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Exposure of Service Station Attendants to Oxygenated Gasoline Containing Methyl Tert-Butyl Ether

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Reported by Calvin K. Cook and Ronald J. Kovein

Summary

In November and December 1994, the National Institute for Occupational Safety and Health (NIOSH) conducted health hazard evaluations at service stations located in the greater Newark, New Jersey, area to assess attendants' exposures to oxygenated gasoline that contained methyl tert-butyl ether (MtBE), an oxygenated compound blended with unleaded gasoline to help reduce vehicle emissions. Environmental measurements were made using two methods: (1) conventional air sampling and (2) video exposure monitoring with the use of real-time instrumentation.

Laboratory analysis of 21 personal breathing zone (PBZ) air samples collected for total hydrocarbons (THCs, as gasoline) and MtBE revealed a geometric mean time-weighed average (TWA) concentration of 1.9 ppm (range: 0.43 to 4.4 ppm) for THCs and a geometric mean TWA concentration of 0.38 ppm (range: 0.08 to 1.3 ppm) for MtBE. These concentrations for THCs and MtBE were well below their most stringent exposure criteria of 300 and 40 ppm, respectively. Real-time exposure monitoring results revealed a high variability of relative THC peak concentrations that were measured as high as 425 ppm. Video exposure monitoring demonstrated that manual refueling is significantly responsible for exposures to oxygenated fuels, particularly peak exposures.

Although full-shift TWA sampling results indicated relatively low exposure concentrations for THCs and MtBE, real-time measurements for THCs revealed elevated peak concentrations as much as about 130 times greater than TWA concentrations. This suggests that similar conclusions can be drawn about MtBE peak exposures. NIOSH investigators concluded that it is not known whether a health hazard exists at the peak THC concentrations measured. Improvement of vapor recovery system effectiveness and attendant work practices suggested in this study could be applied to refueling operations throughout the industry to reduce exposures to oxygenated gasoline.

Introduction

Most oxygenated gasoline marketed in the United States contains MtBE, a compound which is added to oxygenate the fuel, thus increasing the octane rating and reducing the motor vehicle pollution emission.[1] Since the enactment of the Clean Air Act Amendments of 1990, the U.S. Environmental Protection Agency (EPA) has mandated the use of oxygenated fuels (most of which contain MtBE) in 44 urban areas throughout the country where ambient carbon monoxide levels are a major contributor to air pollution. Since the enactment of the act, however, health complaints among service station attendants and self-service customers have increased. Individuals affected generally experience acute health symptoms of nausea, headaches, respiratory depression, and eye irritation which they believe are attributable to oxygenated gasoline exposures.[1]

Full-shift TWA exposures to airborne MtBE (using conventional air sampling methods) have revealed 8-hour TWA exposures of less than 1 ppm, well below the most stringent 8-hour TWA exposure criterion of 40 ppm recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). However, since health complaints have increased, and toxicological data suggest that short-term or peak exposures can cause irritative symptoms, NIOSH investigators decided to develop a measurement strategy to characterize short-term exposures which would provide insight as to why reported symptoms do not correlate with measured TWA exposure. The objective of this research project was to assess service station attendant exposure to oxygenated gasoline using a video exposure monitoring technique. The specific aims of this study were: (1) to characterize short-term airborne exposures to oxygenated fuel, and (2) to identify specific emission sources and work practices that contribute to worker exposure. Currently there are no short-term MtBE exposure criteria established by NIOSH or the Occupational Safety and Health Administration.

Background

Previous Studies

This study was prompted by a series of industrial hygiene evaluations that were conducted by NIOSH and the American Petroleum Institute (API).[2] In October 1990, NIOSH investigators began conducting industrial hygiene assessments of service station attendants' exposures to hydrocarbons, including MtBE, benzene, toluene, and xylenes. In one particular study, API contracted for a parallel study to assess exposures to self-service customers. NIOSH and API made comparative studies that were conducted at service stations equipped with stage II vapor recovery systems and at service stations that were not equipped with vapor recovery. One of the objectives was to evaluate how well vapor recovery systems reduced personal exposure. Vapor recovery systems were developed and designed to control gasoline vapors emitted from the gas tank filler tubes of vehicles when saturated vapors are displaced during refueling.

