

Ozone removal on HVAC filters: Underlying mechanisms, model development, and parameter estimation

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SUMMARY

Ozone reacts with HVAC filters, reducing indoor ozone concentrations but also leading to potentially harmful oxidation products. We developed a model for ozone removal by filters, with parameter estimates based on published data and a series of experiments involving filters challenged with oleic acid particles or diesel soot. Ozone deposition velocities for oleic acid and diesel particles were orders of magnitude greater than typical values for indoor materials. The mean deposition velocity over six oleic acid experiments was 1.8 cm/s (range = 1.5 to 2.4 cm/s), with mass transfer resistance accounting for 75% of total resistance to deposition, on average. The mean deposition velocity over 10 diesel particle experiments was 7.6×10^{-2} cm/s (range = 1.3×10^{-2} to 21×10^{-2} cm/s), with mass transfer resistance accounting for only 3% of total resistance to deposition, on average. Deposition velocity increased with age of diesel particles, suggesting the importance of evaporation of water and less reactive semi-volatile liquids from such particles.

KEYWORDS

Filters, Ozone, Diesel soot, Oleic acid, Model

INTRODUCTION

Ozone is a pervasive air pollutant known to have several associated adverse health effects such as asthma, decreased lung function, increased risk of premature mortality, and increased risk of respiratory symptoms in infants whose mothers have physician diagnosed asthma (Bell et al., 2004; Triche et al., 2006). Ozone is typically found in lower concentrations indoors than outdoors, primarily due to heterogeneous reactions with indoor surfaces (Weschler, 2000). In addition to indoor surfaces, ozone is known to react in varying degrees with heating, ventilating, and air conditioning (HVAC) components including ducts (Morrison et al., 1998) and filters (e.g., Bekö et al., 2006; Hyttinen et al., 2006; Zhao et al., 2007). Lined HVAC ducts remove less than 4% of ozone passing through them, and less is removed on unlined ducts (Morrison et al., 1998). HVAC filters have been observed to remove significantly higher amounts of ozone, ranging from 10-30% at steady state for used polyester and fiberglass filters (Bekö et al., 2006; Hyttinen et al., 2006; Zhao et al., 2007) to 90% at steady state for activated carbon filters (Metts et al., 2005). While ozone removal from indoor air is considered beneficial because of the adverse health effects of ozone, exposure to the resulting oxidation products may outweigh these benefits (Weschler, 2006; Apte et al., 2007).

There is currently a lack of understanding of processes that affect ozone reactions with HVAC filters. In this study we explore the removal of ozone to oleic acid and diesel particles deposited on small PTFE filters. Filters are treated as idealized plug-flow reactors (PFRs), and the resulting reactor model is used to calculate ozone deposition velocities.

METHODS

Model development

An idealized (no axial diffusion or dispersion) one-dimensional PFR model was employed to estimate the removal of ozone across an HVAC filter as:

$$\eta = 1 - e^{\left(-v_d \frac{A_s \delta}{V U}\right)} \quad (1)$$

where η is the ozone removal efficiency of the filter (dimensionless), v_d is the deposition velocity of ozone to the collected dust particles (m s^{-1}), A_s is the total surface area of particles (m^2), δ is the filter thickness (m), V is the total bulk volume of the filter (m^3), and U is the face velocity of the air through the filter (m s^{-1}). The product of the projected cross-sectional area of the filter, A_F (m^2), and filter thickness, δ , can be substituted for V , and $A_F \times U$ can be set equal to the volumetric flow rate of air through the filter, Q ($\text{m}^3 \text{s}^{-1}$). Then, cancelling δ and solving for deposition velocity yields:

$$v_d = \frac{-\ln(1 - \eta)Q}{A_s} \quad (2)$$

Equation 2 can be used to estimate the deposition velocity of ozone to the particles in a filter, given experiment values for η and Q , and a reasonable estimate of A_s .

Since ozone can react with filter fibers or particles deposited on the filter, it is of value to separate the effects of these parallel reactions. The parallel effects of ozone reactions with filter fibers and deposited particles can be represented as:

$$1 - \eta_F = e^{-[(v_{d,f}A_{s,f}) + (v_{d,p}A_{s,p})]/Q} \quad (3)$$

where η_F is the ozone removal efficiency of the filter fiber and particles, $(v_{d,f}A_{s,f})$ is the product of the deposition velocity and the surface area of the filter fibers, and $v_{d,p}$ and $A_{s,p}$ are the deposition velocity and the surface area of the particle cake. The ozone deposition velocity for the particle cake can then be determined by solving for $v_{d,p}$ and equating $(v_{d,f}A_{s,f})$ to $-\ln(1 - \eta_f) \cdot Q$ using Equation 2, and simplifying to obtain Equation 4:

$$v_{d,p} = \ln\left(\frac{1 - \eta_f}{1 - \eta_F}\right) \frac{Q}{A_{s,p}} \quad (4)$$

where η_f is the ozone removal efficiency of a clean filter, i.e., with no deposited particles.

The magnitude of deposition velocity is defined by a combination of transport and surface reaction processes. The overall resistance to deposition is typically modeled as two resistances in series according to Equation 5 (Cano-Ruiz et al. 1993):

$$v_d = \left(\frac{1}{v_t} + \frac{1}{v_s}\right)^{-1} \quad (5)$$

where v_t and v_s are the transport-limited and surface-limited deposition velocities (m s^{-1}), respectively. The transport-limited deposition velocity is affected by advective and diffusive transport processes responsible for movement of molecules to a surface. The surface-limited deposition velocity is affected by the effectiveness of molecular removal by reactions at the surface. The surface-limited deposition velocity can be modeled as (Cano-Ruiz et al. 1993):

$$v_s = \frac{\gamma \langle v \rangle}{4} \quad (6)$$

where γ is the reaction probability between a pollutant and a surface (dimensionless), and $\langle v \rangle$ is the Boltzmann velocity (m s^{-1}). The reaction probability is defined as the number of reactions that occur at a surface normalized by the number of collisions with the surface. The mean Boltzmann velocity for ozone at 293 °K in air is $\langle v \rangle = 3.60 \cdot 10^4 \text{ cm s}^{-1}$ (Cano-Ruiz et al., 1993).

Experiments and parameter estimation

Seventeen PTFE filters (pore size of 2.0 μm and a diameter of 47 mm) were loaded with known amounts of either oleic acid particles or diesel soot. Ozone was passed through the filters, and upstream and downstream measurements were made to determine ozone removal efficiency. Specific methods are summarized below, with additional detail provided in Zhao (2006).

Six filters were loaded with oleic acid particles. A Collison nebulizer was used to generate reagent grade oleic acid aerosols. After passing through the Collison nebulizer, air entered a clean 28 L stainless-steel chamber. The air exited the chamber through a clean PTFE filter placed in a filter holder followed by a vacuum pump with a flow rate of 20 L min^{-1} . The aerosol number concentration distribution upstream of each loaded filter was measured by a Scanning Mobility Particle Sizer (SMPS). The particle number concentrations in 95 channels were averaged and converted to total surface area as described by Zhao (2006). The total mass of oleic acid on each filter was taken as the mass difference before and after loading.

Eleven filters were loaded with diesel soot from the exhaust gas of an idling diesel truck. Inlet copper tubing was placed 5 cm inside the tailpipe of the truck so that all the inlet air came from the truck exhaust without dilution with the surrounding air. The engine was fueled with regular sulfur No. 2-D diesel fuel oil-dyed (sulfur content $\leq 0.5\%$ mass). The diesel exhaust was pumped into 2 m of copper tubing for initial cooling; then passed through 0.6 m of stainless steel tubing. The exhaust then passed through the PTFE filter. The sample stream was drawn by a vacuum pump with an air flow rate of 20 L min^{-1} . The mass of the PTFE filter before and after loading was measured by a micro-balance. Every loaded filter was stored in an ozone-free environment until tested.

The total surface area of oleic acid particles was calculated from the SMPS number concentrations described above. Surface areas for diesel particulate matter reported in the literature range from 52 $\text{m}^2 \text{g}^{-1}$ to 108 $\text{m}^2 \text{g}^{-1}$ (Kittelson et al., 1998; Ghzaoui et al., 2004; Fernandes et al., 2003). An average of 80 $\text{m}^2 \text{g}^{-1}$ was assumed for all calculations.

Ozone concentrations upstream and downstream of the filter were alternately measured by a 2B Technologies UV absorbance ozone analyzer and used to determine ozone removal efficiency across each filter. A controller was programmed to switch the ozone monitor upstream and downstream every three minutes throughout an entire experiment. The

temperature and relative humidity of inlet air was monitored at the beginning and the end of each experiment. Each experiment lasted for 100 hours.

Inlet air was provided from within the general occupied space of the building. Inlet air was mixed with ozone generated by an ozone generator, and was pulled with a volumetric flow rate of 20 L min⁻¹. The air stream was then pre-filtered through a PTFE filter before being conveyed through either a diesel-loaded or oleic acid-loaded test filter set in a PTFE filter holder followed by a vacuum pump with an air flow of 20 L min⁻¹. The air flow rate of 20 L min⁻¹ through the filter was confirmed after each experiment with a bubble flow meter plumbed to the outlet of a vacuum pump. The face velocity through each filter was 0.19 m s⁻¹.

The deposition velocity for each filter was calculated using Equation 2 and the model parameters listed in Table 1. Then, the transport-limited deposition velocity for oleic acid particles was calculated using Equations 5 and 6, and γ from Table 1. Using the overall deposition velocity and the average transport-limited deposition velocity determined from oleic acid experiments, v_s for diesel particles was determined using Equation 5. The assumption that the transport-limited deposition velocity of ozone is the same for oleic acid and diesel particles is reasonable because it is a function of the properties of ozone and the fluid dynamics in the filter, which were likely similar during both types of experiments. Subsequently, the reaction probability for diesel exhaust particles was calculated based on Equation 6. We also evaluated deposition velocity and reaction probability of the diesel particles as a function of time.

Table 1. Summary of parameters and sources for PTFE filter experiments (Zhao, 2006).

Parameter	Symbol	Value
Volumetric airflow through filter ¹	Q	0.000333 m ³ s ⁻¹
Surface area of filter face ^{1,*}	A_F	0.001735 m ²
Face velocity ^{1,†}	U	0.192 m s ⁻¹
Reaction probability between ozone and oleic acid ²	γ_{OA}	8.0·10 ⁻⁴
Surface-limited deposition velocity of ozone to oleic acid [‡]	v_S	7.2 cm s ⁻¹
Boltzmann velocity for ozone ³	$\langle v \rangle$	3.60·10 ⁴ cm s ⁻¹

Sources: 1. (Zhao, 2006), 2. (Moise and Rudich, 2002), 3. (Cano-Ruiz et al. 1993).

* $A_F = \pi/4 \cdot d^2$, where filter diameter, d , = 47mm; † $U = Q/A_F$; ‡ Calculated using Equation 6.

RESULTS

As summary of the particle mass, particle surface area, and ozone removal efficiency appear in Table 2. Deposition velocities for oleic acid and diesel particles are listed in Tables 3 and 4, respectively.

Table 2. Summary of experiments and ozone removal efficiencies for PTFE filters loaded with oleic acid or diesel exhaust particles (Zhao, 2006).

Filter	Filter Age (d)	Particle Mass (mg) \pm 0.3 mg	Surface Area, A_S (m ²)	Ozone Removal Efficiency, η (%)
OA1	0	15.1	0.056 \pm 0.0015	92
OA2	7	16.6	0.062 \pm 0.0016	94
OA3	11	14.4	0.053 \pm 0.0015	95
OA4	0	2.4	0.009 \pm 0.0011	48
OA5	7	2.8	0.011 \pm 0.0011	44
OA6	11	3.1	0.011 \pm 0.0011	39
D1	0	13.8	1.1	0
D2	7	10.6	1.15	36
D3	11	12.1	0.97	65
D4	0	6.1	0.49	26
D5	7	4.8	0.38	51
D6	11	4.4	0.35	70
D7	15	4.1	0.32	73
D8	0	7.9	0.63	62
D9	7	6.9	0.74	47
D10	11	7.1	0.56	76
D11	15	7	0.56	97

D = diesel exhaust, OA = oleic acid; Uncertainties for surface area of oleic acid are calculated based on the uncertainty for particle mass measurements of 0.3 mg, surface areas for diesel exhaust particles are based on an average value of specific surface areas published in the literature, and the mass of particles loaded onto the filter. Uncertainties were not calculated for diesel particle surface area.

Table 3. Calculated values of deposition velocity, transport-limited deposition velocity and contribution to total resistance from v_s , CT_S , for oleic acid captured on small scale filters.

Filter	v_d (m s ⁻¹) \cdot 10 ⁻²	v_t (m s ⁻¹) \cdot 10 ⁻²	CT_S (%)
OA1	1.5	1.9	21
OA2	1.5	1.9	21
OA3	1.9	2.6	25
OA4	2.4	3.7	34
OA5	1.8	2.3	23
OA6	1.5	1.9	21
Mean	1.8	2.4	25

The mean deposition velocity of ozone to oleic acid is approximately one to two orders of magnitude greater than deposition velocities of ozone to a wide range of indoor surfaces, *e.g.*, 0.00015 – 0.00075 m s⁻¹ (Weschler, 2000 and references therein). The overall deposition velocity for ozone and diesel particles ranged from 0.00013 - 0.0021 m s⁻¹ with an average value of $v_d = 0.00076$ m s⁻¹, several orders of magnitude lower than that of oleic acid. The D1 sample removed no ozone from the air for unexplained reasons and was discarded.

Table 4. Calculated values of deposition velocity, surface-limited deposition velocity, contribution to total resistance from v_S , and reaction probability for diesel exhaust particles.

Filter	v_d (m s^{-1}) $\cdot 10^{-4}$	v_S (m s^{-1}) $\cdot 10^{-4}$	CT_S (%)	γ (-) $\cdot 10^{-6}$
D1	0.00	-	-	-
D2	1.29	1.30	99.5	1.45
D3	3.61	3.66	98.5	4.07
D4	2.05	2.07	99.1	2.30
D5	6.26	6.43	97.4	7.14
D6	11.4	12.1	95.2	13.4
D7	13.6	14.4	94.3	16.1
D8	5.12	5.23	97.8	5.81
D9	2.86	2.89	98.8	3.22
D10	8.49	8.81	96.4	9.79
D11	20.8	22.8	91.2	25.4
Mean	7.6	8.0	97	8.9

The values of v_d , v_S , and γ are noticeably higher for diesel exhaust particle samples 6, 7, 10, and 11. These samples were aged longer than the others, *i.e.*, samples were maintained for a longer period before being exposed to ozone. Figure 1 shows a plot of the reaction probability of diesel exhaust particles versus the age of the filters.

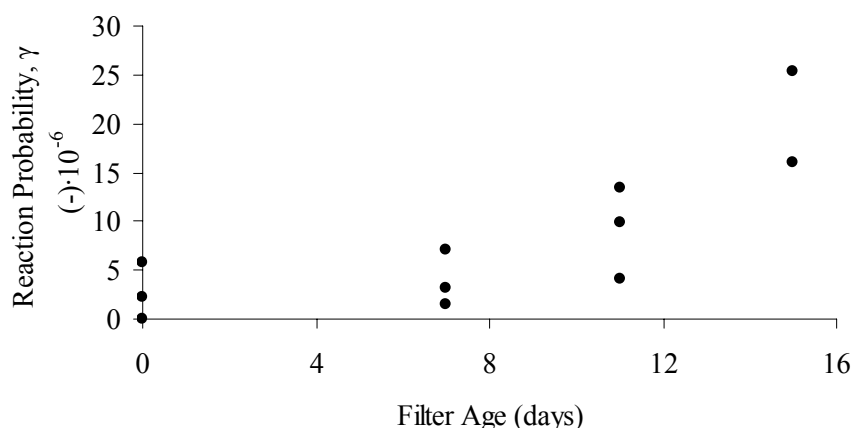


Figure 1. Reaction probability vs. filter age for PTFE filters loaded with diesel exhaust particles. An assumed specific area of $80 \text{ m}^2 \text{ g}^{-1}$, and $v_T = 2.37 \cdot 10^{-2} \text{ (m s}^{-1}\text{)}$ was used to calculate reaction probability.

DISCUSSION

The transport-limited deposition velocities observed in this study were one to two orders of magnitude higher than typical v_i for ozone on indoor surfaces, *i.e.*, $0.0002 - 0.002 \text{ m s}^{-1}$ (Lai and Nazaroff, 2000). These results are reasonable considering that the air velocity flowing through the HVAC filters was 0.2 m s^{-1} , one or two orders of magnitude higher than typical air velocities in indoor spaces of $0.003 - 0.03 \text{ m s}^{-1}$ (Lai and Nazaroff, 2000).

The average contribution of surface reaction resistance to overall resistance was only 25% for oleic acid, which is generally quite reactive with ozone due to an internal carbon-carbon double bond. In contrast, the average resistance contribution of surface reactions for diesel

particles was 97% of the overall resistance to deposition. Unlike oleic acid particles, surface reaction kinetics is the limiting factor in the removal of ozone to diesel exhaust particles. The reaction probabilities of diesel exhaust particles ranged from $1.4 \cdot 10^{-6}$ to $2.5 \cdot 10^{-5}$, with an average value of $8.9 \cdot 10^{-6}$. This agrees reasonably well with the reaction probabilities of various types of soot, including fractal carbon soot, $\gamma = 10^{-7}$, candle soot, $\gamma = 7.5 \cdot 10^{-6}$, and activated carbon, $\gamma = 2.1 \cdot 10^{-5}$ (Zhao et al. 2007, and references therein).

It appears that the reaction probability increases as the age of diesel particles increases. This is consistent with the dual impedance model proposed by Strommen and Kamens (1997) that considers the surface-limited deposition velocity of a diesel exhaust particle as a combined resistance of two layers of material; a solid inner layer which is surrounded by and saturated by a liquid outer layer of semi-volatile organic compounds (SVOCs). The deposition velocity increases due to evaporation of less reactive SVOCs, which decreases the thickness and thus the resistance of the liquid layer. This suggests that used HVAC filters that have large amounts of diesel exhaust or other combustion particles will increase deposition velocity as the filter ages.

CONCLUSIONS

We developed a model for ozone removal by filters, with parameter estimates based on published data and a series of experiments involving filters challenged with oleic acid particles or diesel soot. Ozone deposition velocities for oleic acid and diesel particles were orders of magnitude greater than typical values for indoor materials. The mean deposition velocity for oleic acid was 1.8 cm/s, with mass transfer resistance accounting for 75% of total resistance to deposition, on average. The mean deposition velocity for diesel particles was 0.076 cm/s with mass transfer resistance accounting for only 3% of total resistance to deposition, on average. Deposition velocity increased with age of diesel particles, suggesting the importance of evaporation of water and less reactive semi-volatile liquids from such particles. The results suggest that ozone removal on filters can be predicted with knowledge of the composition and surface area of deposited particles. Similarly, knowledge of the ozone removal efficiency and surface area of deposited particles can be used to evaluate the deposition velocity, and therefore to provide insight into the composition of particles in filter cakes.

REFERENCES

- Apte, M.G., Buchanan, I.S.H., Mendell, M.J. 2007. Outdoor ozone building related symptoms in the BASE study. Lawrence Berkeley National Laboratory, Report LBNL-62419.
- Bell, M.L., McDermott, A., Zeger, S.L., Samet, J.M., Dominici, F. 2004. Ozone and short-term mortality in 95 US urban communities, 1987-2000. *Journal of the American Medical Association*, 292, 2372-2378.
- Bekö, G., Halás, O., Clausen, G., and Weschler, C. 2006. Initial studies of oxidation processes on filter surfaces and their impact on perceived air quality. *Indoor Air*, 16, 56-64.
- Fernandes, B.M., Skjemstad, O.J., Johnson, B.G., Wells, D.J., and Brooks, P. 2003. Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features. *Chemosphere*, 51, 785-795.
- Cano-Ruiz, J.A., Kong, D., Balas, R.B., Nazaroff, W.W. 1993. Removal of reactive gases at indoor surfaces: combining mass transport and surface kinetics, *Atmospheric Environment*, 27A, 2039-2050.
- Ghzaoui, E., Lindheimer, M., Lindheimer, A., Lagerge, S., and Partyka, S. 2004. Surface characterization of diesel engine soot inferred from physico-chemical methods. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 233, 79-86.

- Hinds W.C. 1999. *Aerosol Technology: properties, behavior, and measurement of airborne particles*. 2nd Ed, John Wiley & Sons, Inc., New York, NY.
- Hyttinen, M., Pasanen, P., Kalliokoski, P. 2006. Removal of ozone on clean, dusty and sooty supply air filters. *Atmospheric Environment*, 40, 315–325.
- Kittelson, D.B. 1998. Engines and nanoparticles: A review. *Journal of Aerosol Science*, 29, 575-588.
- Lai, A.C.K., Nazaroff, W.W. 2000. Modeling indoor particle deposition from turbulent flow onto smooth surfaces. *Journal of Aerosol Science*, 31, 463-476.
- Liu, D.L., and Nazaroff, W.W. 2001. Modeling pollutant penetration across building envelopes. *Atmospheric Environment*, 35, 4451-4462.
- Metts, T.A., Batterman, S.A., Fernandes, G.I., Kalliokoski, P. 2005. Ozone removal by diesel particulate matter. *Atmospheric Environment*, 39, 3343–3354.
- Moise, T., Rudich, Y. 2002. Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products. *Journal of Physical Chemistry A*, 106, 6469-6476.
- Morrison, G.C., Nazaroff, W.W., Cano-Ruiz, J.A., Hodgson A.T., Modera, M.P. 1998. Indoor air quality impacts of ventilation ducts: ozone removal and emissions of volatile organic compounds. *Journal of the Air & Waste Management Association*, 48, 941-952.
- Strommen, M., Kamens, R. 1997. Development and application of a dual-impedance radial diffusion model to simulate the partitioning of semivolatile organic compounds in combustion aerosols. *Environmental Science & Technology*, 31, 2983-2990.
- Triche, E.W., Gent, J.F., Holford, T.R., Belanger, K., Bracken, M.B., Beckett, W.S., et al. 2006. Low-level ozone exposure and respiratory symptoms in infants. *Environmental Health Perspectives*, 114 (6), 911-916.
- Weschler, C.J. 2000. Ozone in indoor environments: concentration and chemistry. *Indoor Air*, 10, 269–288.
- 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, 1489-1496.
- Zhao, P. 2006. Ozone interactions with HVAC filters. Doctoral Dissertation, The University of Texas at Austin.
- Zhao, P., Siegel, J.A., Corsi, R.L. 2007. Ozone removal by HVAC filters. *Atmospheric Environment*, 41, 3151–3160.