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Surface removal rate of ozone in residences in China

Mingyao Yao[a], Bin Zhao[a,b,*]

[a] Department of Building Science, School of Architecture, Tsinghua University, Beijing, 100084, China
[b] Beijing Key Laboratory of Indoor Air Quality Evaluation and Control, Tsinghua University, Beijing, 100084, China

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ABSTRACT

Outdoor ozone has been proven to be strongly associated with both morbidity and mortality. The deposition of ozone on indoor surfaces is the main loss of ambient ozone migrating into indoor environments, which is critical for assessing human exposure to ozone. In this study, the surface removal rate due to ozone deposition on indoor surfaces in 14 residences in China was measured. The deposition velocities for the uptake of ozone were measured as well as theoretically calculated. The results indicate that the mean ± standard deviation (SD) of the surface removal rate of ozone in the studied Chinese residential rooms was 2.8 ± 1.1 h^{-1}. The mean ± SD of the measured deposition velocity was 109 ± 34 cm/h, which is much larger than the theoretically calculated value of 27 ± 3 cm/h. The significant difference between the measured and theoretically calculated values might result from the accumulation of organic chemicals on indoor surfaces due to the occupants' daily activities. The measured surface removal rate of ozone in Chinese residences may be further applied for estimating human exposure to ozone in China, where ozone pollution has been increasingly severe.

1. Introduction

Outdoor ozone concentrations have been proven to be associated with morbidity and mortality [1]. Outdoor ozone concentration has been found to be related to acute and possibly chronic health effects, respiratory-related hospital admissions, lost school days and respiratory symptoms [1–5]. Studies have found that indoor ozone exposures were typically 45–75% of the total exposures, with indoor ozone inhalation intakes being typically 25–60% of the total intakes [1]. Considering that modern people spend 80% of their time indoors, indoor ozone concentrations play an important role in people's exposure to ozone [6,7]. In the absence of indoor sources, indoor ozone concentration depends on the outdoor ozone concentration, air change rate, removal rate of indoor surfaces, and chemical reactions between ozone and reactive organic gases in the air. Under typical indoor conditions, the reaction rate between ozone and most indoor pollutants is slow compared with the air change rate and surface removal rate [8]. Therefore, the surface removal rate of ozone is vital in estimating the indoor ozone concentration and corresponding human exposure.

As for China, the outdoor ozone pollution has been increasingly severe [9]. Tang et al. showed that for 22 sites in Northern China, there was an average exceedance of 18.2% of summer days had daily a maximum ozone concentration over 102 ppb [10]. The study investigating the relationship between ozone and daily mortality in Shanghai by Zhang et al. indicated an increase of 10 μg/m^3 in the 2-day average ozone corresponds to 0.45%, 0.53% and 0.35% increase in the total nonaccidental, cardiovascular, and respiratory mortality in whole-year. While for cold-season, the increases are 1.38%, 1.53%, and 0.95%, respectively [11].

The surface removal rate is the first-order rate constant that applies to the removal of ozone by indoor surfaces. Lee et al. measured the surface removal rate of ozone in the living rooms of 43 Southern California homes, reporting a mean surface removal rate of 2.80 ± 1.30 h^{-1} [12]. The surface removal rates of ozone in an aluminum room, stainless steel room, bedroom and office, measured by Muller et al. were 3.24 ± 0.24 h^{-1}, 1.50 ± 0.2 h^{-1}, 7.26 ± 0.24 h^{-1}, and 3.78 ± 0.12 h^{-1}, respectively [13]. Weschler reviewed the studies focused on the surface removal rate of ozone in various indoor environments [8]. The results showed that in offices or laboratories, the surface removal rates ranged from 0.8 h^{-1} to 4.3 h^{-1}, while in homes, the surface removal rates ranged from 2.8 h^{-1} to 7.2 h^{-1}. The surface removal rates of ozone in a department store, museum, and clean room were 4.3 h^{-1}, 4.3 h^{-1}, and 7.6 h^{-1}, respectively. However, all these studies were conducted in western countries, with no research being conducted on the surface removal rate of ozone in China, despite the severe ozone pollution in the country. In cities of China, the surface coverings, building materials, and furnishings are different than the case studies in western countries. For example, carpet is widely used in western homes (about 70% of the floors were covered with carpets in American residences) [14], while it is barely used in Chinese homes

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[*] Corresponding author. Dept. of Building Science, School of Architecture Tsinghua University, Beijing, China.
E-mail address: binzhao@tsinghua.edu.cn (B. Zhao).

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(only 10% of the floors were covered with carpets in Chinese buildings) [15]. Therefore, the ozone deposition velocity is probably different from those measured in western countries. Therefore, a study of the surface removal rate of ozone in Chinese buildings is necessary.

In this study, the surface removal rate of ozone was measured in 15 bedrooms of 14 residences in Beijing, China. The A/V ratios were also measured to obtain the ozone deposition velocities on indoor surfaces from the measured surface removal rate. We also compared the measured deposition velocities with those calculated by theoretical models.

2. Methods

The measurements were conducted in 15 bedrooms of 14 Chinese residences and repeated once for each bedroom during April 2014 to November 2017. The number of occupants were recorded for each bedroom. During the measurements, the bedrooms were unoccupied, with the windows and interior doors of the bedrooms remaining closed. The measured rooms were equipped with neither mechanical ventilation system nor air cleaner during the measurements.

2.1. Measuring surface removal rate and deposition velocity of ozone

In the absence of indoor sources, the indoor ozone concentration can be calculated by

$$\frac{dC_{in}}{dt} = \alpha P C_{out} - (\alpha + k) C_{in} \tag{1}$$

where C_{in} and C_{out} are the indoor and outdoor ozone concentrations (ppb), respectively, α is the air change rate (h^{-1}), P is the ozone penetration factor, and k is the surface removal rate of ozone (h^{-1}).

