

The Influence of Ventilation on Reactions Among Indoor Pollutants: Modeling and Experimental Observations

CHARLES J. WESCHLER* AND HELEN C. SHIELDS

Abstract This study examines the influence of ventilation on chemical reactions among indoor pollutants. We have used a one compartment mass balance model to simulate unimolecular and bimolecular reactions occurring indoors. The initial modeling assumes steady-state conditions. However, at low air exchange rates, there may be insufficient time to achieve steady-state. Hence we have also modeled non steady-state scenarios. In the cases examined, the results demonstrate that the concentrations of products generated from reactions among indoor pollutants increase as the ventilation rate decreases. This is true for unimolecular and bimolecular reactions, regardless of whether the pollutants have indoor or outdoor sources. It is also true even when one of the pollutants has an outdoor concentration that displays large diurnal variations. We have supplemented the modeling studies with a series of experiments conducted in typical commercial offices. The reaction examined was that between ozone and limonene. The ozone was present as a consequence of outdoor-to-indoor transport while the limonene originated indoors. Results were obtained for low and high ventilation rates. Consistent with the modeling studies, the concentrations of monitored products were much larger at the lower ventilation rates (even though the ozone concentrations were lower). The potential for reactions among indoor pollutants to generate reactive and irritating products is an additional reason to maintain adequate ventilation in indoor environments.

Key words Ventilation rates; Air exchange rates; Indoor chemistry; Indoor ozone; Reaction times; Irritating products.

Practical Implications

Conventional wisdom often links poor indoor air quality and low ventilation rates. Low ventilation means less dilution of pollutants with indoor sources and therefore higher indoor concentrations. This paper demonstrates that another mechanism related to ventilation may be even more important in some situations. Several researchers have noted that some reactions between reactive gases (e.g., ozone) and common, benign organic compounds (e.g., certain terpenes) can generate products that are highly irritating. The authors explore the hypothesis that low ventilation rates allow longer times for these reactions to occur and, therefore, cause more of the irri-

tating reactive products to be present indoors. Continuous baseline ventilation should always exist in occupied areas.

Received 3 December 1999. Accepted for publication 22 January 2000.
© Indoor Air (2000)

Introduction

In recent years, investigators have begun to appreciate that some indoor pollutants are affected by chemical reactions as well as by more commonly recognized sources and sinks (see Weschler and Shields, 1997; Wolkoff et al., 1997 and references contained in each). The products of reactions among indoor pollutants are often more irritating than their precursors. For example, the oxidation of alkenes by ozone or the hydroxyl radical produces aldehydes, ketones and organic acids (Finlayson-Pitts and Pitts, 1986, 2000; Weschler et al., 1992), all of which tend to be more irritating than the alkenes themselves. The air oxidation of limonene has been reported to create potent skin allergens (Karlberg et al., 1992). The products of ozone/terpene reactions cause greater airway irritation in mice than would be predicted based on the known responses of mice to ozone or terpenes (Wolkoff et al., 1999, 2000). Some of the products of indoor reactions are, themselves, highly reactive. This is certainly the case for Criegee biradicals, nitrate radicals and peroxyacyl radicals; these species, in turn, lead to other reactive species such as hydroxyl, alkyl, alkylperoxy, hydroperoxy and alkoxy radicals. Many of these products (both stable and reactive) are only present when reactions among indoor pollutants occur.

For reactions among indoor pollutants to occur, there must be sufficient time for the pollutants to interact. Ventilation determines the time available for such interactions – that is, ventilation influences indoor

scripted on peroxyacetyl nitrate (PAN), while much of Table 2/Figures 2 and 3 have been scripted on ozone (pollutant "A") and limonene (pollutant "B").

One of the most commonly encountered indoor reactions is that between ozone (which has been transported from outdoors to indoors) and a terpene such as limonene with an indoor source; this is the 3rd scenario in Table 2 in which "A" originates outdoors, "B" indoors. To obtain a sense of how the bimolecular rate constant affects the relationship between ventilation and product concentrations, it is instructive to examine product concentrations for such a scenario with three different terpenes: α -terpinene, d-limonene, and α -pinene. Atkinson et al. (1990) report second order rate constants at 25°C of $0.756 \text{ ppb}^{-1} \text{ h}^{-1}$ for the ozone/ α -terpinene reaction; $0.0184 \text{ ppb}^{-1} \text{ h}^{-1}$ for the ozone/d-limonene reaction; and $0.00756 \text{ ppb}^{-1} \text{ h}^{-1}$ for the ozone/ α -pinene reaction. Given these rate constants, and otherwise using values for the parameters that are identical to those employed in deriving Table 2, we have calculated steady-state concentrations for a hypothetical product derived from each of these ozone/terpene reactions. Product concentrations as a function of air exchange rate are displayed in Figure 7. The plots illustrate that decreasing the air exchange rate dramatically increases the product concentrations for each of these ozone/terpene reactions. The conditions simulated in deriving Figure 7 are realistic. Outdoor ozone concentrations of 80 ppb are common in urban regions during the summer. A terpene (MW=136 amu) emission rate of 5 ppb/h corresponds to 0.56 mg/h in a 20 m³ room; this is easily achieved when using a terpene

containing wax or solvent. Given that the simulated conditions are representative of conditions encountered in actual indoor environments, the magnitude of the product concentrations displayed in Figure 7 at 0.1 h^{-1} (44 ppb, 12.7 ppb and 6.5 ppb) are especially noteworthy. It is also worth noting in Figure 7 that the slowest reaction is the most sensitive to changes in the air exchange rate. As the air exchange rate decreases from 4.0 to 0.1 air changes/h, the concentration of the reaction product increases a factor of 72 in the α -pinene case, a factor of 64 in the d-limonene case, and a factor of 40 in the α -terpinene case.

