Characteristics of indoor ozone pollution in residential buildings based on outdoor air pollution

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Abstract Ozone pollution can not only cause serious effects on human respiratory tract, lung, cardiovascular and immune system, but also lead to secondary pollution of indoor air environment by reacting with human surface sebum, building materials surface and other indoor compounds. As people stay indoors for more than 90% of their time, indoor ozone exposure is far more harmful than outdoor ozone exposure. Indoor ozone mainly comes from the outdoor environment. Therefore, it is an important prerequisite for controlling indoor ozone pollution to master the characteristics of indoor ozone pollution concentration under the influence of outdoor air pollution. The outdoor ozone concentration of 20 representative cities in the five climatic areas of China were investigated in this study. Meanwhile, indoor ozone concentration was predicted based on I/O ratio (indoor-outdoor concentration ratio). Furthermore, the indoor ozone pollution level affected by window opening time, air change rate and ozone deposition velocity was analyzed. The results show that the increase of air change rate and window opening time leads to the rise of indoor ozone pollution level. Moreover, the growing up of ozone deposition velocity may cause more ozone to be removed by the indoor surface, then the indoor ozone concentration decreases. In addition, indoor ozone pollution is the most serious in cold zone and the least serious in mild zone.

Keywords: ozone concentration, I/O ratio, window opening time, air exchange rate, deposition velocity

1 Introduction

It is well known that the surface ozone pollution can cause adverse effects on human health. A large number of epidemiological studies show that ozone exposure associated with increased short-term mortality[1-2]. Zhang[1] analyzed the relationship between the mortality rate of respiratory diseases and outdoor ozone concentration in China and found that respiratory mortality significantly increased by 0.55% for every 10 mg/m³ increase in the 8-h average concentration of ozone. In addition to respiratory diseases, ozone exposure can also cause lung function damage, airway inflammation, and cardiovascular diseases[4-5]. Moreover, ozone can react with occupant surface sebum and building materials[6-7] to generate formaldehyde, propylene[8-9], acetone and other secondary air pollutants, causing secondary pollution of indoor environment. According to China Environmental Bulletin, in 2020, the number of days exceeding the standard with ozone as the main pollution accounted for 37.1%, while the number of days with heavy pollution or above accounted for 22.0%. After PM2.5 (particles with aerodynamic diameter less than 2.5 µm), ozone become the second-air pollution in China.

The indoor ozone concentration mainly depend on the outdoor ozone concentration. Although indoor ozone concentration is generally lower than outdoor ozone concentration with the partition effect of building envelope, the harm of indoor ozone exposure is far greater than outdoor ozone exposure because people spend more than 90%[11] of their time indoors on average. Chen[12] found that the positive correlation between mortality and outdoor ozone concentration depends on indoor ozone exposure. The harm of indoor ozone exposure to human health can not be ignored. Therefore, many researchers have studied the relationship between indoor and outdoor ozone concentrations. Based on the studies of indoor ozone and outdoor ozone concentration in the California Institute of Technology building, Shair[13-14] found that the indoor ozone concentration was to closely track outdoor concentration and to be dependent on the air exchange rate. In the absence of indoor ozone sources, Weschler[15] analyzed that the indoor-outdoor ozone concentration (I/O) ratio is 0.2-0.3 in offices and hospital, and 0.5-0.7 in classrooms and restaurants without indoor ozone sources. Window opening behavior also affects the I/O ratio. Zou[16] found that the I/O ratio is 0.64 when opening the window and 0.48
when closing the window. In the study of the I/O ratio, most scholars used the average value of the whole sampling period, while Sabersky[16] and Druzk[18] studied indoor and outdoor ozone concentration in continuous time, and they found that the peak indoor ozone concentration would lag behind the peak outdoor ozone concentration.

It can be seen from the existing studies that there is still a lack of systematic analysis and characteristics research on the relationship between indoor and outdoor ozone concentration in different climatic zones in China. Therefore, the main purpose of this study is to determine the indoor ozone concentration characteristics of 20 typical cities in five climatic zones of China. The influence of window opening time, air exchange rate and ozone deposition velocity on indoor ozone pollution level was further analyzed, which may provide guide for effective reducing of indoor ozone concentration.

2 Methods

2.1 Statistical analysis

The daily ozone concentration and surface meteorological elements data of the cities in this paper come from the China Air Quality Online Monitoring and Analysis Platform (https://www.aqistudy.cn/) in 2020. In order to analyze the distribution characteristics of outdoor ozone concentration in different climate zones, Pearson correlation coefficient and correlation test were used for quantitative comparison.

