ASHRAE VIRTUAL ANNUAL CONFERENCE

June 28-30, 2021

Seminar 14: Reducing Ozone: A Critical Factor in Improving IAQ

Ozone Emission Sources and Surface Removal in Indoor Environments

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Learning Objectives

- Understand the impact of ozone on human health and the indoor environment.
- Learn the basic principles of current technologies for ozone removal.
- Learn current methods of removing ozone in indoor environments using various gas-phase air cleaners.
- Provide information that would help to achieve IAQ goals

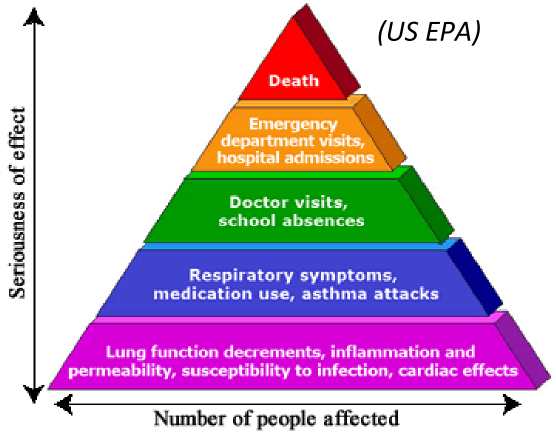
Outline/Agenda

- Background
- Indoor ozone
- Indoor ozone emission devices (IOEDs)
- Indoor ozone removal by building materials
- Indoor ozone estimation tool (single-zone model)
- Conclusions

Background

Ozone is a **reactive gas** that can have negative health effects on human, including increasing in respiratory-related morbidity, cardiovascular morbidity and premature mortality [1].

(US EPA)



Pyramid of health effects caused by ozone [2]

People spend almost 90% of their time indoors.

Indoor ozone exposure accounts for around **60%** of daily ozone exposure, and indoor ozone intake (considering breathing rate) accounts for **40%** of daily ozone intake [3].

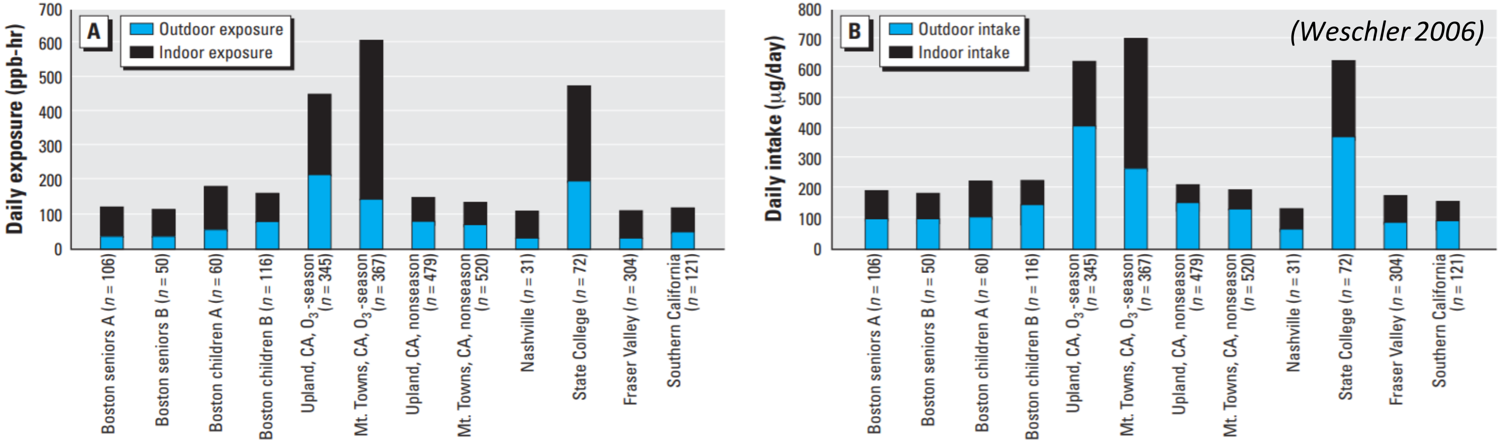


Figure 1. (*A*) Calculated indoor and outdoor ozone exposures. (*B*) Calculated indoor and outdoor ozone intakes (see text for details). Data from Boston, Massachusetts: Sarnat et al. (2005); Upland and Mt. Towns, California: Geyh et al. (2000); Nashville, Tennessee: Lee et al. (2004); State College, Pennsylvania: Liu et al. (1993); Fraser Valley, British Columbia, Canada: Brauer and Brook (1995); Southern California: Linn et al. (1996).

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*
[2] *US EPA. Health Effects of Ozone in the General Population.*
[3] *Weschler, C. J. 2006. Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. Environmental Health Perspectives, 114(10):1489–1496.*

Indoor ozone

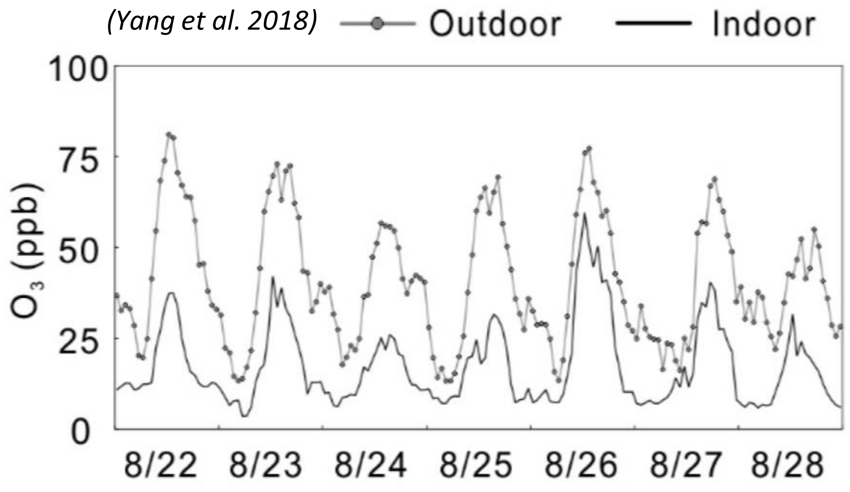
Indoor/outdoor (I/O) ratio indicates the relationship between indoor and outdoor ozone concentrations

