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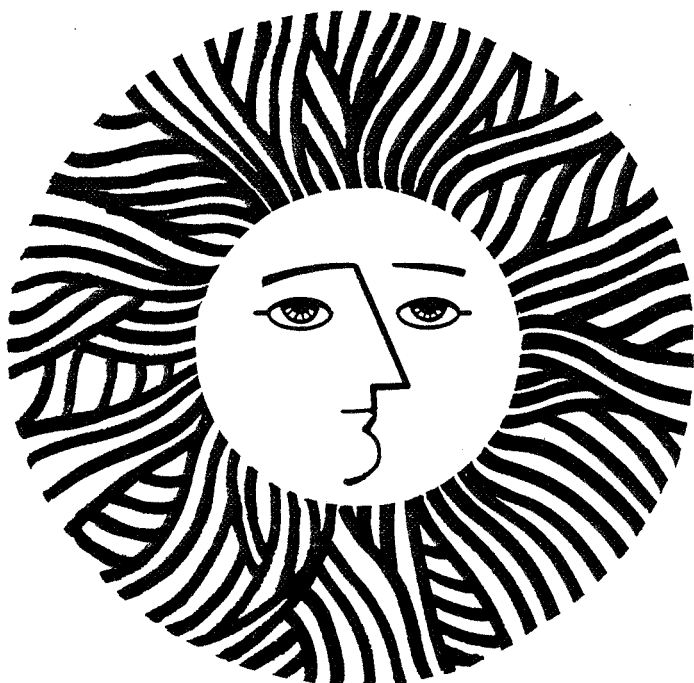
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COMBUSTION-GENERATED INDOOR AIR POLLUTION

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ABSTRACT

The indoor air quality of residential buildings was characterized to determine the types, rates of emissions, and fates of gaseous and particulate air pollutants from typical indoor combustion appliances. Measurements were conducted in occupied residential buildings and during controlled laboratory experiments with combustion appliances. SO_2 , NO , NO_2 , O_3 , CO , CO_2 concentrations and aerosol size distribution were determined on a continuous basis. Total and respirable-fraction particulate samples were collected on membrane filter media for analysis by x-ray fluorescence (XRFA), photoelectron spectroscopy (ESCA), proton activation analysis (PAA), combustion, and wet-chemistry techniques for the determination of particulate elemental composition (S, N, C, etc.) and ionic species such as SO_4^{2-} , NO_3^- , and NH_4^+ . Results of the study indicate that the concentrations of some gaseous and respirable particulate air pollutants in the indoor environment exceed those levels commonly found in the outdoor urban air environment. Such findings may have a large impact on the future design of epidemiology studies, on energy conservation strategies for buildings, and on the need for more stringent control of air pollution from indoor combustion sources.

INTRODUCTION

Air pollution research has focused almost exclusively on pollution in the outdoor environment and has virtually neglected the indoor environment, even though the major proportion of the population spends far more time indoors than outdoors. Recent evidence suggests that the concentrations of some pollutants in residential buildings can frequently exceed those levels commonly occurring in the outdoor environment (ref. 1).

Chemical and biological contaminants, released into indoor environments, are undesirable but unavoidable byproducts of human activity. Typical indoor contaminants include gaseous and particulate pollutants from indoor combustion processes (e.g., cooking, heating, cigarette smoking), toxic chemicals and odors from cooking and cleaning activities, odors and viable micro-organisms from humans, odor-masking chemicals used in several activities, and a wide assortment of chemicals released

from indoor construction materials and furnishings (e.g., asbestos, formaldehyde, vinyl chloride). Table 1 lists some of the major indoor air pollutants and their sources.

TABLE 1

Indoor air pollution in residential buildings

SOURCES	POLLUTANT TYPES
OUTDOOR	
Ambient Air	SO ₂ , NO, NO ₂ , O ₃ , Hydrocarbons, CO, Particulates
Motor Vehicles	CO, Pb
INDOOR	
Building Construction Materials	
Concrete, stone	Radon
Wallboard	Formaldehyde
Paint	Mercury
Insulation	Formaldehyde, Sulfates
Building Contents	
Heating and cooking combustion combustion appliances	CO, SO ₂ , NO, NO ₂ , Particulates
Furnishings	Organics, Odors
Natural gas; water service	Radon
Human Occupants	
Metabolic activity	CO ₂ , NH ₃ , Odors
Human Activities	
Cigarette smoke	CO, NO ₂ , HCN, Organics, Odors
Aerosol spray devices	Fluorocarbons, Vinyl Chloride
Cleaning and cooking products	Hydrocarbons, Odors, NH ₃
Hobbies and crafts	Organics