The NIOSH and API studies revealed surprising results. After comparing exposure levels obtained at each service station and adjusting for exposure variables, such as climatic conditions and fuel composition, the NIOSH study determined that the vapor recovery systems had no effect on reducing exposures to hydrocarbons, including MtBE. In addition, the API study showed no significant reduction in self-service customer exposure to hydrocarbons at service stations equipped with vapor recovery, in comparison to hydrocarbon levels obtained at service stations without vapor recovery. Although worker exposures to specific hydrocarbons were measured below their respective exposure criteria, questions remained as to why the use of vapor recovery systems had little or no effect on reducing MtBE exposures. Based on the results of the NIOSH and API studies, it was believed that personal airborne exposures (workers and self-serve) were caused by gasoline spills or tailpipe emissions.

In both studies, NIOSH Sampling and Analytical Method 1615 was used to determine worker exposure to MtBE based on an 8-hour TWA.[3] NIOSH Method 1615, the only available conventional air sampling method used to measure MtBE, was limited due to its minimum sampling period of about 45 minutes. Consequently, short-term and peak exposures were not measured during the NIOSH and API studies. Because an attendant spent only short periods of time (1 to 4 minutes) refueling vehicles, investigators believed there was a need to characterize MtBE short-term exposures.

Facility Selection and Description

An evaluation of oxygenated gasoline exposures was undertaken to estimate short-term exposure levels using real-time instrumentation. During November and December 1994, exposure to THCs (as gasoline) and MtBE was measured among service station attendants at two retail automotive service stations located in the greater Newark, New Jersey, area. New Jersey was selected because it is one of only a few states that do not permit self-service stations, thus significantly increasing the duration of attendant exposure. Stations in the Newark area were geographically chosen because the formulated gasoline marketed in this area has an MtBE content of 15 percent, the maximum proportion allowed by the EPA. The two stations were also identified based on their relatively high volume of gasoline sales.

The two service stations (A and B) were equipped with stage II vapor recovery systems, and each pump was equipped with locking devices to allow automatic refueling. Station A had four service islands (6 pumps per island, total pumps = 24) and employed about 10 attendants (7 full-time, 3 part-time). These attendants dispensed about 33,000 gallons of gasoline each week. Station B was larger (8 service islands, 6 pumps per island, total pumps = 48) and employed about 14 attendants (10 full-time, 4 part-time) who dispensed about 76,000 gallons of gasoline each week. Unlike other studies that evaluated oxygenated gasoline exposures at service stations, in this study the attendants' primary duty was to refuel vehicles, generally for an 8-hour work period.

Vapor Recovery Systems

Liquid gasoline volatilizes under normal conditions. Controlling fugitive gasoline emissions to the environment is one of the primary means of reducing human exposure to gasoline vapors. Stage I and II controls are the two types of vapor recovery systems that are used at service stations.[1,4]

Gasoline vapors are released when tanker trucks or fuel storage tanks are filled. Gasoline evaporative emissions are captured by stage I control systems and returned to the truck tank from which the liquid gasoline was transferred. Stage I systems have been installed at approximately two-thirds of the nation's bulk terminals, one-half of the nation's bulk plants, and one-half of the nation's service stations.[1]

Stage II controls actively recover vapors released from a vehicle's gas tank when refueled. Stage II controls include a vapor hose attached to the filling nozzle which captures vapor emissions, returning them to service stations' storage tanks. Used in California and the District of Columbia since 1971, these systems are currently installed at about 38,000 of the nation's service stations.[1]

Video Exposure Monitoring

Identifying an activity that causes an elevation in personal exposure can often be difficult, particularly if the activity lasts only a few seconds. Conventional air sampling methods can indicate a certain level of exposure. However, due to the complexity of the process or work cycle, activities contributing to exposure levels may not be identified.

NIOSH researchers have applied video exposure monitoring techniques during a variety of industry studies to help identify specific sources and work activities that affect worker exposure. One video exposure monitoring technique uses response measurements from direct-reading air analyzers that have been connected to datalogging instruments.[5] While a datalogger records concentration measurements, a worker's activities are simultaneously recorded by a video camera. Later, the exposure measurement data collected by the datalogger are downloaded to a personal computer for storage and statistical analysis. In addition to statistical analysis, the personal computer can superimpose a bar graph, proportional to the exposure measurement, upon the edge of each recorded video frame. By replaying the superimposed video recording, this technique can identify tasks that elevate worker exposures to hazardous gases and vapors. These tasks can be coded to the data set as activity variables for subsequent statistical analysis. Video exposure monitoring allows repeated detailed review of the work cycle or process. Though not a substitute for conventional air sampling methods, video exposure monitoring can be a useful compliment to laboratory-analyzed sample media.