2.2 Calculation of indoor ozone concentration

Indoor ozone concentration is mainly determined by outdoor ozone concentration, air exchange rate, indoor sources of ozone, the rate at which ozone is removed by indoor surfaces and the reactions between ozone and other chemicals in the air. According to the study of Shaar[19], for a given building, with a constant air exchange rate and absent varying indoor sources, the indoor concentration divided by the outdoor ozone concentration remains relatively constant. Weschler[15] summarized previous measured data and proposed a method for calculating I/O ratio, as shown in equation (1):

$$\frac{C_{in}}{C_{out}} \times 10 / \theta = \frac{E_{x}}{k_{x}+E_{x}}$$  \hspace{1cm} (1)

where $E_{x}$ is air exchange rate, in units of h$^{-1}$; $k_{x}$ is the ozone deposition velocity, in units of m$^{-1}$h$^{-1}$; A is the total surface area with in the room, in units of m$^{2}$; V is the volume of the room, in units of m$^{3}$.

In the equation (1), the I/O ratio for ozone can be approximated by the ratio of the air exchange rate to the sum of the air exchange rate and the surface removal rate. Based on the fact that dilution and surface removal of ozone are normally much faster than the time variation of the outdoor ozone concentration, this equation can be assumed to be a quasi-steady state situation. Xiang[20] considered the influence of window opening on indoor ozone concentration and proposed Equation (2) to calculate I/O ratio:

$$\frac{1}{\Theta} = \frac{(E_{x, clo} f_{clo} + E_{x, op} f_{op}) p}{k_{d1} + E_{x, clo} f_{clo} + E_{x, op} f_{op}}$$  \hspace{1cm} (2)

where $E_{x, clo}$ is air exchange rate when the window is closed, in units of h$^{-1}$; $E_{x, op}$ is air exchange rate when opening the window, in units of h$^{-1}$; $f_{clo}$ and $f_{op}$ are the fractional time window are closed and open, respectively; p is the penetration factor for ozone.

According to the China Statistical Yearbook, the per capita living area of urban residents in China is about 36m$^{2}$. Therefore, the height of the bedroom calculated in this paper is 2.5m, the total surface area is 132 m$^{2}$, the volume is 90m$^{3}$, and penetration factor for ozone is 0.79 [21].

3 Results and discussion

3.1 Distribution characteristics of outdoor ozone concentration in different climate zones

According to the Environmental Air Quality Standard (GB3095 2012)[22] issued by the Ministry of Environmental Protection of China, the daily maximum 8-h ozone ($O_{8h}$) concentration is 100ug/m$^{3}$ at the first level and 160ug/m$^{3}$ at the second level. Therefore, it is stipulated that when the $O_{8h}$ concentration is greater than 100ug/m$^{3}$, it is first-order exceeding and secondary exceeding standard when the concentration is greater than 160ug/m$^{3}$. In order to analyze the distribution characteristics of outdoor ozone concentrations in different climatic zones, the annual data are divided into four seasons: winter from December to February of the next year, spring from March to May, summer from June to August and autumn from September to November. Fig. 1-5 respectively show the annual distribution of $O_{8h}$ concentration, relative humidity and temperature in typical cities of hot summer and cold winter zone, hot summer and warm winter zone, mild zone, cold zone and severe cold zone in 2020. Table 1-5 show the correlation coefficients between $O_{8h}$ concentration, relative humidity and temperature in different climate zones.
As shown in Fig.1, ozone concentrations in the hot summer and cold winter zone in 2020 increased firstly and then decreased throughout the year. From spring onwards, the ozone concentration began to increase substantially, and the secondary exceeding standard concentration appeared in May to September. After September, the ozone concentration began to decrease gradually and reached its lowest level in winter. Therefore, the ozone concentration level in this climatic zone is summer > spring > autumn > winter. Meanwhile, in order to further analyze the characteristics of outdoor ozone concentration in hot summer and cold winter zone, the calculated correlation coefficients are shown in Table 1. Therefore, from the correlation test, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.496, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.587.

### Table 1

<table>
<thead>
<tr>
<th>variate</th>
<th>Pearson correlation coefficient</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity</td>
<td>-0.496</td>
<td>1.75E-91</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.587</td>
<td>2.86E-136</td>
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</tbody>
</table>

As shown in Fig.1, Scatter plot of annual variation of O₃-8h concentration, relative humidity and temperature in typical cities in hot summer and cold winter zone.
As shown in Fig.2, ozone concentrations in Xiamen and Nanning did not fluctuate significantly throughout the year, while the concentration in Guangzhou and Shenzhen had many peaks throughout the year, and the peak concentration were much higher than this in the other two cities. In this climatic zone, the secondary exceeding concentration mostly appeared in April to May, August to September, and in January, November and December, the secondary exceeding standard concentration also appeared occasionally. Therefore, the ozone concentration level in this climatic zone is autumn > spring > summer > winter. Meanwhile, from the correlation test, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.185, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.239, as shown in table 2. It can be seen that this correlation is not as significant as that in hot summer and cold winter zone, which may be caused by meteorological factors such as marine monsoon.
As shown in Fig.3, the trend of ozone concentration in mild zone in 2020 was first to rise and then to decline. From spring, the ozone concentration began to rise significantly, and the secondary exceeding standard concentration appeared in May to August. Therefore, the ozone concentration level in this climatic zone is spring > winter > summer > autumn. Meanwhile, from the correlation test, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.168, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.137, as shown in table 3. Although the correlation coefficients are not high, P value < 0.05 indicates that these datasets are significantly correlated at the significance level of 0.05.