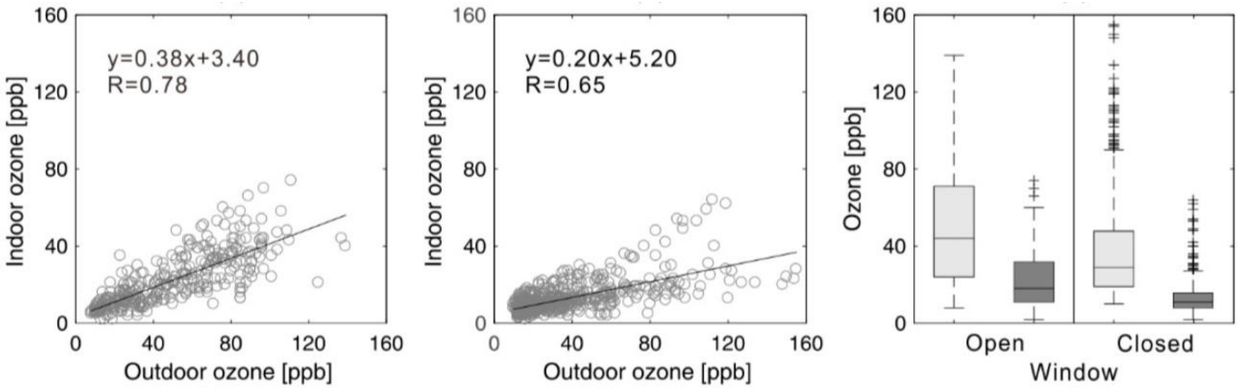
Building	*Location*	*I/O ratio*
145 homes	Mexico City	0.20
126 homes	South California	0.37
70 workplaces	Montpellier, France	0.45
6 apartments	Baltimore	0.5-0.7
3 museums	South California	0.3-0.4
2 schools	South California	0.3-0.7
…	…	…

⇩

I/O ratio is more often in the range of **0.2 to 0.7**.

(Yang et al. 2018)





Ozone concentration inside and outside a college student dormitory during summer in Nanjing [1]

[1] *Yang, Z., J. Shen, and Z. Gao. 2018. Ventilation and Air Quality in Student Dormitories in China: A Case Study during Summer in Nanjing. International Journal of Environmental Research and Public Health.*
[2] *WESCHLER, C. J. 2000. Ozone in Indoor Environments: Concentration and Chemistry. Indoor Air, 10(4):269–288.*

Indoor ozone

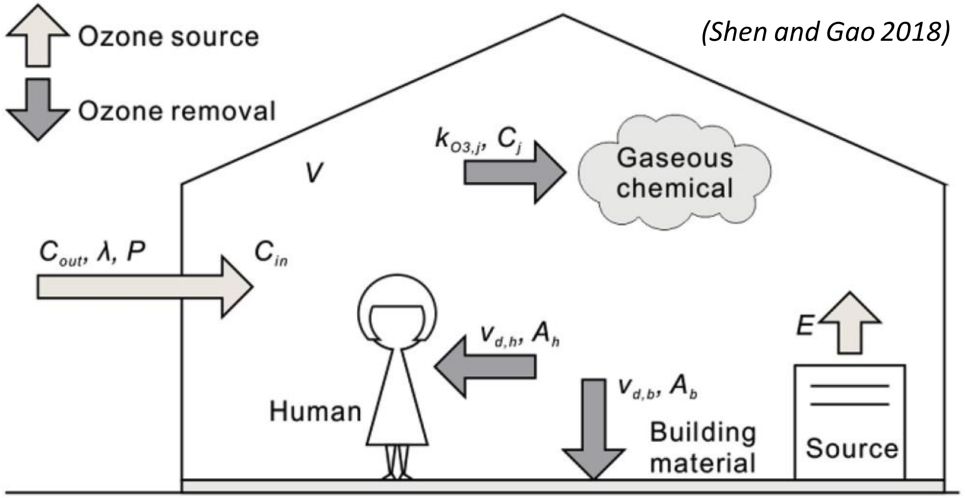
Indoor ozone concentration depends on

Sources from

- Outdoor ozone entering buildings through natural/mechanical ventilation and infiltration
- Indoor ozone emission sources (devices like laser printers, photocopiers, and ionization/ozonolysis air cleaners)

Removal by

- Air changes
- Reaction with gaseous chemicals
- Reaction with indoor material surfaces (e.g. floor, walls and furniture)
- Reaction with human surfaces (e.g. skins)



Schematic illustration of indoor ozone source and sink [1]

$$\frac{dC_{in}}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C_{in} - \sum k_{o3,j} C_j C_{in} - \sum \frac{v_{d,b} A_b C_{in}}{V} - \sum \frac{v_{d,h} A_h C_{in}}{V}$$

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone emission devices (IOEDs)

Appliances such as **disinfectors, air purifiers, and printing devices** have become quite common in households and offices.

Indoor ozone emission devices (IOEDs) can generate ozone through

1) producing a corona discharge or
2) photochemistry by emitting ultraviolet (UV) light,

in the absence of protective measures (e.g. activated carbon filter).

Some IOEDs intentionally generate ozone for disinfection (also known as ozone generators), while others produce ozone as a by-product during operation.

