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Measuring the Penetration of Ambient Ozone into Residential Buildings

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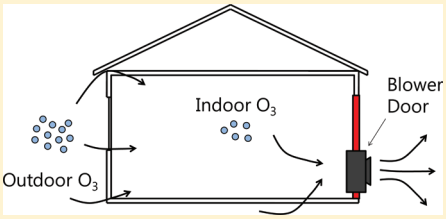
Supporting Information

ABSTRACT: Much of human exposure to ambient ozone and ozone reaction byproducts occurs inside buildings. However, there are currently no experimental data on the ability of ozone to penetrate through building envelopes and into residences. This paper presents a method to determine the penetration factor for ozone in buildings, and applies it in an unoccupied test house and seven single-family residences. The mean (±SD) ozone penetration factor was measured as 0.79 ± 0.13 in the eight homes using this method, ranging from 0.62 ± 0.09 to 1.02 ± 0.15. An analysis of tests across the homes revealed that ozone penetration was significantly higher in homes with more painted wood envelope materials, homes with larger air leakage exponents from fan pressurization tests, and older homes. The test method utilizes a large calibrated fan to elevate air exchange rates and steady-state indoor ozone concentrations to levels that can be accurately measured, so there is a potential for overpredicting ozone penetration factors. However, evidence suggests that this bias is likely small in most of the homes, and, even if a bias exists, the measured ozone penetration factors were lower than the usual assumption of unity in seven of the eight tested homes.



INTRODUCTION AND BACKGROUND

Elevated concentrations of ambient ozone have been associated with increases in mortality,[1−4] exacerbation of asthma symptoms,[5] and infant respiratory and cardiovascular effects.[6] Associations with adverse health effects are usually made in large epidemiological studies using outdoor measurements of ozone; however, because Americans spend the majority of their time indoors, much of their exposure to ozone and byproducts of ozone reactions actually occurs inside buildings.[7−9] In buildings without mechanical ventilation, such as the majority of residential buildings in the U.S., occupants are exposed to ozone and reaction byproducts only after outdoor ozone penetrates through the building envelope.

In the absence of indoor sources, steady-state indoor ozone concentrations (C_{in}) are a function of the outdoor ozone concentration (C_{out}), the air exchange rate (AER, or λ, hr^{-1}), the ozone penetration factor through the building envelope (P, dimensionless), and the first-order indoor ozone decay rate (β, hr^{-1}, or the loss by deposition to interior surfaces and any homogeneous reactions), as shown in eq 1.

$$\frac{C_{in}}{C_{out}} = \frac{P\lambda}{\lambda + \beta} \quad (1)$$

In large residential investigations, Avol et al.[10] and Lee et al.[11] measured mean (±SD) indoor−outdoor (I/O) ozone concentration ratios of 0.37 ± 0.25 in 126 homes and 0.24 ± 0.18 in 119 homes in California, respectively, and found significant differences in I/O ratios due to window opening behavior and the operation of air-conditioning systems. Similarly, Romieu et al.[12] measured mean (±SD) I/O ratios of 0.20 ± 0.18 in 145 homes in Mexico and Cattaneo et al.[13] measured a median I/O ozone ratio of 0.14 in 60 homes in Italy. In two smaller studies, Lee et al.[14] reported weekly mean I/O ratios ranging from 0.03 to 0.15 in 36 homes in Tennessee, and Zhang and Lioy[15] reported mean I/O ratios ranging from 0.22 to 0.62 in six homes in New Jersey. In homes unlikely to have open windows (e.g., during the winter or while operating HVAC systems), measured I/O ozone ratios have been consistently lower, typically ranging from ∼0.01 to ∼0.10,[9,16−18] although it is not clear whether envelope losses or indoor losses contribute most to these lower values.

Several investigations have shown that ozone, once indoors, can react with individual building materials,[19−25] compounds adsorbed to indoor surfaces,[26] and human skin and clothing.[27−29] Some known byproducts of these reactions include organic acids, carbonyls, and free radicals,[8] aldehydes,[30] carboxyl and α-hydroxy ketone groups,[28] and secondary organic aerosols.[31−33] Ozone reactions with materials covered with lead paint have even been shown to increase the release of lead in older buildings.[34] First-order indoor ozone removal rates (β) have been measured in a variety of indoor environments, and have typically ranged from approximately 1 to 7 h^{-1} during normal building operation.[9] Limiting to residences, Mueller et al.[35] measured a decay constant (β) of 7.3 ± 0.2 h^{-1} in a bedroom and Lee et al.[18] measured mean (±SD) values of β of 2.8 ± 1.3 h^{-1} in 43 homes in California. Sabersky et al.[20] found that operating a recirculating HVAC system in a home nearly doubled measured values of β from 2.9 to 5.4 h^{-1}.

