Salonen, Heidi; Salthammer, Tunga; Morawska, Lidia

Human exposure to NO2 in school and office indoor environments

Published in:
Environment International

DOI:
10.1016/j.envint.2019.05.081

Published: 01/09/2019

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Human exposure to NO₂ in school and office indoor environments

Heidi Salonen✉,1, Tunga Salthammer,1, Lidia Morawaska

A Review Article

Contents lists available at ScienceDirect
Environment International
journal homepage: www.elsevier.com/locate/envint

ARTICLE INFO

Handling Editor: Xavier Querol
Keywords:
Air pollution
Nitrogen dioxide
Sources
Indoor/outdoor ratio
School environments
Office environments

ABSTRACT

Background: Although nitrogen dioxide (NO₂) is one of the most common air pollutants encountered indoors, and extensive literature has examined the link between NO₂ exposure and duration causing adverse respiratory effects in susceptible populations, information about global and local exposure to NO₂ in different indoor environments is limited. To synthesize the existing knowledge, this review analyzes the magnitude of and the trends in global and local exposure to NO₂ in schools and offices, and the factors that control exposure.

Methods: For the literature review, Web of Science, SCOPUS, Google Scholar, and PubMed were searched using 42 search terms and their combinations to identify manuscripts, reports, and directives published between 1971 and 2019. The search was then extended to the reference lists of relevant articles.

Results: The calculated median, as well as the mean, concentration of NO₂ in school (median 21.1 μg/m³; mean 29.4 μg/m³) and office settings (median 22.7 μg/m³; mean 25.1 μg/m³) was well below the World Health Organization (WHO) guideline of 40 μg/m³ for the annual mean NO₂ concentration. However, a large range of average concentrations of NO₂ were reported, from 6.00 to 68.5 μg/m³ and from 3.40 to 56.5 μg/m³ for school and office environments, respectively, indicating situations where the WHO guidelines are exceeded. Outdoor levels of NO₂ are reliable predictors of indoor NO₂ levels across seasons, with mean and median Indoor/Outdoor (I/O) ratios of 0.9 and 0.7 in school and 0.9 and 0.8 in office environments, respectively. The absence of major indoor NO₂ emission sources and NO₂ sinks, including chemical reactions and deposition, are the reasons for lower indoor NO₂ concentrations. During the winter, outdoor NO₂ concentrations are generally higher than during the summer. In addition, various building and indoor environment characteristics, such as type of ventilation, air exchange rates, airtightness of the envelope, furnishing and surface characteristics of the building, location of the building (urban versus suburban and proximity to traffic routes), as well as occupants' behavior (such as opening windows), have been statistically significantly associated with indoor NO₂ levels in school and office environments.

Conclusions: Indoor exposure to NO₂ from the infiltration of ambient air can be significant in urban areas, and in the case of high traffic volume. Although reducing transportation emissions is challenging, there are several easier means to reduce indoor NO₂ concentrations, including a ventilation strategy with suitable filters; location planning of new schools, classrooms, and ventilating windows or intakes; traffic planning (location and density); and reducing the use of NO₂-releasing indoor sources.

1. Introduction

A gaseous pollutant, nitrogen dioxide (NO₂), generated from fossil fuel combustion, including sources such as transportation, combustion processes and industrial activities (Demirel et al., 2014), has emerged as one of the most notable ambient air pollutants associated with health effects (Gaffin et al., 2018). Nitrogen dioxide is of concern also as an indoor air pollutant, because there are strong indoor sources, such as building heating, cooking with fossil fuels, and tobacco smoke (Samet, 1991).

As NO₂ is a traffic- and industrial emissions-related pollutant, measured concentrations of NO₂ are generally higher in urban areas than in rural areas (Batisse et al., 2017; Demirel et al., 2014), and generally higher in outdoor air compared to indoor air, if no specific
indoor sources are available (Jelpo et al., 2019; Meier et al., 2015). Sometimes, indoor NO₂ concentrations may exceed outdoor concentrations, and result in higher personal exposure concentrations than outdoor concentrations (Bokzurt et al., 2015).

Recent epidemiological studies have found that exposure to NO₂ early in life may lead to allergic diseases including asthma (Bowatte et al., 2014; Deng et al., 2016) and have long-term effects on lung function affecting respiratory health throughout life (Baoting et al., 2019). Children are a particularly vulnerable subgroup regarding the health impacts of NO₂ exposure, because they breathe more air than adults relative to their body size, and have greater metabolic activities (Dong et al., 2018; Vanos, 2015). There is evidence that among asthmatic children, the threshold for increased symptoms, as long-term exposure, lies below 10 ppb (about 19 μg/m³) (Belanger et al., 2013), which is considerably below the World Health Organization (WHO) guideline of 40 μg/m³ for NO₂ as the annual mean concentration (WHO, 2010). In addition, a concentration–response relation has been determined between long-term NO₂ concentration and mortality throughout the observed range of NO₂ concentrations, with most concentrations below 20 μg/m³ among adults (Raaschou-Nielsen et al., 2012).

However, little is known about exposures to NO₂ in indoor environments, such as in schools and offices, where children and a large fraction of the adult population, respectively, spend about 30% of their time on weekdays; there is, however, more information about home exposures. (Morawska et al., 2017; Whitehouse and Grigg, 2018). Recently, Gaffin et al. (2018) reported that in children with asthma, indoor classroom NO₂ levels can be associated with increased airflow obstruction. In one school study, conducted in Malaysia, Norbäck et al. (2017b) found associations between indoor NO₂ levels and eye symptoms, throat symptoms, and tiredness.

There are several similarities, such as type of ventilation and high occupant density, between non-residential public environments, such as school and office environments, in relation to pollutant exposure (Godish, 2001; Salonen et al., 2015; Salonen et al., 2018). Although there are centralized furnace systems that minimize the combustion exposure in classrooms and office rooms, tobacco smoke is prohibited, and there is no cooking in most school buildings, combustion-related pollutants from outdoor sources can enter indoors through traditional ventilation, and intrude through windows and doors, and the structural imperfections of a building (Gaffin et al., 2018).

In addition to indoor and outdoor sources and occupants’ behavior, indoor levels of nitrogen dioxide may be affected by building and indoor environment characteristics, such as indoor humidity and the size of the building (WHO, 2010). However, information about these factors in school and office environments is very limited.