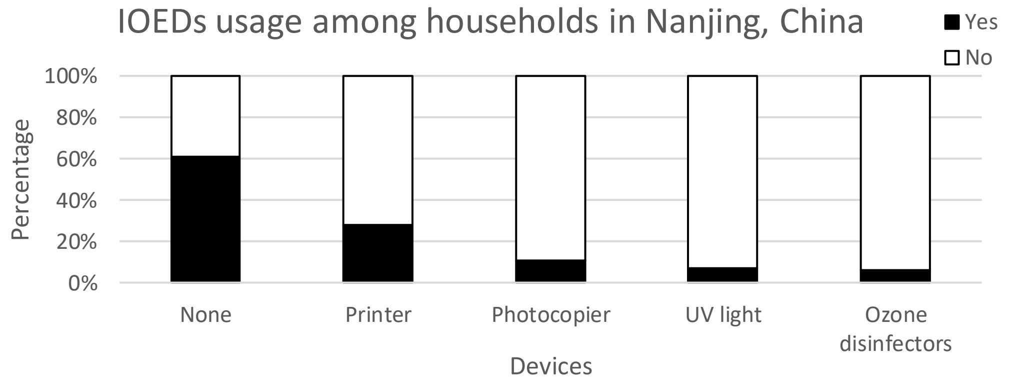


Table 1. Classification of IOEDs in published literature. *(Guo et al. 2019)*

Device Type	Ozone Emission Mechanism	Not Intentional/Intentional[a]
Photocopier	Corona discharge	Not Intentional
Laser printer		
Wearable air purifier		
Pet brush		
Ionic hair device		
Fruit and vegetable washer		Intentional
Refrigerator air purifier		
Laundry/Drinking water treatment device		
Shoe sanitizer	Photochemistry	Intentional
Facial steamer		
Room air purifier	Corona discharge/Photochemistry	Not Intentional
In-duct air cleaner		
Car (dashboard) purifier		
Ozone generator[b]		Intentional

[a] Not intentional emission means ozone is generated as by-product during the device working period; Intentional emission indicates that the device is used to generate ozone intentionally.
[b] The ozone generator here refers to the IOED that intentionally produce ozone in addition to the device already listed.

[1] Guo, C., Z. Gao, and J. Shen. 2019. Emission rates of indoor ozone emission devices: A literature review. Building and Environment, 158:302–318.

Indoor ozone emission devices (IOEDs)

Ozone generation mechanisms for IOEDs

1) Corona discharge

Corona discharge is widely used in printing devices and air purifiers.

$$O_2 + e \rightarrow 2O + e$$

$$O + O_2 + B \rightarrow O_3 + B$$

2) Photochemistry

Photochemical generation of ozone occurs by oxygen decomposition and recombination to form ozone under UV irradiation (185nm, vacuum UV).

Standard low-pressure mercury lamps made of synthetic or natural quartz glass can emit 254nm UV light (UVC, for inactivating microorganisms) and **185nm UV light (VUV, generating ozone through photo chemistry)**.

$$O_2 + h\nu(185\,\mathrm{nm}) \rightarrow O(^1D) + O(^3P)$$

$$O(^1D) + B \rightarrow O(^3P) + B$$

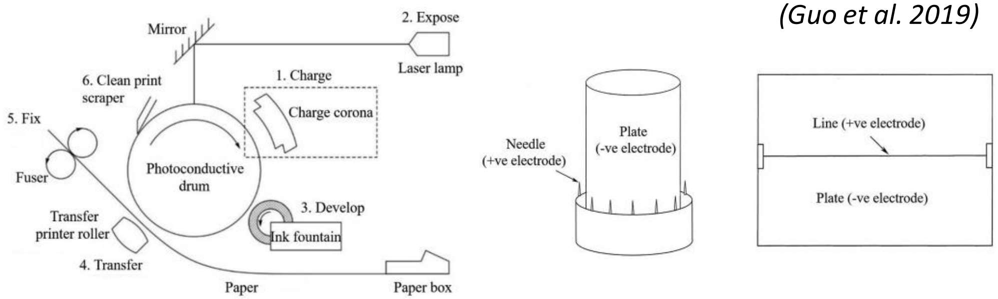
$$O(^3P) + O_2 + B \rightarrow O_3 + B$$

$$O_3 + h\nu(254\,\mathrm{nm}) \rightarrow O_2 + O(^1D)$$

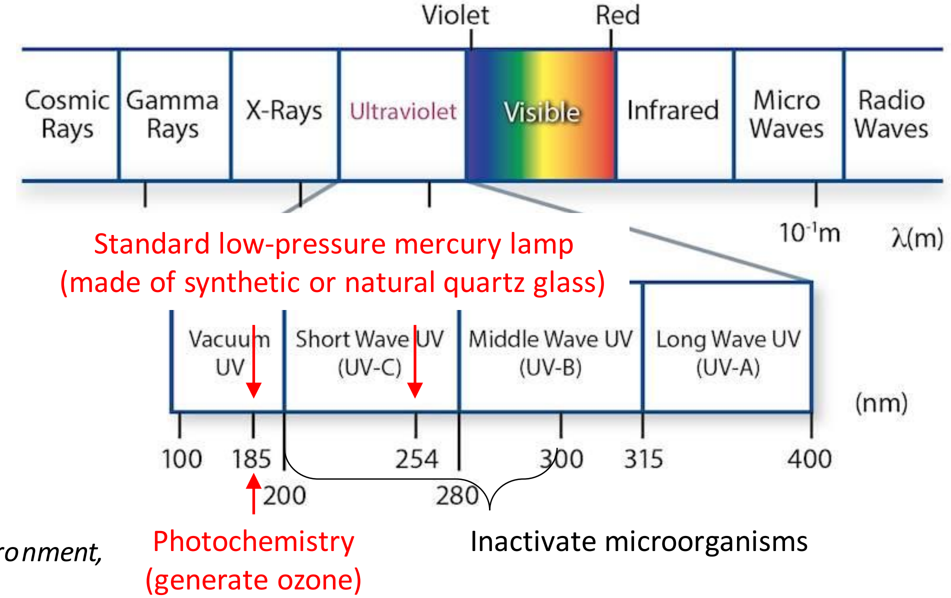
$$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$$

$$O(^3P) + O_3 \rightarrow 2O_2$$

(Guo et al. 2019)



