Experimental study of reactions between ozone and building products

M. Nicolas, O. Ramalho, F. Maupetit*

Centre Scientifique et Technique du Bâtiment (CSTB), F-77421 Marne-la-Vallée, France

ABSTRACT

The purpose of this paper is to present an experimental setup developed to characterize reactions between ozone and building products and document their potential impact on indoor air quality. Preliminary experiments were conducted on four building products: two carpets, a gypsum board and a pine wood board. These preliminary experiments clearly indicate that ozone is significantly removed in contact with the four selected products. Measured ozone removal were around 65% for the two carpets, 70% for the gypsum board and 75% for the pine wood board. In case of exposure to ozone, emissions of building products were modified and reaction products (mainly carbonyl compounds) have been identified. For instance, when exposed to ozone, the carpet with PVC backing shows higher emissions of formaldehyde, the carpet with textile backing emits nonanal and decanal and the pine wood board exhibits increased emissions of hexanal.

INDEX TERMS

Ozone; Indoor chemistry; Aldehydes; Test chambers; Building products emissions

INTRODUCTION

The impact of ozone on indoor air chemistry is receiving special attention of late. Without specific indoor sources (such as laser printers), the indoor/outdoor ozone concentration ratio generally ranges from 0.2 to 0.7 indicating indoor sinks (Weschler, 2000; Kirchner *et al.*, 2002). Ozone removal on surfaces of building products has been demonstrated (Morrison and Nazaroff, 2000, 2002; Kleno *et al.*, 2001). Ozone can also react with NO_x and with some specific volatile organic compounds (VOC), such as terpenes, which are frequently found indoors (Weschler, 2000). Therefore, ozone-induced reactions have a negative impact on indoor air quality since they produce secondary pollutants, mainly aldehydes, which are known irritants (Weschler, 2000; Wolkoff *et al.*, 2000; Morrison and Nazaroff, 2002), odorous compounds (Knudsen *et al.*, 2000; 2002), and also sub-micron particles (Weschler and Shields, 1999; Wainman *et al.*, 2000; Rohr *et al.*, 2003).

In order to document interactions between ozone and building products, an experimental setup based on emission test chamber methods (CEN, 2001) was developed. Its purpose is to document the removal of ozone on the surface of different materials, the influence of ozone on the primary VOC emissions of building products and the identification of secondary emissions. This experimental setup has been tested during preliminary experiments on four building products.

METHODS

The experimental setup has been adapted from emission test chamber methods described in the ENV 13419-1 pre-standard (CEN, 2001). Inert materials (glass and Teflon PFA) have been selected. The setup is composed of two parallel lines containing a mixing chamber and a test chamber where building products are placed (Figure 1). The two lines are supplied with clean air (particles, silica gel, charcoal filtered). The conditions were kept constant during the test (Table 1).

* Corresponding author. E-mail: f.maupetit@cstb.fr

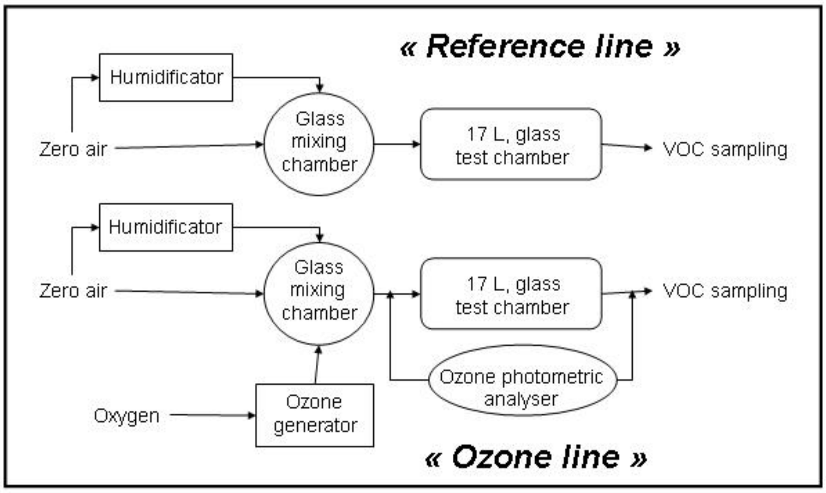

Figure 1 The experimental setup.

