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LIMONENE IN SCHOOL INDOOR ENVIRONMENTS – SOURCE AND LEVEL OF CONTAMINATION

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ABSTRACT. Little information currently exists regarding indoor air pollution with limonene in school environments. This study's aim is to assess the contamination level of limonene and identify possible emission sources inside classrooms because, it is well known that exposure to higher levels of monoterpenes may have important human health effects, children being more susceptible than adults. A field study was conducted in two classrooms from different schools in Alba County, Romania by tracing the evolution of the pollutant over one school day (inside and outside simultaneously) and filling up a specific check-list. Indoor limonene levels ranged between 0.064 – 0.236 mg/m3 for school ro-s1 and 0.022 – 0.164 mg/m3 for ro-s2 school, exceeding in both cases outdoor levels, therefore concluding that indoor sources have been prevalent. Among them, laminate floorings, wooden construction materials, furniture, cleaning agents and living plants have been identified as common for both classrooms. Outdoor air quality didn't have an important effect over the indoor environment, poor ventilation determining the low influence of outdoor concentration levels.

Key words: *indoor air quality, limonene, school, children, source*

INTRODUCTION

Indoor air constitutes a wide variety of pollutants, exposure levels and different possible health outcomes. A good indoor air quality in schools is essential to ensure a safe, healthy and comfortable environment, not only for children, but also for teachers and staff (Annesi-Maesano et al., 2013). The pollutants found in school environments either originate from ambient air or produced indoors from materials, products or activities. The presence of volatile organic compounds (VOCs) has become a serious matter of concern since it was revealed that they can cause eye, nose and throat irritation, cough, headache, skin irritation or even trigger allergies and asthma (European Agency for Safety and Health at Work, 2009, Kovacs et al., 2013).

Some of the VOCs, monoterpenes, for example, can react with pre-existing indoor oxidants (e.g., ozone) and produce secondary pollutants, including secondary organic aerosols, carbonyl compounds (acetone, formaldehyde and methyl ethyl ketone) and reactive hydroxyl radicals, increasing the number of pollutants in the indoor air (Nazaroff et al., 2006).

This present study took as its starting point the SINPHONIE (Schools Indoor Pollution and Health: Observatory Network in Europe) project, a complex research on air quality inside primary schools, developed at EU level in 2010-2012 (in 25 countries). Its main objectives were to produce new exposure data regarding school building/classroom characteristics, and to study interactions between indoor air quality and pollution sources in school environments (Annesi-Maesano et al., 2013).

The aim of this experimental study was to assess the air quality in classrooms from Romania the main objective being highlighting d-limonene concentrations evolution during a common school day, and identifying possible pollution sources.

MATERIALS AND METHODS

The experimental study was carried out in December 2014 in two classrooms from Alba county, Romania, the schools being part of different environments (urban/rural), had different constructions (location, characteristics) and different outdoor exposure sources for limonene.

Three methods had been used in order to assess limonene source and level of contamination in school indoor environments. The first one consisted in limonene and carbon dioxide (CO_2) sampling inside the classrooms and outside the schools, simultaneously; the second method was about applying a checklist and last but not least, calculating the ventilation rate.

Sampling and analysis

The evolution of limonene study over a school day helps establishing the main pollution sources and the influence human activities have over the concentration levels. Thus, six sampling periods had been performed, for 50 minutes each, and the ventilating the classrooms between them by opening windows according to their normal usage. The first sampling period started at 6 a.m., showing limonene concentration level cumulated inside the classroom over night, since children left school. The next sampling period showed the concentration level cumulated inside, without children interfering, the classroom being without any activity. The last four periods presented data about the evolution of limonene during a school day with students being present in the classroom and performing their everyday normal activity. Simultaneously with indoor samplings, outdoor ones had been performed, this time near the school entrances.

The sampling method consisted in the aspiration of a specific air volume on activated charcoal cartridges SKC ANASORB CSC (Coconut Shell Charcoal). The equipment used was composed of: an aspiration device (APEX and Casella - TUFF sampling pumps). A blank sample was used for sampling quality assurance, which consisted in placing an adsorbent cartridge near the sampling point.

Terpenes adsorbed from air on activated charcoal cartridges were extracted by solvent desorption in dichloromethane. The extract was transferred into an auto sampler vial and analyzed by gas chromatography followed by identification and quantification by mass spectrometry with the use of a TG-624 capillary column, 60 m long, 0.25 mm diameter, and 1.4 µm of phase. Gas chromatograph was operated in SIM (selected ion monitoring) method and the concentration was calculated based on calibration curve. Quality control was conducted by analyzing laboratory blank samples of cartridge, field blank samples and by analyzing a standard solution with a known concentration was used to draw a type X control chart.

