

Nitrous Acid, Nitrogen Dioxide, and Ozone Concentrations in Residential Environments

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Nitrous acid (HONO) may be generated by heterogeneous reactions of nitrogen dioxide and direct emission from combustion sources. Interactions among nitrogen oxides and ozone are important for outdoor photochemical reactions. However, little is known of indoor HONO levels or the relationship between residential HONO, NO₂, and O₃ concentrations in occupied houses. Six-day integrated indoor and outdoor concentrations of the three pollutants were simultaneously measured in two communities in Southern California using passive samplers. The average indoor HONO concentration was 4.6 ppb, compared to 0.9 ppb for outdoor HONO. Average indoor and outdoor NO₂ concentrations were 28 and 20.1 ppb, respectively. Indoor O₃ concentrations were low (average 14.9 ppb) in comparison to the outdoor levels (average 56.5 ppb). Housing characteristics, including community and presence of a gas range, were significantly associated with indoor NO₂ and HONO concentrations. Indoor HONO levels were closely correlated with indoor NO₂ levels and were about 17% of indoor NO₂ concentrations. Indoor HONO levels were inversely correlated with indoor O₃ levels. The measurements demonstrated the occurrence of substantial residential indoor HONO concentrations and associations among the three indoor air pollutants. **Key words:** indoor air, indoor/outdoor concentrations, nitrogen dioxide, nitrous acid, ozone, residence. *Environ Health Perspect* 110:145–149 (2002). [Online 10 January 2002] <http://ehpnet1.niehs.nih.gov/docs/2002/110p145-150lee/abstract.html>

Indoor fuel combustion has been identified as one of the most important factors that influences indoor air pollution. Indoor air pollutants arising from gas combustion include nitrogen dioxide and other nitrogen species. NO₂ has been the focus of indoor nitrogen oxides due to its health effects (1). NO₂ is produced by oxidation of atmospheric nitrogen during high-temperature fuel combustion. The oxidant properties of NO₂ can cause adverse health effects, including throat irritation, cough, and dyspnea (2). Several epidemiologic investigations have found an association between NO₂ exposure increased by indoor combustion sources and adverse respiratory health effects (1).

Nitrogen dioxide can react with surface materials commonly present indoors. Nitrous acid (HONO) is one of the possible gaseous products of heterogeneous NO₂ reactions with water on indoor surfaces (3). Indoor HONO concentration from the heterogeneous reactions can be affected by indoor NO₂ concentration, ventilation rate, surface material, available surface area, temperature, and humidity (4). In addition, HONO is formed directly by combustion processes (5). The presence of indoor HONO as a substantial portion of total oxides of nitrogen was suggested by a high removal rate of NO₂ on indoor surfaces, the formation of HONO by heterogeneous NO₂ reactions, and a relatively long lifetime for HONO (5).

A few studies have measured residential HONO concentrations because measurement of HONO at the relevant levels has been technically difficult. However, these limited measurement efforts have demonstrated that indoor levels are higher than outdoor levels. In Albuquerque, New Mexico, 24-hr average concentrations of HONO in 10 homes with gas ranges were between 2 and 8 ppb (6). In southwest Virginia, indoor 24-hr HONO levels were significantly higher than outdoor levels both in summer and winter (7). Winter indoor HONO levels of 5.46 ± 3.75 ppb and 2.43 ± 0.14 ppb were observed in houses with and without gas ranges, respectively. Higher indoor HONO levels were observed at night in a study conducted in Rome, Italy; indoor HONO levels peaked in the range of 10–21 ppb (8). In this study, long-term average residential indoor HONO concentrations were not reported.

Outdoor HONO concentrations are usually lower than indoor levels, reflecting the fact that HONO is photolytically unstable. Annual average ambient HONO levels ranged from 0.1 to 1.4 ppb across 24 U.S. and Canadian communities monitored between 1988 and 1991 (9). The highest annual average ambient HONO concentration recorded was 1.4 ppb in Livermore, California. In an urban area of Sweden, predawn 1-hr maximum HONO levels ranged from 1.3 to 3.9 ppb (10). The outdoor HONO levels were correlated with ambient NO₂ concentrations.

Low, but persistent, daytime HONO levels in Lubbock, Texas, ranged from 0.1 to 0.5 ppb, whereas night levels peaked at 1–2 ppb (11). In Rome, night peak HONO concentrations ranged from 3 to 6 ppb (8).

HONO is one of the generators of hydroxyl radical in photochemical smog formation. The acidity, reactivity, and aqueous solubility of HONO suggest its potential respiratory toxicity. When asthmatics were exposed to 650 ppb of HONO for 3 hr, they demonstrated mild alterations in lung function and reported mild symptoms of lung irritation (12). In other controlled human exposure studies of healthy individuals, irritation to the mucous membrane was determined at concentrations of 77 and 395 ppb of HONO for 3.5 hr (13). However, the effect on human health of long-term exposure to low concentrations of HONO is unknown.

The potential toxicity of HONO and the presence of indoor HONO sources support the need for residential HONO measurements. In addition, many earlier analyses of NO₂ actually measured several oxides of nitrogen, including HONO (14). It is possible that results of previous epidemiologic studies were confounded by the presence of other nitrogen oxides species, including HONO. Indoor HONO can be generated from heterogeneous NO₂ reactions and indoor combustion. In this study we measured residential HONO and NO₂ levels in homes participating in a chronic ozone exposure study conducted in Southern California.

Heterogeneous reactions of nitrogen oxides have been shown to vary with sources, meteorology, and ambient O₃. There are limited data on residential indoor HONO levels in California and elsewhere. Indoor reactions may also vary among indoor locations as well

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as within location across time (15). Additionally, interactions among nitrogen oxides and O₃ have been recognized as important for outdoor photochemical reactions, but little attention has been paid to indoor reactions. In one study in which indoor measurements of multiple pollutants were performed, the authors reported an inverse association between indoor O₃ and nitrogen oxides (15). These measurements were performed in a sparsely occupied, air-conditioned telephone switching building. In our study we substantially expand the information available on indoor residential concentrations of HONO, NO₂, and O₃. We performed the integrated 6-day measurements in 119 residences in two communities in Southern California. The objectives of this study were to measure residential indoor and outdoor HONO levels along with NO₂ and O₃ concentrations and to examine the relationships among housing factors and pollutants.

Materials and Methods

In April and May 1996, HONO, NO₂ and O₃ concentrations were measured in 119 homes. The homes were recruited from an ongoing 12-month study measuring indoor and outdoor concentrations and personal exposure to ozone of elementary school-age children in two communities in Southern California. Details of this “Harvard Southern Chronic Ozone Exposure Study” are described elsewhere (16). Among the 119 houses, 57 were located in Upland (valley site) and the remaining 62 were in towns located in the mountains at the eastern end of San Bernardino County (mountain site). Measurements occurred in the last four sampling cycles of the study, with approximately 25% of the homes sampled each cycle. Complete housing characteristic information was available for 111 houses. Informed consent was obtained.

HONO concentrations were measured using a passive sampler constructed from a 37-mm diameter polystyrene air sampling cassette containing a glass fiber filter coated

with a 2% sodium carbonate solution (17). The exposed filter was analysed by ion chromatography after treatment with hydrogen peroxide. The sampling rate was 100.4 mL/min and the lower detection limit was 0.2 ppb over the 6-day sampling period. Measurements below the detection limit were assigned to 50% of the detection limit, or 0.1 ppb, for the following analyses.

NO₂ concentrations were measured with a filter badge that absorbed NO₂ on a cellulose fiber filter coated with a triethanolamine solution (18). Samples were analyzed spectrophotometrically. The overall mass transfer coefficient of the sampler was 0.1 cm/sec (19). The lower detection limit of the sampler was 0.5 ppb over the 6-day sampling period.

O₃ concentrations were measured using the Harvard passive O₃ sampler (20). The filter of the passive sampler was coated with a nitrite-containing solution. The nitrite ion on the filter of the passive sampler is oxidized to nitrate ion in the presence of O₃. The exposed sampler was analyzed for nitrate ion by ion chromatography. Given sufficient face velocity, sampling rates of the passive sampler were 21.6 cm³/min and 21.3 cm³/min for outdoor and indoor sampling, respectively. The lower detection limit of the sampler was 1.2 ppb over the 6-day sampling period. Measurements below the detection limit were assigned to 50% of the detection limit, or 0.6 ppb, for the following analyses.

Trained field technicians deployed and collected the samplers. Indoor samplers were placed in living rooms, and outdoor samplers were placed near the houses and protected from rain. Residents completed a questionnaire describing housing factors.

Results

Average indoor HONO and NO₂ concentrations were significantly higher than outdoor concentrations, whereas indoor O₃ concentrations were significantly lower than outdoor concentrations, as shown in Table 1. The average indoor HONO concentration was 4.6 ppb, and the average outdoor HONO

concentration was 0.9 ppb. Average indoor and outdoor NO₂ concentrations were 28 and 20.1 ppb, respectively. The mean (± SD) of the ratio of indoor to outdoor NO₂ was 2.08 ± 1.69. Average indoor and outdoor O₃ concentrations were 14.9 and 56.5 ppb, respectively. The mean (± SD) ratio of indoor to outdoor O₃ was 0.24 ± 0.18.

Twenty-two pairs of the HONO passive samplers were collocated. Precision (i.e., the SD of the absolute difference between each pair) of the HONO passive sampler was 0.98 ppb. Relative precision was 23.5%. Twenty-one pairs of the NO₂ passive samplers were collocated. Precision of the NO₂ measurements was 2.5 ppb and relative precision was 12.6%. Results of the duplicate passive samplers are shown in Figure 1.

Housing characteristics of the two communities are shown in Table 2. Housing characteristics were significantly associated with indoor HONO and NO₂ concentrations, including the community (valley vs. mountain), presence of an air conditioner, and presence of a gas range, as shown in Table 3. No single housing characteristic was associated with indoor O₃ concentration, but outdoor O₃ concentrations were significantly higher in the mountain site than in the valley site. Indoor HONO and NO₂ concentrations were significantly higher in the valley site than in the mountain site. When the houses had an air conditioner or gas range, both indoor HONO and NO₂ concentrations were significantly higher. The presence of an air conditioner was significantly associated with the

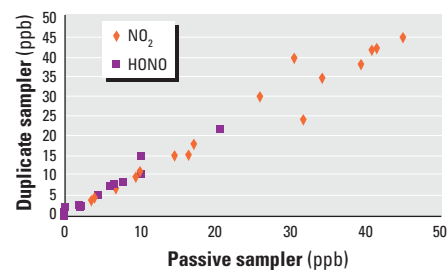


Figure 1. Precision of passive samplers for NO₂ and HONO.

Table 1. HONO, NO₂, and O₃ concentrations (ppb).

Pollutant, location	No.	Mean ± SD	Med	Min	90th percentile	95th percentile	Max	No. < LOD	t-Test	p-Value
HONO										
Indoor	99	4.6 ± 4.3	3.3	0.1	9.7	12.3	21.1	40	7.62	< 0.001
Outdoor	102	0.9 ± 2.3	0.1	0.1	1.7	7.1	12.2	82		
Indoor/outdoor ^a										
NO ₂										
Indoor	92	28.0 ± 12.6	28.9	4.3	43.1	49.3	52.0	0	3.99	< 0.001
Outdoor	88	20.1 ± 14.0	17.4	3.2	39.3	42.1	47.8	0		
Indoor/outdoor	87	2.08 ± 1.69	1.33	0.22	4.51	5.41	10.62			
O ₃										
Indoor	106	14.9 ± 13.3	11.1	0.6	34.2	41.0	67.8	9	-16.38	< 0.001
Outdoor	100	56.5 ± 22.3	49.8	18.4	89.6	95.7	160.1	0		
Indoor/outdoor	96	0.24 ± 0.18	0.19	0.01	0.53	0.65	0.75			

Abbreviations: LOD, limit of detection; Max, maximum; Med, median; Min, minimum.

^aIndoor/outdoor of HONO was excluded due to a large number of measurements < LOD.

community (chi-square test, $p < 0.01$). Ninety-three percent of the valley homes had an air conditioner in contrast to only one mountain home.

Associations between house characteristics and indoor/outdoor ratios for NO_2 and O_3 are shown in Table 4. The indoor/outdoor ratios for HONO were not evaluated because only 14 houses had both indoor and outdoor HONO levels above the detection limit. The indoor/outdoor NO_2 ratio was significantly associated with community, presence of an air conditioner, presence of a gas range, and number of bedrooms. The ratio of indoor to outdoor NO_2 levels was significantly higher in the mountain site, although indoor NO_2 concentrations were significantly higher in the

valley site. The indoor/outdoor NO_2 ratio was higher in the houses with a gas range and more than 3 bedrooms. The ratio of indoor to outdoor O_3 was significantly associated with community ($p < 0.05$), the presence of an air conditioner, and the number of bedrooms ($p < 0.1$).

The relationships between indoor and outdoor concentrations of the three air pollutants were determined by Pearson correlation coefficients, as shown in Table 5. The analysis was confined to houses for which all three pollutants were measured simultaneously. Indoor HONO concentrations were significantly correlated with indoor NO_2 , indoor O_3 , and outdoor NO_2 concentrations. Indoor NO_2 concentrations were significantly correlated

with outdoor NO_2 concentrations. Indoor O_3 concentrations were significantly correlated with outdoor O_3 concentrations.

Associations between indoor HONO, O_3 , and NO_2 and outdoor NO_2 levels were determined by a stepwise multiple regression analysis. Outdoor NO_2 level was excluded from the analysis at a significance level of 0.05. Indoor HONO was correlated negatively with indoor O_3 and positively with indoor NO_2 .

$$\begin{aligned} \text{Indoor HONO} = & 2.65 - 0.13 \\ & \times \text{Indoor } \text{O}_3 + 0.15 \\ & \times \text{Indoor } \text{NO}_2, \quad [1] \end{aligned}$$

where $n = 74$ and $r = 0.65$.

Indoor HONO concentrations were inversely correlated with indoor O_3 concentrations, as shown in Figure 2. Indoor HONO and O_3 concentrations were simultaneously measured in 89 houses. We performed a linear regression analysis for indoor HONO as a function of indoor NO_2 for the 76 houses where both were measured simultaneously (Figure 3). Indoor HONO levels were about 17% of indoor NO_2 levels. The 95% confidence interval for the ratio of indoor HONO to indoor NO_2 was 0.14–0.21. No single housing characteristic was significantly associated with the ratio of indoor HONO to indoor NO_2 concentrations. However, the ratio of indoor HONO to indoor NO_2 was slightly higher in homes with electric ranges

Table 2. Housing characteristics of the two communities.

Variables	Valley	Mountain
No. of houses	56	55
No. of bedrooms (mean \pm SD)	3.6 \pm 0.9	3.7 \pm 1.0
Presence of gas range		
Yes	43	46
No	12	9
Presence of air conditioning		
Yes	51	1
No	4	54
Presence of humidifier		
Yes	15	27
No	41	28
Window open		
Sometimes	12	6
Often	44	4

Table 3. Housing characteristics significantly associated with indoor HONO, NO_2 , and O_3 concentrations

Variable	HONO				NO_2				O_3			
	No.	Mean \pm SD	t-Test	p-Value	No.	Mean \pm SD	t-Test	p-Value	No.	Mean \pm SD	t-Test	p-Value
Community												
Valley	43	5.6 \pm 4.6	2.31	0.023	48	33.8 \pm 9.2	4.97	0.000	49	13.4 \pm 8.5	-1.07	0.286
Mountain	47	3.5 \pm 3.8			47	21.7 \pm 13.4			52	16.3 \pm 17.0		
Presence of air conditioner												
Yes	39	5.4 \pm 4.6	-1.69	0.094	44	32.3 \pm 9.7	-3.26	0.002	45	12.7 \pm 8.1	1.35	0.182
No	50	3.9 \pm 4.0			42	23.8 \pm 13.9			55	16.4 \pm 16.6		
Presence of humidifier												
Yes	32	2.6 \pm 2.6	3.34	0.010	31	24.5 \pm 13.9	2.19	0.032	37	18.0 \pm 16.8	-1.72	0.089
No	58	5.6 \pm 4.7			56	30.5 \pm 11.6			64	13.2 \pm 11.0		
Presence of gas range												
Yes	72	4.8 \pm 4.6	-1.48	0.142	68	30.7 \pm 12.4	-3.45	0.001	83	15.6 \pm 14.1	-0.96	0.338
No	17	3.1 \pm 2.5			18	19.7 \pm 10.4			17	12.1 \pm 11.2		

Table 4. Housing characteristics significantly associated with indoor/outdoor NO_2 and O_3 concentrations.

Variable	Indoor/outdoor NO_2				Indoor/outdoor O_3			
	No.	Mean \pm SD	t-Test	p-Value	No.	Mean \pm SD	t-Test	p-Value
Community								
Valley	45	1.07 \pm 0.25	-7.21	0.000	48	0.28 \pm 0.19	2.59	0.011
Mountain	37	3.24 \pm 2.00			43	0.19 \pm 0.16		
Presence of air conditioner								
Yes	40	1.07 \pm 0.26	6.13	0.000	44	0.26 \pm 0.18	-1.69	0.095
No	41	3.03 \pm 2.01			46	0.20 \pm 0.17		
Presence of humidifier								
Yes	29	1.94 \pm 1.27	0.41	0.683	32	0.28 \pm 0.23	-1.52	0.133
No	53	2.10 \pm 1.95			59	0.22 \pm 0.15		
Presence of gas range								
Yes	64	2.27 \pm 1.88	-2.26	0.027	74	0.24 \pm 0.18	-0.53	0.599
No	17	1.22 \pm 0.52			16	0.22 \pm 0.19		
No. of bedrooms								
≤ 3	39	2.45 \pm 2.12	2.09	0.040	42	0.27 \pm 0.21	1.68	0.096
> 3	42	1.66 \pm 1.19			48	0.21 \pm 0.15		

than in those with gas ranges (0.22 ± 0.21 vs. 0.16 ± 0.14).

Discussion

Indoor and outdoor NO_2 levels were similar to those reported in other studies conducted in Southern California (21). Lower ambient outdoor HONO levels are expected because HONO photolyzes fairly quickly outdoors. However, HONO formed indoors is less susceptible to photolysis. Spicer et al. (5) have shown that HONO has a low surface removal rate, only 0.02–0.05/hr greater than the removal of nonreactive tracer gas due to the air exchange rate. This is significantly lower than the surface removal rate of NO_2 (5). The HONO measurements reported in the present study clearly establish that HONO levels tend to be higher in homes than outdoors.

The precisions of the HONO and NO_2 passive samplers were comparable to previously reported values (17,18). During the entire 12-month sampling period, the relative precision of the passive O_3 sampler was 12% for indoor and 4% for outdoor samplers (16). Forty percent of the indoor HONO measurements were below the 0.2 ppb detection limit for the 6-day monitoring period, and 80% of the outdoor HONO measurements were below the detection limit. The number of HONO samplers that recorded values below the detection limit was significantly higher than expected. Longer sampling times for outdoor HONO samplers may be necessary in future studies.

HONO is a weak acid ($\text{pK}_a = 3.35$), but at the pH of the body fluids that it is likely to come in contact with during respiration, it should be almost completely ionized. The potential physiologic relevance of low levels of indoor HONO might be explored using an approach similar to that described by

Spengler et al. (22) that utilized chamber studies in which children received hydrogen ion doses comparable to those that would be experienced during acid aerosol events. Controlled human exposures of HONO are more limited. If we assume that a dose value of 395 ppb HONO over 3.5 hr is needed to cause mucous membrane irritation (13), the delivered dose is approximately 1,278 μg ($\approx 760 \mu\text{g}/\text{m}^3 \text{ HONO} \times 8 \times 10^{-3} \text{ m}^3/\text{min}$ breathing rate $\times 210$ min). At indoor levels of 10 ppb (90th percentile in this study), an adult (15 m^3/day breathing rate) and a child (10 m^3/day breathing rate) would have the equivalent delivered dose of hydrogen ion from HONO in about 4.5 days and 6.6 days, respectively. This simple estimate assumes constant exposure and does not include activities and concentrations that vary across time. Calculation of the biologically relevant acid dose to children and adults is obviously more complicated than this simple estimation. Nonetheless, the above example demonstrates that indoor exposures to even a weak acid may be relevant. Given the prevalence in the Southern California residences, it is reasonable to consider indoor HONO as an important contributor to hydrogen ion exposures.

A few housing factors were associated with indoor HONO and other pollutants. The community (mountain vs. valley) was significantly associated with both indoor HONO and NO_2 levels. Homes with an air conditioner and a gas range had higher indoor NO_2 concentrations. Homes with an air conditioner had lower O_3 concentrations, indicating either greater removal or lower air exchange rates. Pandian et al. (23) and Suh et al. (24) both have shown that homes with air conditioners have lower air exchange rates. Earlier, Dockery and Spengler (25) reported

that the impact of environmental tobacco smoke concentrations was twice as large for air-conditioned homes than for non-air-conditioned homes, suggesting lower ventilation rates. Because both HONO and NO_2 have indoor sources, it is reasonable to expect high concentrations in the homes that have lower air exchange. However, the lack of a significant association for HONO with the housing factors studied may indicate that there may be other factors that influence indoor HONO concentrations.

Houses with humidifiers had lower HONO levels. Increased humidity from humidifier should have increased moisture on surfaces thus increasing aqueous phase heterogeneous formation of HONO in the presence of NO_2 (15). In addition to a larger formation rate, more moisture on surfaces would also mean a larger reservoir for HONO (5,26). However, our measurements do not support this hypothesis. Unfortunately, we do not have information regarding the use of humidifiers or indoor relative humidity during this study, which limits our ability to interpret the association. The influence of indoor moisture and humidification on HONO production rate needs to be investigated further in more detailed field and chamber studies.

Although HONO was higher in homes with higher NO_2 , the relationship between indoor HONO and cooking on a gas range was not obvious. Because housing characteristics and ambient concentrations of all pollutants were different between the valley and mountain sites, it was difficult to see a clear relationship between indoor HONO and cooking on a gas range. Under controlled conditions, Traynor et al. (27) showed that gas ranges emit HONO at about 11% the rate of NO_2 emissions. Variations in other variables across the homes studied here and the fact that cooking times were not recorded prevented us from examining the direct impacts from cooking on a gas range.

Community was associated with all three contaminants. Indoor and outdoor O_3 levels were higher in the mountain sites than in the valley sites. The difference between communities for indoor O_3 was not statistically significant. However, indoor and outdoor NO_2 levels and indoor HONO levels were significantly lower in mountain sites. In this study, the community was significantly associated with ambient levels and housing characteristics influencing residential ventilation rates. It is possible that the association between community and the three air pollutants may be different when ambient ozone levels are different. Indoor measurements of NO_2 and HONO were made in Albuquerque, New Mexico, during a period when ambient O_3 was low (6). Indoor HONO levels ranged

Table 5. Pearson correlation coefficient between air pollutants.

	Indoor HONO	Indoor NO_2	Indoor O_3	Outdoor HONO	Outdoor NO_2
Indoor NO_2	0.511**	—	—	—	—
Indoor O_3	-0.514**	-0.136	—	—	—
Outdoor HONO	-0.021	-0.186	-0.223*	—	—
Outdoor NO_2	0.352**	0.602**	-0.052	-0.083	—
Outdoor O_3	-0.180	-0.220*	0.556**	-0.092	-0.341**

* $p < 0.05$; ** $p < 0.01$.

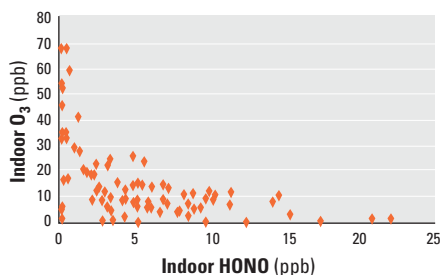


Figure 2. Association between indoor HONO and indoor O_3 concentrations.

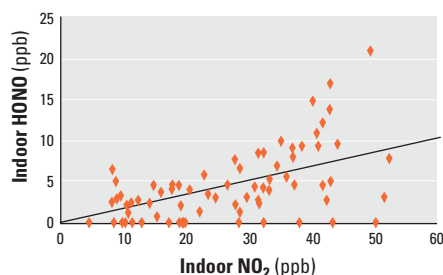


Figure 3. Association between indoor NO_2 and HONO concentrations. $Y = 0.03 + .017X$; $r = 0.51$; $n = 76$.

from 5 to 15% of indoor NO₂ concentrations. The relationship between indoor NO₂ and HONO (6) was less than that found here, suggesting a possible role of O₃ and indoor moisture in the relationship.

Although indoor HONO is partially generated from heterogeneous NO₂ reactions, previously reported associations between HONO and NO₂ levels in residences are available only from a few homes. None of the previous measurements included O₃ concentrations (6,28). In the current study, the average ratio of indoor HONO to indoor NO₂ was 0.17 (95% confidence interval, 0.14–0.21), slightly higher than those recorded in previous studies. Brauer et al. (28) found ratios in two research homes at peak NO₂ concentrations to be on the order of 0.1–0.12. In the Albuquerque study, in which indoor NO₂ concentrations were reported as averages of bedroom, living room, and kitchen NO₂ concentrations, the average ratio of HONO to NO₂ was 0.08 (6). The ratio of HONO to NO₂ levels ranged from 0.03 to 0.15. Indoor HONO is generated by indoor sources and heterogeneous NO₂ reactions; the heterogeneous NO₂ reactions are affected by various environmental conditions. The different ratios may be due to differences of NO₂ concentration, ventilation rate, surface material, available surface area, temperature, and humidity.

Comparisons of indoor HONO and O₃ levels indicate that indoor HONO levels are high only when indoor O₃ concentrations are low. Weschler et al. (15) reported a similar inverse correlation in a telephone switching office. The authors suggested that this reflected the rapid reaction of ozone with nitrite ions in aqueous surface films. HONO in the gas phase is in equilibrium with HONO in sorbed moisture films on surfaces (5,26). HONO in the aqueous surface films, in turn, is in equilibrium with its conjugate base, the nitrite ion. Ozone rapidly oxidizes the nitrite ion to nitrate. When indoor ozone concentrations are elevated, nitrite ions in aqueous surface films are rapidly oxidized to nitrate ions. This process depletes the surface reservoir of HONO, which ultimately reduces the gas phase concentration of HONO. Hence, an inverse correlation between indoor O₃ and indoor HONO is anticipated.

The indoor O₃ and HONO concentrations reported in this study are average concentrations over a 6-day period. However, it is well established that O₃ concentrations vary in a diurnal fashion. If indoor O₃ and HONO concentrations had been measured with sufficient time resolution to fully capture their daily concentration changes, the inverse correlation between these two pollutants would be expected to be even stronger than that observed in the current study.

Differential assessment of health effects associated with NO₂ and HONO may be difficult in community studies because of potential confounding factors. Indoor HONO is correlated with indoor NO₂; however, substantial home variation of HONO is not explained by indoor NO₂ measurements. Potential health effects of HONO would not be completely determined by measuring NO₂ only. Characterization of outdoor NO₂, HONO, and O₃ in the Southern California communities alone did not predict indoor HONO concentrations. Including indoor O₃ improves the correlation between indoor HONO and indoor NO₂, with an increase in the coefficient of correlation from 0.51 to 0.65. However, housing characteristics that could be considered proxies for surface area, surface wetness, and air exchange rates did not lead to any substantial improvement of HONO prediction.

Conclusion

Six-day residential HONO, NO₂, and O₃ concentrations were simultaneously measured using passive samplers. Indoor HONO levels were higher than outdoor HONO levels. Several housing characteristics, including community and the presence of a humidifier, were significantly associated with both indoor NO₂ and HONO concentrations. Additional housing factors, primarily presence of a gas range or air conditioner, were associated with indoor NO₂ levels. No housing characteristic was significantly associated with indoor O₃ concentrations, but factors associated with higher air exchange rates were associated with higher indoor/outdoor ratios for O₃. Indoor HONO levels were correlated with indoor NO₂ levels and inversely correlated with indoor O₃ levels. Indoor HONO levels were about 17% of indoor NO₂ levels. No significant amounts of HONO were measured when indoor O₃ levels were high. The measurements demonstrated the occurrence of substantial residential indoor HONO concentrations and showed association between indoor HONO, NO₂, and O₃ concentrations.

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