

Indoor Chemistry Involving O₃, NO, and NO₂ as Evidenced by 14 Months of Measurements at a Site in Southern California

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For more than 1 year, indoor and outdoor O₃, NO, NO₂* (NO_x - NO), temperature, and relative humidity as well as the air exchange rate have been measured continuously at a commercial building in Burbank, CA. The indoor concentration of a given pollutant is a function of its outdoor level, the air exchange rate, the rate at which it is removed by indoor surfaces, and the rate at which it is produced or removed by indoor chemistry. Several examples of indoor chemistry are inferred from daily and seasonal variations in the collected data. These include homogeneous reactions such as those of O₃ with both NO (fast) and NO₂ (slow) and heterogeneous reactions such as those between NO₂ and indoor surfaces. The latter ultimately contribute to indoor levels of both HONO and NO and are more likely to be observed in the absence of indoor O₃. Indeed, due to the very rapid O₃/NO reaction as well as other slower reactions, the presence or absence of indoor O₃ strongly influences speciation among the indoor oxides of nitrogen.

Introduction

Photochemical pollutants can adversely affect human health, ecosystems, crops, and materials. Our own work has focused on the manner in which these pollutants contribute to failures in sophisticated electronic equipment (1). Most buildings that house such equipment have mechanical ventilation systems that include filters for removing airborne particles. However, very few of these installations have any explicit control measures designed to reduce the outdoor-to-indoor transport of gaseous photochemical pollutants such as ozone, the oxides of nitrogen, or their reaction products. These species can attain indoor concentrations that are a moderate to large fraction of their outdoor levels (see refs 2-4 and references cited therein). This study addresses the consequences of elevated indoor concentrations of photochemical pollutants.

Reactions among ozone (O₃) and the oxides of nitrogen (NO_x) have long been recognized as important components of outdoor tropospheric chemistry, especially in regions with severe photochemical smog (5, 6). However, indoor reactions among these compounds have received little attention. In a 1974 study, Shair and Heitner (7) applied a dynamic one-compartment mass balance model to concentrations of O₃ measured indoors and outdoors; NO and NO_x concentrations were not measured. They included a term for the first-order removal of O₃ by indoor surfaces, but did not include any indoor homogeneous chemistry. In 1982, Ozkaynak et al. (8) developed a model, incorporating simplified NO_x chemistry, to simulate

pollutant concentrations indoors. The oxidation of NO by O₃ to generate NO₂ was one of three reactions included in this model. The authors speculated that indoor O₃ might be generated by the indoor photolysis of NO₂, but they did not appreciate that, at certain times, indoor O₃ could achieve much higher levels as a consequence of outdoor-to-indoor transport. To evaluate the model, they measured indoor and outdoor levels of CO, NO, and NO_x, but not O₃. Given the time and location of measurements (late April in Boston), the influence of outdoor O₃ on the indoor environment was probably small. In 1986 Nazaroff and Cass (9) developed a "general mathematical model for predicting the concentrations of chemically reactive compounds in indoor air". The model included 57 photolytic and thermal chemical reactions. They applied the model to a set of data collected at a Southern California museum. The data set included simultaneous indoor and outdoor measurements of O₃, NO, and NO_x concentrations over a 10-day period. To our knowledge, this is the only previous study that has measured, in real time (i.e., short sampling interval), the indoor and outdoor concentrations of O₃, NO, and NO_x. In 1992, Weschler, Brauer, and Koutrakis (10) examined the indoor reaction between O₃ and NO₂ as a potential pathway to the generation of nitrate radicals, dinitrogen pentoxide, and nitric acid indoors. They applied a simple mass balance model to indoor concentrations of NO₂ (measured) and O₃ (estimated); the results were compared to measured indoor concentrations of nitric acid. The NO₂ and HNO₃ measurements had been obtained using integrated sampling methods.

In the current study, we have continuously measured, in real time, indoor and outdoor concentrations of O₃, NO, and NO₂* (NO_x - NO) for more than 1 year at a telecommunications office in Burbank, CA. Concurrently, we have measured the air exchange rates as well as indoor and outdoor temperatures and relative humidities, parameters that influence outdoor-to-indoor pollutant transport and indoor chemistry. Our objective has been to better understand the factors that govern the indoor concentrations of the monitored pollutants and their reaction products. The extended duration of the study, coupled with its real-time nature, has revealed seasonal variations as well as changes over shorter time intervals; these have been useful in isolating different variables. The results have demonstrated that indoor O₃, NO, and NO₂ are involved in an intricate dance. The concentration of any one of these species is influenced by those of the other two, and indoor reactions involving these species can generate other compounds of concern.

Experimental Section

The reported measurements were made at a telecommunications office in Burbank, CA, 15 mi northeast of

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downtown Los Angeles and 15 mi east of the Pacific Ocean—latitude 34.182°, longitude 118.312°. The Burbank Airport is 1 mi west, and U.S. Interstate 5 passes 0.5 mi northeast of the site; prevailing winds are from the west. The office is a flat roof building with a first floor and basement; each has an area of 930 m² and a volume of 5095 m³. There is no carpeting; the interior walls are unpainted red brick; there is little “fleecy” (high surface area) material within the building. Indoor pollutants were measured on the first floor.

On two occasions, from June 15 to June 16, 1992, and again from January 9 to January 12, 1993, air exchange rates on the first floor were measured using perfluorocarbon tracer techniques (11). During periods of minimum ventilation, the air exchange rate is 0.30 air changes/h (ach or h⁻¹); during periods of maximum ventilation it is 1.9 ach.

Air velocities in the “outdoor-air” plenum, the “return-air” plenums, and the “mixed-air” plenum were measured continuously using TSI air velocity transmitters (anemometers). Outdoor air velocities were used to calculate volumetric flow rates for outside air; these flow rates coupled with the volume of the first floor space were then used to calculate the “continuous” air exchange rates reported in this study. On those occasions when air exchange rates were determined by perfluorocarbon tracer techniques, the measured values and those calculated using the outside air velocities agreed to within 10%.

The outdoor and indoor temperatures and relative humidities were continuously monitored using Omega Model HX93C transmitters. These devices use a thin-film polymer capacitor to sense relative humidity and a thin-film permalloy resistance detector to sense temperature. The sensors are protected by a stainless steel filter.

The sampling details for O₃ have been presented elsewhere (2). In brief, ozone concentrations were measured with UV photometric analyzers (Dasibi Model 1003 AH; wavelength, 254 nm; range, 0–500 ppb; precision, ±1% or 1 ppb, whichever is greater). The instruments were interfaced to a personal computer; data were collected at 1-min intervals. In addition to the raw data, the average and standard deviation of the previous readings were recorded every 15 min. Separate instruments were used for indoor and outdoor O₃ measurements.

Nitric oxide (NO) and total oxidized nitrogen (NO_x) were measured with a chemiluminescence NO_x analyzer (Thermo Environmental Instruments Model 42; range, 0–500 ppb; precision, ±0.5 ppb). A single instrument was interfaced to a computer and a three-port Teflon solenoid valve; the latter was used to alternate sampling between indoors and outdoors on a 15-min cycle. At the start of each indoor or outdoor cycle, the sampling line was purged for 10 min, NO and NO_x values were then read at 30-s intervals for the next 5 min, and finally the average of the 10 readings was recorded.

