TITLE: Characterization of Emissions from Heaters Burning Leaded Diesel Fuel in Unvented Tents

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# Characterization of Emissions from Heaters Burning Leaded Diesel Fuel in Unvented Tents

## Abstract
During and after the Persian Gulf War, a proportion of returned American service personnel was diagnosed as having a "mystery illness" or "Gulf War Syndrome." Only limited information is available to study possible links between environmental exposures and the Gulf War Syndrome.

The purpose of this protocol is to conduct a study that simulates human exposure to aerosols produced by unvented heaters in tents used in the Persian Gulf, so that the contribution of exposure to this in-tent pollutant can be estimated. The specific aims include: (1) physical and chemical characterization of aerosols produced by heaters that burned fuels in an unvented tent, and (2) estimation of exposure to particulate matter, combustion gases (such as CO₂, CO, NOₓ, and SO₂), and other compounds (such as lead and polycyclic aromatic hydrocarbons).
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INTRODUCTION

Approximately 700,000 U.S. military personnel served in the Persian Gulf conflict during 1990 and 1991. During and after the Persian Gulf War, a proportion of returned American service personnel was diagnosed as having a "mystery illness" or "Gulf War Syndrome." Manifestations of the Gulf War Syndrome have varied from person to person, but often include arthralgia, weakness, fatigue, headache, memory loss, and other mental impairments. Skin rashes and hair loss have also been mentioned. A variety of causes have been suspected, including agents of chemical and biological warfare, fumes from both leaded and unleaded fuels, components of smoke from burning oil wells, illicit substitutes for alcohol, and recreational drugs.

Only limited information is available to study possible links between environmental exposures and the Gulf War Syndrome. While environmental exposures may have been important, the data needed for sound epidemiological studies are very limited. Major contributions to air pollution during the Gulf War conflict included oil-well fires in Kuwait, fumes from cook stoves and heaters, pesticides, and naturally occurring pollutants such as sand, dirt, and fauna. Most of these environmental factors have been studied and evaluated to some degree, except the exposures to pollutants produced from unvented heaters in tents. To fully characterize these exposures and the resulting potential health risk to the troops, all pathways of exposure must be evaluated.

Various types of portable space heaters have been widely used in offices and homes. Tu and Hinchliffe studied the emissions from five portable space heaters, including three conventional electrical heaters, one quartz electrical heater, and one kerosene heater. Their results indicated that most aerosols produced were in the ultrafine particle range, and the aerosol concentration in an unvented chamber could be as high as 330 µg/m³ from using a kerosene heater for 1 hour. Particle compositions were primarily carbon black and chromium. The gas phase was not studied. Emissions from gas-fired space heaters were reported by Traynor et al. and Relwani and Moschandreas; the primary pollutants were CO₂, CO, and NO₂ with very low mass concentrations of ultrafine particles. On the other hand, emissions from burning liquid fuels can be substantial in both gas pollutants and particles. For instance, emissions from unvented kerosene space heaters can contribute to indoor air particulate
concentrations in excess of 20 \mu g m^{-3} over background level and over 300 \mu g m^{-3} in a sealed chamber. These space heaters can also emit organic compounds such as polycyclic aromatic hydrocarbons (PAHs), in addition to CO\textsubscript{2}, CO, NO\textsubscript{x} and S\textsubscript{2}O\textsubscript{5}. These semivolatile and particle-bound organics emitted from the kerosene heaters were found to be mutagenic. Indoor air quality can be affected by the use of kerosene heaters; it also can be affected by human activities such as opening doors and windows.

The purpose of this protocol is to conduct a study that simulates human exposure to aerosols produced by unvented heaters in tents used in the Persian Gulf, so that the contribution of exposure to this in-tent pollutant can be estimated. The specific aims include:

1. Physical and chemical characterization of aerosols produced by heaters that burned fuels in an unvented tent.
2. Estimation of exposure to particulate matter (PM), combustion gases (such as CO, NO\textsubscript{x}, and S\textsubscript{2}O\textsubscript{5}), and other compounds (such lead and PAHs).

