Reports

Air Pollutant Emissions from Kerosene Space Heaters

Abstract. *Air pollutant emissions from portable convective and radiant kerosene space heaters were measured in an environmental chamber. Emission factors for nitrogen oxides, sulfur dioxide, carbon monoxide, carbon dioxide, and oxygen depletion are presented. The data suggest that the use of such heaters in residences can result in exposures to air pollutants in excess of ambient air quality standards and in some cases in excess of occupational health standards.*

Efforts to conserve energy by reducing infiltration and ventilation rates, increasing insulation, and using supplementary heat sources have increased the importance of the nonoccupational indoor environment as a source of exposure to air contaminants. Unvented portable kerosene heaters have come into popular use as an efficient, low-cost method of providing supplementary heat in residences. In the past, concern about use of these heaters indoors has focused on their potential for producing fires and asphyxiation (through oxygen depletion). We have performed controlled chamber studies on air contaminant emissions from convective and radiant portable kerosene heaters, and our results indicate that these heaters can produce indoor concentrations of several air contaminants in excess of ambient air quality health standards and in some cases in excess of occupational health standards.

The experiments were carried out in an aluminum-lined chamber (*1*) with a volume of 1200 ft^3 (34 m^3) equipped with an efficient ventilation system that ensured very rapid mixing of outdoor air with the air contaminants generated in the chamber by the kerosene heaters. The chamber is approximately equivalent to a 12 by 12 by 8 foot room. Air enters the chamber through a plenum beneath a perforated floor and flows upward through the floor laminarly to the ceiling. The volume flow (recirculation rate) was set at 2000 ft^3/min (1000 liter/sec) or 100 air changes per hour. Ventilation air could be brought into the chamber at 0 to 400 ft^3/min. The ventilation rate was calibrated by introducing a predetermined concentration of CO_2 into the unoccupied chamber and then measuring the decay of the concentration with an infrared CO_2 analyzer. The

