Indoor air Pollution with Benzene, Formaldehyde, and Nitrogen Dioxide in Schools in Osijek, Croatia

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Abstract
Exposure to air pollution and poor indoor air quality is associated with a variety of adverse health outcomes, especially in schoolchildren. This paper presents results of the pilot study of the formaldehyde, benzene, and nitrogen dioxide measurements in classrooms and at outdoor sites in two schools in Osijek, Croatia, carried out by the Institute of Public Health for the Osijek-Baranya County and WHO. Concentrations of formaldehyde and nitrogen dioxide in classrooms (formaldehyde average weekly concentration = 8.48 μg/m^3, SD = 2.33; NO$_2$ average weekly concentration = 11.12 μg/m^3, SD = 2.49) were below the WHO guideline values for indoor air. The concentration of benzene in indoor air in one school (0.44 μg/m^3) was similar to the level of this chemical in ambient air (0.65 μg/m^3) while the data for another school (1.63 μg/m^3) suggested the presence of indoor sources of benzene. The highest concentration of formaldehyde was observed in a room where mold, dampness, and condensation contamination were visible. School power plants and road traffic affected higher values of indoor air NO$_2$ concentration.

Keywords Indoor air · Benzene · Formaldehyde · Nitrogen dioxide · Passive diffusion samplers

Introduction

If the indoor premises are not efficiently ventilated, unhealthy levels of chemical pollutants, such as formaldehyde, benzene, and nitrogen dioxide, can occur. Exposure to air pollution and poor indoor air quality represents a health risk for schoolchildren (Pilidis et al. 2009; Daisey et al. 2003; Bertoni et al. 2002; Blondeau et al. 2005;

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Sofuoglu et al. 2011). Numerous sources of indoor air pollution are linked to construction materials, indoor equipment, and cleaning products. Polluted ambient air also can affect indoor air quality (Kalenge et al. 2013). Increasing concentrations of indoor air pollutants can be associated with sick buildings syndrome (SBS) (Wargocki et al. 1999; Shan et al. 2016; Šega and Kalinić 1994). Common airborne pollutants in indoor spaces including particulate matters, carbon dioxide, nitrogen dioxide, benzene, and formaldehyde (WHO 2010) have a variety of adverse impacts on human health including skin irritation, eyes, and respiratory organs to carcinogenicity (Gonzalez-Flesca et al. 2000, Salthammer et al. 2010, Nielsen and Wolkoff 2010; Panagopoulos et al. 2011). Products that release benzene and formaldehyde are related to glass wool insulation, paints and varnishes for parquet, cosmetics, carpets and curtains, garments, wallcoverings, disinfectants, and sterilizers. Wooden products often contain phenol formaldehyde or urea-formaldehyde adhesives (Salthammer et al. 2010). Benzene can enter the body through the lung, skin, and digestive system, but inhalation is the most important and most common way of inputting (Gobba et al. 1997). Neurotoxic effects include headache, dizziness, drowsiness, and sometimes loss of consciousness. Most researched are hematopoietic effects:

professional exposure to benzene can lead to a reduction in the number of blood cells, bone marrow hypoplasia and pancytopenia, and in some cases to myelogenous leukemia (Kivistö et al. 1997; Pekari 1994). Formaldehyde can also be formed by ozonolysis of alkenes present in the air of enclosed spaces, most often monoterpenes found in many consumer products, such as air fresheners. The reactions of ozonolysis depend on the concentration of alkenes in the indoor air but also depend on air ventilation (Weschler 2000; Alvarez et al. 2013). Some studies have shown that indoor air levels of formaldehyde were higher during the summer due to increased gas release at higher temperatures (Zhang et al. 2009). The wide population of humans is exposed to low concentrations of formaldehyde (Kalinić 1995; Kalinić and Šega 1996; Šega and Kalinić 1996; Sofuoglu et al. 2011). Most likely, the main route of exposure to the general population of formaldehyde is through inhalation. Since water-soluble formaldehyde is highly reactivated with biological macromolecules and is rapidly metabolized, the first side effects are expected primarily in those tissues or organs with which formaldehyde first comes into contact (e.g., respiratory and digestive tract) (WHO 2002). Combustion processes contribute to an increase in the indoor air concentration of benzene and nitrogen dioxide. Nitrogen dioxide concentration is related to indoor and outdoor air, depending on the distance from busy roads or from other sources of combustion. NO_2 can affect human health irrespective of other present pollutants (Anderson et al. 2013). However, its presence is associated with the emergence or presence of other pollutants and it is difficult to determine which health effects cause only NO_2. There had been no experimental data for the concentration of volatile hydrocarbons and NO_2 in the indoor air in schools in Osijek, Croatia, area until this research. This paper presents results of a pilot survey in two schools carried out by the Institute of Public Health for the Osijek-Baranya County with technical assistance from WHO. For this purpose, passive diffusion samplers were used. Monitoring was conducted during one school week in each school during the heating season. Samples were analyzed by gas chromatography, high-performance liquid chromatography, and UV spectrophotometry. Indoor and outdoor air concentrations of benzene, formaldehyde, and NO_2 were calculated from the individual classrooms and in front school buildings and were considered by the volume, the furniture of the classroom, and the building material.

Materials and methods

The survey was conducted in 2012 in two randomly selected secondary schools in Osijek, Croatia, which are denoted as schools A and B. The survey included a general characterization of school buildings and weekly measurements of average levels of benzene, formaldehyde, and NO_2 concentrations in three classrooms and one outdoor points at each school (outdoor sampling sites are marked as AO and BO). The school A is a public high school located in the urban area approximately 100 m from the traffic road. The school consists of one building that has a ground floor and 1st floor. The total area of the school building is 1789 m^2 and contains 17 classrooms. The school building is a massive building structure older than 50 years and has been renovated in the last 5 years. There were 547 students in the school. The school uses natural ventilation and a centralized heating system connected with the district heating plant. There was a flood in the school during 2011 caused by the broken water pipes. In some parts of the school (classrooms, corridors, and staircases) there were signs of mold, dampness, and damage. The general characteristics of classrooms are presented in Table 1.

Classroom A1 is located on the ground floor of the building and the classroom A2 is on the first floor. The walls and ceilings of these classrooms are made of concrete, brick, and plaster, and are painted in color, and the floor is made of concrete coated with wooden parquet. A1 classroom is equipped by a plain chalkboard, an electronic interactive board, a computer, and a television set. The furniture is constructed from wood and plywood. A2 classroom is equipped by a chalkboard and a TV set. The furniture in the classroom is made of plywood. A3 classroom is on the first floor. The walls, ceiling, and floor are made from the same material as in the first two classrooms, and the floor is covered with tiles. There are chalkboard, computers, and electronic devices. The classroom is equipped with wood furniture and plywood. The walls and ceiling of all three classrooms are painted with color during 2011. The classrooms are cleaned every day

Table 1 Overview of basic classroom characteristics in A school

Classroom	Classroom volume (m^3)	Classroom width (m)	Classroom length (m)	Classroom height (m)	Windows surface (m^2)	Floor
A1	193.9	6.2	9.2	3.4	7.9	0
A2	155.9	6.1	7.3	3.5	3.0	1
A3	199.5	6.0	9.5	3.5	6.0	1

Table 2 Overview of basic classroom characteristics in B school

Classroom	Classroom volume (m^3)	Classroom width (m)	Classroom length (m)	Classroom height (m)	Windows surface (m^2)	Floor
B1	270.3	6.6	9.1	4.5	12.9	1
B2	243.0	6.0	9.0	4.5	7.9	1
B3	221.2	6.1	9.3	3.9	10.6	0

with detergents and are pretty clean. The windows open during the class break and sometimes during the class to make the classrooms ventilated.

School B is also a public high school located in the urban area. This school consists of two buildings that have a basement, ground floor, and 1st floor. The surface of one building is 1098.25 m^2, while the surface of the other is slightly smaller, 780.00 m^2, and has a total of 10 classrooms. The school building is a massive building structure older than 50 years. The air in three classrooms (B1, B2, and B3) and at one outdoor point was sampled. B3 classroom is in a larger building, and B1 and B2 classrooms are in a smaller building. The school attended 835 students. The school uses natural ventilation and the centralized district heating system (Table 2).

