USING OZONE AIR CLEANERS TO REMOVE INDOOR VOLATILE ORGANIC COMPOUNDS

KP Yu, GWM Lee, CP Hsieh, SH Yang

1 Graduate Institute of Environmental Engineering, National Taiwan University
71, Chou-Shan Rd., Taipei, Chinese Taipei

ABSTRACT
Indoor volatile organic compounds (VOCs) are known to cause many human health problems. Ozone air cleaners were claimed to remove the indoor VOCs, but their effectiveness was still unclear. In this study, we selected six ozone air cleaners to evaluate their effectiveness on the control of target VOCs (toluene and formaldehyde). The experiments were conducted in a 11.3-m$^3$ stainless steel environmental test chamber under 25$^\circ$C and 60% relative humidity. The clean air delivery rate for toluene and formaldehyde ranged from 0.0565 to 0.424 m$^3$/hr, and from 0.0068 to 0.747 m$^3$/hr, respectively. The removal rates observed were much high than the removal rates based on the ozone-toluene and ozone-formaldehyde reaction constants measured in previous studies. Thus, the removal of toluene and formaldehyde may result from the other mechanism such as adsorption, and high-voltage electric discharge or ultraviolet lamp, used to generate ozone.

INDEX TERMS
Ozone air cleaner, Toluene, Formaldehyde, Removal Efficiency, Environmental test chamber

INTRODUCTION
Numerous volatile organic compounds (VOCs) could be found in indoor environment. They can cause discomfort such as eye, skin, mucous membrane tissue, and respiratory tract irritation (Elkins 1959). Long-term or high concentration exposure can cause toxic effects to the central nervous system and internal organs. For example, some halogen derivatives VOCs can cause the functional and destructive damage to liver and kidney (Anderson 1981). Furthermore, many VOCs, especially formaldehyde, and some aromatics and halogen derivatives, have been proven to be carcinogens and mutagens (Hines 1993, NAS 1972, Hartwell 1985). Researches show that VOCs in indoor environment is relevant to the cause of sick building syndrome (SBS) (Repace 1981). The sources of indoor VOCs include infiltration of outdoor air pollutants, by-product of combustion generating during cooking or space heating, emission from building elements and furniture, and biological source such as occupants, plants, and fungi.

Owing to the risen general awareness of indoor air pollutions, and increased request for better indoor air quality, a lot of air cleaners appear in the market place, and one of them is ozone air cleaner. Manufactures often assert that ozone air cleaners can generate fresh air and remove many kinds of indoor air pollutants including VOCs. However, some reports suggest that ozone has some negative effects on health such as harm in lung function, exacerbation of asthma, throat irritation, coughing, chest ache and shortness of breath, inflammation of lung tissue, and increase in respiratory infection (Boeniger 1995). Furthermore, there is little information accessible to consumers on the effectiveness of these devices for controlling VOCs.

The objective of this study was to investigate the performance of the ozone air cleaners for controlling VOCs. We selected six ozone air cleaners of different brands for testing. Toluene and formaldehyde were chosen as target pollutants. The tests were conducted in a 11.3-m$^3$ stainless steel environmental testing chamber under around 25$^\circ$C and 60% relative humidity.

RESEARCH METHODS
Experimental methods
The experiments were conducted in a stainless steel environmental test chamber (dimension: 2.2(L)×2.2(W)×2.3(H) m) in static mode, i.e. no mechanical ventilation. The temperature inside the chamber fluctuated between 23$^\circ$C and 26$^\circ$C and the relative humidity was around 55-65%. A fan installed in the test

* Corresponding author email: f89541105@ntu.edu.tw
chamber was used to mix the air. The ozone concentration was detected continuously by a monitor, Ozone Analyzer Model 400A (API Inc.). The sampling port of ozone analyzer was about one meter away from the ozone air cleaner. The VOC solvent was injected into a tube wrapped with heating wire. After the VOC solvent completely evaporated, the vapor was flushed into the chamber, then the air cleaner was switched on, and the experiment started. The outlet air of the chamber was sampled on Tenax TA cartridges (for toluene) or 2,4-dinitriphenylhydrazine (DNPH) solution (for formaldehyde) every 2 hours, and then analyzed by the GC system immediately. The natural decay experiment was conducted with the same procedure while the air cleaner was off.

