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Measuring the Building Envelope Penetration Factor for Ambient Nitrogen Oxides

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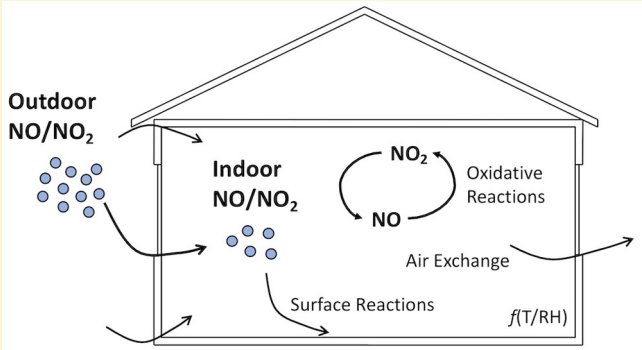
Supporting Information

ABSTRACT: Much of human exposure to nitrogen oxides (NO_x) of ambient origin occurs indoors. Reactions with materials inside building envelopes are expected to influence the amount of ambient NO_x that infiltrates indoors. However, envelope penetration factors for ambient NO_x constituents have never been measured. Here, we develop and apply methods to measure the penetration factor and indoor loss rates for ambient NO_x constituents using time-resolved measurements in an unoccupied apartment unit. Multiple test methods and parameter estimation approaches were tested, including natural and artificial indoor NO_x elevation with and without accounting for indoor oxidation reactions. Twelve of 16 tests yielded successful estimates of penetration factors and indoor loss rates. The penetration factor for NO was confirmed to be ∼1 and the mean (±s.d.) NO_2 penetration factor was 0.72 ± 0.06 with a mean relative uncertainty of ∼15%. The mean (±s.d.) indoor NO_2 loss rate was 0.27 ± 0.12 h^{-1}, ranging 0.06−0.47 h^{-1}, with strong correlations with indoor relative and absolute humidity. Indoor NO loss rates were strongly correlated with the estimated ozone concentration in infiltrating air. Results suggest that envelope penetration factors and loss rates for NO_x constituents can be reasonably estimated across a wide range of conditions using these approaches.



INTRODUCTION

Elevated ambient concentrations of nitrogen oxides (NO_x), most commonly measured as nitrogen dioxide (NO_2), have been associated with a number of short-term and long-term health effects.[1] Although epidemiology studies typically consider outdoor NO_x concentrations (typically as NO_2) as surrogates for human exposures, using either central site monitors[2] or more proximate measures of local ambient concentrations,[3−6] it is critical to understand the mechanisms that drive indoor exposures to ambient NO_x because people in the U.S. and other industrialized countries spend most of their time indoors (mostly at home)[7] and the infiltration of ambient NO_x is an important source of indoor NO_x.[8−11] Therefore, the majority of human exposure to ambient NO_x often occurs indoors, particularly in residences.[12−16] Additionally, NO and NO_2 are principal species involved in indoor oxidative and photochemical reactions.[17−24]

The proportion of ambient NO_x constituents that infiltrate and persist indoors (i.e., the infiltration factor, F_{inf}) is characterized under steady-state or time-averaged conditions by the ratio of indoor and outdoor concentrations in the absence of indoor sources (e.g., cooking and heating) (eq 1).

$$\left.\frac{C_{in}}{C_{out}}\right|_{\text{no indoor sources}} = F_{inf} \tag{1}$$

The dynamic mass balance on specific NO_x constituents will vary according to the constituent and the underlying source and removal mechanisms that govern behavior. For example, the time-resolved indoor NO_2 concentration in the absence of indoor sources can be described generally using eq 2.

$$\frac{dC_{in_{NO_2}}}{dt} = P_{NO_2}\lambda_t C_{out_{NO_2}} - \lambda_t C_{in_{NO_2}} - k_{NO_2}C_{in_{NO_2}} + G_{NO_2,t} \tag{2}$$

where C_{inNO_2} and C_{outNO_2} are the time-resolved indoor and outdoor NO_2 concentrations (ppb), λ_t is the air exchange rate at time t (AER, h^{-1}), and P_{NO_2} is the NO_2 penetration factor through the building envelope (−). k_{NO_2} is the net first-order indoor loss rate of NO_2 attributable to a combination of heterogeneous reaction mechanisms between NO_2 and indoor

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surfaces (reaction R1), including water-mediated disproportionation,[25,26] reduction reactions with organic compounds on surfaces,[27,28] and other NO_2 surface uptake mechanisms that lead to adsorption, nitrate production, or organo-nitrogen formation.[29−31] Note that second-order gas-phase homogeneous reactions of indoor NO_2 (e.g., reactions with O_3, NO, etc.) are excluded from k_{NO_2} in eq 2 because these reaction rates are typically slow enough to be negligible;[11,17,32,33] thus, total NO_2 loss can be approximated by a net first order loss rate k_{NO_2}.[17,34] $G_{NO_2,t}$ is the indoor NO_2 generation rate at time t (ppb/h), assumed to occur primarily due to NO oxidative reactions with ozone (reaction R2) and other oxidative compounds, such as peroxyl and alkylperoxyl radicals (reactions R3 and R4).[11,17,35] $G_{NO_2,t}$ can also include NO_2 formation through nitrate photolysis reactions, although the source strength is typically very low due to low nitrate levels and insufficient light sources indoors,[36] and is excluded herein. Since we focus solely on the indoor proportion of ambient NO_x in the absence of indoor sources, indoor NO_x generation from combustion (e.g., cooking and heating) are not included in the $G_{NO_2,t}$ and $G_{NO,t}$ terms.

$$NO_2 + H_2O/\text{surface} \rightarrow HONO(aq) + HNO_3 \quad (R1)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R2)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (R3)$$

$$RO_2 + NO \rightarrow NO_2 + RO \quad (R4)$$

Similarly, the time-resolved indoor NO concentration in the absence of indoor sources can be described using eq 3.