The first line (hereafter referred to as 'reference line'), where building products are not exposed to ozone, is used for the measurements of primary VOC emissions from the products. In the second line (hereafter referred to as 'ozone line'), ozone is introduced in the mixing chamber and transferred in the test chamber. Secondary emissions of the building products exposed to ozone are measured at the outlet of the 'ozone line'.

A 105 ± 5 ppb concentration of ozone is generated using pure oxygen (Air Liquide, O_2: 99.999%) through UV light generator (Pen Ray, model SOG 1). Ozone is monitored at the inlet and outlet of the test chamber using a photometric analyser (Environnement SA, model O_3 41M).

Table 1 Emission test parameters selected for the experimental setup

Test parameters	Experimental setup
Temperature	23 ± 2°C
Relative humidity	50 ± 5%
Mixing chamber	Glass, 0.003 m^3
Test chamber (V_c)	Glass, 0.017 m^3
Air flow rate	0.204 $m^3\ h^{-1}$
Air exchange rate (AER)	12 h^{-1}
Test duration	90–120 h

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. Fifteen aldehyde compounds (including formaldehyde) were analysed using HPLC (Waters, model Alliance).

VOCs were measured during the carpet with textile backing experiment according to the ISO/DIS 16000-6.2 draft standard (ISO, 2002). Sampling was performed using TENAX TA adsorbent tubes (Perkin Elmer). VOC analyses were then performed by thermal desorption and gas chromatography (GC) using mass spectrometry detector (MSD) for identification and flame ionization detector (FID) for quantification (Perkin Elmer ATD 400, Varian 3800/Saturn 2000). VOC were semi-quantified using the toluene response factor. VOC results have to be examined with caution since no ozone scrubbers were used during sampling.

Four building products were selected for preliminary experiments: carpet with PVC backing, carpet with textile backing, gypsum board and pine wood board. Carpets and gypsum board have been chosen since they are already known as ozone removing products (Morrison and Nazaroff, 2000, 2002; Kleno *et al.*, 2001) and the pine wood board because of the emissions of terpene compounds.

RESULTS

Mean ozone concentrations in the test chamber inlet and outlet during preliminary experiments are illustrated in Figure 2 for the empty glass chamber and for all selected building products.

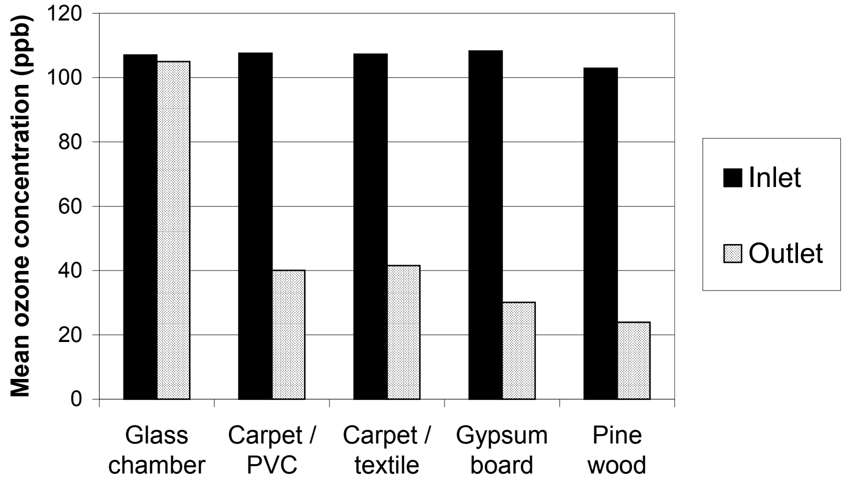

Figure 2 Mean ozone concentration (in ppb) in the test chamber inlet and outlet.

We found a mean ozone removal of 2% in the empty test chamber confirming that glass is relatively inert to ozone and well suited for the setup. The observed mean ozone removal is around 60–65% for the two tested carpets, 70% for the gypsum board and 75% for the pine wood board (Figure 2).

