The emissions of terpene-type VOC from cedarwood in an eco house and the chemical reaction between sesqui-terpenes and ozone

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ABSTRACT

Field measurement on VOC concentrations was conducted in an environmental symbiosis house (‘eco houses’) in Japan. Considering low emission of chemicals, cedarwood was used as an interior material in this house. Very high concentrations of sesqui-terpene VOCs were detected in the house. Then, full-scale chambers (rooms) of test house were used to investigate emission data of terpene VOCs from cederwood. This experiment involved placing samples of cedarwood and an ozone generator in one room of the test house. The sesqui-terpene concentration, under the condition with cedarwood and ozone generator, was much lower than that under the condition with cedarwood and no ozone emission. However, there was no significant difference in the HCHO concentration between two rooms. HCHO is not expected to be formed by the reaction between ozone and the major sesqui-terpenes emitted from cedarwood. However, the analytical techniques in this study were not capable of detecting the anticipated products of reactions between ozone and sesqui-terpenes. Other studies, using different analytical methods, will be necessary to find and identify these products.

INDEX TERMS

Eco house; Sesqui-terpenes; Formaldehyde; Ozone

INTRODUCTION

Building materials, furnishings and consumer products used indoors usually emit Volatile Organic Compounds (VOCs) into the space, being regarded as one of the causes of Sick Building Syndrome (SBS). Avoiding high concentrations of chemical substances, low emission building materials are receiving increased attention from builders and consumers. The houses, which use low emission materials and pay attention to indoor/outdoor environment and sustainability, are called environmental symbiosis houses (or ‘eco houses’). In these eco houses, raw wooden materials are often used as the interior materials or construction materials. These raw wooden materials, however, also emit VOCs such as terpenes. Therefore, the concentrations of VOCs including terpenes were measured in an eco house in southern part of Japan. Also the chemical reaction between terpenes and ozone was investigated.

FIELD MEASUREMENT IN AN ECO HOUSE

The concentrations of VOCs were measured in a wooden house in Kagoshima, Japan. Cedarwood was used as an interior and construction material in the house. The interior view is shown in Figure 1. The field measurement was conducted in May, 1 month after completion of the construction. The room temperature was 23.3°C and the relative humidity 63% at this field measurement. The analysis of VOCs in the air collected on Tenax were carried out by thermal desorption (PE ATD 400) combined with GC/MS system (PE Autosystem and PE Turbomass). Table 1 shows the results of the concentrations of VOCs identified and quantified by GC/MS analysis. It was found that sesqui-terpene concentrations in toluene equivalents

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formed 40% of TVOC concentrations. The gas chromatogram of absorbed VOCs is shown in Figure 2.

Figure 1 Interior of the investigated house.

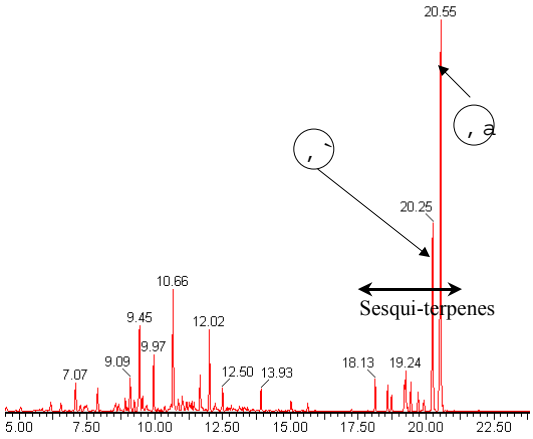


Figure 2 Gas chromatogram of VOCs.

Table 1 VOCs concentrations

VOCs	conc. [ug/m^3]	VOCs	conc. [ug/m^3]
MIB+	18	1,3,5-TMB	20
toluene	146	1,2,4-TMB	69
ethylbenzene	38	1.2.3-TMB	28
p,m-xylene	46	limonene	32
styrene	226	undecane	27
o-xylene	40	decanal	2
α-pinene	101	sesqui-terpenes*	2640
		TVOC*	6850

+ Methyl isobuthyl ketone.

* Concentration in toluene equivalents.

EMISSION EXPERIMENT IN A TEST HOUSE

Methods

The experiment to investigate the chemical reaction between sesqui-terpenes and ozone were conducted in rooms 1 and 2 in the test house at Kagoshima University. Each room with one window facing south has a floor area of 10 m^2 and a volume of 25 m^3. The room air temperature was kept at 25°C by the air conditioner and the room was ventilated with 15 m^3/h of outside air by mechanical ventilation system. To modify the terpene concentration in the room, a cedarwood was introduced in the room (room 1) and not introduced in room 2. The specimen of the cedarwood was newly bought at a store. The samples of the cedarwood with a total surface area of 5.7 m^2 were laid on the floor of the room. The loading factor was 0.23. A plan of the experimental room is shown in Figure 3. The experimental procedure is shown in Figure 4. This emission experiment started from zero (t = 0) and lasted for ca. 600 h. The ozone concentration was elevated by the ozone generator with low emission mode at 360 h and with high emission mode at 480 h after starting the emission experiment.