When these contaminants are generated in indoor environments in excessive concentrations, they may impair the health, safety, or comfort of the occupants. The introduction of outdoor air by infiltration, by opening doors and windows, or by ventilation with fan and duct systems of varying complexity is the usual way in which building occupants are protected from the accumulation of undesirable indoor air contaminants. The primary engineering control for the maintenance of indoor air quality is the use of ventilation, i.e., the use of controlled flows of air to mitigate the levels of air contaminants by 1) dilution with fresh outside air; 2) the use of recirculation systems incorporating chemical and physical contaminant cleaning devices; or 3) both dilution and the use of recirculation systems.

In recent years, there have been several reasons for examination of the use of ventilation in buildings more closely. The study of outdoor air pollution, which indicates that under certain circumstances "fresh" air may be more contaminated than indoor air, has motivated an examination of the use of outside air for building ventilation. Outside air may be unpleasant or even dangerous; and for this reason,

exclusion, reduction, or treatment of outside air must sometimes be considered. Another factor which has directed our attention to ventilation is energy conservation. When indoor air is heated or cooled, exhausting this air for ventilation purposes represents a major energy loss, and suggests minimal ventilation as a good means of energy conservation. As energy becomes less available and more expensive, measures are being taken to make buildings more energy efficient. These include "tightening up" the building structure to reduce leakage and infiltration rates, improving insulation, and reducing ventilation rates. As these measures are implemented and less fresh air is introduced into the buildings, the quality of the indoor air decreases. Ultimately, a balance is sought which will reduce energy consumption as much as possible without compromising the health and comfort of the occupants. At the present time, there are major gaps in the understanding of what positive steps may be needed to assure good air quality in buildings, in light of reduced ventilation.

In particular, the complex mix of indoor air pollutants has only very recently been recognized. Most studies of indoor air pollution have assumed that indoor air pollution arises from and is directly related to outdoor sources. These studies have been concerned mainly with SO₂, CO, O₃, or total suspended particulate matter. They have found in general that the concentrations of these species in indoor air are lower than in outdoor air. Surprisingly little work has been concerned with other potentially important indoor air pollutant species, such as NO, NO₂, nitrates, sulfates, metals, organics, and the respirable fraction of the particulate matter. Even more surprisingly, indoor-generated air pollution has been neglected in most indoor air pollution studies until quite recently although a number of air pollution sources exist inside buildings, notably sources associated with combustion (cooking, heating, and smoking).

The recently recognized importance of indoor air pollution is now expected to have a large impact on 1) the overall assessment of the effect of air pollution on human health, 2) the design of epidemiological studies that must consider indoor as well as outdoor air pollution, 3) energy conservation strategies for buildings that might restrict indoor-outdoor air exchange, and 4) the characterization of exposures of the occupants to the important air pollutants.

BACKGROUND

The Lawrence Berkeley Laboratory (LBL) of the University of California initiated an indoor air pollution research project in 1975 to study the chemical and physical behavior of indoor-generated air pollution in residential and commercial buildings.

The specific goals of this project are to: 1) characterize indoor air pollution; 2) identify the important sources, abundance, and fate of indoor air pollutants; 3) study the abatement of indoor air pollutants; 4) assess the impact of various energy-conservation strategies on indoor air quality; 5) characterize exposures of the occupants to the important air pollutants; and 6) study the health, safety and comfort effects.

Initial phases of this project have focused on combustion-generated indoor air pollution, namely indoor air pollution from gas stoves and heating systems in residential buildings. High concentrations of gaseous indoor air pollutants (e.g., CO, NO_x) from gas stoves have been reported recently (refs. 2-6). The same studies have shown no elevated levels of these gaseous air pollutants from electric stoves. Although emissions of CO, NO, and NO₂ from gas stoves have been extensively investigated, the indoor emissions from other combustion sources, such as heating systems, have not been thoroughly studied and, more important, many nitrogen compounds, particulate as well as gaseous, were not considered in gas stove studies despite the fact that formation of HCN and NH₃, as well as NO and NO₂, is observed in combustion processes (ref. 7). It has also been shown recently that gaseous nitrogen compounds can rapidly undergo catalytic oxidation or reduction to other important air pollution species such as nitrates, nitric acid, ammonium, and organic nitrogen compounds of the amino and pyridino type (ref. 8).

