Evaluation of indoor pollutant emissions from portable air cleaners

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Why portable air cleaners?

- A diverse set of devices is available in a growing market
- There is limited prior research, standards or regulations on pollutant emissions from portable air cleaners
- There is little information on emissions and effectiveness
- In some cases, marketing claims on IAQ benefits seem overstated
- Poorly engineered devices may pose risks by emitting ozone, volatile organic compounds (VOCs), particulate matter (PM) and/or reactive oxygen species (ROS)
- Previous studies showed formaldehyde emissions
The objectives of this study are...

- Evaluate the **primary and secondary emissions** of indoor air pollutants
- Evaluate the devices’ pollutant **removal efficiencies**
- Emphasize a **new generation of equipment, emerging technologies**

**Commonly used in air cleaning**
- HEPA filters
- Activated carbon
- Permanganate + zeolites
- UV light + TiO$_2$

**Newer technologies**
- Photocatalysis
- Non-thermal plasma
- Electron jet, discharge, arc
- Ceramics
- Microbial thermal inactivation
Project Tasks

• Selection and procurement of air cleaners to be studied
  o Photocatalytic oxidation (PCO), non-thermal plasma and microbial inactivation using heated ceramics
  o Designed for room-size application
  o 6 devices purchased from on-line retailers, manufacturers

• Development of a laboratory test protocol
  o Existing methods (VOCs, PM, ozone)
  o Developed a new method to quantify ROS

• Characterization of emissions from air cleaners
  o Systematic evaluation of each of the 6 air cleaners

• Evaluation of the impacts of air cleaners on indoor air quality
  o Determined primary and secondary emission rates
  o Determined pollutant removal efficiencies
  o Predicted impact on exposure
Outline of methods and results

• Description of air cleaners
  • Laboratory methods
  • Representative experimental results
  • Modeled results
  • Discussion and implications
Photocatalytic oxidation (PCO) air cleaners

1. TiO$_2$ is excited with UV lamp(s)
2. Volatile Organic Compounds (VOCs) adsorbed on TiO$_2$ surface
3. VOCs react with photogenerated charges, surface OH & reactive species

Example of catalyst-coated medium: honeycomb monolith

- 1000 cells/m$^2$
- (design/dimensioning constraints)
- (design/dimensioning and physical-chemical constraints)
- (chemical constraints: partially oxidized byproducts)
Different types of UV lamps are used in PCO

**Vacuum UV (VUV)**
- Hg vapor
- $\lambda_{\text{max}} = 185 \text{ nm and } 254 \text{ nm}$
- uncoated quartz
- Produces ozone

**Ozone-free (UVC)**
- Hg vapor
- $\lambda_{\text{max}} = 254 \text{ nm}$
- coated quartz

**Black light (UVA)**
- Hg vapor
- $\lambda_{\text{max}} = 365 \text{ nm}$
- coated quartz
- Do not produce ozone
Three PCO air cleaners were tested in this study.

<table>
<thead>
<tr>
<th>Principle of operation</th>
<th>PAC 1</th>
<th>PAC 2</th>
<th>PAC 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocatalyst (TiO$_2$) + UVA lamp (365 nm)</td>
<td>Photocatalyst + ozone-free UVC (254 nm) + HEPA filter + “oxygenating catalyst”</td>
<td>Photocatalyst + ozone-generating VUV lamp</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Manufacturer’s description</th>
<th>Hydroxyl generator. Targets odors, VOCs, microorganisms</th>
<th>Room air purifier. Targets PM, germs, viruses, mold, mildew and VOCs</th>
<th>Residential air purifier and sanitizer. Targets mold, bacteria, viruses, odors, VOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retail price</td>
<td>$ 450</td>
<td>$ 130</td>
<td>$500</td>
</tr>
</tbody>
</table>
A non-thermal plasma is a partially ionized gas in which the mean energy of the electrons is considerably higher than that of the ions and bulk gas molecules.

