Measurements of primary and secondary emissions with ozone by using a small-scale chamber

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ABSTRACT
Ozone is widely used in rooms for purifying the air and removing the odour. In addition, some copying machines and electrostatic air cleaners produce ozone. Because it is oxidative, ozone reacts with VOCs. It is estimated that secondary source might be produced and affect human health. In this study, primary and secondary emissions with ozone were investigated by using a small-scale chamber, ADPAC. First, ozone concentrations in various locations were measured. It was usually about 10 ppb in the rooms. However it reached over 500 ppb when a copying machine was used. Second, reactivity with ozone was investigated with some building materials. Each material was placed in ADPAC, where high concentration of ozone was supplied, and average concentration of ozone was measured. Ozone concentration in the chamber decreased drastically. It was found that building materials reacted with ozone or adsorbed it. Finally, secondary products were measured with cedar board, PVC board and EPS board. Purified air, 100 ppb and 300 ppb ozone were supplied to the chamber and the emission rates of aldehydes and VOCs were measured. The emission rates of some aldehydes were increased. Especially, formaldehyde increased for all three materials. Toluene and styrene are decreased for EPS. TVOC had changed lot for cedar board and PVC board. It was suggested some unidentified compounds were also produced.

INDEX TERMS
Ozone; Emission; Air quality; VOC; TVOC

INTRODUCTION

Ozone is generated when nitrogen dioxide in car exhaust reacts with hydrocarbons, or when oxygen is irradiated with ultraviolet rays. In addition, some copying machines and electrostatic air cleaners generate ozone (Ito, 1999). Ozone is used widely in rooms for the purpose of purifying the air and removing the odour. Ozone concentrations in rooms rarely become high enough to cause any harm to human health directly. Because it is oxidative, ozone reacts with volatile organic compounds (VOCs) in the room or the building materials (Knudsen *et al.*, 2000). It is suggested that secondary sources might be produced and these might affect human health. For example, styrene reacts with ozone and produces formaldehyde and benzaldehyde. It is important to measure primary and secondary emissions with ozone. Reaction between ozone and unsaturated VOCs is shown in Figure 1.

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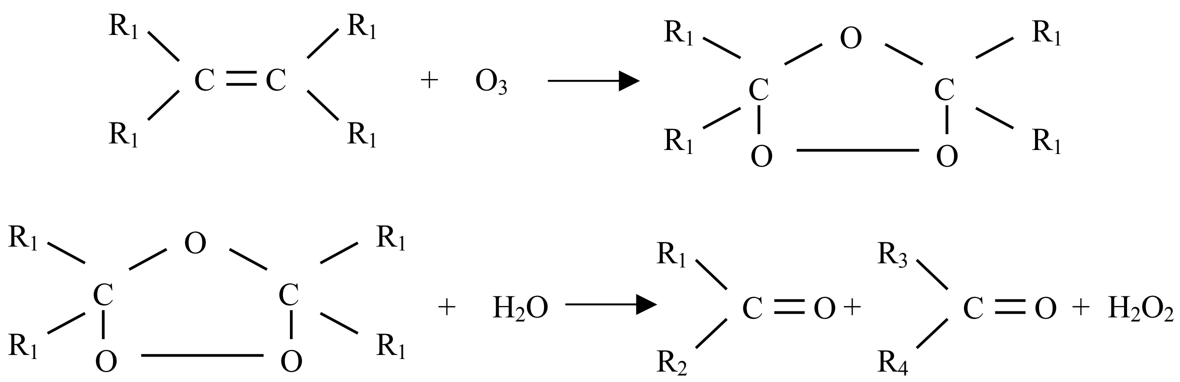

Figure 1 Reaction between ozone and VOCs.

The aim of this experiment was to compare the difference between emission rates with and without ozone. First, ozone concentrations in various locations were measured to investigate the general concentration of indoors and outdoors. Second, reactivity of ozone was measured with PVC board, *tatami* mat (Japanese traditional floor), corkboard, cedar board and EPS board. Finally secondary products were measured with cedar board, PVC board and EPS board.

