

Impact of ozone on indoor air quality: a preliminary field study

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ABSTRACT

The purpose of this paper is to document the potential impact on indoor air quality of outdoor ozone during photochemical pollution episodes. A preliminary one-day experiment was conducted during summer 2002 in a room of the CSTB experimental house MARIA. Ozone, VOC and aldehyde concentrations were monitored outdoors and indoors from 8 a.m. to 8 p.m. Outdoor ozone hourly mean concentrations increased from 30 to 100 $\mu\text{g}/\text{m}^3$ during the day. The indoor to outdoor ratio ranged from 0.10 to 0.25, indicating possible ozone-induced reactions occurring indoors. α -Pinene concentrations decreased from 30 to 15 $\mu\text{g}/\text{m}^3$ suggesting indoor gas phase reactions. At the same time, formaldehyde concentrations increased from 70 to 100 $\mu\text{g}/\text{m}^3$. Both heterogeneous reactions of ozone with building products and gas phase reactions of ozone with some indoor pollutants (mainly terpenes) could produce secondary pollutants, such as aldehydes, as observed during this experiment.

INDEX TERMS

Ozone; Indoor chemistry; Aldehydes; VOC; Modelling

INTRODUCTION

Indoor ozone concentration depends on the outdoor concentration, the air exchange rate (AER), the indoor sources, the ozone removal on indoor surfaces and/or reactions with indoor pollutants. Without specific indoor sources, the indoor/outdoor ozone concentration ratio is generally 0.2–0.7 (Kirchner *et al.*, 2002), indicating ozone-induced reactions occurring indoors (Weschler, 2000).

The ozone removal on surfaces of building products has been experimentally demonstrated (see, e.g., Morrison and Nazaroff, 2002; Nicolas *et al.*, 2003). Ozone can also react with specific volatile organic compounds (VOC) which can be found indoors, if the reaction rate is faster than the AER, e.g. with unsaturated hydrocarbons (Weschler, 2000).

Ozone-induced reactions negatively impact indoor air quality (IAQ) since they produce secondary pollutants, mainly aldehydes which are known irritants (Weschler, 2000; Morrison and Nazaroff, 2002) and odorous compounds (Knudsen *et al.*, 2002), and also sub-micron particles (Wainman *et al.*, 2000).

A preliminary field study was organized in order to document the impact on IAQ of outdoor ozone during summer air pollution episodes. For this purpose, a one-day experiment was conducted in a test room of the CSTB experimental house MARIA under controlled ventilation conditions. Ozone, VOC and carbonyl compounds were monitored indoors and outdoors. This paper presents the results of this first experiment.

METHODS

The experiment was organized on 7 August 2002 in one test room of the CSTB Mechanized house for Advanced Research on Indoor Air (MARIA) (Table 1). MARIA has been presented in detail elsewhere (Ribéron and O'Kelly, 2002). One week before this experiment, a pinewood flooring material has been installed without any adhesive on the concrete floor.

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Ventilation conditions were controlled by a mechanical extraction system placed on the door. Details on the experimental protocol can be found in Akoua *et al.* (2003).

Table 1 Parameters during the experiment

Parameters	7 August 2002
Temperature	Indoors: 21–24°C/outdoors: 15–28°C
Relative humidity	Indoors: 49–61 %/outdoors: 35–89%
MARIA test room volume	32.3 m ³
MARIA test room total surface	12.9 m ²
Pinewood flooring surface	10.8 m ²
Pinewood flooring loading factor	0.334 m ² /m ³
Air exchange rate (AER)	1 h ⁻¹
Test duration	8 a.m. to 8 p.m.

Ozone was monitored alternately outdoors and indoors using a photometric analyser (Environnement SA, O₃ 41M model). Aldehyde compounds were measured according to the ISO 16000-3 standard (ISO, 2001). Sampling was performed using DNPH coated cartridges (Waters) and potassium iodide (KI) ozone scrubbers (Waters) in order to prevent interferences of ozone and sampled compounds during sampling. VOC were measured according to the ISO/DIS 16000-6.2 draft standard (ISO, 2002). Sampling was performed using TENAX TA adsorbent tubes (Perkin Elmer). VOC results have to be examined with caution since no ozone scrubbers were used during sampling. Analytical methods are presented in detail elsewhere (Nicolas *et al.*, 2003).

