Corrections

ENVIRONMENTAL SCIENCES

The authors note that the author name Coralie Schoemaker should instead appear as Coralie Schoemaecker.

The authors note also that, in the affiliations, the text, "Laboratoire de Physicochimie des Processus de la Combustion et de l’Atmosphère, Centre National de la Recherche Scientifique Unité Mixte de Recherche 8522, Université des Sciences et Technologies de Lille, 59655 Villenueve d’Ascq Cedex, Lille, France." should appear as "Université Lille 1 Sciences et Technologies, Physicochimie des Processus de la Combustion et de l’Atmosphère, Centre National de la Recherche Scientifique, Unité Mixte de Recherche 8522, Cité Scientifique Bât. C11, F-59655 Villenneuve d’Ascq, France."

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The corrected author and affiliation lines appear below. The online version has been corrected.

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MICROBIOLOGY

The authors note that Scott H. Robbins, S. Whitney Barnes, and John R. Walker should be added to the author list between Klaus Fütterer and William R. Jacobs. Jr. Scott H. Robbins should be credited with designing research and performing research. S. Whitney Barnes and John R. Walker should be credited with analyzing data.

The authors also note that the author name Kai Johnson should instead appear as Kai Johnsson.

The corrected author line, affiliation line, and author contributions appear below. The online version has been corrected.

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IMMUNOLOGY

The authors note that Fig. 5 appeared incorrectly. The figure has been revised to indicate where gels were rearranged and where extraneous data has been removed. The corrected figure and its legend appear below.

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Fig. 5. FOXO functions. (A) Increased FOXO target gene (Bim) mRNA. Splenic B cells were left untreated (non) or stimulated for 2 or 6 h with 10 μg/mL anti-IgM or 10 μg/mL anti-IgM plus 1 μg/mL CD40L (IgM/CD40). Bim mRNA was determined by qRT-PCR. Data are Bim mRNA relative to 18S RNA. ΔΔCt values were normalized to WT values in untreated controls (fold change, 1). *P < 0.05. (B) Altered proteins. Western blot of FOXO1, p27, Bim, and β-actin proteins in resting WT and KO B cells. (C) Normal FOXO1 mRNA. qRT-PCR of FOXO1 mRNA in resting WT and KO B cells. (D) Restoration of FOXO1 protein by proteasome inhibition. Purified WT and KO B cells were left untreated (−) or treated with MG132 (20 μM) for 1 h at 37 °C. Nuclear (N) and cytosolic (C) fractions of cells were immunoblotted to detect FOXO1 protein, P-S6 ribosomal protein (Ser240/244; p-rpS6), and total S6 ribosomal protein (rpS6; loading control for cytosol). (E) FOXO1 interacts directly with 14-3-3σ protein under overexpression conditions. 293T cells were transiently transfected with plasmid encoding His-tagged 14-3-3σ, without (−) or with (+) plasmid encoding Flag-tagged FOXO1. At 2 d after transfection, total lysates were immunoprecipitated with beads conjugated to anti-His (IP: His) or anti-Flag (IP: Flag) and immunoblotted to detect FOXO1 and 14-3-3σ. (F) FOXO1 interacts directly with endogenous 14-3-3σ in the cytosol. Ramos B cells were left untreated (0) or stimulated with anti-human IgM for 5 or 30 min. Nuclear (N) and cytosolic (C) fractions of cells were immunoprecipitated with anti-14-3-3σ or anti-FOXO1 and immunoblotted to detect 14-3-3σ and FOXO1. (G) Altered signaling downstream of BCR engagement. Purified WT and KO B cells were left untreated (0) or stimulated with 10 μg/mL anti-IgM for the indicated times. Lysates were immunoblotted to detect P-Erk1/2, total Erk1/2, P-JNK1/2, P-Akt (S473), and total Akt.