The aim of this work was to assess the magnitude and trends of the building and indoor environment characteristics, such as indoor humidity and the size of the building (WHO, 2010). However, information about these factors in school and office environments is very limited.

The specific objectives were to (i) assess the concentrations and exposure occurring in school and office buildings, (ii) conclude the apportionment between outdoor air as a source and indoor air source contribution, and (iii) make recommendations for mitigating indoor NO₂ in school and office buildings.

2. Material and methods

A Web of Science, SCOPUS, Google Scholar and PubMed search of the literature published between 1981 and 2019 (until May 2019) was performed. Altogether, 42 search terms (see Table S1 in the supplementary material (SM)) and different combinations of the terms were used. Searches included combinations of at least four terms simultaneously, and each combination included at least two of the following terms each time: NO₂, school, office, environment, exposure, and concentration. The search included original peer-reviewed scientific journal articles, literature reviews, and conference articles (full papers). The search was then extended to the reference lists of relevant articles (based on their abstract and/or full text). The decision to examine certain articles in more detail was based on the article titles. We downloaded of the articles free from the internet, and we also used the electronic databases of Aalto University and Queensland University of Technology. From the > 240 publications identified in the initial search, we selected 208 publications (see the reference list in the manuscript and in the SM) for inclusion in the review analysis. If necessary, the NO₂ concentration was converted from ppm or ppb to μg/m³ (1.0000 ppb = 1.9125 μg/m³ at T = 293 K and P = 1013 mbar).

3. Results and discussion

3.1. Chemical properties and formation of nitrogen dioxide

Nitrogen dioxide (CAS no. 10102-44-0) is a brown gas with a boiling point of 21.2 °C. The paramagnetic molecule is a free radical and stabilizes the unpaired electron via mesomerism. At lower temperatures, NO₂ equilibrates with its dimer N₂O₄. In water, NO₂ hydrolyses to HNO₃ and HNO₂. At room temperature, NO₂ absorbs daylight (< 570 nm), but photodissociates at wavelengths < 420 nm (Finlayson-Pitts and Pitts, 2000). Therefore, NO₂ plays a key role in the formation of tropospheric ozone, as shown in Eqs. (1) and (2). NO₂ also reacts with ozone (Eq. (3)), with the nitrate radical (Eq. (4)), and with the hydroxyl radical (Eq. (5)). NO₂ contributes to atmospheric alkene chemistry (Calvert et al., 2008), and is a precursor of peroxyacetyl nitrate (PAN) (Finlayson-Pitts and Pitts, 2000). Seinfeld and Pandis (2016) pointed out that the oxides of nitrogen, NO and NO₂, are among the most important molecules in atmospheric chemistry. Gilgorovski (2016) considers NO₂ as a powerful source of nitrous acid (HONO) indoors (see Eq. (6)).

\[
\begin{align*}
\text{NO}_2 + \text{hv} (\lambda \leq 420 \text{ nm}) & \rightarrow \text{NO} + \text{O} \\
\text{O}_2 + \text{O} & \rightarrow \text{O}_3 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 \\
\text{NO}_2 + \text{NO} & \rightarrow \text{N}_2\text{O}_5 \\
\text{NO}_2 + \text{OH} & \rightarrow \text{HNO}_3 \\
\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HONO} + \text{HNO}_3
\end{align*}
\]

Nitrogen dioxide is preferably produced via nitric oxide in combustion processes by oxidation of molecular nitrogen or by oxidation of chemically bound nitrogen. Three important mechanisms are known, and were reviewed by Miller and Bowman (1989). The thermal mechanism, also known as the Zeldovich-mechanism, describes the formation of nitric oxide from molecular oxygen (see Eqs. (7) and (8)). The reaction occurs at elevated temperatures, as, for example, in the hot zone of a flame, which is due to the high activation energy:

\[
\begin{align*}
\text{N}_2 + \text{O} & \leftrightarrow \text{NO} + \text{N} \\
\text{N} + \text{O}_2 & \leftrightarrow \text{NO} + \text{O}
\end{align*}
\]

The prompt mechanism was discovered by Fenimore (1971), and describes the formation of NO in a reaction sequence that is initiated by the reaction of hydrocarbon radicals with molecular nitrogen. The fuel-NO mechanism is important for fuels, which contain impurities of nitrogen compounds. In the atmosphere, NO is quickly oxidized to NO₂.

3.2. Methods of measurement

The design of measurements of nitrogen dioxide in indoor air is specified in ISO 16000-15 (2008). This standard defines sampling strategies for short-term measurements (usually 1 h or less) and long-term measurements. The continuous chemiluminescence technique offers a long time resolution, which is essential for monitoring peak
concentrations. This method uses a dual measurement principle and a subtraction calculation method. In one channel, only NO is measured by producing electronically excited NO2 from the reaction with ozone. Light is emitted from the transition of the excited NO2 to the ground state. The NO2 measurement in the second channel is based on catalytic conversion of NO2 to NO before the reaction with ozone. The NO2 concentration is obtained from the difference between the NO2 and NO concentration measurements (DIN EN 14211, 2012). The application of infrared techniques, such as tunable diode laser spectrometry (TLDS) (Finlayson-Pitts and Pitts, 2000), is uncommon in the indoor environment. The discontinuous spectrophotometric ASTM D1607-91 (2018) method is based on the Griess-Saltzman reaction and covers the manual determination of NO2 in the atmosphere. A red azo dye (measured at 550 nm) is formed from the reaction of NO2 with sulfanilic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride in the presence of sodium nitrite and acetic acid. The required sampling time is 10–60 min. Diffusive passive samplers are frequently used for long-term measurements of NO2. Most types are based on a color reaction of NO2 with triethanolamine as described by Palmes et al. (1976). Alternative designs are discussed by Yu et al. (2008). The sampling period of passive dosimeters is usually between 1 day and 1 week.

Very few papers provide a detailed treatment of quality control measures. In the EU network of monitoring stations an objective of 15% is requested for the accuracy of continuous NO2 measurement in ambient air (Gerboles et al., 2003). The uncertainty of mean (95% level) of the Griess-Saltzman method is 10% (ASTM D1607-91, 2018). Cyrys et al. (2000) applied passive samplers and found a 13% difference between duplicate measurements for a 1 week sampling period.

