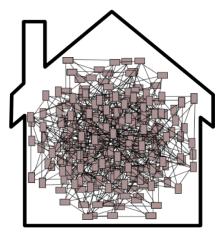
## **Air Cleaners & Indoor Chemistry**





#### Richard L. Corsi, Ph.D., P.E.

H. Chik M. Erzurumlu Dean Maseeh College of Engineering and Computer Science Portland State University

Joe J. King Chair in Engineering #2
Dept. of Civil, Architectural & Environmental Engineering
The University of Texas at Austin

### Ozone + Unsaturated Organic Compounds

$$O_3$$
 +  $R_1$   $C = C$   $R_3$   $R_4$   $R_2$   $C$   $R_3$   $R_4$   $R_2$   $R_3$   $R_4$   $R_4$   $R_5$   $R_4$   $R_5$   $R_5$   $R_6$   $R_8$   $R_8$   $R_9$   $R_$ 

- Σ stable gaseous rxn products can be 2-3 x O<sub>3</sub>
- Reactions occur in air & on surfaces
- · Health effects of products not well understood

Free radicals (OH, HOO, ROO, ..)

Other short-lived intermediates

Carbonyls (mono-, di-)

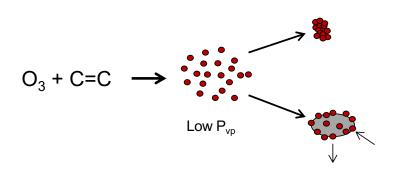
Organic acids

**Peroxides** 

Indoor SOA (iSOA)

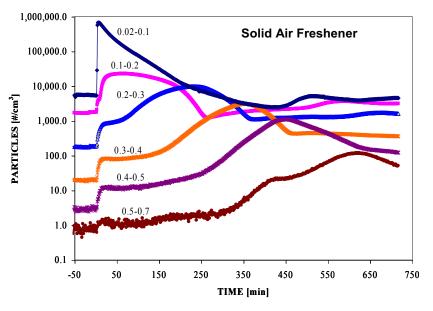
A lot of additional chemistry: OH, NO/NO<sub>2</sub>, HONO, chlorine, ammonia ..

# Indoor Secondary Organic Aerosols



#### **Indoor SOA**

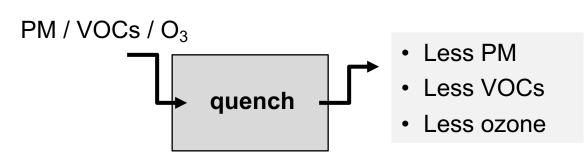
- Ozone + alkenes present
- OH + HC present
- Charged VOCs (ions) present



Sarwar G., et al., *J Air & Waste Man Assoc.*, 54: 367-377 (2004)

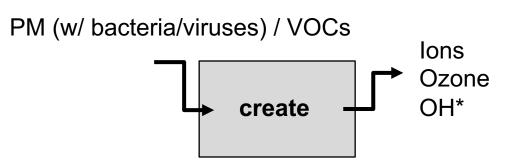
### Quench (Control) vs. Create

In-duct or In-room



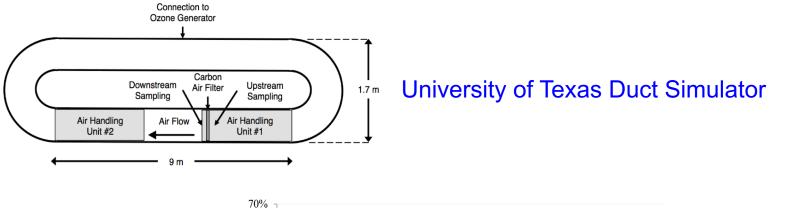
$$C = \frac{pC_o + \frac{E}{\lambda V}}{1 + \sum_{b} \frac{k_b C_j}{\lambda} + \frac{k_d}{\lambda} + \frac{\eta Q_c}{\lambda V}}$$

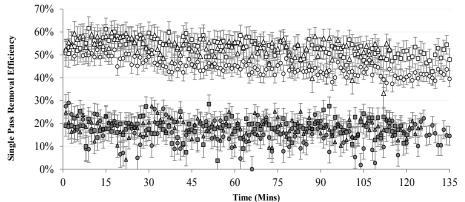
$$\eta Q_c = CADR$$



- Less PM?
- Less VOCs?
- Bacteria kill?
- Virus inactivation?

