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HUMAN EXPOSURE ESTIMATES OF METHYL TERTIARY BUTYL ETHER (MTBE)

Alan H. Huber

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A Research Update

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Abstract

Data on ambient air quality and microenvironmental exposures (e.g., during refueling, inside cars, in personal garages) are too limited for a quantitative estimate of population exposures to MTBE. At best, they can be used to estimate broad ranges of potential exposures. Because of the interest in MTBE, the present evaluation focuses on this compound, even though any potential health effects might result from complex pollutant mixtures of which MTBE is only one component. Furthermore, potential exposures of only the general public, not occupationally exposed groups, were evaluated.

Figure 1 outlines the personal activities that have been considered in developing an annual human exposure estimate. Gasoline fill-up is divided into two parts to cover both the fill-up (1.5 fill-ups per week) and the remaining time spent in the station environment. The distribution of hours spent in each microenvironment is based on reasonable interpretation of available population activity studies. The greatest difficulty arose in trying to distribute the balance of time spent in one's residence, office or outdoors. In this example, meant to represent one exposure scenario, the typical time one spends either at home or in a work place is relatively large. Therefore, if there are elevated concentrations in these microenvironments, they may become the largest contributor to annual average human exposures.

There is a need to estimate both acute and chronic exposures to elucidate health risks. A gasoline fill-up, although brief, results in the highest acute exposures since human exposures are greatest when one is near evaporative emissions. Thus, exposures are greatest when handling gasoline. Figures 2-13 summarizes available concentrations during fill-up, at gas stations, and in-cabin during automobile commutes. New field measurements (Lioy et al., 1993; Johnson, 1993) were collected in New Brunswick, NJ (2 stations with full service and phase II vapor recovery), Westchester County, NY (3 stations with self service and phase II vapor recovery) and Fairfield County, CT (5 stations with self service and no phase II vapor recovery). Ambient air quality was measured in Fairbanks AK, Stamford CT, and Albany NY (Zweidinger, 1993). Details on the study data should be obtained from the authors' presentations and reports. The data analyses should be

considered preliminary. The presentation below is provided to meet an immediate need to present the range of MTBE concentrations in the identified microenvironments and an annual exposure assessment with some margin of safety.

International Technologies Corporation (IT) completed a set of field measurements of MTBE concentrations in the personal breathing zone during fill-up, at the pump island, and around the property line of gas stations (Johnson, 1993). This study was done in coordination with the following EOHSI/RTI study (Lioy et. al.) at the same ten gas stations. All concentrations for the IT study, even those in the intermittent breathing zone, were a four-hour continuous sample. Since the breathing zone collection was video taped IT will try to adjust the breathing zone measurements to reflect a personal exposure during the fill-up. Four-hour average fence-line MTBE concentrations were found to range from 0.018-0.234 mg/m^3 (0.005-0.065 ppm). The highest fence-line MTBE concentrations ranged from 0.36-0.5 mg/m^3 (0.1-0.14 ppm). The highest 4-hour average breathing zone and pump island MTBE concentrations ranged from 0.7-9 mg/m^3 (0.2-2.5 ppm). These breathing zone concentrations are comparable to the 4-hour continuous sample occupational concentrations in a recent NIOSH study (NIOSH, 1993). In the NIOSH study, the mean breathing zone MTBE concentration for station attendants was 2 mg/m^3 (0.58 ppm) with the highest concentrations exceeding 14.4 mg/m^3 (4 ppm). As expected these breathing zone concentrations are lower than reported by the Clayton Environmental Consultant study (Clayton, 1991) which collected samples only during the fill-up period. In the Clayton study mean MTBE concentrations in the breathing zone for 12-13 percent MTBE were 13 mg/m^3 (3.9 ppm) with vapor recovery and 30 mg/m^3 (8.3 ppm) without vapor recovery. The absolute range of the MTBE concentrations was 0.32 to 137 mg/m^3 (0.088-38 ppm).

A wide range of ambient air concentrations within the breathing zone can be expected. Ambient air concentrations measured at a gas station will be highly dependant upon the wind speed and direction. In addition, breathing zone concentrations can be dramatically influenced by how one stands relative to the wind. A typical worst case MTBE concentration in the breathing zone during fill-up would be 36 mg/m^3 (10 ppm) for a few minutes. However, an accidental spill of fuel while filling the tank can dramatically increase the inhaled concentration.

Lioy et al. (1993) provides measurements of MTBE concentrations inside an automobile during an approximate 30 min commute and during a fill-up of the gas tank. A late-new model automobile (1992 Corsica) and an older-model automobile (1985 Caprice or 1986 Monte Carlo) were assigned to each commuter route. The samples were collected in the front passenger side of the automobile. The number of sampling runs (cases) per automobile ranged from 14-20 for the commute and 3-5 for the fill-up. The driver's window was completely open during the fill-up. The average time to complete a fill-up was about 2 min, while the total time at the gas station was approximately 5-10 min. Average in-cabin concentrations of MTBE during the commute were found to range from 0.018 to 0.275 mg/m^3 (0.005-0.075 ppm). Average in-cabin concentrations during the fill-up ranged from 0.036 to 1.8 mg/m^3 (0.1-0.5 ppm). In addition to the measurements inside the automobile, several measurements were collected on the person refueling the gas tank. These concentrations were found to range from 0.7-14 mg/m^3 (0.2-4 ppm). The older model automobiles were found to result in higher inside automobile concentrations which probably reflect differences between the automobile design and "wear".

Figures 14-20 summarize air concentrations collected in Fairbanks AK, Stamford CT, and Albany NY (Zweidinger, 1993). Alaska was not in the MTBE program during the February/March collection. Albany was not part of the MTBE program. Concentrations (except for garage/auto-shop) in Alaska are reduced from 0.0072-0.14 mg/m^3 (0.002-0.04 ppm) range to the 0.0036-0.054 mg/m^3 (0.001-0.015 ppm) range after ending the MTBE program. Concentration inside the house were higher than outside for some cases indicating that there may be a source of MTBE indoors. It is possible that the residential garage may have had a source of evaporative emissions after parking the hot car in the garage or from gasoline being stored in the garage. Figures 21-23 summarize an EPA case study of measured evaporative emissions from an automobile at rest after being run through the Federal Test Protocol (FTP) cycle that was completed to provide an example herein. Approximately 0.5 grams of MTBE was emitted during the 4-hour test. These emissions were then used as the modeled source in a 95 m^3 garage attached to a residential house. This is believed to provide a reasonable worst case demonstration of in-house concentrations due to a hot car parked in a closed residential garage at 75 deg F. A multizonal mass balance model CONTAM88 (Grot, 1991) was used to model indoor concentrations. Peak concentrations were 2.3 mg/m^3 (0.65 ppm) in the garage and 0.12 mg/m^3 (0.035 ppm) in the residence. One-hour averaged concentrations in the garage ranged from 2.5-4.3 mg/m^3 (0.7-1.2 ppm) while concentration in the residence ranged from 0.072-0.32 mg/m^3 (0.02-0.09 ppm). This is a worst-case situation since a newer car or cold winter temperatures would likely have reduced evaporative emission rates resulting in lower concentrations.

Figure 24 summarizes the range of concentrations for the identified microenvironments. The components of an annual average human exposure estimate are shown in Figure 25. The commute and gasoline fill-up are clearly the most important microenvironment unless one has significant evaporative emissions in the residential garage. The annual estimate uses the Figure 25 values for the 4 mo MTBE season and assumes that MTBE concentrations are 10 percent of these values the remainder of the year. This assumption is based on belief that the amount of MTBE in the ambient air is proportional to the amount of MTBE in the fuel (1.5% versus 15% should allow a margin of safety). It's difficult to estimate MTBE levels during the nonoxyfuels season since MTBE is used in premium gasolines and to a lesser extent in some regular gasolines. These exposure values result in an annual estimate of 0.03 mg/m^3 (0.0084 ppm) using the low concentrations and 0.046 mg/m^3 (0.013 ppm) using the high concentrations in Figure 25. The above exposure scenario was calculated to represent a reasonable worst case exposure estimate for the working adult population after factoring-in the margin of safety. Exposure for children is expected to be lower because children do not pump gas and spend less time commuting in heavy traffic.

Acknowledgements:
This presentation could not have been possible without the timely effort of Ted Johnson (ITC), Paul Lioy and Cliff Weisel (EOSHI), Kenneth Knapp (EPA) and Roy Zweidinger (EPA) to share their data files as the data are preliminarily processed. The presented analyses was prepared within several days preceding the conference and was only possible with the assistance of Gary Evans (EPA), John Streicher (EPA), Mike Zelenka (EPA), Azzedine Lanzari (METI) and Graham Glen (METI).

References:

Clayton Environmental Consultants (1991). Gasoline Vapor Exposure Assessment for the American Petroleum Institute. Clayton Project No. 31774.00, July 2, 1991.

Grot, R. A. (1991). User Manual NBSAVIS CONTAM88. Report NISTIR 4585, National Institute of Standards and Technology, Gaithersburg MD.

Johnson, T. (1993). Service Station Monitoring Study. (Abst. and presentation) Conference on MTBE and Other Oxygenates, Falls Church, VA, July 1993.

Lioy, P. J., C. Weisel, E. Pellizzari, and J. Raymer (1993). Volatile Organic Compounds from Fuels Oxygenated with MTBE: Concentration and Microenvironmental Exposures to MTBE in Automobile Cabins. (Abst. and presentation) Conference on MTBE and Other Oxygenates, Falls Church, VA, July 1993.

NIOSH (1993). HETA 88-304-2326 American Petroleum Institute, Washington, DC.

Zweidinger, R. B. (1993) Air Quality Measurements in Fairbanks, Stamford, and Albany. (Abst. and presentation) Conference on MTBE and Other Oxygenates, Falls Church, VA, July 1993.

PERSONAL ACTIVITIES

8760 hours/year

			TIME (hours)
1.	Gas Fill-up	1.5/wk @ 2min	2.6
		other @ 10min	13.0
2.	Commute/ In Vehicle	10hr/week	520
3.	Auto Shop	4/yr @ 15min	1
4.	Public Garage	2/day @ 10min	60.83
5.	Residential Garage	2 min/day	12.16
6.	Residence	10hr/day +weekend	4160
7.	Office	40hr/wk	2080
8.	**OTHER/PUBLIC BUILDINGS**	17/wk	884
9.	Outdoors	20hr/wk	1040

