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COMBUSTION-GENERATED INDOOR AIR POLLUTION

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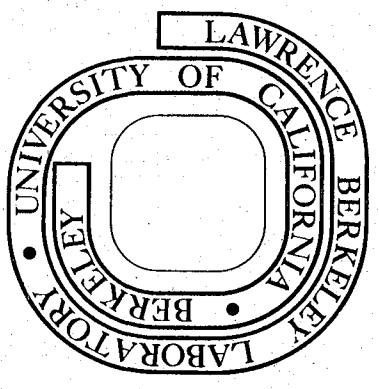

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Introduction

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, however, suggests that levels of pollutants in the indoor environment can frequently exceed those levels commonly occurring in the outdoor environment. The importance of indoor air pollution is only now being recognized. Its significance is expected to have a large impact 1) on the overall assessment of the effect of air pollution on human health, 2) on the design of epidemiological studies that must consider indoor as well as outdoor air pollution, 3) on energy conservation strategies for buildings that might restrict indoor-outdoor air exchange, and 4) on the need for more stringent control of air pollution from indoor combustion sources.

Most studies of indoor air pollution have assumed that indoor pollution arises from and is directly related to outdoor sources. These studies have been concerned mainly with SO_2, CO, O_3, 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.[1,2] Surprisingly little work has been concerned with other potentially important indoor air pollution species, such as NO, NO_2, 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). Although

emissions of CO, NO, and NO_2 from gas stoves have been reported recently, the emissions from other combustion sources, such as heating systems, have not been thoroughly investigated.[2] 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 NH_3, as well as NO and NO_2, is observed in combustion processes.[3] 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.[4]

Experimental Program

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 combustion-generated air pollution in residential and commercial buildings. The broad goals of this project are 1) to characterize indoor air pollution; 2) to identify the important sources, abundance, and fate of indoor air pollutants; 3) to study the abatement of indoor air pollutants; 4) to characterize exposure of the occupants to the important air pollutants; 5) to study the health and welfare effects; and 6) to assess the impact of various energy-conservation strategies on indoor air quality. The work reported here represents the current status of ongoing field and laboratory studies of this project, whose initial goal has been to examine in detail the sources, rates of emissions, dispersion, transformations, and fates of gaseous and aerosol air pollutants in residential buildings.

Other indoor environments in which people spend considerable time are commercial buildings such as office buildings, schools, and other public or semi-public buildings. Modern commercial buildings are usually engineered so that the circulation and infiltration of air are controlled, and public

health regulations often require certain minimum air-circulation rates, usually for the purpose of decreasing transmission of infectious disease. However, significant attention is seldom, if ever, given to the public health role of air pollution generated by indoor sources. Combustion-generated indoor air pollution in these buildings will be studied in subsequent phases of this project.

The principal objective of the field study is to obtain quantitative data on the relationship of indoor to outdoor air pollutant concentrations as a function of gas cooking and heating appliance use. Six occupied single-family residential buildings in Berkeley and Albany, California, were selected for this study. All houses were equipped with gas heating systems. Five had gas stoves, and one had an electric stove. Field measurements reported here were made under conditions simulating typical cooking and heating use. Only the house with the electric stove was characterized during a cool season when the heating system is normally operated, and is therefore the only house to be evaluated for the effect of gas heating systems on indoor air pollutant levels. Field studies in progress are measuring indoor air pollution in several residential and commercial buildings to evaluate the effect of heating systems in detail.

Laboratory studies in experimental buildings are designed to identify various parameters which affect rates of emissions from cooking and heating appliances and air pollution levels in the indoor environment. These parameters include appliance type and its operating characteristics (for example, fuel/air mixture, flame temperature and geometry), venting conditions, and air infiltration rate.

Work in progress concerns the dispersion, transformations, and ultimate fate of combustion-generated indoor pollutants. The physical and chemical transformations depend on the many constituents (gaseous and particulate)

present in the air, on temperature and humidity, and on the effects of walls and other materials on the ultimate fate of various species. This phase of the study involves detailed analysis and experiments with various ventilation and air circulation systems.

At attempt is being made to characterize the range of major pollutant emissions for a cross section of typical American patterns of heating and cooking appliance use. A model will be developed for understanding and estimating indoor air quality in residential and commercial buildings.