The results presented in this paper are specific to the stated conditions. However, the general trends remain the same as long as the time required for reaction is comparable to the air exchange rate. There are certain extreme cases when decreasing the air exchange rate decreases the product concentration. For example, this occurs when the rate of reaction is much faster than the air exchange rate and one or more of the reactants originate outdoors.

Non-Steady-State Modeling (Dynamic Modeling)

As the ventilation rate decreases, more time is required to reach steady-state. At low ventilation rates, in many real-world settings, the concentration of one or more of the reactants may change before steady-state is achieved. This is frequently the case for pollutants that originate outdoors and have strong diurnal variations. The dynamic simulations presented in Figures 4 and 5 indicate that even when there is insufficient time for such a system to reach steady-state, decreased ventilation rates lead to increased product concentrations as a consequence of indoor chemistry.

As just noted, the simulated conditions examined in the non-steady-state sections of this paper involve pollutants with outdoor sources and strong diurnal variations. There are other non steady-state scenarios in which decreases in ventilation result in larger increases in product concentrations. The most sensitive cases occur when the reactant (unimolecular) or both reactants (bimolecular) have predominantly indoor sources. Under such conditions, the linkage between ventilation rate and product formation rate is even more dramatic than that presented in Figures 4 and 5.

Bi-Molecular Reaction - Experimental

The ozone/limonene experiments were conducted in furnished, but unoccupied offices - that is, real world settings. The ozone within the room was not manipulated; it was whatever happened to be present as a consequence of outdoor-to-indoor transport on a summer day in New Jersey. As is apparent from Figure 6,

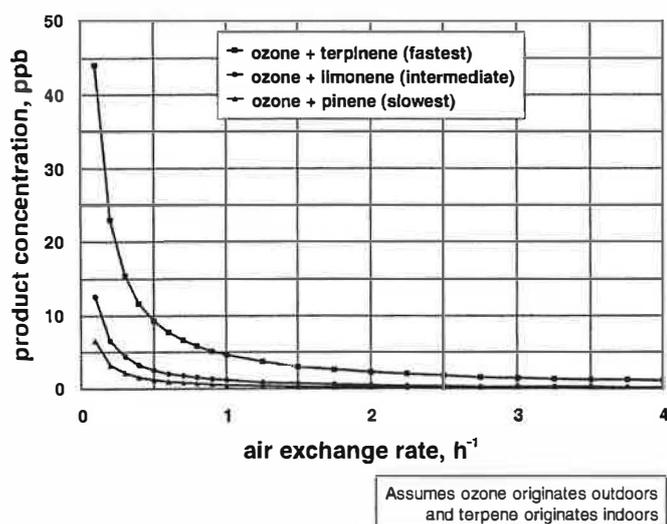


Fig. 7 Calculated concentrations for a hypothetical product generated by the indoor reaction between ozone (transported from outdoors) and a terpene (originating indoors). Squares - ozone/terpinene; circles - ozone/limonene; triangles - ozone/ α -pinene. See text for details

the ozone concentration varied significantly with the time of day. The limonene concentration was manipulated, but the emission rate was realistic. Optical particle counting (of particles in the 0.1–0.2 μm diameter size range) provided a convenient method to monitor the concentration changes of condensed phase products in real time. The conditions under which the ozone/limonene experiments were conducted were similar to the simulated conditions used in deriving Figure 5. The experimental results provide further support for the results obtained using dynamic simulations – simulations of scenarios in which reactant concentrations change before steady-state is achieved.

Conclusions

The results presented in this study illustrate that adequate ventilation is necessary not only to remove pollutants with indoor sources, but also to limit reactions among indoor pollutants. For reactions that occur at rates comparable to the air exchange rate, decreases in ventilation rates result in increases in the concentration of reaction products. This is true even when there is insufficient time to reach steady-state. Since the products derived from the reactions of indoor pollutants are often more irritating than their precursors (Weschler et al., 1992; Karlberg et al., 1992; Weschler and Shields, 1997; Wolkoff et al., 1999a, b), it is prudent to limit their production by maintaining adequate ventilation in indoor environments. Hippocrates warned against drinking from stagnant water (Hippocrates, 1952). In a similar vein, building occupants should be cautious of stagnant air – given time undesirable chemical transformations can occur.

Acknowledgements

This work was conducted with the support of Telcordia Technologies (formerly Bellcore). Portions of this work were presented at Healthy Buildings/IAQ '97, Washington, D.C. and Indoor Air 99, Edinburgh, Scotland.