Evaluation Methods and Instrumentation

Conventional Air Sampling

Environmental measurements were made while station attendants performed routine refueling duties. A total of 21 PBZ and 6 area air samples for THCs and MtBE were collected on 400-mg charcoal tubes using personal air sampling pumps calibrated at a flow rate of 0.20 L/min. Area air samples were collected at service station islands atop refueling pumps. Three area air samples were collected and analyzed qualitatively for individual hydrocarbons. Based on qualitative analysis of the three area air samples, all PBZ samples were analyzed quantitatively by gas chromatography for gasoline vapor (expressed as THC) and for MtBE, in accordance with NIOSH Method 1615.

Six bulk gasoline samples were collected in 10-ml glass vials and later analyzed to determine the percent of MtBE by weight and volume. The six samples included two samples each of three gas-

TABLE 1. Air Sampling Results for MtBE and Gasoline Vapors

Work Activity or Sample Location	Average Sampling Time	Average Sample Volume	Average Concentration (ppm) MtBE	Average Concentration (ppm) THCs (as Gasoline)
Attendant at service station A (PBZ sample)	375 minutes	75 liters	0.57 (range: 0.23 to 1.3)	2.4 (range: 1.1 to 4.4)
Attendant at service station B (PBZ sample)	355 minutes	72 liters	0.51 (range: 0.12 to 1.4)	2.7 (range: 0.6 to 6.2)
Refueling pumps at both stations (area samples)	444 minutes	89 liters	0.19 (range: 0.08 to 0.24)	0.93 (range: 0.43 to 1.4)
Evaluation Criteria				
AIHA workplace environmental exposure level			100	None
NIOSH recommended exposure limit			None	LFC
OSHA permissible exposure limit			None	NA
ACGIH threshold limit value			40	300

Area = general area air sample; LFC = lowest feasible concentration.

oline grades available (octane ratings: 87, 89, and 93).

Video Exposure Monitoring

The Mini RAE® model PGM-75 photoionization detector was used to measure THC exposures using a 10.2 electron volt (eV) ultraviolet discharge lamp. The instrument was worn as a personal dosimeter by attendants while performing routine work activities. The Mini RAE is a lightweight, nonspecific instrument that will detect all components in gasoline vapors that have an ionizing potential less than 10.2 eV. For extended datalogging operation, its analog output was connected to a Metrosonics® DL-3200 datalogger which stored real-time data for up to 4 hours. The instrument was calibrated before each sampling period using the DL-3200 in the sense mode. In the sense mode, the DL-3200 obtained the exact input voltage level from the Mini RAE instrument. One voltage level (160 to 170 mV) was the response to zero gas calibration; the other voltage level (180 to 200 mV) was the response to span gas calibration. Isobutylene (100 ppm) was supplied to the Mini RAE during all calibrations. The DL-3200 was programmed for a 250-ms sampling rate. For every monitoring session, the average value was stored once every second. After each sampling period, real-time data were downloaded to an IBM-compatible personal computer and plotted as a graph over time. Prior to each measurement period in the field, the lamp was cleaned with ethanol and a one-point calibration was performed using 100 ppm of isobutylene span gas.

A total of 12.5 hours of videotape recorded the activities of five individual attendants. Eight separate data files, ranging from 78 to 240 minutes, were compiled at the two service stations. After reviewing the video recordings, the following four specific tasks of the refueling process were selected and coded into each data file so that each task's contribution to the cumulative exposures could be calculated: task 1: gas cap removal/nozzle insertion; task 2: refueling/pumping; task 3: nozzle extraction/gas cap replacement; and task 4: other activities (i.e., transactions, checking under the hood, washing windshield).

These tasks were performed sequentially when there was only one vehicle at an attendant's service island. With multiple vehicles, however, this 1-2-3-4 sequence was usually interrupted. Frequently, the attendant would leave a vehicle being refueled to repeat one or more of the same elements at another island.

To determine how each of the four tasks affected the cumulative exposure, the real-time data were manipulated into a Microsoft® Excel® spreadsheet. The data set consisted of relative concentration measurements and a corresponding 1-second time interval. Each real-time measurement was coded to correspond to one of the four tasks. The cumulative time and exposure for each task were summed to determine average concentration.