Figure 1

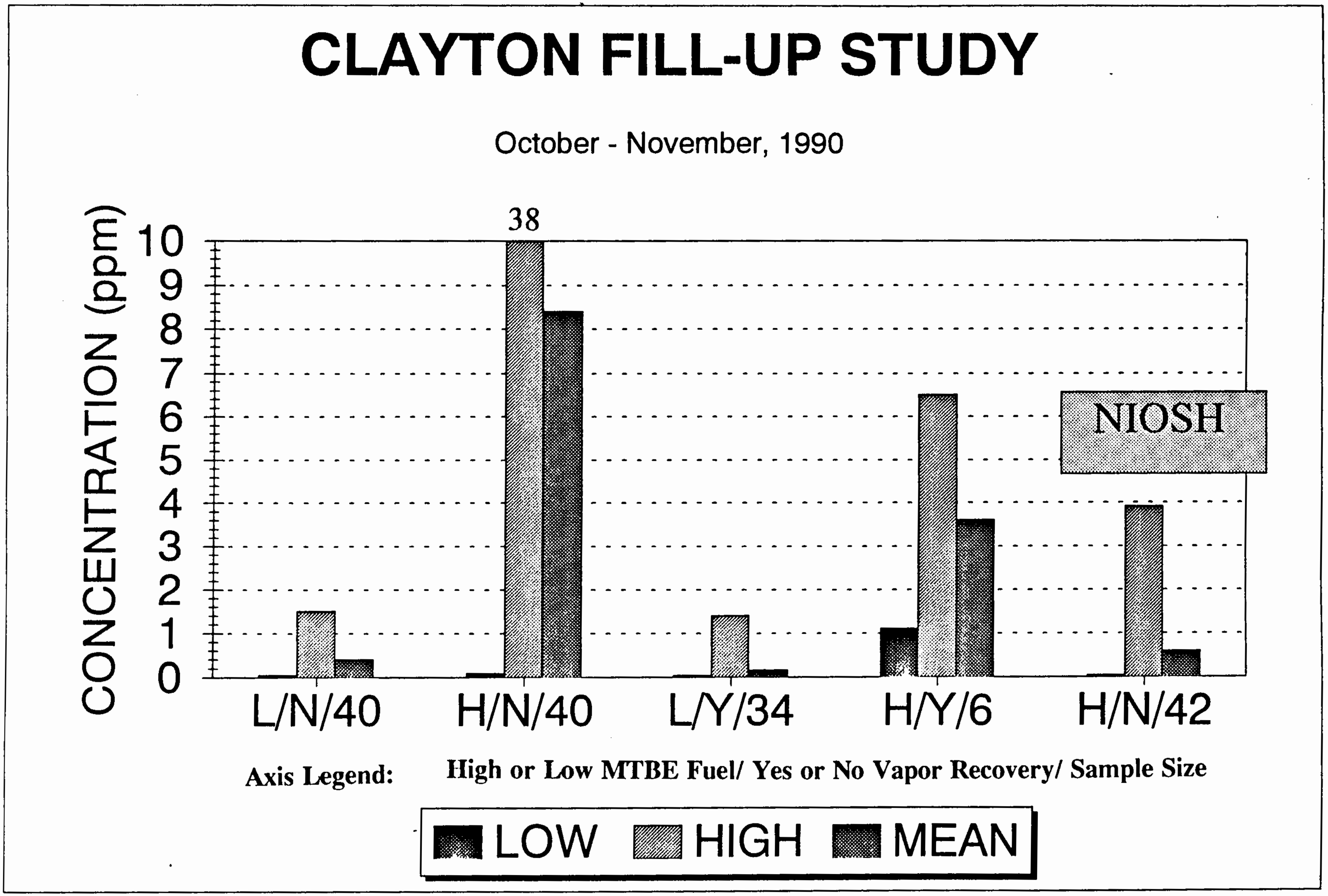
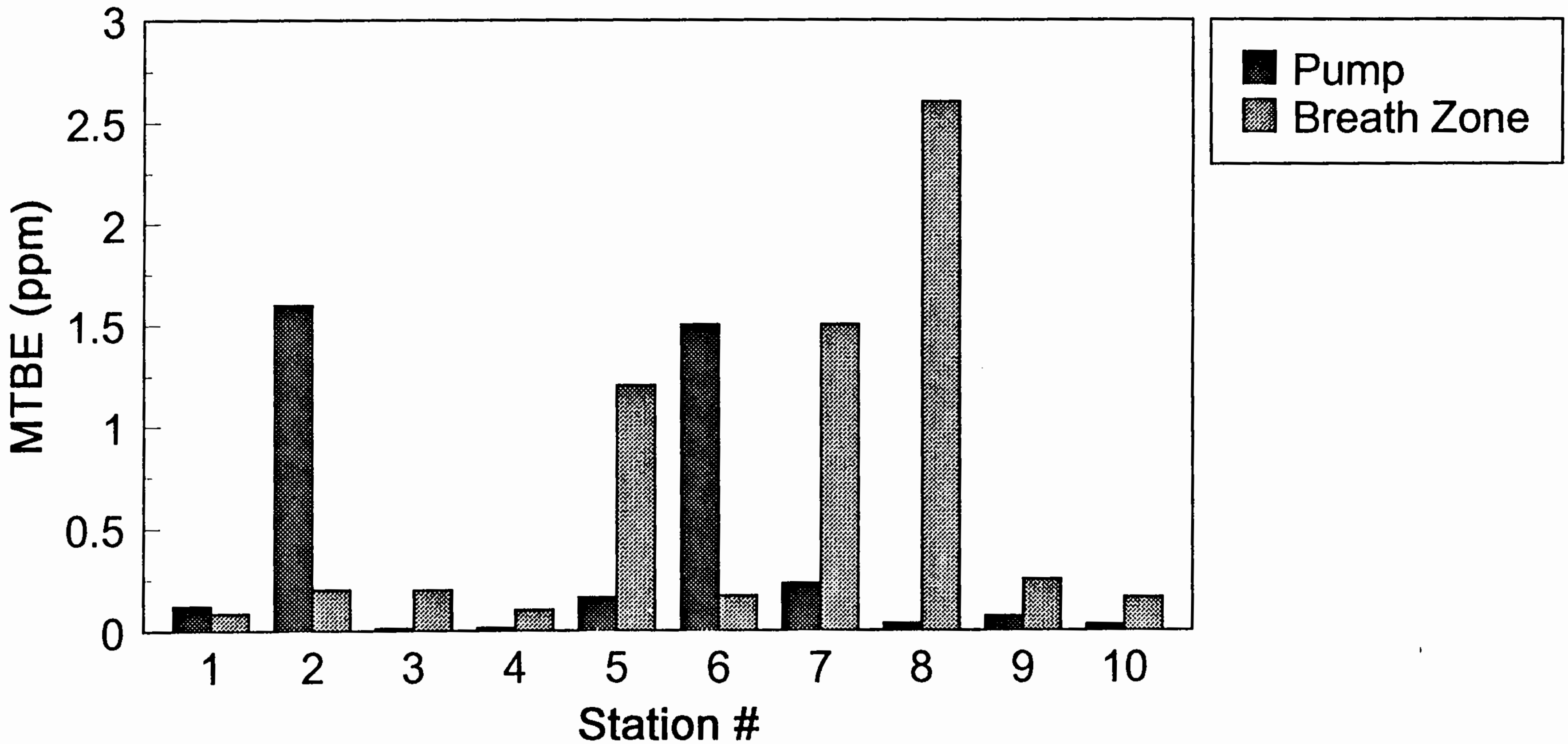

CLAYTON FILL-UP STUDY
October - November, 1990
CONCENTRATION (ppm)
38
0
1
2
3
4
5
6
7
8
9
10
NIOSH
L/N/40
H/N/40
L/Y/34
H/Y/6
H/N/42
Axis Legend:
High or Low MTBE Fuel/ Yes or No Vapor Recovery/ Sample Size
LOW
HIGH
MEAN

Figure 2

Fill-up Stations Data

ITC

AM Samples



4 hr., AM sample

Figure 3

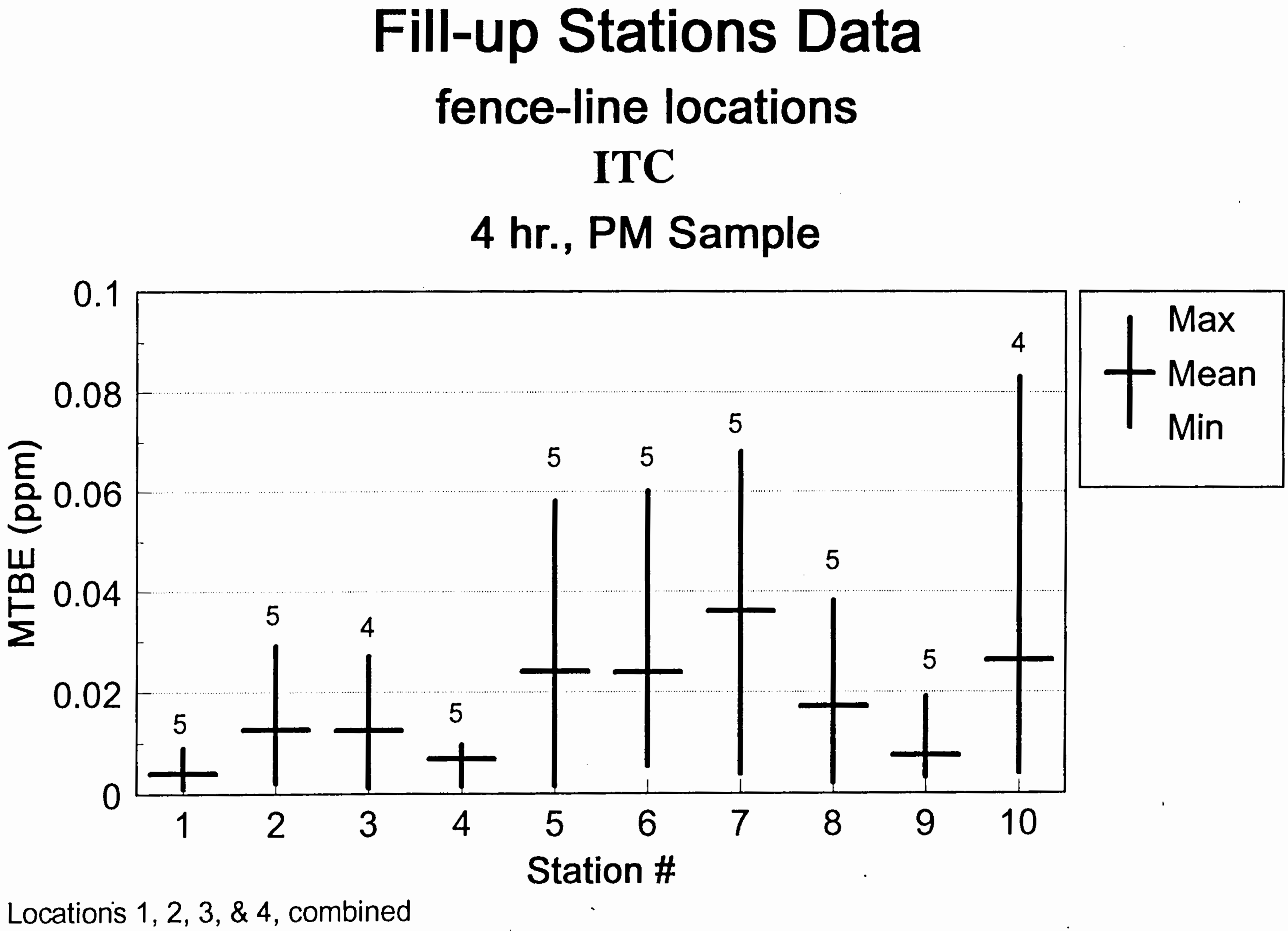

Fill-up Stations Data
fence-line locations
ITC
4 hr., PM Sample
MTBE (ppm)
0.1
0.08
0.06
0.04
0.02
0
Station #
1
2
3
4
5
6
7
8
9
10
5
5
4
5
5
5
5
5
5
4
Max
Mean
Min
Locations 1, 2, 3, & 4, combined