References

- ASHRAE (1989) Ventilation for Acceptable Indoor Air Quality, Atlanta, GA, American Society of Heating, Refrigerating and Air-conditioning Engineers, ASHRAE Standard 62-1989.
- Atkinson, R., Hasegawa, D. and Aschmann, S.M. (1990) "Rate constants for the gas-phase reactions of O_3 with a series of monoterpenes and related compounds at 296 K", *International Journal of Chemical Kinetics*, **22**, 871.
- Atkinson, R., Baulch, D.L., Cox, R.A., Hampson Jr. R.F., Kerr, J.A. and Troe, J. (1992) "Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV", *Journal of Physical and Chemical Reference Data*, **21**, 1125–1568.
- Finlayson-Pitts, B.J. and Pitts, J.N. (1986) *Atmospheric Chemistry*, New York, John Wiley & Sons.
- Finlayson-Pitts, B.J. and Pitts, J.N. (2000) *Chemistry of the Upper and Lower Atmosphere*, New York, Academic Press.
- Graedel, T.E. (1978) *Chemical Compounds in the Atmosphere*, New York, Academic Press.
- Hippocrates (1952) "On Airs, Waters and Places". In: Hutchins, R.M. (ed) *Great Books of the Western World*, Encyclopedia Britannica.
- Karlberg, A., Magnusson, K. and Nilsson, U. (1992) "Air oxidation of d-limonene (the citrus solvent) creates potent allergens", *Contact Dermatitis*, **26**, 332–340.
- Leovic, K.W., Sheldon, L.S., Whitaker, D.A., Hetes, R.G., Calcagni, J.A. and Baskir, J.N. (1996) "Measurement of indoor air emissions from dry-process photocopy machines", *Journal of Air and Waste Management Association*, **46**, 821–829.
- Nazaroff, W.W. and Cass, G.R. (1986) "Mathematical modeling of chemically reactive pollutants in indoor air", *Environmental Science & Technology*, **20**, 924–934.
- Nazaroff, W.W., Gadgil, A.J. and Weschler, C.J. (1993) "Critique of the use of deposition velocity in modeling indoor air quality". In: Nagd, N.L. (ed) *Modeling of Indoor Air Quality and Exposure*, ASTM STP 1205, American Society for Testing and Materials, pp. 81–104.
- Shields, H.C., Fleischer, D.M. and Weschler, C.J. (1996) "Comparisons among VOCs measured in three types of U.S. commercial buildings with different occupant densities", *Indoor Air*, **6**, 2–17.
- VisSim 3.0a (1998) Westford, MA, Visual Solutions, Inc.
- Weschler, C.J., Hodgson, A.T. and Wooley, J.D. (1992) "Indoor chemistry: ozone, volatile organic compounds and carpets", *Environmental Science & Technology*, **26**, 2371–2377.
- Weschler, C.J. and Shields, H.C. (1996) "Production of the hydroxyl radical in indoor air", *Environmental Science & Technology*, **30**, 3250–3258.
- Weschler, C.J. and Shields, H.C. (1997) "Potential reactions among indoor pollutants", *Atmospheric Environment*, **31**, 3487–3495.
- Weschler, C.J. and Shields, H.C. (1999) "Indoor ozone/terpene reactions as a source of indoor particles", *Atmospheric Environment*, **33**, 2301–2312.
- Wolkoff, P., Clausen, P.A., Jensen, B., Nielsen, G.D. and Wilkins, C.K. (1997) "Are we measuring the relevant indoor pollutants?", *Indoor Air*, **7**, 92–106.
- Wolkoff, P., Clausen, P.A., Wilkins, C.K., Hougaard, K.S. and Nielsen, G.D. (1999) "Formation of strong airway irritants in a model mixture of (+)- α -pinene/ozone", *Atmospheric Environment*, **33**, 693–698.
- Wolkoff, P., Clausen, P.A., Wilkins, C.K., Hougaard, K.S., Larsen, S.T. and Nielsen, G.D. (1999b) "Formation of strong airway irritants in terpene/ozone mixtures", *Indoor Air*, **10**, 82–91.

chemistry. The smaller the ventilation rate, the longer the residence time of indoor air. A longer residence time means a longer interval during which indoor pollutants can decompose or react with one another, generating products. Ventilation also influences indoor chemistry, in a secondary manner, by affecting the concentration of the reacting species. As the ventilation rate decreases, pollutants with indoor sources increase in concentration while the converse is true for pollutants with outdoor sources.

As just noted, ventilation drives the transport of pollutants between indoor and outdoor environments. Adequate ventilation is acknowledged to be important for removing pollutants that originate indoors, with historical emphasis placed on body effluents (ASHRAE, 1989). However, the linkage between ventilation and indoor chemistry is often overlooked. A partial explanation for the oversight may lie in the fact that many of the products of indoor chemistry, including free radicals and condensed phase species, are not readily detected using the analytical methods routinely applied to indoor air (Weschler and Shields, 1997). The present study has been designed to examine the relationship between ventilation and indoor chemistry more explicitly. The paper is divided into three parts: steady-state modeling, dynamic modeling and experimental observations. The steady-state modeling illustrates the influence of ventilation on indoor chemistry under conditions when there is sufficient time to achieve equilibrium. However, as the ventilation rate decreases, more time is required to reach steady-state. At low ventilation rates, in many real-world settings, the concentration of one or more of the reactants may change before steady-state is achieved. Under such conditions, it is not apparent that decreasing ventilation rates necessarily lead to increased concentrations of reaction products. The dynamic modeling probes such situations. Finally, the paper concludes with experimental results obtained under conditions that are similar to those modeled in the dynamic bimolecular simulations.

Material and Methods

Modeling Approach

The simulations have been based on a one-compartment mass-balance model that contains appropriate source and sink terms (see, for example, Nazaroff and Cass, 1986; Weschler and Shields, 1996). These include outdoor-to-indoor transport, indoor-to-outdoor transport, surface removal, and kinetic expressions for the reactions of interest. The simulations have been based on commonly occurring indoor situations. Both the

steady-state and non-steady-state simulations will be described in detail in the Results section. The non-steady-state modeling has been accomplished using dynamic modeling software (VisSim, 1998). The indoor chemical reactions are treated as a set of non-linear time dependent differential equations. The integration method was Runge Kutta 4th order with a 0.5 s time step.