Laboratory and field measurements are made with the LBL Mobile Atmospheric Research Laboratory (MARL),[5] which is capable of remote, multipoint sampling for such pollutants as SO_2, NO, NO_2, CO, O_3, aerosol size, and aerosol chemistry. The major components of the MARL gaseous air pollutant measurement system used in this indoor study are identified below:

Parameter measured	Principle of measurement
SO_2	UV fluorescence
$NO/NO_2/NO_x$	Chemiluminescence
O_3	UV absorption
CO	Nondispersive infrared absorption

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), infrared spectroscopy (IR), combustion, and wet chemistry techniques to characterize particulate species such as total sulfur, total nitrogen, SO_4^{--}, NO_3^-, NH_4^+, Pb, Fe, Zn, and total carbon. Aerosol size measurements for the range 0.01-1.0 μm are performed by condensation nuclei formation and electrical mobility analyses. Analytical procedures for HCN and

NH_3 are currently being developed. Gas chromatography/mass spectrometry (GC/MS) analyses for organic aerosol species will be explored in future studies. Meteorology measurements (wind and speed direction, temperature, relative humidity, UV radiation) are conducted in the outdoor environment (and indoor where appropriate). Air circulation, ventilation, and infiltration measurements are made using air flow sensors and sulfur hexafluoride as a tracer gas for air exchange rate determinations. Measurements are conducted by locating MARL near the building being studied and running sampling lines (up to 30 metres in length) to various points of interest (kitchen, living room, bedroom, ambient outdoor air). The parameters are monitored for several hours (or days) under varying normal and controlled conditions.

Results and Discussion

Figure 1 summarizes the average indoor/outdoor data for gaseous air pollutant levels in the six houses under typical occupancy conditions of cooking and heating. The results are consistent with other studies[2] and report for the first time elevated indoor SO_2 levels associated with gas stoves. A small increase in O_3 was observed during use of the electric stove, but no elevated levels of the other gases were seen. Figure 1 also shows the high levels of NO and NO_2 observed in the one house where the effect of a forced-air gas-fired central heating system was studied.

Detailed analyses of gaseous pollutant emissions from gas stoves in some of the houses were made in controlled experiments with various cooking utensils and venting systems. No appreciable differences in gaseous emissions were observed in using utensils constructed of various materials. However, the study clearly demonstrated that gas oven use under poor ventilation conditions can result in elevated levels of CO, NO, NO_2, and even SO_2. The most obvious result

was the high variability of gaseous pollutant emissions among the five gas stoves studied.

The duration of the elevated levels of CO, NO, and NO_2 from gas combustion appliances may be under 1 hour for gas stove use but may be continuous for gas-fired heating system use in cool seasons. Levels of CO and NO_2 were found to approach or exceed existing U.S.A. ambient air quality standards:

Pollutant	Averaging time	Concentration
Carbon monoxide	1 hour	40 mg/m^3 (35 ppm)
	8 hour	10 mg/m^3 (9 ppm)
Nitrogen dioxide	Annual arithmetic mean	100 $\mu g/m^3$ (0.05 ppm)

Nitrogen dioxide levels in kitchens of houses with gas stoves were observed to be as high as 1000 $\mu g/m^3$ with one top burner operating for less than 30 minutes and as high as 1700 $\mu g/m^3$ with the oven operating for 20 minutes. Concentrations of NO_2 were observed to be as high as 1200 $\mu g/m^3$ for 8 hours in the bedroom of a house with a forced-air gas-fired heating system operating under normal conditions. These NO_2 concentrations can be compared with the short-term recommended U.S. and promulgated foreign NO_2 air quality standards[6-9] ($\sim$400 $\mu g/m^3$ for 1 hour) shown in Table 1.

Particulate air samples collected in the six study houses were analyzed by x-ray fluorescence and ESCA techniques. An increase in indoor particulate sulfur was observed 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. No elevated sulfur levels, gaseous or particulate, were found in the house with the electric stove when it was on.

