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Project Summary

Comparison of Measurement Techniques for Quantifying Selected Organic Emissions from Kerosene Space Heaters

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A study was performed to compare the "hood" and "chamber" techniques for quantifying pollutant emission rates from unvented combustion appliances and to assess the semivolatile and nonvolatile organic-compound emissions from unvented kerosene space heaters. In general, the hood and chamber techniques yielded similar emission-rate results for CO, NO, and NO_2. However, when differences were observed, it was concluded that the chamber-technique value was more realistic because this technique allows the oxygen level supplied to the appliance to decrease as it would in residences. A well-tuned radiant heater and a maltuned convective heater were tested for semivolatile and nonvolatile organic pollutant emissions. Each heater was operated in a 27-m^{-3} chamber with a prescribed on/off pattern. Organic compounds were collected on Teflon-impregnated glass filters backed by XAD-2 resin and analyzed by gas chromatography/mass spectrometry. Pollutant source strengths were calculated using a mass-balance equation. The results show that kerosene heaters can emit polycyclic aromatic hydrocarbons (PAHs); nitrated PAHs; alkyl benzenes; pentachlorphenol; phthalates; hydro naphthalenes; aliphatic hydrocarbons, alcohols, and ketones; and other organic compounds, some of which are known mutagens.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The sales and use of unvented kerosene space heaters over the past decade have increased dramatically in the U.S. Unvented kerosene space heaters have been found to emit a wide variety of pollutants including carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), formaldehyde (HCNO), and suspended particles. Other studies using a kerosene-fueled turbulent-diffusion continuous-flow combustor showed that many polycyclic aromatic hydrocarbons (PAHs) are emitted during kerosene combustion. Still other studies also showed that kerosene soot is indirectly mutagenic: one showed that essentially all of the indirect mutagenic activity of kerosene soot was due to unnitrated PAH compounds, and another showed that kerosene heaters emit dinitropyrene. Kerosene soot has also been shown to be directly mutagenic and that most of the direct mutagenic activity could be attributed to dinitropyrenes.

The above studies have shown that: 1) kerosene combustion products can be mutagenic, 2) kerosene combustion can produce PAHs and nitrated PAHs, and 3) it is likely that much of the mutagenic activity of kerosene soot is due to the PAHs and nitrated PAHs. However, it is not known whether the unvented portable kerosene space heaters commonly used indoors in the U.S. produce emissions similar to those emitted by the kerosene combustors used in several earlier studies or whether these portable space heaters produce other potentially harmful organic pollutants.

Two Major Goals

Of the two major goals of this study, the first was to measure selected organic pollutant emissions (including PAH and nitrated PAH emissions) from portable kerosene heaters commonly used in the U.S.

The second, but chronologically first, goal of this study was to compare two techniques for assessing pollutant emissions from unvented combustion appliances. One technique, henceforth called the "chamber" technique, involves placing the unvented combustion appliance in a room-size or large chamber, operating the appliance for a representative period of time, and monitoring the increase in the chamber pollutant concentrations. The pollutant emission rate, expressed as mass of pollutant emitted per unit of fuel consumed often µg/kJ, is then calculated from the chamber and outside pollutant concentrations using a single-equation, mass-balance model. The chamber technique has been used to quantify pollutant emission rates from kerosene heaters. The other technique, henceforth called the "hood" *technique, involves* placing the unvented combustion appliance under a hood large enough to capture all of the pollutant emissions and measuring the ratio of the concentration of each pollutant under investigation to the concentration of CO_2 in the hood exhaust flue. After correcting for background dilution air, the theoretical CO_2 emission rate is used to calculate the emission rate of the pollutant of concern. The hood technique has been used to measure pollutant emission rates from kerosene heaters.

The Tests

For the evaluation of the hood and chamber measurement techniques, one unvented radiant kerosene heater and one infrared unvented (natural) gas space heater (UVGSH) were used. Radiant and infrared combustion space heaters generally have more repeatable emission-rate characteristics than do their convective counterparts; therefore, using such heaters allowed hood vs. chamber technique emission-rate differences to be more easily detected.