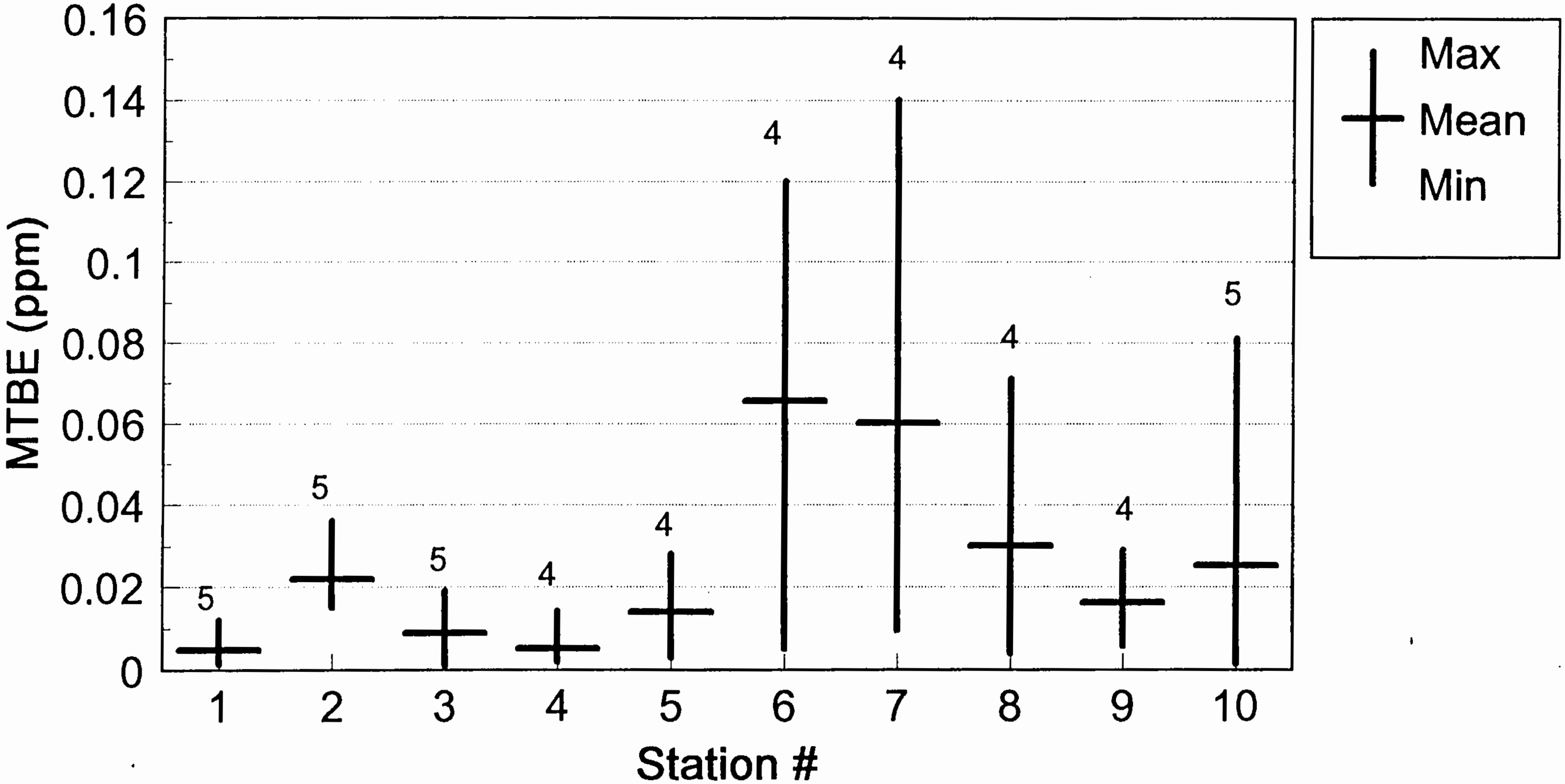
Figure 6

Fill-up Stations Data

fence-line locations

ITC

4 hr., AM Sample



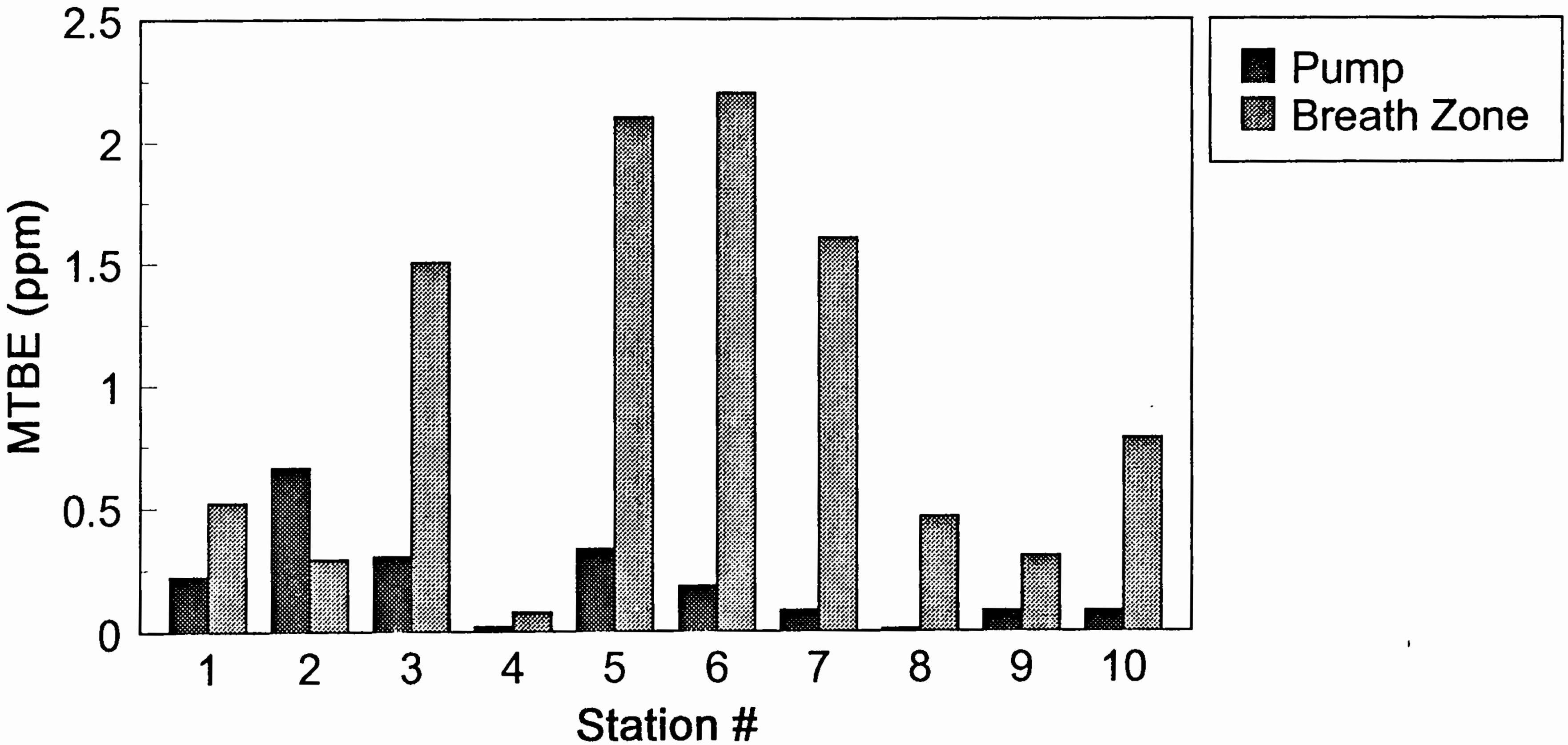
Locations 1, 2, 3, & 4, combined

Figure 5

Fill-up Stations Data

ITC

PM Samples



4 hr., PM sample

Figure 4

In-Cabin Concentrations During Refueling
1985 Caprice

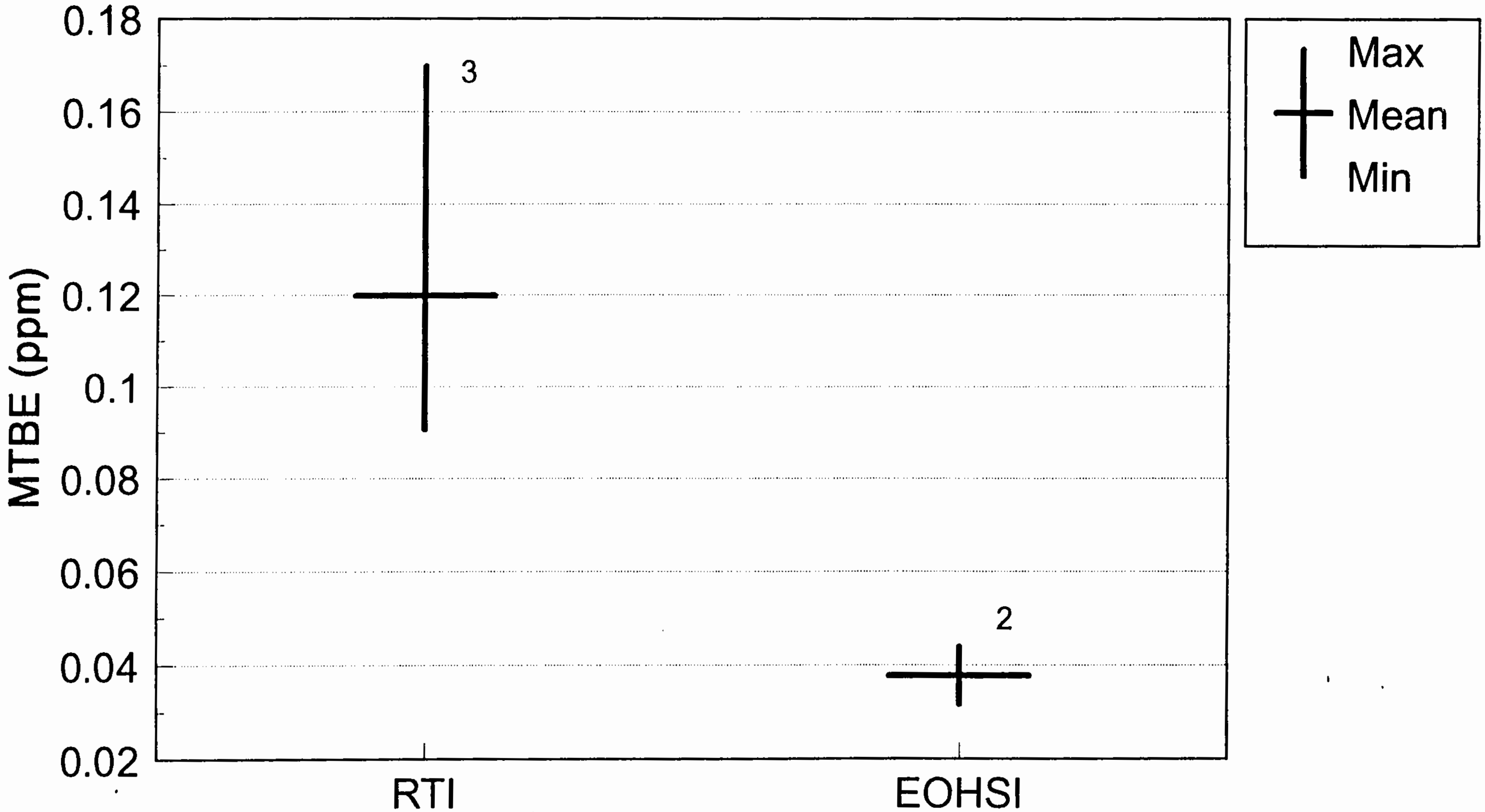


Figure 7

Group 7; NJ during fillup

In-Cabin Concentrations During Refueling
1986 Monte Carlo

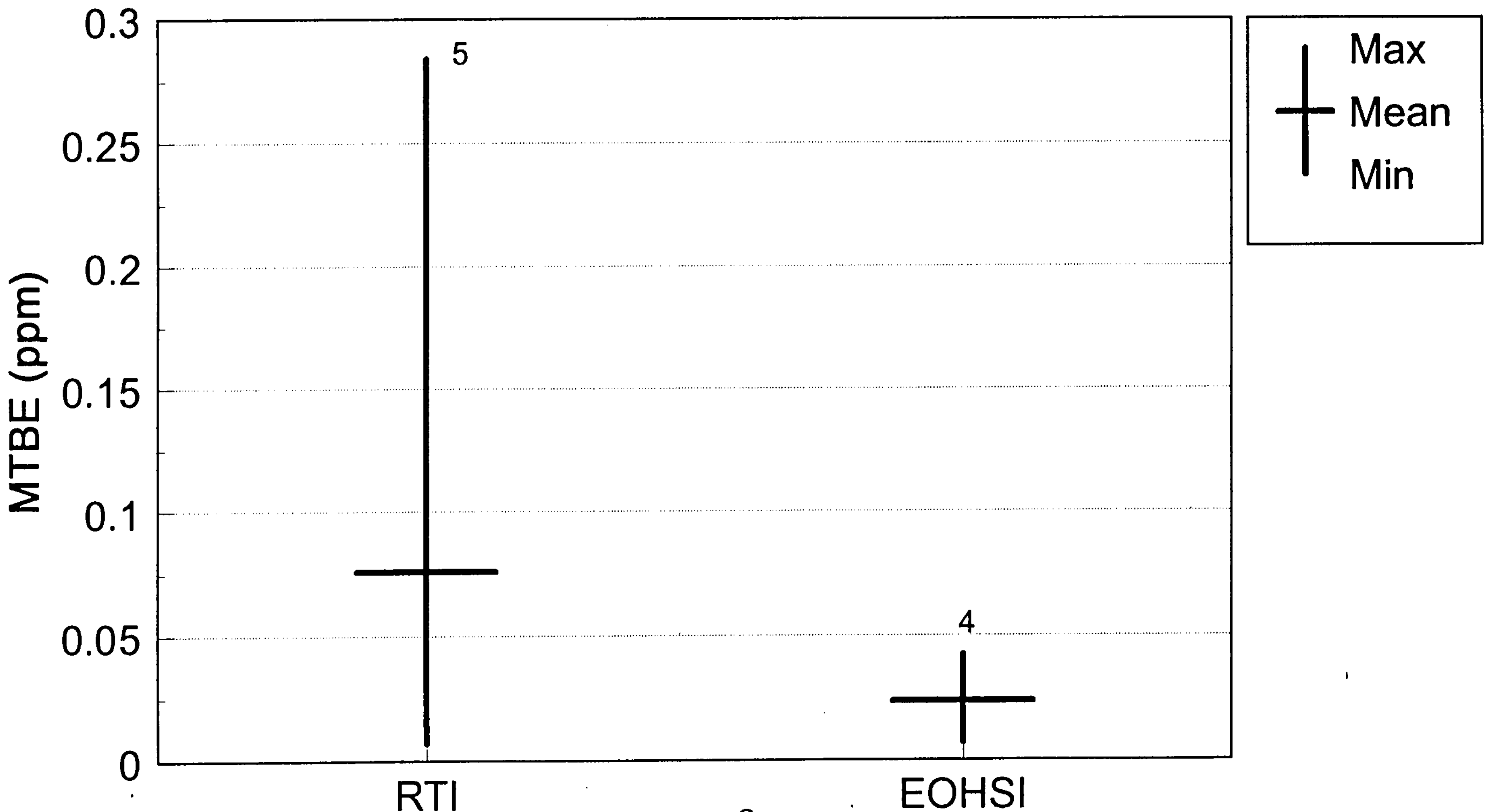


Figure 8

Groups 11 & 13, combined; CT during fillup (full- and self-serve, resp.)