3.3. NO2 guidelines for ambient and indoor air

In 2006, the WHO (2006) published guidelines of 40.0 μg/m3 (the annual mean) and 200 μg/m3 (the 1 h mean) for ambient air. The NO2 air quality standards of the Chinese Ministry of Environmental Protection (MEP, 2012) and the European Environment Agency (EEA, 2018) are identical. The U.S. Environmental Protection Agency (EPA, 2018), the California Air Resources Board (CARB, 2018), and the Australian Government (2005) derived different values.

In 2010, the WHO adopted guidelines for the indoor environment (WHO, 2010). Health Canada (2015) defined critical effects based on toxicological data and derived residential maximum exposure limits of 170 μg/m3 (short term) and 20.0 μg/m3 (long term). Germany established toxicology-based indoor guidelines of 60.0 μg/m3 (1 week) and 350 μg/m3 (30 min) (Englert, 1998). These guidelines were reevaluated and revised by the German Committee on Indoor Guide Values (AIR, 2019). For short-term exposure, the committee recommends 0.25 mg/m3 (1 h mean) as the precautionary guide value and 0.08 mg/m3 (1 h mean) as the health hazard guide value. The committee did not derive a value for long-term exposure but recommended 0.04 mg/m3. However, in this case NO2 should be considered an indicator of combustion-related pollutants, and not a single substance. All national and international guidelines and standards discussed are summarized in Table 1.

3.4. NOx in ambient air

The total flux of reactive nitrogen (NO, NO2, and all compounds that are products of the atmospheric oxidation of NO and NO2) is about 48.8 terra grams (N) per year. Seventy-seven percent of the emissions are anthropogenic, and 23% are natural (Seinfeld and Pandis, 2016). However, the regional tropospheric concentrations of nitrogen oxides differ widely among urban, suburban, rural, and remote sites. Gurjar et al. (2008) compared annual average ambient air concentrations of NO2 for 18 megalopolises, measured in the late 1990s. The values ranged between 20.0 μg/m3 (Buenos Aires) and 170 μg/m3 (Moscow). Other cities with annual NO2 concentration higher than 100 μg/m3 were Beijing (122 μg/m3) and Jakarta (120 μg/m3). For Beijing, Cheng et al. (2018) observed that the annual mean concentration of NO2 decreased from 71.0 μg/m3 in 2000 to 49.0 μg/m3 in 2008, but it did not decrease significantly between 2008 and 2015. Moreover, the number of heavy polluted days per year (days with an air quality index > 200 according to the National Ambient Air Quality Standard) (MEP, 2012) is still around 50, with daily average concentrations of 94.62 ± 7.990 μg/m3.

NO2 concentrations in India between 1991 and 2012, which was attributed to the increase in the number of registered vehicles.

The European Environment Agency (2018) report provides NO2 data for 39 European countries (a total of 3083 stations) from 2016. 23 of the reporting countries recorded concentrations above the European Union’s annual limit value. The stations with concentrations above the annual limit (11.5% of all stations measuring NO2) were widely distributed across Europe. None of these stations were rural background stations and 98% of the concentrations were above the annual limit. The diversity of NO2 concentrations is shown in Fig. 1 for the greater area of Stuttgart. The station Am Neckartor (traffic) usually measures the highest NO2 concentrations in Germany. In 2018, the annual mean was 71.0 μg/m3, and the concentration of 200 μg/m3 was exceeded on 11 days. The annual mean at the station Bernhausen (urban background) was 27.0 μg/m3, and the maximum 1 h value was 119 μg/m3. Finally, the annual mean at the station Schwäbische Alb (rural background) was 7 μg/m3 with a maximum 1 h value of 53 μg/m3.

In most countries, NO2 concentrations are highly variable, and are often related to the traffic density. This was demonstrated by Schieweck et al. (2018), who were able to picture German metropolitan areas and the German motorway network on the basis of NO2 concentrations taken from the Federal Environment Agency database.

3.5. NO2 in indoor air

3.5.1. Schools

We found 47 scientific publications (published between 1986 and 2018) that examined > 963 classrooms (some studies reported only the number of indoor air samples, not the number of studied classrooms) in 354 school buildings, and 42 scientific publications (published between 1991 and 2018) that examined 2760 sampling locations (usually rooms in offices) in 2032 office buildings that reported indoor concentrations of NO2. In several of these studies, the measurements were conducted in summer and winter seasons. In one of the 47 school publications and three of the 42 office publications, the reported concentrations were based on modeling and real NO2 measurement data in selected measurement locations.

A summary of these studies is presented in Tables S2 and S4 in the SM. Detailed information of the studies is available in Tables S3 and S5 in the SM. Table S2 includes reported concentrations from the studied classrooms (reported concentrations from other spaces, such as from laboratories and corridors, were excluded if reported separately).

Based on these studies, the mean concentrations of NO2 in school settings was 30.1 μg/m3, and it varied between 6.00 μg/m3 (in Uppsala, Sweden, during spring/summer) (Smedje et al., 1997) and 68.5 μg/m3 (in Santiago, Chile, during winter) (Rojas-Bracho et al., 2002); see Fig. 2a and Table S2. The calculated median concentration (based on the reported average concentrations) in school settings was 26.1 μg/m3 (Fig. 2a), below the WHO guideline of 40.0 μg/m3 for NO2 as the annual mean concentration (WHO, 2010). However, exposure to higher indoor concentrations of NO2 in school buildings (maximum values in the range of 40.0–262 μg/m3) were commonly encountered (Annesi-Maesano et al., 2012; Janssen et al., 2003; Kim et al., 2004; Mi et al., 2006); see Fig. 2a.

For example, Al-Hemoud et al., 2017 and Annesi-Maesano et al. (2012) reported that the mean concentration of NO2 exceeded the WHO (2010) guideline for long-term exposure (40 mg/m3 for 1-year average) in some classrooms in several schools. In the study by Al-Hemoud et al. (2017), the highest concentration of NO2 in the science room of a one school...
was due to the use of nitric acid (HNO3) and extensive use of Bunsen burners in laboratories. Heating with a low-NOx unflued gas heater was also reported to cause elevated NO2 concentrations (geometric mean 31.60 ppb = 60.44 μg/m3; 95% geometric range 7.400–135.2 ppb = 14.100–258.57 μg/m3), and caused increased respiratory symptoms, particularly in atopic children (Marks et al., 2010).

