Customer Exposure to MTBE, TAME, C₆ Alkyl Methyl Ethers, and Benzene during Gasoline Refueling

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We studied customer exposure during refueling by collecting air samples from customers’ breathing zone. The measurements were carried out during 4 days in summer 1996 at two Finnish self-service gasoline stations with “stage 1” vapor recovery systems. The 95-RON (research octane number) gasoline contained –2.7% methyl tert-butyl ether (MTBE), –8.5% tert-amy1 methyl ether (TAME), –3.2% C₆ alkyl methyl ethers (C₆ AMEs), and 0.75% benzene. The individual exposure concentrations showed a wide log-normal distribution, with low exposures being the most frequent. In over 90% of the samples, the concentration of MTBE was higher (range <0.02–51 mg/m³) than that of TAME. The MTBE values were well below the short-term (15 min) threshold limits set for occupational exposure (250–360 mg/m³). At station A, the geometric mean concentrations in individual samples were 3.9 mg/m³ MTBE and 2.2 mg/m³ TAME. The corresponding values at station B were 2.4 and 1.7 mg/m³, respectively. The average refueling (sampling) time was 63 sec at station A and 74 sec at station B. No statistically significant difference was observed in customer exposures between the two service stations. The overall geometric means (n = 167) for an adjusted 1-min refueling time were 3.3 mg/m³ MTBE and 1.9 mg/m³ TAME. Each day an integrated breathing zone sample was also collected, corresponding to an arithmetic mean of 20–21 refuelings. The overall arithmetic mean concentrations in the integrated samples (n = 8) were 0.90 mg/m³ for benzene and 0.56 mg/m³ for C₆ AMEs calculated as a group. Mean MTBE concentrations in ambient air (a stationary point in the middle of the pump island) were 0.16 mg/m³ for station A and 0.07 mg/m³ for station B. The mean ambient concentrations of TAME, C₆ AMEs, and benzene were 0.031 mg/m³, -0.005 mg/m³, and -0.01 mg/m³, respectively, at both stations. The mean wind speed was 1.4 m/sec and mean air temperature was 21°C. Of the gasoline refueled during the study, 75% was 95 grade and 25% was 98/99 grade, with an oxygenate (MTBE content) of 12.2%. Key words: benzene, gasoline, methyl tert-buty1 ether, oxygenate, pump island, refueling, service station, tert-amy1 methyl ether. 

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Methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) were introduced in the mid-1970s as gasoline additives. MTBE was originally used as an octane enhancer. In the 1990s, however, the reduction of motor vehicle emissions of CO and hydrocarbons has become an important reason for its use and, indeed, for the use of oxygenates in general. Unleaded gasoline that contains oxygenates such as MTBE, TAME, ethanol, methanol, or ethyl tert-butyl ether (ETBE) is commonly used in several western European countries and North America. At present, all of the gasoline used in Austria, Sweden, and Finland is unleaded (1). In Europe, the oxygenates are generally ethers and, unlike in the United States, little ethanol is currently used (2).

In Finland, unleaded gasoline with 11% MTBE has been used since 1991. Reformulated gasoline with a typical MTBE content of 11–12% was put on the market in 1994. In 1995, a new reformulated product was introduced, containing an oxygenate mixture of MTBE, TAME, and other alkyl methyl ethers (AMEs). The new product is based on etherification of the reactive C₅–C₆ isolefins present in fluid catalytic cracking light gasoline fractions (3). The etherification is carried out with methanol and isomylene to obtain TAME, and with methanol and tertiary C₆ olefins to obtain heavier ethers. The result is a mixture of hydrocarbons, TAME, and heavier ethers, such as tertiary hexyl methyl ethers. This mixture is then added to gasoline. MTBE can also be added to the same gasoline pool.

Because MTBE is now the most common oxygenate, its toxicologic effects and, to some extent, human exposure levels have been investigated (mainly in the 1990s) (4–6). The exposure of customers during refueling with MTBE-oxygenated gasoline was assessed in a study carried out at two Finnish service stations (7). No studies have been reported on driver exposure to TAME or other AMEs present in the oxygenate mixture. The aim of this study was to assess the exposure of customers to MTBE, TAME, and C₆ AMEs during refueling. We also measured the exposure to benzene. The field measurements, also including a stationary sampling point at the pump island, were carried out at two Finnish service stations.

There are no set threshold concentrations for such short-term exposures as customer exposure during refueling. For occupational MTBE exposures, there are limit values for an 8-hr working day in some European countries and in the United States, ranging from 90 to 180 mg/m³ (8–11). In Sweden and in The Netherlands, short-term (15 min) occupational exposure limit values of 250 and 360 mg/m³, respectively, have also been set. Furthermore, a reference concentration of 3 mg/m³ has been set by the U.S. EPA as a guideline for long-term exposures via environmental air (12). No threshold limit values (TLVs) exist for TAME and C₆ AMEs.

