. Further investigations would be necessary to evaluate whether these processes might also affect mineral components such as Al_2O_3 or K. A potential contribution to K concentrations by biomass burning emissions was discarded, based on the good correlation between Al_2O_3 and K (r^2 of 0.83, 0.89 and 0.69 in coarse, accumulation and UFPs, respectively), which indicates a common origin for these components, especially in the coarser size fractions. Finally, nitrate (indoors and outdoors), sulphate and ammonium (only outdoors) prevailed as expected ~~show a characteristic unimodal mass size distribution with prevalence~~ in the accumulation mode (>40% in mass for both species). Total nitrate concentrations were much lower indoors than outdoors ($0.4 \mu\text{g}/\text{m}^3$ indoors vs. $1.6 \mu\text{g}/\text{m}^3$ outdoors), a likely result of volatilisation during infiltration of this species as it infiltrates indoors (NH_4NO_3 dissociates to $\text{NH}_3 + \text{HNO}_3$) (Lunden et al., 2003b; Hering et al., 2007). When assessing the nitrate data as a function of season, it was observed that outdoor concentrations were much lower during summer, as expected due to its thermal instability, with a modal shift towards coarse particles (75% of outdoor nitrate was present in the coarse mode, $0.6 \mu\text{g}/\text{m}^3$). This may reflect the effects of summer outdoor volatilisation of NH_4NO_3 as well as the formation of coarser nitrate species, such as NaNO_3 or $\text{Ca}(\text{NO}_3)_2$ by interaction of HNO_3 (gas) with NaCl or CaCO_3 . Similar observations have been reported in other studies in the US (Miguel et al., 2004; Cheung et al., 2011)

Similar size distributions patterns are observed for trace metals, with a limited number of elements showing a marked prevalence in the quasi-UFP range (Ni, Cr and Ba) and the majority being distributed between quasi-UFPs and the coarse modes. Ni and Cr are mostly partitioned in the quasi-ultrafine size range both in indoor and outdoor air, whereas Ba followed this pattern only in outdoor air (probably linked to lubricant oil additives or brake pad emissions). It is unclear why this was not reflected indoors. On the other hand, in indoor air, most of the mass of Cd, Ce, La, Sn, Cu, Zn and Pb is found in quasi-UFPs, whereas most of P, Mn, V, Sr, Rb and Ti are found in the coarse mode (as expected, due to their mineral origin). Similar results were obtained for

outdoor air, with the exception of Cu (mostly coarse in outdoor air) and V (mostly fine indoors).

3.3. Differential exposure to trace metals at traffic and urban background locations

The spatial distribution of metal contents in quasi-UFPs, accumulation and coarse particles across Barcelona was assessed by a graphical mapping approach, but the large variability of location-specific indoor and outdoor sources complicated the identification of distinct spatial patterns. Consequently, a different approach was taken, based on the assessment of the differential exposure to metals at traffic-oriented and urban background (UB) locations. ~~As described in the methodology section, schools were paired as a function of their direct environment (UB or traffic-oriented), and sampling was carried out simultaneously at each pair of schools.~~ Figure 4 summarises the specific Traf/UB ratios for major and trace elements in indoor and outdoor air, ~~for the 3-PM size fractions assessed.~~ Results are only described in detail for quasi-UFPs, for the sake of brevity but also because that size fraction is the focal point of the work discussed in this paper.

This analysis demonstrates different patterns for indoor and outdoor air. The outdoor total quasi-UFP mass is higher at traffic than at UB schools (ratio Traf/UB=1.2), whereas the reverse is true indoors (Traf/UB=0.9). This difference is directly linked to the chemical composition of these quasi-UF particles. As expected, for outdoor air, exposure to typical tracers of vehicular emissions (OM, EC, nitrate) is always higher at traffic schools with regard to UB schools. Conversely, for indoor air, exposure to mineral components (Al_2O_3 , Ca, Fe, K, Mg) is much higher at UB schools (ratios Traf/UB ranging between 0.4 and 0.8), where concentrations of these components are clearly higher than at traffic schools. This was also observed for the coarser size fractions (Figure 4). This enrichment in mineral matter was not observed for outdoor air, where mineral components showed similar and only slightly higher concentrations at traffic schools due to the direct influence of outdoor sources such as road dust and/or city dust (i.e., construction, demolition etc.). The reason behind the higher mineral matter concentrations indoors is likely related to the playgrounds: schools located in the UB tend to have a higher presence of sand playgrounds than traffic schools (58% of schools with sand playgrounds in UB schools vs. only 30% in

traffic schools, where asphalt playgrounds predominate), and thus entrainment of dust by the children (on shoes, clothes etc.) from the playgrounds into the classrooms is higher in UB schools. This interpretation is confirmed by the contribution from mineral dust in quasi-UFPs as a function of the type of playground, on average for all types of schools (traffic + UB) (similar results obtained for accumulation and coarse particles): whereas in indoor air in schools with paved playgrounds mineral matter accounts for 8% ($1.4 \mu\text{g}/\text{m}^3$) of the quasi-UFP mass, its contribution increases to 12% ($1.8 \mu\text{g}/\text{m}^3$) at schools with sand playgrounds. Therefore, mineral dust sources (mainly, entrainment of dust from playgrounds) could play a major role on children exposure in indoor air with regard to all fractions of PM_{10} . The same is true for organic matter originating from human activity ~~(skin cells, textile fibres, etc.) as described above~~, although exposure to this organic component is not dependent on school location.

Exposure to metals and trace elements also shows a distinctly different pattern as a function of the schools' environments. Mineral elements show the same trend described for major elements: exposure to Ti, Rb or Sr is higher by a factor >2 (Traf/UB ratios ranging between 0.3 and 0.5) in indoor UB environments, whereas concentrations are similar (ratios close to 1) in outdoor air. Regarding tracers of vehicular emissions, exposure to metals such as Cu is higher at traffic schools by a factor of 1.3 in both indoor and outdoor air. However, other tracers of vehicular emissions (Sb, Ba, Pb, Cd, Zn), are only slightly enriched at traffic schools in outdoor air (by factors of 1.1-3), and not indoors (ratios Traf/UB close to 1.00). Finally, it is interesting to note that one of the largest differences between traffic and UB schools regarding quasi-UFP composition was obtained for Ni, to which exposure is always higher at traffic schools, by a factor of 2.0 in outdoor air and 1.7 indoors, respectively. A similar enrichment was found for V (also originating from fuel-oil combustion, and shipping emissions), but only for outdoor air. A priori, exposure to fuel-oil combustion tracers (V, Ni) was expected to have been independent of the degree of traffic influence at schools, and thus this enrichment at traffic schools is considered probably coincidental.