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Overall, the wide spread in I/O ratios measured in homes can be attributed to a combination of differences in AERs, HVAC operation, furnishings, and building envelopes, although we are not aware of any measurements of penetration factors (P) for ozone. Without experimental data, it is often assumed that ozone penetrates through building envelopes 100% efficiently (i.e., $P = 1$).[8,36,37] However, models suggest that ozone penetration should vary with the nature of building air leakage paths and the reaction probabilities of envelope materials (reaction probabilities of common building envelope materials range several orders of magnitude, from $\sim 10^{-4}$ for brick to $\sim 10^{-8}$ for aluminum).[38] Thus, this investigation presents a method of measuring the penetration factor for ozone in buildings and applies the method in an unoccupied test house and a sample of seven single-family residences in Austin, Texas.

MATERIALS AND METHODS

Method Development. Because measurements of ozone penetration factors (P) also require accurate measurements of indoor ozone loss rates (β), we manipulated homes to elevate indoor ozone concentrations and measure the subsequent decay. Similar manipulations have been used to measure particle penetration into residences,[39−41] and our method relies on the same general principles of elevation and decay to estimate two unknown parameters (P and β) from one equation.

Our procedure consisted of the following steps performed in a well-mixed unoccupied environment: (1) measurement of ozone and tracer gas (e.g., CO_2) concentrations immediately outside of the building, (2) elevation of indoor ozone concentrations by operating an ozone generator indoors, (3) elevation of indoor concentrations of a tracer gas in order to measure the AER, (4) measurement of the subsequent decay of both indoor ozone and tracer gas at a central location in the building, allowing indoor ozone concentrations to decay toward steady-state levels, and (5) repetition of outdoor ozone and tracer gas measurements.

In all homes, experiments were conducted during times of relatively low outdoor ozone concentrations (e.g., <100 ppb), when steady-state indoor ozone concentrations and outdoor ozone source terms ($P \times \lambda \times C_{out}$) were too low to be accurately measured. Thus, a large calibrated fan and frame (i.e., a "blower door") was installed in a doorway during Step 4 in order to depressurize the space, increase the AER and outdoor ozone source term, and elevate the steady-state value of C_{in} above the level of detection of the monitoring equipment. Depressurizing with the fan provides a single exhaust outlet for indoor air, where the resultant supply air infiltrates through cracks and gaps in the building envelope. It should be noted that the resulting estimates of P may be overpredicted with this high AER configuration relative to normal building operation (due to higher airspeeds and lower residences times in building cracks), and we explore the implications of this configuration in a later section.

Estimation of Parameters. Both the ozone penetration factor (P) and the indoor ozone decay rate (β) were estimated from a three-parameter least-squares estimation using the analytical solution to the dynamic mass balance on indoor ozone shown in eq 2. Indoor data from Step 4 and mean outdoor concentrations from Steps 1 and 5 were used, and P, β, and the initial indoor ozone concentration (C_{in} at $t = 0$) were the three unknown regression parameters. This solution method is referred to as the "dynamic" solution in much of the rest of this work. As a solution check, dynamic estimates of P were also compared to steady-state solutions using eq 3.

$$\frac{dC_{in}}{dt} = P\lambda C_{out} - (\lambda + \beta)C_{in} \quad (2)$$

$$P = \frac{C_{in}}{C_{out}}\frac{\lambda + \beta}{\lambda} \quad (3)$$

Penetration Experiments: Test House. The experimental procedure was first performed in an unoccupied manufactured test house built in 2008 and located on a research campus in Austin, Texas (described in Table 1 and Figures S1 and S2). Ozone measurements were made at 10-s intervals using a UV-absorbance ozone monitor (2B Technologies model 202; accuracy ±1.5 ppb and lower limit of detection ~2 ppb). CO_2 was used as a tracer gas and concentrations were measured using an infrared absorption CO_2 monitor (GE Telaire 7001) installed in the central living room and outdoors, both connected to a data acquisition system (GW Instruments instruNet model 100) logging at 1-min intervals. Indoor ozone concentrations were elevated using a custom ozone generator built from a chemiluminescence NO_x analyzer connected to an oxygen supply; the house was unoccupied during ozone injection to avoid exposure. Indoor CO_2 concentrations were elevated by injection from a compressed CO_2 cylinder connected to a mass flow controller (Omega FMA 5528) routed to all rooms. An oscillating fan was operated in every room to achieve well-mixed conditions throughout the house. AERs were estimated using a least-squares estimation with the analytical solution to the well-mixed mass balance of the concentration of tracer gas (CO_2) in accordance with ASTM E 741,[42] as shown in eq 4. $C_{t,in}$ and $C_{t,out}$ are the indoor and outdoor tracer gas concentrations (ppm CO_2) and there were no indoor sources of CO_2 during the actual decay period.

$$\frac{dC_{t,in}}{dt} = \lambda C_{t,out} - \lambda C_{t,in} \quad (4)$$

Sixteen replicate tests were performed in the test house over a period of four months from April to July 2011. All windows and doors were closed and the house was unoccupied during all tests. An Energy Conservatory blower door fan and frame was installed in the back door (Figure S2) to depressurize the space and elevate steady-state indoor ozone concentrations during each test. Indoor and outdoor climatic conditions were measured using an Energy Conservatory Automated Performance Testing system and a Davis Vantage Pro 2 weather station, respectively; the equipment is described in greater detail in the SI. A downflow air handling unit with ducts located in the crawlspace was operated in the fan-only mode without a filter installed in order to increase mixing and evenly distribute ozone and CO_2 throughout the house.