The measurement of CO_2 concentration levels was important in order to calculate the ventilation rate, the sampling being done the same way as for limonene. It was performed by using two gas analyzers IAQ-CALC model 7545 TSI with NIST Certificate included, that are using infrared detection of CO_2 (non-dispersive infrared sensor with two wavelengths).

Checklist investigation

A checklist specific to each classroom was filled in following observational assessment of the buildings and classrooms and together with teachers and cleaning personnel. Information followed was related to: outdoor characterization (orientation, traffic, and pollution sources), ventilation, indoor air pollution sources (recent renovations, wall and floor coverings, furniture, potted plants etc.) and cleaning (frequency, substances used).

Ventilation rate

The calculation of ventilation rate was made by using CO_2 concentration levels from the end of the sampling period and from the beginning in the following formula:

$$\overline{A} = \frac{[\ln(C(t_2) - C(ext)) - \ln(C(t_1) - C(ext)]}{(t_2 - t_1)}$$, where:

$\overline{A}$ = ventilation rate/h; t = time in hours; C (t) = CO_2 concentration at time t, [pm]; C (ext) = outdoor CO_2 concentration, [pm].

Data analysis

After the assessment of limonene evolution over a school day and the establishment of I/O concentrations relationship, the correlation of indoor with outdoor concentration levels and ventilation rates was evaluated with the Pearson's correlation coefficient "r" by using IBM SPSS Statistics version 22.

RESULTS

Contamination level with limonene

During school hours in S1, d-limonene concentration levels fluctuated between 0.064 and 0.236 mg/m^3 (median: 0.09 mg/m^3 and SD: 0.06) inside the classroom and between 0.012 and 0.085 mg/m^3 (median: 0.06 mg/m^3 and SD: 0.03) outside the school. As seen in figure 1, indoor levels exceeded outdoor levels in all six sampling periods.

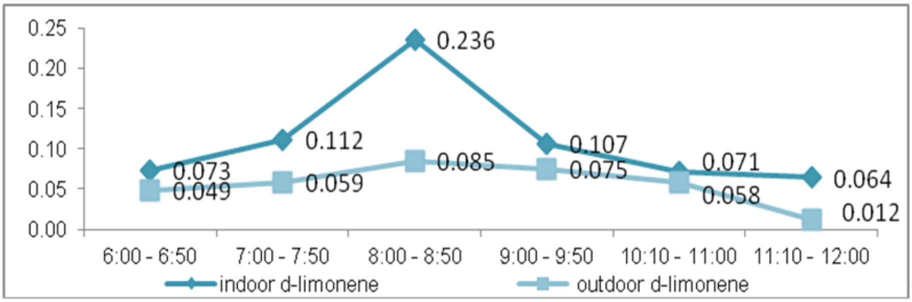

Fig. 1. – *d-limonene concentration levels in S1*

In classroom S2, d-limonene concentration levels were lower than in S1 as seen in figure 2, ranging between 0.022 and 0.164 mg/m^3 (median:0.04 mg/m^3 SD:0.06) in the classroom, and between 0.012 and 0.048 mg/m^3 (median:0.03 mg/m^3 SD:0.02) in outside the school. Most of the time, indoor concentration levels were higher than outdoor ones as well as in S1.

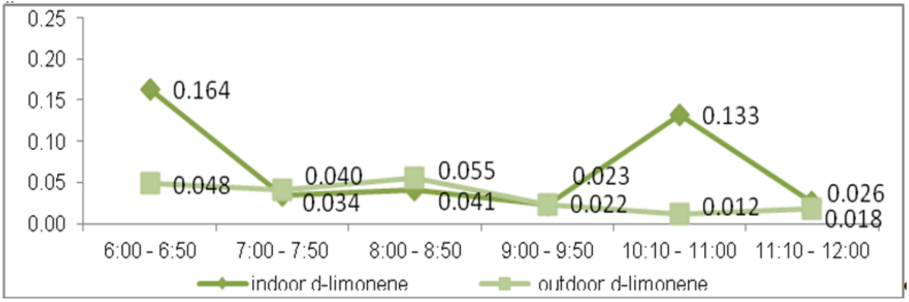

Fig. 2. – *d-limonene concentration levels in S2*

Correlations between indoor and outdoor d-limonene concentrations were positive for both classrooms. For S1, there was a strong correlation (r= 0.7) between indoor limonene and outdoor levels but a very weak one in S2 (r= 0.1).

The results for the correlations between indoor d-limonene concentration levels and the ventilation rates were different from the above. In S1, the obtained coefficient was positive but very weak (r= 0.1) while in S2, the correlation was negative and very weak (r=0.1).