Schematic diagram of corona discharge used in laser printer and air cleaner [1]



[1] *Guo, C., Z. Gao, and J. Shen. 2019. Emission rates of indoor ozone emission devices: A literature review. Building and Environment, 158:302–318.*

Indoor ozone emission devices (IOEDs)

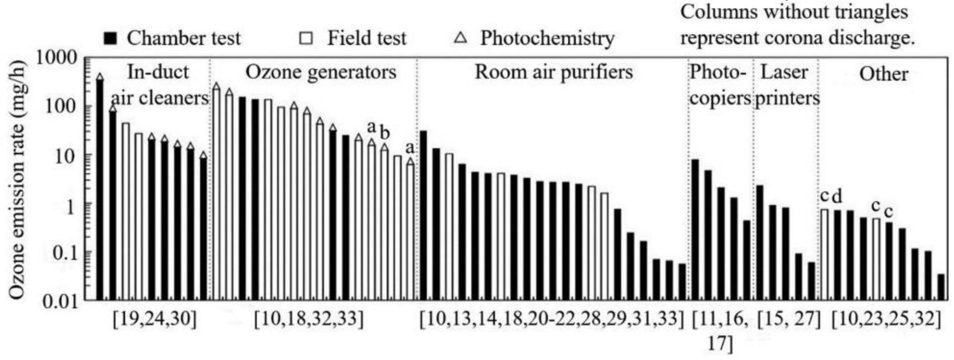
Ozone emission rate (OER) of different IOEDs

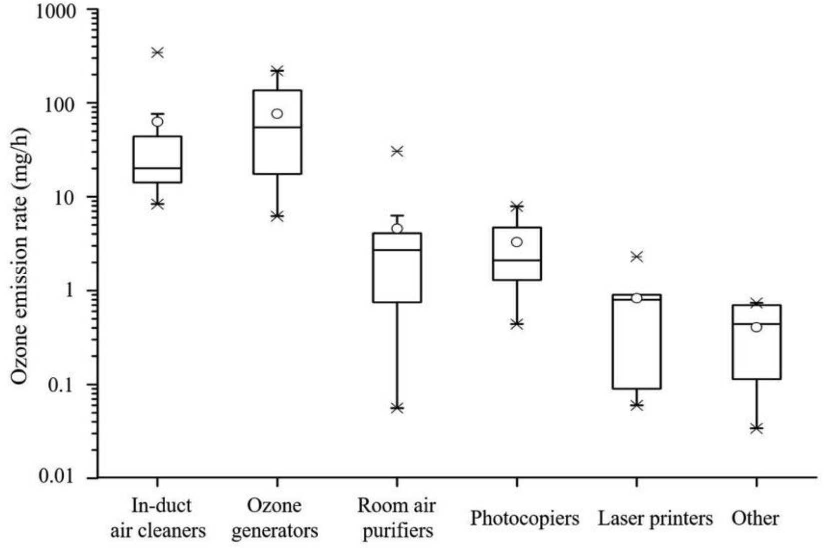
The OER of the IOEDs ranges between 0.034 mg/h (wearable air cleaner) and 344 mg/h (in-duct air cleaner).

Average OERs of IOEDs

IOED	*OER [mg/h]*
In-duct air cleaners	62.8
Ozone generators	76.3
Room air purifiers	4.6
Photocopiers	3.3
Laser printers	0.8
Other small devices	0.4

(Guo et al. 2019)





OERs of IOEDs in literature [1]

[1] *Guo, C., Z. Gao, and J. Shen. 2019. Emission rates of indoor ozone emission devices: A literature review. Building and Environment, 158:302–318.*

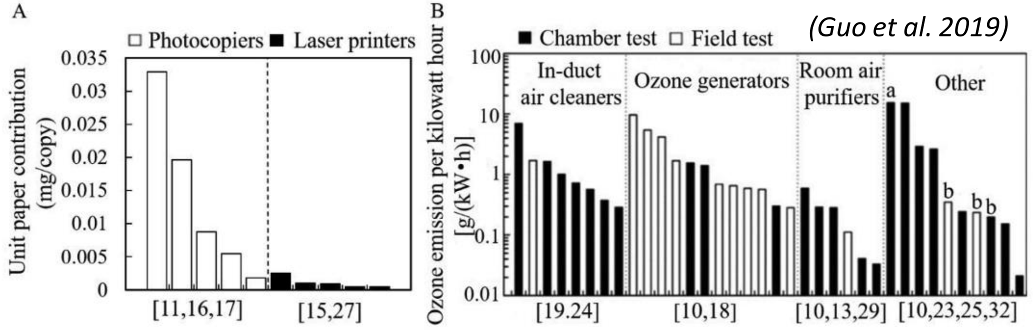
Indoor ozone emission devices (IOEDs)

Ozone emission rate (OER) of different IOEDs

The average ozone emission per paper for laser printer and photocopier is 0.1×10^{-2} and 1.37×10^{-2} mg/copy, respectively.

The average ozone emission per kilowatt hour for in-duct air cleaners, ozone generators, room air purifiers, and other devices is 2.9, 4.1, 0.3, and 7.4 g/(kW·h), respectively.

(Guo et al. 2019)



Ozone emission per unit paper (A) and per kilowatt hour (B) [1]

[1] *Guo, C., Z. Gao, and J. Shen. 2019. Emission rates of indoor ozone emission devices: A literature review. Building and Environment, 158:302–318.*

Indoor ozone emission devices (IOEDs)

Other emissions by IOEDs

VOCs, PM, formaldehyde, acetaldehyde, and NOx were emitted by some IOEDs.

Laser printers and photocopiers also generate considerable heat.

The clean air delivery rate (CADR) of room air cleaners was measured, but no significant correlation was found between CADR and OER.