Upon completion of the experiments, all parameter estimations were conducted using a statistical software package, Stata Version 11.[43] Uncertainty in each parameter was calculated using the relative standard errors of the three regression parameters (P, β, and λ) and the relative standard deviation of outdoor ozone concentrations added in quadrature for the dynamic solution (eq 2), and with the relative standard errors of regression parameters (β and λ) and relative standard deviations of steady-state indoor and outdoor ozone concen-

trations all added in quadrature for the steady-state solution (eq 3), both according to ASHRAE Guideline 2.[44]

Penetration Experiments: Field Sites. The test method was then performed once at each of seven single-family residential buildings in Austin, Texas during June and July 2011. The homes, shown in Figure S1, were a sample of convenience and were all furnished and occupied (but they were unoccupied during our tests). Tracer gas (CO_2) concentrations were measured using an infrared absorption CO_2 monitor (GE Telaire 7001) connected to an Onset HOBO U12 data-logger, both installed in a central living area logging at 1-min intervals. Indoor CO_2 concentrations were elevated to at least 500 ppm above background by releasing the valve on a stainless steel regulator connected to a small (~20 kg full) compressed CO_2 cylinder. Ozone concentrations were measured using the same UV-absorbance ozone monitor that was used in the test house. Indoor ozone concentrations were elevated using ambient air passed through a 13-cm glass corona discharge tube connected to a 1-kV power transformer and an external air pump providing approximately 20 L min^{-1}; again, the homes were unoccupied during ozone injection to avoid direct exposure. The use of ambient air to generate ozone could result in the formation of other compounds (e.g., NO_x) that react with ozone, but the impact is likely small[45] and any additional reactions with ozone should be accounted for in the measured ozone decay rate (β).

Both CO_2 and ozone injection occurred near or directly into the central HVAC return grille in order to use the duct system to distribute the gases throughout the homes, or directly in front of a mixing fan installed in a far corner of the home to avoid local concentration peaks in the central measurement location. Two box fans and all operable ceiling fans were operated throughout the homes, and central HVAC systems were operated in the fan-only mode to aid in mixing (except in Site 6, which had no central HVAC system). HVAC filters were removed before ozone injection at four of the homes because reactions with filter media[46] appeared to inhibit initial indoor ozone concentration increases. The same general test procedure that was used in the test house was followed in the field homes, including the use of a blower door fan installed at one of the doorways to depressurize the space during tests. All windows and doors were closed and the homes were unoccupied during all tests. Parameter and uncertainty estimates were made using the same procedures as in the test house. To track some potentially explanatory variables of ozone penetration, several building characteristics were noted by visual inspection (e.g., materials of the exterior envelope and the number of windows and doors) or by consulting the Travis Central Appraisal District database of home appraisals[47] (e.g., year of construction).

Blower Door Air Leakage Tests. Separate blower door air leakage tests were also performed once in each home in the depressurization mode, which were used to calculate effective leakage areas (ELA, m^2) and the AER at an I/O pressure difference of 50 Pa (ACH_{50}, hr^{-1}), in accordance with ASTM E 1827.[48] Normalized leakage (NL, a dimensionless function of ELA, floor area, and building height) was calculated from blower door data according to ASHRAE Standard 119.[49]

Indoor−outdoor pressure differences (I/O ΔP) were not directly measured during the ozone penetration tests, but because the blower door was also used to depressurize the homes and elevate AERs and steady-state indoor ozone concentrations during the penetration tests, estimates of I/O ΔP were calculated using measured AERs and home volumes in conjunction with blower door leakage parameters (i.e., the leakage coefficient, C, and the exponent, n, from an exponential relationship between airflow and pressure). The I/O ΔP estimation procedure is outlined in more detail in the SI.

Natural Ozone Decay Rates. To compare building envelope reactions to interior losses, ozone decay rates were also measured during "natural" conditions. Because indoor ozone decay rates have been shown to increase with indoor airspeeds,[50] and were likely elevated with the use of a blower door, these measurements were made by injecting indoor ozone and measuring the subsequent decay without a blower door installed, but with the mixing fans and HVAC system still operating. These measurements were repeated three times in the test house and once in each of the field homes. Because "natural" loss rates were measured with mixing, ceiling, and HVAC fans operating, the values are likely to be elevated compared to conditions without the use of fans;[20] however, they still provide an estimate of the relative importance of envelope and indoor reactions in the test homes with HVAC systems operating. These tests followed the same procedure of injection and decay in the unoccupied homes, but only the initial portion of these data unaffected by outdoor ozone penetration was used to estimate natural ozone deposition rates (β_{nat}, hr^{-1}) using a simple first-order decay model (eq 2 without an outdoor source term).