### **Activated Carbon Filtration**





Bulk AC filter replicates

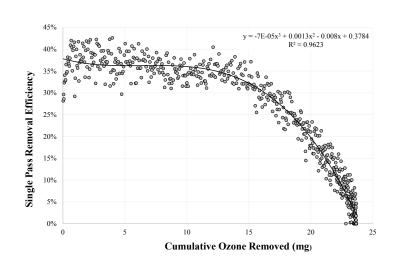
Slurry AC filter replicates

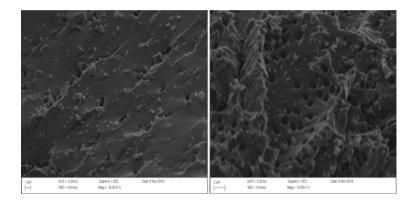
Aldred, J., Doctoral Dissertation, University of Texas at Austin (2015)

### **Activated Carbon Filtration**

- Effectiveness for O<sub>3</sub> removal decreases with time
  - Consumption of reaction sites
  - Acidic surface oxidation complexes
  - Physical decomposition of AcC

Alvarez, P. M., et al. *Industrial & Engineering Chemistry Research*, 47(8), 2545–2553 (2008)

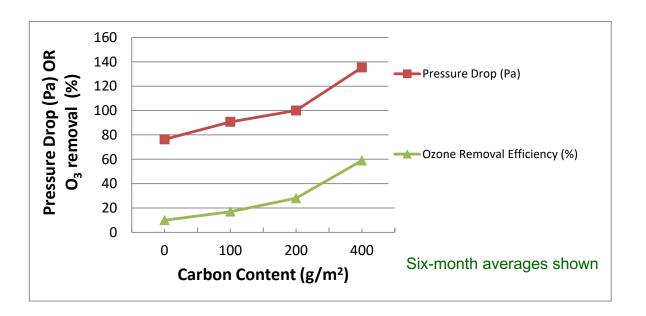




Aldred, J., Doctoral Dissertation, University of Texas at Austin (2015)

### Amount of Activated Carbon / Area Matters

- Six months of continuous field testing (varied g/m²)
- $(0.6 \text{ m x } 0.6 \text{ m x } 0.3 \text{ m}) = (24" \text{ x } 24" \text{ x } 12") \text{ w/} \approx 1,300 \text{ cfm}$

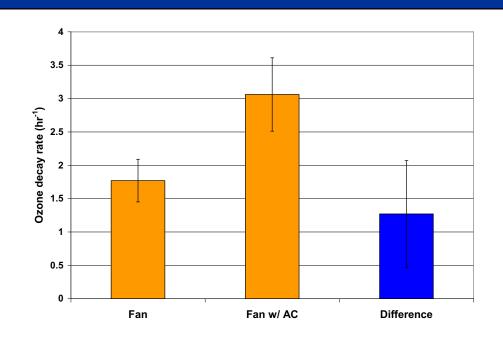


Bekö, G., et al., *Building and Environment*, 44(10), 2114–2120 (2009)

### **Activated Carbon Fan Blade Sleeves**



$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle}$$



- AC on fan blades: Mean O<sub>3</sub> decay increase = 1.25 hr<sup>-1</sup>
- Average 33% decrease in indoor ozone

Kunkel D, et al., Building and Environment, 45: 445-452 (2010)

# Passive Removal Materials (PRMS)

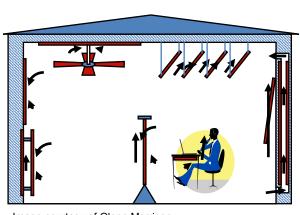
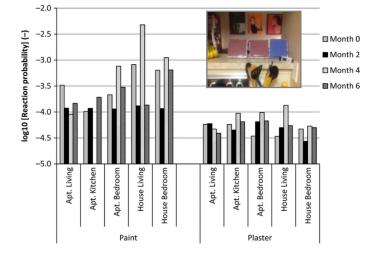


Image courtesy of Glenn Morrison

- High, sustained reactivity w/ O<sub>3</sub>
- Minimal reaction product yield
- Large surface area
- Reduces other O<sub>3</sub> reactions