In summary, results from this study demonstrate that exposure to traffic-derived metals in quasi-UFPs is higher at traffic schools in outdoor air due to the direct influence of traffic emissions. This result alone supports the enforcement in Spanish cities of legislation to determine a minimum distance between major roads and newly built schools, similar to policies already in place in other parts of the world (e.g.,

California, with a minimum distance of 200m). The impact of traffic-derived ultrafine metals on children exposure in indoor air is only detectable for Cu, whereas other metals show similar concentrations at traffic and UB schools. Exposure to mineral matter is consistently higher at UB schools in indoor air, due to entrainment of playground dust into the classrooms, as discussed earlier. Exposure to organic matter is higher in indoor air in traffic and UB schools. Thus, mineral and organic matter in indoor air may be considered two components of concern when assessing children exposure to airborne pollutants in school environments, which originate from school sources and not from traffic.

3.4. Indoor/outdoor ratios and emission sources

Indoor/outdoor (I/O) ratios were calculated on a daily basis for all PM components analysed in the quasi-UF, accumulation and coarse fractions, and then averaged for the entire sampling period (Figure 5 and Table S2). Our results indicate that indoor sources impact more strongly coarser particles than quasi-UFPs, given the larger number of elements and PM components with I/O ratios >1 for coarse particles (17) than for accumulation (10) and quasi-UF (5) particles. This reflects the effect of major indoor sources ~~(, including mineral matter, chalk, from blackboards and indoor dust re-suspension (of playground dust), as well as organic matter) from textiles and children,~~ all of which ~~are generate~~ mostly coarse ~~particles~~. Conversely, major sources of outdoor particles in schoolyards are mineral matter from sandy playgrounds, vehicular exhaust and secondary sulphate and nitrate (mainly from industry, traffic, shipping and long-range transport), usually (excluding the first) with a typically fine and UF grain size distribution.

I/O ratios >1 signify the influence of indoor sources and/or the occurrence of particle evaporation processes in outdoor air, for a given species. In quasi-UFPs, I/O ratios are >1 for OM as well as for Cl⁻ and metals (Cu, Zn, Co) originating from other unspecified indoor sources. It is interesting to observe that certain of these metals (Cu, Zn) are typical tracers of outdoor vehicular emissions, and Cl⁻ is generally considered a tracer of sea spray, whereas the I/O ratios >1 obtained suggest that in addition to infiltration from outdoor air, these elements have specific indoor sources. Known sources of indoor chloride are cleaning agents, plastics (e.g., polyvinyl chloride, PVC) and paints (Zhang and Smith, 2005; WHO, 2010). As for metals, wall paints could be

one of the main sources in indoor dust as a function of the colour; for instance, yellow paint is associated with high levels of Cd, Cu, Pb, and Zn, whereas purple colour is related to Zn and Pb, and green is related to Cu (Chattopadhyay et al., 2003). Other authors have also identified metallic sources (e.g., Cu and Zn) in indoor environments (Koistinen et al., 2004).

I/O ratios <1 indicate the prevalence of outdoor sources, or the occurrence of particle losses or evaporation processes indoors, a pattern shown in quasi-UFPs by the main tracers of outdoor sources such as vehicular exhaust (EC), road dust (Sb, Ba, Ca, Al_2O_3 , Ti, K), shipping emissions (SO_4^{2-} , V, Ni) and secondary inorganic aerosols (SO_4^{2-} , NO_3^- , NH_4^+). Quasi-UFPs are expected to penetrate indoors more efficiently because the effective penetration efficiency is known to be greatest for particles in the 100 to 200 nm range, where particle losses from diffusion and impaction are minimal (Abt et al., 2000). For 0.7-10 μm particles (i.e., the larger fraction of the accumulation mode and the coarse mode), ~~the~~ penetration decreases with increasing particle size, partly because of increased deposition rates associated with increasing particle size.

In the accumulation mode, the elements and species with I/O ratios >1 are Ca, OM, Cl, Na, Co, P, Sr, K, Cd and Ga, reflecting the impact of indoor sources of mineral matter (Ca, P, Sr, Na, K, Ga) ~~originating from re-suspension of settled mineral dust by the teachers and students~~. Other indoor sources are human activity (OM), cleaning agents, plastics, paints etc. (Cl) and metals (Co, Cd), as observed in the quasi-UFP range.

Finally, the analysis of coarse mode particles showed a larger frequency of I/O ratios >1 for OM, Ca, Ti, EC, Mg, Al_2O_3 , Sr, Pb, K, SO_4^{2-} , Ga, As, Cl, V, Cr and Zn. These species again reflect the influence of a mineral dust source (Ca, Ti, Mg, Al_2O_3 , K, Sr, Ga) ~~from the playgrounds~~, which is clearly present across all size fractions. The source of organic material (OM) is also present across all size fractions, ~~originating from human activity~~. In the case of EC, the I/O ratio >1 obtained is driven by 5 of the 12 schools with data available for this component, where indoor EC concentrations exceed those from outdoors by factors of 1.4-3.9. For the majority of the schools, it may be concluded that coarse (and fine) EC infiltrates from outdoors, as suggested by the good correlation obtained in a different study between indoor and outdoor BC (Rivas et al., 2013). However, the results from these specific 5 schools could indicate the presence of an additional indoor source of coarse EC, which could be related to printing and/or

photocopying activities, and/or the use of printed materials by the students and teachers. The coarser size of these EC particles underscores a distinctly different source from outdoor EC ~~particles (mainly originating from vehicular exhaust, having a fine and ultrafine particle size distribution).~~

Another interesting feature of the I/O ratios for coarse particles can be seen for sulphate: while sulphate particles in outdoor air prevail in the accumulation mode (Seinfeld and Pandis, 1998) and thus I/O ratios are <1 , coarse sulphate concentrations in indoor air are slightly higher than outdoors (I/O ratios >1), given that coarse sulphate particles source mainly from the chalk used on blackboards in the classrooms, together with Ca. Finally, the cleaning agents/plastic/paint source (traced by Cl) and the metallic source influencing quasi-UFPs and the accumulation mode also impact coarse particles (in coarse particles for Zn but also Pb, As, V and Cr).

