

# Indoor Exposures to Fine Aerosols and Acid Gases

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Indoor exposures to aerosols and gases are associated with both indoor and outdoor air pollution sources. The identification of sources and the assessment of their relative contribution can be a complicated process due to *a*) the presence of numerous indoor sources, which can vary from building to building; *b*) the uncertainties associated with the estimation of the impact of outdoor sources on indoor air quality; *c*) the interactions between pollutants; and *d*) the importance of reactions between pollutants and indoor surfaces. It is well established that fine particles (diameter  $\leq 2.5 \mu\text{m}$ ) originating from outdoor sources such as automobiles, oil and coal combustion, incineration, and diverse industrial activities can penetrate into the indoor environment. Indoor/outdoor ratios, usually varying between 0.4 and 0.8, depend on parameters such as particle size and density, air exchange rate, and the surface-to-volume ratio of the indoor environment. Determining fine particle elemental composition makes it possible to identify the contribution of different outdoor sources. This paper focuses on the origin and the concentration of indoor aerosols and acid gases by highlighting the results from two indoor air quality studies.

## Introduction

Assessing total human exposures requires knowledge of indoor pollutant concentrations for two primary reasons: individuals spend a great fraction of their life indoors, especially in cold climates; and indoor pollutant concentrations can be significantly different from those outdoors. Indoor exposures to aerosols and gases are associated with both indoor and outdoor air pollution sources. Identifying sources and assessing their relative contribution can be a complicated process due to: *a*) the presence of a number of indoor sources, which can vary from building to building; *b*) the uncertainties associated with estimating the impact of outdoor sources on the indoor environment; *c*) the interactions between pollutants indoors; and *d*) the importance of reactions between pollutants and indoor surfaces. In the proceeding sections, we discuss the origin and the concentrations of indoor aerosols and acid gases by presenting results from two indoor air quality studies.

## Fine Aerosols

From the health effects standpoint, only fine aerosol particles with an aerodynamic diameter  $\leq 2.5 \mu\text{m}$  can affect respiratory health. Coarse particles (aerodynamic diameter  $> 2.5 \mu\text{m}$ ) are efficiently removed by the upper respiratory system. Outdoor

fine particles are mostly secondary particles produced through gas/particle conversions. For example, condensation of metallic vapors during combustion or metal production processes forms fine particles rich in toxic metals. Incomplete combustion of oil, coal, gasoline, and other fuels used for production of electricity or transportation results in the formation of carbonaceous particles containing mutagenic and/or carcinogenic organic compounds; among the more important compounds are polycyclic aromatic hydrocarbons. Reactions of nitrogen and sulfur oxides released from internal or external combustion sources produce a great amount of acidic or metal aerosols such as  $\text{H}_2\text{SO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{NO}_3$ . Finally, biological aerosols such as pollen and spores can significantly contribute to total fine aerosol mass.

A large fraction of outdoor aerosols penetrate indoors and are mixed with particles originating from indoor sources. A great number of indoor aerosol sources, such as smoking, kerosene heaters, wood stoves, humidifiers, electric motors, frying, resuspension of particles, people and pets, or showering, have been identified by previous indoor air quality studies.

One of the most important questions that indoor air quality researchers have to answer before attempting to determine the contribution of indoor sources is what percentage of outdoor pollutants penetrates to the indoor environment. A comparison of the indoor/outdoor ratio of a pollutant that is uniquely associated with only outdoor sources is usually used to provide an estimate of the penetration rate of outdoor particles. Of course, this ratio reflects not only the penetrating ability of the pollutant but also its decay in the indoor environment. The penetration ability is a function of a number of parameters such as the nature of the pollutant, gas or particle, and mechanisms

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of home air exchange. The indoor decay rate of pollutants originating from the outdoor sources depends on the pollutant physicochemical properties and the home characteristics such as house surface and air exchange. Below we present a simple physical model and its application to an indoor air quality study conducted in two New York counties during the period of January 6 through April 15, 1986. Week-long fine particle mass samples were collected indoors and outdoors for a total of 596 samples in 394 homes. These samples were subsequently analyzed for fine mass using a microbalance and elemental composition using X-ray fluorescence. The homes were selected according to their potential indoor aerosol sources such as cigarette smoke, gas stoves, and heating sources. The simple physical model described below allows us to determine the contributions of indoor and outdoor sources to indoor mass and elemental concentrations.