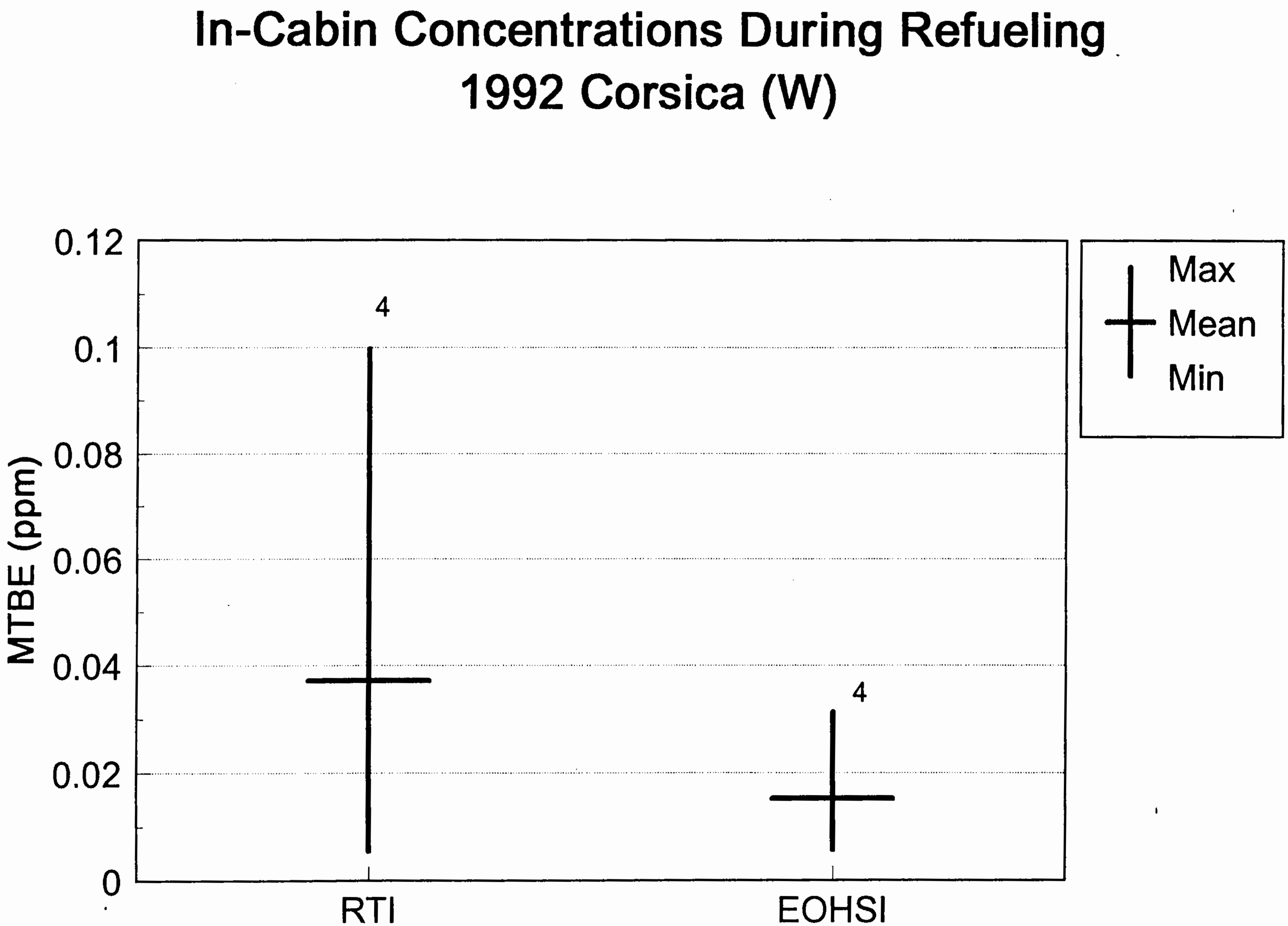


Figure 9

Group 7; NJ during fillup

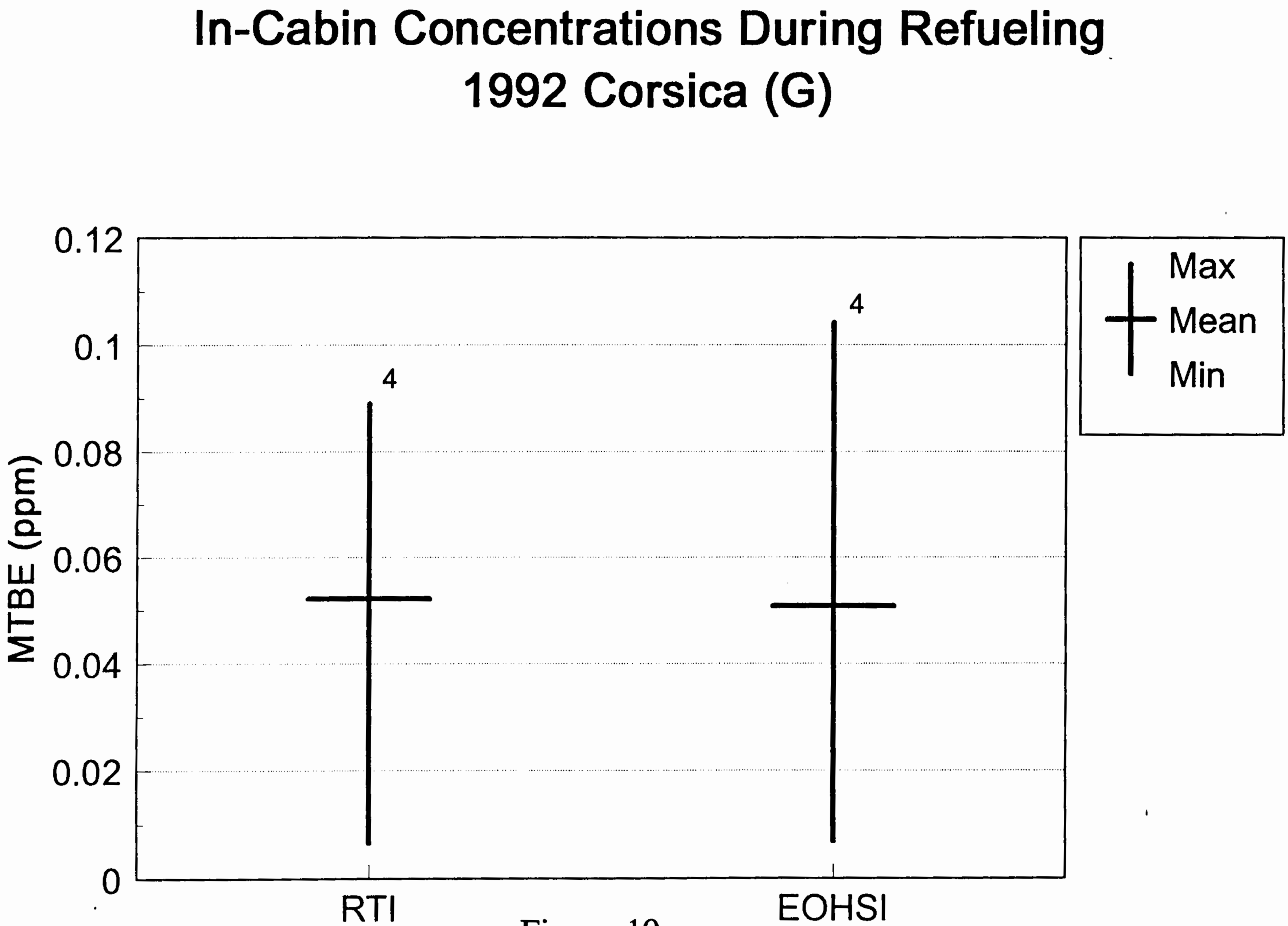


Figure 10

Groups 11 & 13, combined; CT during fillup (full- and self-serve, resp.)