Figure 2 illustrates the elevated indoor particulate nitrogen levels observed in the house where the effect of the gas furnace was studied. The

ESCA spectra illustrate the different nitrogen species (NO_3^-, NH_4^+, N_x [organic nitrogen]) observed indoors and outdoors; the peak areas are proportional to the relative atomic concentrations (as N) of these species. Most of the indoor nitrogen is found as NH_4^+ and N_x; the outdoor nitrogen is found as N_x. In previous outdoor studies, N_x was found to be either the dominant or at least the major component of the total particulate nitrogen. The elevated levels of reduced nitrogen species should be noted because some of these (especially those labeled "N_x" in Figure 2, which are interpreted as NH_2-type compounds) are species whose health implications deserve further study.

In 1976 a bill calling for energy conservation in new and existing buildings was enacted into law by the federal government of the United States.[10] The Energy Conservation Standards for New Buildings Act of 1976 calls for promulgation of performance standards for all new residential and commercial buildings by 1980. It is imperative that consideration of indoor air pollution be given in the development of these standards; the project at LBL is evaluating the impact of various energy conservation measures for buildings on indoor air quality.

Well-constructed new single-family houses have air exchange (ventilation and infiltration) rates on the order of 1 air change per hour (ACPH). Older houses and most new houses have air exchange rates of 2 ACPH or higher. Energy conservation measures which would limit the air exchange rate in new houses to 1/4 to 1/2 ACPH are now being considered by state governments and the federal government. Laboratory studies at LBL using an experimental room with an air volume of 27 m^3 have shown that gas stoves generate extremely high concentrations of such species as CO, NO, NO_2, respirable particulates (size <1.0 μm), and particulate sulfur when the air exchange rate is controlled to less than 1 ACPH. The results of one such experiment are given in Table 2 and are compared with typical polluted urban outdoor air. This experiment was conducted with the

air exchange rate at 1/4 ACPH and with the oven of a new gas stove on for the first hour of a 3-hour measurement period. While these laboratory studies do not necessarily duplicate "real world" situations, they clearly demonstrate the types and levels of air pollutants one could expect under low air exchange rates for buildings; these rates may be required in order to meet new energy conservation performance standards for buildings. Such "real world" findings have already been demonstrated in field experiments with six "leaky" homes where air exchange rates were on the order of a few air changes per hour.

Of particular interest are the high NO_2/NO ratios observed in the laboratory and field studies. Until recently, periodic reports of significant NO_2 formation in flames was discounted as being due to probe errors. In most systems NO_2 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 NO_2 is formed in high concentrations by reactions of NO with HO_2 and/or OH, and that the NO_2 may be reduced subsequently by reactions with oxygen atoms. Evidence for this is provided by Merryman and Levy[11] and by numerical simulations by Kendall et al.[12] Laboratory investigations now in progress include detailed studies of nitrogen compounds in the indoor environment. In addition to NO and NO_2, considerable attention is being given to such gaseous species as HCN and NH_3 and particulate species such as NO_3^-, NH_4^+, and organic nitrogen compounds.

Conclusions

It is obvious from this study that elevated levels of gaseous air pollutants (CO, NO, NO_2, and SO_2) and particulate sulfur and nitrogen compounds are present in indoor environments with gas cooking and heating appliances. High levels of CO and NO_2 approach or exceed promulgated and proposed ambient air quality

standards. Such findings 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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Table 1.

Recommended and promulgated short-term NO_2 air quality standards.

Country	Short-term NO_2 air quality standard (0.1 ppm ≈200 μg/m^3)	Status[a]	Remarks
U.S.A.	0.1 ppm/1 hr[b]	R	Preliminary EPA value pending final review and publication of "Air Quality Criteria for Nitrogen Oxides."
	0.25-0.35 ppm/1 hr[c,d]	R	Conclusions of NAS-NRC Panel on Oxides of Nitrogen based on review of studies on short-term animal and human exposures to NO_2.
	0.13 ppm/24 hr[e]	—	Calculated from U.S. EPA-promulgated long-term 0.05 ppm/year air quality standard for NO_2.
Canada (Ontario	0.2 ppm/1 hr[e]	P	
	0.1 ppm/24 hr[e]	P	
West Germany	0.15 ppm/short-term exposure[e]	P	
Japan	0.02 ppm/24 hr[e]	P	

[a] R = recommended; P = promulgated

[b] Ref. 6

[c] Ref. 7

[d] Ref. 8

[e] Ref. 9

Table 2.