Experimental Approach

The experiments were designed to monitor the concentrations of particles produced in a $3.1 \times 3.1 \times 3.0$ m unoccupied office as a consequence of ozone/limonene reactions (Weschler and Shields, 1999). Two comparable and adjacent unoccupied offices were utilized in these studies. The rooms were located on the 2nd floor of a 3-story building in suburban New Jersey, approximately 27 air-miles from Manhattan and 6.5 air-miles west of the Atlantic Ocean. The rooms were carpeted, had acoustic ceiling tiles, contained standard office furniture, and were fitted with coated, non-opening windows (3.0×2.0 m) facing east. During the experiments the doors were closed and blinds were drawn across the windows. On weekdays, the air-handling system was off from 7:00 p.m. until 6:00 a.m. On weekends, the air-handling system was normally off from 7:00 p.m. on Friday until 6:00 a.m. on Monday, with occasional exceptions. The air-handling system did not recirculate any of the ventilation air (due to the presence of chemical laboratories, as well as offices); the supply air contained only outdoor air.

The condensed phase products of the ozone/limonene reaction were monitored using eight-channel laser particle counters (Particle Measuring System's LASAIR Model 1002). The eight channels correspond to the following size ranges (values are optical diameters): 0.1–0.2 μm , 0.2–0.3 μm , 0.3–0.4 μm , 0.4–0.5 μm , 0.5–0.7 μm , 0.7–1.0 μm , 1.0–2.0 μm and >2.0 μm . The ozone concentration within the room was monitored using a Dasibi Model 1003-AH ultraviolet (UV) photometric analyzer; wavelength, 254 nm; range, 0–500 ppb; precision, $\pm 1\%$ or 1 ppb, whichever is greater. The instruments were interfaced to personal computers for the purpose of data collection. Prior to these studies, both the ozone meter and particle counters were calibrated using equipment and standards traceable to the US National Institute of Standards and Technology. Furthermore, instrument performance checks were conducted throughout the experiments. The concentrations of volatile organic compounds, including limonene, were determined by passive sampling, followed by GC/MS analyses (Shields et al., 1996). The air exchange rate (the rate at which the room air was replaced with sup-

ply air) was measured by releasing SF₆ into a room and recording its decay. SF₆ was monitored using a photoacoustic infrared detection method (Brüel & Kjaer Multi-Gas Monitor Type 1302). d-Limonene was emitted into the room at a constant rate using a custom diffusion vessel. The d-limonene (97% purity) had been obtained from Aldrich Chemical and was used without further purification.

Results

Steady-State Modeling

To illustrate the effect of different ventilation rates on the products formed as a consequence of indoor chemistry we have utilized a simple one-compartment mass balance model. The compartment represents an indoor environment surrounded by outdoors; species can be transported into and out of the environment. We have considered two different types of chemical reactions that can occur in an indoor setting: unimolecular reactions and bimolecular reactions. For each type of reaction we have examined multiple scenarios. Note: the air exchange rates discussed in this study are "effective" air exchange rates – combinations of the air exchange rate and the air change effectiveness (mixing factor).

Unimolecular Reactions – Steady-State. The simplest case is that in which a unimolecular reaction occurs indoors to produce products. Such a reaction is typically a decomposition reaction, although radioactive decay can also be described as a unimolecular reaction. In this type of process reactant "A" is transformed into products in a first order fashion:

$$-d[A]/dt = k_u[A] \quad [1]$$

where [A] is the concentration of the reactant "A", and k_u is a first order rate constant. Under steady-state conditions, the indoor concentration of A, [A]_{in}, is given by:

$$[A]_{in} = (E_x[A_{out}] + ER_A) / (E_x + v_{dA}(A/V) + k_u) \quad [2]$$

where E_x is the air exchange rate (air changes per hour;

either ach or h⁻¹), [A]_{out} is the outdoor concentration of "A" (ppb), ER_A is the emission rate of "A" indoors (ppb/h), v_{dA} is the deposition velocity of "A" (m/h) and A/V is the surface-to-volume ratio (m⁻¹) indoors.

Consider a product that is directly produced by the decomposition of "A" and has no other indoor sources. Under steady-state conditions, the indoor concentration of this product, [prod]_{ss}, is given by:

$$[\text{prod}]_{ss} = (k_u[A_{in}]) / (E_x + v_{dprod}(A/V) + \sum k_{pi}[X_i]) \quad [3]$$

where v_{dprod} is the deposition velocity of the product (m/h), k_{pi} is a second order rate constant (ppb⁻¹ h⁻¹) for the reaction between the *i*th indoor pollutant ([X]_i) and the product; the other parameters have been defined. To simplify this discussion, we have assumed that the terms " $v_{dprod}(A/V)$ " and " $\sum k_{pi}[X_i]$ " are negligible compared to " E_x ". (The reader is cautioned that this is often not the case in decomposition reactions; the products of such reactions can be quite reactive themselves).

We have used Equations 2 and 3 to examine the effect that ventilation has on the steady-state concentration of a hypothetical product generated by the unimolecular decomposition of an indoor air pollutant. We have considered three different scenarios: i) The indoor pollutant originates outdoors; there are no indoor sources. For this scenario we have used an outdoor concentration of 2 ppb; ii) The indoor pollutant originates indoors; there are no outdoor sources. For this scenario we have used an indoor emission rate of 0.15 ppb/h; and iii) The indoor pollutant has both indoor and outdoor sources; the outdoor concentration equals 2 ppb and the indoor emission rate equals 0.15 ppb/h. In each case we have used 1.91 h⁻¹ as the value of k_u (this is the rate at which peroxyacetyl nitrate, PAN, decomposes at 25°C (Atkinson et al., 1992)) and have assumed that $v_{dA}(A/V)$ is negligible compared with E_x . The results are given in Table 1.