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Unexpectedly high indoor hydroxyl radical concentrations associated with nitrous acid

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The hydroxyl (OH) radical is the most important oxidant in the atmosphere since it controls its self-oxidizing capacity. The main sources of OH radicals are the photolysis of ozone and the photooxidation of nitrous acid (HONO). Due to the attenuation of solar radiation in the indoor environment, the possibility of OH formation through photolytic pathways indoors has been ignored up to now. In the indoor air, the ozonolysis of alkenes has been suggested as an alternative route of OH formation. Models and indirect measurements performed up to now according to this hypothesis suggest concentrations of OH radicals on the order of 10−10 molecules per cubic centimeter. Here, we present direct measurements of significant amounts of OH radicals of up to 1.8×105 molecules per cubic centimeter during an experimental campaign carried out in a school classroom in Marseille. This concentration is on the same order of magnitude of outdoor OH levels in the urban scenario. We also show that photolysis of HONO is an important source of OH radicals indoors under certain conditions (i.e., direct solar irradiation inside the room). Additionally, the OH concentrations were found to follow a linear dependence with the product [HONO]·[HONO]. This was also supported by using a simple quasiphotostationary state model on the OH radical budget. These findings force a change in our understanding of indoor air quality because the reactivity linked to OH would involve formation of secondary species through chemical reactions that are potentially more hazardous than the primary pollutants in the indoor air.

The hydroxyl (OH) radical is the key species of the photooxidation cycles in the atmosphere that oxidize primary volatile organic compounds (VOCs) to form secondary oxygenated gas species and aerosols, which can be toxic and often carcinogenic (1).

Considering that people spend on average 80–90% of their time indoors, knowledge about the formation processes of OH radicals (2) and their concentration levels indoors is of crucial importance to assess the impact of human exposure to the secondary pollutants potentially derived from indoor photooxidation processes (3).

Until now, only indirect techniques have been applied to estimate OH concentrations indoors (3–5), which have determined values up to 7×107 molecules per cubic centimeter (molecules cm−3). These studies measure the decay of organic tracers reacting rapidly and exclusively with OH radicals. The OH concentrations determined in this way are averaged over the entire volume of the room with a time resolution in the hour range. However, local and short-term concentrations of OH radicals can be considerably higher. These considerations led Weschler to conclude in his 2011 review (6) that indirect techniques were not fully appropriate to determine OH radical concentrations and that there is a critical need for real-time OH measurements.

In addition, modeling studies (7–10) have been carried out to assess indoor air quality and OH concentrations. Carslaw (10) predicted indoor OH concentrations up to 4×106 molecules cm−3. Potential sources of OH radicals considered in those studies included the reaction between hydroperoxyl (HO2) and nitric oxide (NO2) the reaction between ozone (O3) and alkenes; and the photolysis of O3 (λ < 320 nm), nitric acid (HONO; λ < 400 nm), and hydrogen peroxide (λ < 360 nm). In the work of Carslaw (10), HONO photolysis was assigned a minor contribution of 12% to the total production of OH radicals in indoor environments compared with the 88% attributed to the ozonolysis of alkenes/monoterpenes. The impact of these two reactions on OH radical concentrations in indoor environments was also modeled by White et al. (5). The outcome of this model study (5) exhibited OH values on the order of ~104 molecules cm−3.

Maisey et al. (11) carried out another modeling study on the effect of structural characteristics of buildings on the chemistry of the air indoors by changing four model variables: attenuation of photolysis rates determined by window size and glass composition and surface-to-volume ratios based on room size and air exchange rates. Much higher OH concentrations were calculated from this model (11) than previously reported. However, to perform such calculations, significantly high transmission values of visible (VIS) and UV light through glass were used [up to 0.8 in the VIS light and 0.6 in the UVA light for their high tailored (HT) model reference].

Maisey et al. (12) modeled the seasonal influence on reactive indoor air pollution chemistry. In that study, estimations on OH concentrations were in agreement with Carslaw’s reported values (10). However, unrealistically low HONO concentration values (300 parts per trillion, ppt) (13) were assumed for the calculations, which in reality are more typical outdoors.

