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A PRELIMINARY FIELD STUDY OF INDOOR CHEMISTRY

M Nicolas, O Ramalho and F Maupetit*

Centre Scientifique et Technique du Bâtiment (CSTB), F-77447 Marne-la-Vallée, France

ABSTRACT

In order to document the potential impact of outdoor ozone and NO_x on indoor air quality, a field campaign has been organized from June to October 2004 in the CSTB experimental house MARIA. New building materials have been selected and installed in a test room where ventilation conditions are precisely controlled. During the experiments, the mean I/O NO_x (mainly as NO₂) ratio was close to 0.9 regardless of the AER, while the mean ozone ratio was 0.2, 0.09 and 0.04 with a respective AER of 2.4, 1.0 and 0.6 h⁻¹. This sharp depletion of the I/O ozone ratio is an evidence of ozone-induced reactions occurring in the test room both on indoor surfaces and in the gas-phase with specific VOC emitted by the new materials. Detailed experiments performed during photochemical pollution episodes showed the apparition of ozone-initiated reactions products indoors. In particular, formaldehyde, hexanal and presumably submicron particles peaked indoors just after the ozone peaked outdoors.

INDEX TERMS

Ozone, Indoor chemistry, Aldehyde, VOC, particles

INTRODUCTION

Due to specific indoor sources, improvement of building insulation and lower ventilation rates, many indoor pollutants exhibit indoor-to-outdoor (I/O) ratio higher than 1. In opposite, without specific indoor sources, the I/O ozone concentration ratio remains much lower than 1 (Weschler and Shields 1994, Kirchner et al. 2002, Blondeau et al. 2005), indicating ozone-induced reactions occurring indoors (Weschler 2000).

The ozone removal on building products has been experimentally demonstrated (see, e.g., Weschler et al. 1992, Morrison and Nazaroff 2000, Nicolas et al. 2005). Gas-phase reactions between ozone and specific volatile organic compounds frequently found indoors (e.g., terpenes) can also occur if the reaction rate is faster than the air exchange rate (AER) (Weschler 2000). Ozone-induced reaction products, including odorous compounds (Knudsen et al. 2003) but also airway irritants (Wolkoff et al. 2000) and sub-micron particles (Rohr et al. 2003, Sarwar et al. 2003), are suspected to have more important adverse effects on human health than their precursors (Weschler 2004).

The purpose of this study is to assess the impact of outdoor ozone on indoor air quality (IAQ) during photochemical pollution episodes as documented by a field campaign conducted during summer 2004 in a test room of the CSTB experimental house equipped with new building materials.

METHODS

The experiments were organized in one test room of the CSTB Mechanized house for Advanced Research on Indoor Air (MARIA) from June 14, 2004 to October 12, 2004. MARIA has been presented in details elsewhere (Ribéron and O'Kelly 2002). During all experiments, ventilation conditions in the test room were precisely controlled by a mechanical extraction system placed on the door. Three AER conditions have been studied: 0.6, 1.0 and 2.4 h⁻¹. Ozone was monitored alternately outdoors and indoors with a specific analyzer (Environment SA, O₃ 41M model) during all the studied period (June 14, 2004 to October 12, 2004). Nitrogen oxides (NO_x) and nitric oxide (NO) were monitored alternately outdoors and indoors using a specific analyzer (Environment SA, AC 32M, respectively) from July 23 to October 12, 2004. Nitrogen dioxide concentration is directly calculated by the analyzer (NO₂ = NO_x - NO).

Based on the Paris area outdoor air pollution monitoring network (AIRPARIF) daily forecast, specific periods of high outdoor ozone concentrations were selected. During those periods, detailed measurements of VOC and aldehyde compounds were performed on an hourly basis outdoors and indoors. VOC were sampled on Tenax TA

* Corresponding author email: f.maupetit@cstb.fr

adsorbent cartridges (Perkin Elmer) and analyzed by TD/GC/MS/FID according to the ISO/FDIS 16000-6 pre standard. Aldehyde compounds were sampled using DNPH coated cartridges (Waters) and analyzed by HPLC according to the ISO 16000-3 standard. No ozone scrubbers were used for indoor aldehyde measurements since indoor ozone concentrations were rather low. During the second detailed experiment presented in this paper (July 28 – July 30), ultra fine particles (10 nm to 1 µm) were also measured indoors using a CCN counter (TSI, model 3007).