Assuming steady state, the flux of particles originating from outdoors and indoors,  $Q_{os}$  and  $Q_{is}$ , balances the sum of the two fluxes: transport of aerosols from the indoor to outdoor environment,  $F_{out}$  and, removal of particles onto indoor surfaces by Brownian diffusion, and sedimentation,  $F_d$ .

$$Q_{os} + Q_{is} = F_{out} + F_d \quad (1)$$

The  $Q_{os}$  and  $F_{out}$ , in micrograms per hour for mass or in nanograms per hour for elements, can be expressed as a function of air exchange rate,  $\alpha$ , in exchanges per hour, and the house volume cubic meters:

$$Q_{os} = \alpha C_o V P \quad (2)$$

and

$$F_{out} = \alpha C_i V \quad (3)$$

where  $C_o$  and  $C_i$  are the outdoor and indoor aerosol concentrations, respectively, expressed in micrograms per cubic meter and nanograms per cubic meter for mass and elements, respectively, and  $P$  is the particle penetration efficiency, which is dimensionless.

The flux of indoor sources,  $Q_{is}$ , can be broken down into individual source fluxes:

$$Q_{is} = Q_{smoke} + Q_{wood} + Q_{kerosene} + Q_{other} \quad (4)$$

where

$$Q_{smoke} = c S_{smoke} / t \quad (5)$$

$$Q_{wood} = w S_{wood} / t \quad (6)$$

$$Q_{kerosene} = k S_{kerosene} / t \quad (7)$$

The terms  $Q_{smoke}$ ,  $Q_{wood}$ ,  $Q_{kerosene}$ , and  $Q_{other}$  are the fluxes of smoking, wood, kerosene, and sum of unknown indoor sources, respectively. The number of cigarettes smoked during the samp-

ling period is  $c$ ;  $w$  and  $k$  are, respectively, the use of wood burning and kerosene, expressed in hours. If there are other sources for which the use information is known, more flux terms would be used. No  $Q_{gas}$  was used because it was found that gas stoves do not contribute to mass or elemental concentrations. Furthermore,  $S_{smoke}$ ,  $S_{wood}$ , and  $S_{kerosene}$  are the source emission rates of smoke, wood, and kerosene sources, respectively, expressed in micrograms or nanograms per cigarette, micrograms per hour of wood burning, and micrograms or nanograms per hour of kerosene use, respectively.

The particle deposition flux,  $F_d$ , expressed in micrograms or nanograms per hour, is a function of deposition velocity (by diffusion and sedimentation),  $u_d$  in meters/hour, home floor surface,  $E$  in square meters, and  $C_i$ .

$$F_d = E u_d C_i \quad (8)$$

For a room with dimensions of 3 m  $\times$  4 m  $\times$  3 m, the room surface can be expressed as a function of room volume:  $E_r = 1.7V_r$ . Because the room surface is larger due to the presence of furniture, plants, and other furnishings, one can set  $E_r = 2V_r$  and for the total home surface  $E = 2V$ . Thus, Eq. (7) can be rewritten as follows:

$$F_d = 2V u_d C_i \quad (9)$$

Combining Eqs. (1), (2), (3), and (9) allows the determination of indoor concentration.

$$C_i = \frac{P \alpha C_o + Q_{is} / V}{\alpha + 2 u_d} \quad (10)$$

Since the  $\alpha$  and  $V$  presented little variability,  $0.51 \pm 0.28 \text{ hr}^{-1}$  and  $341 \pm 184 \text{ m}^3$ , respectively, and the variation of  $u_d$  is expected to be significant, one can determine the average penetration rate and contribution of indoor sources for different elements by regressing  $C_i$  and  $C_o$ , as shown in Eqs. (11) and (12).