$$\frac{dC_{in_{NO}}}{dt} = P_{NO}\lambda_t C_{out_{NO}} - \lambda_t C_{in_{NO}} - k_{NO}C_{in_{NO}} + G_{NO,t} \quad (3)$$

where C_{inNO} and C_{outNO} are the time-resolved indoor and outdoor NO concentrations (ppb); P_{NO} is the NO penetration factor through the building envelope (−); and k_{NO} is the net first-order indoor loss rate of NO, which may include a combination of surface removal of NO (which is typically minimal in most indoor environments[11]), oxidative reactions between NO and indoor ozone, hydroxyl radicals, peroxyl radicals, and other oxidative compounds, and other indoor sinks caused by heterogeneous and/or homogeneous reactions.[11,17,20,35,37,38] $G_{NO,t}$ is the indoor NO generation rate (ppb/h), which is plausibly attributable to reactions between NO_2 and HONO on indoor surfaces (reaction R5)[11,39,40] or other mechanisms, such as nitrate photolysis decomposition, but is generally considered to be negligible in most indoor environments.[41]

$$NO_2 + HONO(aq) \rightarrow NO + HNO_3 \quad (R5)$$

Regardless of the nature of transformations that occur between NO_x constituents, the time-resolved total NO_x (i.e., $NO + NO_2$) concentration can also be approximated without specificity between NO_x constituents using eq 4. The utility of this approach is explored in a later section.

$$\frac{dC_{in_{NOx}}}{dt} = P_{NO_x}\lambda_t C_{out_{NOx}} - (\lambda_t + k_{NOx})C_{in_{NOx}} \quad (4)$$

where $C_{in_{NOx}}$ and $C_{out_{NOx}}$ are the time-resolved indoor and outdoor NO_x concentrations (ppb); P_{NO_x} is the total NO_x penetration factor through the building envelope (−); and k_{NO_x} is the net indoor total NO_x loss rate (h^{-1}), which can be approximated as net-first-order for most conditions.

To date, numerous studies have measured indoor and outdoor concentrations of NO_x constituents simultaneously (most commonly as NO_2), often in the presence of indoor sources and often using passive integrated sampling that makes accurate determinations of indoor and ambient contributions in individual buildings challenging.[42−49] Fewer studies have directly measured the ambient contribution in the absence of indoor sources (i.e., F_{inf}),[11,50] while others have approximated F_{inf} through statistical models and mass balance approaches.[15,46,51−54] Several studies have measured indoor loss rates (k), typically by artificial elevation and decay of NO_x constituents (again, chiefly NO_2 in the literature),[17,39,40,46,48,55−58] but we are not aware of any studies that have measured the penetration factor (P) of NO_x constituents through the building envelope. The penetration factor is a key parameter that governs indoor exposure to ambient pollutants and influences indoor reactions, particularly in residences where outdoor air commonly infiltrates through cracks and gaps in the building enclosure assembly.[59−67] Previous studies have assumed that NO_x constituents penetrate through building envelopes with 100% efficiency,[8,46,68] although laboratory experiments have shown that NO_2 can react with a variety of materials commonly used in building enclosure assemblies,[39,69] which suggests that building envelopes might scavenge a portion of ambient NO_x as air infiltrates indoors. However, this has not been experimentally tested to date in part because of a lack of a well-defined test method for measuring penetration factors for NO_x constituents.

Therefore, here, we develop and evaluate methods to measure the penetration factor of ambient NO_x constituents through the building envelope using time-resolved measurements in an unoccupied apartment unit. Repeated measurements were conducted under a variety of indoor and outdoor environmental conditions to provide a data set for evaluating the accuracy and applicability of different approaches to estimate penetration factors and indoor loss rates and to explore the influence of indoor and outdoor environmental factors on the resulting parameter estimates.

■ MATERIALS AND METHODS

Test Apartment. Measurements were conducted in an unoccupied, sparsely furnished apartment unit located on the third floor of a 9-story dormitory on the main campus of the Illinois Institute of Technology in Chicago, IL (described previously[63] and in the Supporting Information (SI)). The majority of measurements were conducted in fall or winter months. All windows were kept closed and the sole perimeter door leading to a corridor was kept closed and taped during testing to minimize potential migration of indoor NO_x sources from the corridor. All internal doors remained open and oscillating fans were operated to enhance mixing. There was no mechanical ventilation and the source of ambient air into the unit was a combination of infiltration from outdoors, outdoor air supplied to the corridor from a supply fan on the roof (which we intentionally minimized by sealing the door), and adjacent apartment units (which we believe was minimal based on the resulting data and experiences from numerous other experiments concerning ozone and particle penetration).[63,64]

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Measurements of NO_2/NO/NO_x Concentrations. Indoor and outdoor NO_2, NO, and total NO_x (NO + NO_2) concentrations were measured using a 2B Technologies Model 405 direct absorbance monitor (manufacturer reported limit of detection of ∼1 ppb and accuracy of 2 ppb or 2% of reading, whichever is greater) located in the main living area, logging at 1 min intervals. NO_2 is directly measured using absorbance at 405 nm, and NO is alternately measured by sequential conversion to NO_2 with internally generated ozone. Total NO_x is calculated by summing the resulting NO and NO_2 concentrations. Interferences in the measurement of NO and NO_2 are expected to be minimal with this instrument,[70] as described in the SI. The NO_x monitor was connected to an electrically actuated three-way ball valve (Swagelok Model SS-43GXS4-42DCX) controlled by an electronic timer (Sestos B3S-2R-24) to alternately monitor indoor and outdoor air. PTFE-lined sampling lines ∼1.5 m in length were used for indoor and outdoor sampling to minimize NO_x losses and to keep any losses approximately equal for both samples. Outdoor samples were drawn through a small (∼0.6 cm) penetration in an acrylic window in the living room with the outdoor sampling line extending ∼0.6 m from the exterior window surface. The total system loss was measured to be <10% for NO_2 and negligible for NO. Because the switching valve requires ∼5 s to transition between indoor and outdoor sampling and the NO_x monitor has a ∼3−5 min functional response time, transition points between indoor and outdoor sampling periods were discarded.