Data analysis
Data analysis procedures followed the previous studies of gaseous pollutant removal by air cleaners (Daisey and Hodgson 1989, Niu et al. 1998). The variation of VOCs concentration within the test chamber may result from removal by air cleaner, adsorption on wall, re-emission from the wall, and leakage of the test chamber. However, we need to take the gas-phase ozone-VOCs reaction into consideration. The experiments were conducted in static mode. Thus, the variation of VOCs concentration in the chamber could be expressed as the differential mass balance equation:

\[
\frac{dC_{VOC}}{dt} = \frac{1}{V} \left( -v_a \eta E_v C_{VOC} - k_n V C_{VOC} + G_{re} - k C_{O3} C_{VOC} \right)
\]

where \( C_{VOC} \) is average VOC concentration in the test chamber, \( V \) is volume of the test chamber, \( v_a \) is air flow rate through the air cleaner, \( \eta \) is removal efficiency of the air cleaner, \( E_v \) is short-circuiting factor, \( k_n \) is natural decay constant of VOC, which is associated to adsorption on wall and leakage of chamber, \( G_{re} \) is re-emission from wall, \( k \) is ozone-VOC reaction constant, and \( C_{O3} \) is average ozone concentration.

The removal efficiency of the air cleaner, \( \eta \), is defined as

\[
\eta = \frac{C_{VOC\,(in)} - C_{VOC\,(out)}}{C_{VOC\,(in)}}
\]

where \( C_{VOC\,(in)} \) and \( C_{VOC\,(out)} \) are the VOC concentration at the inlet and outlet of the air cleaner. The short-circuiting factor, \( E_v \), is defined as \( E_v = C_{VOC\,(in)}/C_{VOC\,(out)} \).

As VOC concentration decreases during experiment, the re-emission from the wall, \( G_{re} \), may occur and it could be described as (Niu et al. 1998):

\[
G_{re} = \frac{dm_{ad}}{dt}
\]

where \( m_{ad} \) is the amount of VOC adsorbed on the wall surface. It equals the amount of injected VOCs minus the amount of initial (maximum) VOC vapor in the chamber and it could be formulated as (Niu et al. 1998):

\[
m_{ad} = \alpha V C_{VOC}
\]

where \( \alpha \) is a constant (in this study, \( \alpha = 0.05 \)). Substituting Eqn.(3) into Eqn.(2), we have:

\[
G_{re} = \frac{d\alpha V C_{VOC}}{dt} = \alpha V \frac{dC_{VOC}}{dt}
\]

The average ozone concentration, \( C_{O3} \), is monitored throughout the testing, and we use a generation-decay model to fit the data. The model is shown as follows (Niu et al. 2001):

\[
V \frac{dC_{O3}}{dt} = E - k_j V C_{O3}
\]

where \( E \) is the ozone emission rate, \( k_j \) is the ozone decay constant, which is relevant to the deposition/reaction on the wall, reaction with VOCs, and removal by the air cleaner itself. The initial condition is that when \( t=0, C_{O3}=C_{O3\,(0)}=0 \). Thus, the general solution of Eqn.(5) is
\[
C_{d3} = \frac{E}{k_dV} \left[ 1 - \exp(-k_d t) \right]
\]  
(6)

Since the VOCs concentration varied during the testing and the aging effect of the wall (Mueller et al. 1973, Sabersky et al. 1973) might occur, it implied that \( k_d \) was not a constant. However, from the experimental result, the effects mentioned above were insignificant. Therefore, the empirical analysis that assumes \( k_d \) was a constant is practicable (Mueller et al. 1973).