A weather station was established at one of sampling sites on each day of the study to monitor wind velocity, tem-

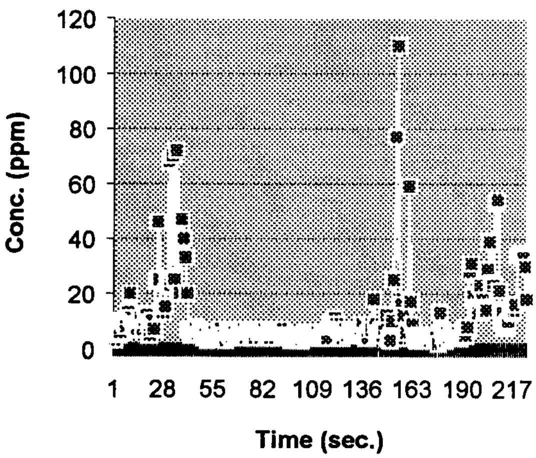

FIGURE 1. Hydrocarbon exposure during typical refueling cycle.

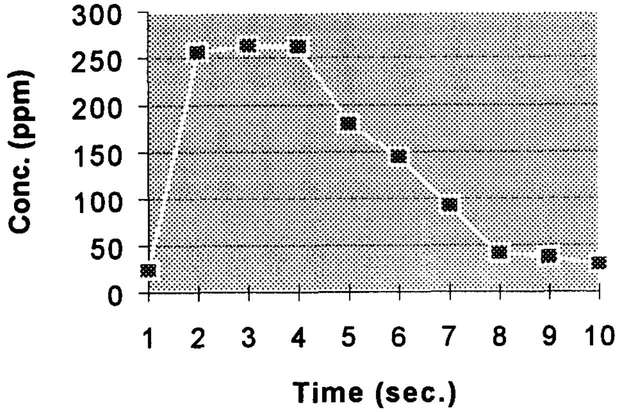

FIGURE 2. Hydrocarbon exposure during task 1, nozzle insertion.

perature, and relative humidity. These conditions were recorded about every hour.

Results and Observations

Conventional Air Sampling

The results of air sampling for THCs and MtBE are summarized in Table 1. The 21 PBZ samples for THCs ranged from 0.43 to 5.9 ppm (geometric mean = 1.9 ppm), well below the ACGIH threshold limit value (TLV) of 300 ppm. The results for the PBZ samples (n = 21) for MtBE ranged from 0.08 to 1.4 ppm, TWA (geometric mean = 0.38 ppm), well below the ACGIH TLV of 40 ppm. Area air samples (n = 3) for MtBE and THCs revealed TWA concentrations that ranged from 0.08 to 0.24 ppm and 1.0 to 1.3 ppm, respectively. A summary of bulk gasoline analysis determined the MtBE liquid volume percent and the percent by weight of each sample. The percent of MtBE in the bulk gasoline samples ranged from 15 to 18 percent (by volume) and 16 to 19 percent (by weight).

Video Exposure Monitoring

Figure 1 illustrates a typical refueling cycle. Figures 2 through 4 characterize the exposure for the three basic job tasks (tasks 1 to 3). The real-time data show the nature and variability of peak hydrocarbon exposures. Although not shown, THC real-time measurements were as high as 425 ppm.

Tasks 1 and 3 were brief in duration, usually lasting about 8 seconds for each task. Although the time required for an attendant to dispense gasoline varied according to the volume being pumped, the average refueling time was about 3 to 4 minutes.

Based on detailed analysis of all real-time data collected, Figure 5 summarizes the contribution of each individual task of the refueling operation to the total activity and total cumulative exposure. Task 2 (refueling/pump), while accounting for only about 25 percent of the total activity time, was responsible for about 45 percent of the total cumulative exposure. While accounting for 64 percent of the total activity time, task 4 (other activities) contributed about 40 percent of the total cumulative exposures. The two tasks involving the removal and replacement of the gas cap only contributed about 7 and 9 percent of cumulative exposures, respectively.

The exposure data spreadsheets were reviewed and elevated peak exposure concentrations (greater than 50 ppm) were collected and summed according to each task. Task 2 (refueling) accounted for about 73 percent of all peak exposures. Peak exposures were generally 1 to 2 seconds in duration.