### Table 3 Pearson correlation coefficient between relative humidity and ozone concentration

<table>
<thead>
<tr>
<th>variate</th>
<th>Pearson correlation coefficient</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity</td>
<td>-0.168</td>
<td>9.34E-11</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.137</td>
<td>1.44E-7</td>
</tr>
</tbody>
</table>

As shown in Fig.4, the trend of ozone concentration in cold zone in 2020 was first rising and then decreasing. As in hot summer and cold winter zone, the ozone concentration in this zone increased significantly from spring, and the secondary exceeding standard concentrations appeared in May to September. After September, ozone concentration began to decrease gradually. Therefore, the ozone concentration level in this climatic zone is Summer > Spring > Autumn > Winter. Meanwhile, as shown in Table 4, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.266, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.789.

### Table 4 Pearson correlation coefficient between O$_3$-8h concentration, relative humidity and temperature in typical cities in cold zone

<table>
<thead>
<tr>
<th>variate</th>
<th>Pearson correlation coefficient</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity</td>
<td>-0.266</td>
<td>4.15E-25</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.789</td>
<td>2.77E-289</td>
</tr>
</tbody>
</table>

As shown in Fig.4, the trend of ozone concentration in cold zone in 2020 was first rising and then decreasing. As in hot summer and cold winter zone, the ozone concentration in this zone increased significantly from spring, and the secondary exceeding standard concentrations appeared in May to September. After September, ozone concentration began to decrease gradually. Therefore, the ozone concentration level in this climatic zone is Summer > Spring > Autumn > Winter. Meanwhile, as shown in Table 4, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.266, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.789.
As shown in Fig.5, the trend of ozone concentration in severe cold zone in 2020 was first to rise and then to decline. From spring, the ozone concentration began to rise significantly, and the secondary exceeding standard concentration appeared in Harbin, Hohhot and Shenyang from May to August, while there was no secondary exceeding standard concentration in Urumqi. After August, ozone concentration began to decrease gradually. Therefore, the ozone concentrations level in this climatic zone is Summer > Spring > Autumn > Winter. Meanwhile, as shown in Table 4, there is a statistical significance negative correlation between relative humidity and ozone concentration, with a correlation coefficient of -0.133, while there is a statistical significance positive correlation between temperature and ozone concentration, with a correlation coefficient of 0.684.

From Table 1-5, it can be seen that the ozone concentration is affected by temperature and relative humidity. On the one hand, temperature can directly affect the rate of chemical reaction. On the other hand, under high temperature, solar radiation is stronger, which promotes the photochemical reaction of ozone generation. Therefore, temperature is positively correlated with the ozone concentration. In atmospheric environment with high relative humidity, solar radiation decays due to the influence of water vapor, which is not conducive to the generation of ozone. Therefore, relative humidity is negatively correlated with ozone concentration. In addition, the influence of meteorological conditions on ozone concentration varies in different climatic zones due to other natural conditions such as terrain.

### 3.2 Analysis and discussion of indoor ozone concentration

#### 3.2.1 Test of the indoor ozone concentration prediction model

In order to verify the above theoretical model, indoor ozone concentration of a residential building in Chengdu in hot summer and cold winter zone was measured by a dual beam UV-absorbance ozone analyzer (Model 205, 2B Technologies). Then, the indoor ozone concentration under different conditions were calculated by equation (2) and the prediction interval of indoor ozone concentration is obtained. As shown in Fig. 6, the measured ozone concentrations were within the predicted range. The test results showed that the ozone I/O ratio of the room was between 0.39 and 0.71, with an average of 0.52, and the measured ozone concentration was between

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**Table 5** Pearson correlation coefficient between O₃-8h concentration, relative humidity and temperature in severe cold zone

<table>
<thead>
<tr>
<th>variate</th>
<th>Pearson correlation coefficient</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity</td>
<td>-0.133</td>
<td>3.36E-7</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.684</td>
<td>9.02E-203</td>
</tr>
</tbody>
</table>

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**Fig.5.** Scatter plot of annual variation of O₃-8h concentration, relative humidity and temperature in typical cities in severe cold zone

(d)Shenyang
16-43ug/m³. The predicted ozone I/O ratio was between 0.13 and 0.79, with an average of 0.47, and the predicted ozone concentration was between 3-46ug/m³. The predictive model calculated a large range of ozone concentration to I/O ratio, because the predictive equation took into account different open-window conditions, while the measurement was only open-window, which also indicated that the model can describe indoor ozone concentration under different conditions.