$$P = \frac{B(\alpha + 2 u_d)}{\alpha} \quad (11)$$

$$Q_{is} = (C_i - B C_o)(\alpha + 2 u_d) V \quad (12)$$

where  $B$  is the slope of the regression  $C_i$  on  $C_o$ . Analysis of data for nonsource homes (no kerosene heaters, wood stoves, or cigarette smokers) reveals, as expected, that for most of the elements with important outdoor sources the regression slopes are significant. Such elements are Pb, Br, Se, Cd, Ni, V, Mn, and Ca, which had slopes equal to 0.52, 0.35, 0.34, 0.38, 0.61, 0.57, 0.52, and 0.59, respectively. The remaining elements and fine mass were found to have nonsignificant slopes. Most of these elements have significant indoor sources, as shown below. For these elements the slope values were set equal to the average of the significant slopes, 0.49. This is a good approximation considering that a small variation in this term will have little effect on the source apportionment of these elements which are mostly associated with indoor sources.

Table 1. Estimated emission rates of cigarette smoke, wood, kerosene, and other indoor sources.

	$S_{\text{smoke}}$ , ng/cigarette		$S_{\text{wood}}$ , ng/hr		$S_{\text{kerosene}}$ , ng/hr		$Q_{\text{other}}$ , ng/hr	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE <sup>a</sup>
Mass <sup>a</sup>	12,657	800	0 <sup>b</sup>	—	0	—	1,156	945
Si	0	—	44,318	15,605	194,767	44,317	10,855	13,131
S	65,410	32,174	0	—	1,514,692	372,550	57,742	80,482
Cl	68,896	10,246	0	—	0	—	2,650	2,278
K	159,215	13,517	92,054	35,160	163,860	60,452	5,952	7,943
Ca	0	—	37,983	14,105	0	—	5,486	6,259
V	373	99	0	—	0	—	159	280
Mn	0	—	0	—	0	—	114	195
Fe	0	—	0	—	0	—	3,071	5,350
Ni	0	—	0	—	0	—	52	119
Cu	0	—	0	—	15,360	2,826	999	1,031
Zn	1,166	420	0	—	0	—	909	1,142
As	0	—	0	—	0	—	61	104
Se	0	—	0	—	0	—	24	36
Br	3,045	435	0	—	0	—	420	704
Cd	318	69	0	—	1,070	273	0	—
Pb	0	—	0	—	0	—	762	2,111

<sup>a</sup>Fine particle mass unit is in micrograms per cubic meter.

<sup>b</sup>The source strength is set to zero if not significant at  $p = 0.05$ .

Assuming a deposition velocity,  $u_d$ , equal to 0.18 m/hr (1), one can calculate the penetration rate for the elements with significant outdoor sources. For instance, the P for Pb is 0.87. Dockery and Spengler calculated the penetration efficiency of fine sulfate particles (2) equal to 0.65. Of course, the value of P can vary among homes and present seasonal variability. Thus the determined value corresponds to these specific groups of homes in the winter season.

Using the determined value of B in Eq. (12), it is possible to estimate the strength of indoor sources,  $Q_{is}$ , for the nonsource homes. Because for these homes the flux of kerosene, smoking, and wood sources is zero,  $Q_{is}$  is equal to  $Q_{\text{other}}$  [see Eq. (4)]. Table 1 presents the calculated emission rates of indoor sources for the nonsource homes.

These results reveal that elements such as Pb, Se, Zn, Ni, Mn, V, Cd, and S are associated (more than 70%) with outdoor sources. However, the elements Si, Cl, K, Ca, Cu, and fine mass have significant indoor sources.

Furthermore, using Eq. (12) again, the flux of indoor sources,  $Q_{is}$ , was determined for the smoking home group. Note that the slopes for the different elements and deposition velocity parameters are the same as previously in the case of nonsource homes. Assuming that for the smoking homes the  $Q_{\text{other}}$  is equal to that estimated above for the nonsource homes, Eq. (4) can be used to determine the flux of the smoke source,  $Q_{\text{smoke}}$ , where  $Q_{\text{wood}}$  and  $Q_{\text{kerosene}}$  are set equal to zero. Subsequently, the emission rate of the cigarette smoke source,  $S_{\text{smoke}}$ , can be estimated from Eq. (5). The same procedure was employed to estimate  $S_{\text{wood}}$  and  $S_{\text{kerosene}}$  using the data from homes with only wood stoves or kerosene heaters, respectively.