In addition to these indoor sources of NO2 pollutants indoors, outdoor sources near school buildings penetrate indoors and cause elevated NO2 levels. For example, mean concentrations of NO2 measured from the schools located near highways or industry areas (mean ranging between 12.9 and 32.1 μg/m3) (Raysoni et al., 2013; Villanueva et al., 2018) or an urban area (mean ranging between 17.6 and 113.0 μg/m3) (Bennett et al., 2018; Chatzidiakou et al., 2015c; Demirel et al., 2014; Guerriero et al., 2016; Stranger et al., 2008; Villanueva et al., 2018; Zhang et al., 2014; Zhang et al., 2011; Zhao et al., 2008) or a suburban area (mean ranging between 13.0 and 55.0 μg/m3) (Demirel et al., 2014; Guerriero et al., 2016; Pegas et al., 2012; Stranger et al., 2008) were generally significantly higher than concentrations measured at rural area schools or at schools located in an area of low traffic density (mean ranging between 6.30 and 13.9 μg/m3) (Pegas et al., 2012; Raysoni et al., 2013; Villanueva et al., 2018). The mean, minimum, and maximum concentrations of NO2 for school environments are shown in Fig. 2 (statistical box plot, based on Table S4). The box-whiskers represent 25% and 75% quartiles, the median is shown by the red line, and the minimum and maximum are shown by the black line. The red plus signs are outliers (not taken into account in the calculations).

When the mean NO2 concentration data across various continents were analyzed, it was observed that the mean NO2 concentration in schools is significantly higher in Oceania and Asia than in Europe. The combined Oceania/Asia dataset has > 60% of the measurements or data points that exceed the 40 μg/m3 guideline, whereas in Europe, only 10% exceeds the limit. Europe has most mean values taken into account (41 values), but Asia also has enough values for good statistics (12 values). The mean school indoor concentration of NO2 shows a clear trend as a function of the continent. Australia (5 values) and Asia have more than a factor of 2 higher mean school indoor concentration magnitudes than Europe and North America (4 values), as illustrated in Fig. 4a. Worsening air pollution, such as NO2 in different parts of Asia, is believed to be due to transport of air pollutants from industrialized areas of mainland China (Guan et al., 2016; Kim et al., 2016), as well as local sources of air pollution such as motor vehicles, industry, and open burning (Mohar et al., 2018; Sun et al., 2018).

### Table 1

National and international guideline and air quality standards for nitrogen dioxide in ambient and indoor air.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Period</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 mg/m³</td>
<td>1 h mean</td>
<td>Health hazard guide value</td>
<td>AIR (2019)*</td>
</tr>
<tr>
<td>0.08 mg/m³</td>
<td>1 h mean</td>
<td>Precautionary guide value</td>
<td>AIR (2019)*</td>
</tr>
<tr>
<td>170 μg/m³</td>
<td>Short term</td>
<td>Health Canada (2015)*</td>
<td></td>
</tr>
<tr>
<td>20 μg/m³</td>
<td>Long term</td>
<td>Health Canada (2013)*</td>
<td></td>
</tr>
<tr>
<td>200 μg/m³</td>
<td>1 h mean</td>
<td>WHO (2010)*</td>
<td></td>
</tr>
<tr>
<td>40 μg/m³</td>
<td>Annual mean</td>
<td>WHO (2010)*</td>
<td></td>
</tr>
<tr>
<td>200 μg/m³</td>
<td>1 h mean</td>
<td>EEA (2018)*</td>
<td></td>
</tr>
<tr>
<td>40 μg/m³</td>
<td>Annual mean</td>
<td>EEA (2018)*</td>
<td></td>
</tr>
<tr>
<td>100 ppb</td>
<td>1 h mean</td>
<td>US EPA (2018)*</td>
<td></td>
</tr>
<tr>
<td>53 ppb</td>
<td>Annual mean</td>
<td>US EPA (2018)*</td>
<td></td>
</tr>
<tr>
<td>0.18 ppm</td>
<td>1 h mean</td>
<td>CARB (2007)*</td>
<td></td>
</tr>
<tr>
<td>0.030 ppm</td>
<td>Annual mean</td>
<td>CARB (2007)*</td>
<td></td>
</tr>
<tr>
<td>0.12 ppm</td>
<td>1 h mean</td>
<td>Australia (2005)*</td>
<td></td>
</tr>
<tr>
<td>0.09 ppm</td>
<td>Annual mean</td>
<td>Australia (2005)*</td>
<td></td>
</tr>
<tr>
<td>200 μg/m³</td>
<td>1 h mean</td>
<td>China (2012)*</td>
<td></td>
</tr>
<tr>
<td>40 μg/m³</td>
<td>Annual mean</td>
<td>China (2012)*</td>
<td></td>
</tr>
</tbody>
</table>

* Indoor air.  
Ambient air.  
1 ppb (ppm) = 1.91 μg/m3 (mg/m³) (P = 1013 mbar, T = 293 K).
values were higher than 40 μg/m³ in many cases. In their study, the lowest and highest median values were 7.00 and 154 μg/m³, respectively. The hourly mean concentration of NO₂ never exceeded the 200 μg/m³ WHO (2006) guideline. The mean, minimum, and maximum concentrations of NO₂ for office environments are shown in Fig. 3 (statistical box plot, based on Table S4).

The corresponding analysis for mean office indoor concentration of NO₂ shows a trend similar to the mean school indoor concentration, but to a somewhat lesser extent (see Fig. 4b). There, Asia has around 40% higher mean indoor concentration than Europe, both having enough statistics with Europe having 36 and Asia 22 mean values taken into account. The statistics for Australia (4 values), North America (3 values) and Africa (3 values) are relatively low to draw clear trends. In European offices, only 4% of the measurement points exceeded the limit; outside Europe the corresponding fraction was 25%.

There are some differences between school and office environments, which may explain our findings; Offices have typically outdoor-air exchange provided by mechanical ventilation, with much smaller contribution from infiltration or natural ventilation. School buildings tend to be more often naturally ventilated, so the infiltration of NO₂ from outdoor air is greater.