The first 6 months after the initiation of the project, we have had extensive discussion with several Army laboratories on tents, tent heaters (US Army, Natick Research Development and Evaluation Center), and fuels (Fuels & Lubricants Technology Team, Mobility Technology Center - Fort Belvoir). Based on these discussions, it was determined that the unvented heaters most likely used in the Gulf War were commercial units that burned kerosene and aviation fuels, primarily JA1 and JP8 fuels which are kerosene-based and have similar compositions. The standard Army heater is vented outside of the tent and is much less a concern for inhalation health effects. After we gathered this information, we then purchased a used Army tent, a Army tent heater, and two kinds of kerosene heaters. The tent was set up, and various instrumentation including samplers for particulate, gases, and vapors were tested. Preliminary data from one kerosene heater using kerosene fuel are reported here.
ASSUMPTIONS

The primary purposes of this study are to characterize, physically and chemically, the aerosols produced from unvented heaters. Aerosols produced from burning fuels are generally formed from vapor condensation produced from burning fuel and from residuals of incomplete combustion. We assume that major exposure in the tent is from emissions by using unvented heaters in tents. We also assume that fuel types, heaters, and air exchange rate are major factors influencing the emission characteristics and therefore, the exposure.

EXPERIMENTAL METHODS

Tent and Heaters

A used canvass with vinyl backing Army tent (GP medium, 16 ft x 32 ft) was purchased following discussion with Army personnel at the Natick Research Development and Evaluation Center. Four unvented heaters were purchased. Two convection type heaters (RMC-95, RMC International, Denver, CO, rated at 22,500 Btu per hr) and two radiant heaters (Model AWHR-1101, Cans Unlimited, Inc., Greer, SC, rated at 10,000 Btu per hr) were purchased. We also purchased a standard Army tent heater (Model H-45, Type II). The fuel was a K-1 kerosene (Parks Co., Fall River, MA). Other fuels will be tested later.

The heaters were placed inside the tent to mimic their use in the Persian Gulf. The tent was set up inside a clamshell structure under a better controlled environment as shown in Figures 1 and 2. The volumes of the tent and clamshell structure were estimated based on the geometry to be 100 and 5000 m³, respectively.
Figure 1. Schematic of the Army tent inside a clamshell

Figure 2. The Army tent and the instrument control panel
Sampling Instruments

Assuming that the aerosols produced by the heaters will be mostly in the fine and ultrafine particle size ranges, and the vapor-phase emission may contain PAHs and lead, the following aerosol sampling instruments were selected for this study:

1. Filter samples with 90 mm mixed cellulose membrane filter (0.8 μm pore size AAWP filter, Millipore, Bedford, MA) were taken for the time-averaged aerosol mass concentration.
2. The Lovelace Multi-jet (LMJ) cascade impactor was used for aerosol size distributions between 0.5 - 15 μm.9
3. Point-to-plane electrostatic precipitator (ESP) samples10 were taken for morphological examination of particles.
4. A continuous flow condensation nuclei counter (CNC) (Model 3020, TSI Inc., St. Paul, MN) was used to continuously monitor the aerosol number concentration versus time, from the time the heater was turned on until steady state, if any, is reached and beyond.
5. A Quartz Crystal Microbalance Cascade Impactor (QCM)(Model PC-2 Air Particle Analyzer, California Measurements, Inc., Sierra Madre, CA) or a Scanning Mobility Particle Sizer (SMPS) system (Model 3932, TSI Inc., St. Paul, MN) were used to size particles in real time. The QCM can size particles ranging from 0.05 - 25 μm, whereas the range for the SMPS is 0.01 - 1.0 μm. The SMPS required a relatively stable aerosol; therefore, the choice of which systems to use will depend on the stability of the aerosol.