B2 and B3 classrooms are on the first floor. The walls are made of bricks, concrete, and plaster, and are painted in color; the floor is made of concrete and coated with laminate flooring. The chalkboard and electronic devices are also located in the classrooms. The classrooms are equipped with furniture made of plywood. Class B3 was painted in 2011 and windows were changed. Class B1 is on the ground floor. The walls, ceiling, and floor are made of the same material as in B2 and B3. The walls are painted in color and partly covered with wood and stucco; the floor is covered with laminate flooring.

The classrooms are equipped with furniture made of plywood, chalkboard, and electronic devices. The walls and ceiling of B1 classroom are painted in color during 2011. Classrooms are cleaned by detergents. The windows are open during the class break and sometimes during the class to ventilate the interior.

Formaldehyde, benzene, and NO_2 were sampled by passive diffusive samplers during April 2012. Radiello Code 165 Passive Sampler with the adsorbent of 2,4-dinitrophenylhydrazine (DNPH) was used for formaldehyde sampling by ISO 16000-1 (2004) and ISO 16000-2 (2004). The method is based on the reaction of the carbonyl group and DNPH resulting in stable 2,4-dinitrophenylhydrazone according to ISO 16000-4 (2004). The resulting derivative is analyzed by high-performance liquid chromatography (HPLC) and ultraviolet (UV) absorption detector operating at 360 nm (Pegas et al. 2012; Gennaro et al. 2014; Chiappini et al. 2011). Radiello Code 130 Passive Sampler with activated charcoal sorbent was used for benzene sampling by ISO 16000-1 (2004). Trapped benzene is eluted with carbon disulfide (CS_2) containing 2-fluorotoluene as internal standard and analyzed by gas chromatography (GC) with a flame ionization detection (FID) (Kot-Wasik et al. 2007; Carrieri et al. 2006; ISO 16200-2 (2000)). NO_2 was sampled by Gradko TDS 15

Table 3 Measured concentrations of formaldehyde, benzene, and NO_2

School A

Sampling point	Duration of sampling (hours)	Concentration CH_2O ($\mu g/m^3$)	Concentration C_6H_6 ($\mu g/m^3$)	Concentration NO_2 ($\mu g/m^3$)
A1 (ground floor)	78	10.7	0.36	11.29
A2 (1st floor)	76	11.7	0.34	7.6
A3 (1st floor)	77	8.5	0.64	9
Outdoor point AO	76	2.3	0.65	15.9

School B

Sampling point	Duration of sampling (hours)	Concentration CH_2O ($\mu g/m^3$)	Concentration C_6H_6 ($\mu g/m^3$)	Concentration NO_2 ($\mu g/m^3$)
B1 (ground floor)	102	5.9	2.52	14.08
B2 (1st floor)	101	7.8	1.18	11.3
B3 (1st floor)	101	6.3	1.21	13.46
Outdoor point AO	102	1.3	0.72	13.44