The United States currently has a short-term standard of 8 mg/m³ and an 8-hr TLV of 1.6 mg/m³ (11) for benzene. In Europe, national standards exist, but the European Union has also set a common limit value of 3.25 mg/m³ (8 hr), which will come into effect with a 3-year transition period from the year 2000; during the transition period, the limit is 9.75 mg/m³ (13).

Materials and Methods

Service stations and gasolines. The study was carried out in summer 1996 at two self-service stations located in the Helsinki, Finland, metropolitan area, representing the typical Nordic station in size and design. Service station A was an urban station with two adjacent main roads with high traffic densities. Service station B was a roadside station. The measurements were carried out on 19–22 August at station A and on 26–29 August at station B.

Both stations had three pump islands in front of the service station building, with a total of 12 pumps at station A and eight pumps at station B for gasoline and diesel oil. At station A, six of the pumps were for dispensing 95- and 99-research octane number (RON) gasoline and six for 98-RON gasoline/diesel oil. At station B, seven of the pumps were for dispensing 95-RON gasoline, three for 98-RON gasoline, six for 99-RON gasoline, and...
three for diesel oil. The gasoline dispenser pistols were equipped with rubber "splash collars," which are in general use in Finland. Both stations had "stage I" vapor recovery systems that collect vapors during gasoline unloading (but not with stage II recovery, which collects vapors released from a vehicle’s gasoline tank during refueling).

All gasoline grades sold during the study (unleaded 95-, 98-, and 99-RON) were of the reformulated type and of summer grade, with the following maximum contents: lead 0.003 g/l, benzene 1% (v/v), and sulfur 0.01% (w/w). The oxygen content was specified as 2.0–2.7% (w/w) and the Reid vapor pressure was 67–68 kPa (at 37.8°C). The density of the fuel was 747–748 kg/m³ (at 15°C).

Table 1. Concentrations of MTBE, TAME, C₈ AMEs, and benzene (% w/v) in 95-RON and 98/99-RON gasoline during the study

|                | Station A          | Station B          |
|----------------|--------------------|--------------------|
|                | 95-RON 19 Aug⁻¹ | 95-RON 19–22 Aug⁻¹ | 95-RON 26 Aug⁻¹ | 95-RON 26–28 Aug⁻¹ | 95-RON 28–29 Aug⁻¹ | 98/99-RON 26–29 Aug⁻¹ |
| MTBE           | 4.0 2.4            | 12.2 (v/v)         | 1.7 2.7         | 3.6 12.2 (v/v)     |
| TAME           | 7.7 8.9            | 0.3 0.00            | 0.3 0.3         | 0.3 0.00            |
| 2,3-Dimethyl-2- | 1.4 1.6            | 0.8 1.0            | 0.4 0.3         | 0.4 0.3             |
| methoxybutane  | 0.13               | 0.08               | 0.0003         | 0.0009             |
| 1-Methoxy-1-    | 0.4 0.3            | 0.4 0.3            | 0.3 0.0         | 0.3 0.0             |
| methylcyclopentane | 2.9 3.2          | 3.5 3.2            | 2.9 0.0         | 0.0003             |
| Sum of C₈ AMEs | 2.9 3.2            | 3.5 3.2            | 2.9 0.0         | 0.0003             |
| Benzene        | 0.8 0.8            | 0.8 0.7            | 0.7 0.7         | 0.0003             |

Abbreviations: MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; AMEs, alkyl methyl ethers; RON, research octane number. Gasoline was delivered to Station A on 19 Aug (1250–1330 hr): 95-RON gasoline, 21,000 liters and 98-RON gasoline, 10,000 liters. Gasoline was delivered to Station B on 26 Aug (0930–1000 hr): 95-RON gasoline, 13,700 liters, and on 28 Aug (1235–1325 hr): 95-RON gasoline, 20,900 liters; 98-RON gasoline, 10,600 liters.

Table 2. Concentrations (mg/m³) of C₆–C₈ AMEs and benzene in ambient air measured at the pump island, concurrent meteorologic parameters, and volumes of gasoline sold

|                | Station A          | Station B          |
|----------------|--------------------|--------------------|
|                | 19 Aug 20 Aug      | 21 Aug 22 Aug      | 26 Aug 27 Aug   | 28 Aug 29 Aug      |
| MTBE           | 0.24 0.069         | 0.13 0.22          | 0.031 0.063     | 0.11 0.074         |
| TAME           | 0.040 0.010        | 0.018 0.0057       | 0.016 0.005     | 0.047 0.026        |
| 2,3-Dimethyl-2- | 0.0008            | 0.0003             | 0.0001         | 0.0006 0.0003      |
| methoxybutane  | 0.0031 0.0014      | 0.017 0.0047       | 0.014 0.0022    | 0.0031 0.0017      |
| 2-Methyl-2-     | 0.0021 0.0008      | 0.010 0.0028       | 0.009 0.0018    | 0.0022 0.0015      |
| methoxy-2-      | 0.0008 <0.0005     | <0.0007 0.001      | <0.0006 0.0008  | 0.0008 0.0006      |
| pentane        | 0.0068 0.0028      | 0.0035 0.0006     | 0.0027 0.0054   | 0.0070 0.0041      |
| Benzene        | 0.015 0.0064       | 0.0097 0.017      | 0.0048 0.0071   | 0.0096 0.0066      |
| Wind speed (m/sec)⁴ | 1.7±0.5            | 2.0±0.6            | 1.9±0.4        | 1.1±0.6             |
| Wind direction | SW,S SW,S SW,S SW,S | N,S,S SE,E SE,E SE,E | SE,E SE,E SE,E SE,E |
| Air temperature (⁰C)⁴ | 23.0±2.4          | 22.9±2.0            | 22.3±1.4      | 22.8±2.4           |
| Relative humidity (%)⁴ | 69±14             | 74±12              | 71±11         | 52±12 70±3 63±5 94±6 63±14 |
| Gasoline sold (liters) | 2,147 1,757 | 1,570 1,689 | 2,077 2,931 | 3,560 2,280 |

Abbreviations: AMES, alkyl methyl ethers; MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; RON, research octane number.

⁴Mean ± standard deviation.

Samples were taken of the 95-RON gasoline to determine its contents of oxygenates and benzene. The samples were taken at the beginning of the exposure measurements and after deliveries of gasoline. The samples were collected in glass bottles, which were then tightly sealed and transferred to a test laboratory of the gasoline supplier (Neste Oy, Porvoo, Finland) for gas chromatographic (GC) analysis. The values obtained are shown in Table 1 together with those for 98- and 99-RON gasolines. The latter were not measured in the present study, but are mean values reported by the supplier for the gasoline blends delivered in August 1996.

The volumes of gasoline sold during the study are presented in Tables 2 and 3. The total amount of gasoline dispensed between 0800 and 1600 hr was higher at station B (14,300 l) as compared to station A (9,700 l).

Measurement of exposures. The exposure services of station customers to oxygenates and benzene were studied by collecting air samples from customers’ breathing zones in charcoal tubes during refueling. Two sampling tubes were placed in the customer’s breathing zone during the refueling operation. One tube was used to collect an individual sample and the other tube was for collection of an integrated sample for each measurement day (consisting of 20–21 refueling operations). The purpose of the integrated sample was to measure components that were expected to occur at very low concentrations (C₆ AMEs and benzene) and would not be found easily in the short-term individual samples. The individual samples were used to measure MTBE and TAME, which were present at higher concentrations in gasoline and therefore at higher amounts in the breathing zone. The individual samples also allowed us to obtain the distribution among customers and to choose an appropriate central value according to the type of the distribution. The integrated samples represented the arithmetic mean exposures for each measurement day, regardless of the distribution of the individual concentrations.

The sampling was started when the person refueling inserted the pump pistol in the fuel tank and ended when he/she replaced the pump pistol in its holder. Only customers who refueled with 95-RON gasoline participated in the study. As a rule, 20 or 21 refuelings (individual samples) were studied at each service station between about 0830 and 1530 hr. During the 4-day measurement period, 83 individual samples were collected at station A and 84 were collected at station B; four integrated samples were collected at each station.
Pump island measurements. The ambient air measurements at the pump islands were carried out on the same days as the breathing zone measurements. The sampling point was in the center of the forecourt between the two pumps on the middle pump island. Two parallel samples were collected in charcoal tubes on each measurement day from 0800 to 1600 hr. This stationary sampling point was 1.5 m above the ground at station A and 1.8 m above the ground at station B.

Meteorologic conditions. Air temperature and relative humidity were measured hourly in the center of the forecourt (pump island sampling point) with a Vaisala HMI 31 Humidity and Temperature Indicator (Vaisala Oy, Vantaa, Finland). Wind speed and direction were measured continuously with a wind gauge (Typ 1482, Wilh. Lambrecht KG, Göttingen, Germany) located on the roof of the service station building about 5 m above the ground.

Method of sampling. The sampling was performed using Du Pont S 2500 pumps (E.I. du Pont de Nemours & Co., Wilmington, DE), which pulled air through the charcoal tubes (SKC 226-01; 150 mg of adsorbent) at 1 l/min (breathing zone samples) or 0.2 l/min (pump island samples). At the service stations, the charcoal tubes were stored in a cooled box (+2°C) after sampling. Each day after sampling, the tubes were stored at -20°C until analysis.

Method of analysis. The analytes were desorbed from the charcoal with 1 ml of benzene-free CS2 (Rathburn Chemicals, Walkerburn, UK) in a glass vial. After 1 hr at room temperature with occasional vibration, the vials were mounted on a GC autosampler (HP 7673; Hewlett-Packard, Palo Alto, CA) and a 2-μl subsample was injected into the GC. The GC instrument was a Hewlett-Packard 5890 equipped with a 5790 A quadrupole mass-selective detector (electron ionization mode). The temperature of the injector was 250°C, and a slow injection was used.

Calibration standards were made by the phase equilibrium method by adding 1 ml of a standard mixture in CS2 to a glass vial containing charcoal, the amount and batch of the charcoal being the same as that used for samples. The mixture was allowed to stand at room temperature for 1 hr before analysis. The stock standard solution was prepared weekly, and the calibration standards were prepared daily. The stock standard solutions of MTBE, TAME, and benzene were prepared from pure solvents (>97%), whereas the calibration standards of C6 AMEs were prepared from an etherified standard mixture containing TAME, C6 AMEs, and hydrocarbons. The mixture was obtained from the oil company (Neste Oy), which also supplied the information on the density and percent composition of the standard mixture.

MTBE, TAME, 3-methyl-3-methoxy-pentane, and 1-methoxy-1-methylcyclopentane were separated in an HP-5 fused silica column (50 m × 0.32 mm × 1.05 μm phase thickness; Hewlett-Packard). The oven temperature program was as follows: 40°C for 6.6 min; increased to 160°C at 30°C/min; and 160°C held for 3.4 min. The inlet pressure of the carrier gas (helium) was 20 kPa, and a split ratio of 1:20 was used. For selected ion monitoring (SIM), two ions were selected for each compound: 57 and 73 (MTBE); 73 and 87 (TAME); 87 and 101 (3-methyl-3-methoxy-pentane); and 85 and 114 (1-methoxy-1-methylcyclopentane).

The abundances of 73 (MTBE), 73 (TAME), 87 (3-methyl-3-methoxy-pentane), and 85 (1-methoxy-1-methylcyclopentane) were used for quantification.

Because 2,3-dimethyl-2-methoxybutane and 2-methyl-2-methoxy-pentane were not separated in the above column, the samples were also analyzed with a PONA column (50 m × 0.2 mm × 0.5 μm phase thickness; Hewlett-Packard), which separated these two compounds well. The concentration of benzene was also determined using this column. The oven temperature program was as follows: 40°C for 7 min; increased to 110°C at 5°C/min; increased to 160°C at 30°C/min; and 160°C held for 0.3 min. The inlet pressure of the carrier gas was 138 kPa and the split ratio was 1:85. The ions monitored were 73, 101 (both AME compounds) and 78, 79 (benzene); 73 (AME) and 78 (benzene) were used for quantitations.

The detection limits were 0.04 μg/ml for MTBE and 0.03 μg/ml for TAME, which correspond to atmospheric concentrations of 0.04 and 0.03 mg/m3, respectively, for a 1-liter air sample and 0.0004 mg/m3 and 0.0003 mg/m3, respectively, for a 90-liter air sample. The detection limits for C6 AMEs and benzene were in the range of 0.02–0.05 μg/ml.

Results

Breathing zone measurements/individual samples. The overall average concentrations of MTBE and TAME in individual breathing zone samples for the two service stations are shown in Table 4. The data were log-normally distributed; therefore, geometric means (GM) were calculated as the central value. In these calculations, each value below the detection limit was assigned a value L/2 (half of the detection limit). At station A, 2/3 MTBE and 2/3 TAME results were below detection limits. At station B, 4/84 MTBE and 3/84 TAME results were below detection limits.

Because the refueling times varied (23–189 sec), average concentrations for 1 min (Cmin) were calculated for all individual samples (concentration measured × refueling time in seconds/60 sec). GMs were also provided for these values (Table 4). The time-averaged values allowed the exposures of individual customers and the average exposures of the two service stations to be compared.

### Table 3. Concentrations (mg/m3) of C6–C8 AMEs and benzene in ambient air measured at the pump island; concurrent meteorologic parameters and volumes of gasoline sold

|               | Station A                  | Station B                  |
|---------------|----------------------------|----------------------------|
|               | 19–22 Aug 1996             | 26–29 Aug 1996             |
| MTBE          | 0.16 ± 0.08                | 0.069 ± 0.031              |
| TAME          | 0.031 ± 0.021              | 0.031 ± 0.013              |
| 2,3-Dimethyl-2-methoxybutane | 0.0007 ± 0.0004          | 0.0005 ± 0.0003            |
| 2-Methyl-2-methoxy-pentane    | 0.0027 ± 0.0009           | 0.0021 ± 0.0007            |
| 3-Methyl-3-methoxy-pentane    | 0.0017 ± 0.0009           | 0.0016 ± 0.0005            |
| 1-Methoxy-1-methylcyclopentane | 0.0006 ± 0.0004        | 0.0006 ± 0.0002            |
| Benzene        | 0.012 ± 0.005              | 0.0070 ± 0.0020            |
| Sum of MTBE and TAME         |                          |                            |
| 0.20 ± 0.10    | 0.10 ± 0.04                |
| Wind speed (m/sec)           | 1.7 ± 0.5                  | 1.0 ± 0.4                  |
| Wind direction              |                           |                            |
| Air temperature (°C)         | 22.7 ± 2.0                 | 18.9 ± 1.2                 |
| Relative humidity (%)        | 67 ± 15                    | 70 ± 12                    |
| Gasoline sold (liters)       | 7.163 (74.2%)              | 10.848 (75.9%)             |
| 95-RON                     | 2,492 (25.8%)              | 3,450 (24.1%)              |
| 98/99-RON                  | 9,655                      | 14,298                     |

Abbreviations: AMES, alkyl methyl ethers; MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; RON, research octane number. Values shown are mean ± standard deviations (range), except where noted.
The GM concentrations of the individual samples were 3.9 mg/m³ (MTBE) and 2.3 mg/m³ (TAME) at station A and 2.4 mg/m³ (MTBE) and 1.6 mg/m³ (TAME) at station B. The corresponding C_{1 min} values were 4.1 and 2.2 mg/m³ (station A) and 2.7 and 1.7 mg/m³ (station B). The differences in the geometric means of the C_{1 min} values were tested using the Student’s t-test. There were no significant differences (95% confidence level) in MTBE or TAME exposures between the two service stations (p = 0.13, MTBE; p = 0.38, TAME).

The C_{1 min} values of MTBE and TAME were added, and these sum values are shown in Figures 1 and 2. The GMs of the sum concentrations were 6.4 mg/m³ (5.0 geometric standard deviation; GSD) at station A and 4.5 mg/m³ (6.7 GSD) at station B. The GM of all C_{1 min} sum values was 5.4 mg/m³ (5.8 GSD; range = 0.02–131 mg/m³).

The presence of a catalytic converter was recorded for each vehicle because the design of the tank is different in vehicles with and without a converter, and we assumed that this might reflect on the exposure levels. The number of vehicles with and without catalytic converters was 87 and 79, respectively. The GM concentrations (C_{1 min}) of MTBE for these groups were 3.9 mg/m³ (5.8 GSD) and 2.7 mg/m³ (6.5 GSD), respectively. The values of TAME were 2.4 mg/m³ (5.3 GSD) and 1.5 mg/m³ (5.8 GSD), respectively. The possible interactions between the independent variables (the presence of catalytic converter and the service station) were tested using a general linear model (SYSTAT version 7.0, SPSS, Inc., Chicago, IL). No statistically significant interaction was observed; the data were tested further by linear regression using the presence of a catalytic converter and the service station as independent variables.

Abbreviations: MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; GM, geometric mean; GSD, geometric standard deviation; C_{1 min} average concentration for 1 min; SD, standard deviation.

Table 4. Overall average concentrations of MTBE and TAME in customers' breathing zones and overall average values for other parameters recorded during the breathing zone measurements.

| Parameter                  | Station A          | Station B          | All measurements |
|----------------------------|--------------------|--------------------|------------------|
| Mean ± SD                  | 63 ± 26            | 74 ± 33            | 68 ± 29          |
| Range                      | 23–154             | 25–169             | –                |
| Total                      | 5,212              | 6,207              | –                |
| Mean ± SD                  | 30.9 ± 17.0        | 29.4 ± 17.4        | 29.7 ± 16.8      |
| Range                      | 3.6–84.0           | 3.7–85.1           | –                |
| Total                      | 2,562              | 2,473              | –                |
| Mean ± SD                  | 1.6 ± 0.6          | 1.0 ± 0.4          | 1.3 ± 0.6        |
| Range                      | 0.2–2.8            | 0.3–1.7            | –                |
| Mean ± SD                  | 22.7 ± 1.9         | 18.8 ± 1.2         | 20.8 ± 2.5       |
| Range                      | 18.1–26.2          | 15.5–21.5          | –                |
| Mean ± SD                  | 67 ± 15            | 70 ± 12            | 69 ± 13          |
| Range                      | 42–91              | 45–92              | –                |

Figure 1. Concentrations for 1 min (C_{1 min}) of methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) in customers' breathing zones at service station A.
variables. The difference in customer exposure between vehicles with and without a converter was not statistically significant (p-value for MTBE was 0.17 and for TAME 0.08).

The sampling site was recorded as the location of the pump island and as a compass point indicating on which side of the pump island the vehicle was parked during refueling. There were 9 sampling sites at station A and 10 at station B. The number of samples taken at each sampling site ranged from 1 to 17. The mean concentrations of more than 12 refuelings (data not shown) were tested using analysis of variance (ANOVA). No statistically significant differences were obtained among the sampling sites.