Table 1. Parameters during the experiments

Parameters	
MARIA test room volume	32.3 m ³
Floor (and ceiling) total surface	13 m ²
Wall total surface	37.5 m ²
Carpet surface on floor	10 m ²
Pine wood surface on walls	16 m ²
Polystyrene tiles on ceiling	11.5 m ²
Air exchange rate (AER)	0.6, 1.0, 2.4 h ⁻¹
Experiment duration	June 14, 2004 to October 12, 2004
Installation of the new materials	June 18, 2004

RESULTS

From July 23 to October 12, 2004, NO_x were generally mainly represented by NO₂, except for several NO pollution episodes observed in September with much higher NO concentrations than NO₂ concentrations. NO_x hourly mean concentrations ranged from 4 to 352 µg.m⁻³ outdoors and from 0 to 175 µg.m⁻³ indoors. We observed no significant differences of the NO_x I/O ratio, ranging from 0.83 to 0.94, with the AER. This observation, in accordance with similar experiments (Weschler and Shields 1994, Kirchner et al. 2002, Blondeau et al. 2005), indicates that, in case of outdoor pollution episodes, conventional ventilation systems transfer almost all outdoor pollutant load indoors. NO₂ hourly mean concentrations ranged from 4 to 95 µg.m⁻³ outdoors and from 0 to 47 µg.m⁻³ indoors. The calculated NO₂ I/O mean ratio was 0.85, 0.88 and 0.99 when the AER was respectively 0.6, 1.0 and 2.4 h⁻¹. NO hourly mean concentrations ranged from 0 to 257 µg.m⁻³ outdoors and from 0 to 140 µg.m⁻³ indoors. The calculated NO I/O mean ratio was 0.60, 0.55 and 0.08 when the AER was respectively 0.6, 1.0 and 2.4 h⁻¹. This NO mean ratio is possibly lowered by all indoor measured concentrations lower than 1 ppb assumed as 0. During all experiments, ozone hourly mean concentrations ranged from 0 to 203 µg.m⁻³ outdoors and from 0 to 38 µg.m⁻³ indoors (Figure 1). The ozone I/O ratio was respectively 0.04, 0.09 and 0.20, depending on the AER: the lower the ventilation rate, the lower the ratio. This sharp depletion of the ozone I/O ratio is an evidence of ozone-induced reactions occurring in the test room both on indoor surfaces and in the gas-phase with specific VOC emitted by the new materials.

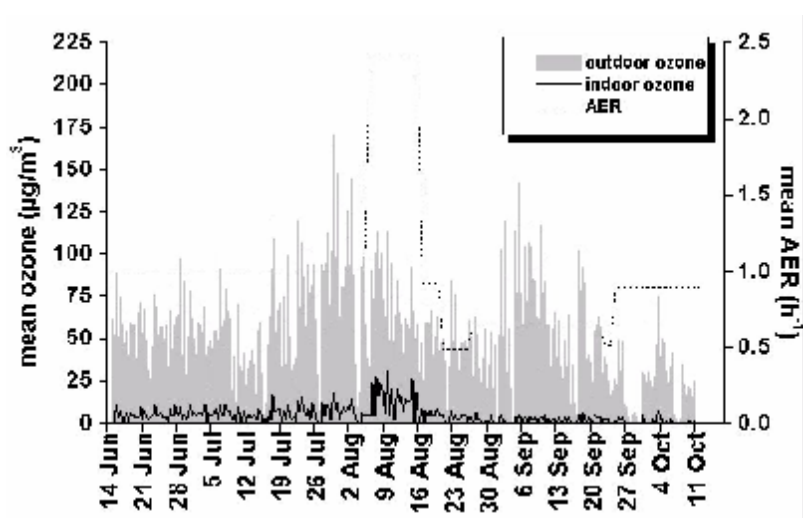


Figure 1. Indoor and outdoor ozone hourly mean concentrations ($\mu\text{g}/\text{m}^3$) and mean AER (h^{-1}) from June 14 to October 12, 2004