Fig. 1 Comparison of the average concentrations of formaldehyde in schools A and B
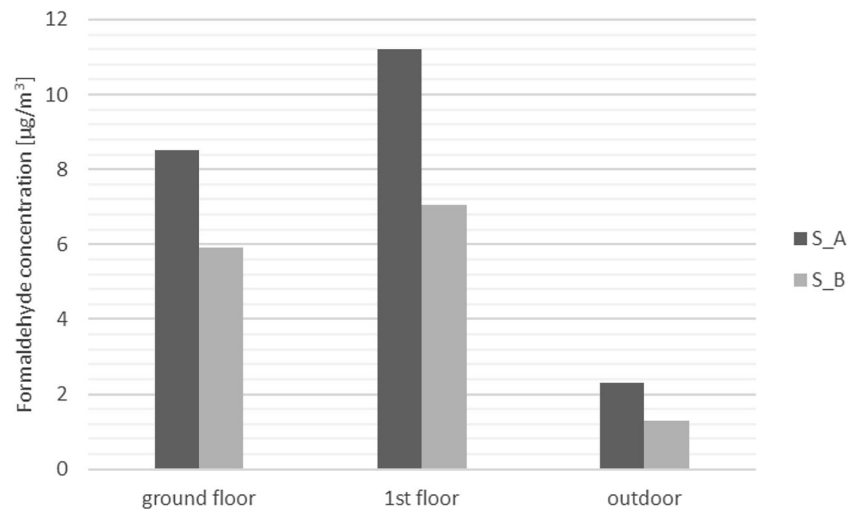
Rapid Air Monitor according to ISO 6768 (1998) and ISO 16000-15 (2008). This sampler provides a high-speed sampling of indoor and outdoor air NO_2. NO_2 diffuses through the air in the sampling device and is trapped as nitrite ion with triethanolamine (TEA) and then the nitrite is extracted with water and detected and analyzed by spectrophotometry (Hamilton and Heal 2004; Hafkenscheid et al. 2009).

Results and discussion

Measured concentrations of formaldehyde, benzene, and NO_2 are shown in Table 3. All the measured concentrations do not exceed the limit values for exposure to hazardous substances.

The concentration of formaldehyde in new houses decreases over the years, so in older houses, the concentration of formaldehyde tends to be below the WHO guideline limit of 0.1 mg/m³.

The mean values of formaldehyde, benzene, and NO_2 from the classrooms on the 1st floor have been used for graphs. The mean concentration of formaldehyde in school A was 4.5 times

higher than the measured value in the outdoor air in front of the school, and at school B, the mean concentration of formaldehyde was 5.1 times higher in indoor than in the outdoor air (Fig. 1). The highest values of formaldehyde concentrations were measured in 1st-floor classrooms in school A. The possible reasons for higher formaldehyde concentrations in 1st-floor classrooms can be linked to short-period windows openings, larger potential sources of wood formaldehyde (wood flooring and furniture). Furthermore, in class A2, condensation on the windows was also observed. In the A3 classroom, the floor is covered with tiles, the furniture is made of wood and plywood, and the window size is larger. Those findings can contribute to a lower concentration of formaldehyde.

Lower formaldehyde concentrations have been measured in school B, same as in the school A; higher concentrations have been measured in the 1st floor. The highest concentration of formaldehyde has been measured in class B2. The cause of high concentration can be linked to laminated flooring (formaldehyde-based adhesive is used), the furniture is made of plywood and the window size is smaller than all three