Penetration Test Procedures. We first attempted several short-term tests (i.e., 4−6 h) in which outdoor NO_x was introduced indoors by opening windows and circulating air throughout the apartment to investigate whether they would yield sufficient fluctuations in the resulting data for estimating P and k for NO_x constituents, similar to methods that we have used to measure ozone and particle penetration factors in the same apartment.[63,64] However, these short-term attempts were not successful because of slow instrument response times and intermittent periods of low ambient and indoor NO_x concentrations. Additionally, indoor reactions between NO_x species (i.e., transformations from NO to NO_2 via oxidative reactions and NO production due to NO_2 surface reactions[11,40]) were difficult to characterize via short-term measurements. Therefore, we switched to longer-term measurements (i.e., ∼24−48 h) for the remainder of testing, following two primary experimental approaches. All parameter estimates were made using Stata Version 13 and the uncertainties associated with estimates of P and k for both experimental approaches were estimated using approaches similar to our previous work,[63] as described in the SI.

Method 1: Natural Elevation and Decay. The first longer-term approach to estimate P and k for NO_x constituents (i.e., Method 1) was similar to that used for ultrafine particles in Rim et al. (2010).[65] Indoor and outdoor NO and NO_2 concentrations were alternately measured at 40 min intervals (i.e., 20 min indoors and 20 min outdoors) over a period of at least 24 h in the absence of indoor sources to capture the natural indoor NO_x concentration elevations and decays that occur due to changes in ambient NO_x concentrations and infiltration rates. To solve for P and k, we applied a nonlinear two-parameter least-squares regression to the discretized solution of eq 4 for total NO_x concentrations (eq 5). The air exchange rate (AER, λ_t) during each test was measured every ∼5 h using CO_2 as a tracer gas,[71] as described in the SI.

$$C_{\mathrm{in}_{\mathrm{NO}x},t} = P_{\mathrm{NO}_x}\lambda_t C_{\mathrm{out}_{\mathrm{NO}x},t}\Delta t + (1 - (\lambda_t + k_{\mathrm{NO}x})\Delta t)C_{\mathrm{in}_{\mathrm{NO}x},t-1} \quad (5)$$

Total NO_x was used as the regression end point in Method 1 because the concentrations of indoor NO_2 or NO were typically too low to yield sufficient natural peaks and decays to solve for P and k for each constituent via nonlinear regression. Using total NO_x also reduced the number of unknown parameters; for example, NO/NO_2 sources required for eqs 2 and 3 could be ignored because total NO_x inherently captures transformations between NO and NO_2 (although this simplification ignores any renoxification from nitrogen-containing reservoir species, for which parametrizations of indoor dynamics remain largely unexplored). Using these estimates of P for total NO_x, P for NO_2 was then estimated assuming that the NO penetration factor was equal to 1, primarily because we are not aware of any literature demonstrating obvious reactions between NO and any materials commonly used in building enclosures. The assumption of $P_{\mathrm{NO}} = 1$ was also later verified experimentally using Method 2. The NO_2 penetration factor was thus calculated by using the estimated P for NO_x (solved using eq 5), weighted by the average outdoor NO_2 and NO_x concentrations during the test period and the assumption of $P_{\mathrm{NO}} = 1$ (eq 6). Finally, the NO_2 net indoor loss rate was approximated using eq 2 with known P_{NO_2} and assuming indoor NO oxidative reactions were negligible throughout the test period.

$$P_{\mathrm{NO}_2} \times \overline{C_{\mathrm{out}_{\mathrm{NO2}}}} + P_{\mathrm{NO}} \times \overline{C_{\mathrm{out}_{\mathrm{NO}}}} = P_{\mathrm{NO}_x} \times \overline{C_{\mathrm{out}_{\mathrm{NO}x}}} \quad (6)$$

We conducted several preliminary natural elevation and decay tests, each lasting 24−48 h. However, we achieved only moderate success with Method 1 because we did not always observe sufficiently large natural peaks and decays in indoor NO_x concentrations to successfully apply the two-parameter regression fit to eq 5. Reasons for insufficient indoor variations included minimal variations in outdoor concentrations or low infiltration rates during the test periods. Moreover, it was clear from the resulting data that indoor NO oxidative reactions were not always negligible, likely because indoor levels of oxidants such as ozone and/or free radicals varied between tests (but were not measured in this study). Therefore, we revised our test procedure to include an artificial elevation and decay approach (Method 2).

Method 2: Artificial Elevation and Decay. In Method 2, we altered the test procedure to also include a short-term artificial elevation and decay of NO_2 and NO concentrations either directly before or directly after the longer-term (24+ hour) natural elevation and decay measurements. The decision to artificially elevate before or after long-term testing was a matter of researcher preference (e.g., injecting either before or after a weekend of longer-term measurements). Indoor NO_2 and NO concentrations were elevated by operating a butane-fueled portable gas stove in one of the bedrooms. Because the NO_2 generation rate of the gas stove was much lower than its NO generation rate, an ozone generator (CAP Model OZN-1) was also operated along with the gas stove to enhance conversion of NO to NO_2 via reaction between NO and O_3.[72] The gas stove and ozone generator were operated for ∼15 min in the bedroom with the door closed and sealed, and the door was kept closed and sealed for another ∼10 min afterward to ensure the generated ozone had time to react completely. The bedroom door was then opened and a box fan was operated to