Table 1 gives the determined  $S_{\text{smoke}}$ ,  $S_{\text{wood}}$ ,  $S_{\text{kerosene}}$ , and  $Q_{\text{other}}$  for the different elements and fine mass using home groups with single sources. Note that homes with fireplace use or pipe and cigar smoking are not included in these calculations.

Using Eqs. (4), (5), (6), (7), and (10), the indoor mass and elemental concentrations can be expressed as a function of parameters that can easily be determined.

$$C_i = BC_o + \frac{cS_{\text{smoke}} + wS_{\text{wood}} + kS_{\text{kerosene}}}{(\alpha + 2u_d)Vt} + \frac{Q_{\text{other}}}{(\alpha + 2u_d)V} \quad (13)$$

Using Eq. (13) we can calculate the contribution of outdoor and indoor sources. By dividing each term by the indoor concentration  $C_i$  and multiplying by 100, we can estimate the average percent contribution of these sources to mass and elemental concentrations. Tables 2 through 5 show the percent source contribution for source categories that contain more than seven homes. These same tables compare the observed mass and elemental concentrations with those predicted using Eq. (13) for the different source categories. For most of the comparisons, the geometric mean relative errors range between 20 and 50%. This suggests that the above calculations could be used to predict indoor aerosol concentrations.

Table 2. Percent source contributions to mass and elemental indoor concentrations for nonsource homes ( $n = 49$ ).<sup>a</sup>

Elements	Outdoor source	Other source	MRE <sup>b</sup>	Observed concentration <sup>c</sup>
Mass	60	40	25	15
Si	56	44	25	108
S	74	26	18	1083
Cl	45	55	30	27
K	56	44	38	67
Ca	57	43	27	79
V	78	22	30	5
Mn	81	19	26	3
Fe	65	35	32	39
Ni	84	16	26	2
Cu	22	78	62	8
Zn	72	28	29	31
As	66	34	35	1
Se	80	20	34	1
Br	63	37	31	6
Cd	100	0	60	0
Pb	84	16	33	28

<sup>a</sup>Number of homes with complete air exchange, house volume, and elemental data.

<sup>b</sup>Geometric mean relative error.

<sup>c</sup>Mass concentration expressed in micrograms per cubic meter, elemental concentration expressed in nanograms per cubic meter.

**Table 3. Percent source contributions to mass and elemental indoor concentrations for smoking homes ( $n = 77$ ).<sup>a</sup>**

Element	Outdoor source	Smoking source	Other source	MRE <sup>b</sup>	Observed concentration <sup>c</sup>
Mass	30	54	16	24	49
Si	57	0	43	46	109
S	69	11	20	23	1235
Cl	14	72	13	31	239
K	19	70	12	34	501
Ca	56	0	44	38	181
V	69	16	15	20	6
Mn	82	0	18	21	3
Fe	67	0	33	19	44
Ni	87	0	13	30	2
Cu	26	0	74	44	8
Zn	65	14	21	27	19
As	67	0	33	43	1
Se	83	0	17	35	0
Br	38	44	17	27	14
Cd	25	75	0	54	1
Pb	87	0	13	27	28

<sup>a</sup>Number of homes with complete air exchange, house volume, and elemental data.

<sup>b</sup>Geometric mean relative error.

<sup>c</sup>Mass concentration expressed in micrograms per cubic meter, elemental concentration expressed in nanograms per cubic meter.

**Table 4. Percent source contributions to mass and elemental indoor concentrations for wood-burning and smoking homes ( $n = 15$ ).<sup>a</sup>**

Element	Outdoor source	Smoking source	Wood source	Other source	MRE <sup>b</sup>	Observed concentration <sup>c</sup>
Mass	31	54	0	15	19	53
Si	41	0	32	27	122	90
S	69	13	0	18	9	1150
Cl	15	71	0	14	30	344
K	14	55	25	7	36	566
Ca	38	0	41	21	37	244
V	61	23	0	17	28	5
Mn	84	0	0	16	33	4
Fe	69	0	0	31	28	55
Ni	85	0	0	15	35	2
Cu	30	0	0	70	26	9
Zn	65	15	0	20	18	27
As	74	0	0	26	26	1
Se	85	0	0	15	35	1
Br	39	43	0	18	24	13
Cd	38	62	0	0	138	0
Pb	85	0	0	15	24	29

<sup>a</sup>Number of homes with complete air exchange, house volume, and elemental data.