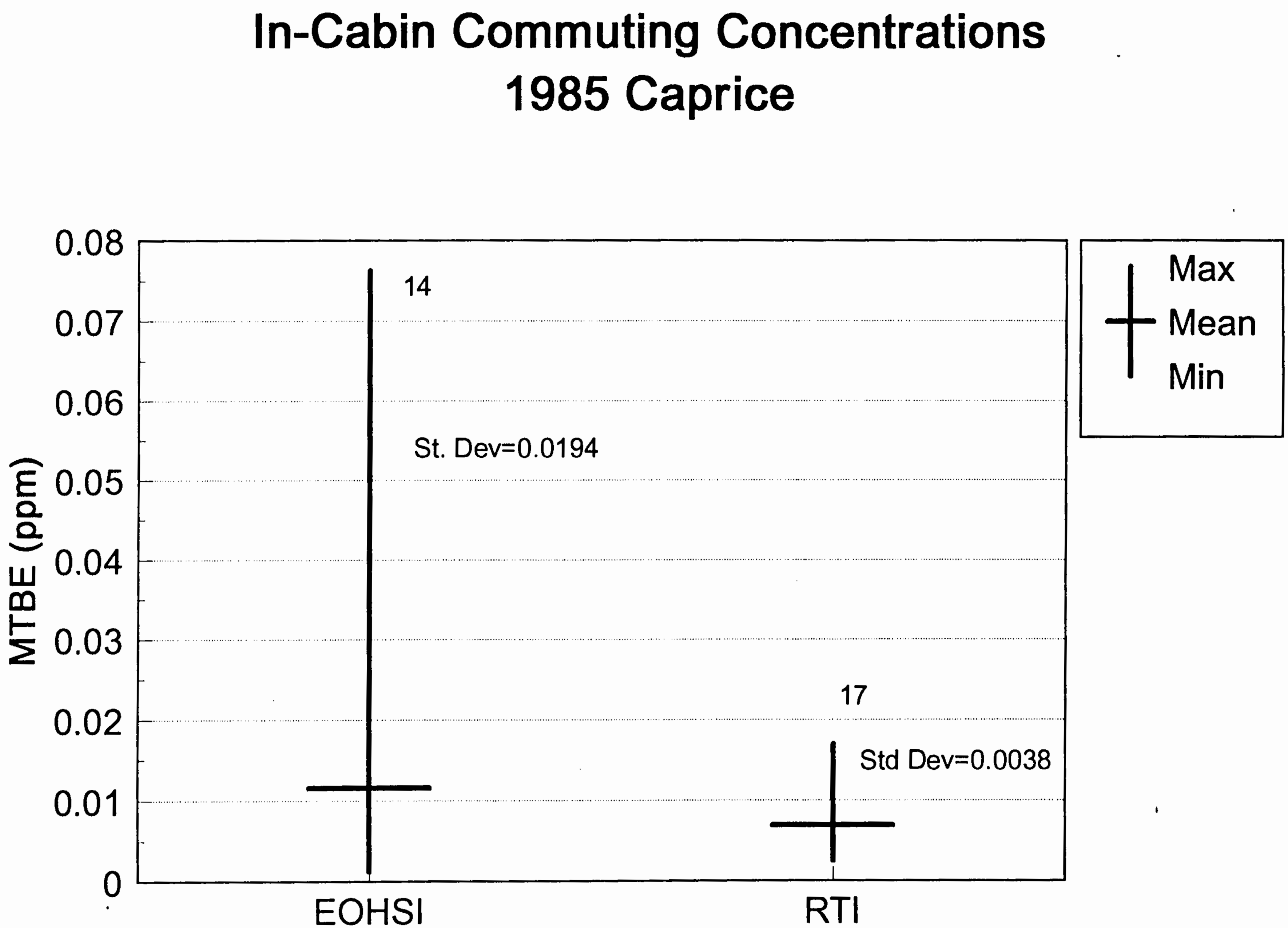


Figure 11

Group 2

In-Cabin Commuting Concentrations
1986 Monte Carlo

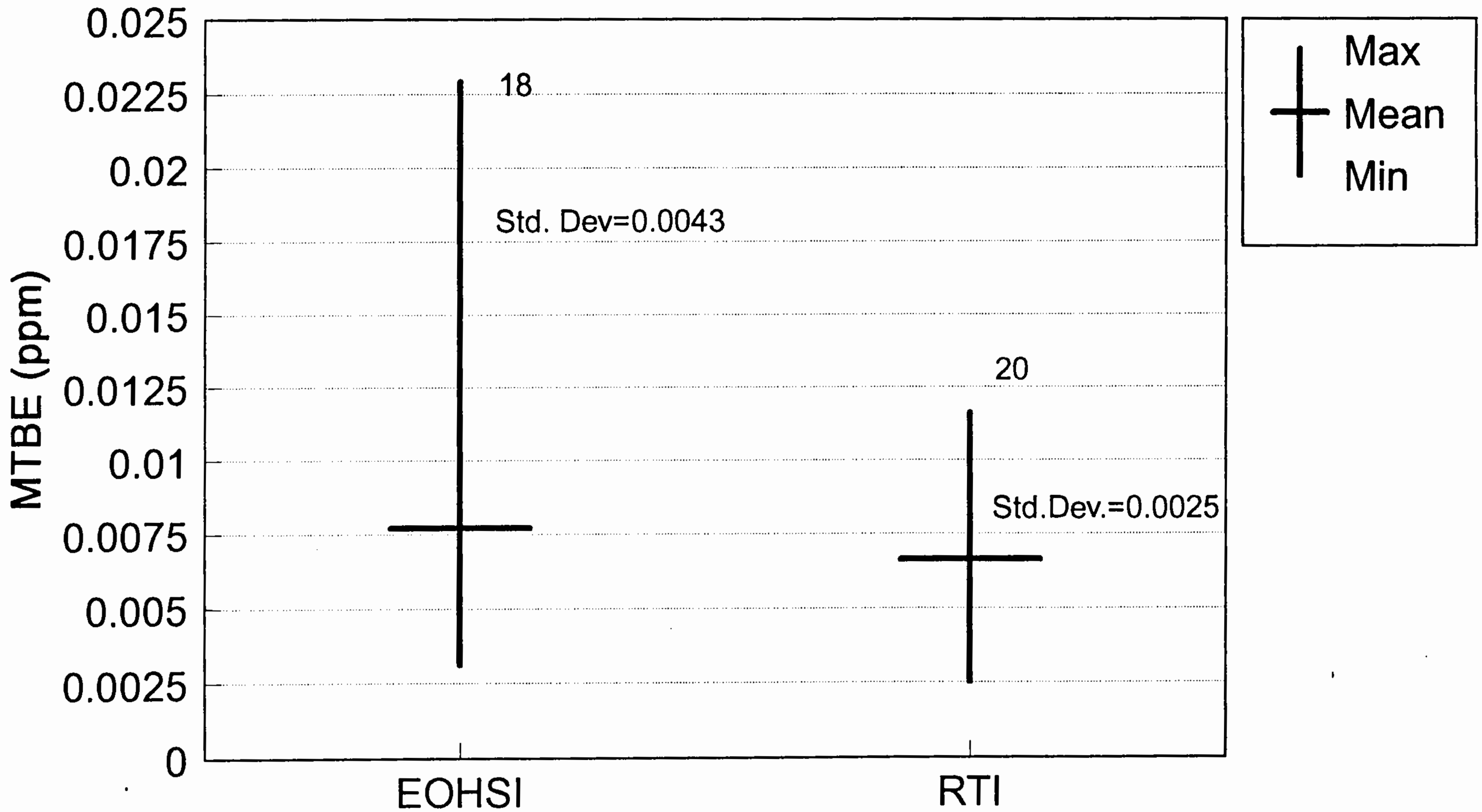


Figure 12

Group 2

In-Cabin Commuting Concentrations
1992 Corsica (W) & 1992 Corsica (G) - combined

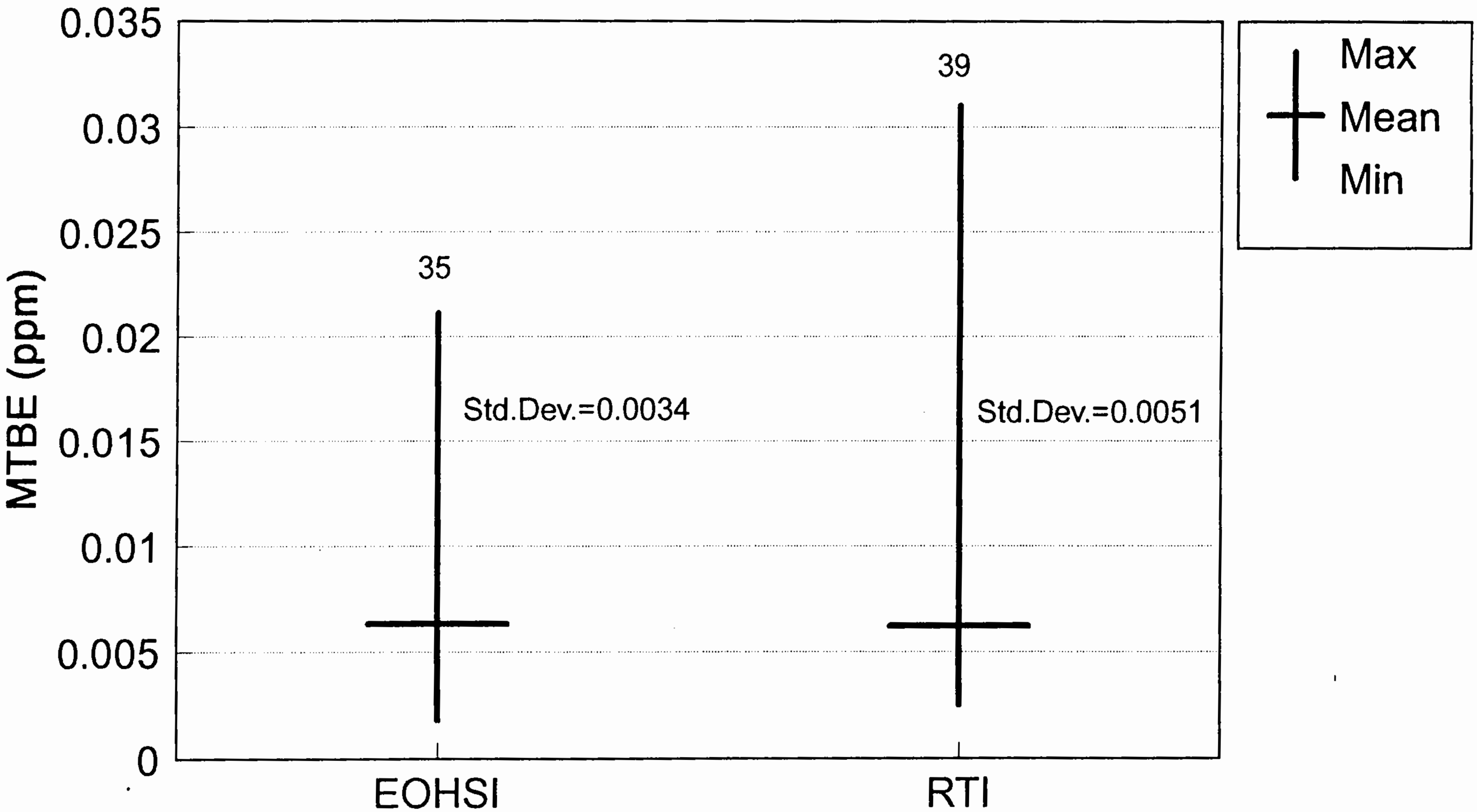
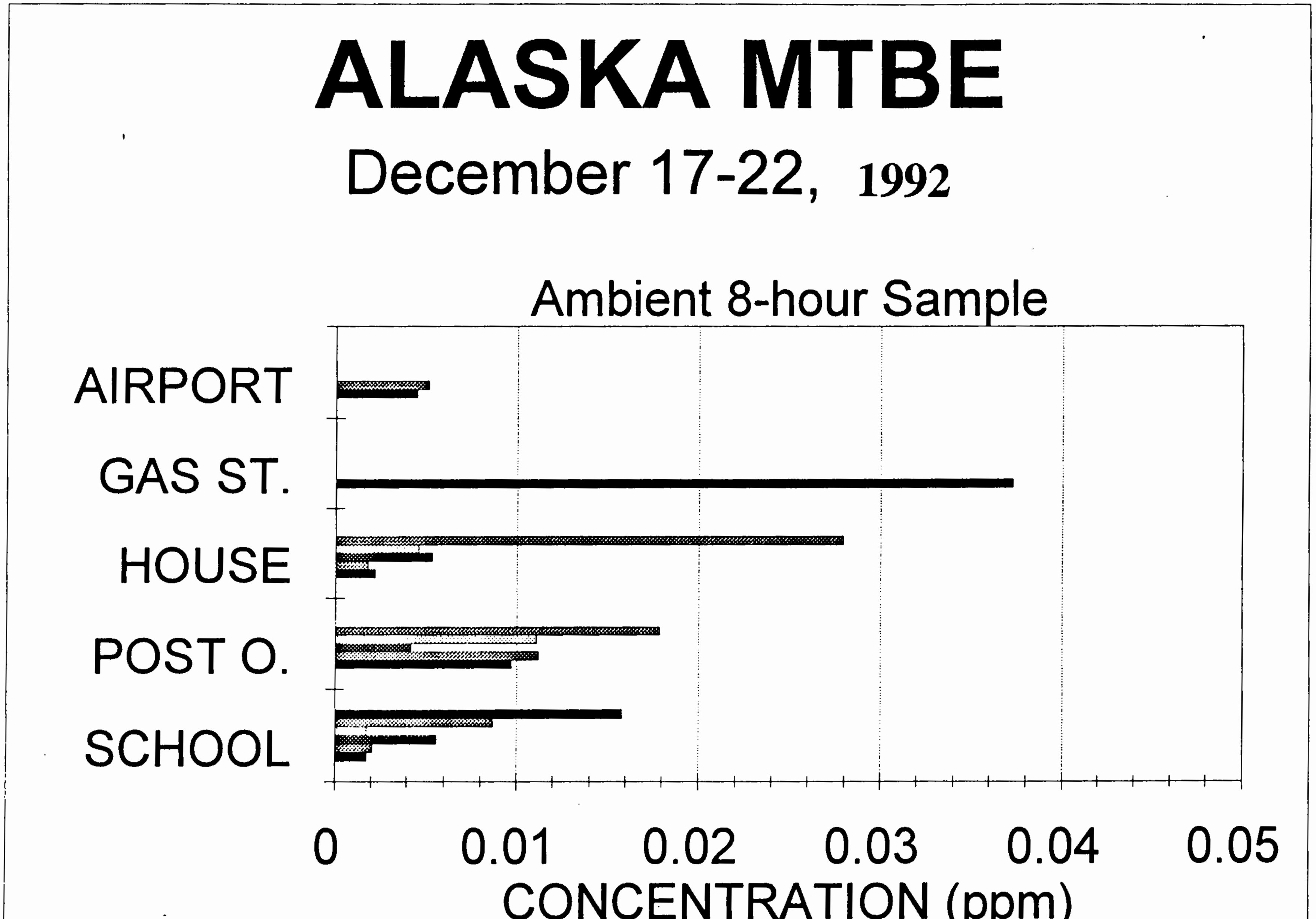


Figure 13

Group 2


ALASKA MTBE
December 17-22, 1992
Ambient 8-hour Sample
AIRPORT
GAS ST.
HOUSE
POST O.
SCHOOL
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)
Figure 14

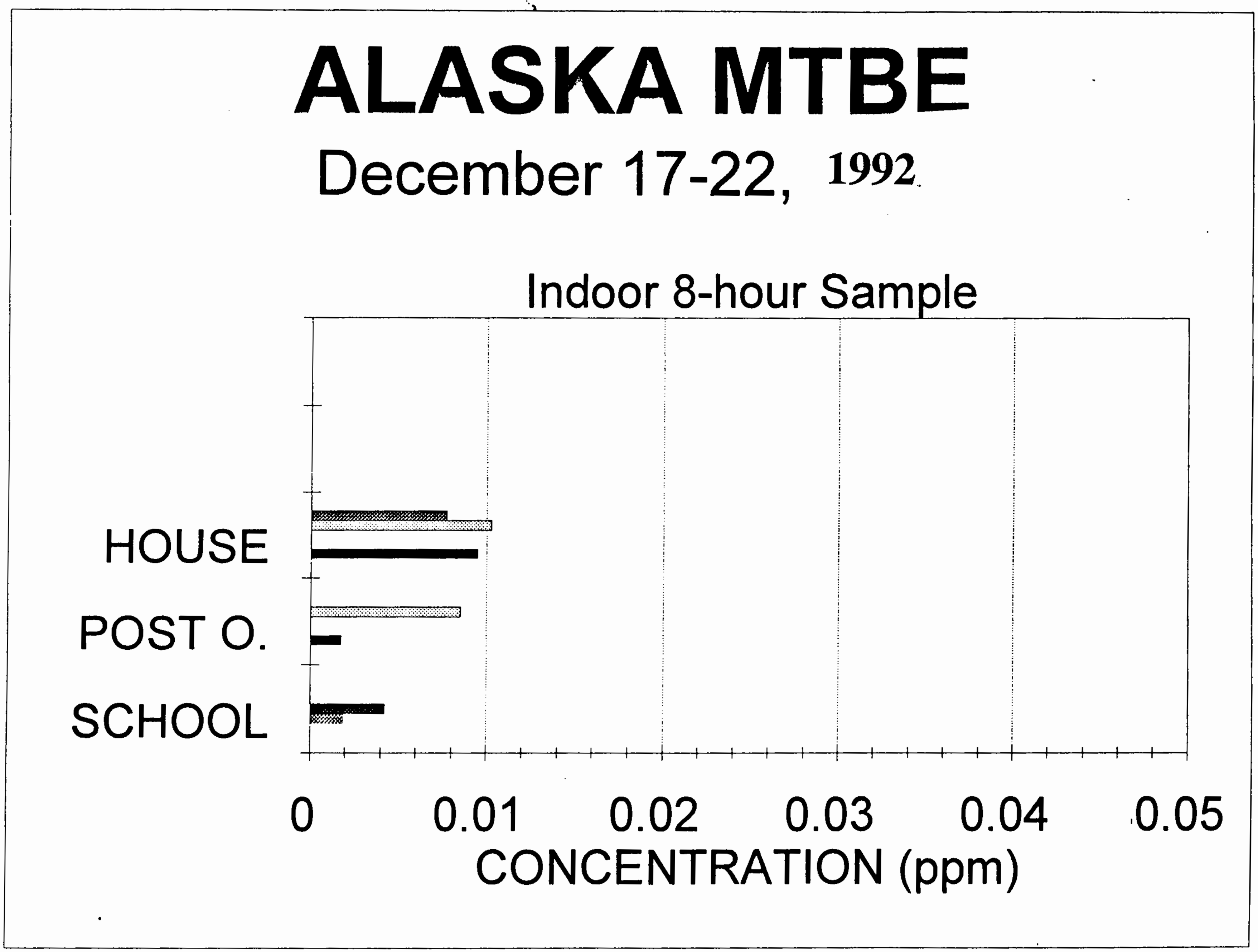

ALASKA MTBE
December 17-22, 1992
Indoor 8-hour Sample
HOUSE
POST O.
SCHOOL
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 15