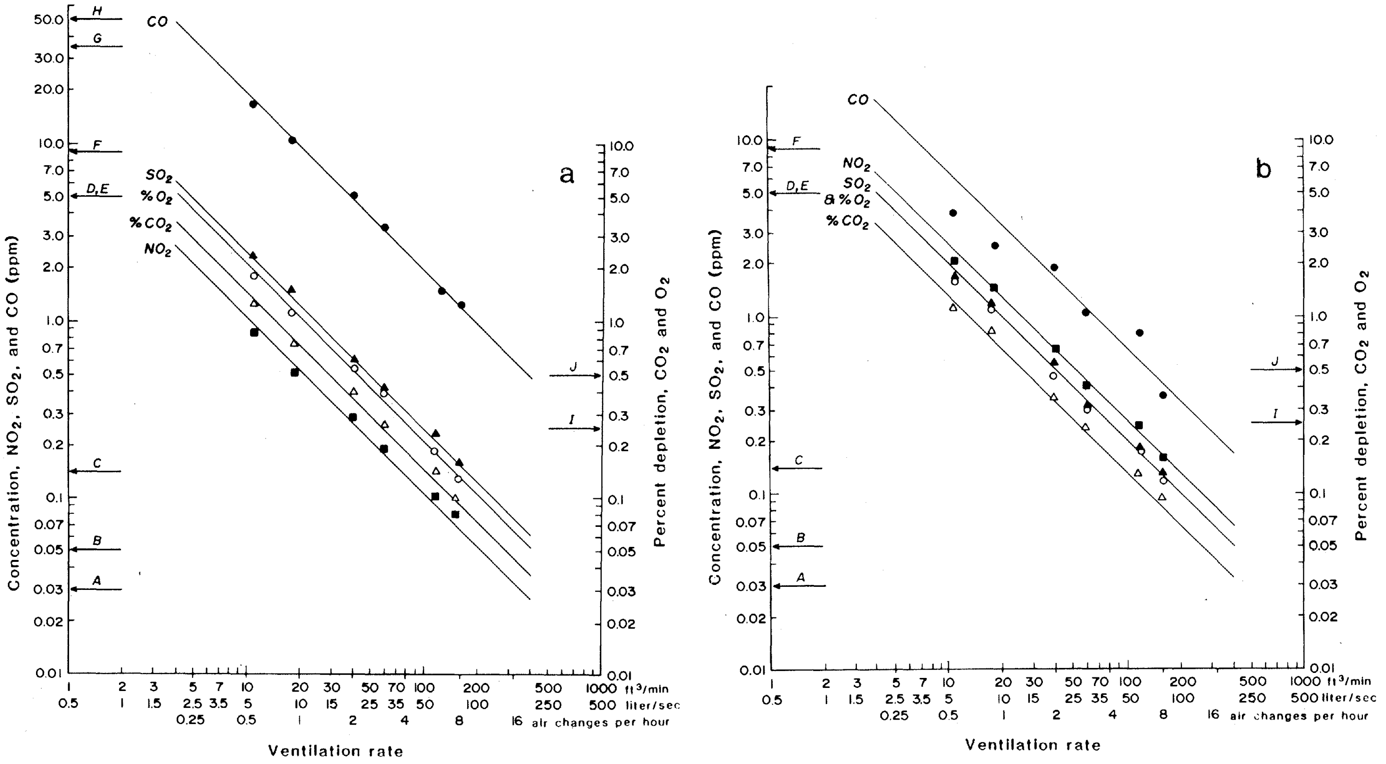

Fig. 1. Steady-state concentrations of air pollutants plotted against ventilation rate for two types of portable unvented kerosene space heaters: (a) radiant type rated at 9600 Btu/hour and (b) convective type rated at 8700 Btu/hour. Experimental conditions are described in the text. Lines represent calculated values based on emission factors from Table 1 for normal flame settings; points represent values measured in the chamber. Health standards are indicated by labeled arrows: *A*, primary ambient air quality standard for SO_2 (annual average) (*4*); *B*, primary ambient air quality standard for NO_2 (annual average) (*4*); *C*, primary ambient air quality standard for SO_2 (24-hour concentration not to be exceeded more than once a year) (*4*); *D*, Occupational Safety and Health standard for NO_2 (concentration not to be exceeded, ceiling value) (*5*); *E*, Occupational Safety and Health standard for SO_2 (8-hour time-weighted average, 40-hour work week) (*5*); *F*, primary ambient air quality standard for CO (8-hour average not to be exceeded more than once a year) (*4*); *G*, ambient air quality standard for CO (1-hour average not to be exceeded more than once a year) (*4*); *H*, Occupational Safety and Health standard for CO (8-hour time-weighted average, 40-hour work week) (*5*); *I*, *ANSI/ASHRAE* guideline for CO_2 (continuous) (*6*); and *J*, Occupational Safety and Health standard for CO_2 (8-hour time-weighted average, 40-hour work week) (*5*). Health standards are presented for reference; actual comparison to health standards requires concentration and duration of exposure.

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Table 1. Pollutant emission factors for two kerosene heaters at three flame settings. Values are means ± standard errors. The values for NO_2 are obtained by subtracting measured NO from NO_x.

Flame setting	Number of runs	Fuel consumption rate (g/min)	Emission factor (mg/g)					
			NO	NO_2	SO_2	CO	CO_2	O_2
				Radiant heater, 9600 Btu/hour				
Normal	3	2.59 ± 0.035	0.0035 ± 0.002	0.217 ± 0.010	0.70 ± 0.25	2.53 ± 0.219	2917.8 ± 99.3	2986.4 ± 130.5
High	3	3.3 ± 0.033	0.0197 ± 0.002	0.192 ± 0.008	0.726 ± 0.018	1.85 ± 0.107	3091.7 ± 61.2	2988.8 ± 110.9
Low	3	1.94 ± 0.033	*	0.256 ± 0.012	0.78 ± 0.004	3.17 ± 0.115	2959.3 ± 5.5	3104.1 ± 122.3
				Convective heater, 8700 Btu/hour				
Normal	3	2.25 ± 0.027	0.508 ± 0.026	0.631 ± 0.014	0.70 ± 0.031	0.97 ± 0.067	3115.1 ± 36.6	3366.2 ± 138.8
High	3	3.63*	0.719 ± 0.013	0.303 ± 0.019	0.66 ± 0.007	0.44 ± 0.179	2994.0 ± 43.3	2964.0 ± 107.7
Low	3	0.857 ± 0.068	0.465 ± 0.039	0.749 ± 0.044	0.77 ± 0.038	1.12 ± 0.204	3620.1 ± 220.2	4182.2 ± 166.5

*Not different from background.

chamber had excellent control of dry bulb (±0.1°C) and dew point (±0.2°C) temperature.

Air contaminant concentrations were measured continuously in the recirculated air, and background levels of air contaminants were measured periodically in the supply or ventilation air. The following air quality parameters were measured: nitrogen oxides (NO_x, NO, and $NO_2 = NO_x - NO$) with a Monitor Labs model 8440 chemiluminescence NO_x analyzer, SO_2 with a Monitor Labs model 8850 fluorescence analyzer, CO with a Beckman model 860 infrared absorption analyzer, CO_2 with a Beckman LB-2 infrared absorption analyzer, O_2 depletion with a Beckman paramagnetic analyzer, and reactive hydrocarbons (total hydrocarbons minus methane) by flame ionization detection with a Bendix model 8201 reactive hydrocarbon analyzer. Background air contaminant levels were subtracted from all concentrations measured in the chamber.