DISCUSSION

On June 15 and 16, a first detailed experiment (hereafter referred to as “without new materials”) was performed in the test room (unpainted concrete as flooring, walls in painted gypsum boards and ceiling in painted concrete) before installation of new building materials. Then on June 18, a carpet with rubber backing was installed on the floor (without adhesive). Pine wood boards were also installed on the half of the total wall surface and polystyrene acoustic tiles fixed on the ceiling of the MARIA test room (Table 1). From July 28 to July 30, a second detailed experiment (hereafter referred to as “with new materials”) was performed. Characteristics of those two detailed experiments are listed in Table 2 and observed data are illustrated on Figures 2 and 3.

Table 2. Parameters during the 2 detailed experiments

Experiment Date	Without new materials June 15-16, 2004		With new materials July 28-30, 2004	
	Indoors	Outdoors	Indoors	Outdoors
	Mean temperature ($^{\circ}\text{C}$)	26	21	28
Mean relative humidity (%)	45	62	39	51
Mean ozone ($\mu\text{g}\cdot\text{m}^{-3}$)	6	60	8	84
Mean formaldehyde ($\mu\text{g}\cdot\text{m}^{-3}$)	105	1	143	5
Mean hexaldehyde ($\mu\text{g}\cdot\text{m}^{-3}$)	10	1	31	1
Mean alpha-pinene ($\mu\text{g}\cdot\text{m}^{-3}$)	2	< 1	238	< 1

The two detailed experiments were relatively similar in terms of mean temperature even if indoor and outdoor temperatures were a little higher on July 29 and 30 than on June 15-16 and July 28. Outdoor ozone hourly mean concentrations were also a little higher on the experiment “with new materials” than on the experiment “without new materials” (Figures 2 and 3) but the ozone I/O mean ratio was similar for the two experiments because ozone is already efficiently removed on raw products of the test room (without new products). As detailed in discussion below; major differences between the two experiments are observed in the identified reaction products.

Formaldehyde and hexaldehyde are the major compounds measured indoors during the two experiments and their outdoor concentrations are negligible compared to their concentrations measured indoors (Table 2). After installation of the new products, the major VOC measured indoors were terpenes: alpha-pinene, beta-pinene, limonene.

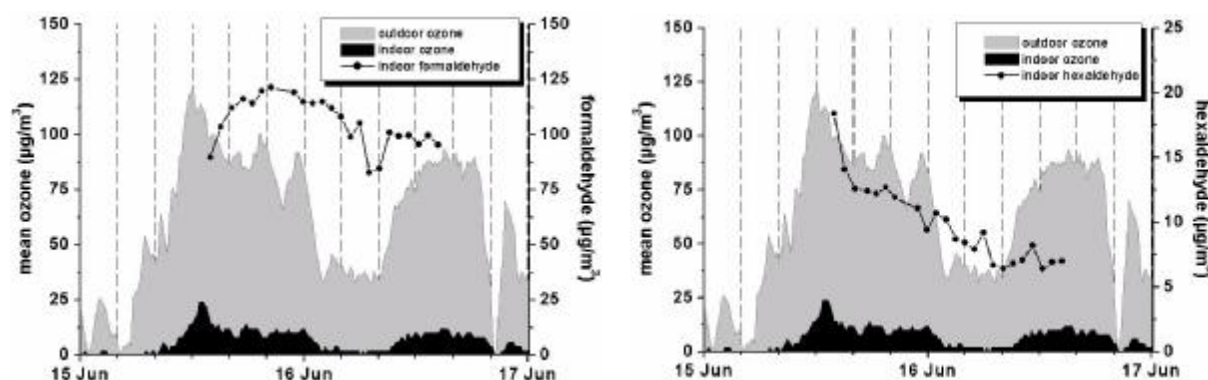


Figure 2. Indoor and outdoor ozone quarter-hour mean concentrations ($\mu\text{g}/\text{m}^3$), indoor formaldehyde (left) and hexaldehyde (right) concentrations ($\mu\text{g}/\text{m}^3$) on June 15 and 16, 2004