<sup>b</sup>Geometric mean relative error.

<sup>c</sup>Mass concentration expressed in micrograms per cubic meter, elemental concentration expressed in nanograms per cubic meter.

Note that data from homes with more than one source were not used in the regression analysis for the determination of the fluxes,  $S_{smoke}$ ,  $S_{wood}$ , or  $S_{kerosene}$ . Therefore, calculation of source contributions for homes with multiple sources are based on source fluxes determined from data for single source homes. This was done for model validation purposes, and, as one can conclude from the data presented in Tables 4 and 5, the model predictions of indoor aerosol concentrations for homes which were not included in the original source flux calculations are also satisfactory.

**Table 5. Percent source contributions to mass and elemental indoor concentrations for kerosene heater and smoking homes ( $n = 13$ ).<sup>a</sup>**

Element	Outdoor source	Smoking source	Kerosene source	Other source	MRE <sup>a</sup>	Observed Conc. <sup>b</sup>
Mass	32	48	0	20	35	71
Si	24	0	53	22	44	290
S	37	7	43	12	37	2947
Cl	15	68	0	17	31	391
K	10	48	34	8	75	528
Ca	50	0	0	50	28	251
V	73	10	0	17	15	6
Mn	81	0	0	19	17	3
Fe	65	0	0	35	23	56
Ni	86	0	0	14	54	2
Cu	9	0	60	31	93	8
Zn	67	11	0	22	21	26
As	70	0	0	30	36	1
Se	83	0	0	17	17	1
Br	45	35	0	20	47	24
Cd	9	38	53	0	48	2
Pb	86	0	0	14	20	48

<sup>a</sup>Geometric mean relative error.

<sup>b</sup>Mass concentration expressed in micrograms per cubic meter, elemental concentration expressed in nanograms per cubic meter.

The preceding calculations allow for examining the origin of fine mass and different elements. For no source, wood burning, and kerosene homes, approximately 60 to 70% of the indoor mass concentrations is associated with outdoor sources, while the rest can be attributed to other indoor sources. Wood burning and kerosene do not contribute to indoor mass concentrations. For homes with smokers, smoking becomes the most important source, accounting for about 54%, while outdoor sources and other indoor sources account for 30 and 16%, respectively.

For all source groups indicated in Tables 2 through 5, Pb, Mn, Se, and Ni appear to be associated mostly with outdoor sources. These elements are tracers of outdoor sources and are expected to have originated from the outdoors exclusively. A small fraction (10–20%) of these elements could originate from resuspension of household dust. Cd is associated only with outdoor sources for the nonsource and wood-burning home groups, whereas for homes with smokers and/or kerosene heaters, outdoor source contributions of Cd range between 10 and 40%. For nonsource and wood-burning home groups, S is associated largely with outdoor sources. For homes with kerosene heaters, approximately 10% of S is associated with outdoor sources. Finally, Br is also associated mostly with outdoor sources. For homes with no cigarette smokers, approximately 70% of Br originates from outdoors, whereas for smoking homes, 40 to 50% comes from outdoors.

Manganese appears to have originated from outdoors, while silicon, which is another soil element, is associated with outdoor sources as well as kerosene heaters, wood burning, and other indoor sources. For no-source and cigarette-smoking homes, outdoor sources account for about 50 to 60% of the total indoor silicon concentration. The remaining 40 to 50% was attributed to other indoor sources which must be the resuspension of indoor dust. Finally, for the other groups, outdoor source contributions are reduced to approximately 30%. Furthermore, Fe, which is also a soil element, originates mostly from outdoor sources (60–70%). Other unknown indoor sources, mostly dust resus-

pension, account for the remaining 30%. No iron contribution of the major iron sources was found.