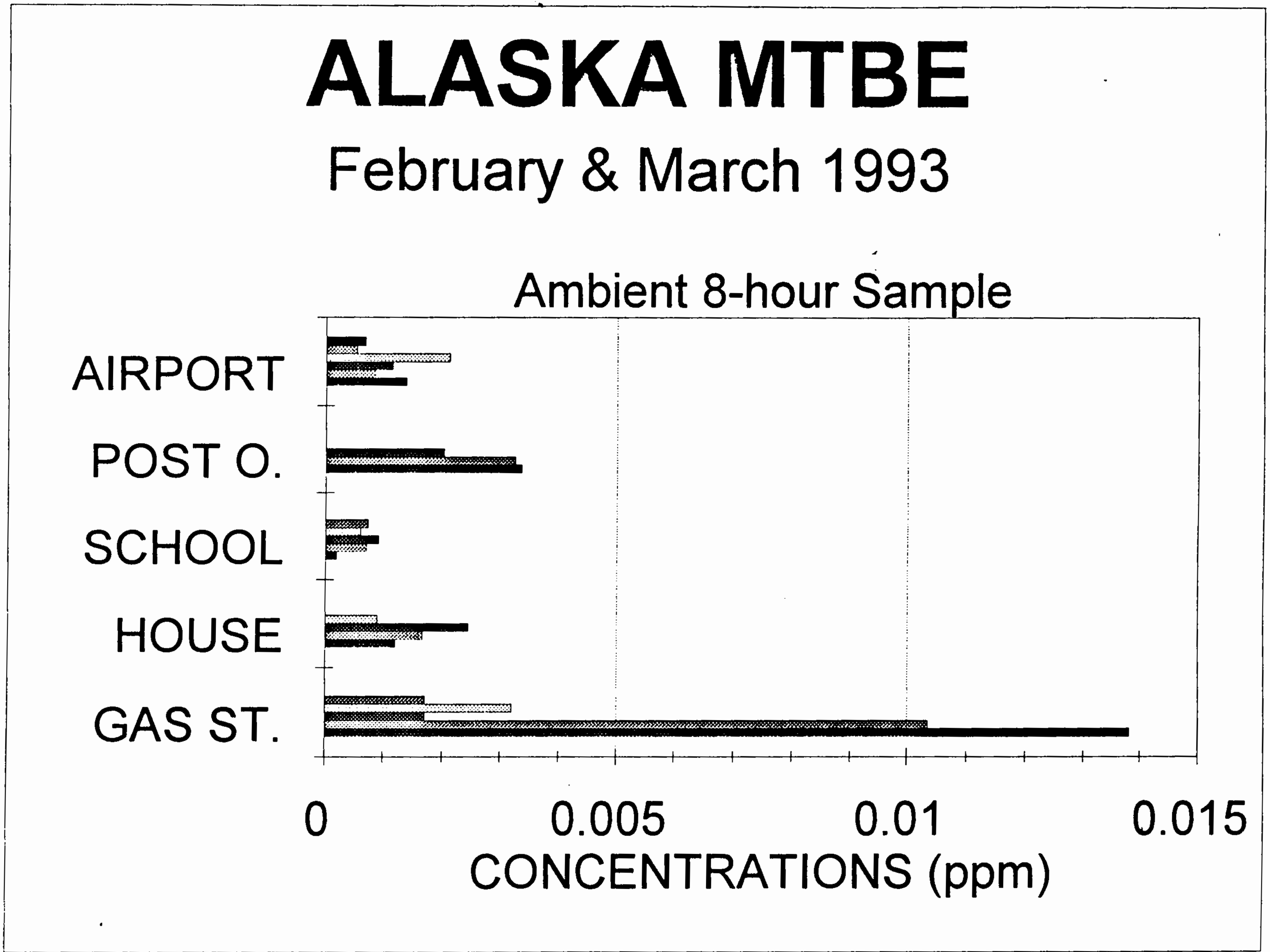
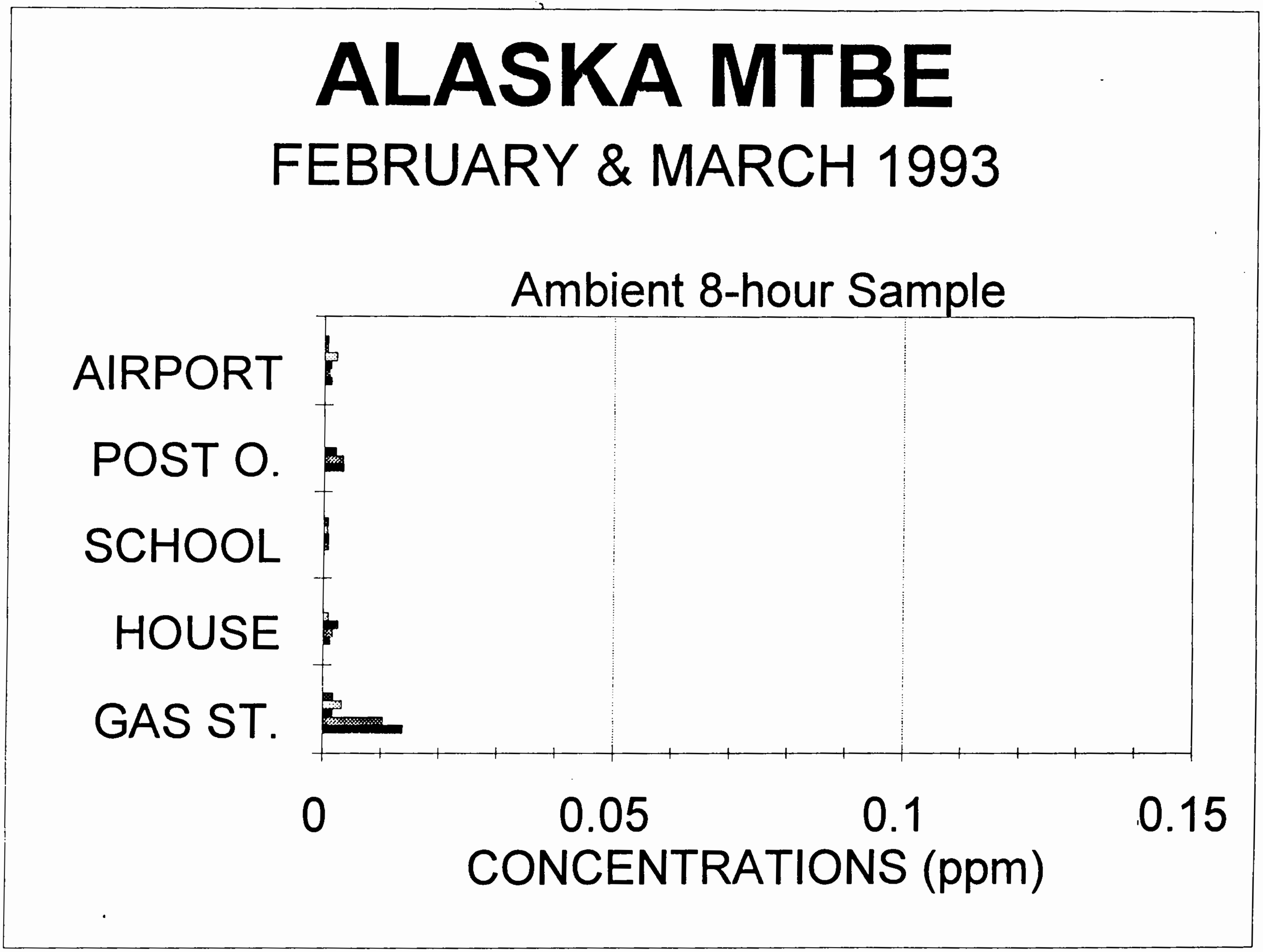

ALASKA MTBE
February & March 1993
Ambient 8-hour Sample
AIRPORT
POST O.
SCHOOL
HOUSE
GAS ST.
0
0.005
0.01
0.015
CONCENTRATIONS (ppm)

Figure 16a



ALASKA MTBE
FEBRUARY & MARCH 1993
Ambient 8-hour Sample
AIRPORT
POST O.
SCHOOL
HOUSE
GAS ST.
0
0.05
0.1
0.15
CONCENTRATIONS (ppm)

Figure 16b

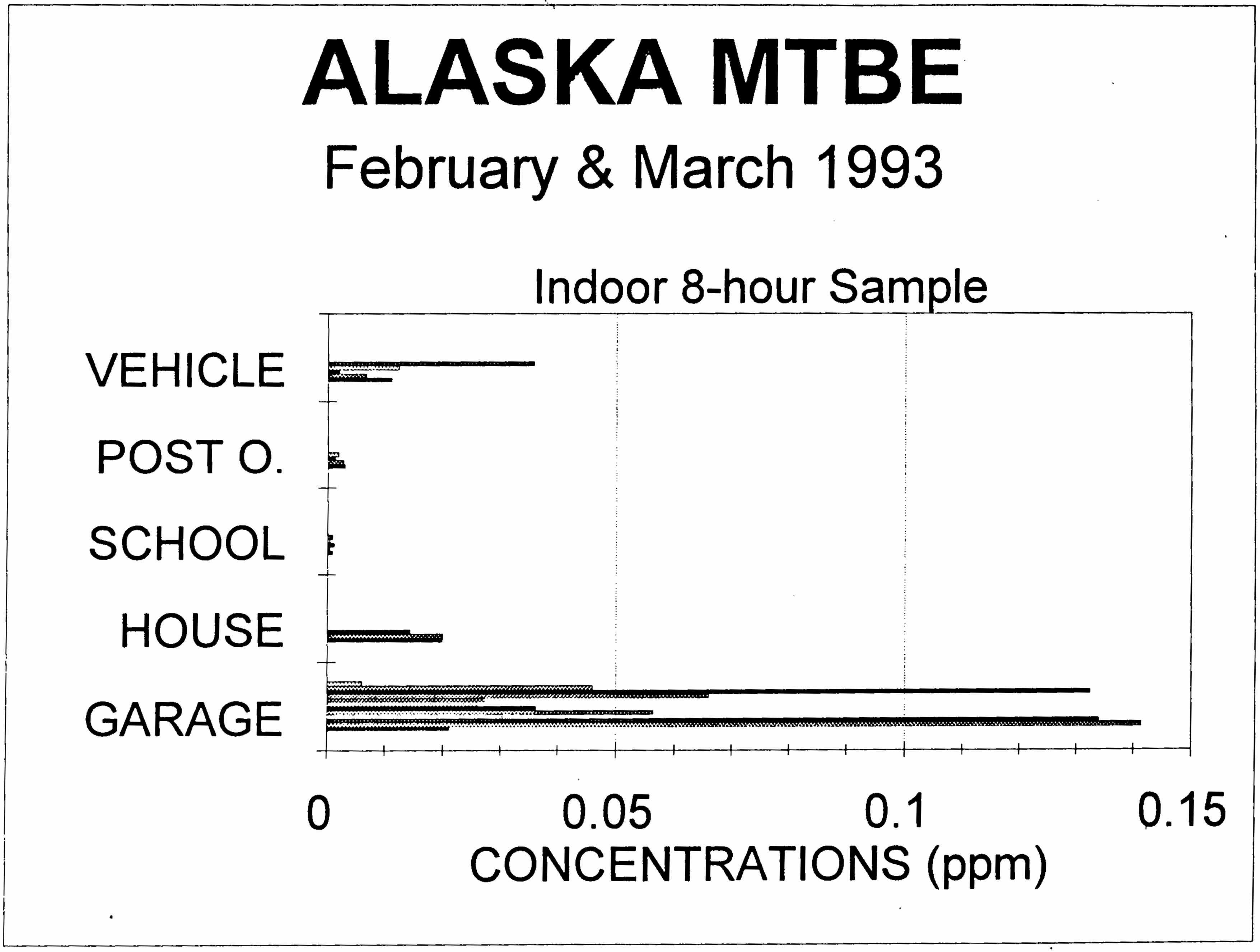
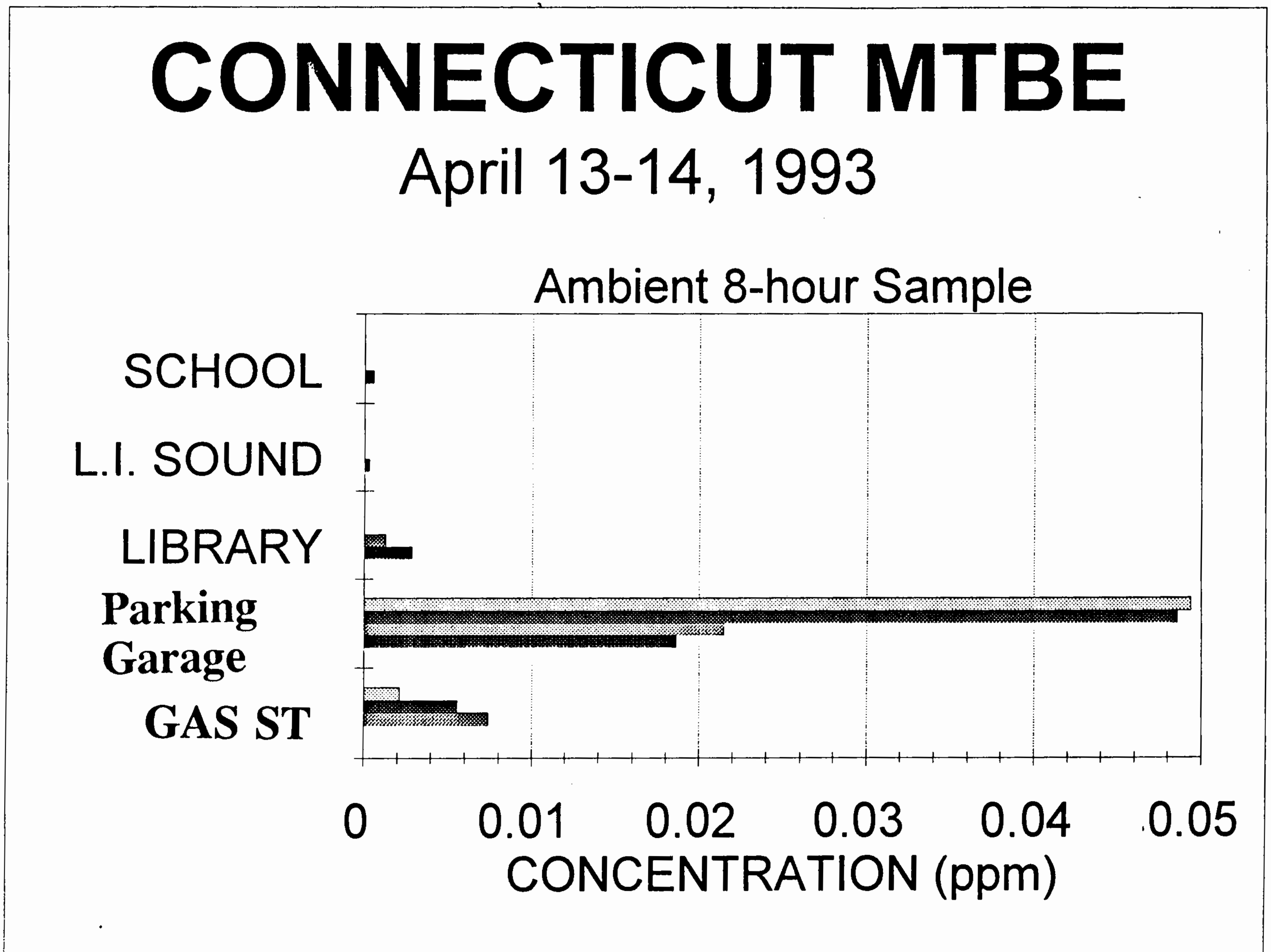

ALASKA MTBE
February & March 1993
Indoor 8-hour Sample
VEHICLE
POST O.
SCHOOL
HOUSE
GARAGE
0
0.05
0.1
0.15
CONCENTRATIONS (ppm)

Figure 17



CONNECTICUT MTBE
April 13-14, 1993
Ambient 8-hour Sample
SCHOOL
L.I. SOUND
LIBRARY
Parking Garage
GAS ST
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 18

