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Environmental test chamber elucidation of ozone-initiated secondary pollutant emissions from painted wooden panels in buildings

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ABSTRACT

Indoor ozone readily reacts with volatile organic compounds (VOCs) and produces formaldehyde as a secondary pollutant. In this study, small-scale environmental chamber experiments are performed using a painted hardwood panel to evaluate the production of VOCs and formaldehyde given different ozone concentrations and reaction times. The results reveal that of the various VOCs emitted by the panel, limonene reacts most readily with ozone. The formaldehyde concentration within the chamber is found to increase by 215.8% given an ozone concentration of 200 ppb and a reaction time of 3.0 h. Consequently, such conditions must be avoided in indoor environments in order to safeguard human health.

1. Introduction

The adverse consequences of global climate change are increasing year by year. Among key indicators, the annual average concentration of ozone in urban indoor environments in Taiwan has increased from 22 ppb in 1998 to 29 ppb in 2006 [1]. According to the United Nations Environment Programme (UNEP) [2], climate change and the greenhouse effect are likely to increase the ozone concentration in the stratosphere by around 10–30 ppb by the end of the 21st century. In Taiwan, indoor environments frequently contain items of office or home equipment which generate ozone (e.g. copy machines, printers, fax machines, and so on). Statistical data from the Environmental Protection Administration (EPA) in Taiwan reveal that the annual average ozone concentration rose from 22 ppb to 29 ppb from 1998 to 2006. Thus, given the background of globally rising ozone levels, the average ozone concentration of 29 ppb (2006) is dangerously close to the maximum limit of 30–50 ppb prescribed by Taiwan's Environmental Protection Administration (EPA) [1].

Many studies have shown that ozone entering a structure from outdoors or generated indoors readily reacts with terpenes and terpenoids to form oxidation products with a wide range of volatility [3–7]. The low volatile products contribute to the production and growth of meaningful quantities of secondary organic aerosols (SOAs). It has been shown that unsaturated organic compounds are particularly liable to act as SOA precursors [8–13].

As mentioned above, many homes and offices in Taiwan contain items of equipment which produce ozone in significant quantities (e.g., copy machines typically produce ozone at a rate of 5.2 mg/h). Furthermore, many indoor environments in Taiwan are extensively decorated in wood. Previous studies have shown that the reaction of indoor ozone with VOCs such as those found within many paints or wooden products (e.g., furniture or floorboards) leads to the formation of formaldehyde as a secondary pollutant [14,15]. Formaldehyde is a known human carcinogen and thus its presence must be carefully controlled in indoor environments. Wu et al. [16,17] showed that the level of formaldehyde in many office spaces in Taiwan is between 100 and 1000 times higher than that regarded as safe for human exposure. Thus, green building materials (GBMs) have attracted significant interest in recent years. However, the reactivity of GBMs with ozone still requires further investigation [18,19]. Accordingly, the present study performs a series of small-scale environmental chamber experiments based on the ASTM D5116-06 standard [20], in which the production of VOCs and formaldehyde by a painted hardwood panel is evaluated for different ozone concentrations and reaction times.

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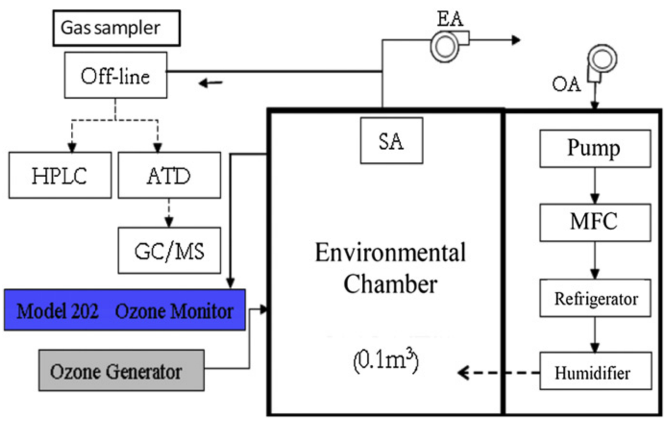

Fig. 1. Schematic illustration of experimental setup.

2. Methods

2.1. Small-scale test chamber

Fig. 1 presents a schematic illustration of the experimental setup. As shown, the major items of equipment include a small-scale test chamber (Vol.: 100 L), a clean air generation system, a monitoring and control system, and a real-time sampling and analysis system. The tests were performed using a painted wooden panel with a surface area of 36 cm^2. The tests were conducted at a temperature of 25 °C with a relative humidity of 50% and a ventilation rate of 0.5 ACH. Gas samples were collected via a sampling pump attached to a stainless steel absorbing tube mounted at the top of the chamber. The samples were desorbed using an automated thermal desorber (ATD) and analyzed in accordance with ISO 16000 (Parts 1–6) via gas chromatography and mass spectrometry (GS/MS). The details of the analysis procedure are summarized in Table 1. The compounds emitted from the wooden panel were identified by cross-matching the GC/MS results with a reference library [21–23].