The Tenax trap was used as the adsorbent for vapor-phase organo-lead vapor. Tenax was chosen rather than the widely used adsorbent XAD-2 because Tenax has been shown to give optimal recoveries of tetraethyl lead.11 Gaseous emission are also monitored using the following instruments:

1. CO infrared analyzer (Model 865 Beckman Instruments, Fullerton, CA)
2. Hydrocarbon analyzer (Model 400 Beckman Instruments, Fullerton, CA)
3. NOX chemilumination analyzer (Model 8440, Monitor Labs, San Diego, CA)
4. SO2 pulsed fluorescent analyzer (Model 43, Thermo Electron Instruments, Hopkinton, MA)
Air Exchange Rate

The air exchange rate in the tent is a major factor in determining the pollutant concentrations inside the tent. The exchange rate was determined using a trace gas method. A trace amount of SF$_6$ was released into the tent and the concentration SF$_6$ was monitored using an Autotrac monitor (Model 101, Lagus Applied Technology, San Diego, CA). The SF$_6$ concentration can be fitted into the following equation:

$$ C = C_0 e^{-\lambda t} $$

(1)

where $C$ and $C_0$ are SF$_6$ concentration in time $t$ and 0; $\lambda$ is the air exchange rate per (hr$^{-1}$). This equation can also be used to estimate the volume of the tent. By injecting a known volume of SF$_6$ and from the fitted value of $C_0$, one can determine the tent volume:

$$ V_{tent} = \frac{C_0}{C_{SF6}} $$

(2)

PROCEDURES

Figure 3 shows the schematic of sampling instruments in the tent. A typical run started at about 3 A.M. Gas analyzers were calibrated and the filter and impactor substrates weighed. The ventilation rate within the tent was measured using a trace gas method as described. A trace amount of SF$_6$ in the compressed gas cylinder was released to give an initial concentration between 10-100 ppb in the tent. Changes in ventilation rate were investigated under various conditions, e.g., changes in wind speeds, or when the tent-doors were opened or closed.

The gas and aerosol monitors were turned on, then the heaters were ignited (usually two identical heaters were used in the test). The heaters were operated under well-tuned condition. Aerosol samples were taken using the filter, the LMJ, and the ESP samples. Real-time aerosol concentration and size distribution were measured using a CNC and the QCM impactor or SMPS. CO, NO$_x$, total hydrocarbon, and SO$_2$ concentrations were monitored continuously. The heaters were turned off after 2 hours, and the monitoring continued for another hour.
The aerosol mass collected on filters and by the LMJ were determined by weighing the filters and substrates before and after each run, using a Cahn-31 electrobalance (Cahn Instruments Inc., Cerritos, CA). The filter samples will be analyzed for lead and PAH. The time-averaged aerosol size distribution were calculated from the weighing data of the LMJ and the stage effective cut-off diameters. The ESP samples were examined for particle morphology using transmission electron microscopy. The CNC data provided aerosol number concentration versus time, and the SMPS data provided aerosol number size distribution versus time.

RESULTS AND DISCUSSION

Air Exchange Rate

The air exchange rate of the tent was adjusted by closing the door and sealing the vent. Figure 4 shows an example of the SF$_6$ concentration profile from a 240-min test. The
curve of \( C = 30 e^{-1.15t} \) was the best fitted curve. The intercept of \( C_0 = 30 \) ppb was the initial concentration, and the air exchange rate, \( \lambda \) was 1.15 hr\(^{-1}\).

**Volume of the Tent**

From the \( \text{SF}_6 \) test we can also estimate the volume of the tent. Three mL of \( \text{SF}_6 \) was injected into the tent for these tests and from fitting equation (1) to the concentration decay data, the initial concentration \( C_0 \) was estimated and the tent volume calculated following equation (2). Based on five separate tests the initial concentration, \( C_0 \) was determined to be 29.6 ± 5.9 ppb, and the tent volume was 98.7 ± 19.7 m\(^3\). The estimated volume was closed to the calculated volume of 100 m\(^3\).