When the indoor pollutant "A" originates outdoors (scenario i), decreasing the ventilation rate produces a modest increase in the product concentration (see 2nd column in Table 1). This particular scenario is displayed in greater detail in Figure 1; the figure contains separate plots for both the product concentration (circles) and the pollutant concentration (triangles). At 4 h⁻¹ the concentration of pollutant "A" is 1.35 ppb and the product concentration is 0.65 ppb, while at 0.1 h⁻¹, the concentration of pollutant "A" is 0.1 ppb and the product concentration is 1.9 ppb. It is interesting to note that the crossover point for the product and pollutant concentrations in Figure 1 occurs at an air exchange rate of 1.9 h⁻¹. This is the point where the rate of air

Table 1 Calculated concentrations (ppb) for a hypothetical product generated as a consequence of the unimolecular decomposition of an indoor air pollutant "A"; results are shown for different air exchange rates and different pollutant origins

Air exchange rate (h ⁻¹)	"A" originates outdoors	"A" originates indoors	"A" originates outdoors and indoors
4.0	0.65	0.01	0.66
2.0	0.98	0.04	1.01
1.0	1.31	0.10	1.41
0.5	1.59	0.24	1.82
0.1	1.90	1.43	3.33

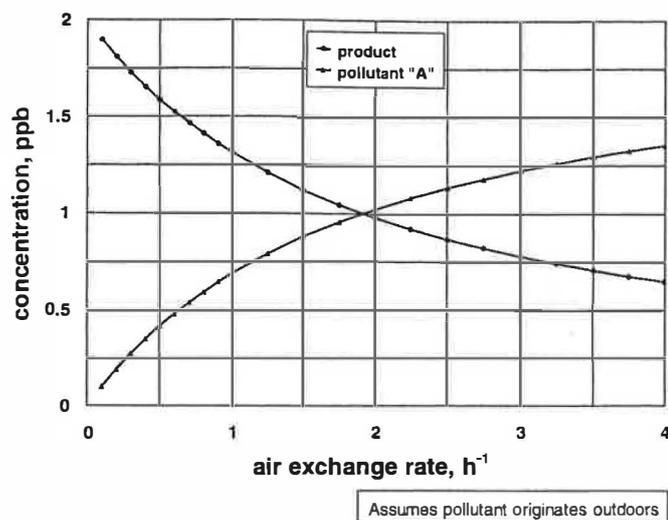


Fig. 1 Effect of ventilation on the indoor concentration of pollutant, "A", that originates outdoors and is transported indoors, and its decomposition product

exchange matches the rate of unimolecular decomposition. When the indoor pollutant "A" originates indoors (scenario ii), the concentration of the hypothetical product increases dramatically with decreasing ventilation rate. At 4 h^{-1} the product concentration is only 0.01 ppb, while at 0.1 h^{-1} , the product concentration is 1.43 ppb (see 3rd column in Table 1). When the indoor pollutant "A" originates outdoors and indoors (scenario iii), the increase in product concentration with decreasing ventilation rate lies between the situations just discussed (see 4th column in Table 1).

Bimolecular Reactions – Steady-State. The more complicated case to consider is that in which a bimolecular reaction occurs indoors to produce products. This is also the more common situation; most of the chemical reactions that occurs indoors are bimolecular processes – "A" reacts with "B" to form products:

$$-d[A]/dt = -d[B]/dt = k_b[A][B] \quad [4]$$

where k_b is a second order rate constant. Under steady-state conditions, the indoor concentration of "A", $[A_{in}]$,

is given by:

$$[A_{in}] = (E_x[A_{out}] + ER_A) / (E_x + v_{dA}(A/V) + k_b[B_{in}]) \quad [5]$$

where the parameters have been previously defined. Similarly, the indoor concentration of "B", $[B_{in}]$, is given by:

$$[B_{in}] = (E_x[B_{out}] + ER_B) / (E_x + v_{dB}(A/V) + k_b[A_{in}]) \quad [6]$$

where ER_B is the emission rate of "B" indoors (ppb/h), v_{dB} is the deposition velocity of "B" (m/h), and the other terms have been defined.

Under steady-state conditions, the indoor concentration of a product that is directly produced by the reaction of "A" with "B", $[prod]_{ss}$, is given by:

$$[prod]_{ss} = (k_b[A_{in}][B_{in}]) / (E_x + v_{dprod}(A/V) + \sum k_{pi}[X_i]) \quad [7]$$

where v_{dprod} is the deposition velocity of the product; the other parameters have been defined. In writing Equation 7 we have assumed that the reaction between "A" and "B" is the only source of the product. To further simplify this discussion, we have also assumed that the terms " $v_{dprod}(A/V)$ " and " $\sum k_{pi}[X_i]$ " are negligible compared to " E_x ". (This may not be the case, especially if the product is a highly reactive free radical).

We have used Equations 5, 6 and 7 to calculate the steady-state concentration of a hypothetical product generated by the reaction between two indoor air pollutants. We have considered five different scenarios: i) The indoor pollutants both originate outdoors; there are no indoor sources. For this scenario we have used an outdoor concentration of 80 ppb for pollutant "A" (comparable to outdoor ozone levels in an urban area during a summer afternoon) and 10 ppb for pollutant "B" (comparable to outdoor limonene concentrations from trees and vegetation on a warm day (see Graedel, 1978, p. 91)). ii) Both pollutants originate indoors; there are no outdoor sources. For this scenario we have used an indoor emission rate of 50 ppb/h for pollutant "A"; this is equivalent to a photocopier emitting ozone at 3

Table 2 Calculated concentrations (ppb) for a hypothetical product generated as a consequence of the bimolecular reaction between indoor pollutants "A" and "B". See text for initial conditions