The ambient measurements, taken every hour for temperature, relative humidity, wind speed, and direction, were neither extreme nor highly variable during the 2 days of this study; therefore, it was considered unlikely that these conditions complicated exposures.

Discussion

Manually dispensing fuel (task 2) had a task duration of only 25 percent of the total time. However, despite a relatively short duration time, task 2 produced the largest proportion of exposure for the operation due to the magnitude of the average concentration measured for this task. Furthermore, task 2 accounted for about 73 percent of peak THC exposures greater than 50 ppm. Controlling this task would be the main priority for controlling gasoline exposures to attendants during the refueling process.

While exposures associated with tasks 1 and 3 cannot be avoided by attendants and self-service customers, exposures during tasks 2 and 4 can be minimized and largely avoided based on visual observations during sample collection. While performing tasks 2 and 4, for example, it was observed that attendants had a significant measurable degree of control regarding exposure. The attendants' proximity to the source (gasoline pump) was the greatest contributing factor. Obviously, an attendant must be near the source of exposure when removing

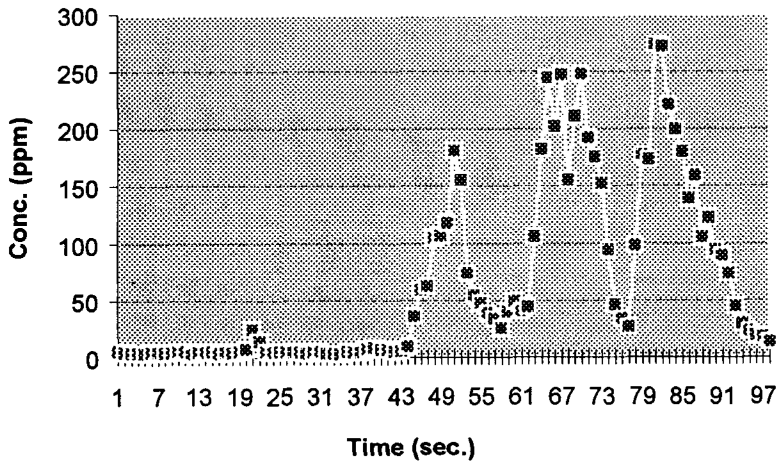

FIGURE 3. Hydrocarbon exposure during task 2, active refueling.

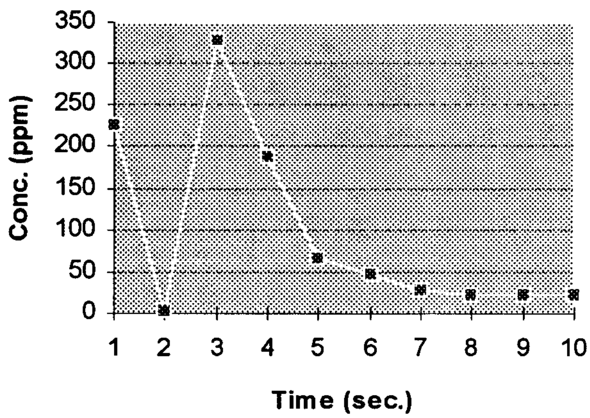

FIGURE 4. Hydrocarbon exposure during task 3, nozzle extraction.

the gas cap and inserting the nozzle into the fuel tube. However, once the nozzle has been triggered and the refueling locking device is used, the attendant need not watch the meter close up. In fact, the attendant can remain a considerable distance (6 to 8 ft) away from the pump and still observe the island meter display unit or hear the audible click of the nozzle when it shuts off automatically. An excellent example of this scenario was illustrated where an attendant was observed refueling a vehicle in the automatic mode. During the first 30 seconds of refueling, the attendant was not manually pumping, but was standing near the active refueling pump. After the first 30 seconds of refueling process, the attendant stepped a few feet away from the pump source. When the attendant was in proximity to the refueling source, peak THC exposures were as high as 217 ppm. However, when he decided to move just a few feet away, his exposures decreased to less than 40 ppm.