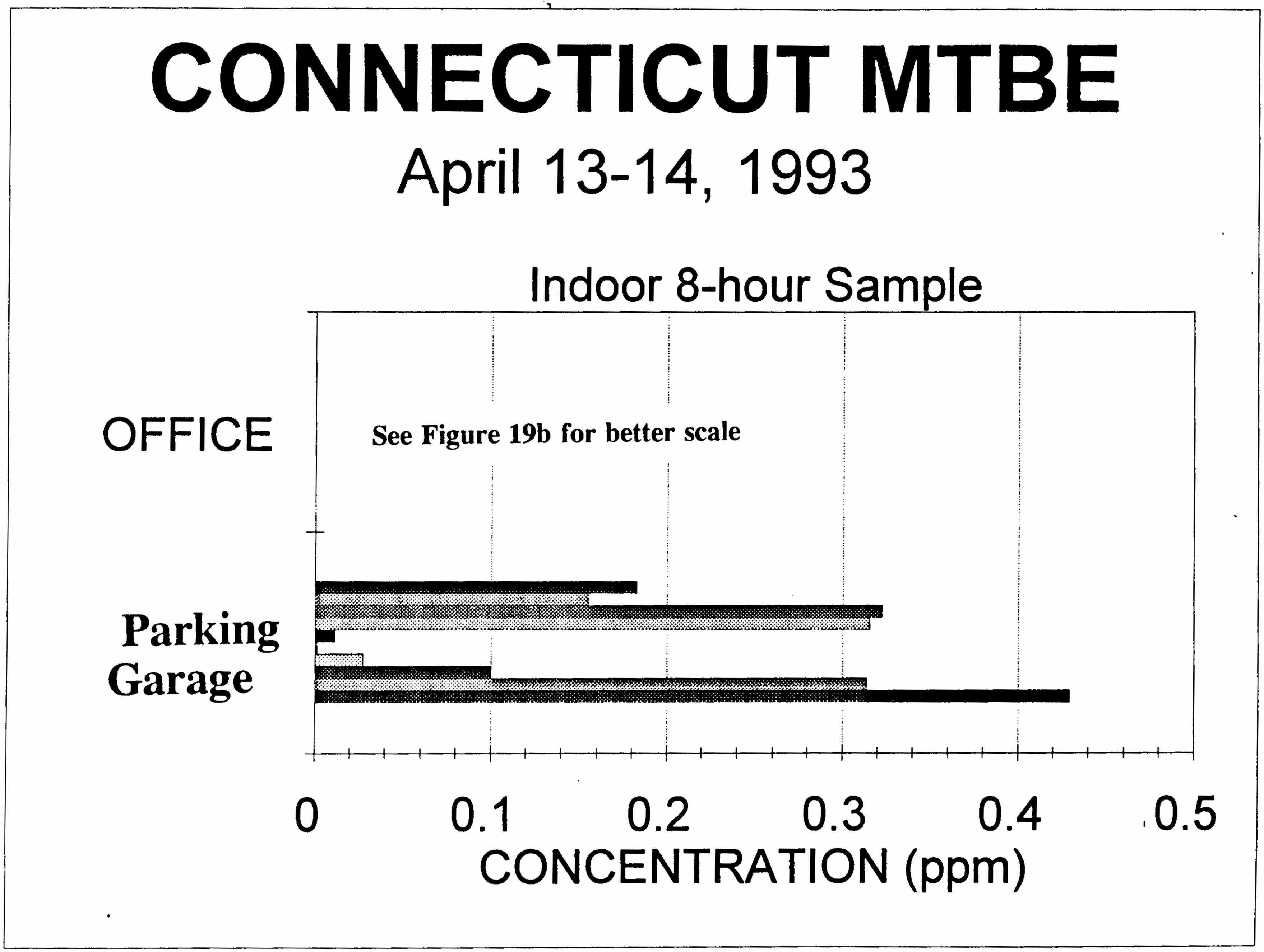

CONNECTICUT MTBE
April 13-14, 1993
Indoor 8-hour Sample
OFFICE
See Figure 19b for better scale
Parking Garage
0
0.1
0.2
0.3
0.4
0.5
CONCENTRATION (ppm)

Figure 19a

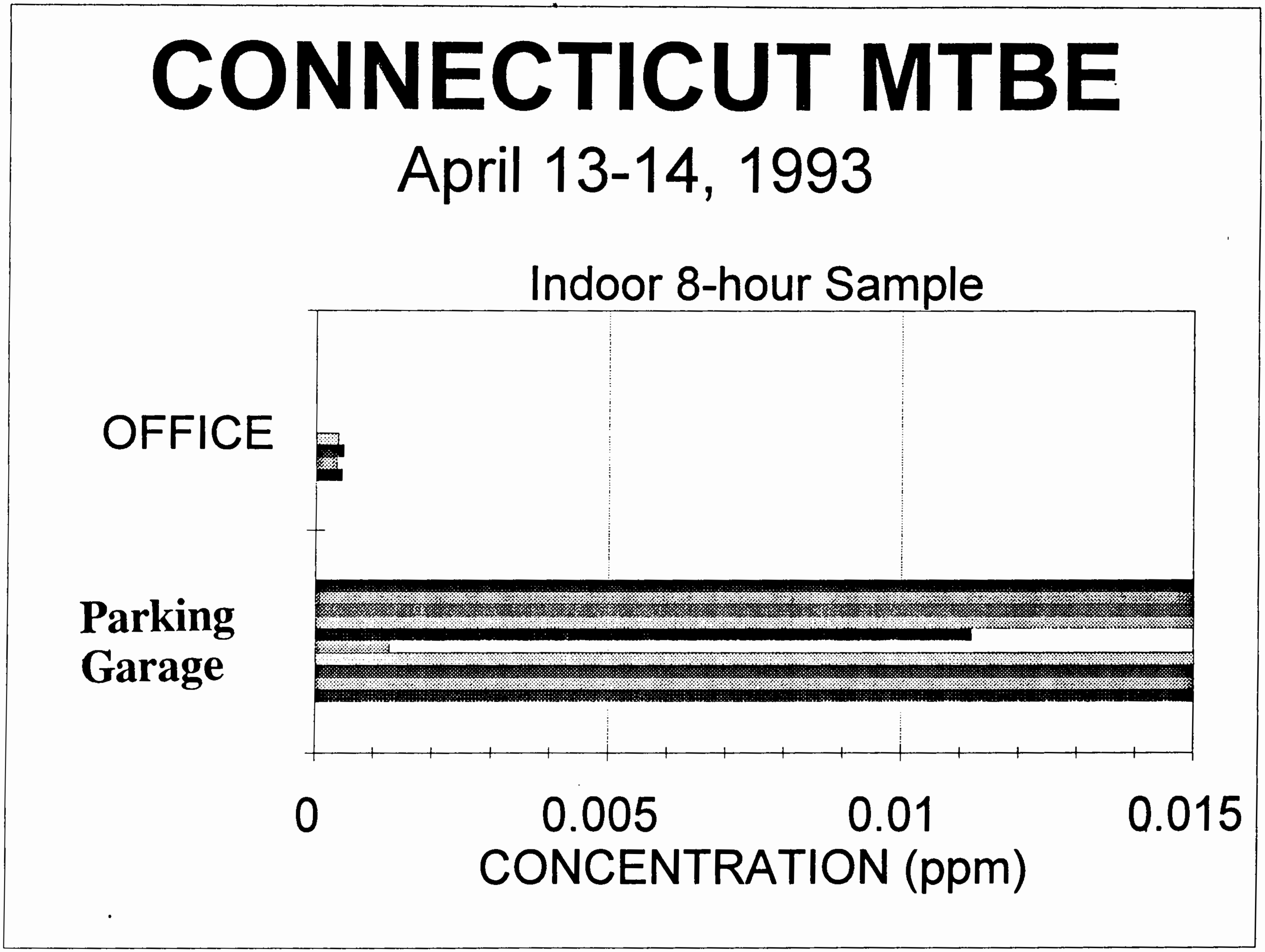

CONNECTICUT MTBE
April 13-14, 1993
Indoor 8-hour Sample
OFFICE
Parking
Garage
0
0.005
0.01
0.015
CONCENTRATION (ppm)

Figure 19b

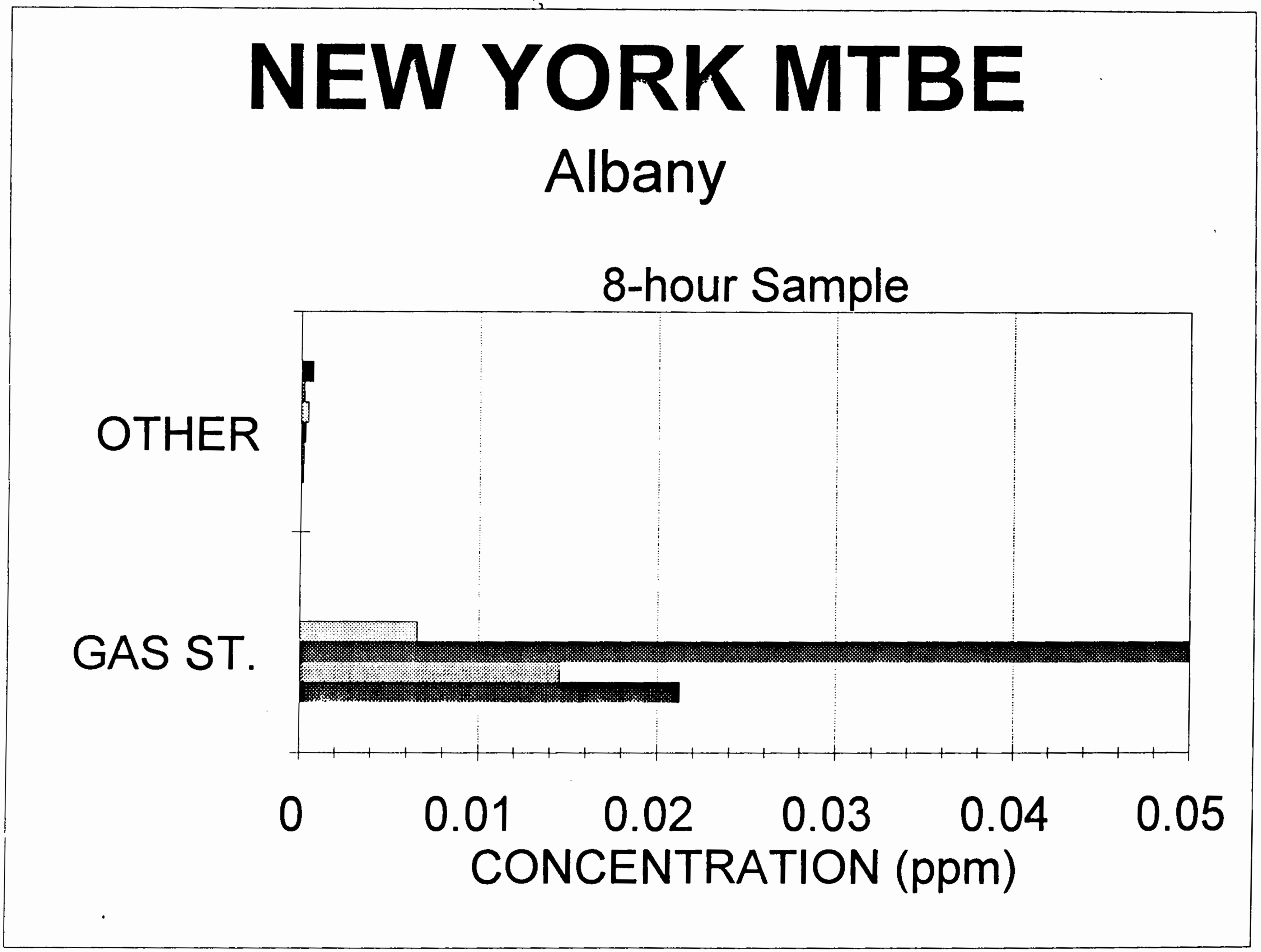

NEW YORK MTBE
Albany
8-hour Sample
OTHER
GAS ST.
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 20