RESULTS AND DISCUSSION

Table 1 provides a summary of the test house and seven field homes, including general building information and descriptions of envelope materials. The year of construction of the eight homes ranged from 1920 to 2008. Sites 2−4 had attached garages with doors closed during testing, and Site 7 shared one narrow wall with a neighboring home's garage. Seven of the homes had recirculating HVAC systems that were operated during testing and one home (Site 6) had a window air-conditioning unit, which was not operated during testing. None of the homes had dedicated mechanical ventilation systems.

Table 1. Building Characteristics of the Test House and the Seven Field Homes

site	year built	floor area, m^2	volume, m^3	exterior envelope materials[a]
test house	2008	110	250	painted fiber cement siding
1	1920	131	372	painted wood siding
2	1996	201	490	~50% brick; ~50% painted wood siding
3	1975	171	443	brick
4	1984	119	311	~80% painted wood siding; ~20% stone
5	1938	92	235	painted wood siding
6	1935	24	56	painted wood siding
7	1961	72	189	painted wood siding

[a]Materials make up approximately 100% of the surface area of walls (excluding windows and doors) unless otherwise noted.

Test House Results. An example of data from one penetration experiment in the test house is shown in Figure 1. The AER during this test was 2.50 ± 0.01 h^{-1} and β was 8.06 ± 0.15 h^{-1}, both elevated due to the operation of the blower door at the back door frame. Estimates of P (±experimental uncertainty) were 0.71 ± 0.05 using the dynamic solution and

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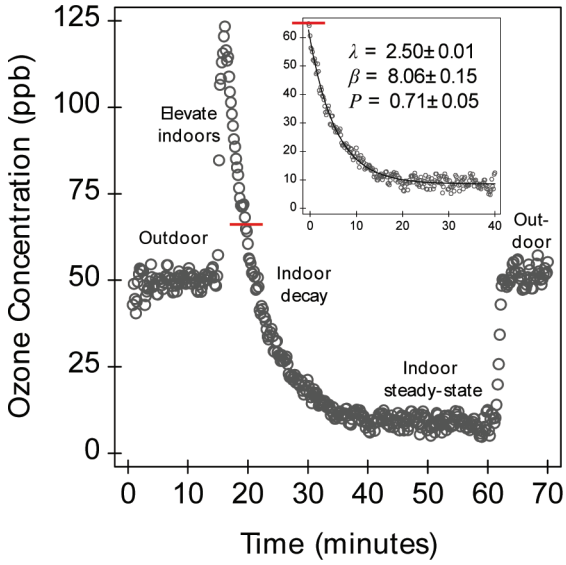

Figure 1. Example test result as performed in the unoccupied test house on May 12, 2011. The entire portion of test data is shown in the larger plot, and the nonlinear regression fit is shown in the smaller plot of a subset of the data.

0.74 ± 0.16 using the steady-state solution from this specific test. Data from all of the test homes followed this same general pattern.

A full summary of the 16 tests performed in the unoccupied test house is provided in Table S2, and values of P and AER measured during penetration tests are shown in Figure 2.

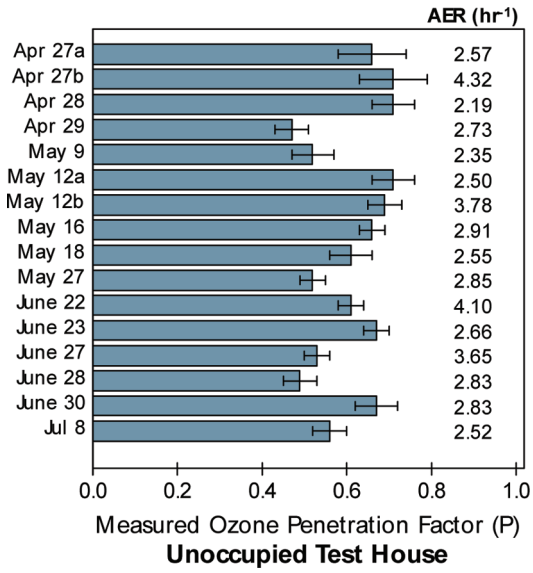

Figure 2. Measured ozone penetration factors (P) and air exchange rates (AER) during penetration tests from 16 replicate experiments at the unoccupied test house. Values of P were estimated using a three-parameter fit to the "dynamic" solution of eq 2.