Weschler and Shields (14) assessed the effect of air exchange rates. Certain chemicals found indoors can hydrolyze under commonly occurring indoor conditions (ref. 6 and references therein). Weschler (6) stated that in the gas phase, these hydrolysis reactions tend to occur too slowly to compete with air exchange processes. However, there is ample time for such reactions to occur on surfaces, on which water adsors, particularly in areas of high relative humidity (RH) like the kitchen or the bathroom.

Since the study of Weschler and Shields (8), other indoor pollutants have been identified that may react with O3 to generate OH. These include terpene alcohols (e.g., terpineol, linalool) and constituents of skin oils, such as squalene and unsaturated fatty acids (15). Although O3/squalene reactions on surfaces may not be a substantial source of gas phase OH, this reaction generates 6-methyl-3-hepten-2-one and geranyl acetone in the gas phase, and O3 can react with these unsaturated gas phase products to generate OH (16).


The authors declare no conflict of interest.

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On the other hand, depending on the fraction of UV-VIS light used as input in the model, a drastic impact on the balance of OH radicals can be predicted. Carslaw (10) recommended the determination of photolysis frequencies of key indoor species over the range of wavelengths commonly observed indoors, since the only two available (17, 18) studies show important discrepancies on the attenuation of light to the indoor environment.

In addition, indoor electric lighting, such as compact fluorescent lamps and lamps using light-emitting diodes (19), could provide sufficient light to initiate photochemistry in the indoor environment. The information on the fluxes at different wavelengths emitted by various types of indoor lighting that could have sufficient flux in the 300- to 400-nm range to photolyze HONO should be the subject of future research.

Photolysis of HONO occurring at wavelengths shorter than 405 nm (20), which are available indoors, makes HONO a good candidate for OH production through the following reaction:

\[ \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \]

[Reaction 1]

In the reaction above, \( h \) is the Planck constant and \( \nu \) represents light frequency.

**Results and Discussion**

The quantification of OH radical indoors and its potential sources was carried out during a 2011 summer campaign in a secondary school classroom in Marseille, France, to verify the potential of HONO photolysis as a source of OH radicals in the indoor settings. A wide range of state-of-the-art instrumentation was deployed to obtain a deeper understanding about the concentration of OH radicals, and hence their reactivity in the indoor environments. These measurements involved the quantification of hydrogen oxide (HOx) radical, HONO, \( \text{O}_3 \), nitrogen oxide (NOx), aldehydes, and VOC concentrations, as well as indoor photolysis frequencies. The effect of different parameters [nitrogen dioxide (\( \text{NO}_2 \)) concentration, RH conditions, or light conditions] on the formation of HONO (Reaction 2) (21, 22) and, consequently, on HOx concentrations was investigated:

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]

[Reaction 2]

The concentrations of \( \text{NO}_2 \) in the room were either ambient (no \( \text{NO}_2 \) externally added) or forced (\( \text{NO}_2 \) externally added). RH was also varied in some of the experiments, adding some extra water vapor. Measurements were taken at different times during the day to vary the ambient light conditions.

In addition to Reaction 2, HONO can be formed in the indoor environments via light-induced heterogeneous reactions of \( \text{NO}_2 \) with various indoor surfaces (22–25).

The reader is referred to *Methods* for more details on the experimental development of the campaign and to Table S1 for a detailed description of the experimental protocol throughout the campaign.