Emissions of building products are quantified using area specific emission rates SER_a (in $\mu g\ m^{-2}\ h^{-1}$) according to CEN (2001):

$$SER_a = C_{VOC} \frac{AER}{\frac{A_{bp}}{V_C}} \quad (1)$$

where C_{voc} is the VOC concentration in the test chamber outlet ($\mu g\ m^{-3}$), AER the air exchange rate (h^{-1}), A_{bp} the building product exposed surface (m^2) and V_c the test chamber volume (m^3).

Specific emission rates of formaldehyde and hexanal for the four selected products exposed or not exposed to ozone are illustrated in Figures 3 and 4. These figures clearly show that the two tested carpets show higher emissions of formaldehyde and hexanal when exposed to ozone and that the pine wood board emissions of hexanal are also increased due to ozone exposure. To a lesser extent, we also noticed higher emissions of acetaldehyde and pentanal for the carpet with PVC backing exposed to ozone. Among the four tested products, the gypsum board, which removes ozone (Figure 2), is the only product that does not present significantly higher carbonyl compounds emissions when exposed to ozone.

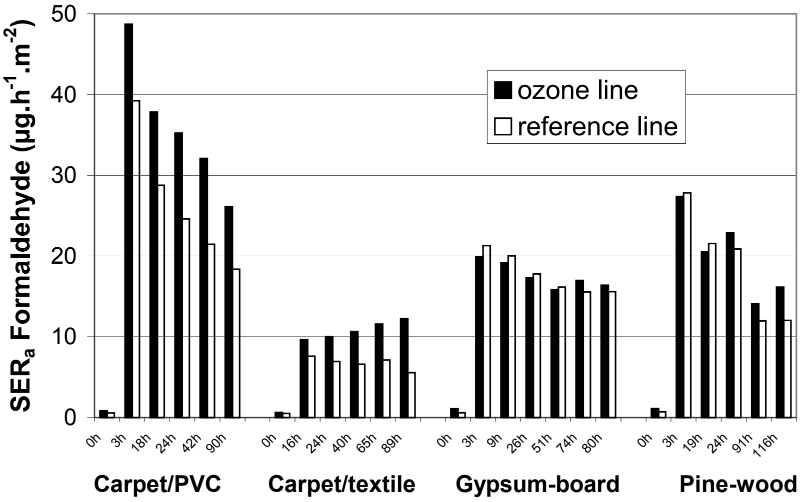

Figure 3 Specific emission rates (µg m^{-2} h^{-1}) of formaldehyde during the tests.

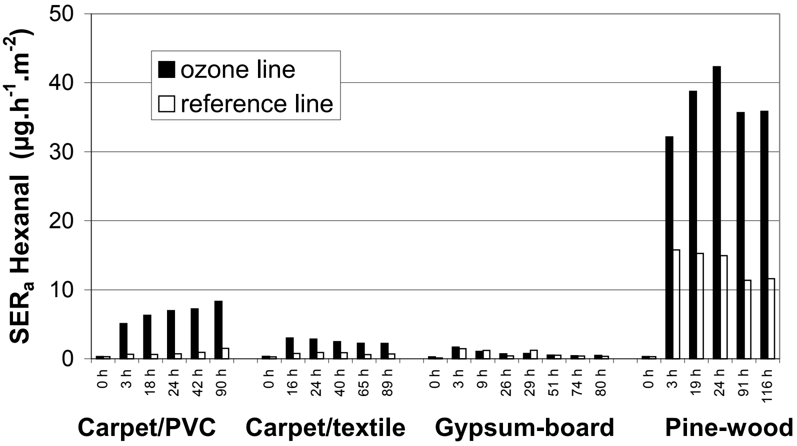

Figure 4 Specific emission rates (µg m^{-2} h^{-1}) of hexanal during the tests.