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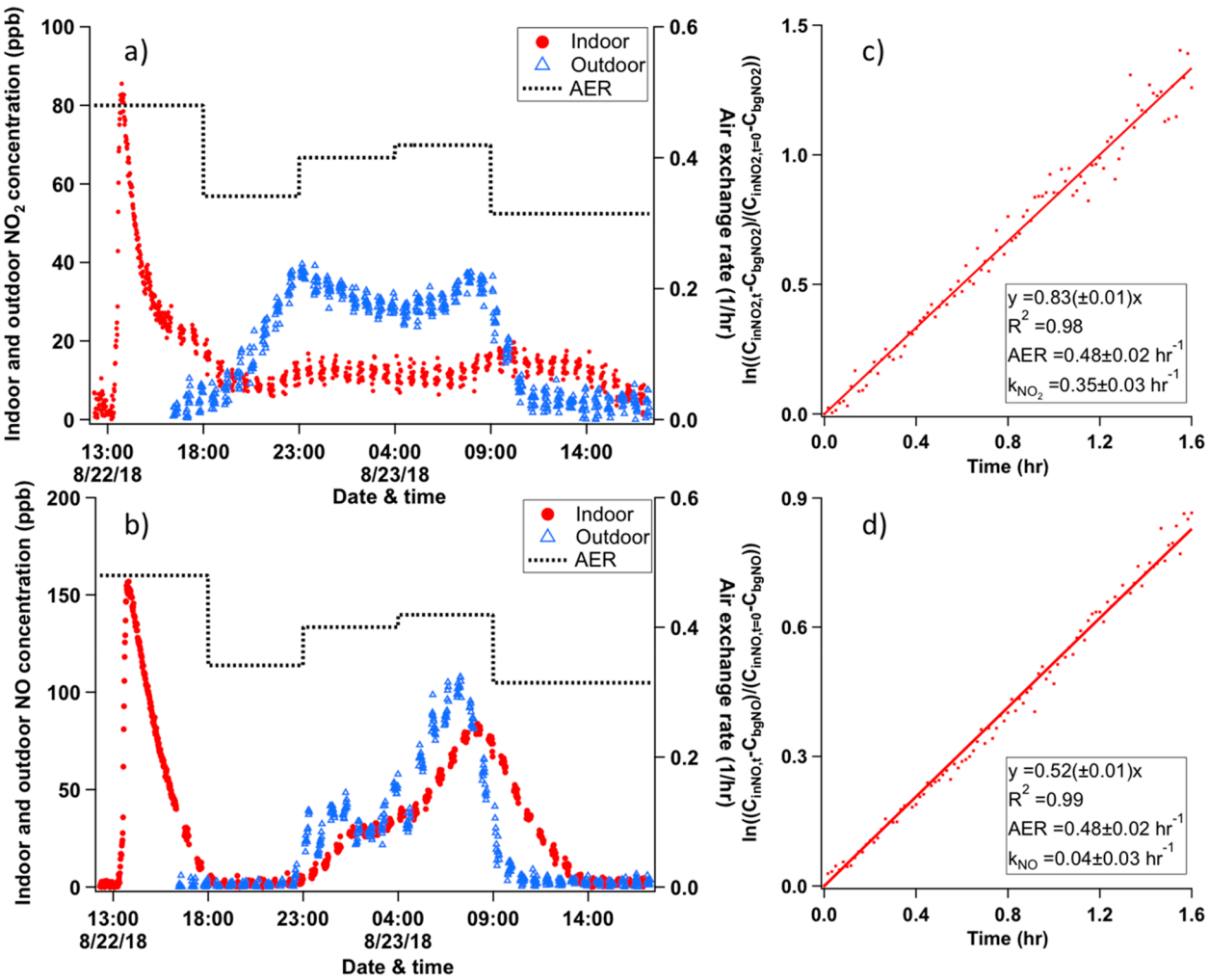

Figure 1. Example test data from a single NO_x elevation and decay period (~14:00−16:00 on 8/22/18) followed by natural variations, with parameters estimated successfully using both Method 1 and Method 2a: (a) time-series indoor and outdoor NO_2 concentrations with 5-h average AER overlaid, (b) time-series NO data from the same test period, (c) log−linear regression used to estimate the first-order NO_2 decay rate constant, and (d) log−linear regression used to estimate the first order NO decay rate constant.

circulate the injected NO_2 and NO throughout the apartment, typically yielding a peak concentration of ~50−100 ppb for both NO_2 and NO in the sampling area. The NO_x monitor was controlled by the two-channel timer (Sestos B2B-2R-220) to measure the indoor NO/NO_2 concentrations only (i.e., no outdoor measurements) for the first 2 h after elevation.

In Method 2, the net indoor NO and NO_2 loss rates (k_{NO} and k_{NO_2}) during the ~2-h decay period were estimated via linear regression of the left-hand side of eqs 7 and 8 versus time, respectively, using the indoor decay portion of the data after the artificial elevation. This assumes there are no indoor sources of NO or NO_2 during the decay period.

$$-\ln \frac{C_{in_{NO},t} - C_{bg_{NO}}}{C_{in_{NO},t=0} - C_{bg_{NO}}} = (\lambda_t + k_{NO})t \tag{7}$$

$$-\ln \frac{C_{in_{NO2},t} - C_{bg_{NO2}}}{C_{in_{NO2},t=0} - C_{bg_{NO2}}} = (\lambda_t + k_{NO2})t \tag{8}$$

where C_{bgNO} and C_{bgNO_2} are the steady-state background indoor NO and NO_2 concentrations measured during ~20 min period immediately prior to NO_x and O_3 injection. Because indoor NO_2 decay rates have been shown to be influenced by relative humidity (RH) in previous studies,[39,40,69] the indoor temperature and RH were measured during the artificial elevation and decay period, as well as during the longer-term indoor/outdoor switching periods, using an Onset HOBO U12 logging at 1 min intervals. Absolute humidity ratio was also calculated from these data. Subsequently, two different approaches were used to estimate the remaining parameters in Method 2 depending on the nature of the observed data (i.e., whether or not NO/NO_2 transformations likely occurred).