As stated above, with respect to HONO formation and OH production, it is essential to characterize the intensity of UV-VIS light available in the indoor environment thoroughly to assess the feasibility of indoor HONO photolysis leading to OH formation. In the present study, we measured the spectral irradiance inside the school classroom with a LICOR LI-1800. This instrument measures spectral irradiance (i.e., photon flux through a flat surface of unity). Actinic fluxes were estimated from spectral irradiance following the procedure described in *SI Methods*. The degree of uncertainty in the estimation of photolysis frequencies (\( J \)) of HONO using a flat collector to determine irradiance and applying the conversion described to estimate actinic fluxes is unknown. Undoubtedly, this estimation will have an impact on the calculations of \( J \) values of HONO, \( \text{NO}_2 \), \( \text{O}_3 \), and formaldehyde performed thereafter.

The calculated \( J \) (HONO) values indoors spanned in the range of \( 1.15 \times 10^{-6} \text{ molecules cm}^{-2} \text{s}^{-1} \) when direct sunlight shone directly into the room (in the evening between 17:00 and 19:00 hours) and decreased to \( 2.5 \times 10^{-7} \text{ molecules cm}^{-2} \text{s}^{-1} \) during the rest of the day. The \( J \) values of other species (\( \text{O}_3 \) and HCHO) that could potentially represent a source of OH were always below the detection limits of the spectroradiometer (\( 10^{-9} \text{ molecules cm}^{-2} \text{s}^{-1} \)), with the only exception being \( \text{HNO}_3 \). (See Fig. S1, corresponding to the July 21, 2011 and July 27, 2011 experiments). This is not surprising, because \( \text{NO}_2 \) is one of the very few atmospheric molecules that absorbs photolyses in the visible range of the solar spectrum (26).

Fig. 1 shows the comparison of the actinic fluxes in the range between 300 and 700 nm measured at different times during the day (July 21, 2011) inside the classroom (at ~2 m from the window).

Maximum actinic fluxes were determined in the afternoon in the period between 17:00 and 19:00 hours. Fig. 1 shows a comparison of the indoor actinic flux (maximum value at 18:38 hours) with the outdoor solar actinic flux obtained at noon on July 21, 2011, using the tropospheric UV and VIS model (version 5.0) (27, 28) at a solar zenith angle of 45°N.

Fig. 2 A and B shows profiles of HONO, OH radicals, \( \text{NO}_2 \), \( \text{O}_3 \), and RH determined in the classroom on the afternoons of July 21, 2011 and July 22, 2011, including the ventilation periods. The conditions shown in Fig. 2 A correspond to ambient conditions, whereas those in Fig. 2 B correspond to manipulated conditions.

The mixing ratios of HONO during the campaign ranged between a few and 12 ppb. These values are in agreement with data reported in the literature (29, 30). It is remarkable that HONO values increased straightaway after closing windows and doors (i.e., after ventilation).

Due to the northwest orientation of the classroom and the season of the year in which the campaign took place, there was no direct irradiation until the sun came down in the evening (between 17:00 and 19:00 hours), providing corresponding peaks of \( J \) (HONO) (Fig. 2 A and B).

Laser-induced fluorescence (LIF) with a fluorescent assay by gas expansion (FAGE) (31), a technique widely used to quantify OH radicals in the atmosphere, was also used in this study to measure OH radical concentration.

The maximum concentrations of OH radicals were attained around 18:00 hours, when direct sunlight shone on the nozzle of the FAGE (hence, coinciding with \( J \) (HONO) peaks). A certain phase lag is observed between the maxima of OH concentrations and \( J \) (HONO) that corresponds to a slight desynchronization of the sunlight on the spectroradiometer and the LIF-FAGE nozzle even though both instruments were placed quite close to each other. This slight phase shift varied between days due to the zenith angle, passing clouds, position of the sun, or even shade from the window frame. These conditions were observed by means of video recordings during the campaign to identify the moments closest to simultaneous irradiation. Due to the fact that the phase lag varied from one couple of peaks to another, even in the same day, we did not attempt to correct for it.

The OH concentrations that we measured at low photolysis frequencies are in agreement with the findings of the modeling study performed by Weschler and Shields (8). Conversely, when direct sunlight was illuminating the room through the windows, an increase in OH concentrations was observed on the order of \( 10^3 \) molecules cm\(^{-2} \) reaching short-term maxima of up to \( 10^4 \) molecules cm\(^{-2} \).