Fig. 2 Comparison of the average benzene air concentrations in schools A and B
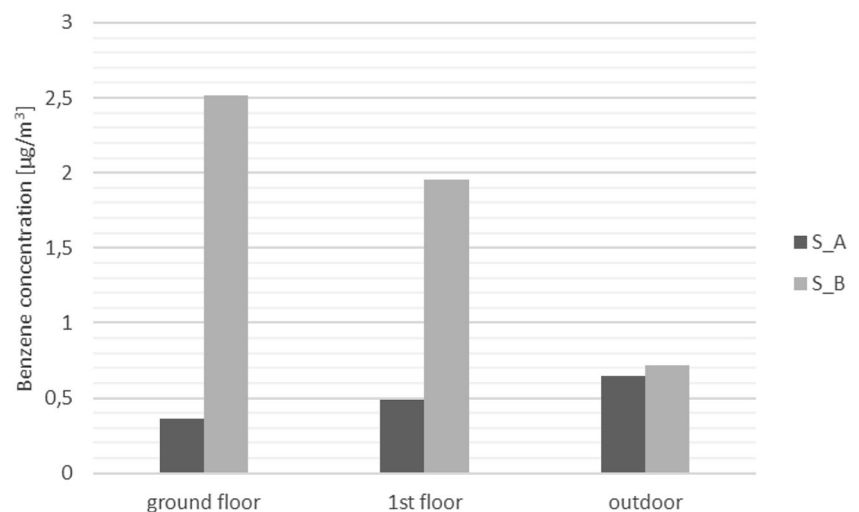
Fig. 3 Comparison of the average NO₂ air concentrations in schools A and B
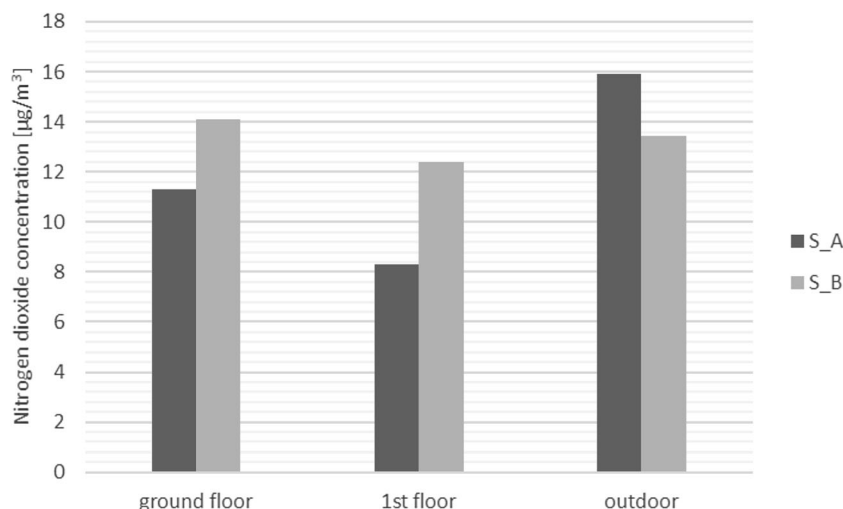
classrooms in B. The measured indoor air formaldehyde concentrations do not exceed the limit value for exposure of 100 μg/m³ according to WHO guidelines (WHO 2015). The Law on Air Protection of the Republic of Croatia (to be checked by the WHO) for formaldehyde prescribes only the limit value for the quality of life and is 30 μg/m³ for 24 h (Vlada 2012). In school B, higher concentrations of benzene were measured in indoor and outdoor air (Fig. 2). The lowest benzene concentration was measured on the ground floor of school A, while in school B, the highest concentration of benzene was measured on the ground floor. Classroom windows (B1) on the ground floor are located on the eastern side where there is a large public traffic road, public traffic garage for buses and trams, and power plant. The power plant consists of a boiler building with two hot-water boilers, one steam boiler and a combined chimney of about 65 m high. Pollutants are released from the chimney. Emissions are related to the combustion of fossil fuels in plants in the process of electrical and thermal energy production and in the production of industrial steam for industrial use.

There is no safe level of exposure to benzene according to WHO guidelines (WHO 2015).

Considering the location of school B, it is not surprising that the measured value of NO₂ in classrooms was higher (Fig. 3). In the outdoor point in front of school A, the air concentration was higher than indoors, and the reason is that school A is very close to the traffic road. The NO₂ level in the air depends on the traffic density and school distance from the road. The measured NO₂ concentrations do not exceed the limit values for short-term exposure of 40 μg/m³ and long-term exposure of 200 μg/m³ according to WHO guidelines (WHO 2015).

Conclusion

The results of the pilot study of benzene air concentrations in school B were a bit higher and it is assumed that a source of

benzene was present there considering that the floor was covered with new laminate, and the windows were located to possible sources of benzene sources. These concentrations are still pretty low; however, constant monitoring is needed. The measured concentration of formaldehyde air is higher in school A, and this could be a result of different equipment present in the classrooms of school A in comparison with the classrooms in school B. The highest concentration of formaldehyde is observed in a room where mold, dampness, and condensation contamination was visible. The measured indoor air NO₂ concentrations are higher at school B which is near the power plant, and higher outdoor air concentration is measured in school A, which is near the road. The measured concentrations of benzene, formaldehyde, and NO₂ do not exceed the limit values for exposure to hazardous substances. These concentrations are affected by indirect pollution sources of indoor air pollutants; therefore, continuous long-term measurements are required to establish typical levels of pollutants in indoor environments. These measurements could provide an insight into potential sources of contamination.

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