Applications:
- Indoor air cleaning
- Treatment of flue gas and industrial effluents
- Antimicrobial / sterilization
- Surface treatments
- Clean combustion
- Analytical instrumentation

Obtained by exposure to strong electrical field:
- Corona discharge
- Dielectric barrier discharge
- Gliding arc
- Electron beam
Plasma & ceramic heater air cleaners tested in this study

<table>
<thead>
<tr>
<th>Principle of operation</th>
<th>PAC 4</th>
<th>PAC 5</th>
<th>PAC 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-thermal plasma with generation of reactive oxygen species</td>
<td>Ceramic room heater with ionizer</td>
<td>Localized high temperatures (400 F) kills microorganisms; does not change room temperature</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Manufacturer’s description</th>
<th>PAC 4</th>
<th>PAC 5</th>
<th>PAC 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air purifier. Targets airborne microorganisms</td>
<td>Room air heater with ionizer. Targets dust, pollen, smoke and pet dander.</td>
<td>Air purifier. Targets airborne microorganisms</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retail price</th>
<th>PAC 4</th>
<th>PAC 5</th>
<th>PAC 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ 170</td>
<td>$ 95</td>
<td>$ 230</td>
<td></td>
</tr>
</tbody>
</table>
Outline of methods and results

• Description of air cleaners
• **Laboratory methods**
• Representative experimental results
• Modeled results
• Discussion and implications
Room-sized chamber setup

well-mixed 20-m$^3$ stainless steel chamber

Air exchange rate: 0.3 to 0.5 h$^{-1}$

clean air

target pollutant mixture

air cleaner

sampling ports for VOCs, aldehydes & ROS

water CPC

ozone monitor

T, RH sensors
## Sample collection and analytical methods

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Mode</th>
<th>Collection method</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>ozone</td>
<td>real-time</td>
<td>continuous</td>
<td>UV photometric</td>
</tr>
<tr>
<td>ultrafine particles (UFP)</td>
<td>real-time</td>
<td>continuous</td>
<td>Water CPC</td>
</tr>
<tr>
<td>volatile organic compounds (VOCs)</td>
<td>integrated</td>
<td>sorbent tubes</td>
<td>GC/MS</td>
</tr>
<tr>
<td>volatile carbonyls</td>
<td>integrated</td>
<td>DNPH-coated silica</td>
<td>HPLC</td>
</tr>
<tr>
<td>reactive oxygen species (ROS)</td>
<td>integrated</td>
<td>fluorescent probes</td>
<td>Fluorimeter</td>
</tr>
</tbody>
</table>
A method was developed to quantify ROS.

<table>
<thead>
<tr>
<th></th>
<th>2',7'-Dichloro fluorescin (DCFH)</th>
<th>Amplex® ultra Red (AuR)</th>
<th>Terephtalic acid (TPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROS detected</td>
<td>$\text{H}_2\text{O}_2$, $\text{HO}^-$, $\text{ROO}^-$, $\text{O}_2^-$</td>
<td>$\text{H}_2\text{O}_2$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>ROS-induced fluorescent byproduct</td>
<td>2,7-dichloro fluorescein (DCF)</td>
<td>resorufin</td>
<td>2-hydroxy-terephtalate (HTPA)</td>
</tr>
<tr>
<td>Excitation / emission (nm)</td>
<td>485 / 530</td>
<td>563 / 587</td>
<td>310 / 412</td>
</tr>
<tr>
<td>Reported detection limit</td>
<td>50 nM</td>
<td>50 nM (10 pmoles)</td>
<td>5 nM (100 fmol)</td>
</tr>
</tbody>
</table>
Each air cleaner was tested in two different conditions

PHASE 1: clean air

CHAMBER BACKGROUND

- ~ 2 ppb formaldehyde
- ~1-3 ppb acetone
- ~ 500 #/cm³ ultrafine particles.
Each air cleaner was tested in two different conditions.