RESULTS

On August 7, 2002, outdoor ozone concentrations increased during the morning and remained around 100 µg/m³ throughout the afternoon (Figure 1). The indoor-to-outdoor (I/O) ozone concentration ratio ranged from 0.10 to 0.25.

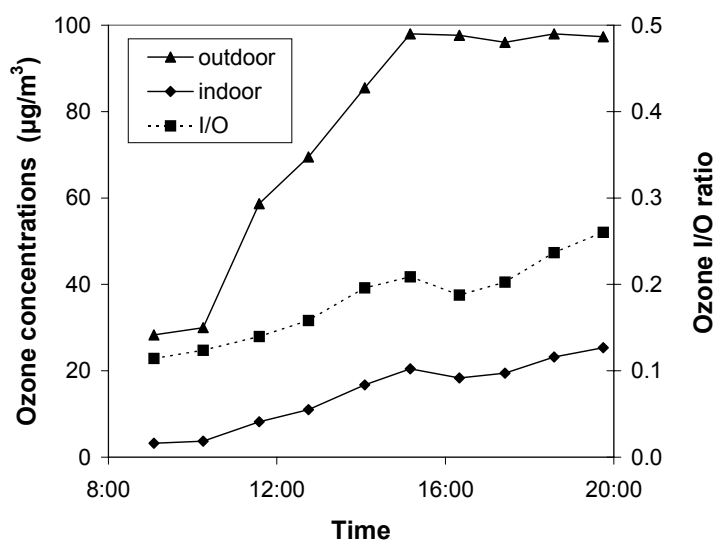


Figure 1 Outdoor and indoor hourly mean ozone concentrations and I/O ratio.

VOC emissions of the flooring material are dominated by terpenes (mainly pinene, limonene and longifolene) and aldehydes (hexanal, octanal and nonanal). α -Pinene and β -pinene concentrations during the experiment are illustrated in Figure 2 (left). A sharp decrease of both α -pinene and β -pinene concentrations in the afternoon (2–6 p.m.) is observed, while

outdoor ozone is at its maximum. Formaldehyde concentrations during the experiment are also illustrated on Figure 2 (right). A peak in formaldehyde indoor concentrations during the afternoon (up to $100 \mu\text{g}/\text{m}^3$) coincides with maximum outdoor ozone concentration.

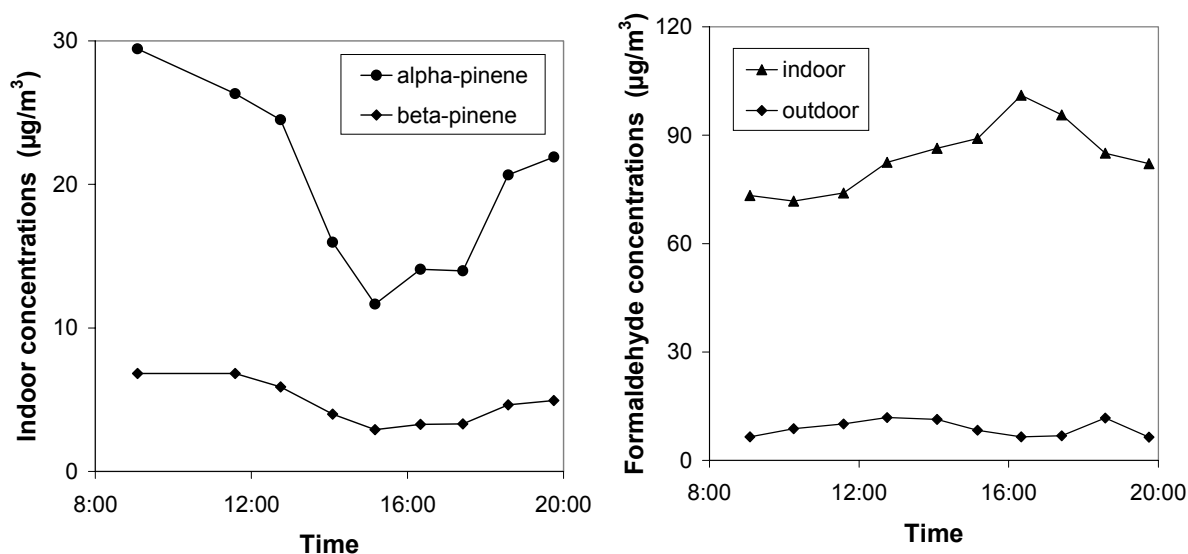


Figure 2 α -Pinene and β -pinene indoor concentrations (left) and formaldehyde indoor and outdoor concentrations (right).