2.2. Materials

The painted floor panel (GBM with EU-ECO label [24]) was placed in the experimental chamber for 24 h (Fig. 2). Ozone (produced by an SW-2000 Ozonizer, Clean King, Taiwan) was abruptly injected into the chamber after 10.5 h, and the variation of the VOC and formaldehyde emissions was monitored until the end of the test period.

2.3. Experimental protocol

According to Weschler [25], Langera et al. [26] and Kagi et al. [27], the half-life period of α-pinene in ozone concentrations of 50 ppb and 100 ppb is 0.75 h and 0.37 h, respectively, while the corresponding half-lives of d-limonene are 1.8 h and 0.9 h, respectively. The guidelines laid down by Taiwan's EPA state that the maximum daily 8 h average indoor ozone concentration should not exceed 35–41 ppb, while the maximum 1 h average ozone concentration during the summer months should be no higher than 100–180 ppb [27]. Accordingly, in the current study, ozone was injected into the chamber with concentrations of 50 ppb, 100 ppb and 200 ppb, respectively, and the gas-phase reaction time (i.e., the ozone injection time) was specified as 1.0 h, 1.5 h or 3.0 h.

Table 1
VOC analysis specification.

Component	Specifications & operating parameter
Analytical column	DB-624 GC 30 m × 0.25 mm × 1.4 μm
Carrier gas	Helium
GC–MS condition	Column temp program: 35 °C, 10 °C/min to 120 °C with 10 min, 10 °C/min to 220 °C with 10 min, Scan range: 50–350 amu (EI)
ATD condition	Tube desorption temp: 280 °C with 5 min, Cold trap low temp: −20 °C, Cold trap high temp: 300 °C with 5 min

3. Results and discussion

The emitted compounds were identified in accordance with the following criteria: (1) a minimum 80% match rate in the GC/MS library search; (2) compounds known to be emitted by GBMs [28,29]; and (3) compounds known to be readily reactive with ozone [14,30,31].

3.1. Ozone reaction in closed ventilation conditions

An initial experiment was performed to investigate the reaction of the VOCs emitted by the painted wooden panel with ozone under closed ventilation conditions. Fig. 3 shows the variation of the VOC concentrations over the first 20 h of the 24 h test period given an ozone concentration of 50 ppb and a reaction time of 1.5 h. Note that the ventilation rate was specified as 0.5 ACH for the first 10 h of the test, but was then reduced to 0 ACH (i.e., closed ventilation conditions) for the remainder of the test. It is seen that the concentrations of toluene, ethylbenzene, undecane, heptane and decane remain approximately constant or increase during the period of 10–12 h. In other words, the results suggest that these particular VOCs do not react significantly with ozone under closed ventilation conditions. However, the concentration of limonene reduces by approximately 23 $\mu g/m^3$ (3.8 ppb) (39.8%) during the reaction period. Thus, it is inferred that limonene reacts with the ozone due to its unsaturated double-bond structure and produces formaldehyde as a secondary pollutant.

3.2. Analysis of gas-phase reactions given different ozone concentrations and ventilation rate of 0.5 ACH

Fig. 4 shows the variation of the formaldehyde concentration given ozone concentrations of 50, 100 and 200 ppb, respectively, and a reaction time of 1.5 h. From inspection, the formaldehyde concentration increases by 46.2 ppb, 64.2 ppb and 103.4 ppb over the period of 10–12 h for ozone concentrations of 50, 100 and 200 ppb, respectively. In other words, the formaldehyde concentration increases with an increasing ozone concentration. Fig. 5 shows the percentage increase in the formaldehyde concentration as a function of the ozone concentration at various intervals in the test period. Applying a regression analysis technique, it is found that a high correlation ($R^2 = 0.9911$) exists between the ozone concentration and the percentage increase in the formaldehyde concentration in the 10–12 h period.

3.3. Analysis of gas-phase reactions given different reaction times and ventilation rate of 0.5 ACH

Fig. 6 illustrates the primary VOC concentrations within the environmental chamber at 10.5 h (i.e., ozone injection) and 12.0 h (i.e., 1.5 h reaction time), respectively. For convenience, the change in the VOC concentrations over the reaction period is summarized on the right-hand side of the figure. It is seen that the decane concentration increases by 122.7 ppb. In other words, no reaction takes place between the decane VOC and the ozone. It is noted that