(Guo et al. 2019)

Device	VOCs	Particles	Others
Laser printer	+ [a]	+	
Laser printer	+		Formaldehyde
Laser printer	+	+	
Photocopier	+	+	Formaldehyde, NO_2
Photocopier	+		Formaldehyde; Acetaldehyde
Room air purifier	+	+	Formaldehyde; Acetaldehyde
Room air purifier	+	+	Formaldehyde; Acetaldehyde
In-duct air cleaner		+	
In-duct air cleaner		+	
Ozone generator			NO_x

Other contaminants emitted by IOEDs [1]

[1] *Guo, C., Z. Gao, and J. Shen. 2019. Emission rates of indoor ozone emission devices: A literature review. Building and Environment, 158:302–318.*

Indoor ozone removal by building surfaces

Building materials can be significant **sinks** for indoor ozone, owing to the **irreversible heterogeneous reactions** between ozone and material surfaces.

Reactions between ozone and material surfaces may also result in **oxidized by-products yields**, including **C1-C13 carbonyls, dicarbonyls and hydroxycarbonyls**, which can adversely affect occupants' health and perceived air quality. Some of these by-products with low vapor pressures can nucleate to new particles or condense on existing particles to form **secondary organic aerosols (SOA)** [1].

		Unsaturated organic compounds (constituting or absorbed on material surfaces)	→	Significant by-products yields + ozone removal
Ozone	+			
		Inorganic materials	→	Negligible by-products yields

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Ozone deposition velocity on surfaces

The rate of ozone removal at the surfaces of building materials, which is typically quantified by **deposition velocity *(v_d)***, is governed by the **transport** of ozone to the material surface and the ozone **uptake** onto the surface.

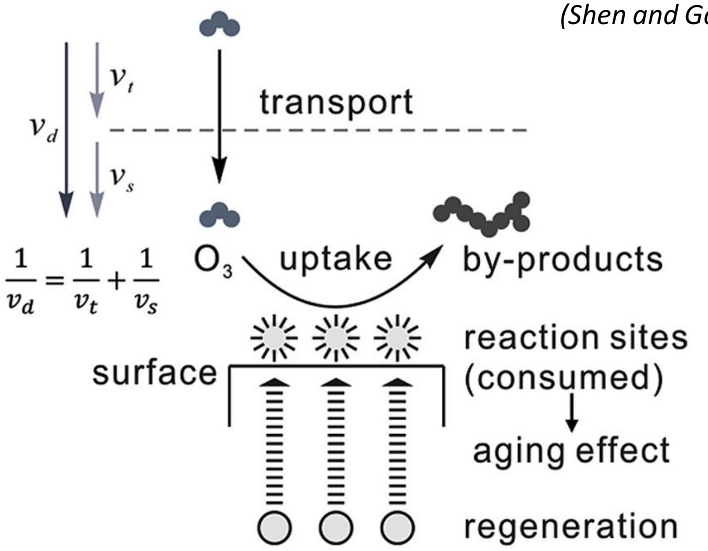
$$\frac{1}{v_d} = r_o = r_t + r_s = \frac{1}{v_t} + \frac{1}{v_s} = \frac{1}{v_t} + \frac{4}{\gamma v}$$

where v_t is the transport-limited deposition velocity (m/h), v_s is the reaction-limited deposition velocity (m/h), γ is reaction probability (−), and <v> is Boltzmann velocity for ozone (<v> = 3.60×10^4 cm/s).

v_t depends on the boundary layer **fluid mechanics** near material surfaces.

v_s can be quantified by **reaction probability γ** (material specific and system-independent), which is the ratio of the removal rate to the collision rate of ozone on the surface.

(Shen and Gao 2018)



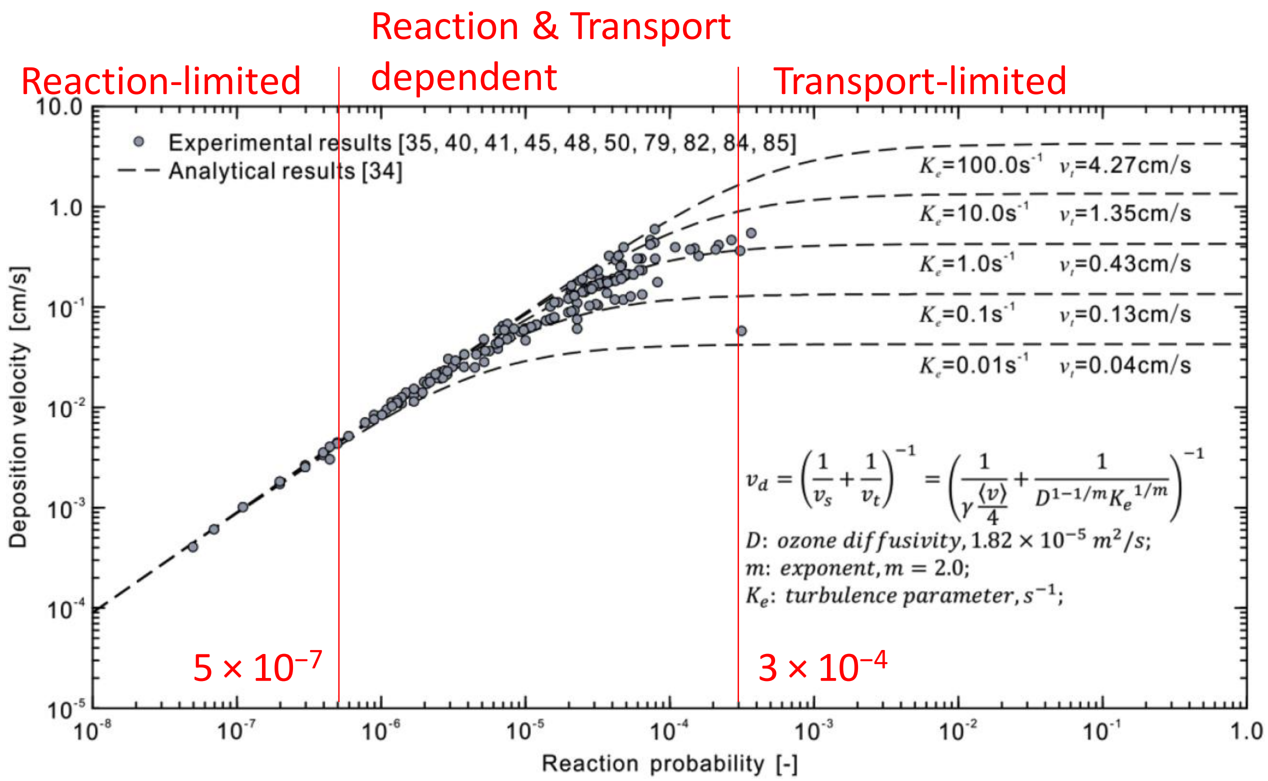
Ozone removal on building surfaces [1]

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Reaction probability on surfaces

Ozone removals on most indoor materials are **dependent on both reaction and transport**.