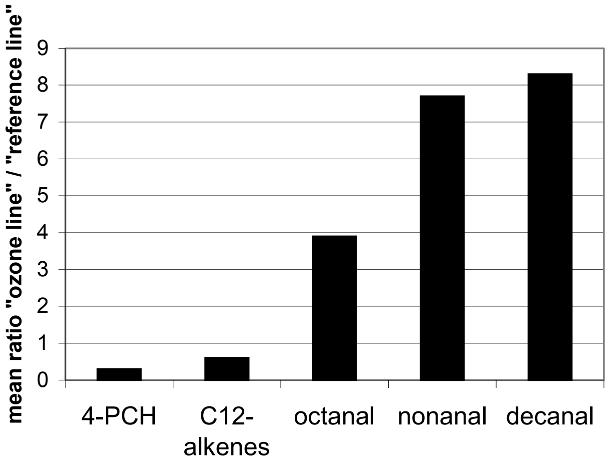

Figure 5 Mean concentration ratio in the 'ozone line' and 'reference line' during the experiment performed on the carpet with textile backing.

During the experiment performed on the carpet with textile backing, VOC were also measured using gas chromatography. The mean ratio of measured concentrations in the 'ozone line' versus 'reference line' are presented in Figure 5 for 4-phenylcyclohexene (4-

PCH), the sum of C12 alkenes, octanal, nonanal and decanal. Even if these preliminary results have to be examined with caution since no particular precautions were taken for VOC sampling on TENAX TA in presence of ozone, they provide indications on the modification of the carpet emissions. For 4-PCH and C12-alkenes, the ratio is lower than 1 suggesting possible reactions of ozone on the unsaturated carbon–carbon bounds. On the contrary, for aldehyde compounds, the ratio is significantly higher than 1 indicating secondary emissions. These preliminary observations are in good agreement with the results of Morrison and Nazaroff (2002).

DISCUSSION

In steady state conditions, the ratio of ozone concentrations in the inlet (C_{in}) and outlet (C_{out}) of the test chamber can be expressed using the following equation (from Weschler, 2000):

$$\frac{C_{out}}{C_{in}} = \frac{\mathrm{AER}}{\mathrm{AER} + k_{dgc}\frac{A_c}{V_c} + k_{dbp}\frac{A_{bp}}{V_c}} \quad (2)$$

where AER is the air exchange rate (h^{-1}), k_{dgc} the deposition velocity of ozone on glass in the test chamber (cm s^{-1}), A_c the test chamber inner surface (m^2), V_c the test chamber volume (m^3), k_{dbp} the deposition velocity of ozone on the building product (cm s^{-1}) and A_{bp} the building product exposed surface (m^2). In Eqn (2), gas-phase reactions are neglected and the microstructure of the building product is not considered (A_{bp} represents the building product exposed surface and not its specific surface). $k_d(A/V)$ (in h^{-1}) represents the first-order removal rate constant of ozone on indoor surfaces (Weschler, 2000).

From the experiment performed with the empty chamber, we calculated the k_{dgc} value. Then, k_{dbp} was calculated for each tested building product. Both ozone surface removal rate constants and deposition velocities measured in the empty glass chamber and on the four tested products are reported in Table 2. Ozone deposition velocities measured in our setup are in good agreement with values reported for indoor surfaces or building products (Weschler, 2000; Kleno *et al*., 2001). The higher ozone deposition velocity is calculated for the pine wood board (neglecting gas-phase reactions). For the follow-up of this study, the setup will be slightly modified in order to differentiate heterogeneous reactions on the product surface from gas-phase reactions.

Table 2 Characteristics of the selected building products

Selected products	Exposed surface A (m^2)	Loading factor A/V ($m^2\ m^{-3}$)	Surface removal rate constant k_d (A/V) (h^{-1})	Deposition velocity k_d (cm s^{-1})
Empty glass chamber	0.3	17.6	0.23	0.00036
Carpet/PVC backing	0.16	9.41	20.4	0.060
Carpet/textile backing	0.16	9.41	18.6	0.055
Gypsum board	0.215	12.65	31.2	0.069
Pine wood board	0.172	10.12	39.5	0.108

CONCLUSION AND IMPLICATIONS

The developed setup appears to be an efficient tool to document interactions between ozone and building products and to investigate whether ozone-induced reactions modify primary emissions of the products. This preliminary study provides another evidence of the capacity of certain building products to remove ozone and indications on the potential impact of ozone on indoor air quality. Indeed, emissions of some building products exposed to ozone are significantly modified. Ozone-induced reactions appears to have a negative impact on indoor air quality, increasing the emissions of carbonyl compounds such as formaldehyde or hexanal.