From this finding, we can conclude that the photolysis of HONO was responsible for the peaks in OH concentrations detected. This value (\( 1.8 \times 10^4 \) molecules cm\(^{-2} \)) is on the same order of magnitude as values determined outdoors in the urban scenario (32).

Fig. 3 displays a plot of the measured values of OH radicals vs. \( J \) (HONO) [HONO] during direct irradiation into the classroom (17:00–19:00 hours), demonstrating that the photolysis of HONO is the main source of OH radicals indoors during this time period. For the graphical representation of measured OH radical concentrations ([OH]f), we systematically used two daily times (18:21 and 18:41 hours) for [OH] vs. \( J \) (HONO) after ascertaining from video recordings that these times corresponded to the times when the differences in the shadows were smallest.
A quasiphotostationary state (quasi-PSS) model (33, 34) was also implemented to assist in our assessment of the main sources determining PSS on the 21st July experiment. Fig. 4 presents a graphical plot of the results of the performed PSS model vs. measured values for the time frame (17:00–19:00 hours).

The black circles in Fig. 4 correspond to the modeled values of [OH]PSS, considering the photolysis of HONO as the only source of OH and the reaction of NOx with OH as a sink (Eq. 1) as a function of [OH]PSS:

\[
[OH]_{\text{PSS}} = \left( \frac{J_{\text{HONO}}[\text{HONO}]}{([\text{KOH}+\text{NO}_2][\text{NO}_2] + [\text{KOH}+\text{NO}][\text{NO}])} \right) .
\]

The other plot (red circles) in Fig. 4 displays [OH]PSS values, also considering the ozonolysis of alkenes in the source term (Eq. 2):

\[
[OH]_{\text{PSS}} = \left( \frac{J_{\text{HONO}}[\text{HONO}] + \sum K_{\text{alkenes}}[\text{alkenes}][\text{O}_3]}{([\text{KOH}+\text{NO}_2][\text{NO}_2] + [\text{KOH}+\text{NO}][\text{NO}])} \right) .
\]

According to Elshorbany et al. (33), the reaction between OH and VOC is typically OH-neutral at high NOx greater than a few hundred ppt (in this study, NOx levels were on the order of tens of ppb); that is, any OH that is consumed by a reaction with VOCs is recovered by recycling. Additionally, it has been shown that the PSS approach reproduces an accurate OH concentration at a high NOx level (above 10 ppb, as is the case in this study) in several environments and that below 10 ppb, there is overestimation of up to a factor of 4 (34). Hence, the PSS model is an appropriate tool with which to estimate the OH concentrations in the classroom under the experimental conditions in this study. Performing a detailed box model is beyond the scope of this study.

For the estimation of [OH]PSS, representative alkenes, in terms of their concentrations indoors and their reactivity toward O3 (8), were initially considered. Fig. S2 shows a typical profile for D-limonene on the 21st July evening experiment. However, due to the limitations of the proton transfer reaction (PTR)-MS analysis technique for the measurement of alkenes, as described in the SI Results and Discussion, only D-limonene, isoprene, and styrene were considered for the estimation of OH concentrations derived from the ozonolysis of alkenes in the final PSS model. The concentration of alkenes corresponding to m/z = 137 by PTR-MS was entirely assigned to D-limonene, which was considered to be the alkene with the highest capacity to generate OH radicals in the indoor environment. It is evident (Table S2) that an increase in alkene concentration values was accompanied by a proportional decrease in O3 concentrations (1.7 ppb of D-limonene for 0.24 ppb of O3). Additionally, the O3 profiles displayed in Fig. 2A and B show evidence of an abrupt decrease in O3 concentration on closing doors and windows after ventilation.