Fig. 6. The relationship between measured indoor ozone concentration and predicted concentration range

3.2.2 Window opening time

As the main way of natural ventilation in residential buildings in China, occupants’ window opening behavior is influenced by outdoor climatic conditions, and the window opening time can be influenced by the outdoor temperature. In order to analyze the indoor ozone concentration under different window opening and closing time, the window opening time ratio was taken as the variable with the range of 0-100%. The assumptions applied to Equation (2) were the air exchange rate of 5.73h⁻¹ when opening the window and 0.31h⁻¹ when closing the window[23], the indoor ozone deposition velocity of 1.09m·h⁻¹[24]. The mean and peak values of indoor ozone concentration are shown in Fig. 7 and 8 respectively.

Fig. 7. Mean value of indoor and outdoor ozone concentration at different window opening time ratio

Fig. 8. Maximum concentration of indoor and outdoor ozone at different window opening time ratio

As can be seen from Fig. 7 and 8, indoor ozone concentration increases with the increase of window opening time. When the window opening time ratio rises from 0 to 20%, the indoor ozone concentration increases by 65%. However, with the further increase of window opening time ratio, the influence on I/O ratio is no longer significant. When the window opening time ratio changes from 80% to 100%, the indoor ozone concentration only increases by 5%. Moreover, the annual mean indoor ozone concentrations range from 11 to 53ug/m³ in hot summer and cold winter zone, from 11 to 53ug/m³ in hot summer and warm zone, from 10 to 50ug/m³ in mild zone, from 12 to 59ug/m³ in cold zone, from 11 to 53ug/m³ in severe cold zone. Meanwhile, when the outdoor concentration reaches the peak value, the indoor concentration can reach 142ug/m³ in hot summer and cold winter zone, 126ug/m³ in hot summer and warm zone, 100ug/m³ in mild zone, 162ug/m³ in cold zone, 136ug/m³ in severe cold zone.

It is worth noting that the window opening duration in spring and autumn is significant longer than that in other seasons. However, according to the previous analysis of outdoor ozone concentration, outdoor ozone pollution in spring and autumn is serious. Therefore, in order to obtain good indoor air quality, the window opening duration in these seasons should be controlled.

3.2.3 Air exchange rate

According to the Design Code for Heating Ventilation and Air Conditioning of Civil Buildings (GB 50736-2012), the minimum air exchange rate of residential buildings with per capita living area of 20-50 m² is 0.5h⁻¹. In order to analyze the indoor ozone concentration under different air exchange rate, it is assumed that the window is always open and the indoor ozone deposition velocity is 1.09m·h⁻¹[24]. The mean and peak values of indoor ozone concentration are shown in Fig. 9 and 10 respectively.
residential buildings in China was 1.09±0.34 m·h⁻¹. In order to analyze the I/O ratio under different ozone deposition velocity, it is assumed that the window is always open and the air exchange rate is 5.73 h⁻¹. The mean and peak values of indoor ozone concentration are shown in Fig. 11 and 12 respectively.

3.2.4 Ozone deposition velocity

Yao [23] measured the removal rate of ozone deposition on the indoor surface of 14 residential areas in China, and the result showed that the ozone deposition velocity of
4 Conclusions
In this paper, the distribution characteristics and concentration level of outdoor ozone in different climate zones were analyzed, and the influence characteristics of window opening time ratio, air exchange rate and ozone deposition velocity on indoor ozone concentration level in different climate zones were studied, and the following conclusions were drawn:

1) The ozone concentration level in hot summer and cold winter zone, cold zone and severe cold zone is summer > spring > autumn > winter, while the ozone concentration level in hot summer and warm winter zone is autumn > spring > summer > winter, and the ozone concentration level in mild zone is spring > winter > summer > autumn.

2) The indoor ozone concentration increases with the increase of window opening time, but with the continuous increase of window opening time, the increment of indoor ozone concentration decreases, and the window opening duration in the spring and autumn should be restricted by outdoor pollution.

3) The indoor ozone concentration increases with the increase of air exchange rate, but the increment of indoor ozone concentration decreases with the continuous increase of air exchange rate.

4) The indoor ozone concentration decreases with the increase of ozone deposition velocity, and the decline range of indoor ozone concentration decreases with the continuous increase of ozone deposition velocity.

5) The indoor ozone pollution in cold zone is more serious than that in other climate zones, and the indoor ozone pollution level in mild zone is the lowest.

References