4 Summary and conclusions

The mass closure and sources of quasi-UFPs ($PM_{0.25}$), accumulation ($PM_{0.25-2.5}$) and coarse ($PM_{2.5-10}$) particles were determined in 39 schools in Barcelona (Spain). The main findings from this work may be summarised as follows:

- Mean quasi-UFP mass concentrations are higher than in other regions of the world ($25.6 \mu\text{g}/\text{m}^3$ outdoors, $23.4 \mu\text{g}/\text{m}^3$ indoors), with organic aerosols and mineral matter as main contributors (OM = 43% and 26% of the mass indoors and outdoors, respectively; mineral matter = 9% in indoor and outdoor air).
- Human activity (skin flakes, textiles, etc.) and playground dust are the main sources of indoor OM and mineral dust. The strong impact of mineral matter in quasi-UFPs is especially notable (9% in terms of mass).
- Bimodal size distributions (coarse and quasi-UFP) are observed for major elements, while unimodal distributions are detected for EC (quasi-UFP) and ammonium salts (accumulation mode). Different size distributions are observed for indoor and outdoor air for certain species (e.g., Al_2O_3 and K partition towards quasi-UFPs in outdoor air, possibly coming from lubricant oil additives). Toxic species such as Ni and Cr show a marked prevalence for quasi-UFPs. This might be of particular relevance for epidemiological studies.

- Our results support the need to enforce targeted legislation to determine a minimum “safe” distance between major roads and newly built schools, given the higher exposure to traffic-derived metals in quasi-UFPs at traffic schools with regard to urban background areas.
- Despite the classification as traffic or urban background schools, we conclude that even background schools are strongly affected by traffic emissions.
- Exposure to mineral matter in indoor air is consistently higher at urban background schools, and this is linked to the entrainment of playground dust by the children into the classrooms.
- Certain particle emission sources are common across all size fractions (e.g., human activity; cleaning products, paints and plastics), while others are size-specific: playground dust (accumulation and coarse modes), blackboards and chalks (coarse sulphate indoors), and printing and/or photocopying (coarse EC indoors, in a limited number of schools).

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1 Table 1a. Mean concentration and standard deviation (Stdev.) for major elements (in $\mu\text{g}/\text{m}^3$) in quasi-UF, accumulation and coarse mode
 2 particles in 39 schools in Barcelona. Mass (grav.): gravimetrically determined mass. Undet.: undetermined fraction. OM: organic mass. EC:
 3 elemental carbon. TC: total carbon. SIA: secondary inorganic aerosols.