The work reported here represents the current status of ongoing field and laboratory studies to systematically examine gaseous and particulate air pollutants in residential buildings. Field and laboratory studies to date have included detailed studies of gaseous and particulate emissions from gas stoves and heating systems.

DISCUSSION

Field and laboratory measurements of indoor air quality are conducted with the LBL Mobile Atmospheric Research Laboratory (MARL) (ref. 9), which is capable of remote, multipoint sampling for such pollutants as SO₂, NO, NO₂, CO, O₃, and for aerosol size and chemistry. The gas phase sample is drawn into MARL through a 10- to 30-meter-long, 6.3-mm I.D. teflon tube with a teflon filter on the inlet side. This teflon particulate filter, changed at intervals ranging from 2 to 24 hours, prevents significant particulate contamination in the sample line. The residence time in a 10-meter sample line is 2.4 seconds. Measurements on laboratory- and field-collected aerosol samples are performed by x-ray fluorescence (XRF), photoelectron spectroscopy (also known as electron spectroscopy for chemical analysis - ESCA), and combustion and wet-chemistry techniques to characterize particulate species such as total sulfur, total nitrogen, SO₄²⁻, NO₃⁻, NH₄⁺, Pb, Fe, Zn, and total carbon. Aerosol collection is by filtration on 1.2-μ cellulose filters for x-ray fluorescence (XRF) analysis; 0.8-μ silver filters for total particulate nitrogen and nitrate analysis by ESCA, and quartz fiber filters for carbon analysis. Size segregated samples for XRF analysis using an Automatic Dichotomous Air Sampler (ADAS) (ref. 10) are also collected. The 50% cut-point for this instrument is 2.5 μ. Aerosol size measurements for the range 0.01-1.0 μm are performed by condensation nuclei formation and electrical mobility techniques.

A list of parameters measured and instrumentation is given in Table 2. In addition to the parameters listed in Table 2, measurements are also made of inside and outside

temperatures and humidities, and the amount of natural gas consumed by the combustion appliances.

TABLE 2
Instrumentation for Lawrence Berkeley Laboratory Indoor Air Pollution Research

PARAMETER	PRINCIPLE OF OPERATION
Field	
Continuous Monitoring Instruments:	
Gases	
SO ₂	UV Fluorescence
NO, NO ₂ , NO _x	Chemiluminescence
O ₃	UV Absorption
CO	Nondispersive Infrared Absorption
CO ₂	Nondispersive Infrared Absorption
N ₂ O	Infrared Absorption
SF ₆	Gas Chromatography/Electron Capture Detection
Aerosols	
Size Distribution	Electrical Mobility Analysis
Number Density	Condensation Nuclei Formation
Visibility (b _{scat})	Nephelometry
Particulate Collection	Virtual Impaction/Filtration
Laboratory	
Aerosols	
Elemental Composition	
Sulfur, Lead, etc (27 elements)	X-ray Induced X-ray Fluorescence (XRF)
Nitrogen	Proton Induced Activation Analysis
Carbon	Combustion/Gas Chromatography
Ionic Composition	
Nitrogen, Sulfur Compounds	X-ray Photoelectron Spectroscopy (ESCA)

Field studies, previously reported (refs. 3,4), have shown that levels of CO and NO₂ approach or exceed existing U.S. ambient air quality standards in some residential buildings with gas appliances. Nitrogen dioxide levels in kitchens of houses with gas stoves were observed to be as high as 1000 $\mu\text{g}/\text{m}^3$ with one top burner operating for less than 30 minutes and as high as 1700 $\mu\text{g}/\text{m}^3$ with the oven operating for 20 minutes. Concentrations of NO₂ were observed to be as high as 1200 $\mu\text{g}/\text{m}^3$ for 8 hours in the bedroom of a house with a forced-air gas-fired heating system operating under normal conditions. These NO₂ concentrations can be compared with the short-term recommended U.S. and promulgated foreign NO₂ air quality standards ($\sim 400 \mu\text{g}/\text{m}^3$ for 1 hour) shown in Table 3. Particulate air samples collected in residential buildings showed an increase in indoor particulate sulfur during periods of gas stove use. The indoor particulate levels for other species (Pb, Zn, Fe, and Ca) were comparable to or lower than the outdoor levels during all periods.

TABLE 3

Recommended and promulgated short-term NO₂ air quality standards¹¹⁻¹⁵

Country	Short-term NO ₂ air quality standard (0.1 ppm \approx 190 $\mu\text{g}/\text{m}^3$)	Status
Canada (Ontario)	0.2 ppm/1 hr 0.1 ppm/24 hr	promulgated promulgated
Japan	0.02 ppm/24 hr	promulgated
U.S.A.	0.1-0.35 ppm/hr	recommended
West Germany	0.15 ppm/short-term exposure	promulgated
WHO/UNEP	0.10-0.17 ppm/hr	recommended

Studies using an experimental room with an air volume of 27 m³ have characterized the emissions from a new gas stove operating in the room with air exchange rates from 1/4 to 10 air changes per hour (ACPH). Well-constructed new single-family houses have air exchange (ventilation and infiltration) rates on the order of 0.5-1.0 ACPH. Older houses and most other new houses have air exchange rates of 0.8-1.5 ACPH or higher. Energy conservation measures which would limit the air exchange rate in new houses to 0.2 to 0.5 ACPH are now being considered by state and Federal agencies.

The laboratory studies have shown that gas stoves generate extremely high concentrations of such species as CO, NO, NO₂, respirable aerosols (size <1.0 μm), and particulate sulfur when the air exchange rate is controlled to less than 1 ACPH (ref. 4). Figures 1 and 2 illustrate the levels of CO and NO₂ observed in the experimental room under various ventilation rates ranging from 0.24 to 7.0 ACPH. These experiments were conducted with the oven of the gas stove operated at 350°F (\approx 180°C) for 1 hour. One can see that the CO concentration exceeded the 1-hour air quality standard only under "tight" conditions. But the NO₂ concentration exceeded the recommended 1-hour standards even with an air exchange rate as high as 2.5 ACPH. Experiments with the top burners of gas stoves also show high levels of NO₂, even under well-ventilated conditions.

Previous studies have shown that emission rates vary considerably from one stove to another (refs. 16,17). There is also considerable variation in a single stove if there is a change in any of the operating conditions such as the primary air supply. Table 4 lists the range of emission rates observed in these studies and compares the results to other studies. It has recently been observed that N₂O is a significant combustion product and its emission rate is on the order to 600 $\mu\text{g}/\text{Kcal}$.

