United States
Environmental Protection
Agency

National Center for
Environmental Assessment
Research Triangle Park, NC 27711

EPA/600/R-95/134
August 1995

EPA

Proceedings of the Conference on MTBE and Other Oxygenates:

A Research Update

EPA/600/R-95/134
August 1995

PROCEEDINGS OF THE CONFERENCE ON MTBE AND OTHER OXYGENATES:

A RESEARCH UPDATE

July 26-28, 1993
Fairview Park Marriott
Falls Church, Virginia

Sponsored by

U.S. Environmental Protection Agency
American Petroleum Institute
Oxygenated Fuels Association

Prepared by

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ACKNOWLEDGMENTS

The sponsors are extremely grateful to numerous individuals and organizations who were instrumental in conducting and presenting the research that was the subject of this conference and to those who contributed to the organization and conduct of the conference and to the preparation of these proceedings.

We especially thank Colleen Rose Schwoerke of Research and Evaluation Associates, Inc. (Chapel Hill, NC), who provided exceptional assistance in the organization of the conference as well as in the development of the proceedings, and Marianne Barrier, John Barton, Suzy Bornemann, Shelia Elliott, Sandra Eltz, and Sheila Lassiter of ManTech Environmental Technology, Inc. (Research Triangle Park, NC), who provided invaluable graphics, editorial, and word processing support.

We also are indebted to the organizing committee for creating a conference with stimulating chairpersons, speakers, and discussants.

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ORGANIZATION AND DESCRIPTION OF THE PROCEEDINGS

The "Conference on MTBE and Other Oxygenates: A Research Update" was held on July 26 through 28, 1993, at Falls Church, Virginia under the sponsorship of the U.S. Environmental Protection Agency (EPA), the American Petroleum Institute (API), and the Oxygenated Fuels Association (OFA). A primary purpose of the conference was to provide a forum for the presentation of results from studies that had recently been conducted on exposure and health effects aspects of methyl tertiary butyl ether (MTBE) and MTBE-oxygenated fuels.

The conference comprised seven sessions: (1) Introduction/Welcome, (2) Emissions and Air Quality under Winter Conditions, (3) Human Exposures, (4) Acute Health Effects of MTBE, (5) Chronic Health Effects of MTBE, (6) New Findings for Other Fuel Oxygenates, and (7) Conference Summary. A chairperson introduced the topic of each session, and after the speakers presented their studies and entertained questions from the audience, a discussant summarized the findings for that session. Following the conference, the speakers were asked to provide abstracts of their presentations and copies of their slides. In addition, the discussants submitted written summaries for their respective parts of the program, including the overall summary of the conference. The discussants' summaries were based on the information available to them ***at that time*** and represent solely their opinions about that information.

These proceedings consist of two parts: Part I contains presentations in the Introduction/Welcome session and the discussant summaries for each of the remaining sessions; Part II contains the abstracts and slides of the speakers. These proceedings of the conference are not a verbatim transcript of the meeting. Speakers and discussants were given an opportunity within the few weeks following the conference to revise their abstracts and slides. Also, oral statements have been edited to reduce the number of verbalisms (although much of the introductory section still has the character of an oral transcript rather than a statement that was intended for publication). In addition, the discussion at the end of each session has been summarized, rather than attempting to identify individual speakers' questions and answers. Otherwise, these proceedings present the information as it was presented in July 1993 or shortly thereafter.

Because many of the studies presented at the conference had only just been completed or were still in the stage of data analysis and interpretation, the material in these proceedings does not reflect analyses that may have been conducted subsequent to the conference. Reports of some of the studies presented at the conference have since been published. These and some related papers are listed below.

Recent Oxyfuel-Related Publications

American Petroleum Institute (1993) Gasoline vapor exposure assessment at service stations. Washington, DC: Health & Environmental Sciences Department; March; API Publication No. 4553.

American Petroleum Institute (1994) Odor threshold studies performed with gasoline and gasoline combined with MTBE, ETBE and TAME. Washington, DC: Health & Environmental Sciences Department; January; API Publication No. 4592.