PHASE 2: challenge mixture

- formaldehyde
- toluene
- benzene
- styrene
- d-limonene
- pyridine
- trichloroethylene
- butanal
- ethanol
- hexane
- o-xylene
- Total concentration: 150 – 200 ppb
Outline of methods and results

• Description of air cleaners
• Laboratory methods
• Representative experimental results
• Modeled results
• Discussion and implications
VOC concentrations measured in the chamber

PAC 1

Overall elimination of indoor VOCs

not included in challenge mixture
VOC concentrations measured in the chamber

Individual VOCs & aldehydes - Phase I

Individual VOCs & aldehydes - Phase 2

Overall increment of indoor VOCs

not included in challenge mixture
Ozone measured in the chamber

**PAC 3**

**Phase 1**

- **Ozone concentration (ppb)**
- **OFF**
- **ON**

**Air cleaner turned on**

**Air cleaner turned off**

**PAC 3**

**PAC 4**

**Phase 1**

**Ozone Concentration (ppb)**

- **Phase 1**
- **Phase 2**

**PAC 4**

**Phase 1**

**Ozone Concentration (ppb)**

- **Phase 1**
- **Phase 2**
UFP measured in the chamber

PAC 3

Phase 1

Concentration (# cm$^{-3}$)

Phase 2

Concentration (# cm$^{-3}$)

Phase 2 (w/limonene & styrene)

Concentration (# cm$^{-3}$)

Phase 1

Concentration (# cm$^{-3}$)

Phase 2

Concentration (# cm$^{-3}$)

Chamber background

Concentration (# cm$^{-3}$)

Time (h)
UFP are formed from ozone reactions with alkenes

- Reactive short-lived species (Criegee intermediates)
- UFP yields from ozone reaction with limonene:
  - 10-15% (Weschler and Shields, 1999)
  - 13% (Alshawa et al, 2007)
- UFP Yields from reaction with styrene: 3-12%
  (Na et al, 2006)
- Formaldehyde yield from ozone reaction with:
  - limonene: ~27% (Destaillats et al, 2006)
  - styrene: 37% (Tuazon et al, 1993)
- OH yields from ozone-limonene reactions:
  - 67% (Aschmann et al, 2002)
ROS measured in chamber and at the air cleaner outlet

In the chamber:

**below detection limit** (Phase 1 & 2)

At the air cleaner outlet:

<table>
<thead>
<tr>
<th>PAC 4</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AuR</td>
<td>300 ppt</td>
<td>[H_2O_2]^{eq}_{gas}</td>
</tr>
<tr>
<td>TPA</td>
<td>47 ppt</td>
<td>[OH]^{eq}_{gas}</td>
</tr>
</tbody>
</table>

Main issues:

Measurements requires background correction as a function of ozone concentration, due to contributions of O_3 to the signal.
Outline of methods and results

• Description of air cleaners
• Laboratory methods
• Representative experimental results
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A box model was used to evaluate the impact on IAQ

Well-mixed chamber

$V_{CH} = 20 \text{ m}^3$

pollutant concentration ($C_i$)

- clean air ($C_{i0}$)
- chamber air flow rate ($F_{CH}$)
- source strength ($E_{iS}$)
- pollutant source
- chamber air
- flow rate ($F_{CH}$)
- pollutant
- concentration
- ($C_i$)
- air exchange rate ($\lambda$)
- air cleaner
- emission rate ($E_{iAC}$)
- air cleaner
- removal rate ($R_{iAC}$)
- deposition rate ($D_i$)
- air cleaner
- flow rate ($F_{AC}$)
- vent

$i = \text{individual pollutant}$
Pollutant emission and removal rates were calculated

Data corresponding to Phase 2:

<table>
<thead>
<tr>
<th></th>
<th>PAC1</th>
<th>PAC2</th>
<th>PAC3</th>
<th>PAC4</th>
<th>PAC5</th>
<th>PAC6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ionizer</td>
<td>ion + heat</td>
</tr>
<tr>
<td>ozone (mg h⁻¹)</td>
<td>-</td>
<td>-</td>
<td>5.9</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UFPs (# particles h⁻¹)</td>
<td>-</td>
<td>6.0E+09</td>
<td>3.10E+10</td>
<td>4.9E+09</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VOCs (μg h⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>-</td>
<td>16</td>
<td>5.4</td>
<td>539</td>
<td>215</td>
<td>7.4</td>
</tr>
<tr>
<td>hexane</td>
<td>582</td>
<td>N/A</td>
<td>116</td>
<td>409</td>
<td>398</td>
<td>202</td>
</tr>
<tr>
<td>butanal</td>
<td>30</td>
<td>-</td>
<td>23</td>
<td>23</td>
<td>62</td>
<td>30</td>
</tr>
<tr>
<td>benzene</td>
<td>34</td>
<td>13</td>
<td>38</td>
<td>99</td>
<td>40</td>
<td>42</td>
</tr>
<tr>
<td>TCE</td>
<td>47</td>
<td>65</td>
<td>74</td>
<td>122</td>
<td>49</td>
<td>37</td>
</tr>
<tr>
<td>toluene</td>
<td>79</td>
<td>147</td>
<td>171</td>
<td>267</td>
<td>96</td>
<td>173</td>
</tr>
<tr>
<td>pyridine</td>
<td>10</td>
<td>-</td>
<td>66</td>
<td>90</td>
<td>19</td>
<td>45</td>
</tr>
<tr>
<td>o xylene</td>
<td>37</td>
<td>40</td>
<td>91</td>
<td>63</td>
<td>71</td>
<td>176</td>
</tr>
<tr>
<td>styrene</td>
<td>7.0</td>
<td>12</td>
<td>133</td>
<td>23</td>
<td>41</td>
<td>134</td>
</tr>
<tr>
<td>d limonene</td>
<td>8.3</td>
<td>-</td>
<td>273</td>
<td>21</td>
<td>111</td>
<td>605</td>
</tr>
<tr>
<td>formaldehyde</td>
<td>33</td>
<td>31</td>
<td>36</td>
<td>25</td>
<td>49</td>
<td>229</td>
</tr>
<tr>
<td>acetone</td>
<td>9</td>
<td>5.0</td>
<td>86</td>
<td>-</td>
<td>89</td>
<td>-</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>-</td>
<td>-</td>
<td>111</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TOTAL VOCs (μg h⁻¹)</td>
<td>792</td>
<td>319</td>
<td>829</td>
<td>1629</td>
<td>992</td>
<td>1343</td>
</tr>
<tr>
<td>% chamber VOCs</td>
<td>-14 %</td>
<td>+15 %</td>
<td>-28 %</td>
<td>-29 %</td>
<td>+12 %</td>
<td>+19 %</td>
</tr>
</tbody>
</table>

Red: emitted  Black: removed
The removal efficiency was estimated with a simple model

OVERALL EFFICIENCY:
The chamber concentration reduction factor is defined as:

$$\omega_i = \frac{C_{i, OFF}^{ON} - C_{i, OFF}^ON}{C_{i, OFF}^ON}$$

CAPACITY:
The recycle ratio is defined as:

$$\rho = \frac{\text{airflow through air cleaner}}{\text{airflow through chamber}} = \frac{F_{AC}}{F_{CH}} = \frac{F_{AC}}{\lambda \cdot V}$$

INTRINSIC EFFICIENCY:
The single pass removal efficiency at steady-state \((ss)\) is defined as:

$$\phi_{i}^{\rho, ss} = \frac{(C_{i, \text{upstream}} - C_{i, \text{downstream}})}{C_{i, \text{upstream}}}$$

These parameters are related by a simple correlation:

$$\omega_i = 1 - \left( \frac{1}{1 + \rho \cdot \phi_{i}^{\rho, ss}} \right)$$
Evaluation of the pollutant removal efficiency

• VOC removal efficiency:
  o evaluated for four devices: PAC1, PAC3, PAC4, PAC6
  o **chamber reduction factors** for individual VOCs were between **0 and 40%**
  o **recycle ratios** were between **0.4 and 1.7**
  o estimated **single-pass efficiencies** for individual VOCs were between **0 and 90%**
  o **styrene and limonene** were reduced by >97% with PAC3 (O$_3$ chemistry)