The mean (±SD) ozone penetration factor at the test house was 0.62 ± 0.09, estimated using a three-parameter fit (unknowns: P, β, and C_{in} at t = 0) to the analytical solution to eq 2. The mean (±SD) experimental uncertainty was 0.05 ± 0.01, or 7 ± 2%, using this "dynamic" method of solving. The steady-state solutions led to similar estimates of P (shown in Table S2), with a mean (±SD) of 0.63 ± 0.10; however, experimental uncertainty was much greater (averaging 0.14 ± 0.04, or 22 ± 6%) due to the reliance on large relative standard deviations of steady-state indoor ozone concentrations.

Overall, a mean penetration factor of 0.61 ± 0.09 in the test house means that reactions with the building envelope diminished outdoor ozone by approximately 39 ± 9% before entering the indoor environment, on average. P ranged from 0.47 ± 0.04 to 0.71 ± 0.08 over the 16 tests. Spearman's rank correlations between P and indoor and outdoor climate conditions (i.e., I/O temperature and RH, outdoor ozone concentration, and wind speed and direction) did not reveal any significant monotonic relationships (p > 0.05 for all comparisons; relationships shown in Figure S3). Importantly, there was also no significant relationship between P and AER or the estimated I/O ΔP, suggesting that the use of the blower door did not have an impact on measurements of ozone penetration factors over the range of test conditions (AER ranged from 2.19 ± 0.10 to 4.32 ± 0.03 h^{-1} and estimated I/O ΔP ranged from 5.8 to 17.7 Pa).

There appeared to be a small nonlinear influence on P by wind direction at the test house, as explored in the SI (and Figure S4); P was higher when wind directions were from the north or west than from the east or south, suggesting that different types of envelope leaks might exist on different sides of the building. The test house is unshielded, so wind direction likely has a larger influence compared to the rest of the field sites. Additionally, to explore the repeatability of our test method, we compared replicate measurements made during similar experimental conditions at the test house. As an example, tests on May 27 and June 27, 2011 were performed with similar mean wind directions and wind speeds, and revealed estimates of P of 0.52 ± 0.03 and 0.53 ± 0.03, respectively, suggesting that the test method is repeatable under similar test conditions.

Field Results. Table 2 provides full experimental results from ozone penetration tests and "natural" decay tests as performed in all eight buildings. Similarly, Figure 3 shows the mean (±SD) ozone penetration factor measured during the 16 experiments at the test house and measurements of P (± associated uncertainty) from single tests at the seven field sites, estimated using three-parameter fits to the analytical solution of eq 2 (the "dynamic" method). Figure 3 also shows measured AERs and estimates of I/O ΔP during ozone penetration tests with a blower door operating.

The mean (±SD) value for the ozone penetration factor measured in the eight test homes was 0.79 ± 0.13, ranging from 0.62 ± 0.09 to 1.02 ± 0.15, as determined using the dynamic solution. The mean (±SD) value of experimental uncertainty from these tests was 10 ± 3%. Similarly, the mean (±SD) value for P as determined using β from the three-parameter fit and the steady-state I/O ozone ratios with eq 3 was 0.82 ± 0.15, ranging from 0.63 ± 0.10 to 1.05 ± 0.30, with a mean (±SD) experimental uncertainty that was much greater than using the dynamic solution (23 ± 6%). The additional uncertainty stems from the reliance on steady-state indoor ozone concentrations, which, even at the elevated AERs during the test periods, remained too near the instrument's minimum detection level to measure with very low uncertainty.

The mean (±SD) value for β measured during penetration test periods with the blower door operating was 11.6 ± 6.0 h^{-1} with a mean (±SD) experimental uncertainty of 4 ± 3% using the three-parameter fit. During the "natural" decay periods, without the blower door operating but with the mixing, ceiling,

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Table 2. Summary of Ozone Penetration Tests in the Eight Test Homes

		during penetration test					natural decay	
site	date	AER, hr^{-1}	β, hr^{-1}	P, dynamic	P, steady-state	outdoor ozone, ppb	AER, hr^{-1}	β_{nat}, hr^{-1}
test house	various[a]	2.96 ± 0.64	7.8 ± 0.8	0.62 ± 0.09	0.63 ± 0.10	54 ± 13	0.24 ± 0.06	6.6 ± 0.6
1	June 29, 2011	3.32 ± 0.04	8.9 ± 0.2	0.89 ± 0.10	0.95 ± 0.17	30 ± 3	0.93 ± 0.02	6.1 ± 0.2
2	July 6, 2011	2.32 ± 0.03	12.4 ± 0.5	0.77 ± 0.08	0.88 ± 0.21	54 ± 3	0.61 ± 0.04	8.2 ± 0.8
3	July 7, 2011	2.26 ± 0.02	6.4 ± 0.1	0.66 ± 0.03	0.65 ± 0.12	59 ± 2	0.33 ± 0.01	3.6 ± 0.1
4	July 11 and 19, 2011[b]	1.94 ± 0.05	9.1 ± 0.7	0.77 ± 0.07	n/a[c]	48 ± 2	0.43 ± 0.01	12.3 ± 1.1
5	July 12, 2011[d]	3.17 ± 0.03	8.7 ± 0.4	0.76 ± 0.07	0.76 ± 0.22	26 ± 2	0.58 ± 0.01	6.7 ± 0.5
6	July 13, 2011	5.20 ± 0.11	24.3 ± 0.6	1.02 ± 0.15	1.05 ± 0.30	27 ± 4	0.19 ± 0.01	16.8 ± 1.1
7	July 18, 2011	2.63 ± 0.02	16.5 ± 0.5	0.85 ± 0.05	0.79 ± 0.22	56 ± 2	0.5 ± 0.02	11.5 ± 0.6
	mean (SD)	2.97 (1.02)	11.6 (6.0)	0.79 (0.13)	0.82 (0.15)	44 (14)	0.48 (0.24)	9.0 (4.3)