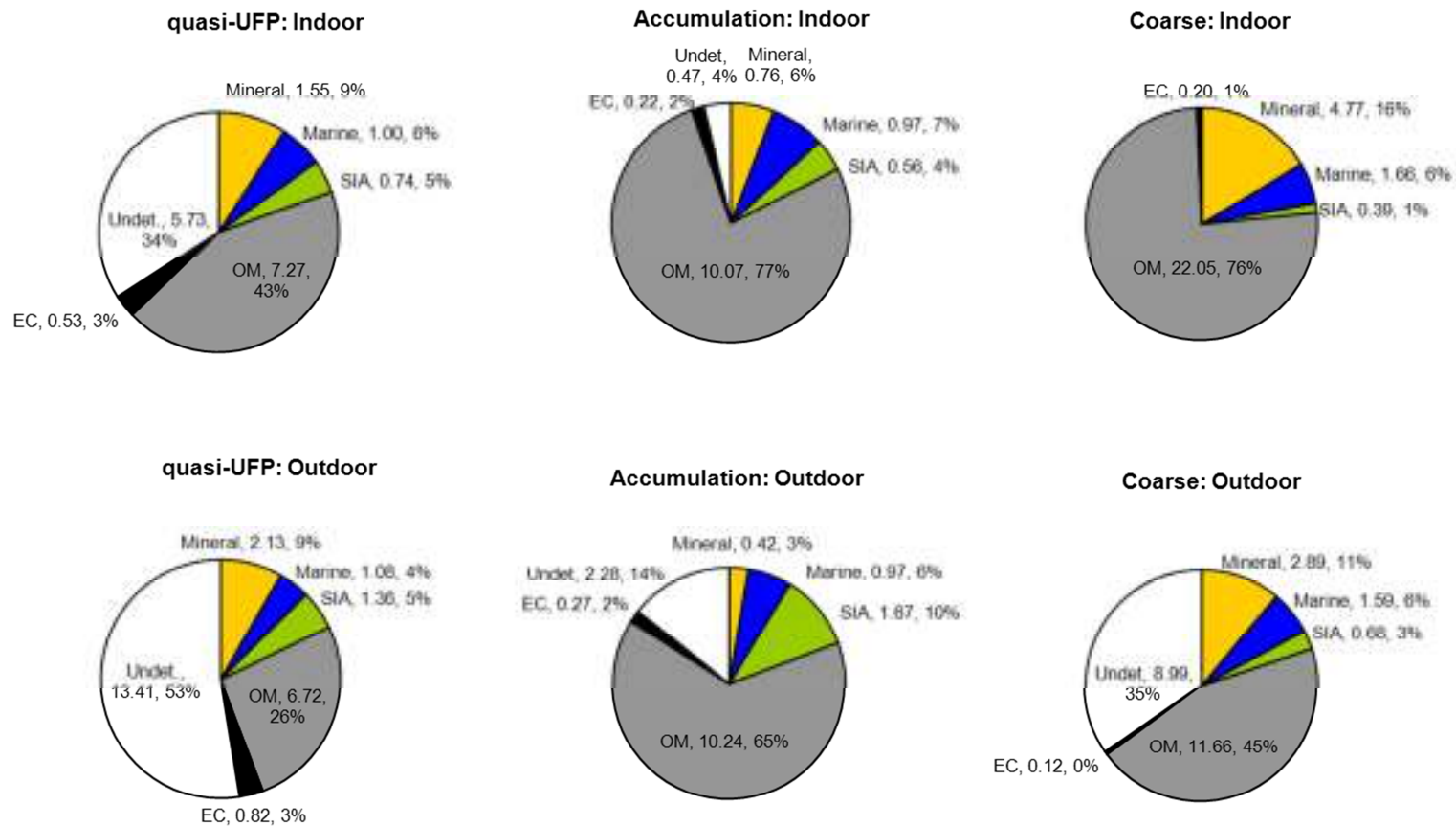
4

$\mu\text{g}/\text{m}^3$	Indoor						Outdoor					
	Quasi-UF (PM _{0.25})		Accumulation (PM _{0.25-2.5})		Coarse (PM _{2.5-10})		Quasi-UF (PM _{0.25})		Accumulation (PM _{0.25-2.5})		Coarse (PM _{2.5-10})	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Mass (grav.)	16.8	7.3	13.1	4.7	24.3	13.7	25.5	10.0	15.8	6.8	26.0	12.2
OM	7.3	3.0	10.1	4.2	22.1	12.2	6.7	3.7	10.2	5.6	11.7	5.5
EC	0.5	0.4	0.2	0.2	0.2	0.2	0.8	0.8	0.3	0.2	0.1	0.2
Al ₂ O ₃	0.7	0.9	0.1	0.3	1.3	2.2	0.9	1.0	0.1	0.3	0.9	1.5
Ca	0.5	0.6	0.5	0.5	2.6	2.2	0.6	0.6	0.2	0.3	1.1	0.8
Fe	0.1	0.2	0.1	0.1	0.6	0.7	0.3	0.4	0.1	0.1	0.6	0.5
K	0.2	0.2	0.0	0.1	0.2	0.4	0.2	0.2	0.0	0.1	0.2	0.3
Mg	0.1	0.1	0.0	0.0	0.2	0.3	0.1	0.1	0.0	0.0	0.1	0.2
Na	0.1	0.2	0.1	0.2	0.4	0.4	0.2	0.3	0.0	0.1	0.5	0.6
SO ₄ ²⁻	0.4	0.4	0.3	0.3	0.2	0.2	0.5	0.4	0.5	0.6	0.2	0.2
NO ₃ ⁻	0.1	0.2	0.2	0.3	0.1	0.3	0.4	0.7	0.7	1.1	0.4	0.5
Cl ⁻	0.9	0.8	0.9	0.9	1.3	1.0	0.9	0.9	0.9	0.7	1.1	0.9
NH ₄ ⁺	0.21	0.23	0.14	0.23	0.06	0.13	0.38	0.42	0.43	0.56	0.08	0.14
EC/TC	0.08	0.04	0.03	0.03	0.01	0.01	0.13	0.15	0.03	0.02	0.01	0.02
Mineral	1.5	1.6	0.8	0.8	4.8	5.4	2.1	2.1	0.4	0.7	2.9	3.0
Marine	1.0	0.8	1.0	0.9	1.7	1.2	1.1	1.0	1.0	0.7	1.6	1.2
SIA	0.7	0.6	0.6	0.6	0.4	0.4	1.4	1.4	1.7	2.1	0.7	0.7
Undet.	5.7	<0.01	0.5	<0.01	<0.01	<0.01	13.4	<0.01	2.3	<0.01	9.0	<0.01

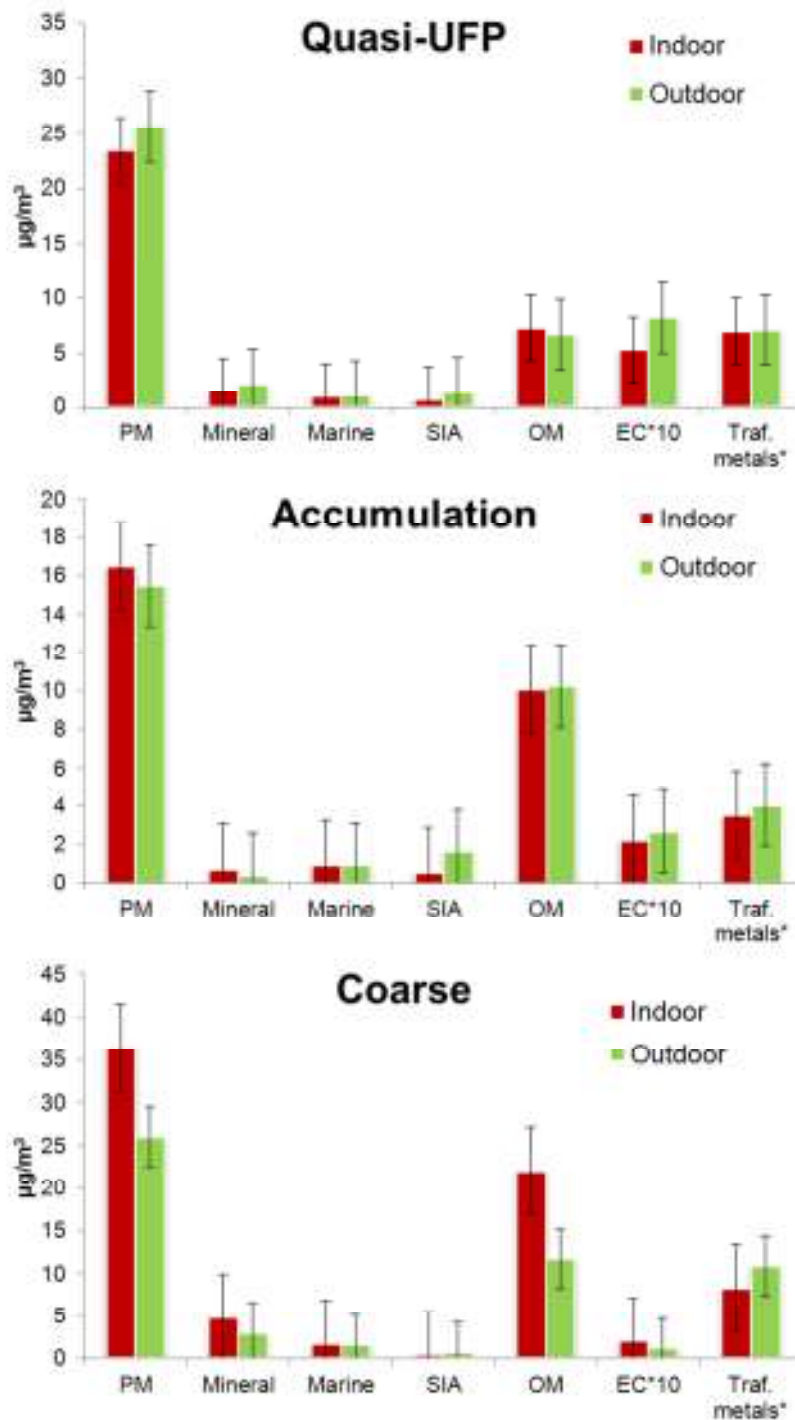
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1 Table 1b. Mean concentration and standard deviation (Stdev.) for trace elements (in ng/m³) including metals in 39 schools in Barcelona.