Air pollutants observed from a gas stove operating in an experimental room at a controlled air exchange rate of 1/4 air changes per hour.[a]

Parameter measured	Background		3-hr measurement period		Typical peak polluted urban levels
	Indoor	Outdoor	Gas oven on (1-hour average)	Gas oven off (2-hour average)	
CO (ppm)	.7	.8	35	60	10-20
NO (ppm)	.005	.040	0.8	1.2	.2-.5
NO_2 (ppm)	.045	.050	2.5	2.5	.2-.5
SO_2 (ppm)	.005	.005	.010	.020	.1-.5
S (as SO_4^{--}) ($\mu g/m^3$)	<1	<2	13	14	10-20
Aitken nuclei ($no./cm^3$)	20K	40K	3000K	200K	100-4000K
Submicron aerosol mass median diameter (μm)	.2-.3	.2-.3	.08	.2	.2-.4

[a] Measurements at center of 27 m^3 room for 3-hr period (gas stove oven operating for first hour only).

Figure Captions

Figure 1. Gaseous indoor and outdoor air pollutant levels observed at houses with various cooking and heating configurations.

Figure 2. Nitrogen (1s) photoelectron (ESCA) spectra of indoor and outdoor particulate samples collected at a house with the gas furnace on. Individual peaks corresponding to NO_3^-, NH_4^+, and N_x (organic nitrogen species) are indicated.

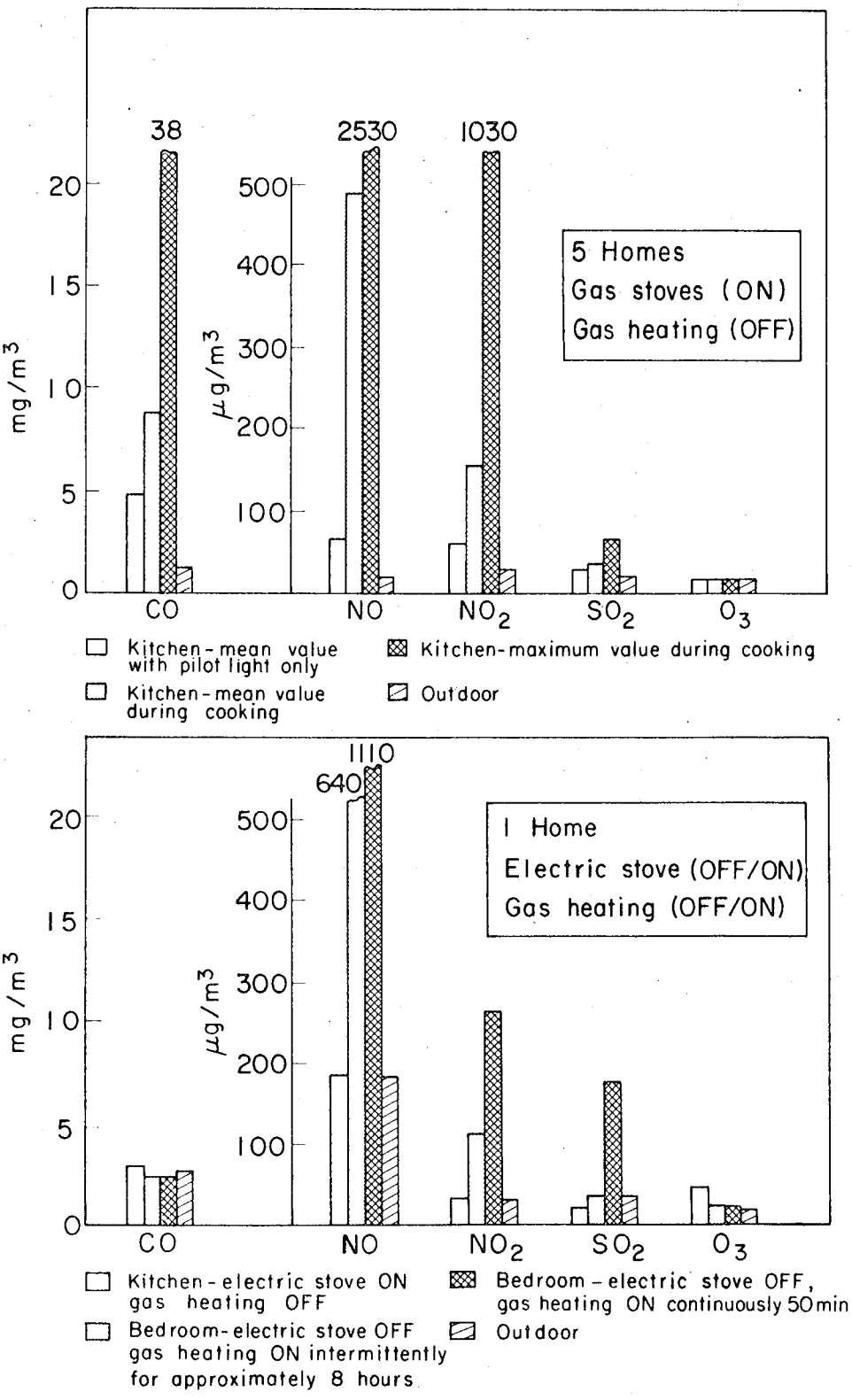
38
2530
1030
5 Homes
Gas stoves (ON)
Gas heating (OFF)
mg/m³
μg/m³
CO
NO
NO₂
SO₂
O₃
Kitchen-mean value with pilot light only
Kitchen-maximum value during cooking
Kitchen-mean value during cooking
Outdoor
1110
640
1 Home
Electric stove (OFF/ON)
Gas heating (OFF/ON)
Kitchen-electric stove ON gas heating OFF
Bedroom-electric stove OFF gas heating ON intermittently for approximately 8 hours
Bedroom-electric stove OFF, gas heating ON continuously 50 min
Outdoor
XBL7510-8561