Air was sampled at the rate of 2 L/min (O₃) or 0.7 L/min (NO_x) using 3.15 mm i.d. Teflon tubing; the maximum length of any sampling line was less than 5 m. Separate sampling lines were used for indoor O₃, outdoor O₃, indoor NO_x, and outdoor NO_x. In-line 0.5-μm Teflon filters were used to remove airborne particles. These filters were replaced every 3 weeks, and instrument performance checks were conducted on a weekly basis. The instruments were periodically calibrated in accordance with the guidelines described in the EPA Quality Assurance

Handbook for Air Pollution Measurement Systems (12) and the EPA's Prevention of Significant Deterioration Guidelines (13). The standards used to perform the calibrations were traceable to the National Institute of Standards and Technology Standard Reference Materials (SRMs).

The computers that were interfaced to the various analytical instruments also were connected to modems. These systems collected data, as described above, and at the same time were available for file transfer initiated from a remote site. In this manner, the data were periodically retrieved from our office—laboratories in New Jersey, 3000 mi from the monitored site.

The chemiluminescence analyzer used in this study is a three-channel instrument that nominally measures NO, NO_x, and nitrogen dioxide (NO₂). The NO₂ value is the difference of the NO_x and NO values. The NO_x channel of this instrument responds linearly and quantitatively to nitrous acid (HONO), nitric acid (HNO₃), and peroxyacetyl nitrate (PAN) in addition to NO₂ and NO (14, 15). In this paper, we have adopted the nomenclature of Nazaroff and Cass (9), who use the symbol NO₂* to signify data determined as (NO_x – NO). HONO, HNO₃, and PAN are expected to have concentrations that seldom exceed 5–10% of the NO₂ concentration (3, 16–19).

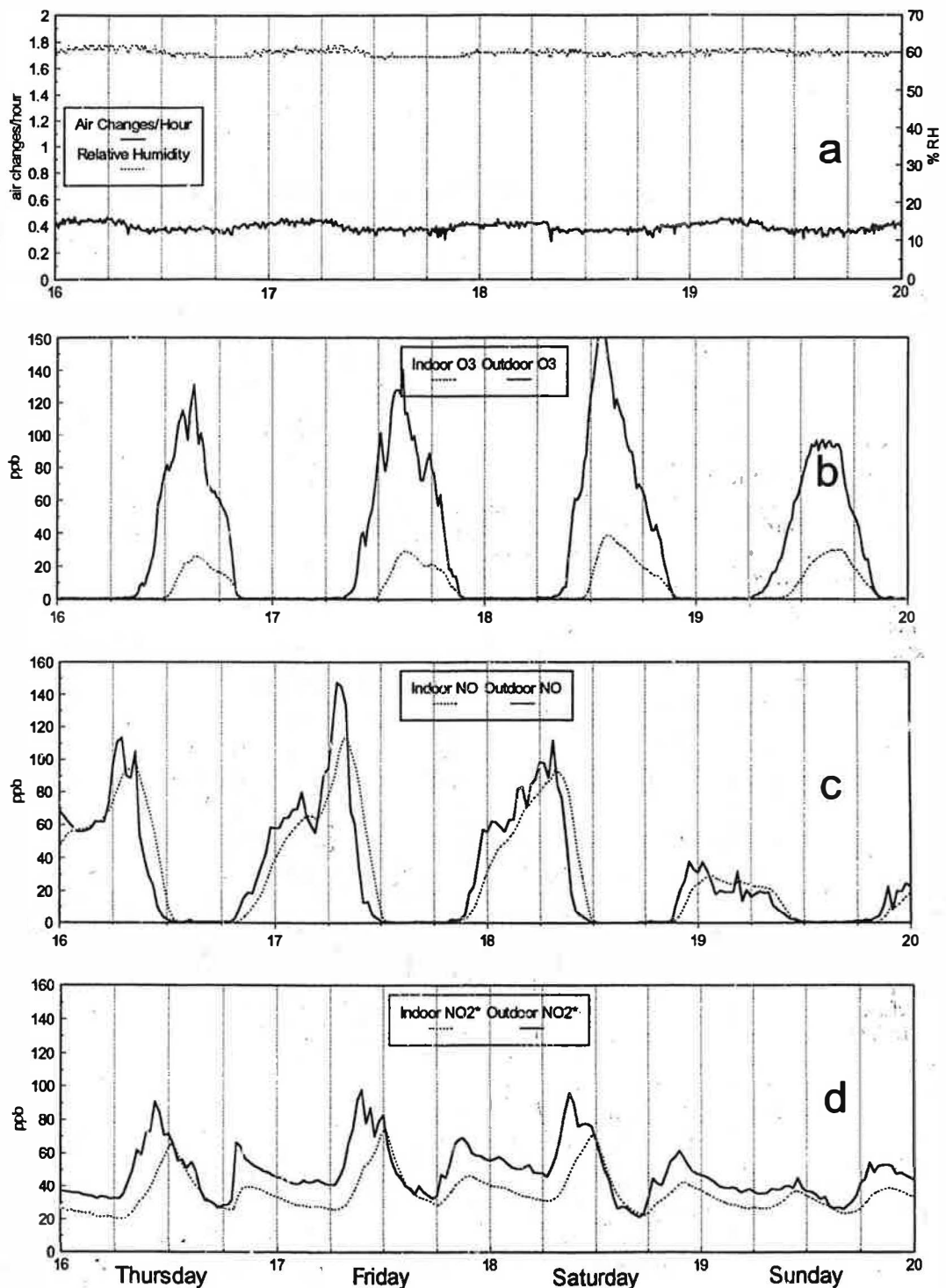
Results

In this paper, we report on measurements made continuously from July 1992 to the end of August 1993 (14 months). Although there are occasional small gaps in the data sets, they are remarkably complete. Space constraints prohibit the presentation of all the data; they are available from the authors upon request. Figures 1–4 show data from representative 4-day periods in the summer, fall, winter, and spring. Figure 1 (7/16–7/19/92), Figure 2 (10/8–10/11/92), and Figure 4 (4/8–4/11/93) show data from a Thursday through Sunday period. Figure 3 (1/2–1/5/93) shows data from a Saturday through Tuesday period.

Air Exchange Rates and Indoor Relative Humidity. Figures 1a–4a show air exchange rates and indoor relative humidities during the representative periods. The air exchange rate, E_x , is a key parameter defining the indoor environment at the Burbank site. For species originating outdoors, E_x is a major factor determining indoor concentrations (appearing in both source and sink terms); it influences the lag time between changes in outdoor concentrations and subsequent changes in indoor concentrations; it determines the amount of time available (residence time) for indoor chemical reactions.

The indoor relative humidity has a major impact on both homogeneous and heterogeneous indoor chemistry. In the latter case, it influences the amount of moisture adsorbed on indoor surfaces. As such, the relative humidity directly affects corrosion processes (20), the rate at which NO₂ is removed by indoor surfaces (21), the rate at which NO₂ is converted to nitrous acid (HONO) on indoor surfaces (22), and the rate at which dinitrogen pentoxide (N₂O₅) is heterogeneously hydrolyzed (5) to nitric acid (HNO₃).