ng/m ³	Indoor						Outdoor					
	Quasi-UF (PM _{0.25})		Accumulation (PM _{0.25-2.5})		Coarse (PM _{2.5-10})		Quasi-UF (PM _{0.25})		Accumulation (PM _{0.25-2.5})		Coarse (PM _{2.5-10})	
	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev	Mean	Stdev
Li	0.14	0.21	0.14	0.16	0.62	0.95	0.33	0.55	0.12	0.10	0.70	1.14
P	0.02	0.02	0.02	0.02	0.04	0.07	0.02	0.04	0.01	0.02	0.03	0.05
Sc	0.34	<0.01	0.34	<0.01	0.36	0.11	0.36	0.08	0.34	<0.01	0.37	0.09
Ti	15.0	21.9	11.5	15.2	80.3	93.1	32.3	43.4	10.1	12.3	76.5	130.1
V	1.9	1.9	1.5	1.6	2.9	4.0	3.6	2.8	2.3	2.2	2.9	2.7
Cr	2.9	5.4	0.2	0.4	0.7	1.4	2.4	3.6	0.1	0.3	0.6	2.6
Mn	4.0	4.9	1.9	2.6	11.8	17.1	7.8	8.2	2.2	3.0	10.9	12.1
Co	0.2	0.0	0.2	0.1	0.2	0.1	0.2	0.0	0.2	0.0	0.2	0.1
Ni	2.2	3.9	0.1	0.2	0.1	0.4	2.9	6.0	0.1	0.4	0.1	0.4
Cu	6.1	6.8	2.9	2.5	7.3	6.6	5.8	5.3	3.3	3.0	9.4	8.0
Zn	23.3	24.8	18.8	19.3	29.2	27.7	22.2	17.8	18.7	16.4	19.0	19.6
Ga	0.30	0.10	0.28	<0.01	0.41	0.35	0.34	0.18	0.28	<0.01	0.39	0.30
Ge	0.75	1.19	0.04	0.14	0.02	0.08	0.64	0.87	0.04	0.12	0.04	0.15
As	0.19	0.27	0.15	0.26	0.37	0.58	0.39	0.56	0.33	0.42	0.35	0.46
Se	0.24	0.39	0.21	0.44	0.33	0.71	0.41	0.70	0.31	0.45	0.30	0.66
Rb	0.31	0.54	0.28	0.39	1.55	1.93	0.69	0.88	0.32	0.33	1.33	1.28
Sr	1.51	2.07	0.60	1.31	5.84	5.92	1.60	1.83	0.24	0.75	2.30	4.09
Zr	7.79	9.73	0.38	0.82	1.07	2.32	6.63	6.71	0.56	1.44	0.90	1.83
Mo	20.3	44.2	0.06	<0.01	0.18	0.66	19.6	29.0	0.22	0.85	0.09	0.19
Cd	0.40	0.27	0.29	0.25	0.22	0.19	0.43	0.26	0.24	0.19	0.22	0.19
Sn	0.92	0.94	0.57	0.67	0.95	0.84	1.23	1.08	0.77	0.82	1.25	1.07
Sb	0.02	<0.01	0.02	<0.01	0.04	0.10	0.04	0.11	0.03	0.09	0.17	0.31
Ba	12.6	22.7	2.6	6.7	13.1	25.4	9.7	17.3	2.1	9.5	6.7	13.9
La	0.27	0.32	0.03	0.09	0.35	0.61	0.33	0.35	0.03	0.08	0.33	0.51
Ce	0.50	0.64	0.08	0.20	0.65	1.17	0.71	0.69	0.06	0.20	0.61	0.92
Pb	2.12	1.76	1.61	1.84	3.17	3.64	2.63	2.12	2.32	2.48	2.04	1.55

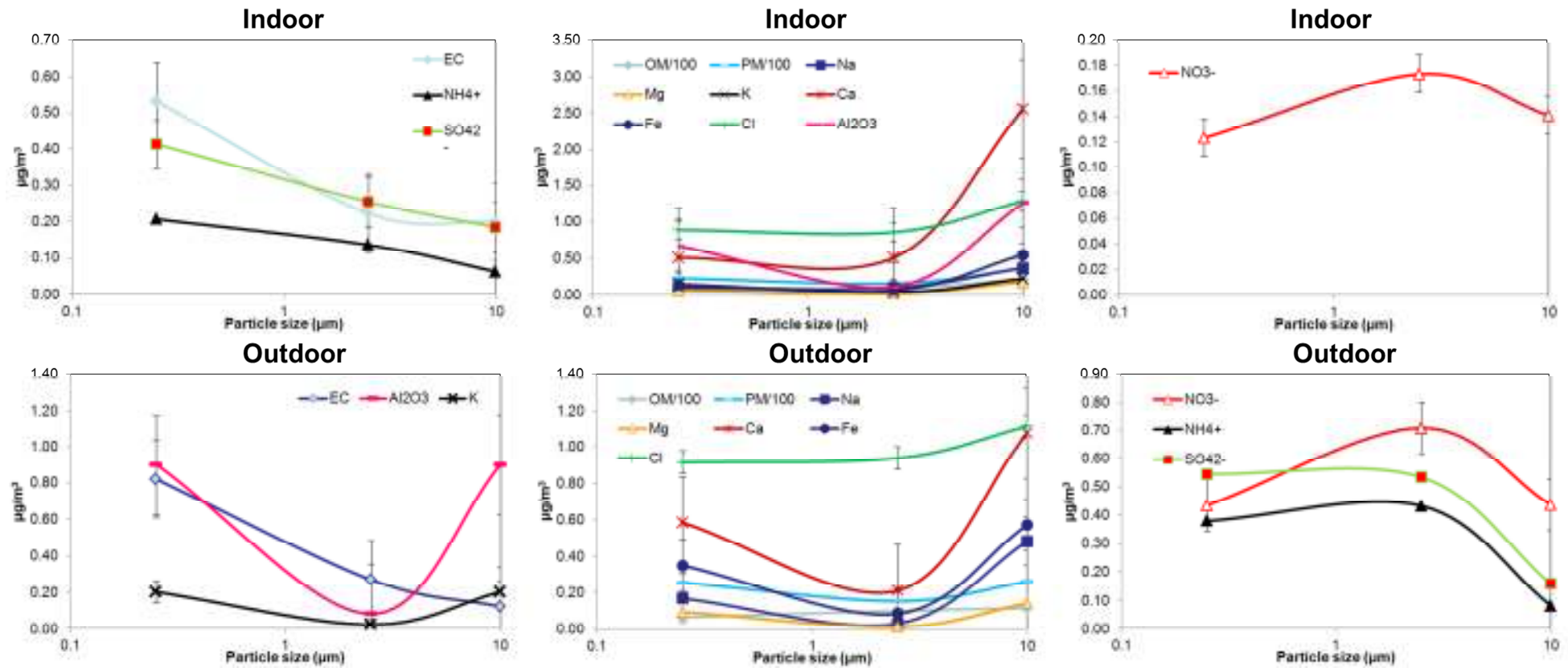


1
 2 Figure 1. Average mass closure of coarse (PM_{2.5-10}), accumulation (PM_{0.25-2.5}) mode and quasi-ultrafine (quasi-UFP, PM_{0.25}) particles in indoor
 3 and outdoor school environments. SIA: secondary inorganic aerosols. OM: organic matter. EC: elemental carbon.