Air exchange rate (h ⁻¹)	Both pollutants originate outdoors	Both pollutants originate indoors	"A" originates outdoors; "B" indoors	"B" originates outdoors; "A" indoors	Both pollutants originate outdoors and indoors
4.0	1.60	0.04	0.20	0.29	2.02
2.0	2.04	0.19	0.52	0.74	3.13
1.0	2.37	0.82	1.20	1.62	5.00
0.5	2.58	3.03	2.58	3.03	8.69
0.1	2.77	34.9	12.6	7.10	43.6

mg/h (Leovic et al., 1996) in a 30 m³ room. The indoor emission rate for pollutant "B" is assumed to be 5 ppb/h, comparable to the rate at which limonene can be emitted from a cleaning product. iii) Pollutant "A" originates outdoors (80 ppb) and pollutant "B" originates indoors (5 ppb/h). iv) Pollutant "B" originates outdoors (10 ppb) and pollutant "A" originates indoors (50 ppb/h). v) The pollutants have both outdoor and indoor sources (80 and 10 ppb, 50 and 5 ppb/h). In each case we have used 0.0184 ppb⁻¹ h⁻¹ as the value of k_b (this is comparable to the rate constant for the reaction between ozone and limonene at 25°C (Atkinson et al., 1990)), 3.6 h⁻¹ for the term $v_{dA}(A/V)$ (a typical value for the removal of ozone by indoor surfaces (Nazaroff et al., 1993)), and have assumed that $v_{dB}(A/V)$ is negligible compared with E_x (a reasonable assumption for an alkene). The results are given in Table 2.

For each scenario summarized in Table 2, as the air exchange rate decreases, the concentration of the hypothetical product increases. The effect is smallest when both pollutants originate outdoors and largest when both pollutants originate indoors. The former scenario has been presented in greater detail in Figure 2, while the latter scenario is detailed in Figure 3. In each figure the line with circles shows the concentration of the hypothetical product, while the line with triangles shows the concentration of indoor pollutant "A" and the line with inverted triangles that of indoor pollutant "B". In Figure 2, as the air exchange rate decreases from 4.0 to 0.1 h⁻¹, the concentration of pollutant "A" decreases from 42 to 2 ppb while that of pollutant "B" decreases from 8 to 7 ppb. Despite the fact that the reactant concentrations are decreasing with decreasing air exchange, the concentration of the product increases

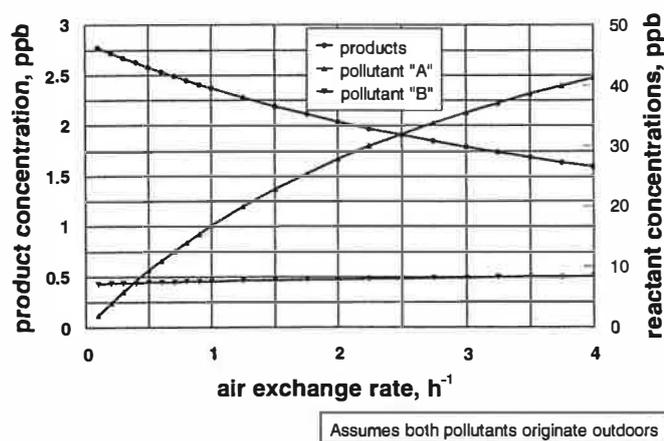


Fig. 2 Effect of ventilation on the indoor production of products from the bimolecular reaction between pollutant "A" and pollutant "B". In this scenario pollutants "A" and "B" originate outdoors. See text for details

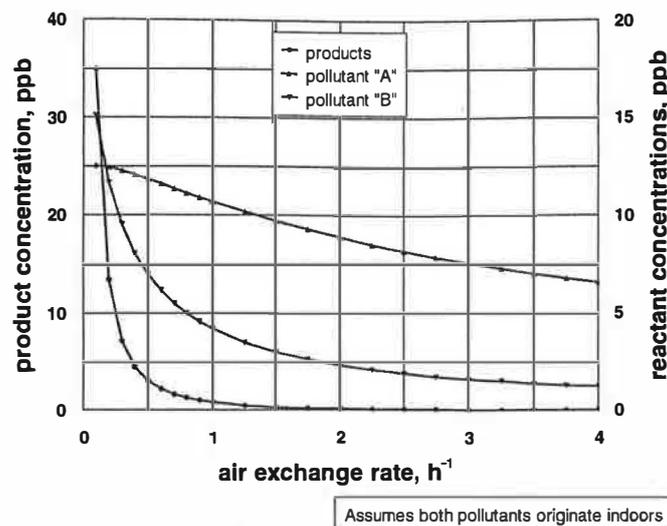


Fig. 3 Effect of ventilation on the indoor production of products from the bimolecular reaction between pollutant "A" and pollutant "B". In this scenario pollutants "A" and "B" originate indoors. See text for details

from 1.6 to 2.8 ppb. In Figure 3, as the air exchange rate decreases from 4.0 to 0.1 h⁻¹, the concentration of pollutant "A" increases from 7 to 12.5 ppb while that of pollutant "B" increases from 1 to 15 ppb. At the same time, the concentration of the product increases from 0.04 to 35 ppb. This increase in product concentration is steepest for the region where the air exchange rate is relatively low – specifically the region from 0.5 to 0.1 h⁻¹. The remaining scenarios presented in Table 2 have results that fall somewhere between the extremes presented in Figures 2 and 3.

Non Steady-State Modeling (Dynamic Modeling)

Space constraints do not permit a case-by-case analysis of the different permutations for uni- and bimolecular indoor chemical reactions (as was done above for the steady-state scenarios). Instead, we will restrict our simulations to two of the more relevant situations for indoor environments: i) the unimolecular decomposition of a pollutant that originates outdoors and ii) the bimolecular reaction between a pollutant that originates outdoors and one that originates indoors.