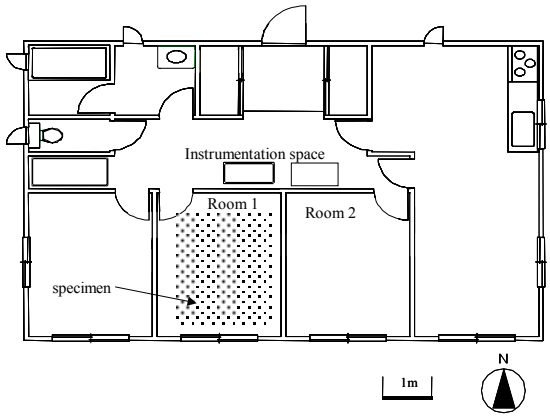
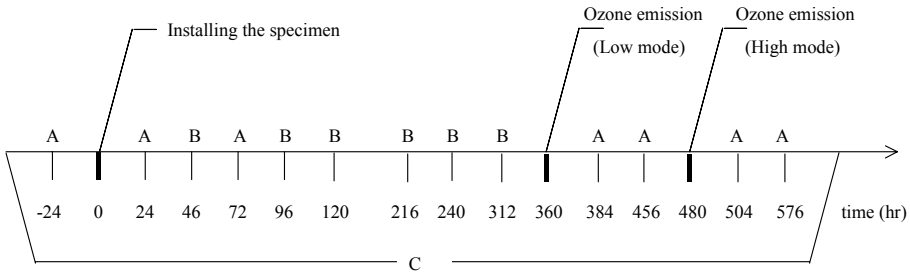


Figure 3 Plan of the test house.



A: Measuring concentrations of VOCs and aldehydes

B: Measuring concentrations of VOCs

C: Measuring air temperature, relative humidity and ozone concentration (continuously)

Figure 4 Experimental procedure.

The concentrations of VOCs, formaldehyde and acetaldehyde were measured during the experiment. The concentrations of VOCs were measured with GC/MS method and the concentrations of formaldehyde and acetaldehyde with the DNPH/HPLC method.

RESULTS

The average ozone concentrations at the centre of room 1, at supply air diffuser and outdoors are listed in Table 2. During the period of no emission mode, the indoor ozone concentration in room 1 was a tenth of outdoor concentration. The indoor ozone concentration was 6 ppb during the low emission period and 30 ppb during the high emission period.

Table 2 Ozone concentrations during the experiment (ppb)

Ozone emission mode	Room 1	Supply air diffuser	Outdoor
No emission $-24 < t < 360$	1.1 ± 0.5*	2.1 ± 1.9	11.8 ± 13.1
Low emission mode $360 < t < 480$	5.8 ± 2.0	3.0 ± 2.0	8.8 ± 10.0
High emission mode $480 < t < 580$	30.6 ± 4.6	3.6 ± 1.9	11.2 ± 9.0

*Average ± standard deviation.

Figure 5 shows the concentration of formaldehyde and acetaldehyde as a function of the

elapsed time. The concentrations of formaldehyde and acetaldehyde were not changed regardless of the ozone emission mode. There was no significant difference in the concentrations of formaldehyde and acetaldehyde between room 1 and room 2.

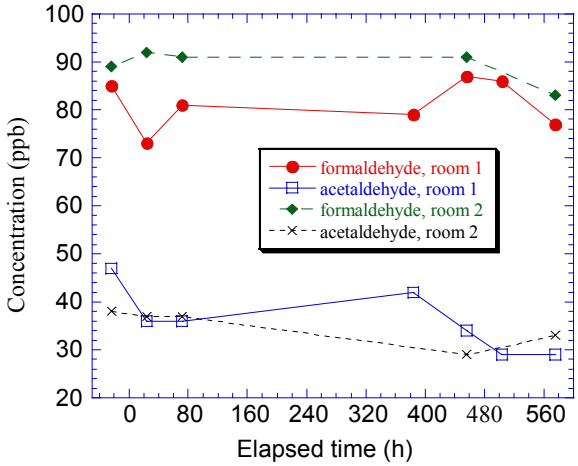


Figure 5 Concentration of formaldehyde and acetaldehyde as a function of the elapsed time.