According to the model calculations, Cl, K, Ca, and Cu are mostly associated with indoor sources. For homes with no cigarette smokers, approximately 50% of the chlorine originates from outdoor sources, and the rest is associated with other unknown indoor sources, which could be related to the use of different consumer products (3,4). For homes with smokers, smoking accounts for 60 to 70% of the total indoor concentration. Similarly, Ca presents significant indoor sources. For non-wood-burning homes, approximately 50% of Ca is associated with outdoor sources, and the rest is attributed to unknown indoor sources which may be resuspension of indoor dust, particles formed during showering, or biological aerosols. For homes with wood burning, outdoor Ca contributions are reduced to 20 to 40% and the rest comes from wood burning and other unknown indoor sources. Potassium is related to all four indoor source types, smoking, wood burning, kerosene, and unknown indoor sources, as well as to outdoor sources. For no-source homes, approximately 56% of K originates from outdoors, while for homes with indoor sources, kerosene, smokers, or wood, outdoor source contributions are less than 30%. These results are in good agreement with those in previous studies (5). Finally, approximately 70 to 80% of Cu is related to indoor sources, possibly due to the use of vacuum cleaners, kitchen ventilation, or fans (4). Kerosene heaters can also contribute to indoor Cu aerosol concentrations.

## Gases

A number of gaseous pollutants with primarily outdoor sources, sulfur dioxide, nitrogen oxides, nitric acid, and ozone, can penetrate indoors. Most of these gases, which are directly related to major air pollution sources, for example, coal and oil combustion and automobiles, have been suspected of causing adverse effects, primarily on respiratory health. Essentially all the available information on exposure to airborne acidity has come from ambient monitoring studies where no indoor air measurements have been made. Epidemiological studies typically explore the relationship between indices of community respiratory health and ambient air concentrations as assessed by one or more fixed location ambient monitors. Such studies neglect indoor/outdoor concentration differences, as will be shown below.

## Indoor Air Quality Studies

In a recent study, simultaneous indoor and outdoor measurements in several private residences in the Boston area were made to determine the indoor infiltration of pollutants of outdoor origin, that is  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{HNO}_3$  (6,7). A total of 11 different homes were used for monitoring, 5 during late winter (March 1989) and 6 during summer (July–August 1989). The homes varied in age (5–120 years), volume (200–2000  $\text{m}^3$ ), and proximity to the urban center (1.25–35 km) in order to provide a varied sample of typical indoor and outdoor concentrations in the Boston area. During the winter phase of the study, all homes used unvented gas ranges for cooking, although all heating was by vented combustion or electricity. One of these homes was occupied by a light smoker. For the summer sampling period, four of the six homes lacked combustion appliances, and the remain

**Table 6. Geometric mean (and geometric SD) indoor/outdoor (I/O) ratios for acid gas species measured during summer and winter sampling periods.\***

Compound	Summer I/O ratio geometric mean (GSD)	Winter I/O ratio geometric mean (GSD)
$\text{SO}_2$	0.39 (1.57)	0.05 (1.71)
$\text{HNO}_3$	0.60 (1.53)	0.19 (3.22)
HONO	2.66 (1.51)	9.41 (2.37)
$\text{NO}_2$	0.94 (1.19)	NA

\*Values presented are mean values for daily indoor/outdoor comparisons. These ratios were skewed, particularly for cases where concentrations were close to the limit of detection, justifying the use of the geometric mean. NA, data not available due to insufficient number of samples.

ing homes used unvented gas ranges for cooking. None of these homes used air conditioners during the sampling periods. Summary results of the winter and summer sampling are represented in Table 6. Consistent with the results of previous investigations,  $\text{SO}_2$  concentrations were lower indoors than outdoors during both seasons. As a result of lower air exchange rates characteristic of weatherized homes in Boston during the winter, indoor/outdoor ratios of  $\text{SO}_2$  were significantly lower in the winter than in the summer. Lower air exchange rates will affect indoor concentrations by increasing the indoor residence time and the probability of gas collisions with indoor surfaces, reflected in terms of an elevated deposition rate. In both seasons indoor and outdoor concentrations were highly correlated with a higher slope for the summer period. These results are indicative of indoor  $\text{SO}_2$  concentrations that are highly dependent on the outdoor concentration and the air exchange rate. Even in the summer, the apparent  $\text{SO}_2$  penetration is quite low, suggesting deposition of the gas on surfaces.