METHODS

Measurement of Ozone Concentration

Ozone concentrations were measured in several rooms and outdoors. Because copying machine is the main emission source of ozone in offices, concentration near the exhaust outlet were also measured to evaluate the effect of using the devices. At each point, the maximum instantaneous value and the averaged value for 3 min were recorded. Temperature and relative humidity were recorded at the same time. The methods for measuring ozone concentrations are shown in Table 1.

Table 1 Methods for measuring ozone concentrations

Target	Method
Ozone concentration	MODEL1150 (Dylec)
Data recorder	AM-7052 (Anritsu Meter Co., Ltd.)
Temperature; humidity	Thermo-recorder; RS-11 (ESPEC)

Measurement of Reactivity with Ozone

Reactivity of ozone was measured with several building materials. Target materials were PVC board, *tatami* mat, corkboard, cedar board and EPS board. The experimental setup is illustrated in Figure 2. Each material was placed in a small-scale chamber, ADPAC (ADvanced Pollution and Air quality Chamber) (Tanabe *et al.*, 2000), where high concentration of ozone was supplied. ADCLEAN supplied purified air and Air Control System controlled humidity of the air. ADPAC chamber was placed in an incubator to maintain constant temperature. ADPAC can measure emissions from building materials exactly under controlled temperature and humidity. Average concentration in the chamber was measured for 20 h.

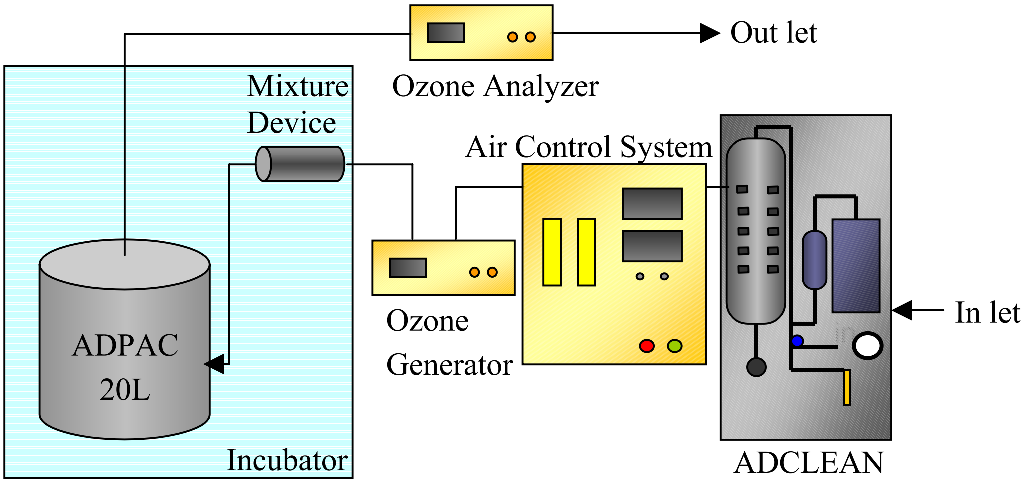

Figure 2 Experimental setup

Measurement of Secondary Products with Ozone

Secondary products of ozone were measured with cedar board, PVC board and EPS board. These materials were selected because they emitted a large amount of VOCs in an earlier study (Funaki *et al.*, 2000). Each material was placed in ADPAC. Purified air, 100 ppb and 300 ppb ozone were supplied to the chamber and the emission rates of aldehydes and VOCs were measured on the first day and the third day after setting the materials. Emission rate was calculated by the emission amount per area and hour ($\mu g/m^2/h$). The sampling conditions and sampling methods are shown in Figures 3 and 4. If the sampled air contained high concentration of ozone, it would affect the sampler, DNPH silica cartridge. Therefore, an ozone scrubber was attached to the sampling tube to avoid the effect of ozone.