American Petroleum Institute (1994) A study to characterize air concentrations of MTBE at representative service stations in the Northeast. Washington, DC: Health & Environmental Sciences Department; April; API Publication No. 4619.

American Petroleum Institute (1995) Petroleum industry data characterizing occupational exposures to MTBE. Washington, DC: Health & Environmental Sciences Department; August; API Publication No. 4622 (in preparation).

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Mannino, D. M.; Schreiber, J.; Aldous, K.; Ashley, D.; Moolenaar, R.; Almaguer, D. (1994) Human exposure to volatile organic compounds: a comparison of organic vapor monitoring badge levels with blood levels. *Int. Arch. Occup. Environ. Health* 67: 59-64.

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Rudo, K. M. (1995) Methyl tertiary butyl ether (MTBE)—evaluation of MTBE carcinogenicity studies. Toxicol. Ind. Health 11: 167-173.

Rudo, K. M.; Pate, W. J.; Smith, C. G. (1995) The public health impact of the oxygenated fuels program in North Carolina. Toxicologist 15: 140.

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Tepper, J. S.; Jackson, M. C.; McGee, J. K.; Costa, D. L.; Graham, J. A. (1994) Estimation of respiratory irritancy from inhaled methyl tertiary butyl ether in mice. *Inhalation Toxicol.* 6: 563-569.

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Session One

INTRODUCTION/WELCOME

Chair: Judith A. Graham, Office of Research and Development, U.S. Environmental Protection Agency

Welcome

Peter Preuss
Director of the Office of Science, Planning, and Regulatory Evaluation, Office of Research and Development, U.S. Environmental Protection Agency

I am very pleased to be here and to welcome all of you to this workshop on behalf of EPA and the Office of Research and Development (ORD). There are a good number of people in the audience here today that I haven't seen in quite awhile. And so I welcome all my friends and colleagues to this meeting.

Basically what we're trying to do with this meeting is very simple. We want to hear what the new scientific evidence on MTBE and MTBE oxyfuels is about. The reason that we're doing this is, in large part, because over the past few months a number of questions have arisen about this topic and we felt it was important both to do research to try to answer some of the questions and to review the information that was available on this topic. So we have a very clear purpose that we've set out for ourselves and that is to look at the science, to try to understand the science, to come to grips with the difficult questions in the science, and to see what it is that we know and determine what it is that we don't know. One of the things that we have to do yet at EPA is take that science and finish our analysis of it and then give it to our program office, the Office of Mobile Sources (OMS) in the Office of Air and Radiation, so that the Agency can make a decision about MTBE and oxyfuels and whatever needs to be done. This is a very critical meeting for us, and I hope all of you will participate and help us to try to clarify what it is that we know, what it is that we don't know, and where the areas of major uncertainties lie, so that any assessment that we do can be as clear as possible.

I think it's very important to both understand and acknowledge what has happened over the past year or so since this issue first was raised. Essentially we've had a group of people, both in EPA and outside of EPA, with sponsorship from API, OFA, and a number of other places, and we have had a number of states involved, coming together trying to understand what it is that people were saying and the kinds of questions that people were asking, and trying to see what kind of scientific data were needed in order to answer some of these questions. One of the things that I'd like to acknowledge here is the very impressive turnaround, the very impressive reaction that all of these groups gave to this, the attention that they gave to this, so that we could in fact, in a very timely way, come together at a workshop like this and discuss it. Much of what we'll be discussing at this workshop really did not exist a year ago.

And so I'd particularly like to make mention of the various EPA laboratories, API, and OFA, who have not only helped us to fashion and put together some of this work, but also have helped us to put together this workshop.

Finally, I'd like to just reemphasize this effort of cooperation. I think the EPA, in particular in the Office of Research and Development, is moving in a somewhat different direction from where we have been in the past. I think we're going to wind up doing a lot more work together with other entities outside of the federal government. Whether it's industry or whether it's state government or whether it's associations or what-have-you, we are trying to come together in the areas where we have common interests, where we have common concerns and where we have common questions; and we are trying to jointly understand what kind of research needs to be done and trying to jointly come together to see that the research is actually done. This is one example; there are other examples in the area of alternative fuels, of tropospheric ozone research—there are lots of areas where EPA is trying to begin to work in this new fashion with groups outside of the federal government. And so as we go through this, I hope you keep that in the back of your mind and see how we can try to develop this kind of an idea and this kind of shared and cooperative research.

So welcome all of you and thank you very much for being here.

Legislative History and Regulatory Overview of Oxygenates and MTBE

Mary Smith
Director of the Field Operations and Support Division
Office of Mobile Sources, U.S. Environmental Protection Agency

After EPA implemented a nationwide oxygenated gasoline program in November 1992, concerns about possible health issues related to MTBE became evident. I will provide some background on the oxygenate program and why we are here to discuss health effects and exposure research on MTBE and other oxygenates. The principal oxygenates used in the program are MTBE and ethanol. Future oxygenates—which we will address on the last day of the conference—include tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE).

In terms of background on oxygenates and mobile source emissions, carbon monoxide (CO) is an odorless, colorless gas, which impairs cardiovascular functions and has particular health effects on infants and unhealthy individuals. Carbon monoxide emissions in motor vehicles represent a large proportion of all CO emissions, about 75%—more so in those cities where there's heavy vehicle traffic and lack of industry. The Washington, DC, area is one of those areas where we have a heavy contribution of motor vehicle CO emissions. Carbon monoxide nonattainment occurs principally in the winter. It's estimated, based principally on lab testing at warmer temperatures, that mobile source emissions of CO from motor vehicles can be reduced by 15 to 20%. Oxygenates can contribute to CO emission reductions because they allow the vehicle combustion process, which is somewhat inefficient in the winter, to be more efficient.

Why do we have an oxygenated gasoline program? When Congress passed the Clean Air Act Amendments in 1990, they had a specific provision in Section 211(m) that required oxygenated gasoline to be used in various areas of the country. Basically, if an area did not attain the CO National Ambient Air Quality Standards, based on 1988 and 1989 data, the area was required to implement an oxygenated gasoline program by November 1 of 1992. Thirty-nine areas met this criterion. Other areas would necessarily be in the program if subsequent data showed that they had a CO nonattainment problem, and this year, in 1993, Salt Lake City meets that criterion. Prior to the implementation of the program in about 39 areas in November 1992, there were seven existing programs operating in the country, including Denver, which started the first oxygenated fuels program in 1988.

Oxygenated gasoline is seen by the states as the major CO reduction strategy in the Clean Air Act amendments. The specific requirement is that gasoline must contain oxygenates to achieve 2.7% oxygen by weight in the gasoline. This is achieved with about 15% by volume MTBE and 7.7% by volume ethanol.

The oxygenate program is not a year-round program because CO is mainly a wintertime problem. Because of differences in climate and the degree of an area's CO problem, the oxygenate program in the 39 areas runs anywhere from 4 to 7 mo each year. Thus,

programs start anywhere from September to November, with the majority running a 4-mo program from November to February.

Oxygenated gasoline was not intended just to be sold only in the CO nonattainment area, which can be small, but must be sold in the entire metropolitan statistical area surrounding the nonattainment area. The rationale was that cars travel in and out of CO nonattainment areas, and it is necessary to encompass all those cars that are contributing to the CO problem in the area. This is a state-enforced program, not a federally enforced program.

Under the Clean Air Act, a state may ask EPA to waive the program based on certain factors, but none of these are relevant to the discussion today. The statute does provide that if an area comes into CO attainment and can demonstrate CO attainment without the program by means of a 10-year maintenance plan, then the area basically does not have to use oxygenated gasoline. There are a few areas applying for such attainment demonstrations without the oxyfuel program. Cleveland is one of them, for example.

On the third day of the conference, other oxygenates will be discussed that are relevant to another section of the Clean Air Act that mandates oxygenates in reformulated gasoline. The reformulated gasoline program starts in 1995 in at least the nine worst ozone nonattainment areas. Other areas that are in nonattainment with ozone may opt into the program. Currently, the opt-in areas are primarily in the northeast where they have a particular problem with ozone nonattainment and where there's a large region of ozone transport. So oxygenates are used in more than one program, and I suspect, in 1995, more of the other oxygenates are going to be used.

We do have a sense of how well the oxyfuels programs performed this past winter. Thirty-six of the programs started on time, although, as I mentioned before, all of the programs do not start at the same time because the control period depends on when CO is elevated. In this past season, 70% of the gasoline had MTBE, 30% had ethanol. The gasoline in these oxygenated gasoline program areas constitutes about a third of the gasoline used in the country. California areas in the program adopted a 2% oxygen requirement, and their petition with regard to this reduced percentage is pending.

Carbon monoxide data for November 1992 to January 1993 have been evaluated. We're still analyzing the February data. The non-California areas were evaluated because these are the areas that had 2.7% oxygen. We did not include data from the older programs because obviously you don't get a good picture of how well oxygenated gasoline has worked when there has been a preexisting program. The evaluation showed that there was about a 95% reduction in the number of CO exceedances. California alone had about an 80% reduction, and even the preexisting programs had about a 50% reduction.

Now for why we're here. As Bill Piel from ARCO Chemical will discuss shortly, oxygenates have been in commerce for a long time, since the early 1980s and even possibly late 1979. And so I don't think anybody anticipated any problems with the oxygenates. But in November of 1992, as Alaska was implementing its program in both Fairbanks and Anchorage, there were a significant number of health complaints registered. The state asked

the Centers for Disease Control (CDC) to investigate the health complaints, which included headaches, nausea, and coughing. The CDC did a study in the November and December time frame and issued a report to Alaska in early 1993, which said that there were some preliminary indications of a correlation between the acute health complaints and the oxygenated gasoline program. I should remind you that 100% of the gasoline in Alaska contains MTBE. The CDC is represented at this meeting and later on will present all their findings, so I defer to them in terms of a more detailed description. There was a lot of press coverage on health concerns. As a result of all of this, Governor Hickel suspended the program. On December 11, we were made aware of that suspension.

Concerns also were raised in other areas, particularly Missoula, MT, where the city convened a health panel. They decided to continue the program to the end of February, but obviously they are very anxious to hear what comes out of this workshop and what conclusions are reached about these health issues. Concerns also were raised later in Anchorage and New Jersey, and the people in these areas also are anxiously awaiting the results of this workshop.

Although unexpected, there was obviously an issue here that needed to have some resolution. So EPA, CDC, and some members of the industry met in January of 1993 to review what we knew about the acute and chronic effects from MTBE and to map out a strategy for research that we felt needed to be completed in 6 mo. Time was limited because, although most of the programs stop for the season at the end of February, they are nonetheless due to resume as early as September 1993. We therefore felt that we had about 6 mo to look at the issue and see what other data we could collect to address a lot of the issues that had arisen, particularly the acute health complaints.

This brings us to the workshop. I would like to reiterate Peter Preuss' compliments (i.e., I think that people worked very well in the 6-mo period on an aggressive research program). People worked hard within EPA, CDC, industry, and other groups to collect data, and to quickly analyze it so that we could target it for presentation at this workshop, in the hope that we could try to come to some sort of resolution and conclusions with regard to MTBE before the next oxyfuel-season started in this country. I must compliment everybody's effort in this regard.

Overview of the Health-Related Issues and Framework for the Research

Judith Graham
Associate Director of the Environmental Criteria and Assessment Office, Office of Research and Development, U.S. Environmental Protection Agency

I would like to expand on the history of the research program to which Mary Smith referred. Discussions on MTBE research actually began in earnest in EPA around 1986 or 1987, resulting early in 1988 in a consent decree between EPA and industry according to the provisions of the Toxic Substances Control Act. The MTBE Task Force, a consortium of a number of industry groups, was created to conduct a large number of research projects investigating acute, subchronic, and chronic inhalation effects of MTBE in animals. Those studies included reproductive and developmental effects.

In 1991, EPA took the subchronic studies that had been completed by the MTBE Task Force and developed a reference concentration, or RfC. An RfC is defined as a concentration (with an uncertainty about it) of a chemical that can be inhaled over a lifetime by even sensitive people, and is thought not to pose an appreciable deleterious noncancer—*noncancer*, I want to emphasize that—health hazard. The 1991 RfC for MTBE was 0.5 $\mu g/m^3$.