Two small portable unvented kerosene space heaters were tested. One was a radiant type with a rated heat output of 9600 Btu/hour and the other a convective type with a rated heat output of 8700 Btu/hour. The heaters were bought commercially and used according to the manufacturer's instructions for several days before the chamber tests. The kerosene used in the heaters was purchased locally. The fuel consumption rate during all chamber tests was monitored continuously by use of a recording Potter scale with a sensitivity of < 1 g.

Two types of chamber experiments were performed. The first set of experiments was designed to determine air contaminant emission factors (milligrams of pollutant per gram of fuel consumed) for each of the space heaters tested, and the second set was designed to assess the levels of exposure to air contaminants that would result from the use of the heaters in residences. In the first set of experiments the recirculation rate was set at 2000 ft^3/min and the ventilation rate at 40 ft^3/min. The temperature of the chamber did not exceed 23°C. The heaters were each operated at three different wick settings: the one recommended by the manufacturer, which gave a normal flame; a high setting which gave a high flame; and a low setting, which gave a low flame. Once the concentrations of all air contaminants had reached a steady state in the chamber under each of the flame settings, these concentrations and the fuel consumption rate were recorded and the emission factors were calculated. After the heaters were shut down, the decay function of each air contaminant from equilibrium was monitored to assess removal of the contaminant surfaces. These observations were repeated three times for each heater and each heater setting.

In the second set of experiments the recirculation rate was set at 2000 ft^3/min and the ventilation rate was varied in six steps from 160 to 11 ft^3/min. Both heaters were operated at wick levels recommended by the manufacturer (normal flame). The steady-state concentrations at each ventilation rate were recorded.

Reactive hydrocarbon concentrations were at background levels during the operation of the heaters but rose to more than 10 ppm (at one air change per hour) when the heaters were extinguished. This increase was presumably due to evaporative emissions from the warm wick.

The emission factors determined from the first set of experiments are shown in Table 1. Nitrogen oxide emissions are considerably higher for the convective heater than for the radiant heater. The NO_x for the radiant heater is almost entirely in the form of NO_2, while NO and NO_2 emission rates from the convective heater are almost equal. Variations in fuel consumption rate had little effect on NO_2 emission factors for the radiant heater, while a high fuel consumption rate in the convective heater lowered the NO_2 emission factor and increased the NO emission factor. The SO_2 emission factors for both heaters at all fuel consumption rates are about equal. The emission rates of SO_2 correspond to a fuel with a sulfur content of approximately 0.035 percent, which is typical for kerosene. The CO emission factors were found to be higher for radiant heaters (less efficient combustion) and higher for lower fuel consumption rates. The ratio of the percent of O_2 consumption to the percent of CO_2 production is approximately what would be predicted from the combustion of fuel. For all contaminants, the decay curves from steady-state conditions once the heaters were extinguished were not significantly different from those expected from the ventilation rate (all unpaired t-test results had $P > 0.1$); hence, there was no measurable removal of contaminants by the chamber surfaces.

The emission rates presented in Table 1, combined with additional information (volume of room in which heater is used, infiltration rate, mixing factor, removal rate by surfaces, flame settings, duration of use, and so on), permit the calculation of concentrations of air contaminants associated with use of kerosene space heaters in residences as a function of time with the general mass balance equation (*2*).

Results of the second set of experiments are shown in Fig. 1. The measured values agree with those predicted from the emission factors in Table 1. Relevant air quality health standards are also shown in Fig. 1 for reference. The exposure in a room with higher or lower ventilation rates under steady-state conditions can be determined from Fig. 1. In order to assess steady-state exposures on the basis of air changes per hour in Fig. 1, it is necessary to adjust the concentration of the air contaminant for a given value of air changes per hour by the volume of the space of interest. Typically, the air infiltration rate for U.S. residences is between 0.5 and 1.5 air changes per hour (*3*). In rooms without perfect mixing the actual exposures could be increased, while furnishings that are present may act as a sink for the contaminants, thereby reducing the levels of exposure.

Figure 1 shows that the use of convective and radiant kerosene heaters can result in concentrations of SO_2 and NO_2 in excess of the relevant ambient air quality standards, and in levels of CO_2 in excess of the guidelines set by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and of the occupational health standard for CO_2, even under the conditions of larger room volume and higher infiltration rates. Concentrations of CO may be of concern if a radiant kerosene heater is used in a small room with a moderate ventilation rate. The concentrations of air contaminants shown in Fig. 1 would be added to the concentrations of the contaminants in the infiltration air.