2.2. Solving equation (1), we may obtain

$$ln\left(C_{in,t} - \frac{ap}{a+k} C_{out}\right) = -(\alpha + k)t + ln\left(C_{in,0} - \frac{ap}{a+k} C_{out}\right) \tag{2}$$

where $C_{in,0}$ and $C_{in,t}$ are the indoor ozone concentrations (ppb) at time $t = 0$, time t, respectively. When indoor ozone reached steady state, the ozone concentration could be expressed as:

$$C_{in,\infty} = \frac{\alpha P C_{out}}{\alpha + k} \tag{3}$$

$C_{in,\infty}$ is the ozone concentration at steady state (ppm). By substituting $\frac{\alpha P C_{out}}{\alpha + k}$ for $C_{in,\infty}$. We obtained:

$$ln(C_{in,t} - C_{in,\infty}) = -(\alpha + k)t + ln(C_{in,0} - C_{in,\infty}) \tag{4}$$

Based on equation (4), air change rate (α), change of ozone concentration with time ($C_{in,t}$) and ozone concentration at steady-state ($C_{in,\infty}$) are required to fit k.

We measured the air change rate with the carbon dioxide (CO_2) decay method. An ozone generator was used to elevate the indoor ozone concentration to 150–250 ppb for each measurement of surface removal rate of ozone. The indoor ozone concentration was monitored by an ozone monitor (2 B Technologies Model 205 Federal Equivalent Method (FEM)) at an interval of 10 s, with an accuracy of ± 1.5 ppb/2% of the reading and lower limit of detection 2 ppb. Each measurement lasted for 3–4 h to ensure that the ozone concentrations decay to steady state. The average ozone concentration of the last 10 min was considered as $C_{in,\infty}$.

With all the parameters required for equation (4), a linear fitting was adopted to obtain the overall indoor removal rate of ozone ($\alpha + k$). By subtracting the measured α, we could obtain the surface removal rate of ozone, k.

Once k is obtained, the deposition velocity for the entire room could be calculated by:

$$v_d = 100k/(A/V) \tag{5}$$

where v_d is the deposition velocity of ozone (cm/h), V is the volume of room (m^3) and A is the total area of indoor surface (m^2). The volume and surface areas of the studied bedrooms were measured before each measurement. Most of the surfaces were rectangular, with some being irregular. The irregular surfaces were approximately rectangular. Under this condition, the lengths and widths of each surface were measured by tape to obtain the surface areas. The projected surface area was used for the calculation. As for the volume, the height, length, and width of the room were measured to obtain the volume of the entire room, while the volume of some furniture, such as closets, were deducted. The net volume was subsequently used to obtain the deposition velocity with equation (5).

2.3. Theoretical calculation of ozone deposition velocities on indoor surfaces

We can also calculate the ozone deposition velocity with theoretical models, as described by Cano-Ruiz et al. [16]. The near-surface air flow was assumed to be laminar, with the deposition velocity on a horizontal surface calculated by:

$$\frac{1}{v_{dh,i}} = \frac{1}{\gamma_i \frac{<v>}{4}} + \frac{\delta_c}{D} \tag{6}$$

where $v_{dh,i}$ is the deposition velocity on a horizontal surface. γ_i is the reaction probability of material i, the value of which is mentioned in Table S1 in Supporting Information (SI). The materials of different indoor surfaces and their positions in each measuring room were recorded for the theoretical calculation of deposition velocities. $< v >$ is the Boltzmann velocity, which is equal to 360 m/s for ozone ($T = 293$ K), δ_C is boundary layer thickness (m) and D is the diffusion coefficient of ozone, the value of which is 1.82×10^{-5} m^2/s according to the study by Cano-Ruiz et al. [16].

To obtain δ_C, equations (7)–(9) were used according to the previous study [17].

$$y^+ = \frac{\delta_c u^*}{\nu} \tag{7}$$

$$u^* = \left(\nu \left.\frac{du}{dy}\right|_{y=0}\right)^{1/2} \tag{8}$$

$$\left.\frac{du}{dy}\right|_{y=0} = \left(\frac{0.074}{\nu \rho_a}\right)\left(\frac{\rho_a U_\infty^2}{2}\right)\left(\frac{L U_\infty}{\nu}\right) \tag{9}$$

where y^+ is the normalized distance from the surface, which is equal to 30 according to the study by Lai et al. [17]. u^* is the frictional velocity (m/s), ν is the kinematic viscosity of air (1.5×10^{-5} m^2/s), ρ_a is the air density, the value of which is 1.2 kg/m^3, L is the characteristic length of the surface (m), and U_∞ was set as 0.15 m/s [17].

For the vertical surface, the deposition velocity is calculated by equation (10), based on the assumption of natural convection laminar flowing past a vertical isothermal plate [16].

$$\bar{v}_{dv,i} = \frac{4}{3}\frac{v_t(H)}{P_i^3}\left\{P_i^3 - 3\left[\frac{P_i^2}{2} - P_i + \ln(1 + P_i)\right]\right\} \tag{10}$$

where $\bar{v}_{dv,i}$ is the average deposition velocity of a vertical surface (m/s), $v_t(H)$ is the transport-limited deposition velocity at a height of H (m/s), which can be expressed as:

$$v_t(H) = 0.50\frac{D}{H} Le^{0.463}\left(\frac{Gr_H}{4}\right)^{1/4} \tag{11}$$

where H is the height of the vertical surface (m), Le is the Lewis number, which is 1.2 for ozone at 293 K [16], and Gr_H is the Grashof number at the height of H, defined by: