Modeling ozone removal to indoor materials, including the effects of porosity, pore diameter, and thickness

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Model input parameters

Inputs to the model described in the accompanying manuscript are shown in Table S1. Full details regarding the determination of the thickness, mass, pore area, median pore diameter by volume, and effective diffusion coefficient are described in Gall et al.[1] Tortuosity is determined from measurements of effective diffusion coefficient and porosity, and estimates of tortuosity are included to facilitate quantitative comparison of test materials; tortuosity is not a direct model input. The parameter "Model grid spacing" refers to the spacing between nodes discretized in space through the thickness of the five test materials. Variable grid spacing was employed for thicker materials (PP, PCC, and ACC). Model run-times were proportional to the number of nodes in materials. Modeled γ_{ipa} were found to be insensitive to wider grid-spacing as test material thicknesses increased, likely a result of lower concentrations due to reactions and diffusion time-scales at greater depths of thicker materials. WF14 and WF15 had 12 total nodes and 96 total nodes for the 0.02 cm and 0.16 cm condition, respectively. Where variable grid spacing was used, each value of Δy was input into the model for ten nodes, for a total of 60 nodes.

The model developed in this work uses median pore diameters by volume, as opposed to median pore diameters by area or characterizations of the distribution of pore diameters in the material. Characterizing the pore geometry on a volume basis was selected as it was considered more aligned with the model assumption of molecular diffusion as the driving force for ozone transport through materials. As noted in the text, future work should explore the model impact of this selection. It is likely to be a more impactful assumption for materials with a wide range of pore diameters, as it may result in a mismatch between the availability of modeled surface area and the transport mechanism in the material substrate that results in material-ozone collisions for certain ranges of pore diameters (e.g., nm-scale pores).

Table S1. Summary of model inputs for test materials.

Material	Thick-ness (cm)	Mass (g)	Pore area ($m^2\ g^{-1}$)	Porosity ε (-)	Median pore diameter (volume), $d_{p,V}$ (µm)	Effective diffusion coefficient, D_e ($cm^2\ s^{-1}$)	Tortuosity, τ (-)	Model grid spacing, Δy (cm)
Cellulose Paper (25 µm retention), WF14	0.02	2.0	14	0.77	13	0.033	3.2	0.00167
	0.16	16						
Cellulose Paper (2.5 µm retention), WF15	0.02	2.0	19	0.78	15	0.024	5.4	0.00167
	0.16	16						
Pervious Pavement, PP	1.27	530	2.5	0.67*	2700#	0.021	4.5	0.00125, 0.00125, 0.002, 0.015, 0.04, 0.07
	2.54	994						0.00125, 0.002, 0.015, 0.04, 0.07, 0.12
Portland Cement Concrete, PCC	1.27	600	13	0.26	0.19	0.0024	14	0.00125, 0.00125, 0.002, 0.015, 0.04, 0.07
	2.54	920						0.00125, 0.002, 0.015, 0.04, 0.07, 0.12
Activated Carbon Cloth, ACC	0.64	5.0	160	0.97*	500#	0.12	1.1	0.00125, 0.00125, 0.002, 0.015, 0.02, 0.25
	1.27	9.5						0.00125, 0.00125, 0.002, 0.015, 0.04, 0.07
	2.54	20						0.00125, 0.002, 0.015, 0.04, 0.07, 0.12

*,# values are corrected to account for large pores not captured by the mercury intrusion porosimeter, as described in full in Gall et al.[1]

Assumption of negligible transport resistance in pore volumes.

To explore the implication of the assumption of negligible transport resistance for uptake of ozone to pore walls, time-scales of effective diffusion along the longitudinal axis of a material pore are compared to time-scales for molecular diffusion along the pore radius of the material. Time-scales for diffusion were estimated from the ratio of the square of the characteristic length to the appropriate estimate of diffusive transport, as shown in eq S5:

$$\tau_e = \frac{y^2}{D_e} or \;\; \tau = \frac{r_p{}^2}{D} \tag{S5}$$

where τ_e is the time-scale for diffusion along the pore longitudinal axis (s), y is the material thickness (cm), D_e is the material-ozone effective diffusion coefficient (cm^2/s), τ is the time-scale for molecular diffusion along the pore radius (s), r_p is the pore radius, and D is the molecular diffusion coefficient of ozone in air (cm^2/s).

Table S2 reports the time-scales for the two characteristics lengths of pores and effective and molecular modes of diffusion. Comparisons were selected for the most conservative condition, that is, the smallest material thickness where the time-scale for diffusive transport along the pore longitudinal axis will be the shortest. Across the five materials, τ_e is greater than τ by 2.5 to 3.5 orders of magnitude. Since Figure 1 in the main text indicates an increase in ozone removal to WF14, WF15, and PP with increasing thickness, this implies that effective diffusion along the pore length is rate-limiting for ozone uptake to materials compared to diffusion to pore walls, and indicates the assumption of negligible transport is a reasonable approximation.

Table S2. Comparison of time-scales for effective diffusion along pore longitudinal axis to molecular diffusion along pore radius.

Material	Thickness, (cm)	Pore radius, (cm)	Material-ozone effective diffusion coefficient, D_e (cm^2/s)	Time-scale for effective diffusion, longitudinal axis of pore, (s)	Time-scale for diffusion to pore walls, D = 0.15 cm^2/s (s)
20-25 µm cellulose Paper, WF14	0.02	0.00065	0.033	0.012	0.000003
2.5 µm Cellulose Paper, WF15	0.02	0.00075	0.024	0.017	0.000004
Pervious Pavement, PP	1.27	0.135	0.021	77	0.12
Portland Cement Concrete, PCC	1.27	0.00095	0.0024	672	0.000006
Activated Carbon Cloth, ACC	0.64	0.025	0.12	3.4	0.004

Discretization of model equations

Equations 2,3,5, and 6, shown in the main manuscript, were discretized in time and equation 5 was also discretized in space. These discretized equations were solved explicitly to determine the best-fit estimate of material-ozone reaction probability accounting for internal pore area and diffusion (γ_{ipa}) as described in the main text of the manuscript. Equation 2 in the main text was discretized in time as shown in eq S1:

$$C_\infty^{t+\Delta t} = \left[\lambda\left(C_1^t - C_\infty^t\right) - \frac{v_{d,w} A_w C_\infty^t}{V} - \frac{1}{\frac{1}{v_t} + \frac{4}{\gamma_{ipa} < v >}} (1-\varepsilon)(A_m)\left(C_0^t\right)\left(\frac{1}{V}\right) - D_e \frac{\left(C_0^t - C_{y,n=1}^t\right)\varepsilon A_m}{\Delta y V} \right] \Delta t + C_\infty^t \quad \text{(S1)}$$

where λ is the chamber air exchange rate (h^{-1}) and Δy is the concentration node spacing in the material (m) and all other terms as defined in the main text. The transport-limited deposition

velocity, v_t, was determined for each material by coating the exposed surface of materials with a solution of potassium iodide and performing an ozone deposition velocity experiment.[2]

Equation 3 in the main text was discretized through time and through $i = n$ nodes in space, incorporating eq 4 from the main text, assuming no advective transport, knowing that the ratio of the control volume diameter to the overall pore diameter, d_p (m) gives the porosity, and solving for concentration explicitly yields eq S2 for i through n number of nodes:

$$C_{y,i}^{t+\Delta t} = \left[\frac{D_e}{\Delta y^2} \left(C_{y,i-1}^{t} - 2C_{y,i}^{t} + C_{y,i+1}^{t} \right) - \frac{\gamma_{ipa} < v > \varepsilon C_{y,i}^{t}}{d_p} \right] \Delta t + C_{y,i}^{t} \tag{S2}$$

where n is chosen based on a number of factors, such as the uniformity of the material, the thickness of the material, and the computational efficiency of the solution to the ultimate system of equations. Values of n are reflected in the reported grid spacing for each test material, shown in Table S1.

The explicit, time-discretized solution to eq 5 in the main text is shown in eq S3:

$$C_o^{t+\Delta t} = \frac{v_t C_\infty^t + D_e \frac{C_{y,1}^t \varepsilon}{\frac{\Delta y}{2}}}{(1-\varepsilon)\frac{\gamma_{ipa} < v >}{4} + v_t + \frac{\varepsilon D_e}{\frac{\Delta y}{2}}} \tag{S3}$$

The explicit, time-discretized solution to the boundary condition at the base of the material, given by eq 6 in the main text, is shown in eq S4:

$$C_{y,i=h}^{t+\Delta t} = C_{y,i=n}^{t} \tag{S4}$$

Sensitivity analysis

Sensitivity analysis was conducted with a univariate approach; that is, model runs were made with one parameter value changed from a base case value to either a “high” or “low” value, for each

of the nine input parameters. Base case, high, and low values of parameters, as well as sensitivity analysis output for each of the five test materials are reported in Tables S2-S6. Sensitivity was assessed by comparing the change in the steady-state predicted concentration reported by the model ($C_{\infty,1200\ s}$) at the high or low parameter value to the base-case condition.

This approach allows an approximation of the uncertainty, however, there are several important limitations to consider. The univariate approach assumes that parameters change independently and that uncertainty in the best-fit estimate of γ_{ipa} is propagated from the uncertainty in the input parameter being varied. However, this simplification does not account for the possibility of covariance between input variables. For example, the effective diffusion coefficient is related to the geometry of the material pore volumes,[3] and therefore is influenced by parameters such as the pore diameter and porosity. Since the pore diameter and the porosity are also model input parameters, it is unlikely that the effective diffusion coefficient could be changed without necessitating a change in one or both of these parameters. Quantifying the covariance between input parameters may be possible for some relationships, for example, Carniglia[4] describes empirical relationships between the tortuosity, pore volume, and surface area of a material. However, detailing these relationships for an improved estimate of uncertainty is beyond the scope of this paper; individual parameters' impact on the uncertainty in the modeled γ_{ipa} are summed in quadrature to approximately quantify the total uncertainty in model predictions of γ_{ipa}.

Table S3. Sensitivity and uncertainty analysis for cellulose paper, WF14. *SI* is the sensitivity index, *EI* is the elasticity index, and S_x is the uncertainty associated with a given parameter.

	Parameter		Base Case	High	Low	*SI*	*EI*	S_x	$\Delta C_{\infty,1200\ s}$ (ppb)	$\Delta\gamma$ (-)	$\Delta\gamma$ (%)
C_{in}	Inlet concentration	ppb	102	112	91.8	0.82	1.0	2%	1.7	1.3×10^{-7}	30%
D_e	Effective diffusivity	$cm^2\ s^{-1}$	0.033	0.036	0.030	-1.7	-0.00070	10%	-0.0060	9.8×10^{-8}	-0.10%
ε	Porosity	-	0.77	0.92	0.62	-6.8	-0.063	20%	-1.1	8.0×10^{-8}	-19%
d_p	Pore diameter	cm	1.30×10^{-3}	1.95×10^{-3}	6.5×10^{-4}	4400	0.069	20%	1.2	1.2×10^{-7}	21%
Q	Flow	$cm^3\ min^{-1}$	36.2	39.8	32.6	0.50	0.20	1%	0.17	1.0×10^{-7}	3.1%
v_t	Mass transfer coeff.	$cm\ s^{-1}$	0.14	0.17	0.11	-21	-0.036	16%	-0.48	9.0×10^{-8}	-8.6%
L_{bq}	Loss to background	hr^{-1}	1.01	1.52	0.51	-5.6	-0.067	20%	-1.1	7.8×10^{-8}	-20%
y	Thickness	cm	0.02	0.08	0.01	-0.56	-0.00010	2%	-0.00020	9.8×10^{-8}	-0.0040%
d	Material diameter	cm	15.2	16.00	14.5	-1.1	-0.20	1%	-0.17	9.5×10^{-8}	-3.0%
γ_{ipa}	Reaction probability	-	9.8×10^{-8}	1.5×10^{-7}	4.9×10^{-8}	-5.7×10^{7}	-0.067	(-)	(-)	(-)	(-)

Table S4. Sensitivity and uncertainty analysis for cellulose paper, WF15.

	Parameter		Base Case	High	Low	*SI*	*EI*	S_x	$\Delta C_{\infty,1200\ s}$ (ppb)	$\Delta\gamma$ (-)	$\Delta\gamma$ (%)
C_{in}	Inlet concentration	ppb	97.0	106.7	87.3	0.78	1.0	2%	1.5	2.6×10^{-7}	28%
D_e	Effective diffusivity	$cm^2\ s^{-1}$	0.020	0.040	0.010	-5.6	-0.0010	10%	-0.011	2.0×10^{-7}	-0.20%
ε	Porosity	-	0.78	0.94	0.62	-6.6	-0.068	20%	-1.0	1.6×10^{-7}	-19%
d_p	Pore diameter	cm	1.50×10^{-3}	2.25×10^{-3}	7.50×10^{-4}	3800	0.076	20%	1.2	2.4×10^{-7}	21%
Q	Flow	$cm^3\ min^{-1}$	35.2	38.7	31.7	0.53	0.25	1%	0.19	2.1×10^{-7}	3.4%
v_t	Mass transfer coeff.	$cm\ s^{-1}$	0.14	0.17	0.11	-38	-0.071	16%	-0.86	1.7×10^{-7}	-16%
L_{bg}	Loss to background	h^{-1}	1.2	1.8	0.60	-5.0	-0.080	20%	-1.2	1.6×10^{-7}	-22%
y	Thickness	cm	0.02	0.04	0.01	-140	-0.038	2%	-0.057	2.0×10^{-7}	-1.0%
d	Material diameter	cm	15.2	16.0	14.5	-1.2	-0.24	1%	-0.18	1.9×10^{-7}	-3.4%
γ_{ipa}	Reaction probability	-	2.0×10^{-7}	3.0×10^{-7}	1.0×10^{-7}	-2.7×10^{7}	-0.072	(-)	(-)	(-)	(-)

Table S5. Sensitivity and uncertainty analysis for pervious pavement (PP).

	Parameter		Base Case	High	Low	*SI*	*EI*	S_x	$\Delta C_{\infty,1200\ s}$ (ppb)	$\Delta\gamma$ (-)	$\Delta\gamma$ (%)
C_{in}	Inlet concentration	ppb	104	114	93.6	0.62	1.0	2%	1.3	5.7×10^{-5}	520%
D_e	Effective diffusivity	$cm^2\ s^{-1}$	0.021	0.023	0.019	-140	-0.046	10%	-0.30	-1.9×10^{-6}	-120%
ε	porosity	-	0.67	0.80	0.54	-2.1	-0.022	20%	-0.28	-1.3×10^{-6}	-120%
d_p	Pore diameter	cm	0.27	0.40	0.13	1.0	0.0042	20%	0.050	1.1×10^{-5}	22%
Q	Flow	$cm^3\ min^{-1}$	35.7	39.2	32.1	0.70	0.39	1%	0.25	1.8×10^{-5}	100%
v_t	Mass transfer coeff.	$cm\ s^{-1}$	0.22	0.26	0.18	-57	-0.20	16%	-2.0	-6.6×10^{-5}	-830%
L_{bg}	Loss to background	h^{-1}	1.89	2.84	0.95	-3.4	-0.098	20%	-1.3	-3.8×10^{-5}	-520%
y	Thickness	cm	1.30	2.50	0.65	0.00	0.00	2%	0.00	9.0×10^{-6}	0%
d	Material diameter	cm	15.2	16.0	14.5	-2.3	-0.55	1%	-0.36	-4.1×10^{-6}	-150%
γ_{ipa}	Reaction probability	-	9.0×10^{-6}	5.0×10^{-5}	5.0×10^{-6}	-2.7×10^{4}	-0.0038	(-)	(-)	(-)	(-)

Table S6. Sensitivity and uncertainty analysis for Portland cement concrete (PCC).

	Parameter		Base Case	High	Low	*SI*	*EI*	S_x	$\Delta C_{\infty,1200\ s}$ (ppb)	$\Delta\gamma$ (-)	$\Delta\gamma$ (%)
C_{in}	Inlet concentration	ppb	110	121	99.0	0.6	1.0	2%	1.3	3.8×10^{-5}	91%
D_e	Effective diffusivity	$cm^2\ s^{-1}$	0.0024	0.0030	0.0016	-480	-0.020	10%	-0.11	1.8×10^{-5}	-7.8%
ε	Porosity	-	0.26	0.31	0.21	0.00	-0.00010	20%	0.00	2.0×10^{-5}	-0.10%
d_p	Pore diameter	cm	1.9×10^{-5}	2.9×10^{-5}	9.5×10^{-6}	1700	0.00050	20%	0.010	2.0×10^{-5}	0.40%
Q	Flow	$cm^3\ min^{-1}$	35.3	38.9	31.8	-0.70	-0.37	1%	-0.25	1.7×10^{-5}	-17%
v_t	Mass transfer coeff.	$cm\ s^{-1}$	0.20	0.24	0.16	-88	-0.26	16%	-2.8	-1.8×10^{-5}	-190%
L_{bg}	Loss to background	h^{-1}	1.8	2.7	0.90	-3.4	-0.093	20%	-1.2	3.1×10^{-6}	-84%
y	Thickness	cm	1.3	2.5	0.65	0.00	0.00	2%	0.00	2.0×10^{-5}	0.00%
d	Material diameter	cm	15.2	16.0	14.5	-2.6	-0.59	1%	-0.39	1.5×10^{-5}	-27%
γ_{ipa}	Reaction probability	-	2.0×10^{-5}	3.0×10^{-5}	1.0×10^{-5}	-7.3×10^{4}	-0.022	(-)	(-)	(-)	(-)

Table S7. Sensitivity and uncertainty analysis for activated carbon cloth (ACC).

	Parameter		Base Case	High	Low	*SI*	*EI*	S_x	$\Delta C_{\infty,1200\ s}$ (ppb)	Δy (-)	Δy (%)
C_{in}	Inlet concentration	ppb	112	123	101	0.60	1.0	2%	1.3	1.2×10^{-7}	21%
D_e	Effective diffusivity	$cm^2\ s^{-1}$	0.13	0.14	0.11	-29	-0.060	10%	-0.37	9.4×10^{-8}	-5.8%
ε	Porosity	-	0.97	0.99	0.95	-9.0	-0.13	20%	-1.8	7.2×10^{-8}	-28%
d_p	Pore diameter	cm	5.0×10^{-2}	7.5×10^{-2}	2.5×10^{-2}	110	0.080	20%	1.1	1.2×10^{-7}	17%
Q	Flow	$cm^3\ min^{-1}$	36.5	40.2	32.9	0.80	0.42	1%	0.28	1.0×10^{-7}	4.4%
v_t	Mass transfer coeff.	$cm\ s^{-1}$	0.39	0.46	0.31	-33	-0.19	16%	-2.0	6.8×10^{-8}	-32%
L_{bg}	Loss to background	h^{-1}	1.8	2.7	0.90	-3.1	-0.090	20%	-1.1	8.2×10^{-8}	-18%
y	Thickness	cm	1.3	2.5	0.60	-3.2	-0.060	2%	-0.084	9.9×10^{-8}	-1.3%
d	Material diameter	cm	15.2	16.0	14.5	-2.4	-0.56	1%	-0.37	9.4×10^{-8}	-5.8%
γ_{ipa}	Reaction probability	-	1.0×10^{-7}	1.5×10^{-7}	5.0×10^{-8}	-6.3×10^{7}	-0.10	(-)	(-)	(-)	(-)

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