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Partitioning of trace elements and metals between quasi-ultrafine, accumulation and coarse aerosols in indoor and outdoor air in schools

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HIGHLIGHTS

- Quasi-ultrafine particles (q-UF) are measured indoors and outdoors in 39 schools.
- Particle size distribution patterns of trace elements and metals are described.
- High proportions of typically coarse elements are found in q-UF particles.
- Potentially health-hazardous metals are found in q-UF in indoor air.
- The location of schools in trafficked areas increases children exposure to q-UF.

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ABSTRACT

Particle size distribution patterns of trace elements and metals across three size fractions (<0.25 μm, quasi-ultrafine particles, q-UF; 0.25–2.5 μm, accumulation particles; 2.5–10 μm, coarse particles) were analysed in indoor and outdoor air at 39 primary schools across Barcelona (Spain). Special attention was paid to emission sources in each particle size range. Results evidenced the presence in q-UF particles of high proportions of elements typically found in coarse PM (Ca, Al, Fe, Mn or Na), as well as several potentially health-hazardous metals (Mn, Cu, Sn, V, Pb). Modal shifts (e.g., from accumulation to coarse or q-UF particles) were detected when particles infiltrated indoors, mainly for secondary inorganic aerosols. Our results indicate that the location of schools in heavily trafficked areas increases the abundance of q-UF particles, which infiltrate indoors quite effectively, and thus may impact children exposure to these health-hazardous particles.

1. Introduction

Most of the concern over atmospheric particles derives from their impact on a number of aspects, ranging from climate (Shindell et al., 2012) or visibility (Cheung et al., 2005), to human health (WHO, 2013). In regard to the latter, aerosol effects are dependent on particle size, with different health effects being associated to different particle diameters (WHO, 2013). Aerosols may be classified based on particle diameter as coarse (aerodynamic diameter > 1 μm), fine (1 μm > aerodynamic diameter > 100 nm), ultrafine particles (<100 nm) and nanoparticles (<50 nm) (Seinfeld and Pandis, 1998). Some of these definitions may vary, especially for the finer size fractions (Kumar et al., 2010). Recent studies have extended the use of the term ultrafine particles to particles up to 250 nm in diameter, referring to this size fraction as "quasi-ultrafine" (Saffari et al., 2013).

Numerous studies have evidenced a wide range of adverse health outcomes on the human cardiovascular and respiratory

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systems linked to the exposure to airborne coarse, fine and ultrafine particles (Cassee et al., 2013). Whereas coarse aerosols impact mostly on respiratory system (Pérez et al., 2008), ultrafine particles have the ability to translocate to the circulatory system and induce inflammation (Oberdorster, 2001).

The partitioning of elements among various sizes depends on their sources and affects their chemical composition and therefore will impact the potential toxicity induced on different regions of the body (Cassee et al., 2013). Based on their chemical composition different types of particles generate reactive oxidative species, with metallic particles such as Cu and Fe being a well-known example (Fu et al., 2014) albeit not the only one (e.g., soluble and mineral particles; Hetland et al., 2001). Because literature results evidence that health effects from airborne particles depend on their chemical composition (e.g., transition metals, combustion-derived organic particles) but also on physical properties (size, particle number; Cassee et al., 2013), it is essential to assess the link between the two by evaluating the concentration of major and trace aerosol components across particle size fractions. This assessment could be used as input data for the assessment of health effects of particles reaching different regions of the body.

In addition to health effects studies, source apportionment analyses of ultrafine particles and nanoparticles by receptor modelling tools also require chemical size distribution data. For coarse and fine aerosols, tracer elements of specific emission sources (e.g., vehicular traffic, mineral dust, sea salt, among others) are well established and have been frequently used in the literature (Bruinen de Bruin et al., 2006). However, studies have indicated that such tracers may not be common across particle size fractions (Lin et al., 2005; Miller et al., 2007; Gietl et al., 2010; Buonanno et al., 2011; Liati et al., 2012; Patel et al., 2012). As an example, whereas Al and Ca are known to be tracers of mineral dust in coarse aerosols, they may be derived from local-scale combustion processes when found in ultrafine particles (Lin et al., 2005). As a result, interpreting Al and Ca as tracers of mineral matter in ultrafine particles may be misleading for specific cases (Sanderson et al., 2014). Similar cases are reported for Fe, Ca, P and Mg in ultrafine particles from lubricating oils (Miller et al., 2007; Patel et al., 2012) and for Ca, Mg, Al and Fe in ultrafine particles from diesel soot (Liati et al., 2012; Sanderson et al., 2014). Consequently, relatively few source apportionment studies of ultrafine particles are currently available (Karanasiou et al., 2007; Sanderson et al., 2014).