1
 2 Figure 2. Mean indoor and outdoor relationships for PM mass, the main aerosol components
 3 (mineral matter; secondary inorganic aerosols, SIA; marine aerosol; organic matter, OM;
 4 elemental carbon, EC) and traffic-related metals (Sn, Sb, Cu, Rivas et al., 2013) in the coarse,
 5 accumulation and quasi-ultrafine modes. * in ng/m³.

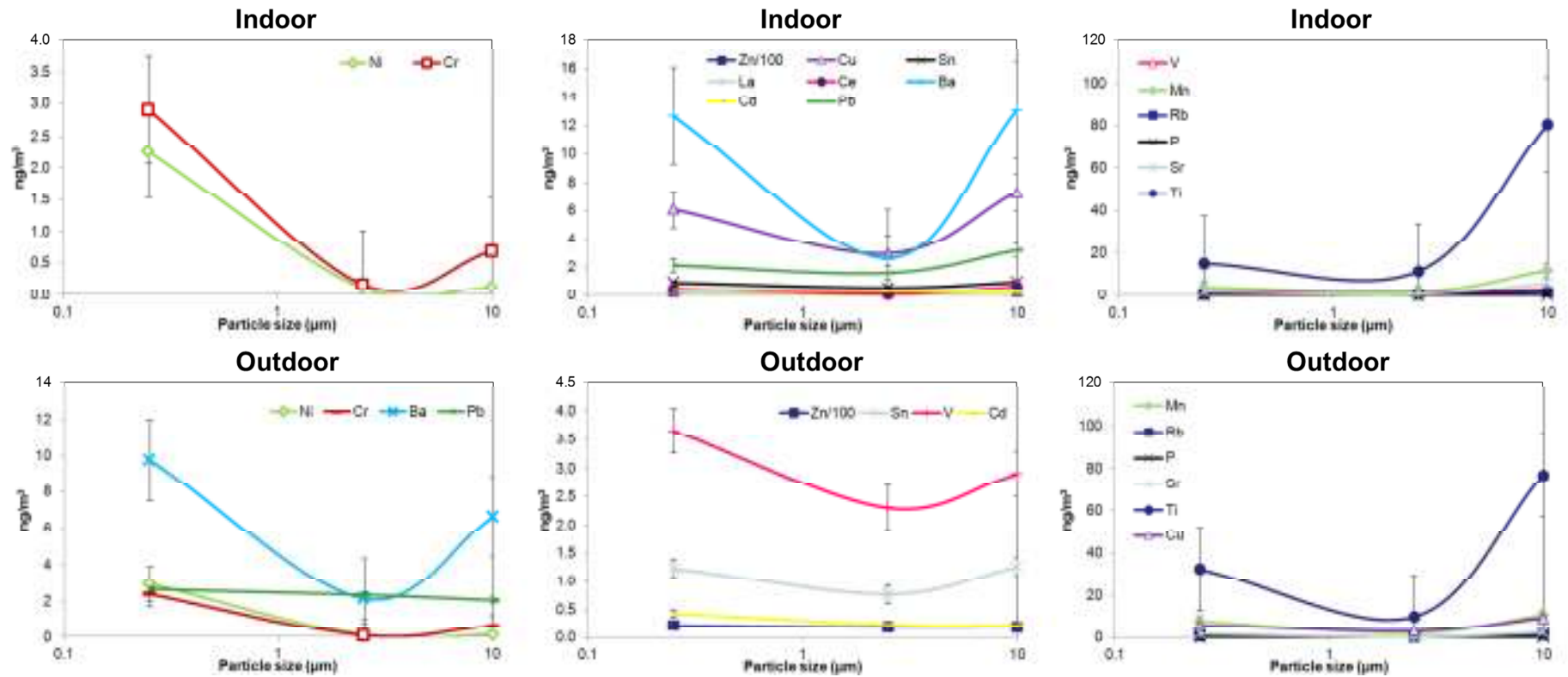
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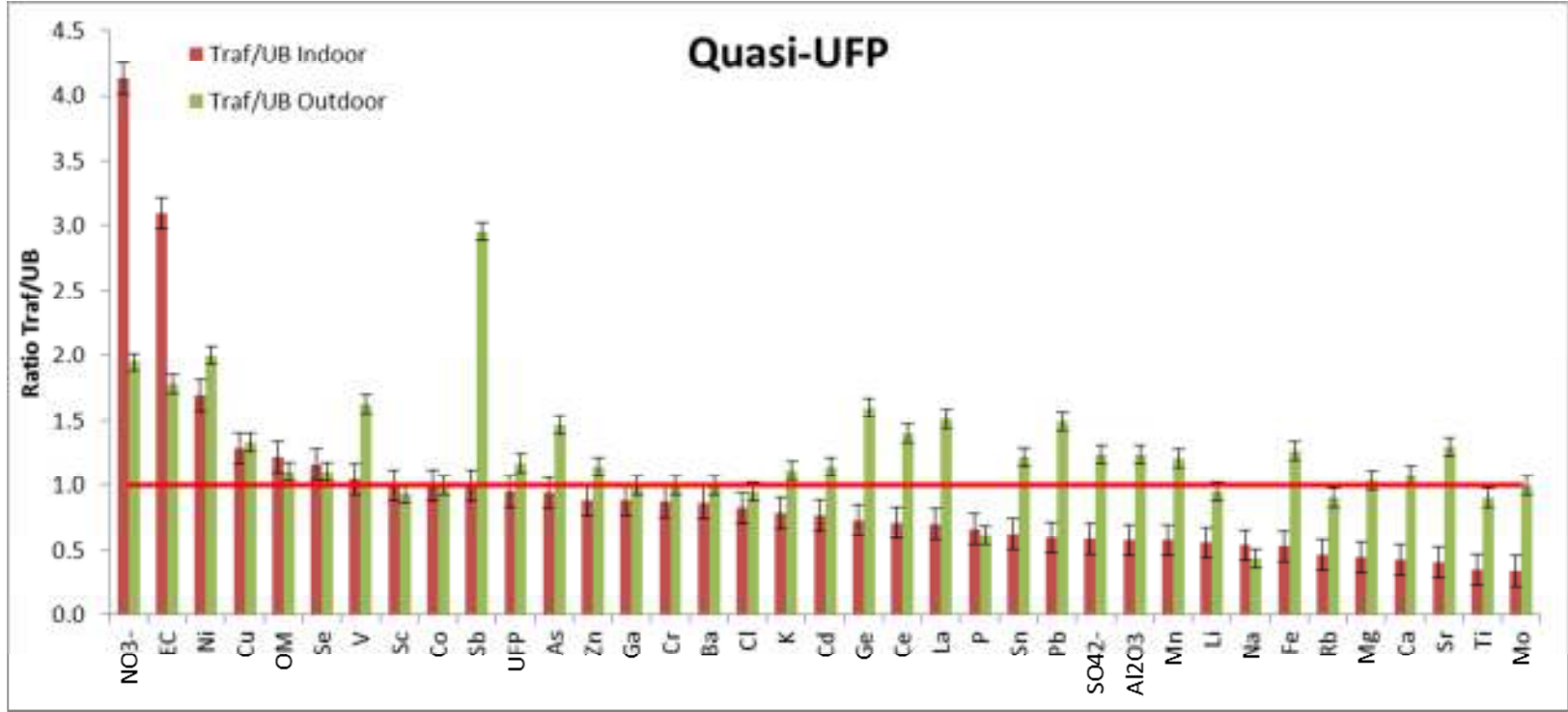
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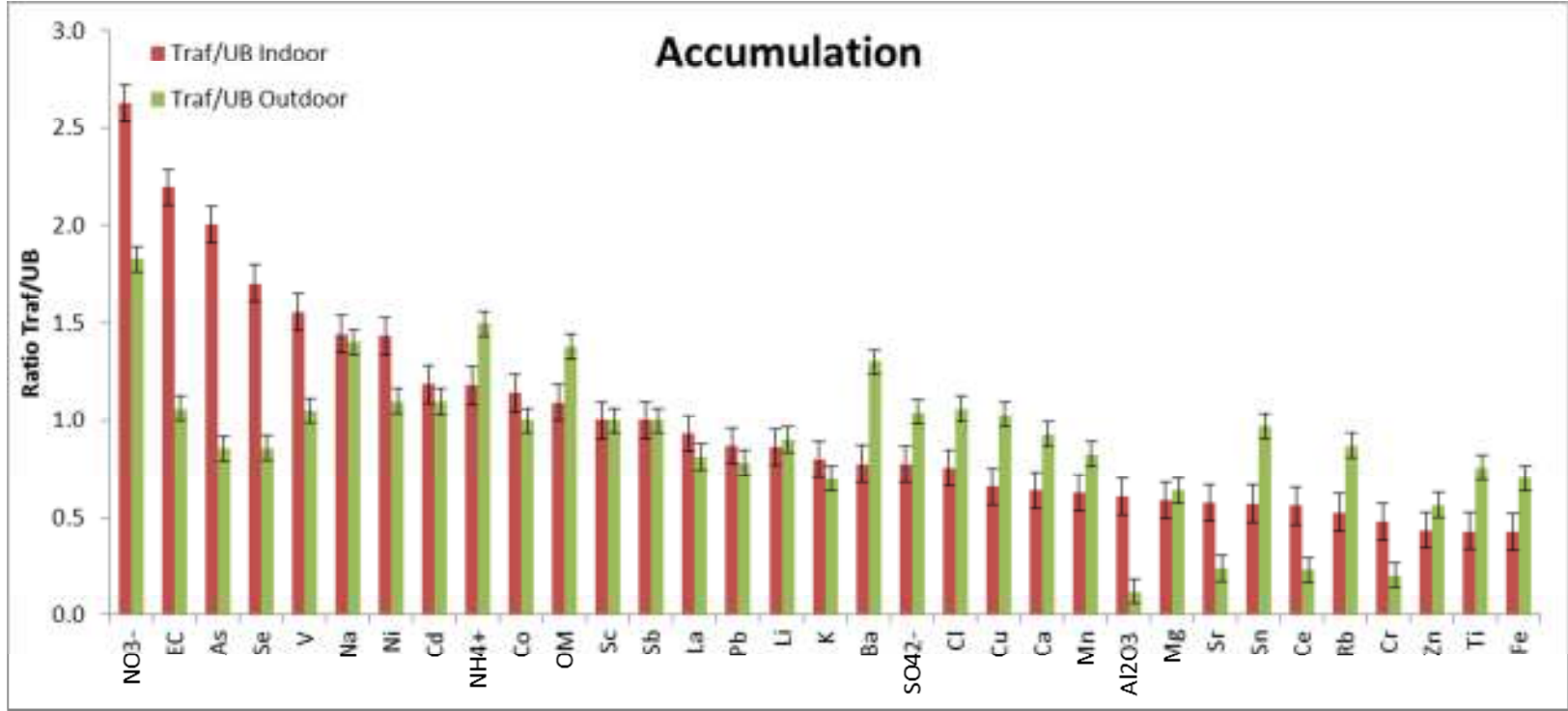
4 Figure 3a. Average size distribution of major PM components in indoor and outdoor air, in terms of mass ($\mu\text{g}/\text{m}^3$) and including standard error
5 bars.