This could be due to the activity of alkenes ozonolysis routes in the generation of OH radicals indoors as reported in the literature. The resulting dynamic transport during this step is unimportant overall but plays an important role in the small deviation between the modeled [OH]PSS and measured levels of OH concentrations.

Finally, OH radical concentrations during the night were within LIF-FAGE noise (Fig. S2). During the day, with higher O3 levels, OH concentrations before and after periods of direct solar irradiance are significantly lower than during sunny periods (Fig. 2). These observations provide further evidence that the main source of the peak of OH radical concentrations was the photolysis of HONO.

It is noteworthy that comparable levels of OH were observed during the ventilation period (between the morning and afternoon experiments in the time range of 14:49–15:24 hours on July 21, 2011 and 15:42–15:23 hours on July 22, 2011) (Fig. 2 A and B), during which the FAGE kept measuring with the windows opened. However, the ventilation was performed in such a way that the indoor/outdoor air exchanges were accelerated using four electric fans at full speed and by opening the windows and doors. The resulting dynamic transport during this step is unrealistic for a room but is more representative of outdoor air. The aim was to ensure efficient flushing of the classroom during ventilation. Due to the short lifetime of OH radicals (τ < 1 s), the most reasonable assumption is that the increased concentration of OH radicals was generated in situ. The OH peaks observed during ventilation periods correspond to a remarkable increase in O3 concentration coming from outside (Fig. 2 A and B). A reactivation of the ozonolysis of alkenes due to the increased levels of O3 could explain this observation.

The increased concentration of OH radicals observed during ventilation could also partially be ascribed to higher NO levels, and consequently to the increased reaction of HO2 + NO as a source of OH radicals. This reaction was not considered when the windows and doors were closed because we assumed that the
radicals formed from this reaction were canceled out by other simultaneous reactions, such as VOC + OH. This reaction, which could have reached a stationary state inside the room at levels of NO of ~5 ppb, could also have reactivated when the windows were opened, because the NO levels increased by a factor of 3 or 4.

Carslaw (10) considered that the contribution of the reactions of O₃ with alkenes and HONO photolysis were less significant sources of OH than radical propagation through the reaction of HO₂ + NO. The study of the chemistry of HO₂ is beyond the scope of this study. However, it should be noted that the measured levels of HO₂ radicals were on the order of 10⁷ molecules cm⁻³, which is an order of magnitude lower than those reported by Carslaw (10) for the base case scenario. In Carslaw’s study (10), the production of OH radicals was estimated at a rate of

Fig. 2. (A) Plots of HONO, J(HONO), OH, NO₂, NO, O₃, and RH(%) profiles for the afternoon experiment on July 21, 2011. The blue band corresponds to the ventilation period. The profiles of OH are given in the form of the moving or running average, with a period of 10. (B) Plots of HONO, J(HONO), OH, NO₂, NO, O₃, and RH(%) profiles for the afternoon experiment on July 22, 2011. The blue band corresponds to the ventilation period.

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∼4·10^5 molecules cm^{-3} for the reaction of HO_2 + NO and at a rate of 5·10^5 molecules cm^{-3} when this reaction was considered as a source of OH radicals, together with the ozonolysis of alkenes. J(HONO) did not increase during ventilation and J(O_3), i.e., the photolysis frequency of ozone, experienced an increase of one order of magnitude (from 10^{-8} to 10^{-7} s^{-1}) during ventilation, which is insufficient to justify the increased OH levels.

**Concluding Remarks**

In this study, we show that OH can peak indoors for certain periods of the day (i.e., when the light intensities are highest during periods of direct sunlight shining through the windows) due to photolysis of HONO. OH can also be detected at similar levels when the windows are opened during ventilation, which was also found to cause a rapid decrease of indoor pollutants, such as HONO. During ventilation, the chemistry at the source of OH is different. Despite the fact that different chemical reaction routes are active when the windows are closed than when the windows are opened, the final OH concentrations measured were very similar. Periods of clouds and rain occurred during the campaign, with more intense irradiation through the windows for a short time frame in the evening. Additionally, direct irradiation was only observed at sunset, which posed problems in synchronization of the spectrometer and LIF-FAGE measurements. In future studies, it is strongly recommended to perform campaigns during periods of favorable meteorology and with longer periods of homogeneous irradiation to observe the distribution of OH radical concentrations.