The gas chromatogram of absorbed VOCs in room 1 at 24 h after starting the experiment is shown in Figure 6. As seen in Figure 2, the peaks of sesqui-terpenes (nos. 1–8) are very large. These VOCs could be emitted from cedarwood. Especially peak nos. 5 and 6 are significantly large. The retention times of peak nos. 5 and 6 in Figure 6 agree with the retention times of peaks A and B in Figure 2. The mass spectra of these peaks in Figure 6 also agree with those in Figure 2. Figure 7 shows the sum of the concentration of nos. 5 and 6 as a function of the elapsed time. This figure also shows the indoor ozone concentration. Emission process of the cedarwood gave rise to concentrations of the sesqui-terpenes in the room 1, which, starting from zero, increased with time, passed through a maximum at ca. 50 h and then declined toward a plateau at ca. 200 h. The plateau concentration of the sesqui-terpenes was 320 μg/m^3 during the no ozone emission period. During the low ozone emission period, the concentration of the sesqui-terpenes decreased to 150 μg/m^3. It decreased to 50 μg/m^3 during the high ozone emission period.

Figure 6 Gas chromatogram of VOCs in the air of room 1 (t = 24 h).

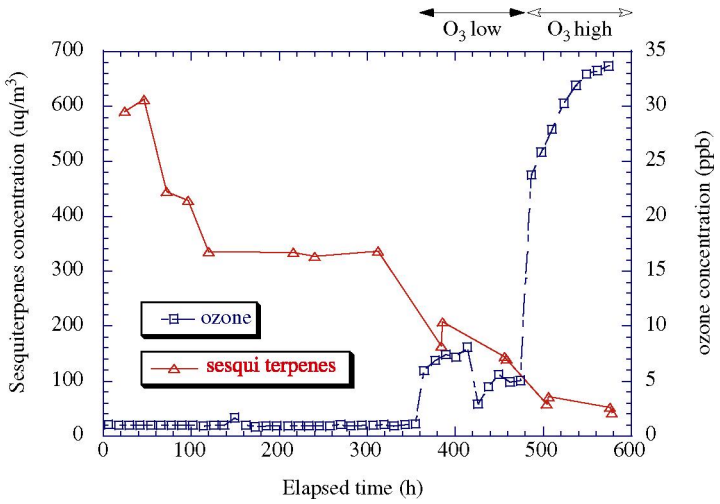


Figure 7 The sum of the concentrations of sesqui-terpenes of nos. 5 and 6 and the indoor ozone concentration.

DISCUSSION

In Figure 7, the higher the indoor ozone concentration, the lower the sesqui-terpenes concentration. The sesqui-terpenes might have been consumed by the reaction with indoor ozone during the experiment. Then, what are secondary products caused from the chemical reaction between sesqui-terpenes and ozone? Since the concentrations of formaldehyde and acetaldehyde were not changed regardless of the change of ozone concentration, the above chemical reaction might not have produced formaldehyde or acetaldehyde. It is described that the principal constituents of cedar oil essence are cedrene, thujopsene and cedrol (see Figure 8, Kirk-Othmer, 1996). Ozone is not expected to react with cedrol—no double bonds. Ozone is expected to react with cedrene and thujopsene. In each case, as a first step, ozone is expected to attach the double bond, leading to ring opening. As these VOCs do not have a terminal double bond, formaldehyde in not an anticipated product. Similarly, having no terminal double bond with CH_3 and H on a terminal carbon, acetaldehyde is not an anticipated product. Weschler and Shield (1999) described that ozone/terpene reactions can be a significant source of sub-micron particles in indoor settings. The measurement on indoor particles is needed to research on secondary products from ozone/sesqui-terpene reactions.

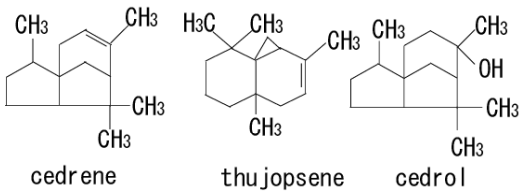


Figure 8 Principal constituents of cedar oil.

CONCLUSIONS

The concentrations of sesqui-terpenes were found to be high in an eco house, where raw wooden materials of cedarwood were used as interior and construction material. The concentrations of sesqui-terpenes emitted from cedarwood were measured in a test house during the no ozone emission period, low ozone emission period and high ozone emission period. It was found that the higher the indoor ozone concentration, the lower the sesqui-terpenes concentration. The sesqui-terpenes might have been consumed by the reaction with indoor ozone during the experiment. The concentrations of formaldehyde (HCHO) and

acetaldehyde were not changed regardless of the change of ozone concentration. HCHO is not expected to be formed by the reaction between ozone and the major sesqui-terpenes emitted from cedarwood. Other analytical tools are necessary to identify the major products of these reactions.

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