DISCUSSION

Ozone may react with unsaturated indoor species if the reaction rate is faster than AER. Among these compounds, terpenes are compounds that can react fast enough (Weschler, 2000).

We have calculated the ‘ozone loss’, the difference between measured outdoor and indoor ozone concentrations:

$$[\text{O}_3]_{\text{loss}} = [\text{O}_3]_{\text{outdoor}} - [\text{O}_3]_{\text{indoor}} \quad (1)$$

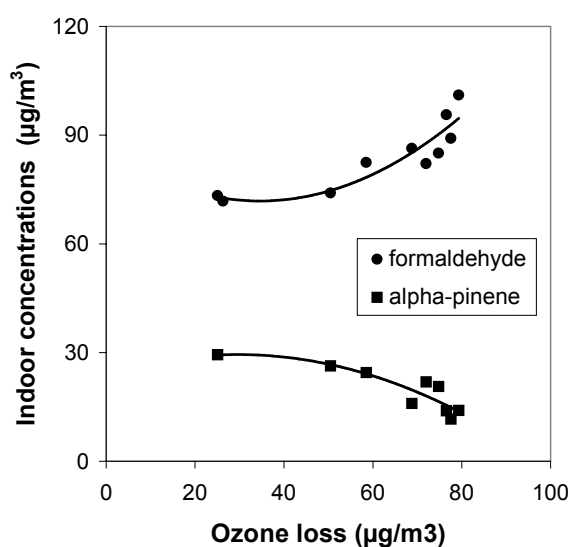


Figure 3 α -Pinene and formaldehyde indoor concentrations as a function of the ‘ozone loss’.

In Figure 3, we have plotted indoor α -pinene and formaldehyde concentrations as a function of the ‘ozone loss’. Indoor variations of α -pinene concentrations decrease as a function of ‘ozone loss’ besides an increase in formaldehyde indoor concentrations. These observations

suggest that gas phase reaction of ozone with α -pinene occurred indoors depleting α -pinene concentrations and that secondary pollutant were generated indoors. Formaldehyde was the main identified secondary pollutant, but we also observed a slight increase of hexaldehyde and acetaldehyde concentrations.

We have calculated indoor ozone concentrations using two different models. The first model is a steady-state model (Nazaroff *et al.*, 1993, Weschler, 2000) assuming no gas phase reactions:

$$\frac{d[O_3]_{\text{outdoor}}}{dt} = \text{AER} \cdot [O_3]_{\text{indoor}} + \Phi_{O_3}(t) - [O_3]_{\text{outdoor}} \cdot \left\{ v_d \left(\frac{S}{V} \right)_{\text{tr}} + \text{AER} \right\} \quad (2)$$

In Eqn (2), $[O_3]$ is the ozone concentration, AER is the air exchange rate, Φ_{O_3} is the indoor ozone emission source, $v_d(S/V)_{\text{tr}}$ is the first-order removal rate constant of ozone in the test room.

We also used the time model (Shair and Heitner, 1974), which also neglects indoor gas phase reactions:

$$V_{\text{tr}} \cdot \frac{d[O_3]_{\text{indoor}}}{dt} = \Phi_{O_3}(t) + v_d \left(\frac{S}{V} \right)_{\text{tr}} \cdot V_{\text{tr}} \cdot [O_3]_{\text{indoor}}(t) + p \cdot \frac{\text{AER}}{V_{\text{tr}}} \cdot [O_3]_{\text{outdoor}}(t) - \frac{\text{AER}}{V_{\text{tr}}} \cdot [O_3]_{\text{indoor}}(t) \quad (3)$$

In Eqn (3), $[O_3]$ is the ozone concentration, AER is the air exchange rate, Φ_{O_3} is the indoor ozone emission source, $v_d(S/V)_{\text{tr}}$ is the first-order removal rate constant of ozone in the test room, V_{tr} is the volume of the test room, p is the penetration coefficient of ozone in this room. In this experiment, there was no indoor specific source of ozone ($\Phi_{O_3} = 0$). Penetration coefficient of ozone in the room is assumed to be 1.