#### Clay paints & plasters (kaolinite)

- Removal of organic acids
- Buffers water vapor
- Improves PAQ

Lamble, SP, et al., Atmos Environ, 45: 6965-6972 (2011); Darling, E, et al., Building and Environment, 57: 370-376 (2012); Darling, E., et al., Building and Environment, 106: 33-44 (2016); Darling E. & Corsi RL, Indoor Air, 27 (3): 658-669 (2017)

### Ion Generators

lonized hydrogen peroxide systems

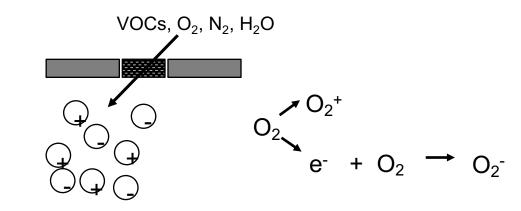
"...contain a high concentration of Reactive Oxygen Species (ROS), consisting mostly of hydroxyl radicals (OH) as the killing agent."

Ion generators (plasma, unipolar, bipolar)

"...vastly superior to most air purification methods because it works "in the space" ... doesn't wait for pollutants to find their way into the filter.."

#### Claims: Ion generators

- PM charged agglomerate → surfaces/filters
- Viruses inactivated
- Odors neutralized oxygen ions break down VOCs



### Ion Generators

Ionization Energy (IE) = energy required to remove an electron from atom (molecule)

- High energy input = more ions = better performance = O<sub>3</sub>
- Manufacturers that claim no O<sub>3</sub> generally aim for ≤ 12 eV
- Aged/dirty electrodes shown to increase O<sub>3</sub>

Dorsey, JA., & Davidson, JH, IEEE Transactions on Industry Applications, 30(2): 370-378 (1994)

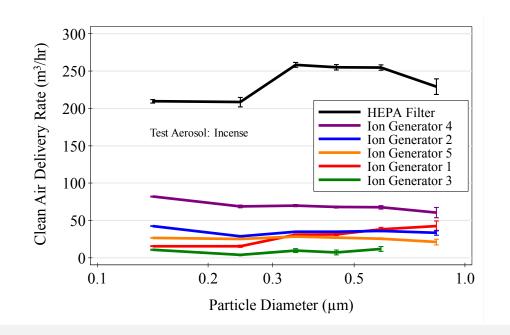
IE (eV): 
$$O_2 = 12.07$$
;  $N_2 = 15.6$ ;  $H_2O = 12.6$ 

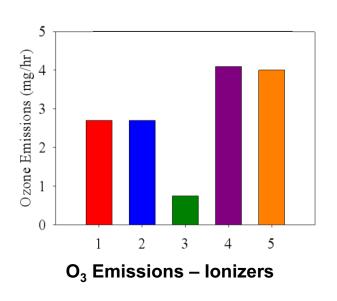
Ionizers designed to avoid ozone are insufficient to ionize major components of air

Most ions will be generated by VOCs

e.g., limonene (8.3); xylenes (8.6); toluene (8.8); HCHO (10.88); ethanol (10.48)

### Ion Generators: Effectiveness & Ozone





CADR: HEPA (not a great HEPA) > IG (CADR =  $\eta Q_c$ )

Ion generators: lowest ozone emitter = worst CADR; highest ozone emitter = best CADR

Yu, X., et al., Indoor Air 2005, Proc. 10th Intl' Conf on Indoor Air Quality and Climate, Beijing, China (2005)

### Ion Generators

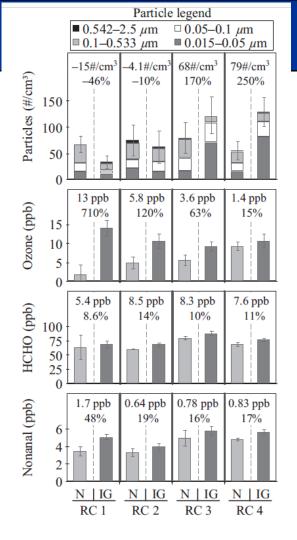
Field study - 27 m<sup>3</sup> room in residence @ 0.5.h

**RC 1**: Original flooring of sealed/stained concrete, without air freshener

**RC 2**: Installed flooring of carpet with padding, without air freshener

**RC 3**: Original flooring of sealed/stained concrete, with air freshener

**RC 4**: Installed flooring of carpet with padding, with air freshener



Waring, M.S. & Siegel, J.A., *Indoor Air, 21: 267-276* (2011)