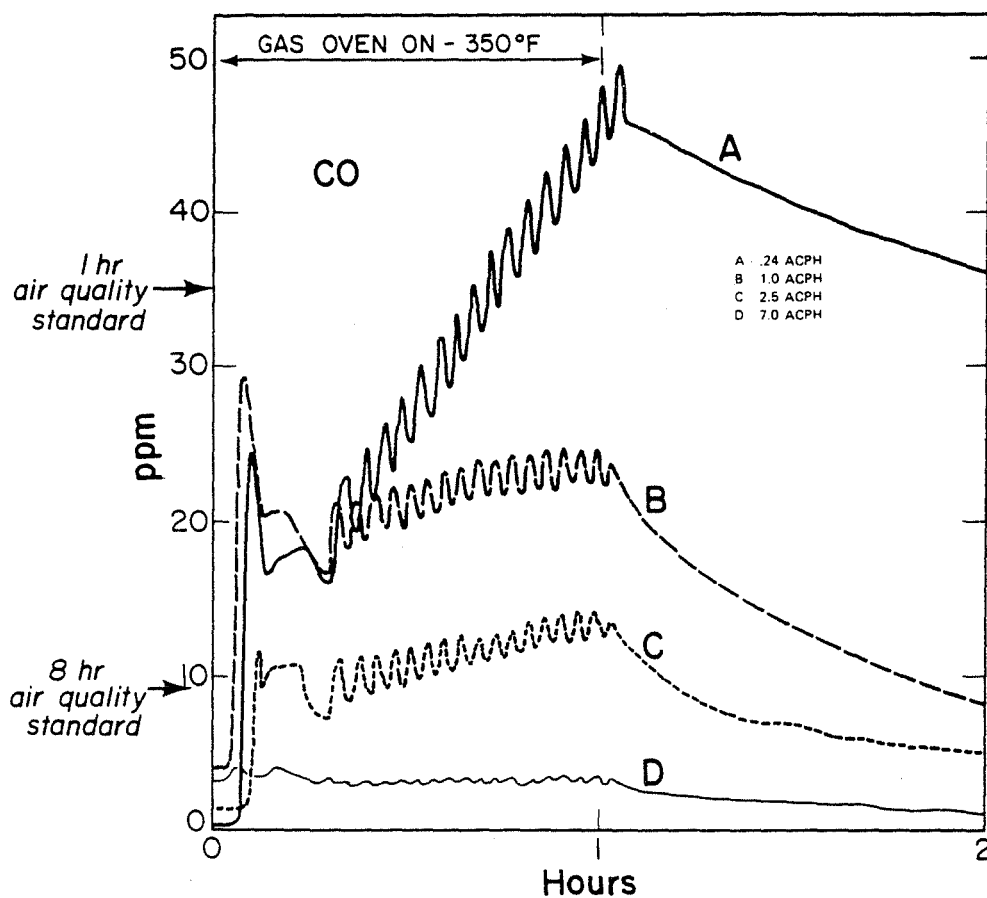


Fig. 1. Carbon monoxide concentrations in a 27-m³ experimental room at various air exchange rates. Gas oven operated for 1 hour at 350°F ($\sim 180^{\circ}\text{C}$).

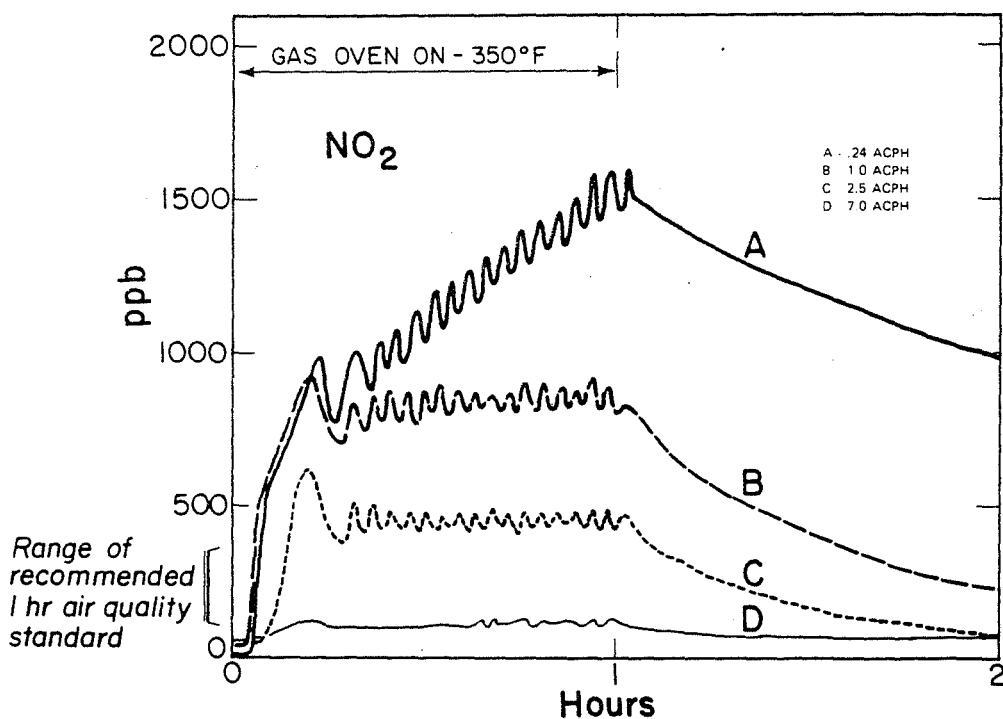


Fig. 2. Nitrogen dioxide concentrations in a 27-m³ experimental room at various air exchange rates. Gas oven operated for 1 hour at 350°F ($\sim 180^{\circ}\text{C}$).

TABLE 4

Oven emission rates ($\mu\text{g/Kcal}$)

Pollutant	Lawrence Berkeley Laboratory	The Research Corporation of New England (TRC) ¹⁸		British Gas Corporation ¹⁹	American Gas Association Standard ²⁰
	Oven at 350° F	Old Stove Oven (Steady State)	New Stove Oven (Steady State)	Oven (General)	
CO	600-1300	530	1620		645
NO	20-50	91.4	77.9	}	85
NO ₂	30-60	73.1	50.4		
SO ₂	.5-1.0				
Kcal/hr	2000	2200	2200		

Laboratory investigations now in progress include detailed studies of particulate sulfur, nitrogen, and carbon compounds in the indoor environment. The sulfur content of natural gas in California varies between 0.5 and 1.2 $\mu\text{g/Kcal}$ (ref. 21). An average emission rate of particulate sulfur from gas stoves has been measured to be 0.02 $\mu\text{g/Kcal}$. The increase in sulfate in a typical kitchen is calculated and observed to be approximately 2 $\mu\text{g/m}^3$ after operating a gas oven for 1 hour.