[a]Penetration test values for the test house are mean (±SD) values from 16 tests conducted over a 4-month span, and natural decay values are the mean (±SD) values from 3 separate decay tests. All other values represent single test periods. [b]Tests were conducted over 2 separate days: a natural decay test on the first day and a penetration test on the second day. [c]Steady-state conditions were not achieved due to time constraints. [d]Because indoor concentrations could not be elevated high enough to provide a large inflection point in the data (for some unknown malfunction with the ozone generator), β was first estimated from a two-parameter least-squares estimation of eq 2 (the other parameter was C_{in} at time $t = 0$), using only the first portion of an indoor decay test without an outdoor source term (i.e., when outdoor sources were negligible). Then P was estimated using both dynamic and steady-state solutions, forcing the first estimate of β.

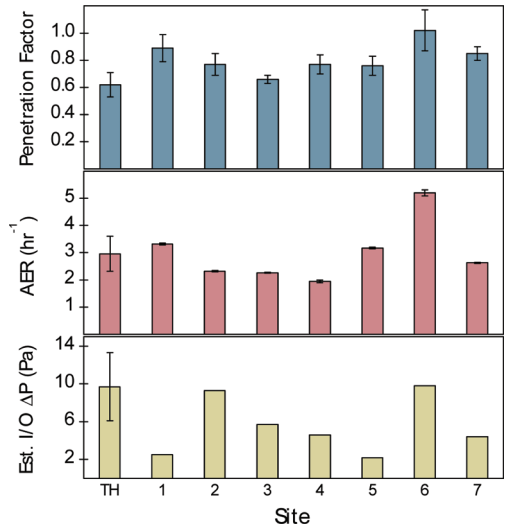

Figure 3. Measured ozone penetration factors (P), air exchange rates (AERs), and estimated indoor−outdoor pressure differences (I/O ΔP) during ozone penetration tests using a blower door at the eight homes. "TH" values represent mean (±SD) values from 16 tests at the unoccupied test house; all others represent one experimental value at each home (± experimental uncertainty for P and AER). The estimated uncertainty in I/O ΔP was likely ∼15%, although only the SD of the mean is shown for the test house.

and HVAC system fans still operating, the mean (±SD) value for β_{nat} was 9.0 ± 4.3 h^{-1}, with a small change in mean uncertainty: 6 ± 3%. The mean value for β_{nat} was similar to those measured in a bedroom by Mueller et al.,[35] but were much greater in all but one home (Site 3) than observed in Lee et al.,[18] likely due to increased mass transfer caused by the operation of mixing and HVAC fans.[20,50] Additionally, HVAC filters were removed at the test house and Sites 1 and 3−5, but used filters were left installed at Sites 2 and 7, which can also contribute to additional ozone loss.[46]

Because steady-state indoor concentrations were generally too low to measure with reasonable certainty, we estimated I/O ozone ratios using eq 1 and measured values of P from penetration tests and values of β_{nat} and AER from the "natural" decay tests. Across the eight sites, the combination of envelope and indoor losses during normal conditions with the HVAC fans operating would lead to a mean (±SD) steady-state I/O ratio of 0.05 ± 0.03 (ranging from 0.01 to 0.12), shown in Table S5. These I/O ratios are on the low end of those measured in most previous residential studies,[9−15] but in the range typically measured in homes without open windows and with HVAC systems likely operating (e.g., ∼0.01 to ∼0.10).[9,16−18] Thus, although the operation of mixing fans and HVAC fans likely increased values of β_{nat} relative to what they would be with only the HVAC fan operating, and estimates of penetration factors might be elevated due to the operation of the blower door, these I/O ozone estimates using measured values of P and β_{nat} are still reasonable for closed homes with HVAC systems operating.