BRIAN P. LEADERER
John B. Pierce Foundation Laboratory,
Department of Epidemiology and
Public Health, Yale University
School of Medicine,
New Haven, Connecticut 06519

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Dehalogenation: A Novel Pathway for the Anaerobic Biodegradation of Haloaromatic Compounds

Abstract. *Microorganisms of lake sediment and sewage sludge anaerobically metabolized halobenzoates by a novel pathway. The primary degradative event was loss of the aryl halide without the alteration of the aromatic ring. Dehalogenation required strict anaerobic conditions and depended on the halogen and position, but not the number of halogen substituents. A stable methanogenic bacterial consortium was enriched from sludge and found capable of dehalogenating and often mineralizing a variety of halobenzoates to* CH_4 *and* CO_2*. The results suggest that reductive dehalogenation of aromatics could be important in removal of some chlorinated xenobiotics from the environment.*

Halogenated aromatic compounds are pollutants of major concern because they often enter the environment in substantial quantities, are toxic and resistant to degradation, and accumulate in sediments and biota (*1*). Although these compounds are recognized as persistent contaminants, satisfactory methods of degradation are still needed. The biodegradation potential of anaerobic microorganisms in habitats like sediments, sludges, ground waters, and landfills has largely been ignored. We report here a novel pathway for the reductive dehalogenation of aromatic substrates by the anaerobic microflora from these environments.

Halogenated benzoates were chosen as model substrates because they are used as herbicides (Amiben, 2,3,6-trichlorobenzoic acid, and dicamba) and are degradation products of other xenobiotic materials such as pentachlorobenzyl alcohol, Bidisin, and the polychlorinated biphenyls (*2*). There is also a wide range of benzoates with different substituents available which allowed us to characterize the specificity and rates of metabolism.

Anaerobic sediment or sewage sludges were transferred as 100 ml slurries to serum bottles (160 ml) with the use of strict anaerobic techniques (*3*). Substrates (0.2 to 0.8 m*M*) were injected by syringe into bottles; incubation was in the dark at 20°C for sediment and 37°C for the sludges. Parent substrate depletion, the appearance of intermediates, and the net amount of gaseous end products were determined by high-performance liquid chromatography (HPLC) and gas liquid chromatography (GLC) methods (*4*).

Initial screening for complete substrate mineralization to CH_4 and CO_2 indicated that both sediment and sludge possessed the ability to anaerobically metabolize halobenzoates. The organisms responsible for halobenzoate degradation were enriched from sludge by their ability to grow on 3-chlorobenzoate in a mineral salts medium (*3*). The specificity of this dehalogenating bacterial consortium was assayed by measuring substrate depletion after a 4-week incubation period.

The ability of sediment microflora and the enriched sewage consortium to metabolize halobenzoate substrates is summarized in Table 1. Microbes from both habitats degraded mono-, di-, and trihalogenated aromatic compounds. Significant halobenzoate metabolism occurred immediately in the enriched consortium, whereas sediment and sludges often exhibited a lag period before biodegradation proceeded. However, once acclimated to halobenzoate degradation, both sediment and sludge metabolized subsequent substrate additions without a lag.

On the basis of sequence and identity of the intermediates and final products observed (*5*), the primary degradative event for halobenzoates in anoxic environments was the removal of the aryl halides from the aromatic ring (Table 1). This reaction did not occur in sterile sediment, sludge, or enrichment culture, or in acclimated sediment incubated aerobically.

We conclude that dehalogenations of this type are biologically catalyzed and occur only in anaerobic habitats. Anaerobic dechlorination of compounds like DDT and lindane are well known (*6*), but the displaced chlorines are on alkyl rather than aromatic structures. The only previous reports of anaerobic dechlorination of an aromatic ring are for pentachlorophenol and Techlofthalam, which are degraded to a mixture of partially dehalogenated intermediates (*7*). These dehalogenations occur in anaerobic soil but have not been well characterized. In contrast, aerobic metabolism of aromatic compounds can be characterized by (i) direct replacement of the halogen by a hydroxyl group (*8*), (ii) the occasional nonenzymatic loss during NIH shifts (*9*), and (iii) removal of the halogen from the alkyl moiety after cleavage of the ring, which is the most frequently cited case (*10*).

A variety of halogens can be removed from the aromatic ring by dehalogenation (Table 1). Bromo- and iodo- substituents are degraded after a shorter lag time than their chloro- or fluoro- counterparts, which suggests that the Br and I species are more readily dehalogenated. In addition, meta halogens are more susceptible to microbial attack when com-

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