Substituting Eqn.(4) and Eqn.(6) into Eqn.(1) and then rearranging, we have:

\[
\frac{dC_{VOC}}{dt} = -\left( v_d \eta E_d + k_a V + \frac{kE}{k_dV} \left[ 1 - \exp(-k_d t) \right] \right) \frac{C_{VOC}}{V(1+\alpha)} = -k_a C_{VOC}
\]  
(7)

where \( k_a \) is the decay constant when air cleaner is running (although the ozone concentration varied with time, this effect was negligible. And we will discuss this later). When air cleaner is off, the Eqn.(4) can be reduced to

\[
\frac{dC_{VOC}}{dt} = -\frac{k_a}{(1+\alpha)} C_{VOC} = -k_n' C_{VOC}
\]  
(8)

where \( k_n' \) is the natural decay constant when re-emission occurs. The clean air delivery rate (CADR) is defined as:

\[
\text{CADR} = V \left( k_a - k_n' \right)
\]  
(9)

RESULTS
Natural Decay
Figure 1 (a) and Figure 1 (b) showed the natural decay of toluene and formaldehyde in the chamber, respectively, where \( C_{VOC(0)} \) represent the initial VOC concentration. The measured data were fitted with Eqn.(8) and the natural decay constants for toluene and formaldehyde were 0.0543 and 0.0549 hr\(^{-1}\), respectively. Natural decay of VOCs in the chamber was relevant to the adsorption on wall, re-emission form the wall, and leakage of chamber.

\[\text{Figure 1. Natural decay (exponential) of (a) toluene and (b) formaldehyde in the chamber}\]

Removal of VOCs by Ozone-VOC Reaction
As described in Eqn. (7)–(9), the effects of ozone-VOC reaction and air cleaner on the decay and CADR of VOC coexist during the testing. The method we used to determinate the effect of ozone-VOC reaction on the removal of VOC based on the result of previous studies regarding the gas-phase ozone-VOC reaction. Using Eqn.(6) to regress the variation of ozone concentration with time observed in the chamber, we got the ozone emission rate, \( E \), and the ozone decay constant, \( k_d \). (The \( R^2 \) of the regression curve > 0.995). From previous study, the ozone-toluene and ozone-formaldehyde reaction constants were \( 3.69 \times 10^{-12} \text{ ppb}^{-1} \text{s}^{-1} \) and \( 5.17 \times 10^{-14} \text{ ppb}^{-1} \text{s}^{-1} \), respectively (Atkinson and Carter 1984, Boeniger 1995). According to Eqn.(7)–(9), the CADR result from ozone-VOC reaction was

\[
\frac{kE[1-\exp(-k_d t)]}{(1+\alpha)} k_d V
\]

and the values of the test six air cleaners ranged from \( 8.34 \times 10^{-14} \) to \( 8.92 \times 10^{-13} \text{ m}^3/\text{hr} \) for toluene, and from \( 1.17 \times 10^{-15} \) to \( 1.25 \times 10^{-14} \text{ m}^3/\text{hr} \) for formaldehyde. Comparing with the whole CADR, the part of CADR caused by the ozone-VOC reaction was very insignificant (~0%).
Consequently, the removal of VOCs may arise mainly from the air cleaners themselves rather than the ozone they emit.

**Removal of VOCs by Air Cleaners**

According to Eqn. (7)–(9), the CADR rise from air cleaner was $v_\alpha \eta E_d/(1+\alpha)$. And this value was $V(k_a-k_n)$ minus $kE[1-exp(-kd)t]/(1+\alpha)k_dV$ (CADR result from ozone-VOC reaction). Since the part of CADR that rise from ozone-VOC reaction was negligible, the removal of toluene and formaldehyde resulted mostly from (~100%) the effect of air cleaner, and the mechanism might be adsorption by filter, and high-voltage electric discharge or ultraviolet lamp, used to generate ozone. And this needs further research and discuss. As shown in Table.1, the product of the removal efficiency of air cleaner, $\eta$, and the short-circuiting factor, $E_d$, ranged from 1.45 to 6.92% for toluene, and from 0.77 to 11.4% for formaldehyde, and the air flow rate through air cleaner, $v_\alpha$, ranged from 1.75 to 9.07 m$^3$/hr. NO.6 was the best among these air cleaners for removing toluene and formaldehyde.