Table 2 Sampling conditions

Chamber volume	20 l
Loading factor	2.2 m^2/m^3
Temperature	25°C
Relative humidity	50% RH
Ventilation rate	0.5 h^{-1}

Table 3 Sampling methods

	Aldehydes	VOC
Sampling tube	Sep-Pak DNPH-Silica (short type) (Waters)	Tenax TA (60/80 mesh) 200 mg inside (ATD/TCT tube)
Sampling airflow	0.167 l/min	0.167 l/min
Sampling volume	10 l	3.2 l

RESULTS AND DISCUSSION

Measurement of Ozone Concentration

The results of ozone concentration are shown in Table 4. Ozone concentrations were usually about 10 ppb in rooms, and about 30 ppb outdoors. Majority of the measured values were very low and safe, but when some copying machines were used, concentration reached over 500 ppb regionally. The maximum instantaneous value was 776 ppb.

Table 4 Ozone concentration

Measure point			Max. instantaneous value (ppb)	Average concentration (3 min) (ppb)	Temperature (°C)	Relative humidity (%RH)
Room A			8	7.3	25.5	43
Near copying machine A			24	11.4	30.0	36
Corridor	Upper		18	17.0	24.4	46
	Lower		18	14.0	24.3	45
Room B			11	8.1	26.3	43
Copying machine B	Paper tray		36	15.5	31.1	43
	Exhaust outlet	1st	776	343.4	39.9	30
		2nd	581	137.1	43.5	23
Outdoors			43	37.5	23.9	46

Measurement of Reactivity with Ozone

The results of ozone concentrations are shown in Figure 3. Ozone concentrations with building material decreased drastically compared to an empty chamber. Average concentrations were 55 ppb for cedar board, 77 ppb for *tatami* mat, 88 ppb for corkboard, while that of the empty chamber was about 263 ppb. It was found that ozone reacted with VOCs emitted from materials. Ozone might be adsorbed by the material itself since large decrease in ozone concentrations was observed for porous materials such as cedar board, *tatami* mat and corkboard.

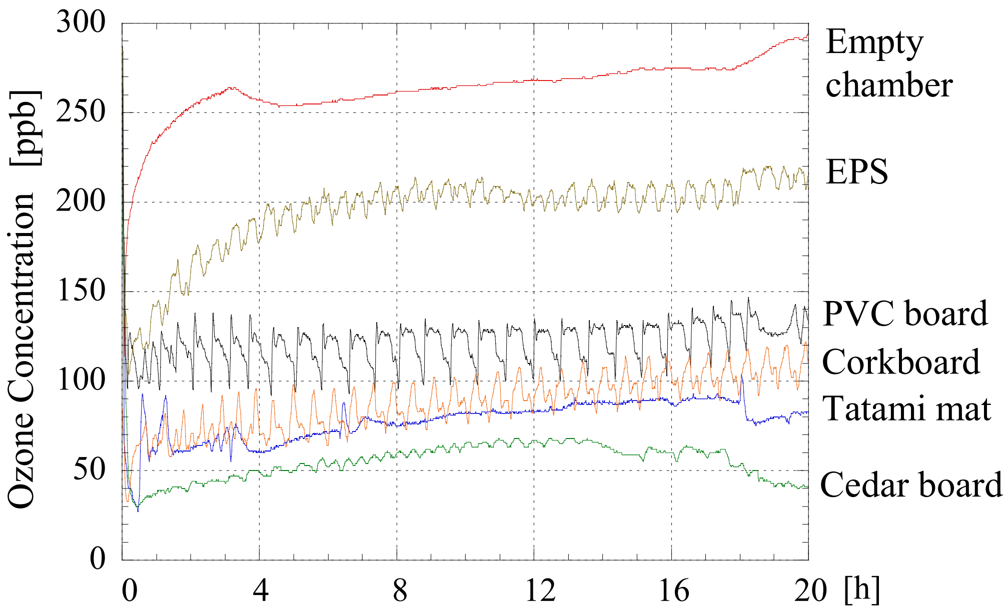

Figure 3 Ozone concentrations.