• UFP removal efficiency:
  o evaluated for two devices: PAC2 (recycle ratio: 1.8) and PAC4 (recycle ratio: 0.7)
  o **PAC2** removed **80-90%** of particles (HEPA filtration)
  o **PAC4** (plasma) removed **35-50%** of particles, above the predictions of the simple model, suggesting that ions or radicals emitted to indoor air adhere to particles and accelerate their deposition
Outline of methods and results

- Description of air cleaners
- Laboratory methods
- Representative experimental results
- Modeled results
- Discussion and implications
Predicted impacts on indoor air quality (IAQ) (i/iii)

We calculated contributions to indoor concentration ($\Delta C$) in two model scenarios:

<table>
<thead>
<tr>
<th></th>
<th>Indoor air volume, $V$ (m$^3$)</th>
<th>S/V ratio (m$^{-1}$)</th>
<th>Air exchange rate (h$^{-1}$)</th>
<th>Number of devices (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBNL chamber</td>
<td>20</td>
<td>2.2</td>
<td>0.3 to 0.5</td>
<td>1</td>
</tr>
<tr>
<td>Scenario #1: 1,500-ft$^2$ house</td>
<td>1115</td>
<td>2.5</td>
<td>0.12</td>
<td>3</td>
</tr>
<tr>
<td>Scenario #2: small furnished room</td>
<td>30</td>
<td>3.5</td>
<td>0.05</td>
<td>1</td>
</tr>
</tbody>
</table>

Worst-case scenario
Predicted impacts on indoor air quality (IAQ) (ii/iii)

• **OZONE:**
  o PAC3 in **scenario 2**: $\Delta C = 22 - 191 \, \mu g \cdot m^{-3}$, exceeded:
    ✓ California REL for acute levels ($180 \, \mu g \cdot m^{-3}$)
    ✓ California outdoor air quality standards (1-h: $180 \, \mu g \cdot m^{-3}$; 8-h: $140 \, \mu g \cdot m^{-3}$)
    ✓ ARB regulations on air cleaner emissions ($100 \, \mu g \cdot m^{-3}$)
  o PAC 3 in **scenario 1**: $\Delta C = 2 - 19 \, \mu g \cdot m^{-3}$
  o PAC 4 in **scenario 2**: $\Delta C = 0.6 - 5.5 \, \mu g \cdot m^{-3}$

• **FORMALDEHYDE:**
  o PAC1, PAC2 and PAC4 in **scenario 2** increased indoor levels by $\Delta C = 22, 20$ and $17 \, \mu g \cdot m^{-3}$ respectively, exceeding California REL for chronic exposure ($9 \, \mu g \cdot m^{-3}$)
  o Other three devices removed formaldehyde in similar amounts
Predicted impacts on indoor air quality (IAQ) (iii/iii)

- **BENZENE:**
  - PAC2 and PAC5 in *scenario 2*: $\Delta C = 9$ and $27 \, \mu g \cdot m^{-3}$ respectively, exceeded California’s Prop 65 levels for inhalation exposure ($0.8$ and $3 \, \mu g \cdot m^{-3}$)
  - The other four devices removed benzene from indoor air

- **UFP:**
  - PAC3 emitted a significant level of UFPs in the presence of ozone-reacting VOCs (limonene, styrene)
  - The *yield* of secondary organic aerosol was 1-5% (consistent with values measured previously for these reactions)

- **ROS:**
  - Higher-than background levels measured directly at the outlet of PAC4
Conclusions and recommendations

- Emissions of pollutants from portable air cleaners were observed, exceeding California reference levels for three pollutants in realistic scenarios (ozone, formaldehyde and benzene).

- One device (not certified by ARB) emitted ozone at potentially harmful levels, exceeding State and EPA’s standards; led to UFP formation.

- Standard test procedures are needed to measure harmful emissions and verify the validity of marketing claims.

- VOC removal efficiencies were < 40%. There is a great opportunity for improving VOC removal performance.

- There is a need for developing and implementing better engineering controls to prevent harmful pollutants from being released indoors (e.g., filters/catalysts to remove ozone or ROS downstream of a plasma generator).

- Use of ozone-generating VUV lamps should be discouraged.
Questions?