Formaldehyde and hexaldehyde indoor concentrations slowly decrease but no clear daily pattern seems to appear during the “without new materials” experiment (Figure 2).

During the “with new materials” experiment (Figure 3), outdoor (and indoor) ozone concentrations peak between 12 a.m. and 8 p.m. (UT). Both formaldehyde and hexaldehyde indoor concentrations exhibit the same daily evolution with a maximum around 8 p.m. (UT) when ozone concentrations begin to decrease. We also plotted submicron particles measured indoors on Figure 3. Since we had only one particle counter available, outdoor particles were not measured. Nevertheless, a maximum of indoor submicron particles is also observed around 8 p.m. (UT) on July 28, July 29 and presumably July 30, in a striking coincidence with formaldehyde and hexaldehyde.

Even if we cannot totally rule out an effect of temperature on formaldehyde emission by building materials (since indoor temperature slightly increases during the day), those measurements suggest that formaldehyde, hexaldehyde, and presumably submicron particles are produced in the test room by ozone-initiated reactions. Since we did not observe such reactions during the “without new materials” experiment, the presence of terpene, and in particular of pinene and limonene, seems to play a key role in ozone-initiated reactions. But contrary to preliminary observations in MARIA where both indoor concentrations of alpha- and beta-pinene were depleted while formaldehyde concentrations increased (Nicolas et al. 2003), no clear evolution of indoor concentrations of alpha-pinene and limonene (not presented in the paper) was observed during the experiment “with new materials”.