Measurement of Secondary Products with Ozone

There were no difference between the results of the first day and those of the third day. The emission rates of cedar board, PVC board and EPS board on the first day are shown in Figures 4–6.

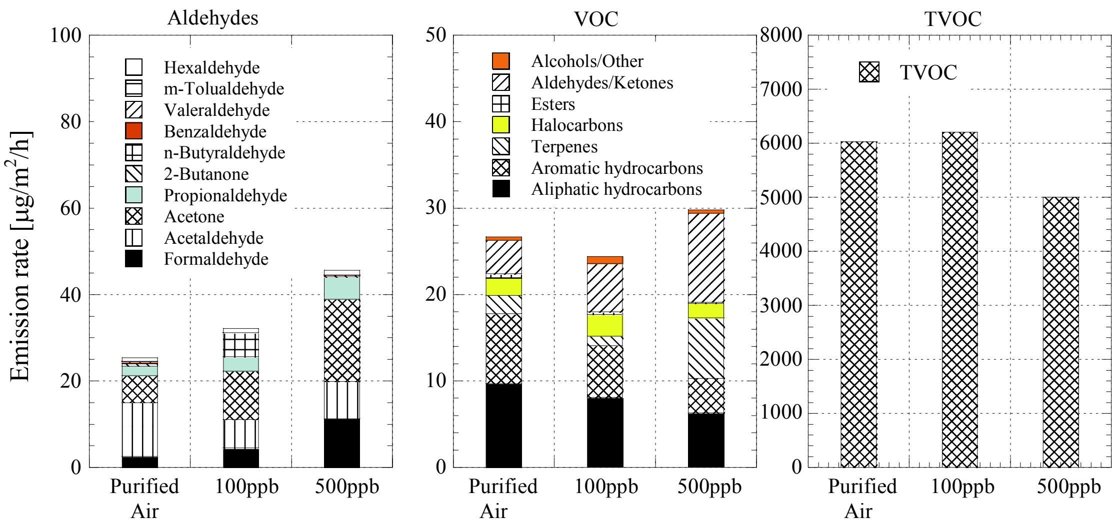

Figure 4 Emission rates of cedar board.

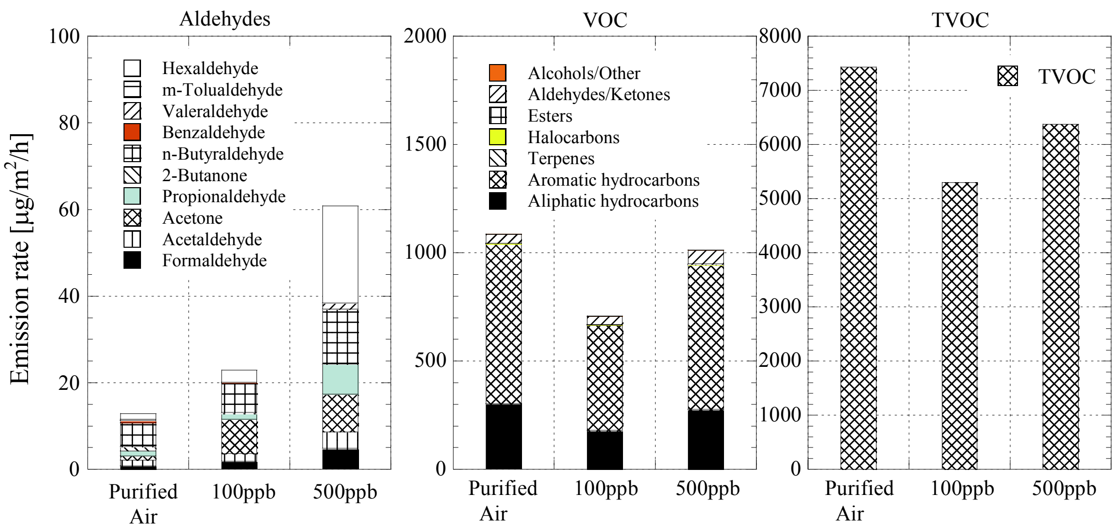

Figure 5 Emission rates of PVC board.