The air exchange rate on the first floor of the Burbank office varies from a low of 0.3 ach to a high of 1.9 ach. The ventilation system is operating on an economizer cycle. When the outdoor air temperature is greater than the return air temperature, the damper is closed; when outdoor air temperature is less than the return



July 16 to July 19, 1992

Figure 1. Parameters measured at the Burbank office from July 16 to 19, 1992. (a) Air exchange rates (solid line) and indoor relative humidities (dotted line). (b) Indoor O₃ (dotted line) and outdoor O₃ (solid line). (c) Indoor NO (dotted line) and outdoor NO (solid line). (d) Indoor NO₂* (dotted line) and outdoor NO₂* (solid line).

temperature, the damper is open; an adjustable throttling range is superimposed upon these criteria. Hence, during the warm summer months, the outside air damper tends to be at a minimum setting (see Figure 1a), and the air exchange rate may remain low for several consecutive weeks. [Note that even at the lowest air exchange rate, the ventilation exceeds the minimum ventilation rate recommended for the occupant density of this building (23).] During the cooler months, it is common for the

outside air damper to close during the day and open overnight. Even in December and January, it often gets warm enough at midday that the outdoor air damper closes (see Figure 3a). It should be noted that on May 13, 1993, the minimum setting of the outdoor air damper was changed. Prior to this time, the minimum damper setting resulted in an air exchange rate of ~0.3 ach; following the change, the minimum damper setting resulted in an air exchange rate of ~0.7 ach.

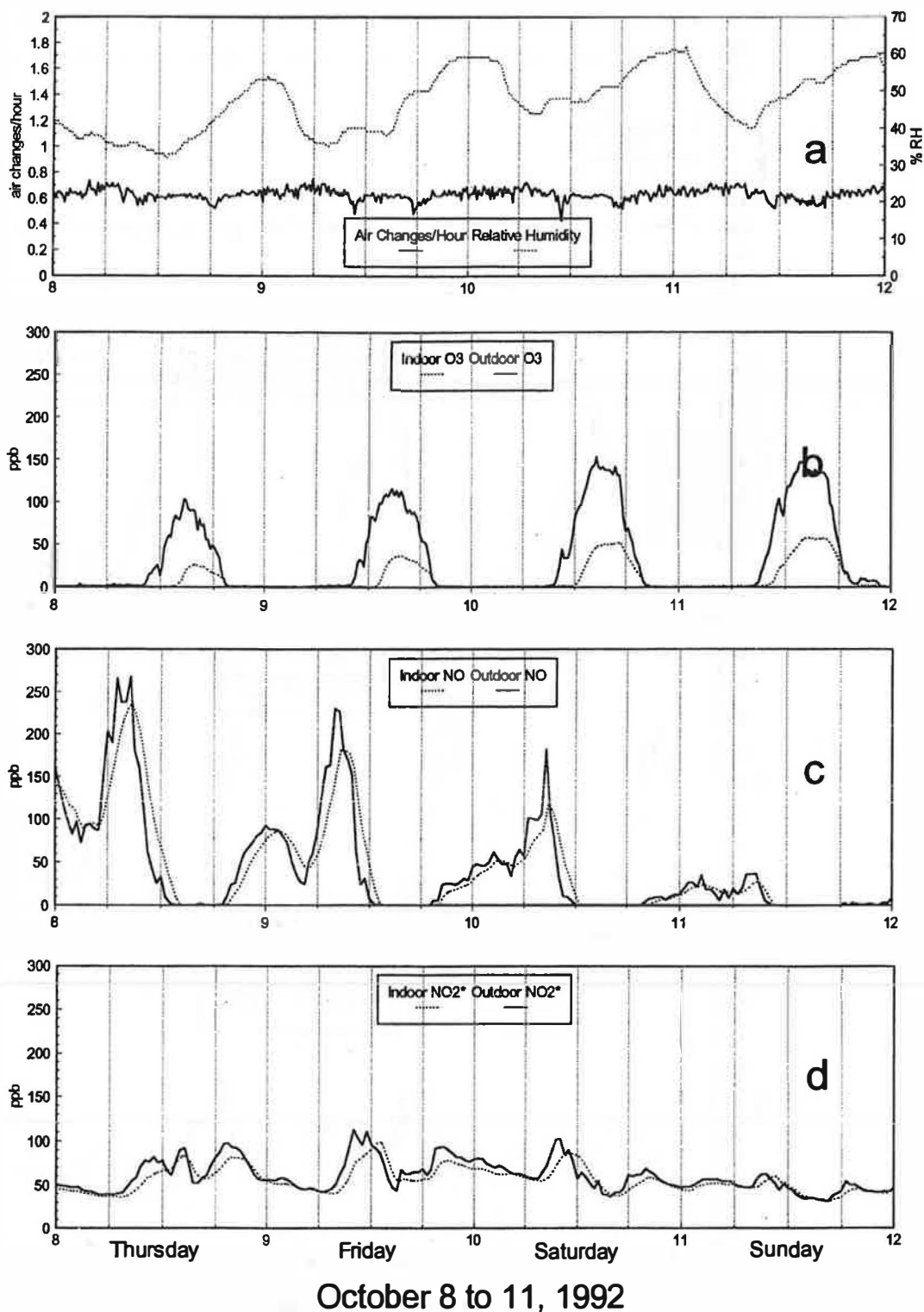


Figure 2. Parameters measured at the Burbank office from October 8 to 11, 1992. (a) Air exchange rates (solid line) and indoor relative humidities (dotted line). (b) Indoor O_3 (dotted line) and outdoor O_3 (solid line). (c) Indoor NO (dotted line) and outdoor NO (solid line). (d) Indoor NO_2^* (dotted line) and outdoor NO_2^* (solid line).

The relative humidity values plotted in Figures 1a–4a are those measured indoors on the first floor. The relative humidity at this location has ranged from lows of 12% in late fall and early winter to highs of 65% during the summer. The temperature at the measurement location is normally between 22 and 25.5 °C. The upper limit for the relative humidity appears to be determined by the maximum water content of the conditioned air (14 °C) immediately downstream of the wet cooling coils. During

the summer months, the relative humidity frequently stays at values close to the maximum for several consecutive weeks. From November through January, inclusive, there are periods when the relative humidity drops below 20%.