In late 1992, the chronic inhalation studies from the MTBE Task Force became available and the oxyfuel program began. Very soon after the program began, numerous people started complaining of health symptoms in some areas. Especially noteworthy were the complaints coming from Fairbanks and Anchorage, AK, and from Missoula, MT. There were a number of more isolated complaints coming from citizens in New Jersey and some other areas. There were still other areas of the country using oxyfuels, such as Denver, where a significant number of complaints were not made.

Due to complaints in Alaska, the state requested that the CDC conduct an evaluation. The CDC, working with the state, initiated some epidemiology studies in Fairbanks while MTBE was still being used. As part of these studies and as part of an EPA interest in obtaining even more information, there was a collaborative effort to measure MTBE air levels as well as other compounds in the air, in some sites in Fairbanks. At the same time, the Environmental and Occupational Health Sciences Institute in New Jersey conducted some pilot studies of exposure levels inside vehicles, using commuting scenarios. In some of the scenarios, people stopped and refueled their cars with gasoline, whereas in other scenarios they didn't.

The Office of Research and Development within EPA also conducted initial studies of emissions from vehicles down to temperatures as low as 0 °F. In February 1993, ORD issued a report that evaluated the public health issues and indicated numerous uncertainties and gaps in the information available. I think it's important to spend a few moments here on the conclusions of ORD's February report, so that everybody can have a sense of where we were when the research started and so that we can think clearly about where we are when the

research is completed. It also gives you an idea of the genesis of some of the research projects that were undertaken.

We had concluded that the use of MTBE oxyfuels can decrease CO emissions from vehicles at temperatures as low as 0 °F, and perhaps even lower. But we really didn't go lower than that, leaving the emission effects at lower temperatures undefined. One of the main concerns was that in the state of Alaska it can get down to −30 °F or even −50 °F.

From limited emission studies, it appeared that MTBE oxyfuels would reduce the total mass (the net emissions) of 1,3-butadiene, benzene, and formaldehyde. The data showed that concentrations of formaldehyde increased and concentrations of butadiene and benzene decreased. But the net overall effect was a decrease. We don't know what this decrease implies for health. If there's a decrease in total cancer risk—and that's a big if—that decrease would likely be very small.

At the end of February when we issued this report, we really couldn't draw any definitive conclusions about the potential for MTBE oxyfuels to cause acute health symptoms. But the initial reports that came out from CDC and the anecdotal reports that were received from various areas of the country were suggestive of a problem, although they were not definitive.

When we evaluated the RfC for MTBE and compared it to very—emphasis on the word "very"—limited preliminary exposure data, it didn't appear at that time that MTBE was going to pose a significant risk of chronic noncancer health effects.

As we looked at the results of chronic inhalation toxicity studies in February, we noted that tumors were observed in some of the animals at high MTBE concentrations. But we decided that an assessment was needed and that we had to evaluate the data in depth before reaching conclusions. It also became apparent that although there were numerous studies of MTBE itself, we couldn't find any controlled studies of MTBE oxyfuels, and that precluded drawing conclusions about the effects of the mixture. Our bottom line was that research was needed.

When we talked about research needs, we did think in terms of a major goal: to conduct research that would provide information by midsummer. We wanted to get information before the next MTBE oxyfuel season began, and we wanted the data to increase our understanding of the potential for health risks. We wanted to be able to develop risk assessments, insofar as possible, with the new data. And we also wanted to identify any residual uncertainties to determine whether it was advisable to think about more of a long-term research program.

The primary groups that have funded this research are API, OFA, and various organizations within EPA. (If I've left anybody out, I really do offer my sincere apologies.) There was widespread collaboration and interaction among the groups.

I have dealt with research for a long time, and as Peter Preuss mentioned earlier, this program really is remarkable in that we had states, several federal organizations, several

groups within EPA, industry groups, and several academic institutions, who were all working toward the same goal. And although communication can always be improved, I think it was a good example of a lot of different minds coming together to work on a common problem.

The risk assessment paradigm developed by the National Academy of Sciences several years ago describes how research feeds into risk assessment and how risk assessment feeds into risk management. Briefly, research would consist of laboratory and field studies, not only of health effects, but some preliminary exposure data as well. It then becomes important to identify or determine whether there is there a hazard; that is, does the agent cause an effect?