The work of Weschler and Shields (14) focused on the investigation of air exchange rates on the reactivity in the indoor environments. It concluded that the reaction rates of typical indoor pollutants should be of a higher order of magnitude than the air exchange rate in order for the processes induced by reactivity to have a significant impact indoors. We found this to be the case in our study. To illustrate this, we calculated the air removal rate of \( \alpha \)-limonene, the alkene with the highest capacity to generate OH indoors by ozonolysis reactions according to Weschler and Shields (8). A simple calculation to compare the lifetimes of \( \alpha \)-limonene by reactions with OH, O_3, and air exchange shows that the most important removal process for
D-limonene is reaction with OH at ~54 min (at the maximum OH concentration calculated in this work of 1.8 × 105 molecules cm−3). Removal by air exchange would take 1.7 h (taking the average exchange rate calculated in this work of 1.6 × 10−9 s−1; SI Methods). Finally, removal by reactions with O3 would take 11.2 h [rate constant values for reaction with OH and O3 are taken from ref. 8 and references therein]. This calculation indicates that because the levels of concentration of OH radicals found in this study are one order of magnitude higher than predicted before, reactivity with OH becomes relevant because these reactions take place on a smaller time scale than typical air exchange rates indoors.

The conclusions drawn from this study should motivate specific actions aimed at better characterization and understanding of the chemistry of the interior atmosphere. This study’s direct measurements of significant OH radical concentrations in indoor environments should induce a change in our scientific views of indoor air quality and potentially reshape our understanding of indoor chemistry. We observed levels of OH radicals higher than had hitherto been predicted by both models (4, 7) studies. We prove that photolysis of HONO is the primary source of OH radicals under direct sun irradiation inside the room. This finding leads to the possibility of higher chemical reactivity in the indoor environment, which has previously been neglected. Reactions of alkanes and aldehydes, which are ubiquitous indoors, and of aromatics with OH radicals thus may lead to the increased formation of potentially harmful secondary organic aerosols inside.

Methods

The measurements were carried out between July 19 and July 30, 2011, in a classroom of the following dimensions: 7.00 m (length) × 6.50 m (width) × 3.74 (height) m (total volume of 170 m3). There were two large windows with approximate dimension of 2.5 m × 1.2 m. The classroom was oriented northwest. Acetonitrile was added as dilution tracer through the main door before the experiments to measure the air exchange rates. Four powerful fans were installed in the plenum of the roof, ensuring a good mixing in the classroom. The effect of the following parameters on the formation of HONO indoors was tested: RH(%), light intensity, and concentration of NO2. For each of these parameters, four levels were tested. [NO2] was tested at ambient levels and at 50, 70, and 150 ppb. RH% was varied with the aid of a humidifier and was tested at ambient levels and at 50%, 60%, and 90%. Finally, the effect of light intensity on the production of indoor HONO was tested by injecting 50 ppb (base case) of NO2 into the classroom at ambient RH% and performing the experiment at three different periods per day, corresponding to different light intensity levels: (i) (11:00 to 15:00 hours), (ii) (15:00 to 19:00 hours), and (iii) (21:00 to 00:30 hours). Each combination of parameters was repeated at least twice.

The following instruments were used: an O3 analyzer (42i; TEI), a NOx analyzer (49i trace level; TEI), a specific analyzer for the measurement of HONO (NITROMAC), a LIF-FAGE instrument for direct measurements of OH and NO2 radicals, a PTR-TOF-MS for online monitoring of VOCs, and a spectroradiometer (LiCOR) for measuring the spectral irradiance (Table S3).

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