Figure 1

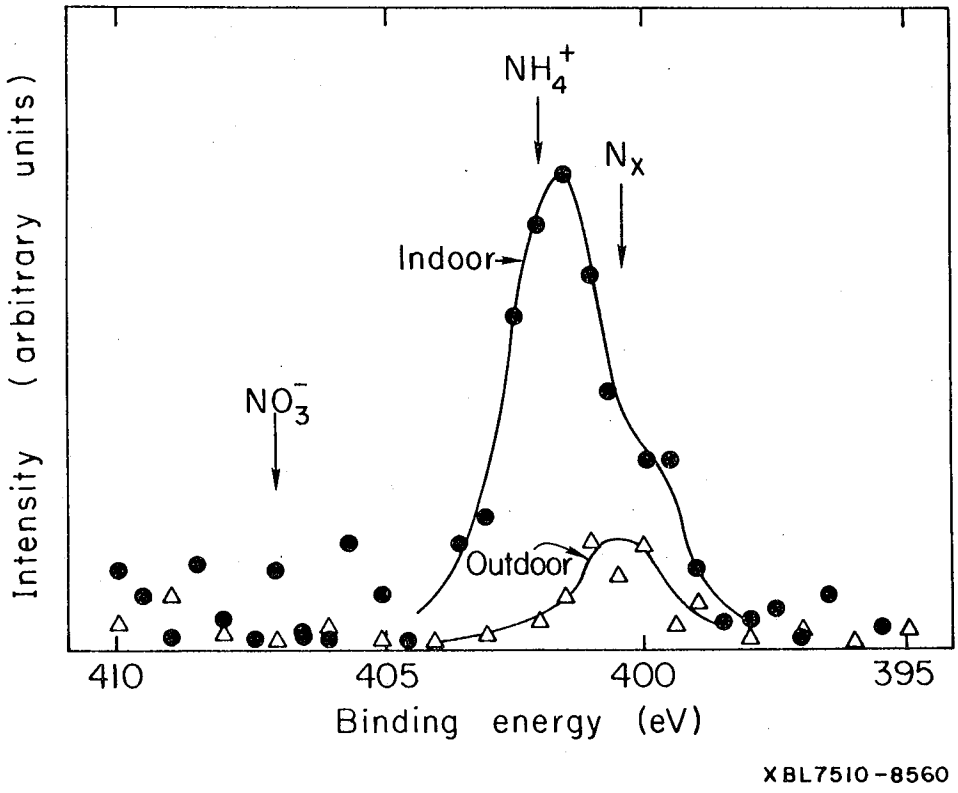
NH_4^+
N_x
Indoor
NO_3^-
Outdoor
Intensity (arbitrary units)
410
405
400
395
Binding energy (eV)
XBL7510-8560

Figure 2

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