

HETA 88-304-2326
JUNE 1993
AMERICAN PETROLEUM INSTITUTE
WASHINGTON, D.C.

NIOSH INVESTIGATORS:
Richard W. Hartle, M.P.H., C.I.H.
John E. Kelly, M.S.
Nancy Clark Burton, M.P.H., M.S.
Calvin Cook

I. SUMMARY

The National Institute for Occupational Safety and Health (NIOSH) was contacted by the American Petroleum Institute (API) regarding the expanding uses of methyl tert-butyl ether (MTBE) as an oxygenate and octane enhancer in gasoline. Discussions on the feasibility of assessing airborne exposures to MTBE led to API's request for a NIOSH Health Hazard Evaluation of gasoline-related exposures among service station attendants and operators.

Exposure to the gasoline components MTBE, benzene, toluene, and xylene was measured among attendants at six retail automotive service stations. To reflect the multiple uses and potential exposures of MTBE, two of these facilities were selected to represent its ubiquitous use as an octane enhancer (generally blended at less than 1% of the fuel), two facilities were selected to represent requirements to use MTBE as an oxygenate (blended at 12-15% of the fuel), and two facilities equipped with phase II-type vapor recovery were selected to determine the relative effectiveness of these engineering controls.

Only one of the 16 personal breathing zone (PBZ) samples for MTBE collected at stations using less than 1% MTBE as a fuel additive was above the lowest detectable concentration (LDC), at 0.16 part per million (ppm). At stations using fuels blended with approximately 12% MTBE, 41 PBZ samples ranged from 0.03 to 3.89 ppm, averaging 0.54. At the stations equipped with phase II vapor recovery 15 of the 48 PBZ samples were detectable, with concentrations ranging from 0.02 to 0.73, averaging 0.18 ppm. No evaluation criteria have been established for occupational exposure to MTBE. At the two stations using less than 1% MTBE, 28 of 32 PBZ samples for benzene were above LDC, ranging from 0.01 to 0.29 ppm, averaging 0.06. At the high volume MTBE stations, the 41 measured benzene exposures ranged from 0.01 to 0.52 ppm, averaging 0.07. At stations equipped with vapor recovery, 31 detectable benzene exposures ranged from 0.01 to 0.19, averaging 0.07 ppm.

The multiple sites provided for a wide range of climatic and work practice conditions, as well as the presence/absence of vapor recovery. Linear regression analysis indicates that exposure levels are affected most significantly by wind velocity, followed by the amount of fuel dispensed by the attendant. Comparison of the benzene and MTBE exposure data collected at vapor recovery and non-vapor recovery service stations indicates that vapor recovery systems had no significant effect upon exposure levels, even after adjusting for climatic and work practice variables.

MTBE exposure averaged less than 1 ppm, even at service stations using 12% MTBE motor fuel blends. Based upon the available toxicity information, no health hazard would be expected from these exposures, other than the possibility of transient irritative symptoms. Benzene exposures are apparently not affected by MTBE content of motor fuels. At the service stations monitored, vapor recovery had no effect on reducing exposures to MTBE or benzene. Recommendations for further evaluation of service stations equipped with vapor recovery are made in Section VII of this report.

KEYWORDS: SIC 5541 (Gasoline Service Stations), Methyl tert-butyl ether (MTBE), Benzene, Toluene, Xylene, Vapor recovery, Gasoline

II. INTRODUCTION

The United States currently consumes over seven million barrels of gasoline per day. Estimations on the number of general retail automotive service stations in the U.S. range from 150,000 to 210,000. With the addition of government and private sector fuel dispensing facilities, the total number is estimated to be greater than 400,000.¹ Although the number of service station attendants dramatically decreased with the introduction of "self service", there remains a vast population of workers with occupational exposure to gasoline through fuel dispensing operations.

During the 1980's, methyl tert-butyl ether (MTBE) was initially used as an octane enhancer following the Environmental Protection Agency's lead phase-down program. Currently, MTBE is also used as an oxygenated fuel additive in "reformulated" gasolines, to reduce carbon monoxide emissions. Termed "the world's fastest growing petrochemical", the demand for MTBE could be as much as 300,000 barrels per day by mid-1993.²

Due to this new, extensive use in gasoline, an evaluation of MTBE exposures among service station attendants and operators was undertaken at the request of the American Petroleum Institute (API). In October-November 1990, exposure to the gasoline components MTBE, benzene, toluene, and xylene was measured among attendants at six retail automotive service stations. To reflect the multiple uses and potential exposures of MTBE, two of these facilities were selected to represent its ubiquitous use as an octane enhancer (generally blended at less than 1% of the fuel), two facilities were selected to represent requirements to use MTBE as an oxygenate toward reduction of carbon monoxide exhaust emissions (blended at 12-15% of the fuel), and two facilities equipped with phase II-type vapor recovery were selected to determine the relative effectiveness of these engineering controls. An interim report was distributed to API in March, 1991 describing the evaluation methods and techniques, including summary statistics for all environmental data.

III. BACKGROUND

In 1977, the Division of Surveillance, Hazard Evaluations, and Field Studies of NIOSH conducted an extensive evaluation of benzene exposures among retail automotive service station attendants. This activity was at the request of the Occupational Safety and Health Administration (OSHA), in support of the Emergency Temporary Standard for benzene. A total of 141 personal breathing zone samples were collected at 28 service stations located in various geographical areas of the U.S. API's knowledge of this evaluation prompted their original communication with NIOSH in 1988, concerning a similar potential for occupational exposure to MTBE from its use as a fuel additive. API judged that the evaluation techniques used by NIOSH for benzene exposures would also be suitable for determining exposures to MTBE.

Related mutual interests included the potential influence of MTBE blending on exposures to other constituents of gasoline (particularly benzene), factors affecting the extent of exposure (i.e., work practices), and the effectiveness of vapor recovery systems in limiting exposures.

API contracted for a parallel effort to determine community exposures to MTBE at locations surrounding service stations, and for assessment of exposures to self-service customers, at the same time as the NIOSH occupational evaluations. Under this concept, API contracted for the determination of "gasoline" exposures to self-service customers (breathing zone samples), plus community exposures via service station fence-line monitoring.

To apply any findings/conclusions from the NIOSH study to an audience beyond the evaluated sites, statistical analysis was designed to address 1) the significant climatic and work practice variables affecting exposure, and 2) determine the degree of exposure reduction at service stations equipped with vapor recovery systems.

IV. **METHODS**

A. Site Selection

In consideration of the three basic use/exposure scenarios (low MTBE content, high MTBE content, vapor recovery) three geographic areas reflecting these conditions were selected. Cincinnati, Ohio was chosen to represent the low MTBE category (MTBE used only as an octane enhancer). API member companies identified two service stations in the greater Cincinnati area which had the highest volume of sales, and relatively large full service capacity. It should be noted that at the time of evaluations, fuel prices had recently undergone a substantial increase due to the Middle East crisis. The relative increase in full service fuel prices was in the range of 20 - 40% at the stations evaluated. This had a major impact on the number full service customer visits.

Phoenix, Arizona represented the high-MTBE use category. From November through March, at least 12.6% MTBE is required in all gasoline sold in the Phoenix metropolitan area. Similarly, two service stations in Los Angeles, California were identified to assess exposures associated with the use of vapor recovery systems.

B. Statistical Discussion

To determine an appropriate sample size, preliminary information and intended goals of the evaluation were submitted for statistical assessment. Based on an assumed CV of .40% (derived from results of the similar, 1978 NIOSH study) it was determined that sampling consist of approximately 60 shifts, with 16 sampled shifts from Cincinnati, and 22 sampled shifts each from Phoenix and Los

Angeles. The two primary objectives identified for statistical analysis were 1) identify the climatic and work practice variables with the most impact on exposure variation, and 2) determine the effectiveness of vapor recovery. The sample size of 60 would produce 95% confidence intervals on exposure factors within 25% of the mean. Weighted multiple linear regression was used for this analysis (sample time as the weighting factor; samples collected over a relatively longer period had more influence in the analysis).

The data set consisted of 121 personal breathing zone samples collected for approximately 4-hr periods (half-shift samples provided greater variability among dependant/independent variables). As mentioned earlier, the cities selected provided a range of environmental conditions (temperature, humidity, wind velocity) as well as the presence or absence of vapor recovery systems, and the presence or absence of MTBE. In addition to the dependant variables (PBZ exposures) a number of independent variables were used, including the number of gallons of the various grades of fuel pumped by the attendant, total fuel through put of the station, number and size of spills, temperature, wind speed, relative humidity, total number of pumping occurrences, and the liquid volume % of the target components in the fuel. Created variables included "area" conversions of the spill data ($3.14 \times (\text{diameter}/2)^2$), and the "sum" of all gallons of fuel pumped by the attendant.

All four dependent variables showed a distribution of their residuals in the regression models that was highly skewed. Therefore, a log transform for each of the four dependent variables was used. The analysis was confined to no more than second order models (no more than two-way interactions, or quadratic terms for continuous independent variables) due to the number of variables and the straightforward objectives of the analysis.

C. Data Collection

Several work practice and climatic variables were measured during environmental sample collection. These included:

1. liquid volume percent (LV%) MTBE, benzene, toluene, and xylene present in the various grades of fuels during sampling.

It has been suggested that the relationship between airborne exposures at service stations and the amount of the target chemical in the fuel is approximately one-third dependant on the mixture in the auto fuel tank and approximately two-thirds dependant on the mixture of the delivered fuel.² This relationship is undoubtedly quite unstable, depending on a number of conditions, including fuel remaining in the tank, fuel temperature, recent use of the automobile, etc. Because

of the number of autos serviced, collection of representative samples from each auto was impractical. However, bulk samples were collected of each grade dispensed at the station during the evaluation. The samples were collected at the beginning of the evaluation, and following each bulk fuel delivery (4-6 hours after delivery to allow for mixing in the storage tanks and purging of the pumps and hoses). The 10 milliliter samples were analyzed for MTBE, benzene, toluene, and xylene (v/v). A total of 79 samples were collected from the six stations.

2. amount and grade of fuel dispensed by the attendant and at the service station during the sampling period.

At each refueling, the amount and grade of fuel dispensed by the attendant was recorded. For each environmental sample, a corresponding weighted average liquid volume % was calculated for each of the measured components in the grade of fuel.

3. amount of time required for each "re-fueling."

As in most situations involving exposures to airborne contaminants the extent of exposure is greatly affected by the proximity of the worker to the source of the contaminant. We defined this relationship in this evaluation as amount of time the attendant was in the vicinity of the vehicle while fuel was actually being dispensed. For each refueling, a summation of this time was recorded, along with the type and amount of fuel dispensed. In the statistical analysis, this information was used in the form of total time spent refueling during the sample period, number of refueling events during the sampling period, and percent of the sampling period or work shift actually spent pumping fuel.

4. number and size spills during re-fueling.

If a spill occurred during refueling (i.e., tank over-fill or residual fuel in the nozzle spilled prior to, or after refueling) the NIOSH investigator recorded the number and size. Size was estimated as the diameter of the spill. This information was later converted to area ($3.14 \times (\text{diameter}/2)^2$), for statistical analysis.

5. climatic conditions including temperature, relative humidity, and windspeed.

Temperature and relative humidity were measured using a battery operated psychron. Readings were recorded approximately every hour. Windspeed and direction was measured at the sites with a Climatronics cup anemometer equipped with a strip chart recorder. The mechanism was placed near the fuel pumps on a 5 foot tripod. Because two stations were monitored during the same time period, logistics required that we use the windspeed/direction information generated by the API contractor (coinciding API evaluation of community exposures). A similar device was used; however, the contractor elected to place their anemometer on the roof of the service station. All climatic data were averaged over the duration of the sampling period.

D. Sampling and Analysis

1. MTBE, Benzene, Toluene, and Xylene in Air

A sampling and analytical method (NIOSH Method 1615) was formally developed by NIOSH to measure airborne MTBE. The solid sorbent tubes consisted of two charcoal tubes in series; the front tube containing 400 milligrams (mg) of coconut shell charcoal, and the back tube containing 200 mg. Specified flow rates were 0.1 to 0.2 liters per minute; however, higher flow rates were used for a portion of the evaluation due to less than expected levels of exposure to the gasoline components (resulting from unusual work practice and climatic situations - to be discussed later). Analysis of the backup tubes for "breakthrough" at the increased flow rates was negative. Samples were collected for one-half the work shift, or two per 8-hr shift. The sampling media were attached to the lapel of the worker for acquisition of "breathing zone" samples. The samples were connected to battery-operated pumps calibrated at flow rates of 0.1 to 0.5 liters per minute (lpm).

In addition to MTBE, NIOSH method 1615 was suitable for benzene, toluene, and xylene.

Desorption Process:	30 minutes in 2 ml of carbon disulfide.
Gas Chromatograph:	Hewlett-Packard Model 5890 equipped with a flame ionization detector.
Column:	50 meter by 0.3 millimeter fused silica capillary coated internally with 0.5 micro meter of HP-1.
Oven Conditions:	-15° C for seven minutes, up to 25° C at a rate of 5° C per minute. Following, up to 250° C for 5 minutes at a rate of 25° C per minute.

The analytical limit of detection for each compound follows:

<u>Compound</u>	<u>Limit of Detection*</u>
MTBE	0.01 - 0.02 mg/sample
Benzene	0.001 - 0.03 mg/sample
Toluene	0.01 - 0.02 mg/sample
Xylene	0.01 - 0.03 mg/sample

*Detection limits varied by analytical "run."

2. Bulk Sample Analysis

Bulk samples of the various grades of fuel were collected at the beginning of each site evaluation, and following fuel deliveries. Analysis was similar to that of the charcoal tubes, except that samples were diluted and directly injected into the gas chromatograph/flame ionization detector according to NIOSH Method 1615.

V. EVALUATION CRITERIA

A. General

As a guide to the evaluation of the hazards posed by work place exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other work place exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled to the level set by the evaluation criterion. These combined effects are not often considered by the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the work place are: 1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), and 3) the U.S. Department of Labor (OSHA) Permissible Exposure Limits (PELs). The OSHA PELs may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended exposure limits, by contrast, are based primarily on concerns relating to the prevention of occupational disease. When considering the exposure levels and the recommendations for reducing the levels found in this report, it should be noted that industry is legally required to meet those levels specified by an OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

B. Substance Specific Evaluation Criteria

1. Gasoline

Gasoline is a clear, volatile liquid with a characteristic odor. Although it can theoretically contain as many as 1500 different hydrocarbons, gasoline is typically made up of 150-250 branched-chain paraffins, cycloparaffins, and aromatics. The relative concentrations of these constituents in the final blended gasoline vary with production techniques, seasonal variability, and the addition of proprietary additives.^{2,3} From a health perspective, benzene is the most significant component of gasoline. Benzene content generally ranges from less than 1% to 2% (liquid volume percent), although it may contain as much as 4.8%.^{4,5} A previous NIOSH evaluation involving 28 service stations measured benzene contents of 0.5 to 2.3%.

Acute toxicity is similar for all gasolines. They act generally as an anesthetic and are mucous membrane irritants. Acute symptoms of intoxication include headache, blurred vision, dizziness, and nausea. The threshold for immediate mild intoxication is 900-1000 ppm.⁶ Although human population studies on the chronic effects of exposure to gasoline are rare, a NIOSH study of cancer mortality patterns (standardized mortality odds ratio) by occupation for white males in the state of Massachusetts using death records for the years 1971-1973 suggests an increased mortality from bladder cancer among gas station owners and managers (SMOR = 586).⁷ In a study of all deaths recorded from 1975 to 1985 among New Hampshire white

male residents (proportionate mortality ratio: measure of proportion of deaths attributable to a disease), workers in the service station industry were found to have a significant leukemia mortality excess (PMR = 328; dubrn = 3) and mental and psychoneurotic and personality disorders (PMR = 394; n = 3).⁸ NIOSH considers gasoline to be a potential occupational carcinogen, and recommends that exposures be limited to the lowest feasible level. The OSHA PEL specifies an 8-hr TWA of 300 ppm, and an STEL of 500 ppm.

2. Methyl tert-Butyl Ether (MTBE, $\text{CH}_3\text{OC}(\text{CH}_3)_3$)

MTBE is a colorless, volatile liquid derived from the catalytic reaction of methanol and isobutene. It has a terpene-like odor, with an odor threshold of 0.6 ppm.

Several studies on the acute toxicity of MTBE revealed the following:⁹

Toxicity Assay	Data	Toxicity Ranking
Oral LD ₅₀	3.0-3.8 g/kg bd. wt.	low
Dermal LD ₅₀	>10 g/kg bd. wt.	very low
Inhalation LC ₅₀	23,630 - 33,000 ppm	very low
Skin Irritation	Moderate Reddening	Not a primary irritant
Eye Irritation	Transient Effects	No irreversible effects
Skin Sensitization	Response	Not a skin sensitizer

Data on chronic health effects from exposure to MTBE are limited. However, several animal studies are underway to identify any carcinogenic, mutagenic, or teratogenic properties.

Recent irritative symptoms attributed to MTBE among occupational and public groups in Alaska are currently being investigated by the Centers for Disease Control and Prevention (Centers for Environmental Health) and the Environmental Protection Agency.

3. Benzene

Benzene is a colorless, volatile, highly flammable liquid. The lowest reported odor threshold is 4.5 mg/m³. Acute exposure results in central nervous system depression, headache, dizziness, nausea, convulsion, coma, and death. The most significant toxic effect of benzene exposure is an insidious and often irreversible injury to the bone marrow. Accumulated

case reports and epidemiologic studies suggest a leukemogenic action of benzene in humans; the leukemia tending to be acute and myeloblastic in type, often following aplastic changes in the bone marrow. Benzene may also induce chronic types of leukemia.¹⁰ A series of NIOSH studies analyzed the mortality of workers exposed to benzene at two rubber hydrochloride manufacturing locations, which demonstrated an excess risk of leukemia. One of these studies demonstrated a Standardized Mortality Ratio (SMR) of 337 for leukemia and 409 for multiple myeloma (an SMR of 100 is the normal value of an excess is not observed; an SMR of 200 represents a 100% excess risk above normal).¹¹ The NIOSH REL for benzene is reflected in its testimony on the OSHA Benzene final rule which states; "The data on benzene leave no doubt regarding the human carcinogenic potential of this chemical. NIOSH recommends that occupational exposure to benzene be controlled so that no worker is exposed to more than 0.1 ppm as an 8-hour time-weighted average (TWA) and that short-term exposure be controlled so as not to exceed 1 ppm as determined in any 15-minute sampling period." The OSHA PEL is a TWA of 1 ppm, with an STEL of 5 ppm as averaged over any 15-minute period. However, the PEL does not apply to "...storage, transportation, distribution, dispensing, sale or use of gasoline, motor fuels, or other fuels containing benzene subsequent to its final discharge from bulk wholesale storage facilities, except that operations where gasoline or motor fuels are dispensed for more than 4 hours per day in an indoor location..."¹²

4. Toluene

Toluene is a clear, colorless, noncorrosive liquid with a sweet, pungent, benzene-like odor (odor threshold between 8 and 150 mg/m³). Toluene may cause irritation of the eyes, respiratory tract, and skin. Repeated or prolonged contact with the liquid may cause removal of natural lipids from the skin, resulting in dry, fissured dermatitis. The liquid splashed in the eyes may cause irritation and reversible damage. Acute exposure predominantly results in central nervous system depression. Symptoms and signs include headache, dizziness fatigue, muscular weakness, drowsiness, incoordination with staggering gait, skin paresthesia, collapse and coma.¹³ Toluene exposure does not result in the hematopoietic effects caused by benzene. The myelotoxic effects previously attributed to toluene are judged by more recent investigations to be the result of concurrent exposure to benzene present as a contaminant in toluene solutions.¹⁰ The NIOSH REL is 100 ppm TWA with provision for an STEL of 150 ppm. The OSHA PEL is the same as the REL.

5. Xylene

Xylene is a colorless liquid, primarily used as an industrial solvent. The lowest reported odor threshold is 0.35 mg/m³. The vapor is an irritant of the eyes, mucous membranes, and skin. At high vapor concentrations, it may cause narcosis, pulmonary edema, anorexia, nausea, vomiting, and abdominal pain. The NIOSH REL is 100 ppm TWA with an STEL of 150 ppm. The OSHA PEL is identical to the REL.

VI. **RESULTS**

A. Descriptive Statistics

Figure 1 presents a summary of MTBE and benzene sample results by site, within each of the three municipalities (individual sample results are presented in Tables 1-6), while Figure 2 presents overall mean exposure concentrations by region. For each data "set" (i.e., all samples collected for a particular compound from a single facility), averages are not reported if greater than one-half the values were below the lowest detectable concentration (LDC). If greater than one-half of the results were above the LDC, non-detected samples were assigned a value of LCD/2^{1/2}.¹⁴ The following focuses on attendant exposures MTBE and benzene.

Figure 1. Mean Exposure Concentration (ppm)

LOCATION	CNTI		PHNX		L.A.	
SITE	I	II	I	II	I	II
MTBE (arthmtc)	*	*	0.82	0.28	*	0.25
MTBE (geo)	*	*	0.68	0.21	*	0.20
Benzene (arthmtc)	0.10	0.02	0.11	0.03	0.07	0.06
Benzene (geo)	0.08	0.02	0.10	0.03	0.06	0.05

Figure 2. Mean Exposures (ppm)

	CNTI	PHNX	L.A.
MTBE (arthmtc)	*	0.54	*
MTBE (geo)	*	0.37	*
Benzene (arthmtc)	0.06	0.07	0.07
Benzene (geo)	0.04	0.05	0.06

As previously discussed, the Cincinnati area was selected as representing the majority of service station "exposure" scenarios in the U.S., where MTBE is used only as an octane enhancer. As shown in Tables I and II, only one of the 32 4-hour, half-shift samples collected from attendants was above the LDC reported at 0.2 ppm (LDC - 0.02 ppm @ 0.2 m³ air sample). As anticipated, only minor amounts of MTBE were detected in the bulk fuel samples; the highest being 0.18 LV% MTBE (Fig. 3; Tables 7-8). Exposure to benzene at the Cincinnati stations averaged 0.1 ppm at Site I, and 0.02 ppm at Site II (Tables 1-2). The highest measured 4 hr sample was 0.52 ppm.

Fig. 3 Bulk Fuel Analysis (LV%)

	MTBE		BENZENE		TOLUENE		XYLENE	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
CNTI I	0.00-0.18	0.09	0.29-1.60	0.63	2.70-8.40	3.90	3.30-22.0	5.20
CNTI II	0.06-0.17	0.12	0.36-1.30	0.80	2.40-3.80	2.97	4.60-13.0	8.95
PHNX I	12.0-14.0	12.6	1.10-1.90	1.57	4.10-6.60	4.75	4.50-7.70	5.46
PHNX II	12.0-13.0	12.7	1.30-1.50	1.39	3.90-7.60	4.95	5.40-9.90	6.60
L.A. I	0.00-0.20	0.02	1.30-1.90	1.69	4.90-13.0	9.16	6.00-14.0	10.3
L.A. II	0.00-11.0	4.58	2.00-3.10	2.62	8.00-12.0	9.54	8.70-11.0	9.53

At both Phoenix sites, MTBE content of the gasoline averaged approximately 12.5 LV% (range 12-14 LV%; Fig. 3, Tables 9-10). Only one of the 42 4-hr MTBE samples was below the LDC. Half shift exposures ranged from 0.11 to 3.88 ppm at Site I (averaging 0.82 ppm). At the second site, exposures ranged from 0.04 to 2.12 ppm, averaging 0.28 ppm. Overall, MTBE exposures averaged 0.54 ppm between both Phoenix sites. Benzene exposures ranged from 0.02 to 0.52 ppm, averaging 0.11 at Site I, and 0.01 to 0.15 ppm, averaging 0.03 ppm at Site II. The overall average for both Phoenix locations was 0.07.

The MTBE content of the fuels at the Los Angeles-area stations equipped with vapor recovery was quite variable, ranging from "non-detected" to a high of 11% (Fig.3, Tables 11-12). No explanation was obtained for the cause of this variability. Of the two stations tested, the overall MTBE contents were reported at 0.02 and 4.58%, respectively. At the station with low MTBE content, only 5 of 20 PBZ samples were above the analytical limit of detection, all ranging below 0.1 ppm. At the "high" MTBE station, the five PBZ samples ranged from 0.1 to 0.6 ppm. Benzene exposures among attendants at both locations ranged from 0.02 to 0.19, averaging 0.07 ppm.

B. Statistical Analysis

BENZENE

After careful examination of all potential exposure factors, three factors seemed to dominate all other variables. These were temperature, wind velocity and total gallons of fuel pumped by the attendant (Table 13). When it became apparent that a combination of environmental conditions and work practices were the primary determinants of benzene exposure, certain variables were isolated in each category to try and improve the model fit. For example, relative humidity appeared to be a contributor in some models, but when both wind velocity and temperature were included, relative humidity was no longer significant.

Similarly, other combinations of work practices were investigated to see if they explained changes in benzene exposure better than total gallons of fuel pumped. While total time pumping fuel and total number of trips to the pumps were each significant, neither were as strong as total gallons.

After these three factors were identified, tests of linearity of each of the three were conducted, i.e., quadratic terms were introduced for each. All three non-linear terms were non-significant. A number of two-way interactions were likewise not significant.

After settling on the three factor model as our best effort, the vapor recovery variable was introduced which was coded as "1" if vapor recovery was used and "0" otherwise. Results showed that vapor recovery showed no significant reduction ($p = .278$) in benzene concentrations when corrected for environmental and work practice factors. In addition, the direction of the effect was such that benzene concentrations were slightly higher where vapor recovery was used. This effect persisted even after the weighted average of benzene in the fuel was forced into the model.

MTBE

The analysis of MTBE was very similar to the analysis of benzene. The three factors identified in the benzene analysis (temperature, wind velocity and gallons of fuel) were also found to be important in the MTBE analysis. There was one additional significant factor: the weighted average content of the MTBE in the fuel (Table 13). Note that this analysis was based only on the three sites using the MTBE additive and therefore the sample size was 56. Two observations were eliminated because of being outliers or exceedingly influential to the analysis. However, the nature of the results was similar even when they were included.

As with the benzene analysis, no quadratic or two-way interactions were detected. Vapor recovery with MTBE was based on one Los Angeles station, but again there was no significant effect and the direction of the effect was counter-intuitive.

When sampling location was added to the model for MTBE, no significant difference was found. Therefore, for MTBE, correction for the environmental and work practice factors removed any significant differences in mean exposures across the three stations.

TOLUENE

Results of the analysis of toluene were slightly different than those for benzene or MTBE. The best fitting model involved three factors: wind velocity, total area of spills, and total gallons of fuel pumped by the attendant (Table 13). No interactions or non-linear term were detected for toluene.

Again, there was no significant effect of vapor recovery ($p = .112$). There was, however, a significant difference among stations even after correction for the other exposure factors ($p = .001$).

XYLENE

The analysis of the xylene data showed somewhat different exposure factors than the previous three components. The only two significant factors were percent vicinity time and wind velocity (Table 13). No other exposure factors, non-linear terms or two-way interactions were found.

Again, there was no significant effect of vapor recovery systems ($p = .975$). There were also no significant differences among stations after correcting for the effect of wind velocity and percent vicinity time ($p = .320$).

VII. CONCLUSIONS/RECOMMENDATIONS

The goals of this investigation were 1) determine the extent of exposure to MTBE, given its new use patterns in today's fuel markets, and identify those parameters most responsible for variations in exposure, 2) determine whether the use of MTBE as a fuel additive affects exposure levels to benzene, and 3) ascertain the effectiveness of vapor recovery in limiting exposures to gasoline component vapors.

Occupational exposure to MTBE among service station attendants at stations required to use at least 12% MTBE were less than 1 ppm (overall arithmetic average of 0.54; overall geometric average of 0.37 ppm). Exposures were generally less than 0.1 ppm (below the analytical limit of detection) at stations using MTBE at less than 1% of the fuel. Of all variables monitored, three were observed to dominate variations in exposures to MTBE and benzene; temperature, wind

speed, and amount of fuel pumped by the attendant. Of interest here is that these variables would not only effect exposures from the station's standpoint, but also from remaining fuel in the automobile being serviced (with amount of fuel pumped being directly related to proximity to the auto). This finding certainly does not rule out the importance of the auto being serviced on variations in exposure.

There was no significant relationship between benzene exposures and MTBE content, even when controlling for other dependant variables. If a positive (or negative) relationship does exist, it does not appear to be substantial.

Surprisingly, and of major interest, was the finding that vapor recovery had no significant effect on reducing exposure to MTBE or benzene, when corrected for environmental and work practice factors. Furthermore, the direction of the effect was such that higher levels were measured at stations equipped with vapor recovery. This is especially surprising given the results of the similar 1977 NIOSH investigation, where an approximate twelve-fold reduction in exposures was measured at two stations equipped with vapor recovery. This finding may be a combination of a number of factors, i.e., the VR not working to specification, benzene/MTBE exposures from the automobile being serviced, etc. Another possibility involves the surface porosity of the asphalt/cement near the pumps. Although the number and size of spills was recorded, the actual amount of fuel spilled would not be accurately recorded if there were large differences in surface characteristics (i.e., an ounce of fuel spilled on a smooth surface would cover a larger area than an ounce spilled on a rough, porous surface). The possibility of spills having a major impact on exposures is reinforced by investigator reports of large, uncontrolled spills occuring during the sampling periods. These spills reportedly occurred at the self-service islands, typically involving motorists apparently unfamiliar with the vapor recovery appartus.

Further evaluation of service stations equipped with vapor recovery may be best suited to the real time, direct infrared imaging system recently developed by NIOSH.¹⁵ With this method, both the source and path of emissions can be identified, thus enabling identification of any malfunction or alternate exposure source.

VIII. REFERENCES

1. ENVIRON Corporation [1990] Summary report on individual and population exposures to gasoline. ENVIRON Corporation, Arlington, VA, November 28, 1990.
2. Ainsworth SJ [1991] Booming MTBE demand draws increasing number of producers. C&EN 69(23):13-16 (June 10, 1991).
3. Sax NI, Lewis RJ [1987]. Condensed chemical dictionary. 11th ed. New York, NY: Van Nostrand Reinhold Company Inc, pp. 554.
4. Phillips CF, Jones RK [1978] Gasoline vapor exposure during bulk handling operations. Am Ind Hyg J 39:119
5. McDermott HJ, Vos GA [1979] Service station attendants' exposure to benzene and gasoline vapors. Am Ind Hyg J 40(4):315-321.
6. ACGIH [1990]. Threshold limit values and biological exposure indices for 1990-1991. Cincinnati, OH: American Conference of Governmental Industrial Hygienists.
7. NIOSH [1984]. Occupational characteristics of cancer victims in Massachusetts 1971-1973. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-109.
8. Schwartz E [1987]. Proportionate mortality ratio analysis of automobile mechanics and gasoline service station workers in New Hampshire. Am J of Ind Med 12:91-99.
9. Kneiss JJ [1991]. An overview of the MTBE toxicology testing program. Unpublished paper presented at the National Conference on Octane Markets and reformulated gasoline, San Antonio, TX, March 19-20, 1991.
10. Proctor NH, Hughes JP, Fischman ML [1988]. Chemical hazards of the workplace. 2nd ed. Philadelphia, PA: JB Lippincott Company, pp. 90-95.
11. Rinsky RA, Smith AB [1987] Benzene and leukemia: an epidemiologic risk assessment. N Eng J Med 316:1044-1050.
12. Code of Federal regulations [1987]. Occupational Exposure to benzene; final rule. Washington, DC: U.S. Government Printing Office, Office of the Federal Register. [29 CFR 1910 (Sept. 11, 1987)].
13. NIOSH [1977]. Occupational diseases - a guide to their recognition. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 77-181.
14. Hornung RW, Reed LD [1990] Estimation of average concentration in the presence of nondetectable values. Appl Occup Env Hyg 5(1):46-51
15. NIOSH [1992]. Analyzing Workplace Exposures Using Direct Reading Instruments and Video Exposure Monitoring Techniques. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 92-104.

IX. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by:	Richard W. Hartle Regional Operations Coordinator
Field Assistance	John Kelly Nancy Burton Calvin Cook
Statistical Analysis	Richard Hornung Associate Director
Analytical Support	John Palassis Chemist
Originating Office:	Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations, and Field Studies

X. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report may be freely reproduced and are not copyrighted. Single copies of this report will be available for a period of 90 days from the date of this report from the NIOSH Publications Office, 4676 Columbia Parkway, Cincinnati, Ohio 45226. To expedite your request, include a self-addressed mailing label along with your written request. After this time, copies may be purchased from the National Technical Information Service (NTIS), 5825 Port Royal Road, Springfield, Virginia 22161. Information regarding the NTIS stock number may be obtained from the NIOSH Publications Office at the Cincinnati address.

Copies of this report have been sent to:

1. American Petroleum Institute, Washington, D.C.
2. NIOSH
3. OSHA Region II

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

TABLE 1

Assessment of Exposures to Gasoline Constituents

SITE I
CINCINNATI, OHIO

HETA 88-304

October 16-19, 1990

#	Date	Time		Concentration (ppm)	Concentration (ppm)			
		On	Off		(min)	MTBE	Benzene	Toluene
s01	1016	0753	1120	227	nd*	0.11	0.17	0.10
s02	1016	1125	1500	215	nd	0.06	0.10	0.03
	TWA**	0753	1500	442	--	0.08	0.13	0.06
s03	1016	1520	1854	205	nd	0.05	0.07	nd
s04	1016	1925	2230	185	0.16	0.06	(0.05)***	nd
	TWA	1520	2230	390	--	0.06	0.06	--
s05	1017	0710	1055	225	nd	0.08	0.12	nd
s06	1017	1100	1458	238	nd	0.13	0.23	0.10
	TWA	0710	1458	463	--	0.11	0.18	--
s07	1017	1515	1855	220	nd	0.02	(0.05)	nd
s08	1017	1930	2236	186	nd	0.03	(0.05)	nd
	TWA	1515	2236	406	--	0.02	0.05	--
s09	1018	0733	1113	220	nd	0.05	0.06	nd
s10	1018	1118	1440	202	nd	0.05	(0.05)	nd
	TWA	0733	1440	422	--	0.05	0.05	--
s11	1018	1513	1904	231	nd	0.08	0.06	nd
s12	1018	1942	2250	188	nd	0.09	0.15	nd
	TWA	1513	2250	419	--	0.09	0.10	--
s13	1019	0820	1148	208	nd	0.10	0.13	nd
s14	1019	1155	1458	183	nd	0.22	0.29	0.13
	TWA	0820	1458	391	--	0.15	0.20	--
s15	1019	1526	1926	240	nd	0.29	0.45	0.15
s16	1019	2004	2244	160	nd	0.19	0.34	0.15
	TWA	1526	2244	400	--	0.25	0.41	0.15
Site Average:		Arithmetic			****	0.10	0.16	****
		Geometric			****	0.08	0.11	****

* nd = non-detected; below the lowest detectable concentration (LDC)

** TWA = Time-weighted Average

*** If greater than 1/2 the values of a sample set were above the LDC, nd's

were assigned values at LDC/2^{1/2}. (x.xx) indicates "calculated" value. **** Less than 1/2 the values were above the LDC; averages not reported.

TABLE 2

Assessment of Exposures to Gasoline Constituents

SITE II
CINCINNATI, OHIO

HETA 88-304

October 18-23, 1990

#	Date	Time		Concentration (ppm)				
		On	Off	(min)	MTBE	Benzene	Toluene	Xylene
b01	1018	0710	1105	235	nd*	(0.01)**	nd	(0.04)
b02	1018	1105	1525	260	nd	(0.01)	nd	0.09
	TWA***	0710	1525	495	--	0.01	--	0.06
b03	1018	1540	1905	205	nd	(0.02)	nd	(0.04)
b04	1019	0705	1103	238	nd	(0.01)	nd	(0.03)
b05	1019	1107	1500	233	nd	0.03	0.05	0.04
	TWA	0705	1500	471	--	0.02	--	0.04
b07	1019	1505	1906	229	nd	0.02	nd	0.01
b08	1020	0720	1100	220	nd	0.01	nd	0.02
b11	1020	1100	1510	250	nd	0.02	nd	0.02
	TWA	0720	1510	470	--	0.02	--	0.02
b12	1020	1512	1859	228	nd	0.02	nd	0.02
b13	1022	0745	1056	191	nd	0.01	0.02	0.06
b14	1022	1100	1455	235	nd	0.03	0.05	0.08
	TWA	0745	1455	426	--	0.02	0.04	0.07
b15	1022	1500	1810	190	nd	0.01	nd	0.05
b16	1023	0710	1115	245	nd	0.06	0.12	0.11
b17	1023	1115	1515	240	nd	0.03	0.07	0.12
	TWA	0710	1515	485	--	0.05	0.09	0.11
b18	1023	1523	1904	221	nd	0.04	0.06	0.07
b19	1023	1909	2300	231	nd	0.01	nd	0.10
	TWA	1523	2300	452	--	0.03	--	0.09
Site Average:		Arithmetic			****	0.02	****	0.05
		Geometric			****	0.02	****	0.04

* nd = non-detected; below the lowest detectable concentration (LDC)

** If greater than 1/2 the values of a sample set were above the LDC, nd's were assigned values at LDC/2^{1/2}. (x.xx) indicates "calculated" value.

*** TWA = Time-weighted Average

**** Less than 1/2 the values were above the LDC; averages not reported.

TABLE 3
 Assessment of Exposures to Gasoline Constituents
SITE I
PHOENIX, ARIZONA
 HETA 88-304
 October 29-November 2, 1990

#	Date	Time		· (min)	Concentration (ppm)			
		On	Off		MTBE	Benzene	Toluene	Xylene
e01	1029	0625	0930	185	0.38	0.06	0.40	nd*
e02	1029	1015	1400	225	0.65	0.07	0.41	nd
	TWA**	0625	1400	410	0.53	0.07	0.41	--
e06	1029	1608	2015	247	0.48	0.08	0.22	nd
e05	1029	2015	2200	105	1.08	0.13	0.15	0.10
	TWA	1608	2200	352	0.66	0.10	0.20	--
e07	1030	0625	1005	220	0.22	0.02	0.11	nd
e08	1030	1045	1410	205	1.17	0.12	0.13	0.08
	TWA	0625	1410	425	0.68	0.07	0.12	--
e09	1030	1505	1800	175	3.88	0.52	0.97	0.46
e10	1030	1800	2200	240	0.35	0.04	0.13	nd
	TWA	1505	2200	415	1.84	0.24	0.48	--
e11	1031	0630	1005	215	0.68	0.06	0.19	nd
e12	1031	1040	1350	190	0.93	0.15	0.97	nd
	TWA	0630	1350	405	0.80	0.10	0.56	--
e13	1031	1430	1830	240	1.65	0.41	0.33	0.07
e14	1031	1830	2200	210	1.04	0.08	0.18	nd
	TWA	1430	2200	450	1.37	0.26	0.26	--
e15	1101	0643	1008	205	0.41	0.04	0.07	nd
e16	1101	1023	1400	217	0.34	0.04	0.16	nd
	TWA	0643	1400	422	0.37	0.04	0.12	--
e17	1101	1415	1800	225	0.11	0.20	0.05	0.05
e18	1101	1805	2200	235	0.17	0.03	0.14	nd
	TWA	1415	2200	460	0.14	0.11	0.10	--
e19	1102	0640	1008	208	0.38	0.04	0.15	nd
e20	1102	1024	1400	216	1.42	0.11	0.14	nd
	TWA	0640	1400	424	0.91	0.08	0.15	--
e21	1102	1415	1800	225	(0.04)***	(0.01)	0.04	nd
e22	1102	1810	2100	170	2.07	0.15	0.24	0.07
	TWA	1415	2100	395	0.91	0.07	0.13	--
Site Average:		Arithmetic			0.83	0.11	0.25	****
		Geometric			0.68	0.10	0.21	****

* nd = non-detected; below the lowest detectable concentration (LDC)

** TWA = Time-weighted Average

*** If greater than 1/2 the values of a sample set were above the LDC, nd's were assigned values at LDC/2^{1/2}. (x.xx) indicates "calculated" value.

**** Less than 1/2 the values were above the LDC; averages not reported.

TABLE 4
 Assessment of Exposures to Gasoline Constituents
SITE II
PHOENIX, ARIZONA
 HETA 88-304
 October 29 - November 2, 1990

#	Date	-----Time-----		· (min)	-----Concentration (ppm)-----			
		On	Off		MTBE	Benzene	Toluene	Xylene
t01	1029	0621-1026		245	0.11	0.10	0.05	0.38
t02	1029	1052-1354		209	0.13	0.01	0.03	0.09
	TWA*	0621-1354		454	0.12	0.06	0.04	0.25
t03	1029	1416-1805		229	0.12	0.01	0.09	0.08
t06	1029	1805-2257		292	0.17	0.02	0.05	0.02
	TWA	1416-2257		521	0.15	0.02	0.07	0.05
t04	1029	1414-1800		228	0.54	4.15***	0.12	0.08
t05	1029	1800-2257		297	0.12	0.02	0.05	0.02
	TWA	1414-2257		525	0.30	0.02	0.08	0.05
t07	1030	0614-1015		241	0.74	0.07	0.07	0.06
t08	1030	1016-1400		224	0.55	0.05	0.07	0.04
	TWA	0614-1400		465	0.65	0.06	0.07	0.05
t09	1030	1415-1755		220	2.12	0.15	0.15	0.13
t10	1030	1755-2250		295	0.06	0.01	0.07	0.02
	TWA	1415-2250		515	0.94	0.07	0.12	0.07
t11	1031	0614-1023		249	0.13	0.02	0.04	0.02
t12	1031	1023-1356		213	0.57	0.05	0.08	0.09
	TWA	0614-1356		462	0.33	0.03	0.06	0.05
t13	1031	1405-1745		220	0.38	0.04	0.08	0.03
t15	1031	1745-2250		305	0.11	0.02	0.04	0.02
	TWA	1405-2250		525	0.22	0.03	0.06	0.02
t16	1101	0611-1020		249	0.11	0.02	0.04	0.02
t17	1101	1021-1356		215	0.08	0.02	0.03	(0.02)**
	TWA	0611-1356		464	0.10	0.02	0.04	0.02
t18	1101	1410-1803		233	0.19	0.03	0.05	0.02
t19	1101	1805-2145		220	0.05	0.02	0.10	0.02
	TWA	1410-2145		453	0.12	0.03	0.07	0.02
t20	1102	0603-1015		252	0.04	0.01	0.02	0.02
t21	1102	1015-1356		221	0.45	0.05	0.07	0.08
	TWA	0603-1356		473	0.23	0.03	0.04	0.05
t22	1102	1406-1804		238	0.23	0.03	0.07	0.08
t23	1102	1804-2158		234	0.05	0.01	0.02	(0.02)
	TWA	1406-2158		472	0.14	0.02	0.05	0.05
Site Average:		Arithmetic			0.30	0.03	0.06	0.06
		Geometric			0.23	0.03	0.06	0.04

* TWA = Time-weighted Average

** If greater than 1/2 the values of a sample set were above the lowest detectable concentration (LDC), non-detectable values were assigned LDC/2^{1/2}. (x.xx) indicates "calculated" value.

TABLE 5
 Assessment of Exposures to Gasoline Constituents
SITE I
LOS ANGELES, CALIFORNIA
 HETA 88-304
 November 5-9, 1990

#	Date	-----Time-----		(min)	-----Concentration (ppm)-----			
		On	Off		MTBE	Benzene	Toluene	Xylene
u01	1105	0623	1035	252	nd*	0.07	0.12	0.07
u05	1105	1035	1410	215	nd	(0.06)**	0.07	0.04
	TWA***	0623-1410		467	--	0.06	0.10	0.06
u02	1105	0620	1025	245	0.02	0.10	0.13	0.08
u06	1105	1025	1410	225	0.03	(0.06)	0.07	0.04
	TWA	0620-1410		470	0.03	0.07	0.10	0.06
u03	1105	0644	1041	237	nd	(0.06)	0.07	0.04
u07	1105	1046	1411	205	nd	(0.07)	0.05	0.05
	TWA	0644-1411		442	--	0.06	0.06	0.05
u04	1105	0655	1035	220	nd	(0.06)	0.12	0.06
u08	1105	1038	1411	213	nd	(0.06)	0.08	0.04
	TWA	0655-1411		433	--	0.06	0.10	0.05
u09	1106	0625	1025	240	nd	(0.05)	0.11	0.04
u15	1106	1026	1418	232	nd	(0.06)	0.11	0.06
	TWA	0625-1418		472	--	0.05	0.11	0.05
u10	1106	0632	1026	234	nd	0.08	0.16	0.06
u16	1106	1030	1410	220	nd	(0.06)	0.05	0.04
	TWA	0632-1410		454	--	0.06	0.11	0.05
u11	1106	0639	1016	217	nd	(0.06)	0.07	0.04
u13	1106	1020	1418	238	nd	(0.06)	0.05	0.04
	TWA	0639-1418		455	--	0.06	0.06	0.04
u12	1106	0630	1022	232	nd	(0.06)	0.07	0.04
u14	1106	1025	1410	225	nd	(0.06)	0.03	0.02
	TWA	0630-1410		457	--	0.06	0.05	0.03
u17	1107	0608	1018	250	nd	0.06	0.11	0.11
u21	1107	1018	1355	217	nd	(0.04)	0.06	0.06
	TWA	0608-1355		467	--	0.05	0.09	0.09
u18	1107	0612	1016	244	nd	(0.03)	0.04	0.09
u22	1107	1016	1350	214	nd	(0.04)	0.06	0.05
	TWA	0612-1350		458	--	0.03	0.05	0.07
u19	1107	0615	1020	245	0.02	0.10	0.17	0.11
u23	1107	1020	1403	223	nd	(0.06)	(0.02)	(0.02)
	TWA	0615-1403		468	--	0.07	0.10	0.06

* nd = non-detected; below the lowest detectable concentration (LDC)

** If greater than 1/2 the values of a sample set were above the lowest detectable concentration (LDC), non-detectable values were assigned LDC/2^{1/2}. (x.xx) indicates "calculated" value.

*** TWA = Time-weighted Average

TABLE 5 (cond.)
 Assessment of Exposures to Gasoline Constituents
SITE I
LOS ANGELES, CALIFORNIA

#	Date	-----Time-----		(min)	-----Concentration (ppm)---			
		On	Off		MTBE	Benzene	Toluene	Xylene
u20	1107	0710-1015		185	nd*	0.10	0.17	0.11
u24	1107	1015-1406		231	nd	(0.06)**	0.12	0.08
	TWA***	0710-1406		416	--	0.07	0.14	0.09
u25	1107	1405-1800		235	nd	0.06	0.07	0.10
u26	1107	1410-1800		230	nd	0.10	0.14	0.08
u27	1108	0618-1031		253	nd	0.09	0.13	0.06
u33	1108	1032-1433		241	nd	0.08	0.11	0.04
	TWA	0618-1433		494	--	0.09	0.12	0.05
u28	1108	0615-1015		240	0.03	0.06	0.08	0.05
u31	1108	1016-1414		238	nd	0.05	0.08	0.05
	TWA	0615-1414		478	--	0.06	0.08	0.05
u29	1108	0632-1015		223	nd	0.12	0.16	0.06
u32	1108	1015-1417		242	nd	0.04	0.07	0.04
	TWA	0632-1417		465	--	0.08	0.11	0.05
u35	1109	0617-1016		239	nd	0.14	0.22	0.14
u41	1109	1016-1420		244	0.11	0.09	0.13	0.09
	TWA	0617-1420		483	--	0.12	0.18	0.12
u36	1109	0614-1015		241	nd	0.04	0.07	0.07
u40	1109	1015-1415		240	nd	0.04	0.07	0.17
	TWA	0614-1415		481	--	0.04	0.07	0.12
u37	1109	0622-1005		223	0.06	0.19	0.24	0.14
u39	1109	1005-1415		250	nd	0.05	0.09	0.08
	TWA	0622-1415		473	--	0.12	0.16	0.12
Site Average:		Arithmetic			****	0.07	0.10	0.07
		Geometric			****	0.06	0.09	0.06

* nd = non-detected; below the lowest detectable concentration (LDC)

** If greater than 1/2 the values of a sample set were above the LDC, nd's were assigned values at LDC/2^{1/2}. (x.xx) indicates "calculated" value.

*** TWA = Time-weighted Average

**** Less than 1/2 the values were above the LDC; averages not reported.

TABLE 6

Assessment of Exposures to Gasoline Constituents
SITE II
LOS ANGELES, CALIFORNIA
 HETA 88-304
 November 5-9, 1990

#	Date	-----Time-----		(min)	-----Concentration (ppm)-----			
		On	Off		MTBE	Benzene	Toluene	Xylene
c01	1105	0706	1101	235	0.73	0.19	0.20	0.08
c02	1105	1101	1456	235	0.45	0.09	0.11	nd*
	TWA**	0706	1456	470	0.59	0.14	0.16	--
c03	1106	0904	1230	206	0.32	0.06	nd	nd
c04	1106	1230	1559	209	(0.04)***	0.01	nd	nd
	TWA	0904	1559	415	0.17	0.04	--	--
c05	1107	0814	1216	242	0.09	0.02	nd	nd
c06	1107	1216	1558	222	0.08	0.02	nd	nd
	TWA	0814	1558	464	0.09	0.02	--	--
c07	1108	0818	1214	236	0.14	0.03	nd	nd
c08	1108	1214	1557	223	0.17	0.05	nd	0.48
	TWA	0818	1214	459	0.16	0.04	--	--
c09	1109	0808	0930	082	0.21	0.07	0.11	0.06
c10	1109	1209	1555	226	0.22	0.06	0.09	nd
	TWA	0808	1555	308	0.22	0.06	0.10	--
Site Average:		Arithmetic			0.25	0.06	****	****
		Geometric			0.20	0.05	****	****

* nd = non-detected; below the lowest detectable concentration (LDC)

** TWA = Time-weighted Average

*** If greater than 1/2 the values of a sample set were above the LDC, nd's were assigned values at LDC/2^{1/2}. (x.xx) indicates "calculated" value.ref.

**** Less than 1/2 the values were above the LDC; averages not reported.

TABLE 7

Bulk Sample Results; Liquid Volume Percent

**SITE I
CINCINNATI, OHIO**

HETA 88-304

October 16-19, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
10/16/90				
Regular	00.18	1.60	08.3	11.0
Premium	00.16	0.93	08.0	07.1
Super	00.05	0.77	08.4	22.0
10/16/90				
Regular	00.09	0.59	03.0	03.7
Premium	00.09	0.55	04.5	04.0
Super	00.00	0.29	03.1	07.2
10/17/90				
Regular	00.10	0.60	03.0	03.5
Premium	00.09	0.54	04.4	03.9
Super	00.00	0.31	03.3	07.8
10/18/90				
Regular	00.10	0.57	02.8	03.3
Premium	00.09	0.54	04.4	03.8
Super	00.00	0.29	03.1	07.3
10/19/90				
Regular	00.10	0.59	02.7	03.4
Premium	00.09	0.58	04.7	04.1
Super	00.00	0.33	03.3	07.6
10/19/90				
Regular	00.10	0.60	02.8	03.5
Premium	00.11	0.78	06.3	05.5
Super	00.00	0.35	03.6	08.4
<u>SUMMARY</u> (Means)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	00.11	0.76	3.8	04.7
Premium	00.11	0.65	5.4	04.7
Super	00.01	0.39	4.1	10.1
<u>SUMMARY</u> (Ranges)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	0.09-0.18	0.57-1.60	2.7-8.3	3.3-11.0
Premium	0.09-0.16	0.54-0.93	4.4-8.0	3.8- 7.1
Super	0.00-0.05	0.29-0.77	3.1-8.4	7.2-22.0

TABLE 8

Bulk Sample Results; Liquid Volume Percent
SITE II
CINCINNATI, OHIO
 HETA 88-304
 October 16-19, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
10/18/90				
Regular	00.17	1.10	03.3	05.3
Premium	00.11	0.64	02.6	09.7
Super	00.06	0.36	02.4	12.0
10/19/90				
Regular	00.11	0.62	02.5	09.5
Premium	00.17	1.20	03.3	04.6
Super	00.06	0.40	02.7	13.0
10/22/90				
Regular	00.17	1.30	03.8	05.3
Premium	00.12	0.81	03.2	13.0
Super	00.06	0.43	02.5	12.0
<u>SUMMARY (Means)</u>	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	0.15	1.10	3.2	6.7
Premium	0.13	0.88	3.0	9.1
Super	0.06	0.40	2.5	12.3
<u>SUMMARY (Ranges)</u>	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	0.11-0.17	0.62-1.30	2.5-3.8	5.3- 9.5
Premium	0.11-0.17	0.64-1.20	2.6-3.3	4.6-13.0
Super	0.06-0.06	0.36-0.43	2.4-2.7	12.0-13.0

TABLE 9

Bulk Sample Results; Liquid Volume Percent

SITE I**PHOENIX, ARIZONA**

HETA 88-304

October 29 - November 02, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
10/29/90				
Regular	12.00	1.80	04.1	04.5
Premium	13.00	1.30	04.2	05.8
Super	13.00	1.10	06.3	07.4
10/30/90				
Regular	13.00	1.90	04.1	04.5
Premium	13.00	1.30	04.3	06.0
Super	14.00	1.10	06.6	07.7
10/31/91				
Regular	12.00	1.80	04.2	04.7
Premium	13.00	1.30	04.6	05.9
Super	14.00	1.10	06.6	07.7

<u>SUMMARY</u> (Means)	MTBE	Benzene	Toluene	Xylene
Regular	12.33	1.83	4.1	4.6
Premium	13.00	1.30	4.4	5.9
Super	13.67	1.10	6.5	7.6
<u>SUMMARY</u> (Ranges)	MTBE	Benzene	Toluene	Xylene
Regular	12.00-13.00	1.80-1.90	4.1-4.2	4.5-4.7
Premium	13.00-13.00	1.30-1.30	4.2-4.6	5.8-6.0
Super	13.00-14.00	1.10-1.10	6.3-6.6	7.4-7.7

TABLE 10

Bulk Sample Results; Liquid Volume Percent

SITE II**PHOENIX, ARIZONA**

HETA 88-304

October 29 - November 02, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
10/29/90				
Regular	12.00	1.50	04.2	05.6
Premium	13.00	1.30	04.5	06.0
Super	13.00	1.30	07.6	09.9
10/31/90				
Regular	13.00	1.40	03.9	05.4
Premium	13.00	1.30	04.4	05.9
Super	13.00	1.30	07.5	09.7
<u>SUMMARY</u> (Means)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	12.50	1.45	4.1	5.5
Premium	13.00	1.30	4.5	6.0
Super	13.00	1.30	7.6	9.8
<u>SUMMARY</u> (Ranges)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	12.00-13.00	1.40-1.50	3.9-4.2	5.4-5.6
Premium	13.00-13.00	1.30-1.30	4.4-4.5	5.9-6.0
Super	13.00-13.00	1.30-1.30	7.5-7.6	9.7-9.9

TABLE 11
 Bulk Sample Results; Liquid Volume Percent
SITE I
LOS ANGELES, CALIFORNIA
 HETA 88-304
 November 5-9, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
11/05/90				
Regular	00.00	1.30	06.2	07.4
Premium	00.00	1.50	08.3	09.1
Super	00.00	1.90	12.0	12.0
11/05/90				
Regular	00.00	1.60	06.5	08.4
Premium	00.00	1.60	08.6	09.8
Super	00.00	1.70	11.0	12.0
11/06/90				
Regular	00.00	1.70	06.6	08.4
Premium	00.00	1.70	08.6	10.0
Super	00.00	1.70	11.0	12.0
11/07/90				
Regular	00.00	1.70	06.5	08.3
Premium	00.00	1.80	10.0	11.0
Super	00.00	1.70	11.0	12.0
11/08/90				
Regular	00.00	1.80	06.7	08.4
Premium	00.00	1.70	08.3	09.4
Super	00.00	1.70	11.0	12.0
11/09/90				
Regular	00.20	1.40	04.9	06.0
Premium	00.20	1.60	08.0	08.7
Super	00.00	1.80	13.0	14.0
<u>SUMMARY</u> (Means)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	00.03	1.58	6.23	7.82
Premium	00.03	1.65	8.63	9.67
Super	00.00	1.75	11.50	12.33
<u>SUMMARY</u> (Ranges)	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
Regular	00.00-00.20	1.30-1.80	4.9-6.7	6.0- 8.4
Premium	00.00-00.20	1.50-1.80	8.0-10.0	8.7-11.0
Super	00.00-00.00	1.70-1.90	11.0-13.0	12.0-14.0

TABLE 12

Bulk Sample Results; Liquid Volume Percent

SITE II**LOS ANGELES, CALIFORNIA**

HETA 88-304

November 5-9, 1990

	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Xylene</u>
11/05/90				
Regular	00.20	2.50	08.3	08.7
Premium	00.00	2.00	08.8	11.0
Super	09.90	2.90	11.0	10.0
11/06/90				
Regular	00.20	2.40	08.0	09.0
Premium	00.00	2.00	08.8	11.0
Super	10.00	3.00	11.0	10.0
11/07/90				
Regular	00.20	2.40	08.2	08.9
Premium	00.00	2.10	08.7	10.0
Super	10.00	3.00	11.0	10.0
11/08/90				
Regular	00.20	2.30	08.3	09.2
Premium	00.00	2.10	08.8	11.0
Super	11.00	3.10	12.0	10.0
11/09/90				
Regular	00.20	2.30	08.2	09.7
Premium	00.00	2.20	09.5	11.0
Super	09.40	2.80	11.0	10.0

<u>SUMMARY</u> (Means)	MTBE	Benzene	Toluene	Xylene
Regular	00.20	2.38	8.2	9.1
Premium	00.00	2.08	8.9	10.8
Super	10.06	2.96	11.2	10.0
<u>SUMMARY</u> (Ranges)	MTBE	Benzene	Toluene	Xylene
Regular	00.20-00.20	2.30-2.50	8.0-8.3	8.7-9.7
Premium	00.00-00.00	2.00-2.20	8.7-9.5	10.0-11.0
Super	9.40-11.00	2.80-3.10	11.0-12.0	10.0-10.0

Table 13
 Final Models
 HETA 88-304
 November 1991

Benzene (log benzene)			
<u>Exposure Factor</u>	<u>Regression Coefficient</u>	<u>Std Error</u>	<u>p-value</u>
Intercept	-4.68	.464	<.001
Temperature	0.020	.006	0.001
Wind Speed	-0.104	.023	<.001
Gallons of fuel*	0.006	.001	<.001
	$R^2 = 0.36$		
MTBE (log MTBE)			
<u>Exposure Factor</u>	<u>Regression Coefficient</u>	<u>Std Error</u>	<u>p-value</u>
Intercept	-8.15	1.03	<.001
Temperature	0.057	0.014	<.001
Wind Speed	-0.089	0.041	0.036
Gallons	0.013	0.002	<.001
AWAM**	0.164	0.027	<.001
	$R^2 = 0.62$		
Toluene (log Toluene)			
<u>Exposure Factor</u>	<u>Regression Coefficient</u>	<u>Std Error</u>	<u>p-value</u>
Intercept	-2.52	0.132	<.001
Wind Speed	-0.084	0.025	<.001
Gallons	0.003	0.001	<.001
Cumulative Spill Area	0.001	.0005	0.003
	$R^2 = 0.24$		
Xylene (log Xylene)			
<u>Exposure Factor</u>	<u>Regression Coefficient</u>	<u>Std Error</u>	<u>p-value</u>
Intercept	-2.99	0.152	<.001
Wind Speed	-0.059	0.026	0.028
% Vicinity Time	0.026	0.008	0.001
	$R^2 = 0.17$		

* Pumped by attendant

** Weighted average of MTBE content; fuel pumped by attendant