Our review paper is based on the previous published studies, and therefore the comparisons we have made may have some uncertainties. The results reported in the literature were obtained using various measurement methods, with each of them of their own weaknesses and error possibilities. It is believed that the longer the measurement time, the higher the accuracy and lowered the error of the measured average pollutant concentration can be achieved (Mui et al., 2006). It has been...
3.6. Indoor/outdoor ratios

Numerous studies investigated the penetration of outdoor NO₂ into the indoor environment and indoor to outdoor (I/O) NO₂ ratios. The calculated mean and median I/O ratios (based on the reported or calculated mean I/O ratios) in school settings were 0.9 and 0.7, respectively (Fig. 5a). The reported I/O ratios in school environments varied between 0.3 and 4.3 (Fig. 4a, Table S2). The I/O-ratios > 1 were reported in 16% of the studies, > 2 in 6% of the studies and > 2.5 in only one study. The highest, and a very unusual I/O ratio for NO₂ was measured for schools having fuel-burning heating systems and located in the Ciudad Real and Puertollano rural areas in Spain (Villanueva et al., 2018). The lowest I/O ratio was measured in Utrecht, the Netherlands, in the “ring road background school” (Van Roosbroeck et al., 2007). According to several school studies, the building envelope provided little protection from outdoor NO₂, and the peaks in indoor concentrations reached the extremes of the outdoor concentrations (Chatzidakiou et al., 2012).

The calculated mean and median I/O ratios in office settings (based on reported or calculated I/O ratios) were 0.9 and 0.8, respectively (Fig. 5b). Reported I/O ratios varied between 0.2 and 2.7 (Fig. 5b and Table S4) (Liao et al., 1991; Saraga et al., 2011). The highest I/O ratio occurred in Athens, Greece, in naturally ventilated office buildings (Saraga et al., 2011), and the lowest was measured in Hong Kong in mechanically ventilated office buildings (Liao et al., 1991). A relatively high I/O ratio was also measured in Mexico (mean I/O ratio, 1.7). In Mexico, the highest I/O ratio was obtained in Mexico City (1.9), while Guadalajara and Monterrey had the lowest ratios (1.2 and 1.3, respectively). These ratios show that, on average, in Mexico, indoor concentrations were higher than outdoor concentrations. For example, in Mexico City more office workers experienced environmental tobacco smoke and kept their windows closed than in the other cities during the study. Both situations contributed to increased indoor NO₂ concentrations (Ramirez-Aquilan et al., 2002).

Challoner and Gill (2014) found I/O NO₂ ratios increased statistically significantly overnight, as outdoor concentrations decreased to a much greater extent than indoors. The authors concluded that finding indicated a benefit in promoting increased air exchange between the outdoors and indoors during nighttime periods to flush out air NO₂.

Indoor surfaces can remove some of the NO₂ present in indoor air. Spicer et al. (1989, 1993) determined material-dependent surface removal rate constants kNO₂ up to 8.50 h⁻¹, but most values were between 0.80 h⁻¹ and 1.45 h⁻¹. The results reported by Gronsfelt and Raychaudhuri (2004) came close to those of Spicer et al. (Saltzhammer et al., 2018). Photocatalytic wall paint also accelerates the degradation of NO₂. Under laboratory conditions, a kinetic decay constant of k₁ = 2.19 h⁻¹ was determined; the air exchange rate was λ = 0.40 h⁻¹ (Saltzhammer and Fuhrmann, 2007).

In the absence of indoor sources and under the assumption that the indoor NO₂ concentration is primarily determined by air exchange λ (h⁻¹) and the surface removal rate constant kNO₂ (h⁻¹), the I/O ratio can be estimated with Eq. (9):

\[
\frac{I}{O} = \frac{\lambda}{\lambda + k_{NO_2}}.
\]  

As in the case of ozone (Salonen et al., 2018), we used Eq. (9) to consider two different situations, presented in Fig. 6. The left part of the figure presents a scenario with low air exchange rates (0.1–1.0 h⁻¹), while the right part presents a scenario with high rates (1.0–5.0 h⁻¹). In both cases, the removal rates kNO₂ were between 0 h⁻¹ and 5 h⁻¹. When typical indoor kNO₂ values of 1.0 h⁻¹ were considered, I/O ratios of 0.3–0.6 and 0.4–0.9 were calculated for low and high air exchange rates, respectively.

3.7. Predictors affecting indoor NO₂ concentrations and exposure

3.7.1. Outdoor air (via infiltration)

Chithra and Shiva Nagendra (2018) concluded in their recent review paper that outdoor air is an important source of indoor NO₂ pollution in school buildings, with the typical sources of NO₂ emissions in the indoor environment, gas appliances, heaters, and cigarette smoking playing a very limited role in most of the schools. Several studies have found that in the absence of indoor emission sources, NO₂ levels in classrooms generally correlated well with outdoor NO₂ levels, and were
the main contributors to indoor levels (Chatzidiakou et al., 2015c; Lee and Chang, 2000; Stranger et al., 2008). Sá et al. (2017) reported recently in their study of nursery and primary schools that intrusion from outdoor air was the main source of NO2 in rural and urban areas.

Guerriero et al. (2016) estimated (based on a multilevel regression analysis) that > 80% of the variation in indoor NO2 levels is explained by outdoor levels alone, and therefore, outdoor levels are a reliable predictor of indoor levels across seasons in the absence of indoor emission sources (Chatzidiakou et al., 2015a; Sá et al., 2017). The poor correlation between indoor and outdoor levels of NO2 reported by Zhao et al. (2008) indicated that the indoor NO2 exposure was largely determined by room-specific characteristics, such as ventilation. Their study illustrates the need to measure indoor NO2 levels in different indoor environments. Wichmann et al. (2010) concluded that in Stockholm, Sweden, NO2 indoor levels had a stronger association with outdoor levels, and with some exceptions, were lower, and that children's indoor environments offer little protection against combustion-related particles and gases in outdoor air.