Of particular interest are the high NO₂/NO ratios ($\sim 1:1$) observed in the laboratory and field studies. In addition to NO and NO₂, considerable attention is being given to such gaseous species as HCN and NH₃ and particulate species such as NO₃⁻, NH₄⁺, and organic nitrogen compounds. In most systems, NO₂ accounts for less than 5% of the NO_x emissions, but higher values can be encountered when flames are rapidly quenched. One probable explanation is that NO₂ is formed in high concentrations by reactions of NO with HO₂ and/or OH, and that the NO₂ may be reduced subsequently by reactions with oxygen atoms. Evidence for this is provided by Merryman and Levy (ref. 22) and by numerical simulations by Kendall et al. (ref. 23). Possible intermediate species in such a process include HCN, NH₃, amines, and various nitrates. The concentrations of some of these compounds in the post-combustion gas may be significant, and we plan to quantitatively characterize HCN, NH₃, and other gaseous nitrogen compounds in the indoor environment.

We have also observed elevated indoor particulate nitrogen levels from gas stoves and heating systems in recent experiments. The analyses have been performed by proton activation analysis (for total N) and ESCA (for NH₄⁺, NO₃⁻, and organic amines). A recent paper by Benarie (ref. 24) reports higher levels of NH₄⁺ and NO₃⁻ inside buildings than outside; these results are similar to our findings. Although the results of our study are not definitive, they clearly indicate the need for systematic

studies to assess the significance of particulate nitrogen compounds in the indoor environment. These studies are in progress.

As assessment of the potential health impact of gas stove emissions under low ventilation rates is now in progress at the Lawrence Berkeley Laboratory. A recent study in England (ref. 25) has reported that 2554 children living in homes in which gas was used for cooking had significantly more respiratory illness than did 3204 children from homes in which electric stoves were used. In this study, the analysis of data collected took account of age, of individuals' social class, latitude of residence, population density, family size, crowding in the home, outdoor level of smoke and sulfur dioxide and the type of fuel used for heating the home. Smoking habits of parents were not considered in the analysis, but known relationships between smoking and social class were believed by the authors to allow for avoidance of at least some of the potential bias from this source. The prevalence of bronchitis in homes using gas stoves was 5.7 and 4.7 percent for boys and girls respectively. The prevalence in homes with electric stoves was 3.1 and 2.0 percent respectively. Smaller but still statistically significant increases in "day or night cough", "morning cough", and "colds going to chest" were found for both boys and girls living in homes with gas stoves. Girls in these homes also had a significantly increased prevalence rate for "wheeze". The investigators concluded that elevated levels of oxides of nitrogen from gas stoves might have caused the increased respiratory illness.

CONCLUSIONS

Studies in an environmental chamber with a controllable ventilation rate of 1/4 to 10 air changes per hour have characterized the emissions from gas stoves. These laboratory studies have shown that gas stoves generate extremely high concentrations of such species as CO, NO, NO₂, respirable aerosols and particulate sulfur, nitrogen, and carbon compounds when the air exchange rate is controlled to less than one air change per hour. Air exchange rates in current conventional residential buildings are typically 0.8 to 1.5 ACPH. Energy conservation measures which could limit air exchange rate in new houses to below 0.5 ACPH are now being considered by state and Federal agencies in the United States.

It is obvious from this study that elevated levels of gaseous air pollutants (CO, NO, and NO₂) and particulate sulfur and nitrogen compounds are present in indoor environments when gas appliances are in use. Observed levels of CO and NO₂ approach or exceed promulgated and proposed ambient air quality standards. At this point, there are several possible strategies that need to be explored. One such solution might be to filter or scrub out the pollutants inside the home by utilizing a recirculating ventilation system. Another solution might be to actively vent the combustion products outside during the use of the appliance, but to completely shut off the venting system when the appliance is not consuming gas.

The field and laboratory measurements carried out thus far certainly indicate a potential impact of combustion-generated indoor air pollution on human health; and if borne out by further work, they may ultimately have a large impact on the future design of epidemiological studies, on energy conservation strategies for buildings, and on the need for more stringent control of air pollution from indoor combustion sources.

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