## **Bipolar Ionization**

- Several studies show benefits (PM, VOCs, pathogens)
  - Small volumes, near source
  - Extreme ion concentration =  $10^6 10^7 \text{cm}^{-3}$
- Indoor air w/ in-room or in-duct ionizer: 2,000 20,000 cm<sup>-3</sup>
  - Background ≈ 100 to 1,000 cm<sup>-3</sup>
  - Context: 1 ppb VOC ≈ 2.5 x 10<sup>10</sup> cm<sup>-3</sup>
- Independent studies limited
  - PM removal: Translatable info?
  - Viruses: Inactivation mechanism(s)?
  - VOCs: Removal pathways? Adducts?
  - Rxn Products: Neglected. Pathways?

# Chamber Test: Bipolar Ionizer (BPI)

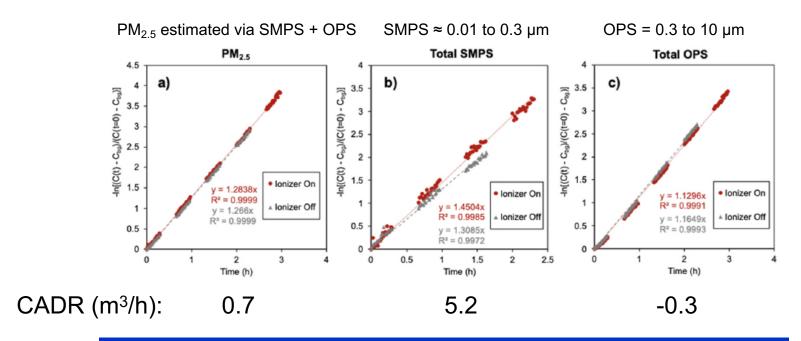




- Chamber: 36.7 m<sup>3</sup> equipped w/ aged emission sources
- Single pass ventilation w/ charcoal fiber filtered lab air @ 1.2 1.6/hr
- BPI system intended to ionize molecules w/ IE < 12.07 eV (less than O<sub>2</sub> = 12.07 eV)
- Ion concentration w/ ionizer off = 300 700 cm<sup>-3</sup>; on = 1,400 to 2,000 cm<sup>-3</sup>

# Particle Decay: BPI On & Off

Particle decay (based on incense in chamber)



Comparison: Good portable HEPA air cleaner: CADR = 500 m<sup>3</sup>/h

Zheng, Y., et al., *Building and Environment*, 195 (2021) doi.org/10.1016/j.buildenv.2021.107750

### BPI in Chamber: VOC Formation & Decay

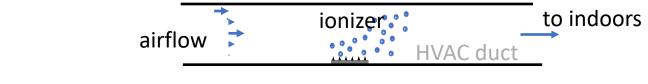
	% Change in
Analyte	I/O Ratio <sup>1</sup>
Formaldehyde	+2%
Acetaldehyde	+13%
Acetone	+73%
Butanal	+28%
Toluene	+15%
1,2-Dichloroethane	< -42%
Ethylbenzene	< -64%
m,p-Xylene	< -78%
Dichlorodifluoromethane	< -17%
Summed TOC	-19%

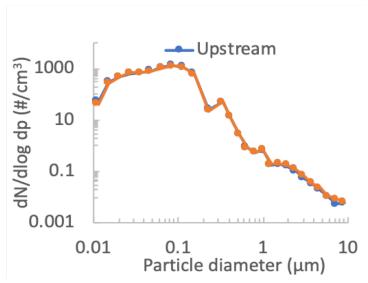
- Negligible ozone formation
- Higher MW VOC decay
- Toluene formation
- Low MW OVOC formation
  - IE < energy input</li>
  - Rate of formation >> removal
  - Reaction pathway?