(Shen and Gao 2018)

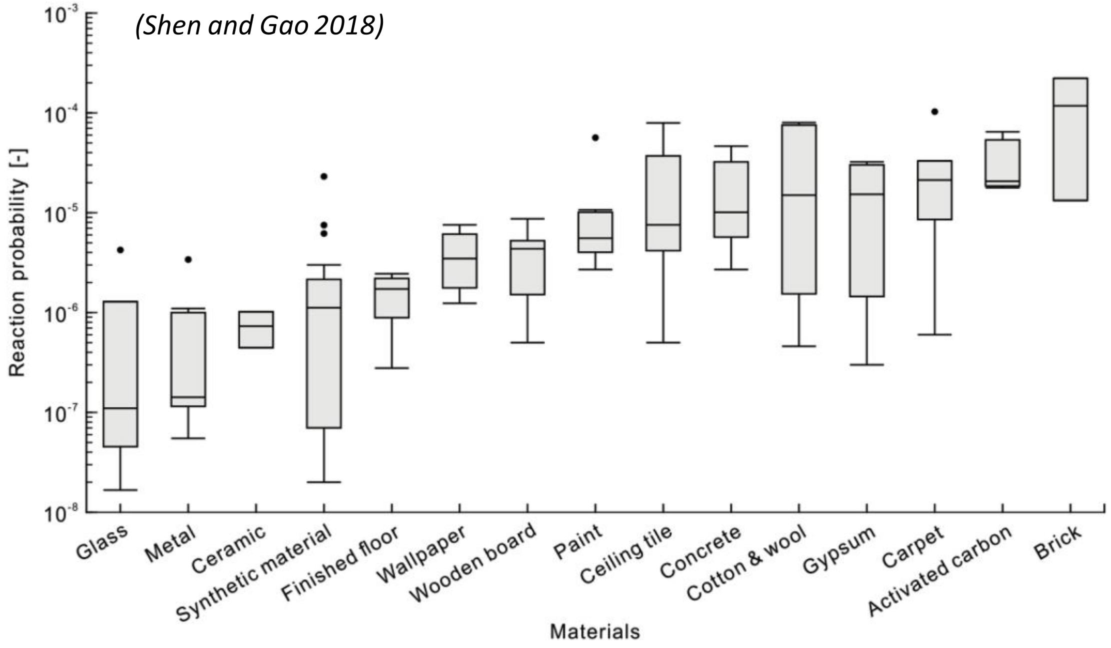
Relationship between deposition velocities and reaction probabilities in different air flow conditions in literature [1]

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Reaction probability of different materials

The reaction probabilities of different materials range from 10^{-8} (e.g. glass) to 10^{-4} (e.g. brick and activated carbon) [1].



Reaction probabilities of different materials presented in literature [1]

Table 1. Values of reaction probability (γ) for ozone. *(Shen et al. 2017)*

Material	γ (-)	Material	γ (-)
Glass[11,14,19,20,26]	6.06E-08	Wall plaster, clay[16,28]	2.20E-05
Lucite[14]	5.50E-08	Sunflower[15]	3.78E-06
Metal, aluminum[11,14,19]	1.08E-07	Cork[15]	5.67E-06
Metal, stainless steel[11]	1.30E-06	Wheat[15]	5.22E-06
Metal, galvanized steel[19,21]	1.10E-06	Nylon[11,14]	5.50E-08
Ceramic[15]	4.44E-07	FEP Teflon[14]	5.50E-07
Stone material, soft dense[11]	7.82E-06	Rubber[16,26,28]	6.86E-06
Stone material, hard dense[11]	1.67E-08	Neoprene[14]	1.90E-06
Floor, wooden[24]	1.20E-06	Polyethylene sheet[14]	1.10E-06
Floor, finished hardwood[16,28]	2.45E-06	Medium density fiberboard[27]	4.50E-06
Floor, finished bamboo[16,28]	1.95E-06	Particle board[27]	5.00E-07
Porcelain clay tile[16,28]	1.02E-06	Plywood[11,14,19]	5.80E-07
Resilient tile[16,28]	1.11E-06	Bamboo[15]	4.44E-07
Ceiling tile, perlite[16,17,28,29]	1.02E-05	Cedar[26]	5.20E-06
Ceiling tile, mineral fiber[16,28]	4.65E-05	Woodwork, fine, hard[11]	5.59E-07
Ceiling tile, fiberglass[16,28]	3.74E-05	Woodwork, course, soft[11]	4.16E-06
Concrete, course[11]	9.65E-06	Cloth, <1 year old[11]	8.99E-06
Concrete, fine[11]	4.20E-06	Cloth, >1 year old[11]	7.06E-07
Wallpaper[11,19,20,26]	4.28E-06	Linoleum[11]	7.89E-07
Fabric wall covering[16,28]	5.30E-06	Linen[11,14]	6.30E-07
Paint, latex[16,19,20,28]	1.47E-06	Carpet, recycled[16,17,28,29]	3.20E-05
Paint, clay[16,28]	5.65E-05	Carpet, fabric-backed[16,28]	2.30E-05
Paint, water-based[26]	4.90E-06	Carpet, nylon[22,28,30]	1.38E-05
Paint, oil-based[26]	6.10E-06	Carpet, olefin[22,28,30]	1.01E-05
Paint, collagen[16,28]	3.15E-06	Carpet, wool[11]	1.06E-05
Gypsum board, painted[11,17,28,29,33]	4.72E-06	Brick[11]	1.59E-05
Gypsum board, untreated[11]	1.73E-05	Activated carbon cloth[11,25,28,29]	2.24E-05