Appropriateness of Blower Door Use. As mentioned, an important potential limitation in the penetration test method is that the operation of a blower door fan to artificially elevate AERs and steady-state indoor ozone concentrations may not provide accurate estimates of the ozone penetration factor during normal building operation. The mean (±SD) AERs during the blower door penetration test periods and natural decay tests were 2.97 ± 1.02 h^{-1} and 0.48 ± 0.24 h^{-1}, respectively. The mean (±SD) estimate of I/O ΔP during ozone penetration tests was 6.0 ± 3.2 Pa (ranging from approximately 2 to 10 Pa, shown in Figure 3 and Table S3), but I/O ΔP tends to average near zero during typical residential building operation, with fluctuations typically below ∼4 Pa.[39,51,52] Ozone penetration through cracks in building envelopes is a function of ozone deposition velocity,[38] which is a function of both the reaction-limited and mass-transport-limited deposition velocities (which are functions of specific envelope materials and fluid mechanics, respectively). Thus, it is possible that elevated pressure differences and airspeeds due to blower door operation could increase transport-limited deposition velocities through cracks, reduce residence times, and overestimate ozone penetration factors.

To investigate this possibility, we estimated airspeeds using an analysis in the SI (results in Table S3). We estimated that the mean (±SD) airspeed through building envelopes in the test sites was approximately 3.3 ± 1.2 m s^{-1} during penetration test conditions with the blower door operating (range of 1.8−5.0 m s^{-1}) and approximately 0.5 ± 0.3 m s^{-1} during more

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typical operating conditions (range of 0.2−1.2 m s^{-1}). Walker et al.[53] applied the modeling methods from Liu and Nazaroff[38] and demonstrated that all but the largest (albeit idealized) cracks in the most reactive building materials are likely reaction-limited at airspeeds as low as 0.1 m s^{-1}; thus, our estimate that airspeeds are likely above 0.1 m s^{-1} during all test conditions suggests that ozone penetration was always reaction-limited in the homes. Therefore, it may be reasonable to assume that the use of blower door fans during the test conditions did not drastically affect ozone penetration factors relative to normal operating conditions.

Additionally, estimated I/O ΔP values during penetration tests (2−10 Pa) were in the range of those used in the idealized models in Liu and Nazaroff,[38] who estimated a maximum increase in P of ∼0.30 when I/O ΔP increased from 4 to 10 Pa, which provides a likely upper bound of the amount of overprediction that the use of a blower door might introduce. However, Spearman's rank correlation tests revealed no significant correlation between measured values of P and estimates of I/O ΔP during replicate tests at the test house or across the eight homes (Spearman's $\rho = -0.005$ and p-value = 0.98 across 16 tests in the test house; Spearman's $\rho = -0.02$ and p-value = 0.96 across all homes), which again suggests that elevated indoor−outdoor pressure differences and airspeeds did not have a significant impact on measured values of P.

Unfortunately, because our experimental data were collected for cracks of unknown geometries in real buildings, we cannot accurately model ozone penetration with the idealized models from Liu and Nazaroff[38] and cannot confirm the actual magnitude of any bias that might be introduced by the operation of a blower door. However, even if the measured values of P herein are somewhat overpredicted, they still represent the first measurements of ozone penetration factors in residences of which we are aware, and the values were typically lower than what is normally assumed in the absence of actual measured data (i.e., $P = 1$). Additionally, our measured values of P and β_{nat} lead to estimates of steady-state I/O ozone concentration ratios that fall in the range of I/O ratios measured in closed residences with HVAC systems likely operating.[9,16−18] Still, the test method should be validated further under normal building operation (i.e., lower AERs without a blower door) in areas of higher ambient ozone concentrations or with more sensitive instrumentation. If discrepancies are observed between the two methods, better estimates of a potential bias could be made.

Exploration of Parameters Affecting Ozone Penetration. Several potential explanatory variables were noted or measured in all of the homes, including blower door leakage parameters (described in Table S1), the year of construction, the estimated fraction of exterior envelope covered in brick/stone or painted wood, and the number of doors and windows. Spearman's rank correlations were performed between P and 16 of these factors across the eight homes; results are shown in Figure S5 and Table S4. The only significant associations (p-value <0.05) with P were for the estimated fraction of painted wood as an exterior envelope material ($\rho = +0.77$) and the leakage exponent (n) from blower door tests ($\rho = +0.75$). The year of construction was also considered marginally significant ($\rho = -0.71$, p-value = 0.05). These associations suggest that P increased significantly with the prevalence of exterior painted wood cladding and with longer cracks in the envelopes (values of n close to 0.5 and 1.0 are expected to describe short orifice-type holes and long crack-like leaks, respectively), and P decreased in newer homes (more ozone penetrated through the envelopes of older homes).