For the tests measuring organic pollutant emissions from kerosene heaters, two heater/tuning conditions were chosen based, in part, on previously reported particulate emission data. The previous study showed that particulate emissions from a well-tuned properly operated convective kerosene heater were negligible, but that particulate emissions from a radiant heater were not. Therefore, it was reasoned that significant organic emissions would be more likely to be observed from a radiant heater rather than from a convective heater. A well-tuned radiant heater was chosen as the first heater/tuning combination to be tested. The other heater/tuning combination chosen for testing was a maltuned convective heater. This choice was based, in part, on conversations with kerosene-heater users and testers, who indicated that it was easier (more likely) for a convective heater to soot (i.e., emit a visible stream of particles) than it was for a radiant heater. In fact, altering the burner assembly itself was the only way the radiant heater tested in this study could be made to "soot." The convective heater was maltuned by lifting the exterior shell of the heater by approximately 1 cm, thereby providing excess air to the wick. Only two heater/tuning combinations were tested because each test had to be conducted many times to collect enough samples for mutagenicity testing.

All experiments were conducted at the Lawrence Berkeley Laboratory (LBL). Battelle's Columbus Division prepared and analyzed filters and resins used by LBL to collect selected organic pollutant emissions and provided sample extracts to the Health Effects Research Laboratory of the U.S. EPA.

Test Results

In general, the hood and chamber emission-rate measurement techniques yield similar results for CO, NO, and NO_2. However, when discrepancies were observed, they were believed to be caused by differences in combustion-air oxygen levels. The chamber method results were judged to be more accurate since this method allows the oxygen content of the combustion air to drop, as would occur in actual residences. The hood method appears to be adequate for quantifying CO, NO, and NO_2 emission rates from appliances that are not oxygen sensitive or from appliances that marginally affect a residence's oxygen level, such as a gas range. The chamber method was preferable for measuring total suspended particulate emissions primarily because it was easier to implement. No disadvantages to the chamber method were discovered.

With regard to *organic pollutant* emissions from kerosene heaters, this study has confirmed the results of other studies; i.e., that the kerosene combustion process can emit PAHs and nitrated PAHs. One-nitronaphthalene is clearly emitted by well-tuned radiant and maltuned convective kerosene space heaters. One-nitronaphthalene was found almost entirely in the semivolatile fraction for the radiant-heater tests. For the maltuned-convective-heater tests, 30% of the nitronaphthalene was collected on the filter. This is presumably due to the heavy loading of fresh soot on the filter during the maltuned-convective test. Emissions of 9-nitroanthracene were observed in the XAD fraction of one of the radiant-heater tests and in the filter fraction of the maltuned-convective test. Emissions of 1-nitropyrene were also observed in the filter fraction of both radiant test samples, whereas only trace amounts of 3-nitrofluoranthene were observed in one of the two series of radiant-heater tests in the filter-collected fraction.

In addition, kerosene heaters were found to emit many other organic compounds, including aliphatic hydrocarbons, alcohols, and ketones; phthalates; and alkyl benzenes. Additional analysis is needed to correlate these results with health-effects data to determine the risk associated with these organic emissions. PAH and nitrated-PAH emissions are sufficiently important to justify additional quantitative studies; furthermore, examinations of other organic compounds of toxicological significance and of unvented combustion sources should be expanded.

One very important observation of this study was that some estimates of the indoor reactivity of SVOCs were higher than 2 h^{-1}. This implies that reactivity rates for some SVOCs are more important than ventilation rates for determining indoor concentrations. Clearly, this indicates that future studies must quantify the indoor reactivity process for individual SVOCs in order to gain insight into potential indoor exposures to these compounds.

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James B. White is the EPA Project Officer (see below).
The complete report, entitled "Comparison of Measurement Techniques for Quantifying Selected Organic Emissions from Kerosene Space Heaters," (Order No. PB 90-187 022/AS; Cost: $15.00, subject to change) will be available only from:
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