Potential pollution sources

After analyzing the two checklists, multiple potential indoor and outdoor limonene sources had been identified for both classrooms. The most important outdoor source identified was represented by trees (conifers) surrounding the buildings. Regarding indoor sources, the following have been identified: recent renovation work that was done prior to the sampling, wooden origin flooring or furniture, use and storage of products with irritant smell inside the room (only in S1) and potted plants (Seung et al., 2012; Pio et al., 2001; Yang et al., 2009).

Cleaning is very important in controlling the indoor pollution level. Depending on the cleaning frequency, materials and substances that are used, it can become a source of pollution/recycling. In both classrooms, the trash cans were emptied, floorings were swept and surfaces were dusted daily. Surfaces were polished and other objects (e.g. doors) dusted once a week, while windows had been washed once a month and curtains once a year. In the cleaning process, the vacuum cleaner was not used in any of the classrooms. A disinfectant-free detergent was used for washing the floorings, spray for polishing the surfaces, liquid polishing products for polishing the floorings and ammonia-free detergent for washing the windows.

Ventilation

In both classrooms, ventilation was exclusively natural. According to checklists, windows were opened generally for two reasons: ventilation during cleaning and heat. Classrooms were ventilated differently, in classroom S1 windows being opened less often in comparison to classroom S2.

DISCUSSIONS

The monoterpen d-limonene isn't regulated in any national or international indoor air quality law or guideline, instead, a German national committee, an ad hoc working group consisted of technical experts from Indoor Air Hygiene Commission (IRK) of the Federal Environment Agency and the Permanent Working Group of the Highest State Health Authorities have established a guideline that has two categories for d-limonene concentration levels. The first, RW-I, is a precautionary guideline, anticipating that even with lifelong exposure below the recommended value, no adverse effects on human health are to be expected. The second, RW-II is an effect-related value, that if exceeded, an acute need for action is indicated (Heine and Eckhardt, 2014). D-limonene concentration levels inside the classrooms was between 0.022 - 0.164 mg/m^3 in S1, and 0.064 - 0.236 mg/m^3, both levels being below the recommended RW-I limit of 1mg/m^3 and RW-II of 10 mg/m^3.

Correlations between indoor and outdoor d-limonene concentrations were positive for both classrooms, meaning the main source of contamination being indoors. Also, I/O ration calculated for S1 (mean: 1.7) and S2 (mean: 1.2) enforces the statement. Same results have been found in other studies (Takigawa et al., 2009; Seung et al., 2012). The main indoor pollution sources identified for both classrooms were: recent wall renovations, wooden origin flooring or furniture and potted plants.

Regarding the correlation between indoor concentration level and ventilation rate, for S2 it was a very weak negative one, meaning the outdoor levels having an influence over the indoor ones. In this case, trees around the school building represented the main outdoor d-limonene source (Krol et al., 2014; Zabiegala et al., 2009).

A major concern however, is children's inhalation of VOC's from cleaning products since organic chemicals are widely used as ingredients. All household cleaning products such as detergents, disinfectants, softeners or cleaning solutions for carpets contain VOCs, d-limonene being especially found in those with orange fragrance (Smedje and Norbäck, 2001; Nazaroff et al., 2006). Studies showed that monoterpenes and oxygenated monoterpenes species concentration levels were determined mainly due to the consumption of cleaning products and air fresheners indoors (Huang et al., 2011). This can be the case after floors are scrubbed (once a day in S1 or once a week in S2) or when surfaces are polished, windows washed, mostly once a month in the evaluated classrooms.

Higher ventilation rate can dilute pollutants in the indoor environment, resulting in lower concentration levels (Huang et al., 2011). This was not the case for the classrooms that took part of this study. It is important that in both classrooms windows were opened during cleaning activities, but in the rest of the time, ventilation was poor. A study (Ridley et al., 2003) showed that due to their specific particularity of thermal insulation, double glazed windows with PVC frames reduce significantly the ventilation rate, thus keeping or even increasing the pollutant concentration levels in the classroom, this being the case of both classrooms.

CONCLUSION

Indoor air quality, especially d-limonene in school indoor environments, is very important to study, due to its association with impact over children's health. In the two classrooms evaluated in this experimental study carried out in 2014 in Romania, concentration levels were below the recommended international guidelines available; even in low concentrations, their presence in the indoor air is important since environmental parameters including ventilation rate, temperature and relative humidity have significant influences on the formation of secondary organic pollutants after the reactions between d-limonene concentrations and ozone, increasing the number of pollutants affecting children's health. Several indoor sources have been identified: renovations, furniture, flooring, plants or cleaning activities. Guidance regarding cleaning and disinfection should be given in schools since there is evidence that use of cleaning products, and disinfectants can harms children's health. D-limonene indoor pollution sources identified in this study are rather common in most schools in Romania, making it possible to generalize the obtained results.

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