Finally, understanding the way in which elements partition across particle size fractions also allows us to interpret changes in such particle size distributions, especially those induced by physical and/or chemical processes, such as particle infiltration from outdoor to indoor air. Infiltration processes may alter particle size distribution and aerosol composition for specific aerosols, e.g., volatilization of ammonium nitrate (Hering et al., 2007). The assessment of the chemical size distribution data of aerosol components should enhance our understanding of the extent to which infiltration processes affect indoor aerosols, and provide better insights on indoor exposures. In the present study, this analysis targets children and their exposure to indoor airborne pollutants during school hours. Previous studies on indoor air quality in schools (Blondeau et al., 2005; Diapouli et al., 2007; Weichenthal et al., 2008; Morawska et al., 2009; Mejía et al., 2011; Mazaheri et al., 2014) concluded that research on indoor air quality in typical schools is vital to students' health and their performance, given that numerous outdoor airborne pollutants are present in schools.

This work aims to quantify the distribution of major metals and trace elements across three particle size fractions in urban outdoor and indoor air. This assessment was carried out in primary schools in Barcelona, both indoors and outdoors, and at different distances from traffic emissions. Our results provide qualitative and quantitative descriptions of particle size distribution patterns for metals and trace elements, with a special focus on their emission sources in each particle size range.

2. Methodology

2.1. Sampling locations

Measurements were carried out in 39 schools across Barcelona (Spain), selected in the framework of the Advanced ERC Grant BREATHE. Schools were divided into those representative of the city's urban background pollution levels and of high traffic emissions (Rivas et al., 2014), and then grouped into pairs (one school of each type) for concurrent sampling. In each school, indoor and outdoor sampling was carried out simultaneously. Further details of the sampling locations are provided elsewhere (Rivas et al., 2014; Viana et al., 2014). Two six-month sampling campaigns took place between January 2012 and February 2013, at a rate of 2 schools per week. Sampling was carried out at each school twice.

2.2. Sample collection and analysis

Filter samples were collected using Personal Cascade Impactor Samplers (PCIS; Misra et al., 2002) connected to SKC Leland Legacy pumps, operating at 9 l pm. Four PCIS were placed simultaneously (2 indoors, 2 outdoors) in each school. Samples were collected only during school hours (9:00–17:00 local time, 8 h) over a period of 4 consecutive days (Monday to Thursday). Thus, samples accumulated 32 sampling hours on the same filters and were representative of weekly (4-day) school-hour concentrations.

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

After collection, mass concentrations were gravimetrically determined by weighing the filter substrates on a Mettler-Toledo Microbalance. All samples were then analysed for major and trace elements. For each school, week and environment (indoor and outdoor), 2 parallel samples (with 3 filter substrates each) were available: A and B. The mass concentration on samples A and B was comparable. The filters from PCIS A were acid digested (HNO_3:HF:$HClO_4$) to determine major and trace elements by ICP-MS and ICP-AES (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 (q-UF, accumulation and coarse).

In total, the number of valid samples for outdoor air was 84 and 144 for sampling campaigns 1 and 2, respectively, and 75 and 126 for indoor air for sampling campaigns 1 and 2.

3. Results and discussion

3.1. Mean indoor and outdoor concentrations

The size-fractionated mean concentrations of major and trace components, as well as the gravimetrically determined mass, for indoor and outdoor air samples, are shown in Fig. 1. The data shown are the mean concentrations for both sampling campaigns,