Twenty-nine different makes of cars refueled at both stations, the most abundant being Toyota \(n = 26\), Opel \(n = 16\), Nissan \(n = 15\), and Volvo \(n = 13\). There were 1–6 different models within one make, for a total of 68 models. The data did not allow correlation of the make and model of the vehicle with the time spent in refueling or with the exposure levels. The mean refueling time was 63 sec at station A and 74 sec at station B (overall mean 68 sec).

Breathing zone measurements/integrated samples. The results of the breathing zone measurements by integrated sampling are shown in Table 5. Each sample consisted of 20–21 refueling operations, thus corresponding to daily arithmetic means of individual samples. The variation among the 4 sampling days at each station was small; therefore, the arithmetic mean was chosen as the central value for the integrated samples.

The arithmetic mean concentrations of the four integrated samples were 9.7 mg/m\(^3\) MTBE and 5.3 mg/m\(^3\) TAME at

![Figure 2](image-url) Concentrations for 1 min \(C_{1\text{min}}\) of methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) in customers' breathing zones at service station B.

| Table 5. Concentrations (mg/m\(^3\)) of C\(_4\)–C\(_6\) AMEs and benzene in customers' breathing zones (integrated samples) |
|----------------------------------------------------------------------------------------------------------------------------------|
| **Station A**                                                                                                                   | **Station B**                                                                                         |
| **19 Aug** | **20 Aug** | **21 Aug** | **22 Aug** | **19–22 Aug\(^*\)** | **26 Aug** | **27 Aug** | **28 Aug** | **29 Aug** | **26–29 Aug\(^*\)** |
| MTBE       | 11.6      | 10.7      | 8.9        | 7.7        | 9.7 ± 1.8  | 6.0        | 5.7        | 10.9        | 6.9        | 7.4 ± 2.4  |
| TAME       | 4.9       | 7.3       | 4.6        | 4.3        | 5.3 ± 1.4  | 4.2        | 4.0        | 4.8         | 4.4        | 4.4 ± 0.3  |
| 2,3-Dimethyl-2-methoxybutane | 0.067 | 0.096 | 0.060 | 0.058 | 0.070 ± 0.018 | 0.050 | 0.051 | 0.051 | 0.050 | 0.051 ± 0.001 |
| 2-Methyl-2-methoxypentane | 0.30 | 0.44 | 0.27 | 0.27 | 0.32 ± 0.08 | 0.22 | 0.23 | 0.22 | 0.22 | 0.22 ± 0.01 |
| 3-Methyl-3-methoxypentane | 0.17 | 0.25 | 0.15 | 0.15 | 0.18 ± 0.05 | 0.14 | 0.13 | 0.15 | 0.14 | 0.14 ± 0.01 |
| 1-Methoxy-1-methycyclopentane | 0.067 | 0.10 | 0.063 | 0.064 | 0.074 ± 0.018 | 0.057 | 0.055 | 0.065 | 0.057 | 0.059 ± 0.004 |
| C\(_4\) AMEs | 0.61 | 0.89 | 0.54 | 0.54 | 0.65 ± 0.17 | 0.47 | 0.49 | 0.49 | 0.47 | 0.48 ± 0.01 |
| MTBE plus TAME | 16.5 | 18.0 | 13.5 | 12.0 | 15.0 ± 2.7 | 10.2 | 15.7 | 15.7 | 11.3 | 11.7 ± 2.7 |
| C\(_4\)–C\(_6\) AMEs | 17.1 | 18.9 | 14.0 | 12.5 | 15.6 ± 2.9 | 10.7 | 16.2 | 16.2 | 11.8 | 12.2 ± 2.7 |
| Sampling volume (liter) | 18.8 | 25.4 | 21.3 | 20.8 | 21.6 ± 2.8 | 24.2 | 25.1 | 25.1 | 25.7 | 25.5 ± 1.1 |
| Refuelings (n) | 20 | 21 | 21 | 21 | 83 | 21 | 21 | 21 | 21 | 84 |

Abbreviations: MTBE, methyl tert-butyl ether; TAME, tert-amyl methyl ether; AMEs, alkyl methyl ethers.

\(^*\) Arithmetic mean ± standard deviation.
station A and 7.4 and 4.4 mg/m³, respectively, at station B. The highest means of the C⁵ AMEs were measured for 2-methyl-2-methoxypentane: 0.32 mg/m³ at station A and 0.22 mg/m³ at station B. The lowest mean concentrations were measured for 2,3-dimethyl-2-methoxybutane: 0.051 mg/m³ (station B) and 0.070 mg/m³ (station A). The mean concentration of benzene was 1.0 mg/m³ at station A and 0.77 mg/m³ at station B.

Sum concentrations calculated for the group of C⁶ AMEs were 12% (station A) and 11% (station B) of the corresponding mean concentrations of TAME, and 4.2% (station A) and 3.9% (station B) of the total amounts of C⁴-C⁶ AMEs measured. The mean benzene concentration was 6.4% (station A) and 6.3% (station B) of the total amount of C⁴-C⁶ AMEs measured. In all, the mean proportions of each individual component measured in the breathing zone were very similar at the two stations.