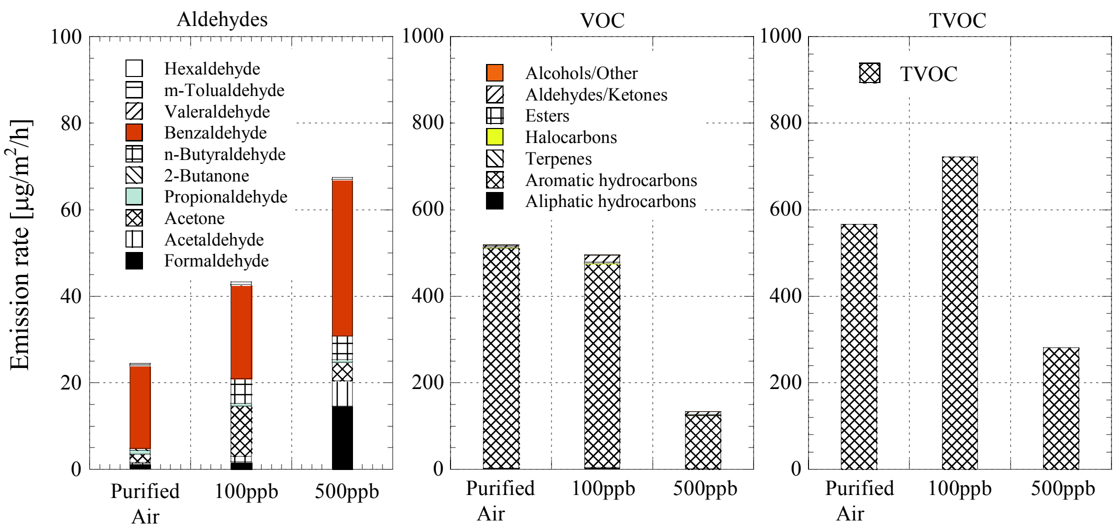

Figure 6 Emission rates of EPS board.

Aldehydes

Emission rates of chemicals such as acetone from cedar board, hexaldehyde, *n*-butyraldehyde, acetone from PVC board and benzaldehyde, acetaldehyde from EPS were increased. Formaldehyde was increased for all three materials. The list of increased aldehydes due to high ozone concentration is shown in Table 5.

Table 5 List of increased aldehydes due to high ozone concentration

Cedar board	Formaldehyde, acetone, propionaldehyde
PVC board	Formaldehyde, acetaldehyde, benzaldehyde
EPS board	Formaldehyde, acetone, propionaldehyde, *n*-butyraldehyde, hexaldehyde

VOCs and TVOC

The number of identified VOCs was 50. TVOC was calculated by toluene equivalent from the peaks from *n*-hexane to *n*-hexadecane. As for cedar board and PVC board, emission rate of identified VOCs were almost the same due to high ozone concentration. However, these TVOC decrease was higher. It indicated that reaction with ozone produced some compounds that were not identified. As for EPS board, aromatic hydrocarbons, especially toluene and styrene, decreased largely due to high ozone concentration. It was found that each material reacted with ozone and some VOCs increased or decreased significantly.

CONCLUSIONS

Some copying machines were found to produce high concentration of ozone. Then ozone reacted with aldehydes and VOCs in the room and produced secondary sources. In this experiment, a lot of secondary products were observed. In addition, these experiments demonstrated that a large variety of secondary products were produced due to high reactivity of ozone. To evaluate the effect of ozone exactly, further analytical work is needed in the future. Measurements of ozone concentration in several buildings are also needed to investigate the general concentration.

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