**Table 1. Summary of effectiveness of the 6 tested ozone air cleaners for removing toluene and formaldehyde**

<table>
<thead>
<tr>
<th></th>
<th>NO.1</th>
<th>NO.2</th>
<th>NO.3</th>
<th>NO.4</th>
<th>NO.5</th>
<th>NO.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_\alpha$ (m$^3$/hr)</td>
<td>1.8</td>
<td>7.49</td>
<td>4.05</td>
<td>9.07</td>
<td>1.75</td>
<td>6.9</td>
</tr>
<tr>
<td>$\eta E_d$ for toluene (%)</td>
<td>3.28</td>
<td>2.07</td>
<td>6.92</td>
<td>1.45</td>
<td>6.35</td>
<td>6.42</td>
</tr>
<tr>
<td>$k_a$ for toluene (1/hr)</td>
<td>0.059</td>
<td>0.0674</td>
<td>0.078</td>
<td>0.0654</td>
<td>0.0637</td>
<td>0.0918</td>
</tr>
<tr>
<td>CADR for toluene (m$^3$/hr)</td>
<td>0.0565</td>
<td>0.148</td>
<td>0.268</td>
<td>0.125</td>
<td>0.106</td>
<td>0.424</td>
</tr>
<tr>
<td>Air cleaner contribution</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
</tr>
<tr>
<td>Ozone contribution</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
</tr>
<tr>
<td>$\eta E_d$ for formaldehyde (%)</td>
<td>3.08</td>
<td>0.77</td>
<td>3.47</td>
<td>3.37</td>
<td>0.81</td>
<td>11.4</td>
</tr>
<tr>
<td>$k_a$ for formaldehyde (1/hr)</td>
<td>0.059</td>
<td>0.0592</td>
<td>0.0662</td>
<td>0.0802</td>
<td>0.0555</td>
<td>0.121</td>
</tr>
<tr>
<td>CADR for formaldehyde (m$^3$/hr)</td>
<td>0.0463</td>
<td>0.0486</td>
<td>0.128</td>
<td>0.286</td>
<td>0.0068</td>
<td>0.747</td>
</tr>
<tr>
<td>Air cleaner contribution</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
<td>~100%</td>
</tr>
<tr>
<td>Ozone contribution</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
<td>~0%</td>
</tr>
</tbody>
</table>

**DISCUSSION**

From our experimental results, the effectiveness of the tested ozone air cleaners on the removal of VOCs (toluene and formaldehyde) was relatively low, comparing with other air cleaners (Niu et al. 1998, Ao and Lee 2005). The chamber provided an isolated environment where many confounding factors could be eliminated. Therefore, the performance of the air cleaner observed here may be different from those in the real condition. For example, some material like duct liners and carpets may react with ozone and emit VOCs (Morrison et al. 1998, Weschler et al. 1992). And, the adsorption/re-emission effect of the wall varies with material to material. However, the chamber test still provided a practical method for examining the performance and operation characteristic of the ozone air cleaners. And the effect of other environmental factor, such as relative humidity, air change rate and temperature, could be taken into consideration in future studies.

**CONCLUSION AND IMPLICATIONS**

Based on the results of this study, the removal efficiencies of VOCs, which possess low VOC-ozone reaction constants, by ozone air cleaner are very low, and these VOCs include most frequently encountered indoor VOC species. The removal of VOCs may be mainly caused by the filter, and high-voltage electric discharge or ultraviolet lamp, used to generate ozone from oxygen, of the air cleaners. Ozone that emit from these air cleaners may cause some health problems when the concentration is higher than health standards. Furthermore, ozone could react with some materials used in indoor environment, and this may result in the damage of these materials and VOCs emission. Therefore, when using these air cleaners, the operation characteristic of these devices should be well understood to make sure that the use of these devices would not cause any health problem to the occupants.

**ACKNOWLEDGEMENTS**

The authors would like to thank National Science Council for funding the research project under contract number 91-EPA-Z-241-001.

**REFERENCES**


