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Indoor and outdoor air concentrations of volatile organic compounds and NO_2 in schools of urban, industrial and rural areas in Central-Southern Spain

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HIGHLIGHTS

- Twenty eight VOCs including carbonyl compounds and NO_2 were quantified in the schools in the province of Ciudad Real, Spain.
- The most abundant pollutants at schools were the aldehydes formaldehyde and hexanal
- The higher concentration of benzene in the industrial area reflects the magnitude of the contribution by petrochemical plant
- The persistent cyclic volatile methylsiloxanes were identified in all schools

GRAPHICAL ABSTRACT

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ABSTRACT

Thirty two VOCs including alkanes, aromatic hydrocarbons, terpenes and carbonyl compounds together with NO_2 were investigated in a kindergarten classroom, a primary classroom and the playground in 18 schools located in rural areas, an urban area (Ciudad Real) and an industrial area (Puertollano) in the province of Ciudad Real in central southern Spain. The most abundant pollutants at schools were the aldehydes formaldehyde and hexanal. After carbonyls, n-dodecane was the most abundant compound in the study areas. The NO_2 concentrations were higher in the urban area, followed by industrial area and rural areas. For benzene, its concentration in the industrial area was significantly higher than in the urban and rural areas which reflects the magnitude of the contribution to the indoor air by petrochemical plant during the sampling period. Principal component analysis, indoor/outdoor ratios, multiple linear regressions and Spearman correlation coefficients were used to investigate the origin, the indoor pollutant determinants and to establish common sources between VOCs and NO_2. Seven components were extracted from the application of PCA to the indoor measurements accounting for 77.5% of the total variance. The analysis of indoor/outdoor ratios and correlations demonstrated that sources in the indoor environment are prevailing for most of the investigated VOCs. Benzene and n-pentane have a major relevance as outdoor sources, while aldehydes, terpenes, alkanes and most aromatic hydrocarbons as indoor sources. For NO_2, ethylbenzene and toluene both indoor and outdoor sources probably contributed to the measured concentrations. Finally, the

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results reported in this paper demonstrate that during the measuring period there were not great differences in the indoor air quality of the schools of the three study areas.

1. Introduction

In Spain, kindergarten and primary education requires the attendance of children at school from ages 3 to 12 for about 5–7 h daily. This means that children spend a lot of time exposed to indoor chemical pollutants in classrooms, which could have a great impact on their respiratory system due to their lower body mass index and their breathing pattern which is more susceptible to pollutants than adults (Xi et al., 2011). Poor indoor air quality in schools has been linked to reduced school attendance, respiratory infections, asthma, allergies, and compromised performance (Yoon et al., 2011; Daisey et al., 2003). Demirel et al. (2014) and Sofuoglu et al. (2011) demonstrated that children personal exposure concentrations correlated highly with indoor concentrations which poses cancer risk and Madureira et al. (2015) found that children exposed to higher total VOC concentrations had a twofold increased risk of having asthma-related symptoms. The main pollutants present in indoor air are volatile organic compounds, VOCs, including carbonyl compounds. Floor surface materials such as PVC/vinyl or linoleum, environmental tobacco smoke, personal care products, cleaning products, perfumes, glues, paints, solvent based products and some building and construction materials are the main indoor sources of VOCs (Demirel et al., 2014) and parquet, particle board, plywood furniture containing formaldehyde-based resins, paints and cleaning products are the major sources of carbonyls (mainly formaldehyde and acetaldehyde) (Madureira et al., 2016). Specifically, there is a large quantity of possible sources of formaldehyde emissions at schools from building and furnishing materials. Poulhet et al. (2014) reported through a mass balance model that formaldehyde concentrations could be decreased by 87–98% by removing the main source of emission and by increasing the air exchange rate to 1 h^{-1}.

Traffic was identified as the main source of outdoor VOC exposure in urban areas (Mishra et al., 2015). VOCs react in the atmosphere contributing to the formation of ozone under some conditions of temperature and radiation (Carter and Seinfeld, 2012). Gaseous pollutants such as VOCs can be brought in or infiltrate from outdoor to indoor environment, then indoor/outdoor ratio is a useful tool to evaluate the grade of infiltration in urban areas (Raysoni et al., 2013).