Further experiments will be conducted in order to determine the influence of different parameters (e.g. air exchange rate, ozone concentration, relative humidity) on ozone reactions with building products and to differentiate heterogeneous reactions on indoor surfaces from gas-phase reactions with some indoor VOC.

ACKNOWLEDGEMENTS

This work has been supported by CSTB and the French Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) through 02-04-002 grant.

REFERENCES

CEN (2001). CEN Pre-standard ENV 13419-1 2001, Building products—Determination of the emission of volatile organic compounds—Part 1: Emission test chamber method.

ISO (2001). International Standard ISO 16000-3 2001, Indoor air—Part 3: Determination of formaldehyde and other carbonyl compounds—Active sampling method.

ISO (2002). Draft International Standard ISO/DIS 16000-6.2 2002, Indoor air—Part 6: Determination of volatile organic compounds in indoor and chamber air by active sampling on TENAX TA sorbent, thermal desorption and gas chromatography using MSD/FID.

Kirchner, S., Laurent, A.M., Collignan, B., Le Moullec, Y., Ramalho, O., Villenave, J.G. and Flori, J.P. (2002). Impact of the urban pollution on the indoor environment—experimental study on a mechanical ventilated dwelling. *Proceedings of the 9th International Conference on Indoor air Quality and Climate—Indoor Air 2002*, Monterey, Vol. 1, pp. 164–169.

Kleno, J.G., Clausen, P.A., Weschler, C.J. and Wolkoff, P. (2001). Determination of the ozone removal rate by selected building products using the FLEC emission cell. *Environmental Science & Technology* **35**, 2548–2553.

Knudsen, H.N., Nielsen, P.A., Clausen, P., Wilkins, C.K. and Wolkoff, P. (2000). Sensory evaluation of the impact of ozone on emissions from building materials. *Proceedings of the 6th International Conference on Healthy Buildings—Healthy Buildings 2000*, Espoo, Vol. 4, pp. 217–222.

Knudsen, H.N., Afshari, A., Ekberg, L. and Lundgren, B. (2002). Impact of ventilation rate, ozone and limonene on perceived air quality in offices. *Proceedings of the 9th International Conference on Indoor air Quality and Climate—Indoor Air 2002*, Monterey, Vol. 4, pp. 217–222.

Morrison, G.C. and Nazaroff, W.W. (2000). The rate of ozone uptake on carpets: experimental studies. *Environmental Science & Technology* **34**, 4963–4968.

Morrison, G.C. and Nazaroff, W.W. (2002). Ozone interactions with carpet: secondary emissions of aldehydes. *Environmental Science & Technology* **36**, 2185–2192.

Rohr, A.C., Weschler, C.J., Koutrakis, P. and Spengler, J.D. (2003). Generation and quantification of ultrafine particles through terpene/ozone reaction in a chamber setting, *Aerosol Science and Technology* **37**, 65–78.

Wainman, T., Zhang, J., Weschler, C.J. and Lioy, P.J. (2000). Ozone and limonene in indoor air: a source of submicron particle exposure. *Environmental Health Perspectives*, **108**, 1139–1145.

Weschler, C.J. (2000). Ozone in indoor environments: concentration and chemistry. *Indoor Air* **10**, 269–288.

Weschler, C.J. and Shields, H.C. (1999). Indoor ozone/terpene reactions as a source of indoor particles, *Atmospheric Environment* **33**, 2301–2312.

Wolkoff, P., Clausen, P.A., Wilkins, C.K. and Nielsen, G.D. (2000). Formation of strong airway irritants in terpene/ozone mixtures, *Indoor Air* **10**, 82–91.