**Pump island measurements.** The daily and the mean concentrations of C⁴-C⁶ alkyl methyl ethers and benzene in ambient air measured in the middle of the pump island are presented in Tables 2 and 3. Each day, the highest concentrations were measured for MTBE. The daily levels of C⁶ AMEs were low but mostly detectable; only four of the values were below the detection limit.

The arithmetic mean concentration of MTBE was 0.16 mg/m³ at station A and 0.069 mg/m³ at station B. The mean concentration of TAME was the same at both service stations (0.031 mg/m³). The mean concentrations of C⁶ AMEs were also very similar at the two stations, ranging from 0.0005 mg/m³ (2,3-dimethyl-2-methoxybutane) to 0.0027 mg/m³ (2-methyl-2-methoxypentane). The benzene level was slightly higher at station A (0.012 mg/m³).

For daily TAME concentrations and wind speed, the Pearson’s coefficient of correlation (r) was 0.95 (p = 0.05) at station A and 0.99 (p = 0.01) at station B. At station B, MTBE (r = 0.96; p = 0.04) and benzene (r = 0.99; p = 0.006) were also highly correlated with the daily wind speed. At station A, the r values for MTBE and benzene were also rather high (0.71 and 0.88), but because of the small number of samples (n = 4), they did not reach statistical significance.

**Discussion**

**Breathing zone measurements.** The concentrations of MTBE in customers’ breathing zones were higher than those of TAME in over 90% of the samples, although the amount of TAME in 95-RON gasoline was at least three times the MTBE concentration. This is explained by the clearly higher vapor pressure of MTBE (55 versus 17 kPa at 37.8°C) (4). Nevertheless, there was great variation in the TAME/MTBE ratio among the samples. The concentration of TAME was on average 60–70% of the MTBE concentration but, as can be seen in Figures 1 and 2, the TAME/MTBE ratio ranged from 0.1 to 1.0 in individual samples. This variation may have been partly due to gasoline fumes in the car tank from a previous fill-up. The oxygenate composition of these fumes may have been different from that of the gasoline added.

The levels of both MTBE and TAME in the individual samples varied widely, from below detection limits to concentrations at least 1,000 times higher, resulting in a GSD of up to 7 for the overall mean concentrations. Because of the high sensitivity of the method, only six samples remained below detection limits. Low exposures were the most frequent. At least 50% of C₁ min values were below 5 mg/m³ for MTBE or 3 mg/m³ for TAME, although the highest exposure levels (C₁ min) measured were around 100 mg/m³ for MTBE and 70 mg/m³ for TAME.

High variations in the data contributed to the fact that a Student’s t-test showed no statistically significant difference between the two service stations, despite the higher overall GMs for MTBE and TAME at station A. At station A, the air temperature was higher (4°C), as was the wind speed, which should in turn reduce the exposures. In all, the weather conditions at both stations were representative of north or central European summer conditions. The mean volume of gasoline dispensed was almost the same at both stations, but the mean refueling time was 11 sec shorter at station A. The difference in mean refueling time may be explained by different adjustments of gasoline flow in the pump pistons.

The integrated samples (corresponding to arithmetic means of the individual samples) gave almost the same MTBE and TAME concentrations as the arithmetic means of the individual samples at station B (Fig. 3). At station A, however, the integrated samples yielded higher arithmetic mean concentrations than did the individual samples. As can be expected for a highly skewed log-normal distribution, the GM values (representing the proper central values for the exposure concentrations) are much lower than the arithmetic means. The integrated samples and the arithmetic means overestimate the average exposure during refueling.

Despite the above, the integrated samples were useful in clearly showing the differences in the volatilities of the components measured. Figure 4 presents the average concentrations in liquid gasoline and the corresponding average airborne concentrations measured by integrated sampling. For example, the proportions of MTBE and C⁶ AMEs were rather similar in gasoline, but the amount of MTBE found in air samples was 15 times higher. The Reid vapor pressure of benzene (22 kPa) is only slightly higher than that of TAME (17 kPa), but according to our results, benzene is much more easily volatilized than TAME. This may be due to a positive discrepancy of Rauholt’s law, which has been observed for benzene in hydrocarbon mixtures (14).

In the Finnish service station study conducted in 1995 (7), an overall GM value of 6 mg/m³ was obtained for MTBE during a 1-min refueling time. The range for four measurement periods was 4.6–8.2 mg/m³, and the MTBE content of the gasoline was 11%. In the present study, the
gasoline used for refueling contained on average 2.7% of MTBE, and the corresponding overall average concentration of MTBE in air was 3.3 mg/m³. The latter figure seems to be higher than expected on the basis of the much lower MTBE content of the gasoline (averaging 25% of the MTBE content in the aforementioned study). One explanation may be gasoline vapors from the car tanks, originating from a previous refueling, as explained above. Nevertheless, the highest atmospheric concentrations measured in the 1995 study were about 200 mg/m³, as compared with 50 mg/m³ measured in the present study.