Unimolecular Reaction – Dynamic Modeling. We have used the same rate constant for the decomposition of "A", 1.91 h⁻¹, that was used in the section entitled *Unimolecular Reactions – Steady-State*. In the simulation we have assumed that the outdoor concentration of pollutant "A" varies in a diurnal fashion from 0 to 2 ppb, with the peak concentration occurring at midday. We have further assumed that there are no indoor sources of pollutant "A" and that the removal of pollutant "A" by indoor surfaces is negligible. Figure 4 shows the re-

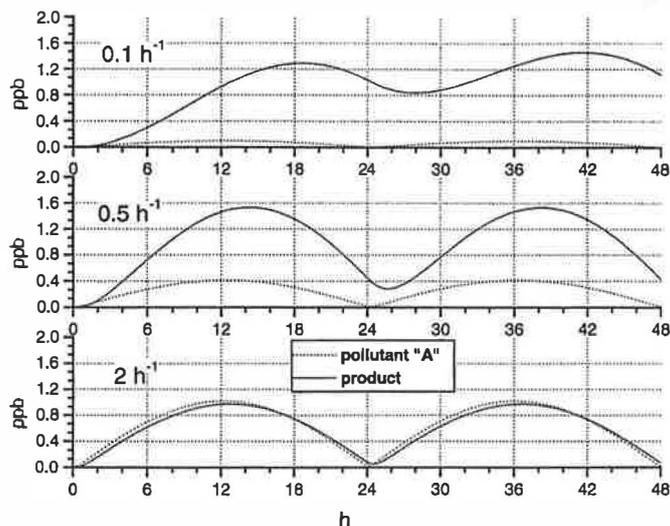


Fig. 4 Production of products from the unimolecular decomposition of pollutant "A" at three different ventilation rates. In this scenario pollutant "A" originates outdoors and displays a large diurnal variation

sults of the simulation, over a 48-h period, for three different air exchange rates.

At 2 h^{-1} the concentration of pollutant "A" and its decomposition products display quite similar trends. During the first 24 h the indoor concentration of pollutant "A" (dotted line) climbs to about 1 ppb before falling to near zero. The product concentration (solid line) climbs and falls slightly behind that of pollutant "A", reaching almost the same peak value. This pattern is repeated during the next 24 h.

At 0.5 h^{-1} the indoor concentration of pollutant "A" is lower and the net concentration of its decomposition products are higher than those observed at 2.0 h^{-1} . During the first 24 h the indoor concentration of pollutant "A" climbs to about 0.4 ppb before falling to near zero. The product concentration climbs to almost 1.6 ppb at 14 h and falls to about 0.3 ppb at 26 h. The pattern is similar during the next 24 h.

At 0.1 h^{-1} the indoor concentration of pollutant "A" is even lower than that observed at 0.5 h^{-1} , while the concentration of its decomposition products approaches the maximum level achieved at 0.5 h^{-1} . To be more specific, during the first 24 h the indoor concentration of pollutant "A" climbs to slightly less than 0.1 ppb before falling to near zero. The product concentration climbs to almost 1.3 ppb at 19 h, but falls only partially, reaching a minimum of about 0.8 ppb at 28 h. During the next 24 h the concentration of pollutant "A" repeats the pattern of the first 24 h, while the product concentration reaches an even larger value than it did during the first 24 h ($\sim 1.5 \text{ ppb}$).

Bimolecular Reaction – Dynamic Modeling. We have

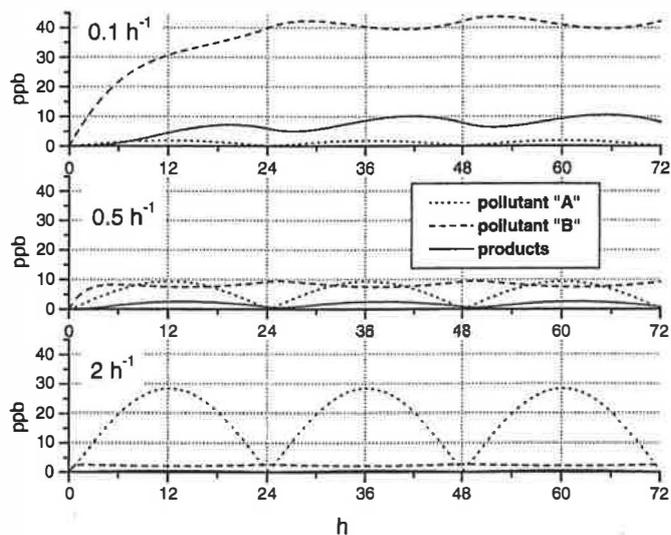


Fig. 5 Production of products from the bimolecular reaction between pollutant "A" and pollutant "B" at three different ventilation rates. In this scenario pollutant "A" originates outdoors and displays a large diurnal variation, while pollutant "B" is emitted indoors at a constant rate

used the same rate constant for the reaction between "A" and "B", $0.0184 \text{ ppb}^{-1} \text{ h}^{-1}$, that was used in the section entitled *Bimolecular Reactions – Steady-State*. In the simulation we have assumed that pollutant "A" originates outdoors and pollutant "B" originates indoors (a common occurrence). We have further assumed that the outdoor concentration of pollutant "A" varies in a diurnal fashion from 0 to 80 ppb, with the peak concentration occurring at midday; pollutant "B" is assumed to have a constant indoor emission rate of 5 ppb h^{-1} . Indoor surfaces are modeled identically to the steady-state simulation – as a significant sink for pollutant "A" but a negligible sink for pollutant "B". Figure 5 shows the results of the simulation, over a 72-h period, for three different air exchange rates.