NO_2 peak concentrations in the urban atmosphere usually coincide with rush traffic hours, which suggests that vehicular emissions are the major source of this pollutant (Malik and Tauler, 2015). Once in the troposphere NO_2 acts as a precursor of ozone (Itano et al., 2007) and causes adverse health effects in human respiratory system (WHO, 2010). The most important indoor sources of NO_2 include tobacco smoke and gas-, wood-, oil-, kerosene- and coal-burning appliances. Outdoor nitrogen dioxide also influences indoor levels (WHO, 2010).

Studies in different countries have focused on the analysis of indoor air quality at schools and their health effects in France (Banerjee and Annesi-Maesano, 2012), Turkey (Ekren et al., 2017; Scheepers et al., 2010), Sweden (Wang et al., 2015), USA (Mukerjee et al., 2009) and India (Mathew et al., 2015). However, very few studies have been carried out in the indoor and outdoor air at schools in Spain with the objective of determining different air pollutants and their impact in children's health. Only some studies in Barcelona have been carried out in order to quantify fine particles, NO_2 and ultrafine particle concentrations at schools (Amato et al., 2014; Rivas et al., 2014; Reche et al., 2014). But to our knowledge, no studies have been carried out regarding VOCs in the indoor air of schools. Consequently, in this work we present the first study about the levels of VOCs including carbonyl compounds and NO_2 at eighteen primary schools located in the province of Ciudad Real in three different areas (rural, urban and industrial).

The major objectives of this study were: (a) to measure the levels of VOCs including carbonyl compounds and NO_2 in kindergarten classrooms and primary classrooms of schools in different locations (rural areas, an urban and an industrial area), (b) to compare the concentrations between classrooms within the same area and between the different locations (c) to compare the indoor and outdoor concentrations and (d) to investigate the origin of pollutants and establish common sources between them.

2. Materials and methods

2.1. Areas of study

Indoor and outdoor measurements were conducted in 18 primary schools. Six of the schools were located in Ciudad Real, a small city from Spain in the centre of the Iberian Peninsula (38°59′N, 03°56′W) with around 72,000 inhabitants. Another six schools were located in an industrial city, Puertollano with almost 52,000 inhabitants at approximately 42 km from Ciudad Real (38°41′N, 04°06′W). The presence of a petro-chemical pole, situated about 5–6 km southeast from the town center, is an important source of air pollution in this city. The existent industries include refinery, chemical industry, two power plants and a coal mine. The rest of schools were located in rural areas at a distance between 8 and 24 km from Ciudad Real: Alcolea de Calatrava (38°59′N, 04°07′W), Valverde (38°58′N, 04°02′W), Picón (39°03′N, 04°04′W), Las Casas (39°02′N, 03°59′W), Poblete (38°56′N, 03°59′W) and Corral de Calatrava (38°51′N, 04°05′W). Fig. S1 in the Supplementary Information (SI) shows the location of the study areas. Two classrooms per school (a kindergarten classroom and a primary classroom), comprised of children aged 3 to 12 years old, were simultaneously investigated. Kindergarten classrooms were usually located either on the ground floor of the main school building or in another building and primary classrooms were usually located on the first floor of the main school building. As a result, a total of 36 classrooms were selected. Two samplers for VOCs and for carbonyl compounds, and one sampler for NO_2 were exposed in each classroom. Air samples were collected simultaneously outside on the playgrounds in each school. The sampling was carried out from February to April, during the year 2013.

2.2. Questionnaire

A questionnaire was completed for each school and indoor space to document information about the following parameters and conditions: course, floor, number of students, walls, building construction age, if it has been renovated recently, kind of floor covering, area, ventilation habits (time), orientation of classroom (playground-, main road- or street-facing), sort of heating and kind of blackboard. The results are summarized in Table 1.

2.3. Sampling and analysis

The analysis, the analytical system and the operating conditions for VOCs, carbonyl compounds and NO_2 were described in previous works (Villanueva et al., 2013b, 2014; Martín et al., 2010). Radiello® passive samplers (Fondazione Salvatore Maugeri, Padova, Italy) were used for monitoring VOCs (RAD 130, activated charcoal), carbonyl compounds