The relationships between painted wood siding and year of construction are somewhat intuitive, as newer homes are increasingly more airtight[54] and painted wood has a lower ozone reaction probability than porous materials such as stone and brick.[38] The positive relationship between P and n is somewhat counterintuitive because long crack-like leaks should provide more surface area for ozone to react with and actually lower P, although this relationship was not observed, potentially because n does not account for the width of leaks or because differences in n were too small to establish a real relationship (n does not vary widely across homes[55] and only varied from 0.61 to 0.76 in this study). Variables from air leakage tests such as ELA, NL, and ACH_{50}, which were expected to be associated with P, were not significantly associated, potentially because ozone penetration is actually more a function of material than air leakage, or because we did not have a large and diverse enough sample size to find significant relationships.

Comparison of Envelope Losses and Indoor Losses. Some building envelopes with lower measured values of P provided more protection against the infiltration of outdoor ozone than others. The relative contributions of envelope losses and indoor losses to I/O ozone ratios are likely important determinants of exposure to ozone and ozone byproducts because of the different pathways for reactions involved. To investigate the roles of building envelopes and indoor environments in reducing indoor concentrations of outdoor ozone, Table S5 and Figure S6 show the contribution to indoor ozone reductions attributed to (1) losses in the building envelopes (due to $1 - P$) and (2) losses indoors due to β_{nat} (with mixing fans, ceiling fans, and HVAC fans operating) for the eight homes in this study. On average, losses in the building envelope accounted for 21 ± 13% of the total ozone loss; indoor losses accounted for the remaining 74 ± 13%. These values sum to 95% ozone loss, or a mean I/O ratio of 0.05, as previously mentioned. Thus, indoor losses accounted for a factor of 3.5 more indoor ozone removal than the envelope, on average, although the relative importance of envelope reactions would increase with lower values of β_{nat} measured without HVAC systems operating.

The ratio of indoor losses to envelope losses was approximately 1.6 in the most protective home (the test house), while envelope losses accounted for no ozone reduction in the least protective home (Site 6), suggesting that different building envelopes might provide different levels of protection against the infiltration of outdoor ozone and subsequent byproduct formation from indoor reactions. Reactions between ozone and material surfaces are hypothesized to mainly involve unsaturated C−C bonds,[9] with known harmful byproducts including formaldehyde, acetaldehyde, and "heavy" aldehydes.[56−58] Molar yields and emission rates of some of these byproducts from ozone reactions with indoor surfaces (e.g., flooring, countertops, painted walls, and particularly carpet) have been shown to be higher[22,57] than those resulting from reactions with some typical building envelope materials (e.g., drywall and pine wood).[58] Additionally, indoor surfaces are often contaminated with human skin oils, which react with ozone to produce potentially irritating or toxic ketones and dicarbonyls.[27,28,59] Given the absence of human contact, this reaction is unlikely to occur in building envelopes. Whereas specific experiments are needed on more envelope materials and further exploration of subsequent

transport of envelope byproducts indoors is warranted, it is possible that limiting the penetration of ozone through envelopes may be a preferred first line of defense against indoor exposures to outdoor ozone and its byproducts.

The decreasing trend noticed herein with measured ozone penetration factors and year of construction is an encouraging sign that construction practices and materials may be inadvertently protecting building occupants from exposure to ozone and reaction byproducts, as both AER and P decreased in newer homes. The least protective home (Site 1), with a measured value of $P = 0.89 \pm 0.10$ and a natural AER of $0.93 \pm 0.02\ h^{-1}$, would have an outdoor ozone source term ($P \times$ AER) of $1.82 \pm 0.21\ h^{-1}$, which is more than twice the estimated mean outdoor source term of $0.86 \pm 0.25\ h^{-1}$ in the most protective home in our sample (the unoccupied test house, where mean values of $P = 0.62 \pm 0.09$ and natural AER = $0.24 \pm 0.06\ h^{-1}$). There is some evidence that building characteristics may play a role in indoor ozone exposures and mortality,[37,60] but continued investigations in a larger and more diverse sample of buildings may be able to identify architectural details, building envelope materials, or construction practices that can be used to inhibit the transport of ozone indoors.

We performed these tests in homes with doors and windows closed and HVAC systems operating, which is generally appropriate because sensitive individuals are often recommended by public health agencies to stay indoors during times of elevated outdoor ozone (which often occur during periods of hot weather in Texas, when HVAC systems are likely operating in most homes). However, the methods herein could also be used to investigate impacts of window openings on ozone penetration. Ultimately, broader application of ozone penetration tests could enable more accurate estimates of exposures to indoor ozone and reaction byproducts. Additional work should also be performed to quantify byproduct formation and transport from ozone reactions with typical building envelope materials, both individually and combined as envelope structures.

■ ASSOCIATED CONTENT

Supporting Information

Photos of the homes, test house schematics, equipment details, additional methods, additional tables and figures of experimental results, additional analysis of explanatory variables at all homes, and a more detailed investigation of the appropriateness of using a blower door during the penetration tests. This information is available free of charge via the Internet at http://pubs.acs.org/.

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