Indoor–Outdoor O_3 , NO, and NO_2^* . Figures 1b–4b, 1c–4c, and 1d–4d display indoor and outdoor concentrations of O_3 , NO, and NO_2^* , respectively, for the representative 4-day periods. For each of these species, during all four seasons, the indoor concentrations closely track

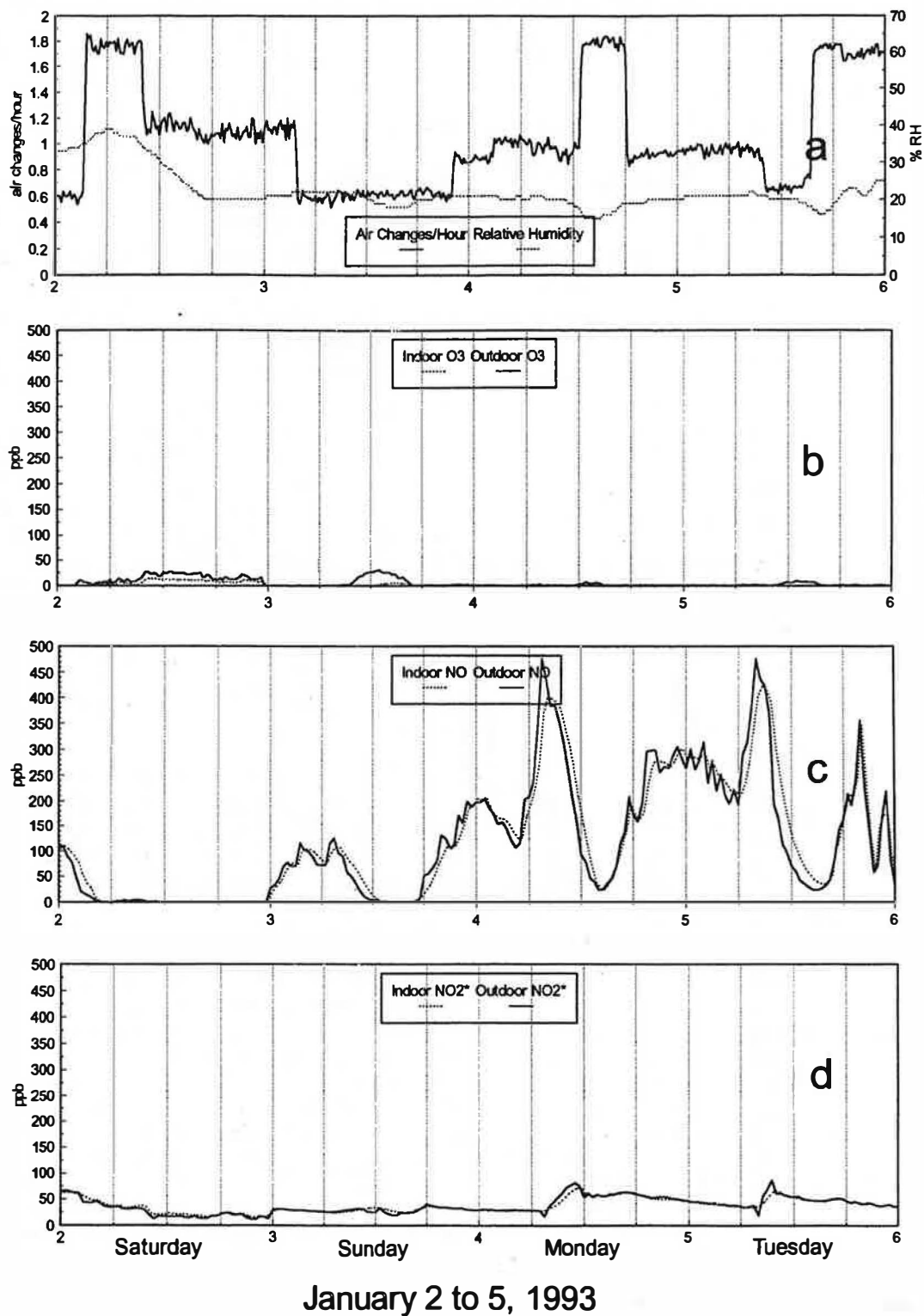


Figure 3. Parameters measured at the Burbank office from January 2 to 5, 1993. (a) Air exchange rates (solid line) and indoor relative humidities (dotted line). (b) Indoor O₃ (dotted line) and outdoor O₃ (solid line). (c) Indoor NO (dotted line) and outdoor NO (solid line) and outdoor NO₂* (solid line). (d) Indoor NO₂* (dotted line) and outdoor NO₂* (solid line).

the outdoor concentrations, indicating the importance of outdoor-to-indoor transport. Indeed, apart from chemical transformations occurring indoors (see below), no indoor sources for any of these species have been identified. (Possible O₃ sources, such as electrostatic precipitators, photocopiers, or laser printers, and NO_x sources, such as combustion appliances or smoking, are not present.) As expected, the air exchange rate strongly influences how closely the indoor levels approach the outdoor levels (see

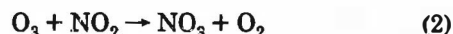
ref 2 and references contained therein). During steady-state conditions, the indoor O₃ values are roughly 70% of the outdoor values at maximum air exchange rates and about 30% of the outdoor values at minimum air exchange rates. The indoor/outdoor ratios (*I/O*) for NO and NO₂* are larger than those for O₃. For a given air exchange rate, *I/O* (NO) > *I/O* (NO₂*) > *I/O* (O₃). This is consistent with a smaller surface removal rate for NO₂ than for O₃ (24) and a smaller surface removal rate for NO than for

increase (see Figure 4). The O_3/NO reaction has several effects: (i) The decay of indoor NO is faster than expected from its outdoor profile and the air exchange rate. (ii) Conversely, the growth of indoor O_3 is slower than expected from its outdoor profile, the air exchange rate, and the rate at which it is scavenged by indoor surfaces. (iii) Indoor NO_2^* tends to peak very close to the region where the falling NO concentration equals the rising O_3 concentration (the crossover point); furthermore, this indoor NO_2^* peak is often higher than expected from the corresponding outdoor profile, the air exchange rate, and the rate at which NO_2 is scavenged by indoor surfaces. Such behavior is evident in Figure 4 (April 8, ~12:30 p.m., and April 11, ~10:30 a.m.) Crossover points also occur when NO is rising and O_3 is falling (in the early evening). Near these evening crossovers: (i) the decay of indoor O_3 is faster than expected; (ii) the growth of indoor NO is slower than expected; and (iii) indoor NO_2^* again peaks. The observations just described are evident at selected times during spring, summer, and fall (e.g., in addition to Figure 4, see Figures 1 and 2—the reader is cautioned to examine periods when the air exchange rate is constant). At the indoor crossover points, NO and O_3 coexist at concentrations high enough for the reaction between them to contribute significantly to indoor levels of NO_2 . This interplay among indoor O_3 , NO, and NO_2 is not observed in the winter months, presumably because the indoor levels of O_3 , even at their maxima, are quite small (see Figure 3).

Outdoor sources of NO are present 24 h a day. The near-zero levels of NO that are often recorded from early afternoon to early evening reflect titration of emitted NO by photochemically generated oxidants coupled with high afternoon mixing depths. Although it is still emitted, NO is not accumulating during these periods. In a related sense, the measured concentration of outdoor O_3 reflects an ongoing titration between O_3 and NO; it is a *net* concentration. The measured amount of *indoor* O_3 also is a *net* concentration; it is the concentration that remains after any NO accumulated indoors or introduced from outdoors has been titrated. An analogous statement holds true for indoor NO.