![Graph](image)

**Figure 4** \( \text{SF}_4 \) Concentration decay as a function of time

**Preliminary Data**

Typical emission data for the convection heater (RMC-95) are shown in Figures 5-9. The air exchange rate was high at 4.2 h\(^{-1}\). Figure 5 shows the temperature rise as a function of
Figure 5. Temperature profile inside the tent during a test run with two RMC-95 heater time, suggesting a rapid rise after the heater was ignited and a rapid decline after the heater was turned off. Figures 6-8 show concentration profiles of NO\textsubscript{x}, CO, and total hydrocarbon indicating the rises and falls of gases generated from the combustion process. It appears that the NO\textsubscript{x} concentration reached a plateau after the continuous operation of the heater, whereas the CO and total hydrocarbon concentration peaked about 20 min after heaters were turned on, then the concentration decreased. A small second peak appeared after the heaters were turned off. Figure 9 shows the particle number concentration as a function of time, which suggests peak concentrations after the heaters were turned on and turned off. Figure 10 shows the particle size obtained with the LMJ cascade impactor. The size distribution shows a bimodal distribution with modes at 10 and 1 \( \mu \)m.
Figure 6. NOx concentration profile in a test

Figure 7. CO concentration profile in a test
Figure 8. Total hydrocarbon concentration

Figure 9. Particle number concentration
Table 1 summarizes particulate and gaseous concentrations for three tests on the convection heaters. These tests were done at air exchange rates between 2.35 and 4.24. The mean particulate concentrations during the 2 hours of heater operation decreased with increasing air exchange rate, indicating dilution effects due to air exchange. A similar trend can be found for gaseous concentrations. Particle concentrations were quite high, even after the heaters were turned off.

Figure 10. Particle size distribution from LMJ impactor
Table 1 Summary of Emission Data

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<tr>
<td>Air exchange rate</td>
<td>2.35</td>
<td>2.95</td>
<td>4.24</td>
</tr>
<tr>
<td>(h⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Concentration</td>
<td>0.433</td>
<td>0.277</td>
<td>0.119</td>
</tr>
<tr>
<td>in the first 2 hr (mg m⁻³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Concentration</td>
<td>0.131</td>
<td>0.465</td>
<td>0.308</td>
</tr>
<tr>
<td>1 hr after heaters were turned off (mg m⁻³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean CO concentration</td>
<td>NA</td>
<td>NA</td>
<td>1.22</td>
</tr>
<tr>
<td>in the first 2 hr (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak CO concentration (ppm)</td>
<td>NA</td>
<td>NA</td>
<td>1.62</td>
</tr>
<tr>
<td>Mean NOₓ concentration</td>
<td>2.39</td>
<td>1.25</td>
<td>1.43</td>
</tr>
<tr>
<td>in the first 2 hr (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak NOₓ concentration (ppm)</td>
<td>3.20</td>
<td>1.84</td>
<td>1.85</td>
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<tr>
<td>Mean SO₂ concentration</td>
<td>0.013</td>
<td>0.02</td>
<td>NA</td>
</tr>
<tr>
<td>in the first 2 hr (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak SO₂ concentration (ppm)</td>
<td>0.021</td>
<td>0.98</td>
<td>NA</td>
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<tr>
<td>Mean HC concentration</td>
<td>5.18</td>
<td>7.59</td>
<td>4.78</td>
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<tr>
<td>in the first 2 hr (ppm)</td>
<td></td>
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<td></td>
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<tr>
<td>Peak HC concentration (ppm)</td>
<td>7.40</td>
<td>10.4</td>
<td>6.94</td>
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CONCLUSIONS

In the first year, we did a substantial literature search and have consulted extensively with Army experts on tents, heaters, and fuels used in the Gulf War for the experimental design. Our current design emphasizes the role of commercial kerosene heaters that have been extensively used in the Gulf War. Because these are unvented heaters, their emission is released directly in the tent. Substantial emission of PMs and gases can accumulate in a tent
depending on the fuels and air exchange rates.

Our preliminary data indicate a high concentration of PM, NO\textsubscript{x} and CO concentrations. PM concentration remained high 1 hour after the heaters were turned off. We also found out that the air exchange rate is an important factor on the emission concentration inside the tent. The air exchange rate (between 1-4 per hour) was higher than within a home (between 0-2 per hour), because it is difficult to seal the tent especially during windy weather conditions. We will continue to investigate the role of fuels and heaters on emission characteristics. These data will be applied in calculating respiratory doses of particles for assessing exposure to pollutants of the troops who served in the Gulf War.
IV. REFERENCES


Bibliography of Pubs/Mtg. Abstracts: None