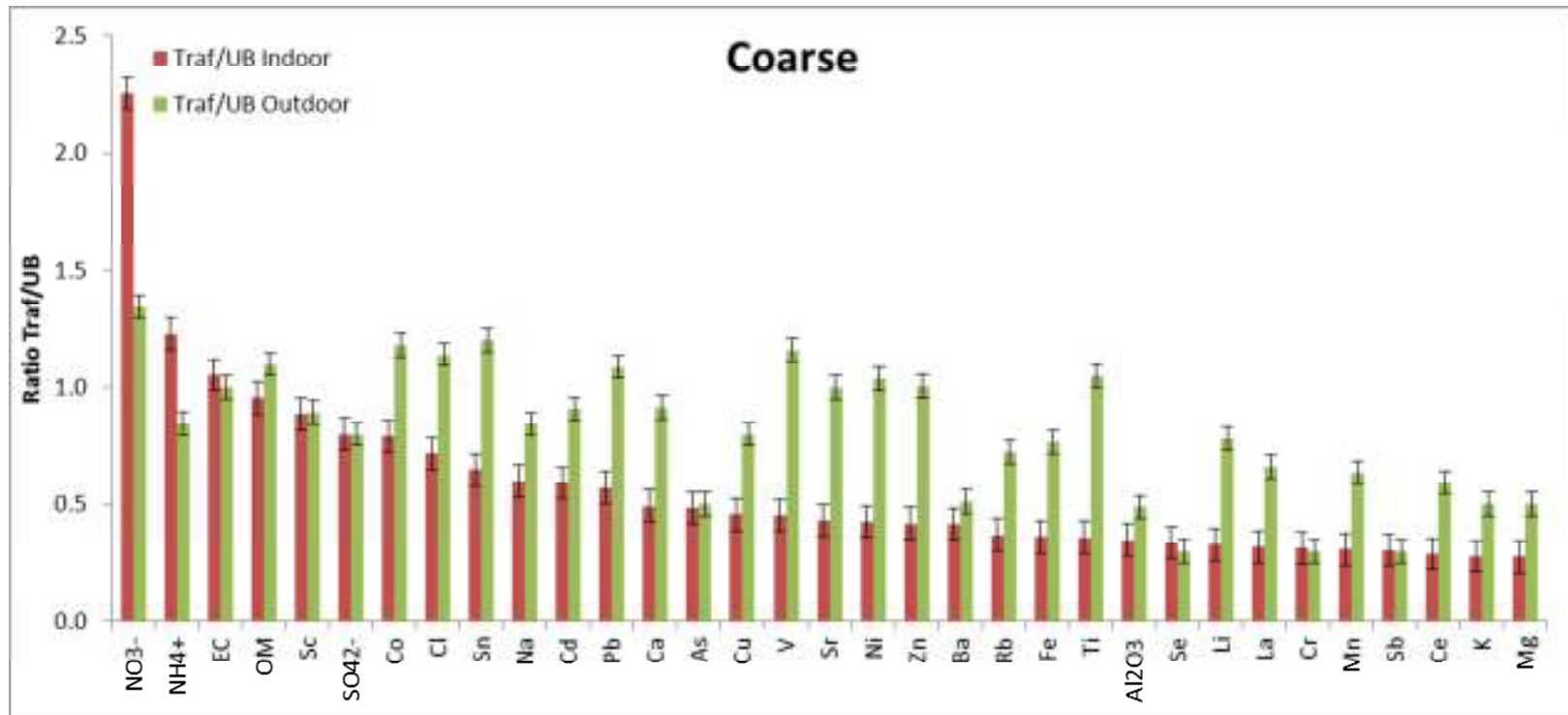
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 2 Figure 3b. Average size distribution of trace components (including metals) in indoor and outdoor air, in terms of mass (ng/m³) and including
 3 standard error bars.
 4