The arithmetic mean concentration of benzene calculated for the eight integrated samples was 0.9 mg/m³. This equals the value obtained in an earlier study in which 228 refuelings were measured in Cincinnati, Ohio [15]. The benzene concentration of the regular unleaded gasoline was 0.92% (v/v) in this study, whereas in our study (7) it was slightly lower: 0.75% (w/w) corresponding to 0.64% (v/v). When the results of the two studies are calculated for a 1-min refueling time, 1.4 mg/m³ and 1.0 mg/m³ mean concentrations are obtained for the Cincinnati study and our study, respectively. These values are consistent with the slightly different benzene concentrations of the gasolines in these studies. In a previous study from 1984–1985 [16], 21 self-fill operations were measured, and an average benzene concentration of 4.3 mg/m³ was obtained for a 2-min refueling time, which corresponds to 8.6 mg/m³ calculated over a 1-min period. The average benzene content of the gasoline was reported to be 4% (w/w). Again, this result is consistent with ours.

When the individual exposures found in the present study are compared with the occupational short-term limits (15 min), it can be concluded that even the highest MTBE and benzene concentrations at the customer breathing zone are well below these limits. The highest MTBE exposure (C100) was 106 mg/m³, and the highest benzene exposure was estimated (based on integrated samples) to be 1/10 of the MTBE C100 value, 10 mg/m³. The upper 95% confidence limit (UCL) for a 1-min refueling time was calculated to be 114 mg/m³ for MTBE and 56 mg/m³ for TAME. For the sum of MTBE and TAME, the 95% UCL was 169 mg/m³.

**Pump island measurements.** The daily concentrations of the components measured correlated well with the wind speed especially at station B. No such correlation was found in our 1995 study [17]. This may be due to the shifting wind during that study, whereas the wind was rather stable throughout the measurements for the present study.

The average pump island concentrations were either similar (TAME, C₆ AMEs, benzene) at the two stations or higher (MTBE) at station A, although the wind speed was higher and the volume of gasoline sold was lower at that station. These factors should contribute to lower air concentrations. In this case, the lack of contribution from these factors might be explained by the sampling sites being closer to the pumps at station A. Emissions from passing traffic are unlikely to have markedly affected the impurity levels at the pump island, as evidenced by our previous study carried out in the vicinity of two service stations [17].

The mean pump island concentrations of MTBE measured in the summer in a previous study [17] were on average 0.9 mg/m³. The MTBE content of the gasoline was 11% and the volume of gasoline dispensed was 21,000 l/24 hr. In the present study, the corresponding mean concentration was slightly lower (0.11 mg/m³) when considering the average MTBE content of the gasolines, which was estimated to be around 5%. The volume of gasoline dispensed was 12,000 l/8 hr. It should be noted, however, that the sampling points are not fully comparable because the service stations were not in the same in the two studies. However, the air temperature and wind speed were rather similar in both studies.

In two Italian service station studies [18], mean MTBE concentrations of 0.11 mg/m³ (2.1% MTBE) and 0.25 mg/m³ (2.7% MTBE) in gasoline were measured at the pump island. In a U.S. service station study [19], an overall GM of 0.39 mg/m³ was obtained for MTBE at five non-station II self-service stations when the MTBE content of the gasoline was around 15%. The overall means (0.11 mg/m³; 5% MTBE in gasoline) of our study are not inconsistent with the above studies.

For benzene, the overall GM concentration at the pump island in the U.S. study was 0.032 mg/m³ (range 0.003–0.17 mg/m³) [19]. The benzene content of the gasoline averaged 1.3% (v/v); the benzene content in our study was about 0.64% (v/v). Again, there is no discrepancy between the U.S. study and ours: the overall benzene concentration at the pump island was 0.01 mg/m³ in our study.

**Conclusions**

The individual exposure measurements in customers’ breathing zones yielded widely distributed concentrations, with low concentrations being the most frequent. Due to the higher volatility of MTBE, its concentration was higher in most samples than the TAME concentration, despite the threefold higher content of TAME in the gasoline. On average, a customer was exposed to an MTBE concentration of 3.3 mg/m³ and to a TAME concentration of 1.9 mg/m³ for 1 min. No statistically significant difference was observed in customer exposures to MTBE or TAME between the two service stations or between vehicles with and without catalytic converters. The average concentrations of benzene and C₆ AMEs in customers’ breathing zones were about 1/10 and 1/15, respectively, of the average MTBE concentration.

The pump island measurements showed the highest overall mean concentration for MTBE (0.11 mg/m³), and second highest for TAME. The concentrations of benzene and C₆ AMEs were low but measurable. A correlation was found between wind speed and daily pump island concentration.
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