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*
[2] *Shen, J., J. Chen, X. Zhang, S. Zou, and Z. Gao. 2017. Outdoor and Indoor Ozone Concentration Estimation Based on Artificial Neural Network and Single Zone Mass Balance Model. In Procedia Engineering (Vol. 205, pp. 1835–1842). Elsevier Ltd.*

Indoor ozone removal by building surfaces

Reaction probability of different materials

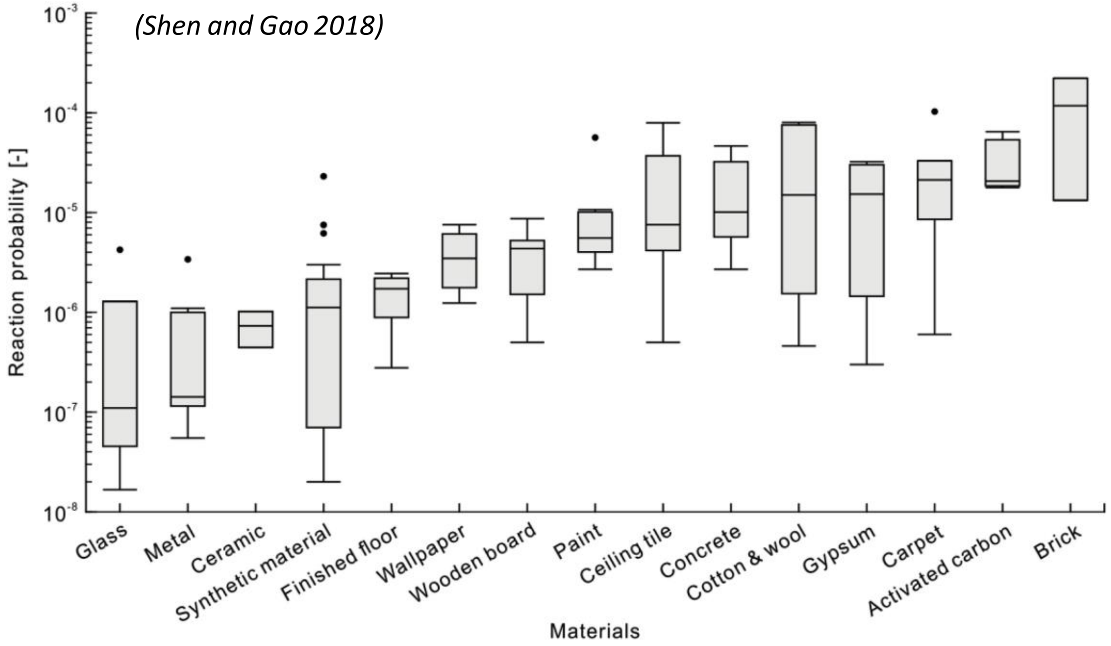
Reaction probabilities of building materials depend on

1) **Material chemical compounds**

- Unsaturated **organic compound** (e.g. cotton, wool, and carpet) are highly reactive with ozone, and may produce oxidized by-products.
- Materials containing **clays** (e.g. brick, gypsum, clay-based paintings and ceiling tiles) consume ozone readily while exhibits negligible by-products yield, probably due to the reaction catalyzed by metals presented in the clay.

2) **Surface characteristics** (e.g. roughness and porosity)

- **Fleecy and porous** materials, e.g. activated carbon cloth and carpet, exhibit higher reaction probabilities than **smooth, non-porous** surfaces, e.g. glass, metal and ceramic.
- **Specific surface area** of the building material is more closely related to ozone reaction probability than total pore volume.
- **Paints or covering materials** are probably more important than the underlying material in determining ozone deposition.



[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Transport-limited deposition velocity

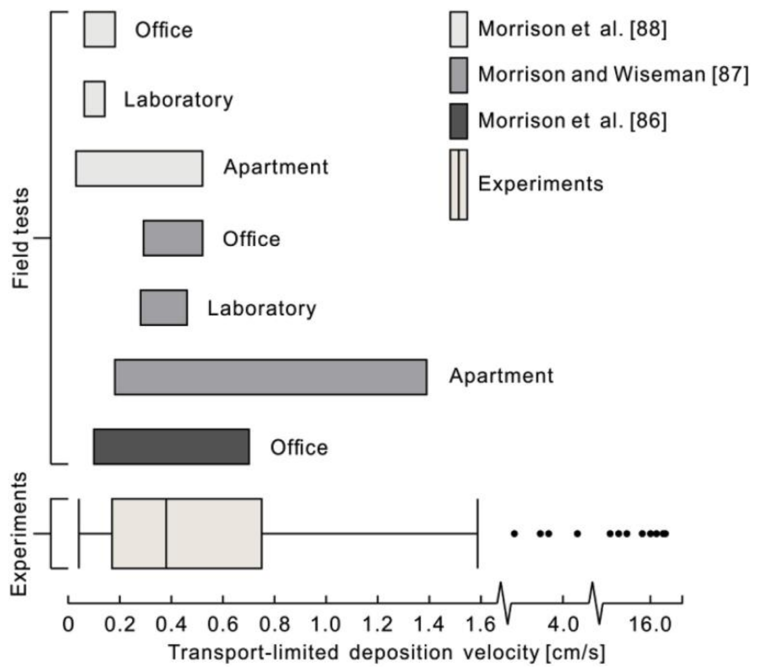
v_t in field tests mainly between 0.1 and 0.7 cm/s

v_t in laboratory experiments roughly between 0.1 and 0.8 cm/s

Values of v_t can vary over an order of magnitude in the same room and can be influenced by air movement.