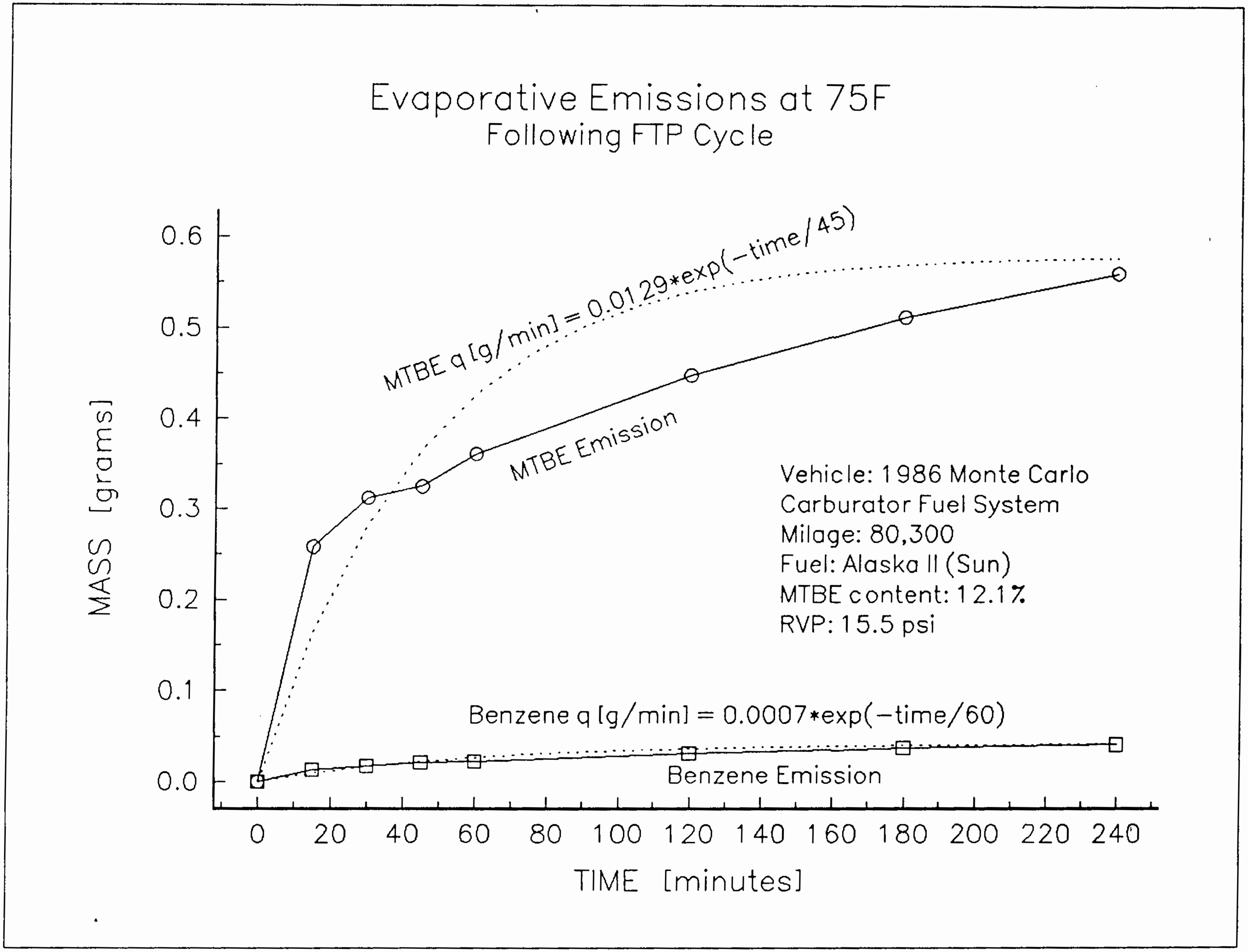

Evaporative Emissions at 75F
Following FTP Cycle
MTBE q [g/min] = 0.0129*exp(-time/45)
MTBE Emission
Vehicle: 1986 Monte Carlo
Carburator Fuel System
Milage: 80,300
Fuel: Alaska II (Sun)
MTBE content: 12.1%
RVP: 15.5 psi
Benzene q [g/min] = 0.0007*exp(-time/60)
Benzene Emission
MASS [grams]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
TIME [minutes]
0
20
40
60
80
100
120
140
160
180
200
220
240

Figure 21

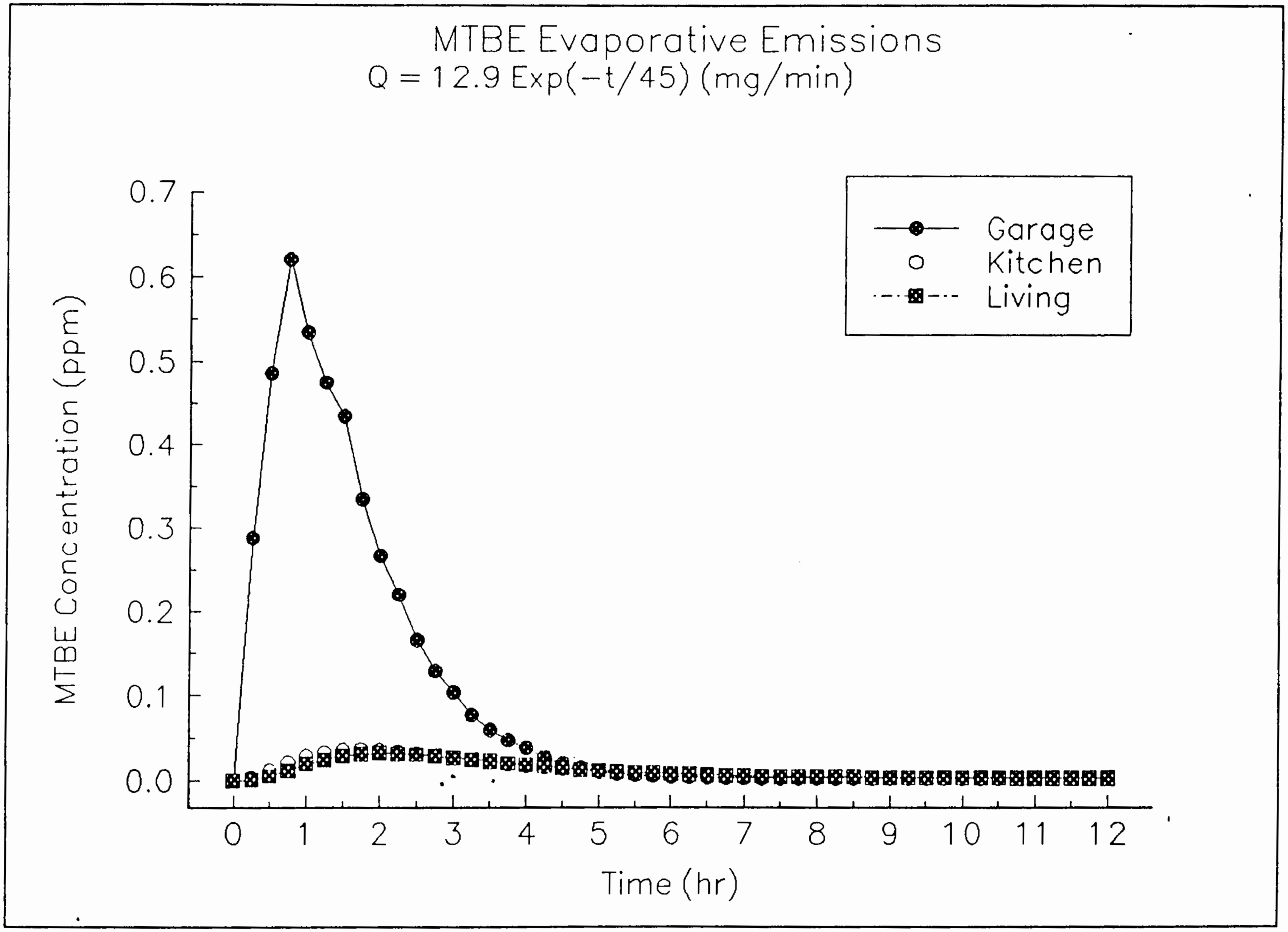

MTBE Evaporative Emissions
Q = 12.9 Exp(−t/45) (mg/min)
Garage
Kitchen
Living
MTBE Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
6
7
8
9
10
11
12
Time (hr)

Figure 22

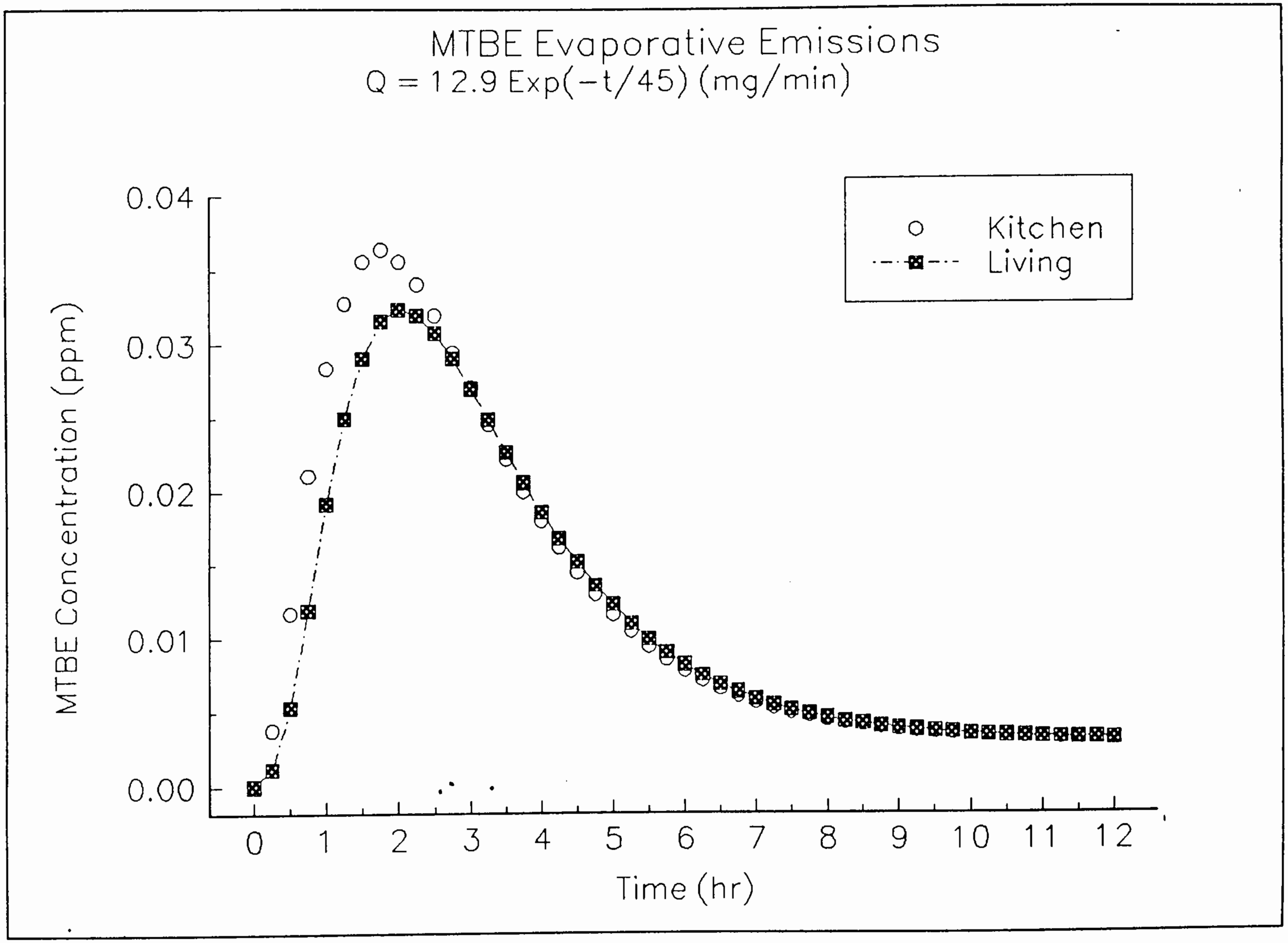

MTBE Evaporative Emissions
Q = 12.9 Exp(−t/45) (mg/min)
Kitchen
Living
MTBE Concentration (ppm)
0.04
0.03
0.02
0.01
0.00
0 1 2 3 4 5 6 7 8 9 10 11 12
Time (hr)

Figure 23

MICROENVIRONMENT CONCENTRATIONS

EPA ESTIMATE

1. Gas Fill-up	Pump	1-10 ppm (36 mg/m3)
	Other	0.1-1 ppm (3.6 mg/m3)
2. Commute/ In Vehicle		0.005-0.1 ppm (0.36 mg/m3)
3. Auto Shop		0.1-0.5 ppm (1.8 mg/m3)
4. Public Garage		0.1-0.5 ppm (1.8 mg/m3)
5. Residential Garage	High	0.1-1 ppm (3.6 mg/m3)
	Low	0.001-0.005 ppm (0.018 mg/m3)
6. Residence	High	0.005-0.01 ppm (0.036 mg/m3)
	Low	0.001-0.005 ppm (0.018 mg/m3)
7. Office		0.001-0.01 ppm (0.036 mg/m3)
8. School/ Public Buildings		0.001-0.01 ppm (0.036 mg/m3)
9. Outdoors	High	0.01-0.1 ppm (0.36 mg/m3)
	Low	0.001-0.01 ppm (0.036 mg/m3)

Figure 24

METHYL TERTIARY BUTYL ETHER EXPOSURE ESTIMATES

Activity	Occurrence	Time/Year (h)		Concentration (mg/m^3)	Exposure ($mg/m^3 \cdot h$)
1. Gas fill-up	1.5/week @ 2 min	2.6		36.0	93.6
	Other @ 10 min	13.0		3.6	46.8
2. Commute/in vehicle	10 h/week	520		0.36	187.2
3. Auto shop	4/year @ 15 min	1.0		1.8	1.8
4. Public garage	2/day @ 10 min	60.83		1.8	109.5
5. Residential garage	2 min/day	12.16	high	3.6	43.8
			low	0.018	0.22
6. Residence	10 h/day + weekend	4,160	high	0.036	149.8
			low	0.018	74.9
7. Office	40 h/week	2,080		0.036	74.9
8. School/public buildings	17 h/week	884		0.036	31.8
9. Outdoors	20 h/week	1,040	high	0.36	374.4
			low	0.036	37.4

Figure 25

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/A-94/255	2.	3.RECI
4. TITLE AND SUBTITLE Human Exposure of Methyl Tertiary Butyl Ether (MTBE)		5.REPORT DATE
		6.PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Alan H. Huber		8.PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Research and Exposure Assessment Lab HEFRD/HEMB U.S. Environmental Protection Agency Research Triangle Park, NC 27711		10.PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research and Exposure Assessment Lab HEFRD/HEMB U.S. Environmental Protection Agency Research Triangle Park, NC 27711		13.TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Data on ambient air quality and microenvironmental exposures (e.g., during refueling, inside cards, in personal garages) are too limited for a quantitative estimate of population exposures to MTBE. At best, they can be used to estimate broad ranges of potential exposures. Because of the interest in MTBE, the present evaluation focuses on this compound, even though any potential health effects might result from complex pollutant mixtures of which MTBE is only one component. Further more, potential exposures of only the general public, not occupationally exposed groups, were evaluated.

17. KEY WORDS AND DOCUMENT ANALYSIS

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