3.7.2. Seasonality

Several studies (Bozkurt et al., 2015; Kodama et al., 2002; Kornartit et al., 2016; Mandin et al., 2017; Monn, 2001; Tong et al., 2018; Wichmann et al., 2010) reported higher indoor NO2 concentrations during the winter. For example, Bozkurt et al. (2015) found 1.3–4.3 times higher NO2 concentrations in winter than in summer, and concluded that the higher winter concentrations were mainly due to NO2 from the outdoors, originating from burning fossil fuels for space heating and transportation. Bozkurt et al. (2015) also mentioned that although during the winter the school environment was ventilated poorly to ensure heat isolation, and this poor ventilation allowed less NO2 penetrate from the outdoor environment, pollutants could accumulate in the indoor air due to higher outdoor concentrations than in the summer.

Bozkurt et al. (2015) detected that during the summer, the concentration of NO2, as well as of other inorganic gases, in schools’ indoor environments started to increase after 08:00. The NO2 concentrations exhibited a bimodal diurnal variation, peaking at 12:00 (could be due

![Fig. 5. a) The reported I/O ratios (and calculated median value) in school environments; b) the reported I/O ratios (and calculated median value) in office environments.](image)

Fig. 5. a) The reported I/O ratios (and calculated median value) in school environments; b) the reported I/O ratios (and calculated median value) in office environments.

![Fig. 6. Contour plots of calculated NO2 I/O ratios as a function of air exchange rates and surface removal rates km (see Eq. (5)). Low air exchange rates (0.1–1.0 h⁻¹) were assumed in the left part, while high air exchange rates (1.0–5.0 h⁻¹) were assumed in the right part. In both cases, the ozone surface removal rates km ranged from 0.1 h⁻¹ to 5.0 h⁻¹.](image)
to the outdoor to indoor NO2 transition) and 19:00 (could be the result of the reaction of O3 with NO to form NO2). In the daytime, the NO2 concentrations were at their lowest levels. The diurnal variation in the NO2 concentrations was generally due to ventilation of the school rooms. In office environments, NO2 concentrations increased during the morning hours of the summer season. Indoor NO2 concentrations started to decrease after midday, just as the outdoor NO2 concentrations. This finding by Bozkurt et al. (2015) shows that in summer, office environments are not completely isolated from the outdoors; the intrusion of outdoor air decreases NO2 concentrations. In winter, the variations in the NO2 concentrations were almost the same as in summer.

Recently, Al-Hemoud et al. (2018) found in a study of modern offices lower NO2 concentrations during summer periods than during pre- and post-summer periods. Mandin et al. (2017) reported in their study of office buildings across Europe (the OFFICAIR study) that in winter, higher NO2 emission rates from combustion sources, such as heating systems, combined with a higher atmospheric stability (low mixing layer height and low wind speed), occur outdoors and impact the indoor air quality. Based on these results, Mandin et al. (2017) concluded that, during a 1-year time frame, a spot measurement during one working week may be inadequate to characterize the long-term exposure of office workers inside a building. Despite the similarities in previous findings, there are also some contradictory findings. In Turkey, Yurdakul et al. (2017) found higher concentrations of NO2 in offices during summer (mean 25.4 μg/m³) than during winter (mean 22.7 μg/m³).

3.7.3. The proximity of traffic and industry (location of the building)

NO2 concentrations have been reported to be higher in urban schools and classrooms compared with suburban schools and classrooms (Chatzidiakou et al., 2015c; Guerriero et al., 2016). Recently, Villanueva et al. (2018) found in a study of schools that the NO2 concentrations were higher in urban areas, followed by industrial areas and rural areas. This finding supported Al-Hemoud et al.'s (2017) study which revealed statistically significant differences between urban and industrial areas in NO2 concentrations (p = 0.001); the average concentrations were slightly higher for urban schools than for schools located near the oil and gas industrial region. Blaszczyk et al. (2017) compared NO2 concentrations in schools located in urban-industrial areas and in rural areas, and found the statistically higher concentration of NO2 in urban-industrial areas.

Chaix et al. (2006) discovered that exposure to nitrogen dioxide at the place of residence and school of attendance (in Malmö, Sweden) regularly increased as the socioeconomic status of a child's neighborhood of residence decreased. Their findings showed that even in a fairly equal welfare state with widespread state intervention for social equity, social segregation points to traffic-related air pollution as in other Western countries as well (Jerrett et al., 2001; O'Neill et al., 2003).

The distance of buildings from roadways or high traffic roads, as well as traffic density, appears to have a significant impact on indoor nitrogen dioxide levels in school buildings (Chatzidiakou et al., 2015b; Guerriero et al., 2016; Janssen et al., 2001; Kodama et al., 2002; Kühler et al., 1988; Nakai et al., 1995; Nitta et al., 1993; Norbeck et al., 2000; Rivas et al., 2014; Rodes and Holland, 1981; Roorda-Knape et al., 1998; Vassura et al., 2015; WHO, 2010). It was also reported that the NO2 concentrations in and outside schools near motorways are significantly associated with traffic composition, and percentage of time downwind (Janssen et al., 2001). In offices, the maximum NO2 concentrations are present early in the morning (about 7:00) and late in the evening (about 10:00) due to the increase in traffic (Saraga et al., 2011).

3.7.4. Indoor sources and occupants' behavior
3.7.4.1. Combustion processes and heating

An EU report (CEC, 1989) identified indoor combustion as the major source of NO2 in the indoor environment. Samet (1991) and Cyrys et al. (2000) concluded from the results of studies in the US and in Germany that gas cooking was the major source of indoor-generated NO2. Today, the use of gas heating and gas cooking systems has strongly decreased in Europe. Nevertheless, gas heaters are still in use in many parts of the world, and may considerably increase indoor NO2 levels in school buildings. In New South Wales, Australia, Marks et al. (2010) measured indoor NO2 levels in classrooms heated with low-NOX unflued gas heaters and classrooms heated with flued gas heaters, and found an almost twofold higher geometric mean concentration of NO2 in the classrooms with flued gas heaters (33.5 μg/m³). In Canada, Australia, Pilotto et al. (1997) found a more than two times higher mean concentration of indoor NO2 in unflued gas heated classrooms (67.9 μg/m³) than in electrically heated classrooms (24.9 μg/m³).