The islands at both stations were equipped with computerized systems that allowed dollar amounts ($5, $10, and $20) to be keyed in by an attendant; once the pump was triggered by the attendant, refueling a given dollar amount was performed automatically without requiring the attendant to be close to the refueling. Observations from this study also showed that four of the five attendants evaluated routinely stood in proximity (less than 2 to 3 ft) to the pump while refueling in the automatic mode. The attendant who did not routinely stand in close proximity to the refueling pumps had real-time exposure measurements and charcoal tube measurements that were consistently lower than the other four attendants evaluated. When the attendant with the lowest exposures was asked why he consistently avoided being in close proximity to an active pump, he replied that because he did not like the irritating odor of the new formulated gasoline, he stood away to avoid exposure to the gasoline vapors.

Based on previous NIOSH studies, gasoline spills during the refueling process were expected to contribute significantly to exposures. The absence of gasoline spills during this evaluation may have been the result of improved dispensing nozzles or the experience of the attendants. Attendant exposures from vehicle exhaust emissions were also expected. However, review of the video exposure monitoring data suggested that vehicle exhaust emissions did not contribute to exposures. This was probably due to the requirement that customers shut off their vehicles prior to refueling.

Finally, the limitations of this study should be addressed. The video exposure monitoring technique uses relative THC real-time measurements as a surrogate to characterize short-term oxygenated fuel exposures. Due to constraints of the real-time instrument used for this study, absolute quantitative short-term exposure data could not be obtained specifically for MtBE; however, surrogate measurements definitely suggest elevated concentrations of peak gasoline exposures. Also, the THC exposure data were referenced to 100 ppm of isobutylene. For future studies to determine quantitative exposure data specifically for THCs and MtBE, the use of a portable gas chromatography/mass spectrometry may be preferable.

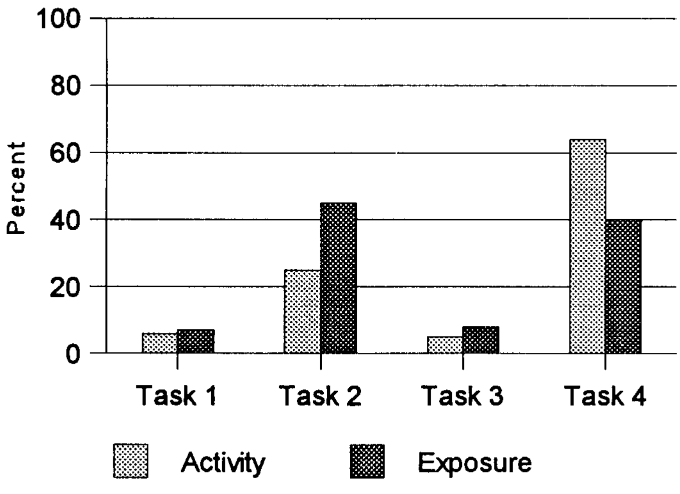

FIGURE 5. Contribution of refueling tasks to total activity and exposure.

Conclusions

Consistent with previous studies, full-shift TWA sampling results indicated low exposure concentrations for THCs and MtBE. However, real-time monitoring results indicated that elevated short-term or peak THC exposures may be more than 130 times greater than TWA concentrations for 1 to 2 seconds in duration. Similar inferences can be drawn about MtBE peak exposures. Since the mean TWA concentration for MtBE is about 0.50 ppm, conservative estimated peak exposures may be as high as approximately 70 ppm. [A similar calculation to estimate MtBE peak concentrations revealed similar results (85 ppm) when considering the ratio of MtBE and THCs in vapor phase.] However, there are no human toxicity data available suggesting that brief peak MtBE exposure at 70 ppm causes symptoms reported by attendants and self-service customers. Also, a ceiling limit for MtBE has not been established by a recognized organization which should be considered.

Based on the frequency of elevated peak THC exposures measured, it was concluded that peak exposures to oxygenated gasoline occurred during refueling. Because of the elevated THC concentrations measured during this study, and based on the conclusions of previous NIOSH and API studies, it was believed that vapor recovery systems may not be very effective in controlling gasoline vapor emissions. A similar study may be necessary to evaluate the effectiveness of stage II vapor recovery systems.

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Editorial Note: Calvin K. Cook is with the Hazard Evaluation and Technical Assistance Branch of NIOSH. Ronald J. Kovein is with the Division of Physical Sciences and Engineering of NIOSH. More detailed information on this evaluation is contained in Health Hazard Evaluation Report No. 94-0220-2526, available through NIOSH, Hazard Evaluation and Technical Assistance Branch, 4676 Columbia Parkway, Cincinnati, Ohio 45226; telephone: (800)35-NIOSH; fax: (513) 533-8573.