Indoor/outdoor ratios of  $\text{HNO}_3$  were slightly higher than those of  $\text{SO}_2$ . The low indoor concentrations of  $\text{HNO}_3$  are due to the lack of indoor  $\text{HNO}_3$  production and its high deposition velocity (2.5–0.7 m/hr). As expected, outdoor concentrations were higher during the summer due to increased photochemical activity. Extremely little  $\text{HNO}_3$  was detected in the winter indoor samples, with nearly all measurements below the method detection limit (0.07 ppb). This result is consistent with reduced infiltration during winter. A significant correlation between indoor and outdoor  $\text{HNO}_3$  concentrations was found in the summer periods supporting our hypothesis that the major source of indoor  $\text{HNO}_3$  in these homes was the infiltration of the gas from outdoors. Furthermore, the temperature gradient between the bulk indoor air and the indoor wall surfaces will be greater in the winter than in the summer, consequently yielding a decreased aerodynamic resistance and a higher deposition velocity.

For reactive gases such as  $\text{SO}_2$  and  $\text{HNO}_3$ ,  $\alpha < u_d/h$ , thus  $\alpha$  can be omitted from the denominator of Eq. (13). Also, if no indoor sources exist,  $Q_{is} = 0$ , Eq. (13) can be rewritten as follows:

$$C_i = \frac{P \alpha C_o h}{u_d} \quad (14)$$

Thus,  $C_i/C_o$  is proportional to air exchange rate.

Indoor nitrous acid concentrations were greater than outdoor values in all homes, as shown in Table 6. In particular, indoor nitrous acid concentrations were elevated even in homes with no combustion appliances. This result, consistent with our previous investigation, is indicative of indoor nitrous acid production via

**Table 7. Regression of indoor acid gas concentrations on the corresponding outdoor concentrations.**

Compound	Season	<i>n</i> <sup>a</sup>	Slope $\pm$ SE	Intercept $\pm$ SE	<i>R</i> <sup>2</sup>
SO <sub>2</sub>	Summer	28	0.55 $\pm$ 0.04	NS <sup>b</sup>	0.89
SO <sub>2</sub>	Winter	16	0.12 $\pm$ 0.02	NS	0.73
HNO <sub>3</sub>	Summer	28	0.46 $\pm$ 0.09	NS	0.47
HONO	Summer	28	1.40 $\pm$ 0.32	1.05 $\pm$ 0.30	0.42
HONO	Winter	22	3.16 $\pm$ 1.05	3.15 $\pm$ 0.92	0.30
NO <sub>2</sub>	Summer	29	0.87 $\pm$ 0.07	NS	0.84

<sup>a</sup> Number of valid observations above limit of detection. Relationships not included in the table had nonsignificant slopes ( $p < 0.01$ ).

<sup>b</sup>NS, not significant at  $p < 0.01$ .

reactions of nitrogen oxides that have penetrated indoors from the outdoor air. Reduction of NO<sub>2</sub> on indoor surfaces results in the formation of nitrous acid. Formation of nitrous acid through homogeneous gas-phase reactions is not important due to the fact that the characteristic time of these reactions is longer than the residence time of air indoors. Due to the lack of photochemical reactions indoors, the indoor environment has been considered an inert reservoir where indoor and outdoor pollutants are mixed. Results from recent indoor air quality studies strongly suggest that heterogeneous processes are of paramount importance and can affect human exposures.

Finally, indoor/outdoor NO<sub>2</sub> ratios were less than unity for homes without unvented combustion, suggesting some reactive decay of NO<sub>2</sub> indoors. In homes with gas ranges, the ratios were greater than or equal to 1. This is in good agreement with previous studies (8,9). Furthermore, as seen in Table 7, the indoor and out

door concentrations were highly correlated in the summer, the only period for which sufficient NO<sub>2</sub> samples were collected.

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