Negligible particle removal

<sup>&</sup>lt;sup>1</sup> values with < indicate measured value inside the chamber was below MDL

# Application of BPI in Office Building

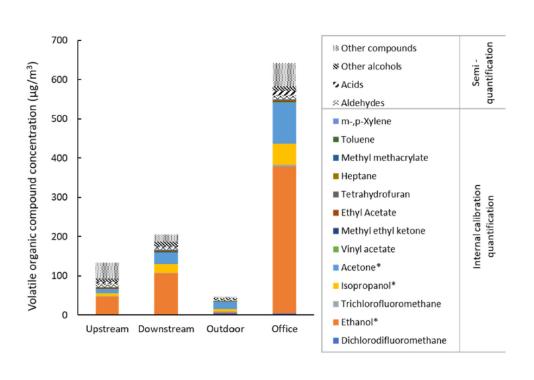




- Negligible particle removal
- Negligible O<sub>3</sub> formation
- Some OVOC production
- Some non-oxygenated HC removal

Plot/graphic courtesy of Elliott Gall, Portland State University

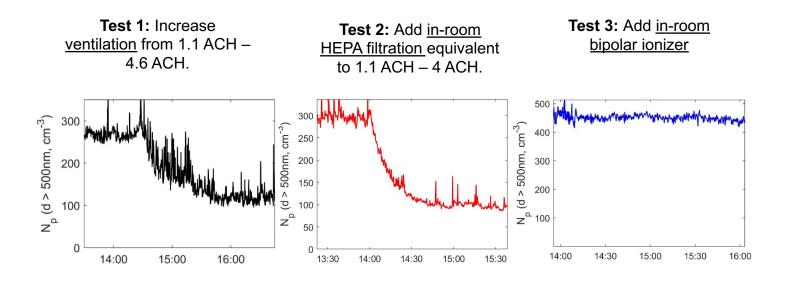
### **VOCs: BPI in Office Building**



- Formed: several OVOCs
- Near vicinity of ionizer
  - 0.75 m downstream
- Significant increase out of duct

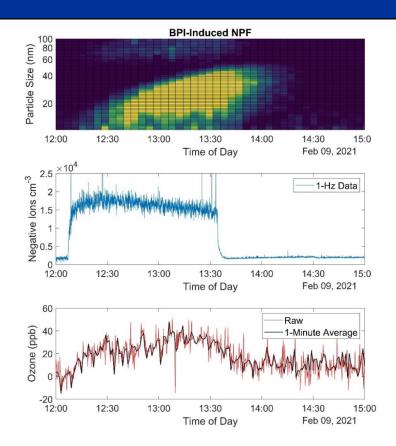
### In-Room BPI v. Proven Approaches

Classroom: 363 m<sup>3</sup>; NaCl aerosol particles (mean  $d_p$  = 2 µm); SS to intervention



Plots/findings courtesy of Bertram Research Group, U of Wisconsin-Madison

### BPI in Classroom: UFP, Ions, Ozone



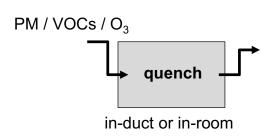
- Strong UFP formation driven by ion-induced nucleation + in room VOC
- 2. UFP = fn(ion gen rate, existing aerosol  $A_{surf}$ , VOCs ...)
- 3. In room ion lifetime < 1 min (Ion Decay rate > 110 h<sup>-1</sup>)
- 4. Rapid ion loss rates make in-duct ion delivery prohibitive
- 5. BPI can sustain in-room ion concentrations of 1-2 x 10<sup>4</sup> ions cm<sup>-3</sup> with strong spatial gradients (ventilation 1 ACH)
- 6. No evidence of enhanced particle deposition by charging
- 7. BPI O<sub>3</sub> production

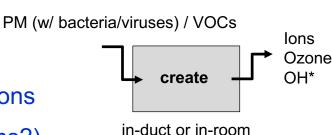
Red text added

Plots/findings courtesy of Bertram Research Group, U of Wisconsin-Madison

### Summary

- Air cleaners can quench indoor ozone chemistry
- Ionizers cause some indoor chemistry
- Less energy = less  $O_3$  = less ions = less effective
- Ionizers (becoming popular again)
  - Literature incomplete / problematic
  - Do not appear relevant for PM removal
  - Inactivation of viruses at extreme ion concentrations
  - Some VOCs degrade / OVOC form (mechanisms?)
  - Implications of by-products?
  - Speciation of ions?





## Acknowledgements

Dr. Timothy Bertram, U of Wisconsin-Madison

Dr. Elliott Gall, Portland State University

Former students & colleagues who contributed to work herein:

Dr. Josh Aldred Jeff Siegel

Dr. Erin Darling Glenn Morrison

Donna Kunkel

Dr. Golam Sarwar

Dr. Michael Waring