Method 2a. Method 2a was used to estimate parameters if the average indoor NO concentration measured during the test was similar to the average outdoor NO concentration. In this case, indoor oxidative reactions involving NO were assumed to be negligible (i.e., k_{NO} should be ~0 h^{-1}). To confirm this assumption, the indoor NO loss rate during the decay period (k_{NO}) was estimated using eq 7. If the estimate of k_{NO} made using eq 7 was close to zero (i.e., < 0.1 h^{-1}), then we assumed G_{NO} = 0 and solved for P_{NO} using a one-parameter least-squares regression to the discretized solution of eq 3 for NO concentrations (eq 9) with a known k_{NO}. In these cases, P_{NO} would be expected to be close to 1 based on prior understanding of a lack of heterogeneous reactions between

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Table 1. Summary of Parameter Estimates for the 12 Successful Experiments

date	method	P_{NO_2}	k_{NO_2} (h^{-1})	P_{NO_x}	k_{NO_x} (h^{-1})	k_{NO} (h^{-1})	k_{NO} (h^{-1})[a]	AER (h^{-1})	NO_2 (ppb)	NO (ppb)
2018/9/26	1	0.73 ± 0.10	0.33 ± 0.03	0.85 ± 0.10	0.04 ± 0.01			0.33 ± 0.05	17.0	14.0
	2a	0.76 ± 0.11	0.35 ± 0.05	0.87 ± 0.14	0.05 ± 0.01	0	0.01 ± 0.01			
2018/9/12	1	0.73 ± 0.14	0.14 ± 0.06	0.79 ± 0.10	0.10 ± 0.02			0.29 ± 0.02	13.0	3.6
	2b	0.74 ± 0.17	0.42 ± 0.03	0.79 ± 0.20	0.10 ± 0.03	0.23 ± 0.09	0.16 ± 0.01			
2018/8/23	1	0.74 ± 0.10	0.32 ± 0.03	0.89 ± 0.10	0.05 ± 0.02			0.36 ± 0.06	19.8	24.4
	2a	0.78 ± 0.12	0.35 ± 0.04	0.91 ± 0.14	0.06 ± 0.01	0	0.04 ± 0.03			
2018/3/12	1	n/a	n/a	n/a	n/a			0.83 ± 0.13	11.0	4.0
	2b	0.67 ± 0.13	0.06 ± 0.05	0.76 ± 0.16	0.01 ± 0.02	2.05 ± 0.21	0.20 ± 0.02			
2017/12/13	1	n/a	n/a	n/a	n/a			0.82 ± 0.11	16.7	5.3
	2b	0.81 ± 0.09	0.12 ± 0.10	0.85 ± 0.13	0.12 ± 0.02	0.66 ± 0.22	0.24 ± 0.05			
2017/12/12	1	n/a	n/a	n/a	n/a			0.88 ± 0.21	13.7	11.9
	2a	0.75 ± 0.09	0.12 ± 0.10	0.87 ± 0.13	0.03 ± 0.03	0	0.24 ± 0.05			
2017/12/1	1	0.61 ± 0.08	0.15 ± 0.02	0.83 ± 0.10	0.01 ± 0.01			0.45 ± 0.08	25.6	33.9
	2a	0.72 ± 0.09	0.26 ± 0.04	0.88 ± 0.12	0.03 ± 0.01	0	0.03 ± 0.01			
2017/11/29	1	n/a	n/a	n/a	n/a			0.50 ± 0.04	9.5	2.9
	2b	0.88 ± 0.15	0.32 ± 0.06	0.91 ± 0.20	0.22 ± 0.06	0.38 ± 0.19	0.14 ± 0.02			
2017/11/20	1	n/a	n/a	n/a	n/a			0.68 ± 0.21	10.7	4.2
	2b	0.73 ± 0.10	0.18 ± 0.12	0.80 ± 0.15	0.14 ± 0.04	0.71 ± 0.16	0.25 ± 0.09			
2017/11/9	1	0.67 ± 0.10	0.16 ± 0.03	0.82 ± 0.11	0.01 ± 0.03			0.48 ± 0.17	24.7	20.3
	2a	0.65 ± 0.09	0.16 ± 0.09	0.81 ± 0.11	0.01 ± 0.01	0	0.45 ± 0.07			
2017/10/25	1	0.64 ± 0.09	0.42 ± 0.08	0.83 ± 0.11	0.03 ± 0.03			0.40 ± 0.04	17.3	18.7
	2a	0.66 ± 0.09	0.47 ± 0.05	0.83 ± 0.12	0.04 ± 0.01	0	0.04 ± 0.01			
2017/10/19	1	0.68 ± 0.11	0.34 ± 0.08	0.79 ± 0.08	0.05 ± 0.01			0.38 ± 0.08	12.9	7.0
	2a	0.69 ± 0.10	0.38 ± 0.04	0.80 ± 0.13	0.05 ± 0.02	0	0.06 ± 0.01			
mean	1	0.69 ± 0.10	0.27 ± 0.04	0.83 ± 0.10	0.04 ± 0.02			0.52 ± 0.10	16.0	12.5
	2 a and b	0.75 ± 0.11	0.27 ± 0.07	0.84 ± 0.15	0.08 ± 0.02					

[a]Estimated from decay period only (conditions may have changed during remaining natural measurement period). n/a = not applicable (i.e., could not solve).

NO and material surfaces (this assumption is later verified experimentally). Additionally, since G_{NO_2} in eq 2 is assumed to occur primarily due to reactions between NO and oxidants, such as ozone, hydroperoxy radicals, and alkylperoxy radicals, then we could assume that G_{NO_2} was also negligible when k_{NO} was near zero. Therefore, P_{NO_2} could be solved for using a one-parameter regression on the discretized solution of eq 2 for NO_2 concentrations (eq 10), using k_{NO_2} from eq 8 and assuming $G_{NO_2} = 0$.

$$C_{in_{NO},t} = P_{NO}\lambda C_{out_{NO},t}\Delta t + (1 - (\lambda_t + k_{NO})\Delta t)C_{in_{NO},t-1} \tag{9}$$

$$C_{in_{NO2},t} = P_{NO_2}\lambda C_{out_{NO2},t}\Delta t + (1 - (\lambda_t + k_{NO_2})\Delta t) C_{in_{NO2},t-1} + G_{NO_2}\Delta t \tag{10}$$