There are many other indoor-related combustion processes with potential relevance for the formation of NO2. Derudi et al. (2014) determined concentrations of around 5 ppm in the exhaust gas of burning candles. Lee and Wang (2004, 2006) measured the release of NO2 from burning incense, candles, and mosquito coils in a 18.26 m² chamber. The highest NO2 concentrations indoors must be expected from non-vented fireplaces using ethanol fuel. The experiment was carried out with gelled ethanol in a 48 m³ stainless steel chamber, and the air exchange rate was 0.43 h⁻¹ (see Schripp et al. (2014) for the experimental details). During the burning period, the NO2 concentration reached a maximum of 0.76 mg/m³, and then decayed strictly exponentially. Temperatures up to 1000 °C are reached, and therefore, it is assumed that the majority of NO2 is formed by the thermal mechanism. Open ethanol flames are not common in schools and office environments, but the example demonstrates the efficiency of NO2 production from combustion processes.

3.7.4.2. Door and window opening

In a study of schools, Zhang et al. (2011) reported that relying on window opening as a tool for ventilation in China is difficult because increased ventilation decreases the CO2 levels but increases the indoor NO2 and SO2 levels. In Kuwait, Al-Hemoud et al. (2018) found statistically significantly higher mean concentrations of NO2 in a modern office building when the doors were closed.

3.7.4.3. Smoking

One possible source of indoor NO2 might be smoking (Can et al., 2015; Moir et al., 2008). Although smoking is not allowed in many schools and offices today, in some countries, such as Turkey, for example, face-to-face interviews by Can et al. (2015) showed that students sometimes smoke during their activities in painting workshops and in corridors which may also explain the relatively high NO2 concentrations measured at those places (including offices inside the university building).

3.7.5. Other building and indoor environment characteristics
3.7.5.1. Envelope airtightness

There is evidence of the effect of envelope airtightness on the penetrability of NO2 (Chatzidiakou et al., 2015c; Guerriero et al., 2016). For example Chatzidiakou et al. (2015c) reported that estimated I/O NO2 ratios suggest that the penetration ability of a pollutant indoors depends on the airtightness of the building envelope. In their study, the ability of more airtight buildings to filter NO2 and protect occupants was clearly seen during the non-heating season in urban and suburban schools by the higher I/O NO2 ratios (0.8–0.9). The ability was also seen in the heating season, reflected in the lower ratios estimated in contemporary more airtight schools ranging from 0.3 to 0.5 compared with 0.6–0.8 in less airtight schools. The ability of more airtight buildings to filter NO2 and protect occupants was further strengthened by the higher I/O NO2 ratios (0.8–0.9) estimated in the non-heating season in urban and suburban schools (Chatzidiakou et al., 2015c).
### 3.7.5.2. Surface characteristics, building furniture and the window material.

Surface characteristics, such as reactive decay on interior surfaces (WHO, 2010), as well as building furniture, may affect the indoor air concentrations of NO2 pollutants. Chemical reactions on material surfaces accelerate the depletion of indoor NO2. Ozone and NO2 contribute to gas phase indoor chemistry by formation of the nitrate radical (Arata et al., 2018; Waring and Wells, 2015; Weschler et al., 1994). Gomez Alvarez et al. (Gómez Alvarez et al., 2014) state that household chemicals have the potential to generate HONO indoors through light-enhanced NO2 heterogeneous reactions. There is also some evidence, that the window’s material affect the indoor NO2 concentrations; Rivas et al. (2015) found an increase of 8 μg/m3 of indoor NO2 for wood framed windows.

### 3.7.5.3. Ventilation.

Several studies have demonstrated that the ventilation type and the air exchange rate affect IAQ (Irga and Torpy, 2016; Spengler et al., 2001), and that inadequate ventilation favors accumulation of pollutants, such as NO2 (Pegas et al., 2011). In Stockholm, Sweden, Wichmann et al. (2010) found that the ventilation type and the air exchange rate influence infiltration factors of NO2, and that NO2 infiltrated better with mechanical than natural ventilation. However, if outdoor NO2 concentrations are relatively close to those found indoors, ventilation rates will likely cause negligible changes in indoor NO2 concentrations (Kornarit et al., 2010).

In Korea, Moon et al. (2015) tested the effect of mechanical ventilation on indoor NO2 concentrations, and found a higher mean NO2 level in classrooms when mechanical ventilation was off (50.7 μg/m3) than when mechanical ventilation was on (45.3 μg/m3). They concluded that the operation of ventilation systems could decrease the levels of indoor pollutants in the classrooms and that adequate ventilation by means of a mechanical ventilation system can play a key role in improving the IAQ in school buildings. In Australia, Challoner and Gill (2014) found that lower indoor NO2 concentrations were present in naturally ventilated buildings compared to buildings with centralized mechanical ventilation systems. These observations were attributed to the deposition of NO2 on the internal surfaces as well as to possible heterogeneous reactions in these older buildings.

### 3.8. Health effects of indoor exposure to NO2

In several school studies, exposure to concentrations ranging from 34.8 to 44.0 μg/m3 were related to several health effects, such as increased respiratory symptoms, exacerbation of allergies, current wheeze, current itchy skin, and current conjunctivitis, as well as asthma occurrence (Janssen et al., 2003; Kim et al., 2004; Mi et al., 2006; Van Roosbroeck et al., 2007). For example, Mi et al. (2006) found a significant association between indoor NO2 current asthma (odds ratio, OR = 1.18 for 10 μg/m3; P < 0.01) and asthma medication (OR = 1.45 for 10 μg/m3; P < 0.01). Zhao et al. (2008) concluded, in their study carried out in a coal-burning city in north China, that pupils’ asthmatic symptoms – either wheeze or daytime or nocturnal attacks of breathlessness – were positively associated with indoor and outdoor SO2, NO2, or formaldehyde. Recently, Gaffin et al. (2018) found that NO2 levels were associated highly with airflow obstruction (each 10 ppb increase in NO2 concentration was associated with a 5% decrease in FEV1 (forced expiration)/FVC (forced vital capacity) ratio). The percent predicted forced expiratory flow between the 25th and 75th percentile of forced vital capacity was also inversely associated with higher NO2 exposure. There was no significant association of NO2 levels with the percent predicted FEV1, fraction of exhaled nitric oxide, or with asthma symptoms. In addition, there was no effect modification of atopy on lung function or symptom outcomes.

