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Measurements and modeling of the spectral properties of sunlight at the irradiated volume and surface of an indoor environment: The impact on the oxidation capacity

Adrien Gandolfo^{1*}, Sabrine Tlili¹, Hui Chen², Alexander Kukui², Amandine Durand¹, Brice Temime-Roussel¹, Jörg Kleffmann³, Henri Wortham¹, Sasho Gligorovski^{1,4}

¹Aix Marseille Université, CNRS, LCE, UMR 7376 Marseille, France
²Université d'Orléans, CNRS-INSU, LPC2E, Orléans, France
³Physical and Theoretical Chemistry, University of Wuppertal, Germany
⁴Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

*Corresponding email: ad.gandolfo@gmail.com

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1 Introduction

The ultraviolet (UV) and visible (VIS) fraction of the sunlight initiates photochemistry in the atmosphere by photolyzing certain molecules into highly reactive species such as the hydroxyl radical (OH). In indoor environments, several field campaigns demonstrated the variability of the actinic flux (and the corresponding photolysis frequencies) depending on windows cut off wavelength of ca. 330-390¹⁻³ nm pointing to the need for direct measurements. In addition, indoor, sunlight irradiation is spatially and temporally variable. A recent model study has illustrated the spatial heterogeneity of compounds as OH, HO₂ and oxidation products under direct irradiation or in the shade⁴. It clearly appears that correctly and accurately assess indoor irradiated volume is of primary importance. To do so, the use of an architectural model can greatly help indoor scientific community¹. Here, we present for the first time, a comprehensive architectural model in combination with direct solar flux measurements to predict the sun irradiation variability in an office indoor environment under various light conditions, different window types and season.

2 Materials/Methods

Time-resolved measurements of key indoor species and actinic flux have been conducted during October 2016, in a building office in Martigues, situated in the southeast of France. Two kinds of glass were studied: one commercial double glass safety window, SP510 Verrissima[®] (Anti-UV) and one simple borosilicate glass (UV-transparent). To model the sunlight beam penetration within the experimental room, we performed a combination of two software: Revit 2018[®] and Autocad 2016[®]. The first was used to construct the building model in his virtual environment and to determine the sun pathway in the shy depending on the time of the day and the day of the year. The second was used to calculate the irradiated surface and volume within the room. The model outputs provide hourly data from 9 am to 5 pm.

3 Results and Discussion

The variation of the irradiated volume within the modeled room is displayed in Figure 1. For the of measurements campaign days (set as the 30^{th} of October), the irradiated volume ranges 0.9 to 6.6 m³ with a maximum at noon and a minimum in the late afternoon (17h). Thus, between ~3 to 20 % of the total volume of the room undergoes



Figure 1: irradiated volume model outputs in Martigues $(43^{\circ}25'0''N, 5^{\circ}2'35''E)$. December, March/September and June are representative of the winter, spring/fall and summer periods. October is representative of the period in wich measurements have been performed

photochemistry involved by direct sunbeam irradiation. Because of the high solar zenithal angle, December is the period that depicted the largest irradiated volume (the chosen modeled day is December the 21^{st} and represents the days subset in the winter period). The maximum is 9.7 m³ at noon and represents almost 30 % of the total volume of the room. At the opposite, in June, the room is not directly irradiated by sunbeams due to the low solar zenithal angle (20° at noon in Martigues). Between both extremes, in March and in September at noon the irradiated volume is $1.7m^3$ (~5% of the total volume).

Indoor cutoff by windows occurs at 320 and 390 nm for the UV-transparent and Anti-UV glasses respectively. Around noon under direct irradiation, the transmittance by the windows, defined as the ratio between the outdoor TUV modeled and indoor measured actinic fluxes, are on average in the range of 0.6 % and 36 % $(300 < \lambda < 400 \text{ nm})$ and 72 % and 83 % $(400 < \lambda < 660 \text{ nm})$ nm) and for the anti-UV and the UV-transparent windows, respectively. The difference of transmittance observed in the visible range between the two glass windows can be ascribed to the quality and the thickness of the glass³. In the near-UV range, the difference between the transmittance values is much more pronounced due to the UV treatment of the Anti-UV window. The photolysis frequencies associated with the measured actinic flux are summarized in table 1. Compounds with a large absorption band in the UV region (HONO, H₂O₂, O₃ or HCHO) present differences in photolysis frequencies between both glass types of 2 to 3 orders of magnitudes. NO₂ and HOCl which both absorb in the UV and in the VIS are less impacted by the UV treatment of the Anti-UV window (a factor of 10 and 5.5 is

measured between photolysis frequencies with both glass windows, respectively).

Table 1: photolysis frequencies of indoor key species under direct sunlight irradiation as a function of window types around noon

	Photolysis frequencies	
	(s^{-1})	
	UV-trans	Anti-UV
$J(HONO)$ (HONO \rightarrow HO+NO)	$4.8 \cdot 10^{-4}$	$4.9 \cdot 10^{-7}$
$J(H_2O_2) (H_2O_2 \rightarrow 2HO)$	$1.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-8}$
$J(O^1D)$ (O ₃ \rightarrow O ₂ +O(¹ D))	9.5·10 ⁻⁷	BDL^{b}
$J(HCHO)_r (HCHO \rightarrow H+HCO)$	$3.5 \cdot 10^{-6}$	BDL^{b}
$J(NO_2) (NO_2 \rightarrow NO+O(^3P))$	$3.1 \cdot 10^{-3}$	$3.1 \cdot 10^{-4}$
$J(NO_3)_m (NO_3 \rightarrow NO+O_2)$	$1.44 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$
$J(NO_3)_r (NO_3 \rightarrow NO_2+O(^3P))$	$1.1 \cdot 10^{-1}$	$1.0 \cdot 10^{-1}$
$J(HOC1)$ (HOC1 \rightarrow HO+C1)	6.2.10-5	3.4.10-6

Nitrate radicals which are VIS sensitive are de facto (quasi) not impacted by the glass changing. Accordingly to the mixing ratio levels observed indoor², HONO depicted the higher OH production rate $(5.9 \cdot 10^7 \text{ molecules.cm}^{-3}.\text{s}^{-1})$ while HOCl photolysis presents intensive OH and Cl radicals production rate events linked to specific cleaning activities with bleach $(3.1 \cdot 10^8 \text{ molecules.cm}^{-3}.\text{s}^{-1})$.

4 Conclusions

We demonstrate that in a south-oriented room in the middle latitude of the northern hemisphere, the integrated irradiated volume is the largest in December. Since under direct irradiation, indoor actinic fluxes are not affected by the season¹ and the distance from the windows², the winter season is the period when the indoor oxidative capacity is the greatest, the latter being mainly drive through HONO photodissociation.

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