Method 2b. Method 2b was used to estimate parameters if the average indoor NO concentration measured during the test period was *lower* than the average outdoor NO concentration. These cases were assumed to be indicative of indoor oxidative reactions between NO and certain (albeit unmeasured) indoor oxidant compounds (e.g., ozone, $^{\bullet}OH$, HO_2, or RO_2). If oxidation reactions cannot be ignored, then estimates of k_{NO} from application of eq 7 to the short decay period data cannot be extrapolated to the entire test period, as concentrations of these oxidants are well-known to have high temporal variations indoors[11,48] (although, again, they were not measured). Instead, the time-averaged indoor NO loss rate (k_{NO}) throughout the test period was estimated by one-parameter regression of eq 9 with the assumption of $P_{NO} = 1$. Here, we assumed that k_{NO} was due entirely to gas-phase oxidation of NO and thus the time-averaged value of k_{NO} estimated from eq 9 was assumed to be equal to the indoor NO oxidative reaction rate. In these cases, the indoor NO_2 generation rate at each time step was assumed to be equal to the indoor NO consumption rate (eq 11) using the simplifying assumption that oxidation reactions with NO produced NO_2 at a 1:1 molar ratio (i.e., reactions R2 and R3).

$$G_{NO_2,t} = k_{NO}C_{in_{NO},t-1} \tag{11}$$

Note that the assumption of 1:1 conversion of NO to NO_2 may be limiting; for example, during periods of high indoor OH levels where NO may react without accompanying formation of NO_2 or if renoxification processes generate NO_x from NO_z species. Also, because there are possibly slow and continuous reactions between NO_2 and HONO on indoor surfaces that will reproduce NO indoors, estimating k_{NO} using eq 9 and assuming $P_{NO} = 1$ may underestimate k_{NO} by ignoring indoor NO production. As a result, the NO_2 penetration factor may be overestimated under these conditions.

RESULTS AND DISCUSSION

A total of 16 tests were attempted, each involving 24+ hours of natural elevation and decay, as well as an artificial elevation and decay period immediately before or immediately after the natural test period. Twelve of the tests were successful, meaning they yielded logical estimates of P and k for NO_x constituents using one or more of the solution methods (i.e., $0 \leq P \leq 1$ and $k \geq 0$). The four failed tests occurred due to low

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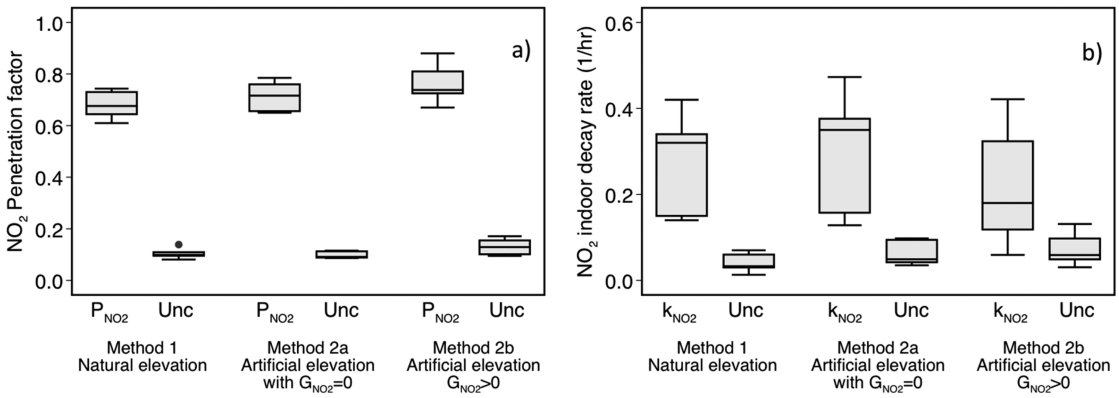

Figure 2. Parameter estimates and absolute uncertainties (labeled "Unc") made using three different methods for (a) NO_2 penetration factor and (b) NO_2 indoor loss rate. Boxes represent 25th, 50th, and 75th percentiles. Whiskers represent upper and lower adjacent values (1.5 times the differences between the 25th and 75th percentiles) and dots are outlier values.

ambient and indoor NO_x concentrations (3 of 4, with <5 ppb outdoor and <2 ppb indoor) or drastic weather changes that caused rapid changes in indoor RH, meaning that the estimate of k_{NO_2} from the decay period could not be used to represent the rest of the measurement period (1 of 4).

Example Test Data without NO Oxidative Reactions. An example of resulting data from one artificial elevation and decay experiment followed by ∼24 h of alternating indoor and outdoor concentrations without indoor sources is shown in Figure 1. The AER during the decay period was 0.48 ± 0.02 h^{-1} and ranged from 0.31 to 0.42 h^{-1} during the following 24 h of measurements. k_{NO_2} and k_{NO} were estimated to be 0.35 ± 0.03 and 0.04 ± 0.03 h^{-1}, respectively, by applying eqs 7 and 8 to the decay period data (Figure 1c and 1d). Because k_{NO} was close to zero and the average indoor and outdoor NO concentrations during the subsequent 24 h of measurements were similar (mean of 24.8 versus 24.4 ppb), Method 2a was used assuming that indoor oxidative reactions with NO were negligible (setting $k_{NO} = 0$). Therefore, G_{NO_2} was also assumed to be zero. Note that using $k_{NO} = 0\ h^{-1}$ or $k_{NO} = 0.04\ h^{-1}$ did not meaningfully impact subsequent parameter estimates; both values were applied to a one-parameter regression with eq 9 to estimate P_{NO} for this test, yielding estimates of $P_{NO} = 1.04$ and 1.06, respectively. Since these estimates were close to 1, we considered the use of $k_{NO} = 0$ and $P_{NO} = 1$ to be reasonable assumptions. We hypothesize that an estimated value of P_{NO} that is slightly greater than 1 may be indicative of NO_2 reactions with surface HONO to produce additional NO; although this reaction is poorly characterized, it is thought to be small compared to the NO source from infiltration.[11] Continuing with these assumptions, P_{NO_2} was estimated to be 0.78 ± 0.11 for this test using one-parameter regression with eq 10 and prior estimates of k_{NO_2} and λ_t. To compare across solution methods, Method 1 was also used to solve for P_{NO_x} using a two-parameter solution to eq 5 with data from the 24-h indoor and outdoor measurements without the artificial decay period, which yielded estimates of $P_{NO_x} = 0.89 \pm 0.10$ and $k_{NO_x} = 0.05 \pm 0.02$. When combined with the assumption of $P_{NO} = 1$ and average ambient NO_2 and NO concentrations of 19.8 and 24.4 ppb during testing, respectively, P_{NO_2} was estimated to be 0.74 ± 0.10 using eq 6, which was within ∼5% of the Method 2a solution. Data from another example test solved using Method 2b (with NO oxidative reactions) is also shown in the SI (Figure S2).