Zhang et al. (2011) reported that NO2 was associated with mucosal symptoms (OR = 1.13 per 10 μg/m3), and symptoms improved when away from school (OR = 1.13 per 10 μg/m3). Later Zhang et al. (2014) found that outdoor NO2 levels were associated with SBS. There were positive associations between NO2 concentration and increased incidence of skin, mucosal and general symptoms and a decreased remission of school-related symptoms. Chatzidakiou et al. (2015a) concluded that exposure to traffic-related pollutants, such as NO2, ozone (O3) and tetrachloroethylene (T4 CE), associated with mucosal symptoms, also increased dissatisfaction with indoor air quality (IAQ) and, therefore, perceived IAQ might be a first indication of exposure. Annese-Maiano et al. (2012) discovered an increased prevalence of past year asthma in the classrooms with high levels of PM1.5 (OR 1.21; 95% CI (confidence interval) 1.05 to 1.39), acrolein (OR 1.22; 95% CI 1.09 to 1.38) and NO2 (OR 1.16; 95% CI 0.95 to 1.41) compared with others. Norbäck et al. (2017b) found that indoor NO2 in school buildings was associated with ocular symptoms (p < 0.001) and fatigue (p = 0.01) among students in Malaysia. In their other school study in Malaysia, Norbäck et al. (2017a) concluded that there were no associations between NO2 in classroom air and respiratory health. Concentration of NO2 in schools has been associated also with increased behavioral problems in schoolchildren (Forns et al., 2016).

There is some evidence suggesting that the indoor peak concentrations might be more important than the average exposure. Pilotto et al. (1997) found that exposure to NO2 at hourly peaks of the order of > or = 80 ppb (=153 μg/m3), compared with background levels of 20 ppb (=38.3 μg/m3), was associated with a significant increase in sore throat, colds and absences from school. This reported hourly peak levels are below the WHO (2010) guideline of 200 μg/m3 for peak NO2 concentrations. Marks et al. (2010) concluded that, when compared with exposure to flued gas heaters, classroom exposure to newer-style low-NOx unflued gas heaters (mean NO2 31.6 ppb = 60.4 μg/m3) increased respiratory symptoms, particularly in atopic children, but was not associated with measurable adverse changes in lung function.

There are only few studies reporting health effects of NO2 exposure in offices; Mennies et al. (1996) reported that mucosal symptoms were increased with the 52 μg/m3 average concentration of NO2. Liao et al. (1991) found that NO2 levels (median 16 μg/m3) did not show any relationship to occupier comfort or sick-building syndrome (SBS) complaints. Gupta et al. (2007) studied the relation between the average SBS score (quantification of the perceptions of the users regarding IAQ was done by converting their responses to a SBS score) and indoor concentrations of four pollutants, namely NO2, SO2 (sulphur dioxide), SPM (suspended particulate matter) and CO (carbon monoxide), and they found a direct relation only between the average SBS score and CO2 concentration. Glas et al. (2015) concluded that no consistent differences in NO2 exposure (NO2 concentration 0.26–110 μg/m3) odds ratios were found between cases and controls or for individual symptoms.

### 4. Conclusions

This review was prepared with the goal of providing a summary of the existing knowledge on global and local exposure to NO2 in school and office environments as well as on the factors controlling the exposure. Our study revealed that there were considerable correlations between indoor and outdoor NO2 concentrations for school and office buildings, and NO2 concentrations in ambient air differ widely, depending on the region, local conditions, traffic volume, and season. The calculated median and mean concentration of NO2 in school and office buildings was considerably lower than the WHO guideline of 40 μg/m3 for NO2 as the annual mean concentration. However, there are situations in school and office settings in which the WHO guideline was exceeded. In addition to the main sources of indoor NO2 pollutants – nearby traffic and industry – the type of indoor air heaters considerably affected the indoor NO2 concentrations. The mean indoor NO2 concentration in schools and in offices was considerably higher in Oceania and Asia than in Europe, and generally higher during the winter season. The type of ventilation and air exchange rates were significantly related to indoor NO2 concentrations.
associated with indoor NO2 levels and chemical reactions on material surfaces accelerated the depletion of indoor NO2. Ozone and NO2 contribute to gas phase indoor chemistry by formation of the nitrate radical. In the discussion of guideline values (ambient and indoor air), it should always be kept in mind that NO2 is the most important precursor for tropospheric ozone in ambient air. On sunny days, high NO2 concentrations trigger high ozone concentrations.

Although it is difficult to identify a priori cost-effective strategies for reducing traffic pollution in most cities, the following important things should be considered for reducing the indoor NO2 concentration to below the WHO guideline: i) city planning to situate new schools away from roads with heavy traffic; ii) reduction in the use of NO2-releasing heaters, iii) indoor environment planning (placing classrooms facing parks, yards, or the calmest street around the school instead of facing the busiest road); iv) increased attention to the efficiency of the ventilation systems and to appropriate and sufficient exchange of air in rooms, mechanical ventilation with an air purification system in new school buildings; v) Location planning of ventilating windows or intake for new schools considering outdoor sources of NO2 and keeping windows closed when the ambient NO2 concentration is high; and vi) reduction of the permeability of NO2 by increasing the airtightness of the building envelope.

When evaluating individual exposure, the ambient NO2 concentration alone is not a suitable surrogate, and factors affecting personal NO2 exposure, especially activity patterns (e.g., opening windows and using NO2-releasing devices), and outdoor activities should be taken into account. Short-term peak levels of exposure are also important in relation to adverse respiratory effects associated with NO2 exposure.

Declaration of Competing Interest

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

Acknowledgements

H. Salonen is grateful to the Business Finland (grant 4098/31/2015), for financial support for her research visit to the Queensland University of Technology (Brisbane, Australia) and working with this research. T. Salthammer and L. Morawska are grateful to the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) (grant IG II 2 - 45083-4/0) for financial support. The authors thank the German Committee on Indoor Guide Values (AIR) for communicating their results before publication. The authors also thank PhD (Tech) Tuomas Tala for his help with Figs. 2–5, PhD student Nini Pang for her help with SM Table S5, and PhD (Tech) Claudia Dell’Era for the language editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.05.081.

References