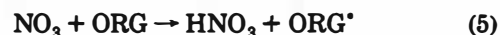
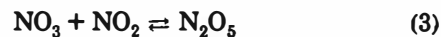
Axley et al. (26) have recently developed and applied a series of dynamic mathematical models to a subset of this data—the period from September 15 to 24, 1992. The data were modeled with and without homogeneous chemistry. The simulation that included the O_3/NO reaction matched the observed indoor measurements much better than the simulation without this chemistry.

Homogeneous Reaction between O_3 and NO_2 . The gas phase reaction



has a second-order rate constant, k_2 , of 7.87×10^{-7} ppb⁻¹ s⁻¹ (0.0028 ppb⁻¹ h⁻¹) at 25 °C (25). Outdoors, during daylight hours, this reaction is of little consequence since the nitrate radical, NO_3 , is photolytically unstable. On the other hand, outdoors, at night, nitrate radical concentrations as high as 430 ppt have been measured (27) with concomitant O_3 and NO_2 concentrations of 79 and 35 ppb, respectively. Indoors, given the absence of direct sunlight, reaction 2 may be comparably important. Once formed, the nitrate radical and NO_2 are in equilibrium with dinitrogen pentoxide, N_2O_5 , reaction 3; either dinitrogen pentoxide reacting with water, reaction 4, or the

nitrate radical reacting with an organic (ORG), reaction 5, can contribute to the formation of nitric acid indoors (9, 10):



Given that indoor concentrations of volatile organic compounds are normally larger than those outdoors (29, 30), the nitrate radical abstraction of an H-atom from an organic (reaction 5) may be the dominant pathway to gas phase nitric acid indoors (10). Reaction 4, the homogeneous hydrolysis of N_2O_5 is relatively slow (28). Evidence suggests that the analogous heterogeneous reaction, mediated by surface moisture, is much faster. Indoors, with large surface-to-volume ratios, this heterogeneous process may be important. The resulting hydrolysis, producing dissociated nitric acid (H^+ and NO_3^-) in moisture adsorbed on indoor surfaces, will not contribute to gas phase nitric acid but may cause damage to materials.

The O_3/NO_2 reaction is not expected to have a significant effect on the indoor concentration of either reactant (see Sources and Sinks). However, this reaction does appear to be, at times, a significant source of indoor nitric acid. Such is the case during the majority of mid-afternoon periods from April through October. During these periods, the indoor O_3 concentration is normally greater than 25 ppb, the indoor NO_2^* concentration is normally greater than 30 ppb, and the reaction sequence described in eqs 2–5 has the potential to generate indoor nitric acid at greater than 2.1 ppb h⁻¹. At this rate, the contribution of the O_3/NO_2 reaction to indoor nitric acid would be more than 0.7 ppb, assuming an air exchange rate of 1 h⁻¹ and a surface removal rate for HNO_3 of 2 h⁻¹ (about twice the value for O_3 at Burbank). This estimate is supported by more detailed calculations, using dynamic models, that Axley et al. have applied to a September 1992 subset of the Burbank data (26).

Since indoor NO_2^* at the Burbank site has a median concentration close to 40 ppb and seldom drops below 25 ppb, indoor O_3 is expected to normally be the limiting reagent in the production of indoor nitric acid via the O_3/NO_2 reaction. That is, indoor nitric acid production by chemical reactions is expected to rise and fall with indoor O_3 levels.

Heterogeneous NO_2 Reactions Producing HONO. From the data collected during this study and a simple mass-balance model (2, 24), we have calculated first-order rate constants for the surface removal of NO_2^* at the Burbank facility. The values are derived from indoor/outdoor ratios (I/O) under steady-state conditions and corresponding air exchange rates, excluding periods when the O_3/NO reaction might contribute significantly to indoor NO_2 . The resulting surface removal rates are between 0.10 and 0.16 h⁻¹ and tend to increase with increasing relative humidity, matching the observations of Yamanaka (21). These rates are significantly smaller than those reported in the literature (see Table 5 in ref 24 and Table 1 in ref 16). The difference apparently is due to the unusually small surface-to-volume ratio (A/V) at the Burbank office. [The first-order rate constant for surface removal is the product of v_a and A/V (24).] In the offices

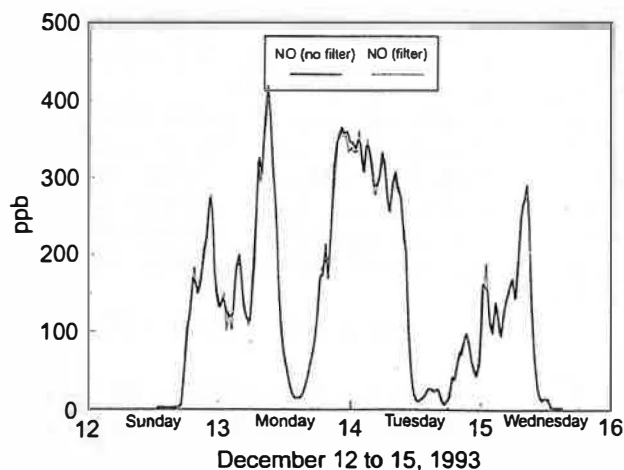


Figure 5. Indoor NO concentrations measured using two different sampling lines, one with a sodium carbonate filter (dotted line) and the other without (solid line).

and test homes described in previous studies, A/V 's were estimated at between 2.5 and 3.3 m^{-1} . At Burbank, the nominal value for A/V is 0.5 m^{-1} . Even if the actual value is closer to 1.0 m^{-1} , due to other surfaces present within the Burbank office, the surface-to-volume ratio is still much less than in the earlier studies. If one assumes a value for A/V at the Burbank switching office of 0.8 m^{-1} , then the values for $v_d \text{NO}_2$ lie between 3.5×10^{-3} and 5.6×10^{-3} cm/s.

The salient point is that NO_2 is scavenged by indoor surfaces at a rate that makes surface removal a significant sink. For the rates of air exchange at the Burbank site, 0.3–1.9 ach, and in the absence of O_3/NO chemistry, we anticipate an indoor/outdoor ratio for NO_2^* between roughly 0.7 and 0.95. However, from late fall through early spring, there are numerous periods when I/O (NO_2^*) is larger than one would calculate from the measured air exchange rate. For example, in Figure 4, during the period from April 9 at 8:00 p.m. to April 10 at 4:00 a.m., at which point the air exchange rate E_x increased sharply, one would anticipate I/O (NO_2^*) to be about 0.85 [$I/O = E_x / (v_d \text{NO}_2(A/V) + E_x) = 0.7 / (0.12 + 0.7)$]. Instead, I/O (NO_2^*) is close to unity during this period. This raises the question: which compound(s) among the species that constitute NO_2^* —namely, NO_2 , HNO_3 , HONO , and PAN—is(are) responsible for the greater than anticipated indoor concentrations of NO_2^* ? For reasons that follow, we suggest that HONO , produced indoors, is responsible for the observed “excess” amounts of indoor NO_2^* (i.e., higher than expected I/O).

For a period from 12/12 to 12/15/93, the NO_x meter was modified so that air sampling alternated between two indoor lines rather than between indoors and outdoors. The switching cycle was the same as that used for indoor/outdoor measurements (see Experimental Section). The only difference between the two indoor sampling lines was that one of them contained a 47-mm quartz fiber filter impregnated with sodium carbonate. The sodium carbonate filter efficiently removes HONO and HNO_3 from the sampled air without affecting the NO and NO_2 concentrations. The NO measurements made with the two different sampling lines are shown in Figure 5; there is no significant difference between measurements made with either line. The NO_2^* measurements made with the two different sampling lines are shown in Figure 6. In this case, the measurements made with the line containing the sodium carbonate filter are often 5–10 ppb lower than

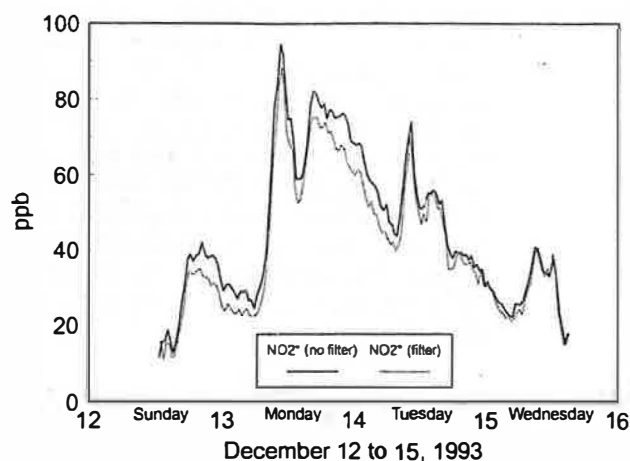
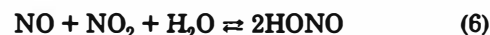


Figure 6. Indoor NO_2^* concentrations measured using two different sampling lines, one with a sodium carbonate filter (dotted line) and the other without (solid line).

those made with the line that did not contain the filter. The differences are attributable to HONO and/or HNO_3 in the indoor air. However, for several reasons, indoor HNO_3 concentrations during this period are inferred to be close to zero: (i) from 12/12 to 12/15/93, sunrise occurred at $\sim 6:50$ a.m.; sunset occurred at $\sim 4:45$ p.m.; the maximum elevation of the sun above the horizon was 33° ; and, consequently, photochemical production of HNO_3 is expected to be small (5). (ii) The expectation of low HNO_3 levels is reinforced by earlier HNO_3 measurements, covering an entire year, at a Burbank location (31). In this data set, the month of December had the lowest HNO_3 concentrations, with all measurements during December below 1.3 ppb (see Figure 3 in ref 31). Assuming an I/O for HNO_3 of 0.5, this means that corresponding indoor HNO_3 never exceeded 0.7 ppb. (The I/O of 0.5 was calculated using a simple mass balance model, assuming a surface removal rate for HNO_3 at Burbank that is twice that of O_3 , and using the measured air exchange rate from 12/12 to 12/15/93 of 1.7 ach.) (iii) Throughout the period from 12/12 to 12/15/93, the outdoor ozone concentrations at the Burbank site never exceeded 25 ppb, and for 80% of the time, the outdoor levels were less than 2 ppb. Using O_3 as a surrogate for HNO_3 (9), this implies that outdoor HNO_3 never exceeded 2.5 ppb, while indoor HNO_3 never exceeded 1.8 ppb and, actually, was close to zero for most of the experiment. Assuming then that the NO_2^* differences in Figure 6 are due to HONO , did the HONO infiltrate from outdoors, or was it produced indoors? HONO is photolytically unstable and does not accumulate in the presence of sunlight. Hence, during daylight hours, it appears that the differences in the NO_2^* measurements (e.g., see Figure 6, Monday, between 6:50 a.m. and 4:45 p.m.) are due primarily to HONO that has been produced indoors. During hours of darkness, additional HONO may enter the office from outdoors. However, in Figure 6 day/night differences in the amounts of “excess” NO_2^* cannot be distinguished.

A number of studies have demonstrated the formation of HONO in indoor settings or in large exposure chambers (see ref 16 and references cited therein). Pitts et al. were the first to make such an observation (17). The homogeneous reaction



is too slow, compared with typical air exchange rates, to

serve as the source of HONO; the forward rate constant has a value of $1.3 \times 10^{-13} \text{ ppb}^{-2} \text{ h}^{-1}$ while the reverse rate constant has a value of $8.4 \times 10^{-5} \text{ ppb}^{-1} \text{ h}^{-1}$ (32). Hence, indoor HONO generation has been presumed to be a consequence of heterogeneous chemistry. Among the more recent studies, Spicer et al. (16) have demonstrated the indoor production of HONO from the reaction of NO_2 with surfaces inside a test house; a production rate of $0.055 \text{ h}^{-1} [\text{NO}_2]$ was observed. They postulate that HONO is derived from the disproportionation of NO_2 in aqueous surface films, reaction 7, followed by the equilibration shown in reaction 8:

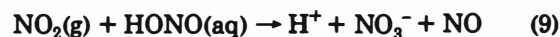


They demonstrate the occurrence of the latter reaction through an experiment in which a room containing HONO(g) is ventilated and resealed; HONO offgases from surfaces to establish a new equilibrium. Brauer et al. (22) have reported HONO production as a result of NO_2 /surface reactions in a series of chamber studies and have noted that the production increases with increasing relative humidities and decreasing air exchange rates. Spengler et al. (33) measured HONO in homes located in Albuquerque, NM, and found HONO concentrations ranging from 5% to 15% of the measured indoor NO_2 concentrations. The differences shown in Figure 6 are comparable. The cited studies support the conclusion that, at times, the heterogeneous production of HONO occurs within the Burbank office.

HONO and O_3 Indoors. Examination of the data collected during this study suggest that indoor HONO(g) is not present in significant amounts when indoor O_3 concentrations are high [i.e., during such periods, $I/O (\text{NO}_2^*)$ is not higher than expected, taking into account the periodic influence of the O_3/NO reaction]. A possible explanation involves the aqueous surface films alluded to in reactions 7 and 8. In aqueous solution, HONO with a pK_a of 3.29 (6), is in equilibrium with its conjugate base, the nitrite ion (NO_2^-). The latter species is oxidized by O_3 at a rate that increases with pH; at 25°C , the reported rate is $200[\text{H}^+]^{-1}[\text{NO}_2^-][\text{O}_3(\text{aq})] \text{ s}^{-1}$ (34). Is this reaction fast enough to play a role in indoor chemistry at the Burbank site? Assuming an O_3 concentration of 30 ppb within the Burbank office and given a Henry's law coefficient of 0.01 M atm^{-1} at 25°C (6), the O_3 concentration in an aqueous surface film can be estimated to be about $3 \times 10^{-10} \text{ M}$. If the aqueous surface film has a pH of 5, then the half-life of NO_2^- in such a solution is approximately 2 min. [We recognize the limitations of an aqueous surface film calculation based on bulk water measurements (20); the calculation is for illustrative purposes.] This simple estimate suggests that the aqueous reaction between O_3 and NO_2^- is potentially fast enough to be significant when indoor O_3 concentrations are high. Additional details regarding reactions and rate expressions for the aqueous-phase oxidation of nitrite to nitrate have been presented by Seinfeld (see pp 229–234 in ref 6). In summary, if HONO is present in aqueous films on indoor surfaces, NO_2^- will also be present; as O_3 enters this environment, it will oxidize nitrite to nitrate; the rate of this process, as well as the HONO/ NO_2^- ratio, depends on the pH. If HONO(g) is in equilibrium with HONO(aq),

and if the indoor O_3 concentration is greater than the sum of HONO(g) + HONO(aq), this process has the potential to convert most of the HONO within the building to nitrate in aqueous surface films.