NO_x Penetration Factors and Indoor Loss Rates from All Tests. Table 1 shows parameter and uncertainty estimates made for the 12 successful experiments using both Methods 1 and 2 (either 2a or 2b, as applicable). Seven of the 12 tests yielded sufficient natural peaks and decays to solve for P and k via Method 1, and all 12 of the tests yielded sufficient data to solve for P and k via Method 2, including 7 tests solved via Method 2a (negligible NO oxidation) and 5 tests solved via Method 2b (including NO oxidation). The 7 tests with P and k solved via both Methods 1 and 2 provide an opportunity to compare different solution methods on the same test data. Overall, all methods were shown to yield reasonable estimates for P and k for NO_2 and NO_x, but Method 2, with its two variants of solution approaches, was shown to be more adaptable for different environmental conditions and improved the overall success rate of experiments (Figure S3). Figure S4 shows predicted versus measured indoor NO_2 and NO_x concentrations for each time interval of each test to explore the accuracy of estimates solved using both test methods and variants of solution approaches.

Figure 2 shows distributions of parameter estimates and uncertainties for P_{NO_2} and k_{NO_2}. Distributions of P_{NO_x} and k_{NO_x} estimates and uncertainties are shown in the SI (Figure S4). The mean (±s.d.) estimates of P_{NO_2} solved by the natural elevation and decay approach (Method 1; n = 7), artificial elevation without indoor NO_2 generation via NO oxidation (Method 2a; $n = 7$), and artificial elevation with indoor NO_2 generation via NO oxidation (Method 2b; $n = 5$) were 0.69 ± 0.05, 0.72 ± 0.05, and 0.76 ± 0.07, respectively, ranging from 0.61 to 0.88 with an overall mean (±s.d.) of 0.72 ± 0.06. In other words, reactions within the building envelope mitigated an average of ∼28% of ambient NO_2 exposure. Using Wilcoxon rank-sum tests, differences in estimates of P_{NO_2} made using (i) Methods 1 and 2 (lumping 2a and 2b together) and (ii) Methods 1, 2a, and 2b (treated separately) were not statistically significant ($p > 0.05$). The mean (±s.d.) estimates of the relative uncertainty in P_{NO_2} using Methods 1, 2a, and 2b were 15 ± 2%, 14 ± 1%, and 17 ± 4%, respectively, which are similar in magnitude to prior estimates of uncertainty in penetration factors for both particles[62,64,65,67,73] and ozone.[61,63]

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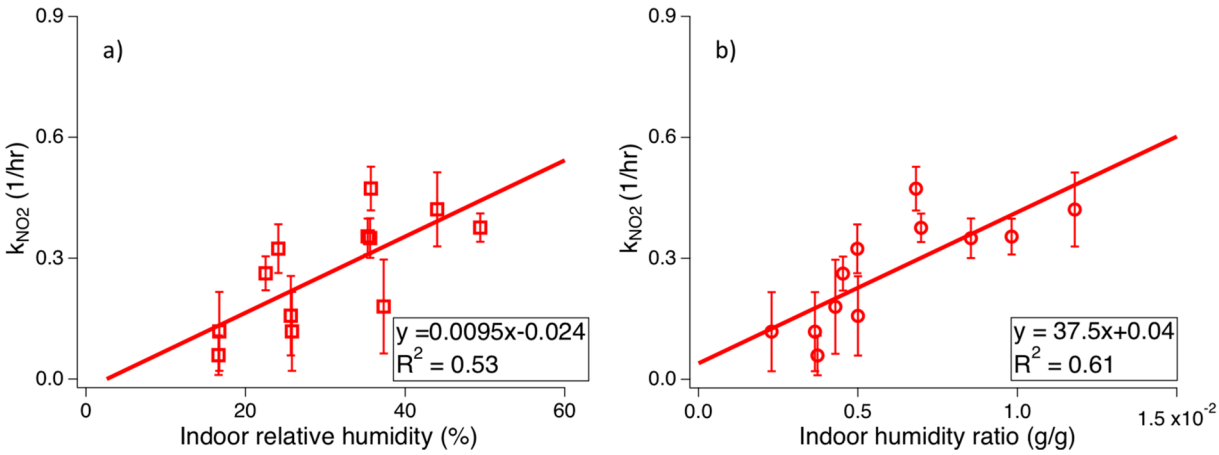

Figure 3. Estimates of indoor NO_2 loss rates (k_{NO_2}) versus average indoor (a) relative humidity and (b) humidity ratio during testing.

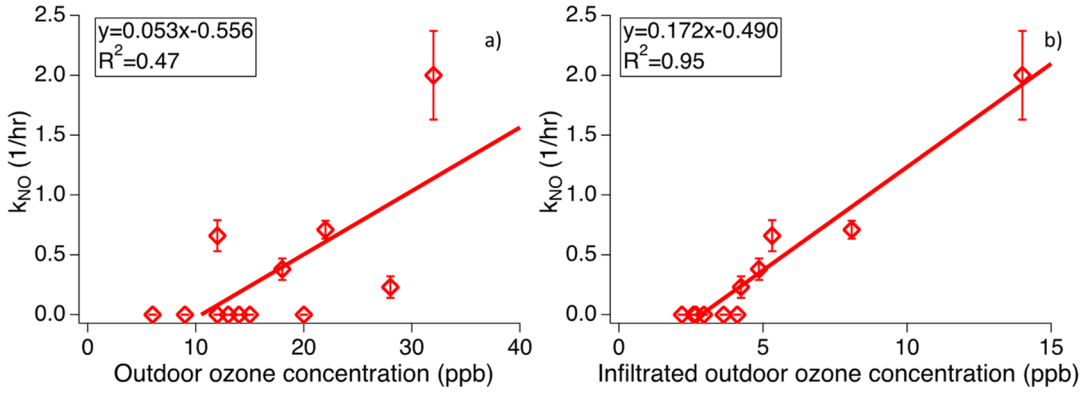

Figure 4. Estimated indoor NO loss rates (k_{NO}) versus (a) average outdoor ozone concentrations measured at the nearest regulatory monitor ∼10 km away and (b) the estimated average concentration of infiltrated outdoor ozone.