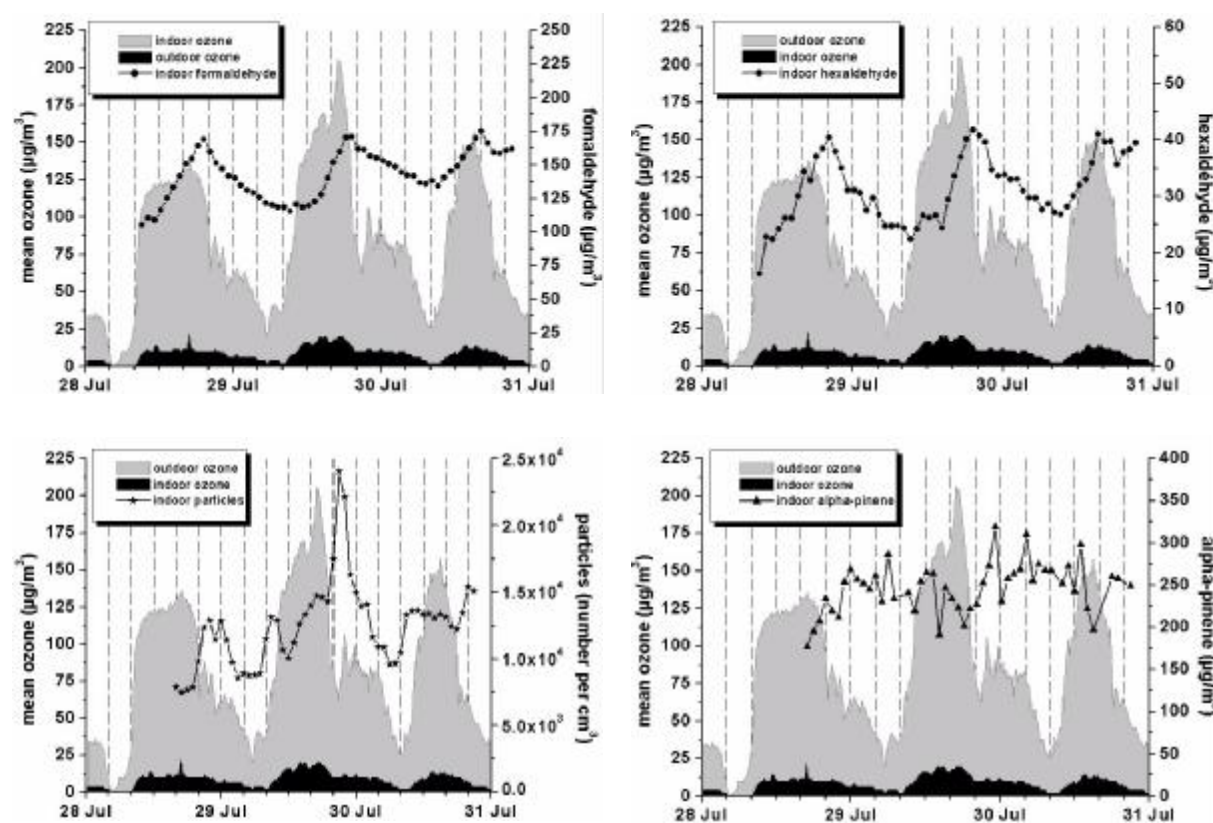


Figure 3. Indoor and outdoor ozone quarter-hour mean concentrations ($\mu\text{g}/\text{m}^3$), indoor formaldehyde (top left), hexaldehyde (top right), particles (bottom left) and alpha-pinene (bottom right) concentrations ($\mu\text{g}/\text{m}^3$) on July 28-30, 2004

At this stage, it is relatively difficult to differentiate the relative contributions of heterogeneous reactions on indoor surfaces and gas-phase reactions. Because of large surface-to-volume ratio of indoor environments, reactions on indoor surfaces represent a significant sink of ozone (Nazaroff et al. 2003). The ozone removal on the polystyrene ceiling tile, the carpet and the pine wood board (tested separately) is respectively 27%, 55 %, and 77 % (Nicolas et al. 2005). For the ceiling tile and the carpet, this removal is presumably totally due to surface reactions. During the two detailed experiments, the ozone removal measured in the MARIA test room is higher (90 %) than measured on each of the materials. This observation is caused by an increase of indoor surfaces potentially available for reaction with ozone and by the occurrence of gas-phase reactions. Increasing available indoor surfaces (simulated by adding acoustic tiles in a room) enhances ozone removal (Kirchner et al. 2002). Submicron particle formation in the test room supports the hypothesis of the occurrence of homogeneous reactions between ozone and terpenes (Rohr et al. 2003, Sarwar et al. 2003) in addition to heterogeneous reactions on surfaces.



CONCLUSION AND IMPLICATIONS

Field experiments conducted from June 14 to October 12, 2004 in the CSTB experimental house MARIA provide indications of the impact of photochemical pollutants on indoor chemistry. NO_x concentrations measured indoors represent almost 90 % of outdoor concentrations, regardless of the AER, indicating that conventional ventilation systems transfer almost all outdoor pollution load indoors. On the other hand, ozone concentrations measured indoors represent only 5 % to 20 % of outdoor concentrations, depending on the AER. This observation is an evidence of ozone-induced reactions occurring indoors on indoor surfaces and in the gas-phase with specific VOC. In particular, when terpene compounds are emitted indoors from building materials (as simulated in our experiments) or from other sources such as cleaning products or air fresheners, secondary emissions of carbonyl compounds (formaldehyde, hexaldehyde) and submicron particles are identified. In case of outdoor ozone pollution forecast, people with respiratory problems are advised to avoid important activities outdoors and to stay at home. Therefore indoor chemistry has to be taken into consideration, for instance in ventilation system design, in order to prevent the occurrence indoors of ozone-induced reaction products, which can be more harmful than their precursors.

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