Heterogeneous NO_2 Reactions Producing NO. In a series of chamber studies, Spicer et al. (35) have demonstrated that NO_2 /surface reactions also are a source of NO. Depending on the nature of the surface, the NO may result from direct reduction of NO_2 on the surface or may be produced from a mechanism, such as



Common building materials that reduced NO_2 in these studies included masonite, ceiling tile, plywood, plasterboard, bricks, polyester carpet, wool carpet, acrylic carpet, and oak paneling. In some cases up to 15% of the NO_2 scavenged by indoor surfaces was re-emitted as NO.

At Burbank, there are times when the indoor level of NO actually exceeds the outdoor level. For example, at the beginning of the day on January 4, 1993 (Figure 3), the indoor NO concentration actually peaked at a slightly higher value than outdoor NO. Furthermore, as can be seen in Table 1, the median value of indoor NO during the month of December 1992 was slightly larger than the corresponding outdoor value (85 vs 82 ppb); a similar relationship between the median values occurred during the month of January 1993 (63.9 ppb indoors vs 60.8 ppb outdoors). There are no combustion sources within the Burbank facility, yet an indoor source of NO is needed to explain these observations. The most likely source is the set of NO_2 /surface reactions just discussed. The modeling studies by Axley et al. (26), referenced earlier, support this hypothesis. They have found that an indoor source of NO is needed to explain the manner in which the indoor NO concentration varies with the outdoor NO concentration. Their dynamic models produced a better fit to the measured data after a term was added that accounted for NO_2 -to-NO conversion on indoor surfaces.

Sources and Sinks. The relative importance of the various "sources" (rates at which a pollutant enters indoor air) and "sinks" (rates at which a pollutant is removed from indoor air) for O_3 , NO, and NO_2 can be examined in the context of a one-compartment mass balance model (7). Expressions for the sources and sinks at the Burbank site and values for the relevant parameters are summarized in Table 2. It is the balance among these terms, often changing in periods as short as a few minutes, that determines the resultant indoor concentrations measured at any particular point in time.

The only identified source of indoor O_3 at the Burbank site is outdoor air that is either introduced intentionally (ventilation) or unintentionally (infiltration): $E_x[\text{O}_3]_{\text{out}}$, where E_x is the air exchange rate and $[\text{O}_3]_{\text{out}}$ is the outdoor concentration of O_3 .

There are two identified sources for NO: ventilation/infiltration from outdoors and surface reactions involving NO_2 . It is difficult to compare the relative magnitudes of these two sources. The latter depends on the nature of the surface and other factors that are not well understood, including indoor O_3 which may retard the surface-mediated reduction of NO_2 . During most of the periods monitored in this study, ventilation/infiltration dominates any NO produced by NO_2 /surface reactions. For a further discussion of the latter, see Spicer et al. (35).

Table 2. Sources and Sinks for O₃, NO, and NO₂ within the Burbank Office

pollutant	source	measured values	comments
O ₃	$E_x[\text{O}_3 \text{ outdr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
NO	$E_x[\text{NO outdr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
NO	$k_{s \text{ sur}}[\text{NO}_2 \text{ inodr}]$	$k_{s \text{ sur}}$; surface dependent	variable
NO ₂	$E_x[\text{NO}_2 \text{ outdr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
NO ₂	$k_1[\text{O}_3 \text{ inodr}][\text{NO inodr}]$	$k_1 = 1.6 \text{ ppb}^{-1} \text{ h}^{-1}$	variable
pollutant	sink	measured values	comments
O ₃	$E_x[\text{O}_3 \text{ inodr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
O ₃	$v_d \text{ O}_3(A/V)[\text{O}_3 \text{ inodr}]$	$v_d \text{ O}_3(A/V) = 0.8\text{--}1.0 \text{ h}^{-1}$	significant
O ₃	$k_1[\text{NO inodr}][\text{O}_3 \text{ inodr}]$	$k_1 = 1.6 \text{ ppb}^{-1} \text{ h}^{-1}$	variable
O ₃	$k_2[\text{NO}_2 \text{ inodr}][\text{O}_3 \text{ inodr}]$	$k_2 = 0.0028 \text{ ppb}^{-1} \text{ h}^{-1}$	negligible
NO	$E_x[\text{NO inodr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
NO	$v_d \text{ NO}(A/V)[\text{NO inodr}]$	$v_d \text{ NO}(A/V) < 0.02 \text{ h}^{-1}$	negligible
NO	$k_1[\text{O}_3 \text{ inodr}][\text{NO inodr}]$	$k_1 = 1.6 \text{ ppb}^{-1} \text{ h}^{-1}$	variable
NO ₂	$E_x[\text{NO}_2 \text{ inodr}]$	$E_x = 0.3\text{--}1.9 \text{ h}^{-1}$	significant
NO ₂	$v_d \text{ NO}_2(A/V)[\text{NO}_2 \text{ inodr}]$	$v_d \text{ NO}_2 = 0.1\text{--}0.16 \text{ h}^{-1}$	variable
NO ₂	$k_2[\text{O}_3 \text{ inodr}][\text{NO}_2 \text{ inodr}]$	$k_2 = 0.0028 \text{ ppb}^{-1} \text{ h}^{-1}$	negligible

There also are two identified sources for NO₂: ventilation/infiltration and the O₃/NO reaction. The O₃/NO reaction can be comparable in magnitude to ventilation/infiltration at crossover points (see Table 2; e.g., if [NO₂ outdr] = 40 ppb and [O₃ inodr] = [NO inodr] = 5 ppb). However, at most other times, when the concentration of either indoor O₃ or indoor NO is close to zero, the O₃/NO reaction is a negligible NO₂ source.

Potential sinks for O₃ are transport from indoors to outdoors (exhaust/exfiltration), $E_x[\text{O}_3 \text{ inodr}]$; removal by indoor surfaces, $v_d \text{ O}_3(A/V)[\text{O}_3 \text{ inodr}]$; reaction with indoor NO, $k_1[\text{NO inodr}][\text{O}_3 \text{ inodr}]$; and reaction with indoor NO₂, $k_2[\text{NO}_2 \text{ inodr}][\text{O}_3 \text{ inodr}]$. The relative importance of the various sinks can be gauged by comparing typical values for each of these terms (Table 2, third column). The air exchange rate, E_x , and the rate constant for surface removal, $v_d \text{ O}_3(A/V)$, are comparable—0.3–1.9 and 0.8–1.0 h⁻¹, respectively. The O₃/NO reaction has a rate constant of 1.6 ppb⁻¹ h⁻¹ at 25 °C; a simple calculation reveals that even an indoor NO concentration as low as 0.5 ppb creates a sink comparable to exhaust/exfiltration or surface removal. However, when the indoor NO concentration approaches zero, this sink also approaches zero. The O₃/NO₂ reaction occurs at a rate much slower than the other terms and is only significant when the indoor NO₂ concentration is quite high (>100 ppb). In summary, the important sinks for indoor O₃ are air exchange, scavenging by indoor surfaces, and at times the O₃/NO reaction. This last sink varies with time and is likely to be most significant at crossover points.