Estimates of k_{NO_2} across the 12 successful tests were more widely distributed, regardless of which solution method was used (Figure 2b). The mean (±s.d.) estimates of k_{NO_2} solved by Methods 1, 2a, and 2b were 0.27 ± 0.10, 0.30 ± 0.11, and 0.22 ± 0.13 h^{-1}, respectively, ranging from 0.06 to 0.47 h^{-1} and with an overall mean (±s.d.) of 0.27 ± 0.12 h^{-1} across all solution methods. The mean k_{NO_2} value is somewhat lower than those reported in several other studies in real homes (commonly ranging ∼0.5−1 h^{-1})[17,39,40,46,48] but is similar to that measured in apartment units in Northern California and in one commercial building in Southern California.[11,56] Lower observed k_{NO_2} values are likely due in part to the test apartment unit being sparsely furnished with a low surface-area-to-volume ratio. Moreover, many of our tests were conducted in the winter with low RH, which has been shown to influence k_{NO_2} in previous studies[17,40,74] and herein (see Figure 3). The mean (±s.d.) estimates of the relative uncertainty in k for NO_2 made using Methods 1, 2a, and 2b were 16 ± 8%, 28 ± 25%, and 52 ± 33%, respectively. Uncertainties in k_{NO_2} were highest using Method 2b, primarily because of the smaller values of k_{NO_2} under this condition (absolute uncertainties were similar across each method). Similar to that of P_{NO_2}, distributions of k_{NO_2} estimated using Methods 1, 2a, and 2b were not significantly different from each other (Wilcoxon rank-sum $p > 0.05$). The relative consistency in parameter estimates across each solution method suggests that the approaches defined, herein, can reasonably capture P and k for NO_x constituents across a wide range of test conditions.

Influence of Indoor Environmental and Ambient Conditions. Estimates of P and k and associated uncertainties for NO_2 and NO_x from the 12 successful tests were combined with several potentially influential indoor and outdoor environmental factors for subsequent analysis, including averages of indoor and outdoor temperature and RH, outdoor ozone concentrations, and wind speed and direction during the test (Table S1). Results did not reveal any significant relationships between P_{NO_2} and any of these parameters (Spearman's rank correlations $p > 0.05$). However, k_{NO_2} was correlated with indoor RH and humidity ratio measured during the test periods (Figure 3), which is consistent with previous studies of the impact of RH on indoor NO_2 removal.[40,48,74] The correlation between k_{NO_2} and indoor humidity ratio (a measure of absolute humidity that is not a function of temperature) was stronger than with RH (R^2 = 0.61 vs 0.53).

We also explored the relationship between estimates of k_{NO} and ambient ozone concentrations and estimates of indoor ozone concentrations during testing (which were not measured). Figure 4a shows estimates of k_{NO} from each test versus the average outdoor ozone concentration measured during the test period at the nearest ambient regulatory monitor. Similarly, Figure 4b shows estimates of k_{NO} from each test versus the estimated average ozone concentration in the infiltrating air, which was estimated by multiplying the average

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outdoor ozone concentration from the regulatory monitor during testing by the air exchange rate measured during the test and the average ozone penetration factor of this test apartment previously measured under natural infiltration conditions (P_{O_3} = 0.54).[63] This measure serves as a surrogate for how much ambient ozone likely infiltrated indoors during testing in the absence of concurrent indoor O_3 measurements. Estimates of k_{NO} were more strongly correlated with the estimated ozone concentration in the infiltrating air (R^2 = 0.95) compared to ozone in ambient air alone (R^2 = 0.47). However, the slopes of both regressions were lower (i.e., 0.05 and 0.17 ppb^{-1} h^{-1}) than previously reported reaction rate constants between NO and O_3 (i.e., 1.6 ppb^{-1} h^{-1}),[11,17] which indicates that indoor NO loss was probably not dominated by direct reactions with ozone but also with other oxidants that were present but not measured, such as hydroperoxyl, alkylperoxy, or hydroxyl radicals.[75]

LIMITATIONS

There are several limitations of the approaches described herein. First, in Method 2, estimates of k_{NO_2} were made using data from an artificial indoor elevation and decay period, which requires an assumption that k_{NO_2} is constant throughout the rest of the test period. Consistency in indoor temperature and, in particular, relative and absolute humidity, throughout the test periods were used as indicators that this could hold true, but it may not be the case throughout the entire test period due to other factors. Further, if these methods are applied in the field, then fluctuations in indoor and outdoor environmental conditions that are beyond control can lead to test failure (in fact, one out of our 16 test attempts resulted in failure for this reason). Second, as discussed, our approximation of G_{NO_2} assumed a 1:1 molar ratio between NO loss and NO_2 production; the importance of NO_x recycling from N-containing reservoir species is an important topic for future research that may improve the models developed here. Third, in Method 2b, calculation of k_{NO} ignores any indoor NO generation from NO_2 reactions with surface HONO, which, while expected to be of modest impact, may underestimate k_{NO} and, as a result, overestimate P_{NO_2} and P_{NO_x}. Last, other indoor reactions within NO_x and NO_y species that have not been characterized here may also affect the test results. Despite these limitations, the methods presented herein were shown to yield reasonable estimates of P and k for NO_x constituents under a variety of conditions. However, measuring P and k for NO_x constituents remains more challenging than for ambient ozone and particulate matter, and further work should improve upon the methods introduced here to refine the practicality of testing in larger samples of buildings to elucidate these key parameters that affect understanding of human exposure to ambient NO_x and byproducts from indoor NO_x chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02920.

Additional methods, including test house characteristics, NO_x monitor interference potential, air exchange rate measurements, and uncertainty estimates, and results, including example test data, parameter estimates for total NO_x, comparisons of the accuracy of different solution methods, and an exploration of the influence of environmental and ambient conditions (PDF)

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Notes

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