The first-order ozone removal rate constant in the test room is the combination of pinewood on the floor and walls and ceiling surfaces. For the modelling, we used ozone deposition velocity on pinewood experimentally measured by Nicolas *et al.* (2003) and ozone deposition velocity on walls and ceiling of a dwelling observed by Kirchner *et al.* (2002). Table 2 presents the parameters used for both simulations.

Table 2 Parameters used for indoor ozone concentration simulations

	Pinewood	Walls and ceiling
S	10.8 m ²	54.1 m ²
V	32.3 m ³	32.3 m ³
AER	1 h ⁻¹	1 h ⁻¹
v_d	3.9 m/h	1.6 m/h
$v_d(S/V)$	1.3 h ⁻¹	2.7 h ⁻¹

A satisfactory agreement is found between the two models and between predicted and measured indoor ozone concentrations (Figure 4). At the end of the experiment (6–8 p.m.), measured ozone concentrations are slightly higher than predicted.

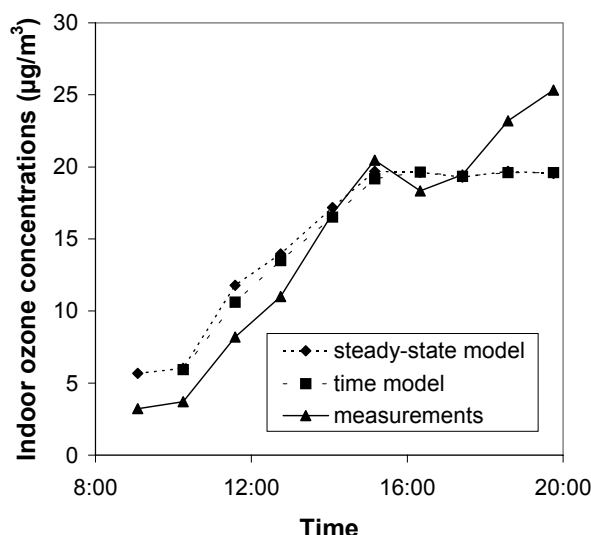


Figure 4 Indoor ozone concentrations measured in test room and predicted.

The observed differences may be due to gas phase reactions which are not taken into account by the two simple models. On the other hand, during this experiment, we have not monitored nitrogen oxides (NO_x), which are closely linked to the ozone chemistry and, therefore, may explain differences in outdoor and indoor ozone concentrations.

It should be noted that the experimental results presented in this paper are limited by the small range of conditions observed during this one-day experiment and that under different outdoor concentrations, climate conditions and air exchange rates, the results would likely have differed, perhaps significantly. Therefore, extended field experiments are necessary to better understand and document the potential impact of outdoor ozone on indoor air quality. Further laboratory experiments are also needed in order to model reactions mechanisms with a broader range of parameters (air exchange rate, outdoor ozone concentration and indoor terpene concentrations).

CONCLUSION AND IMPLICATIONS

This preliminary one-day field experiment organized in the MARIA test house provides indications on the influence of ozone on IAQ during photochemical pollution episodes.

If ozone is significantly removed when transferred indoors, ozone induced reactions with indoor surfaces and with specific VOC affects IAQ and produces secondary pollutants. During this experiment, we have presumably identified both gas phase reactions with terpenes (as indicated by the α -pinene sharp decrease) and heterogeneous reactions on indoor surfaces. Formaldehyde was the major by-product of these ozone-induced reactions.

Further experiments will be conducted in order to describe with more detail the global impact of ozone during photochemical pollution episodes and to better identify secondary pollutants (possibly including sub-micron particles) produced indoors.

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