The major sinks for NO are exhaust/exfiltration, $E_x[\text{NO inodr}]$ and during appropriate conditions, reaction with indoor O₃, $k_1[\text{O}_3 \text{ inodr}][\text{NO inodr}]$. Surface removal is not a significant sink for NO, as is apparent from the results in this study and reports from other studies (16). The argument comparing E_x and $k_1[\text{O}_3 \text{ inodr}]$ as potential NO sinks is analogous to that presented above for potential O₃ sinks; the $k_1[\text{O}_3 \text{ inodr}]$ sink will be most significant at crossover points.

Air exchange, $E_x[\text{NO}_2 \text{ inodr}]$, and surface removal, $v_d \text{ NO}_2(A/V)[\text{NO}_2 \text{ inodr}]$, are the major sinks for NO₂. The latter process is somewhat variable since the deposition velocity, $v_d \text{ NO}_2$, increases with increasing relative humidity. The rate of the O₃/NO₂ reaction is relatively slow. Unless

indoor O₃ concentrations are unusually high (>100 ppb), this reaction is a negligible sink for NO₂.

Other Reactions Involving Indoor O₃. The measurements made in this study clearly demonstrate the presence of O₃ within a commercial building. From mid-March through October, between the hours of 2 and 5 p.m., the indoor concentration of O₃ is normally above 25 ppb. These observations are of interest not just in terms of O₃ exposures, but also in terms of a wide variety of indoor chemistry driven by O₃. Indoor O₃ reacts with selected unsaturated organic compounds yielding aldehydes and organic acids (36–38). Furthermore, indoor O₃ chemistry may be a source of free radicals indoors. Reactions of indoor O₃ with monoterpenes and other alkenes can generate hydroxyl radicals (ref 39 and references cited therein). The O₃/NO₂ reaction generates nitrate radicals, and these, in turn, may contribute to the formation of peroxy and hydroxy radicals indoors (40).

Implications for Materials. Preliminary measurements at Burbank suggest that gas phase species, as opposed to airborne particles, may contribute more than 90% of the nitrogen-containing salts found on active metal surfaces. (This work will be the subject of a future publication.) Some of these species may result from the reaction of gas phase nitric and nitrous acid with the metal surface. Others may be derived from the disproportionation of NO₂ on surfaces to yield nitrous and nitric acid. This is likely given the high median concentration observed for indoor NO₂* throughout the year (35–45 ppb) and its relatively high surface removal rate (~0.10–0.16 h⁻¹). Indoor O₃ may eventually oxidize some of the surface nitrites to nitrates. The relative importance of these processes remains to be determined. However, it is apparent that particulate filters, which do not remove these gaseous pollutants, are not sufficient to prevent the accumulation of nitrate and nitrite salts on electronic equipment surfaces. Such salts are not only corrosive but over time can also bridge conductive paths on circuit packs—paths that are intended to be electrically insulated from one another (1). Such contaminated packs are poised to fail as a consequence of current leakages and shorts when the relative humidity exceeds the deliquescence point of the accumulated salts.

Summary and Conclusions

The photochemical pollutants measured at Burbank are common to southern California, a region that contains almost 10% of the U.S. population. However, these pollutants are not limited to this area. Most major metropolitan regions in the United States experience elevated levels of photochemically generated pollutants, especially during the summer months. Results derived from the Burbank Study have broad applicability.

Buildings exist to protect their occupants and their contents from the outdoor environment. The Burbank building successfully guards against wind, rain, and temperature extremes. However, this study demonstrates that it provides only fractional, if any, protection from gaseous pollutants such as O₃, NO, and NO₂* (NO_x - NO). The indoor concentration of each of these species roughly tracks its outdoor concentration. Indoor O₃ concentrations at the Burbank site vary from 30 to 70% of outdoor levels and can reach values in excess of 100 ppb. Indoor NO concentrations are close to those outdoors and can exceed

500 ppb. The levels of indoor NO₂* are consistently high throughout the year (median value ~40 ppb); at times, nitrous acid, nitric acid, and PAN contribute to this value.

Although outdoor concentrations are a major factor influencing the indoor concentrations of O₃, NO, and NO₂*, detailed analyses of the data reveal significant chemical interactions among these indoor compounds. (i) Indoors, O₃ reacts rapidly with NO to produce NO₂. The process is most apparent during periods when the indoor concentrations of O₃ and NO cross, typically late morning and early evening. The evidence for the reaction includes faster decay and slower growth of the respective reactants coupled with a larger peak in the indoor concentration of NO₂* than would be anticipated if the reaction did not occur. (ii) Indoors, O₃ also reacts with NO₂, although more than 500 times slower than with NO. The reaction has a much greater relative effect on the concentrations of its products, which include HNO₃, than its reactants. Its occurrence is inferred from periods, typically mid-afternoon from late spring to early fall, when the indoor concentrations of O₃ and NO₂ are large enough that the rate of reaction should be comparable to the air exchange rate. (iii) The reaction of NO₂ with indoor surfaces can ultimately produce gas phase HONO. Evidence for the production of HONO within the Burbank site includes occasional I/O ratios for NO₂* that require an indoor source (most often observed from late fall to early spring) as well as a set of December 1993 measurements using sodium carbonate filters. The latter indicated the indoor presence of an acidic nitrogen oxide; this was presumably HONO since, for several reasons, the indoor concentration of HNO₃ was deemed negligible at the time of the experiment. (iv) Indoor NO₂ also can react with surfaces to produce NO. The evidence that this occurs at Burbank comes from periods when the I/O ratio for NO was greater than unity. Since there are no indoor combustion processes at this site, the only apparent source is NO₂/surface reactions similar to those reported by Spicer et al. (35).

Indoor O₃ and NO do not coexist at high concentrations, since O₃ rapidly oxidizes NO to NO₂. The indoor formation of both HNO₃ and HONO are favored by high relative humidities and low air exchange rates. HNO₃ is produced when O₃ and NO₂ coexist at elevated levels, while the NO₂/surface reactions that generate HONO and NO are more likely to be observed in the absence of O₃. Indeed, the presence or absence of indoor O₃ strongly influences speciation among the indoor nitrogen oxides.

A number of recent studies have indicated that chemistry (i.e., molecular transformations) occurs in indoor environments (8-10, 16, 36-38). This study further demonstrates that indoor pollutants can interact with one another, altering their own concentrations and those of their products. We seek to understand the factors that influence the indoor concentration of a given pollutant. This study demonstrates that such understanding requires attention not only to the pollutant in question but also to any pollutant to which it is related through chemistry (as either a reactant or product).

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