At 2 h^{-1} the daily indoor concentration of pollutant "A" (dotted line) climbs to 28 ppb and falls to near zero (while the daily outdoor pollutant "A" concentration climbs to 80 ppb and falls to zero). After an initial rise, the pollutant "B" concentration (dashed line) remains close to 2 ppb, with a slightly higher value when pollutant "A" is at a minimum and a slightly lower value when pollutant "A" is at a maximum. The product concentration (solid line) barely rises above 0.5 ppb.

At 0.5 h^{-1} the indoor concentration of pollutant "A" is lower and both pollutant "B" and the product concentrations are higher than those observed at 2.0 h^{-1} . The indoor pollutant "A" concentration climbs to 10 ppb and falls to near zero. After an initial rise, the pollutant "B" concentration fluctuates between 7 and 10 ppb, depending on the pollutant "A" level. The product concentration varies daily from zero to 2.5 ppb.

At 0.1 h^{-1} the indoor concentration of pollutant "A" is even lower and the concentrations of pollutant "B" and reaction product are even higher than those observed at 0.5 h^{-1} . The indoor pollutant "A" concentration cycles between 0 and 2 ppb (consistent with its outdoor origins). The indoor pollutant "B" concentration climbs to larger levels each day, reaching 43 ppb on the third day (52 h). The product concentration climbs to 7.5 ppb on the first day, 10 ppb on the second day, and 11 ppb on the third day; the product-peaks occur approximately 6 h after the pollutant "A"-peaks. It is apparent that the air exchange rate is too small to flush the product from the indoor setting during those periods when the production of product is small (i.e., when the pollutant "A" level is near zero).

Bi-Molecular Reaction – Experimental

The reaction between ozone and limonene generates both vapor phase and condensed phase products. The production of condensed phase products can be followed in near-real time with an optical particle counter (Weschler and Shields, 1999). Figure 6 shows results from an experiment that utilized adjacent, identically furnished offices. One office contained a limonene source; the other did not. In both offices, the ozone was present due to outdoor-to-indoor transport, and varied with time of day and ventilation rate. The difference in particle concentrations between the two offices (in the $0.1\text{--}0.2 \mu\text{m}$ diameter size range) was used as a metric for product formation as a consequence of the ozone/limonene reaction. (See Weschler and Shields, 1999 for additional details).

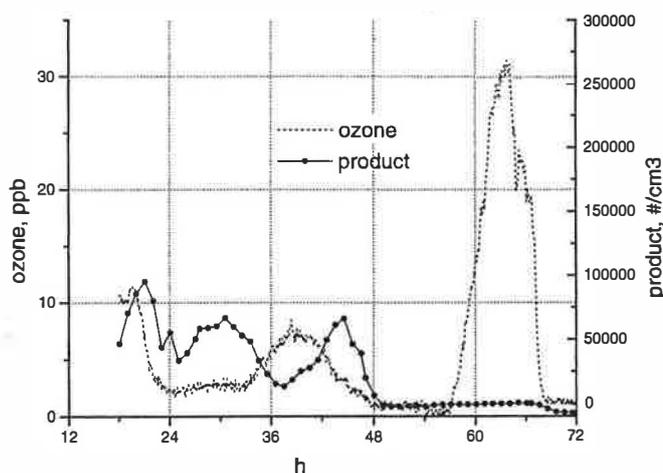


Fig. 6 Measured production of products from the ozone/limonene reaction at two different ventilation rates: 0.1 h^{-1} from 18 to 54 h and 12 h^{-1} from 54 to 72 h. In this experiment ozone originated outdoors, while limonene was emitted at a constant rate indoors. Left Y-axis and dashed line: ozone concentration. Right Y-axis and line with solid circles: differences in particle concentrations between the two offices (see text for details)

During the initial period shown in Figure 6 (18–54 h), the ventilation rate in each office was approximately 0.1 h^{-1} . During this same period the product concentration roughly tracked the ozone concentration with a slight lag; on several occasions it exceeded $50,000 \text{ counts/cm}^3$. From 54–72 h the ventilation rate in each room was increased to approximately 12 h^{-1} , but conditions were otherwise unchanged. During this period there was no detectable product formation (i.e., no observable difference in the concentration of particles between the two offices) despite the fact that indoor ozone levels reached a concentration of 30 ppb. The latter ozone level was almost three times larger than the level reached under low ventilation conditions when product formation was readily apparent. In effect, the large ventilation rate swept ozone and limonene out of the room before they had had sufficient time to interact and produce a detectable amount of product.

Discussion

Steady-State Modeling

For the conditions examined, the concentrations of the reaction products increase as the air exchange rate decreases (see Tables 1 and 2 and Figures 1 to 3). The magnitude of this increase depends on whether the indoor reactants originate outdoors or indoors. Decreasing ventilation rates have the greatest effect on product concentrations when the reactants originate indoors. As the air exchange rate decreases, the time available for reaction increases and the reactant concentration increases. For the 2nd scenario reported in Table 1 (unimolecular reaction, "A" originates indoors), the hypothetical product has a concentration that is more than 140 times greater at 0.1 h^{-1} than at 4 h^{-1} . Similarly, for the 2nd scenario reported in Table 2 (bimolecular reaction, both pollutants originate indoors), the hypothetical product has a concentration that is more than eight hundred times greater at 0.1 h^{-1} than at 4 h^{-1} .

The difference between product concentrations at high and low ventilation rates is lowest when the reactants originate outdoors (see Tables 1 and 2). As the air exchange rate decreases, the time available for reaction increases but this is partially or wholly offset by the fact that the reactant concentrations decrease (slowing down the rate at which product is produced). For the simulated conditions, the product concentration still displays a modest increase as the air exchange rate decreases.

In preparing Tables 1 and 2 and the related figures we deliberately chose concentrations and rate constants typical of situations encountered in the real world. Hence, much of Table 1/Figure 1 have been