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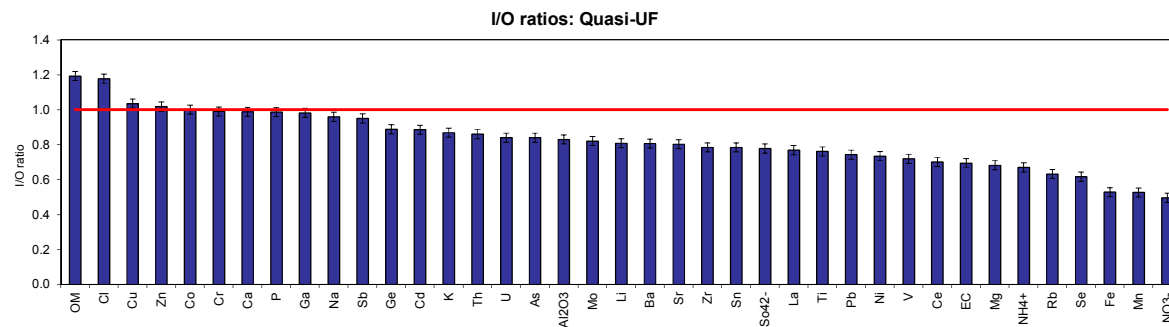


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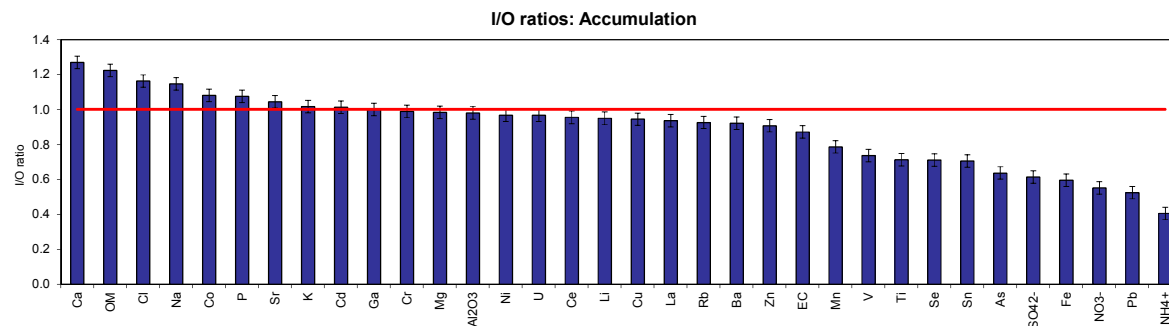


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 2 Figure 4. Mean concentration ratios for concentrations measured at schools located in traffic (Traf) and urban background (UB) environments,
 3 for in quasi-UFPs, accumulation and coarse mode particles.
 4

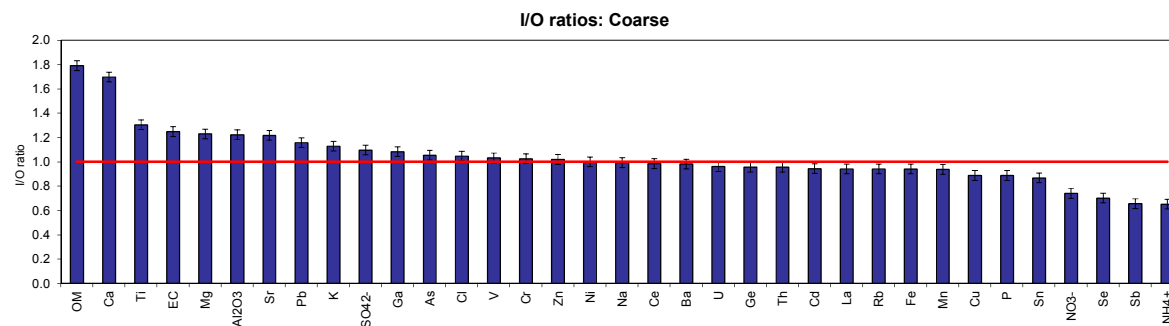
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Figure 5. Mean I/O ratios for quasi-UF, accumulation and coarse mode particles, with standard errors.