Location	*v_t [cm/s]*
Under cabinet	0.06
Under desk	0.09
Near hood	0.12
Near operating computer	0.14
Near window & supply vent	0.52

(Shen and Gao 2018)



Transport-limited deposition velocities in field tests and experiments in literature [1]

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Ozone-initiated by-products yields

Reactions between ozone and material surfaces may result in the formation of oxidized by-products, including **C1-C13 carbonyls, dicarbonyls** and **hydroxycarbonyls**. These by-products are usually produced from reactions between ozone and the **unsaturated organic compounds** that constituting or adsorbed on material surfaces.

Studies observed high by-products yields dominated by **C9 aldehyde** for various kinds of **carpets**.

Human skin oil is highly reactive with ozone and may result in high yields of oxidized by-products, which mainly consist of **acetone, C9-10 aldehydes, 6-methyl-5-hepten-2-one** and **4-oxopentanal**.

Inorganic materials usually exhibit negligible by-products yields

→ some inorganic materials, e.g. bricks, clay-based plasters and perlite-based ceiling tiles, are usually considered as the most promising **passive removal materials (PRMs)** for indoor ozone, since they can remove substantial ozone while yield negligible by-products

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone removal by building surfaces

Ozone removal during long-term period

Materials may become less reactive after a relative short period of ozone exposure, e.g. several months, which is likely due to the consumption of available **surface reaction sites**.

However, during a **longer-term** exposure to ozone, some materials in occupied environments may exhibit remained surface reactivity on account of the **replenishment of the reactive compounds** on material surfaces, which is believed to be closely associated with **human occupants (e.g. surface soiled by skin oil) or occupant activities (e.g. cooking and cleaning).**

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*

Indoor ozone estimation tool (single-zone model)

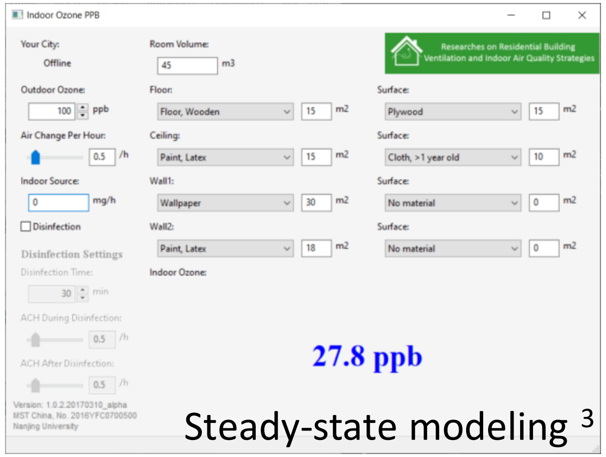
(Shen 2017)

Indoor ozone estimation tool

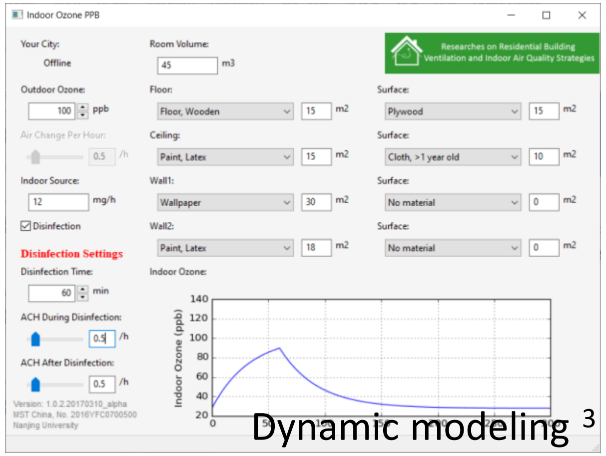
- Single-zone mass balance model $\frac{dC_{in}}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C_{in} - \sum k_{o3,j} C_j C_{in} - \sum \frac{v_{d,b} A_b C_{in}}{V} - \sum \frac{v_{d,h} A_h C_{in}}{V}$
- Database of reaction probabilities between building material and ozone
- Database of ozone emission rates of typical IOEDs

Validated by field data measured in a college student dormitory during summer in Nanjing, China.

(I/O ratio)	*Window closed*	*Window open*
Measured	0.30	0.44
Simulated	0.33	0.49



Steady-state modeling [3]



Dynamic modeling [3]

[1] *Shen, J., and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.*
[2] *Shen, J., J. Chen, X. Zhang, S. Zou, and Z. Gao. 2017. Outdoor and Indoor Ozone Concentration Estimation Based on Artificial Neural Network and Single Zone Mass Balance Model. In Procedia Engineering (Vol. 205, pp. 1835–1842). Elsevier Ltd.*
[3] *Shen, J. 2017. https://github.com/jialeishen/Indoor-Air-Assistant*

Conclusions

- The average OERs of in-duct air cleaners, ozone generators, room air purifiers, photocopiers, laser printers, and other small devices are 62.8, 76.3, 4.6, 3.3, 0.8, and 0.4 mg/h, respectively.
- The reaction probabilities of different materials range from 10^{-8} (e.g. glass) to 10^{-4} (e.g. brick and activated carbon)
- Reaction probabilities of building materials depend on material chemical compounds and surface characteristics (e.g. roughness and porosity).
- Reactions between ozone and unsaturated organic compounds on material surfaces may result in the formation of oxidized by-products, while inorganic materials usually exhibit negligible by-products yields
- Materials may become less reactive after a relative short period of ozone exposure likely due to the consumption of available surface reaction sites. During a longer-term exposure to ozone, some materials in occupied environments may exhibit remained surface reactivity on account of the replenishment of the reactive compounds on material surfaces, which is believed to be closely associated with human occupants (e.g. surface soiled by skin oil) or occupant activities (e.g. cooking and cleaning).

Bibliography

1) **Shen, J.,** and Z. Gao. 2018. Ozone removal on building material surface: A literature review. Building and Environment, 134:205–217.
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Questions?

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