But then we need to know at what concentration does an agent cause a problem? What exposures actually cause effects, and what are those concentrations in humans? Often laboratory studies have to be extrapolated from high to low dose or from animal to human.

Once we know that a certain exposure causes a certain effect, another significant question follows—does that exposure actually occur? And if it occurs, is it one person that gets such an exposure or 50 million people that get such an exposure? That's the importance of exposure assessment, which needs to be supported by field measurements and characterization of populations.

All of these pieces of information are integrated together and judgments are made about risk characterization, which is the estimated incidence of the effect in a given population. It then becomes the task of risk managers and policy makers to decide how to take that information and develop regulatory options. Regulatory options consider a number of issues including health issues, social issues, and the different impacts of the regulatory options. From these, the Agency makes decisions. So these processes, the risk assessment process and the risk management process, are different.

This brings us to the research that will be presented here at the conference. I'm going to give you a brief overview of what people are going to present without giving you any information on the results of their studies.

The Environmental and Occupational Health Sciences Institute (EOHSI) has been conducting a lot of work on exposure in commuting scenarios, including monitoring inside vehicles. The International Technology (IT) Corporation has been performing some extensive work characterizing MTBE and other pollutant levels at several gas stations. The EPA/ORD has looked at vehicular emissions at subzero temperatures. Those emission studies also have been conducted in collaboration with Environment Canada, using their facilities as well to look at the effects of low temperatures. And both the ORD and OMS worked with Alaska and New York, as well as several of the EPA regions, to analyze the ambient air samples.

For the health studies, we took a combination approach of epidemiology, human clinical, and animal toxicology studies; each one of these approaches has its own strengths and its own limitations. In the interest of time, I won't go into them here today. Together,

these approaches are synergistic. When we look at the results of all of these approaches as a whole, it minimizes the inherent weaknesses of each and it maximizes the strengths of each.

In terms of epidemiology, CDC has done a number of studies. As you recall, originally they were called in by the state of Alaska to look at Fairbanks while MTBE was being used. They went back after MTBE had been removed and looked at symptom complaints; they measured blood levels of MTBE and other compounds and conducted some other associated studies. They later used similar approaches to compare Stamford, CT, which uses MTBE, to Albany, NY, which does not use MTBE.

The EOHSI, as part of a broader program, also did some epidemiological evaluations. They had a panel of people who were already known to be chemically sensitive, so they were able to investigate symptoms in relation to gasoline exposures in that panel. Because different areas of New Jersey either had or didn't have MTBE at a particular period of time, they also were able to compare symptom prevalences within New Jersey.

The API surveyed industry to see what kind of symptom complaints were arising with workers who were more closely and frequently involved with fuels. Also, the Municipality of Anchorage looked at health insurance records to see if there was any kind of an increase in claims that possibly could be associated with MTBE use.

Two human clinical studies were conducted, one at the EPA Health Effects Research Laboratory (HERL) at Research Triangle Park and the other at Yale University. In both studies, volunteers were exposed acutely to MTBE and evaluated for self-reported symptoms, nasal and eye irritation, and neurobehavioral changes. Previously, API had odor threshold studies performed for pure MTBE, but further studies were conducted to include MTBE-blended gasolines.

As I mentioned, the MTBE Task Force sponsored a whole series of animal studies. There were some uncertainties associated with effects on rat kidneys, and so they did further evaluation of tissue samples and conducted some new studies to help clarify some of the effects on kidneys.

In the realm of assessment, the EPA/ORD developed a tentative or draft cancer classification. When EPA develops a cancer assessment, a particular group of scientists—in this case, scientists from the Office of Health and Environmental Assessment—develop a draft that goes to an Agency-wide work group for verification. So at this point, the cancer assessment is still in that early draft stage; it has not gone to the EPA-wide verification group.

The ORD also revised the RfC for MTBE. If you recall, the first RfC was based on subchronic studies. We were able to take advantage of the new chronic information and derive a new RfC. This is an official reevaluation; the EPA work group just recently met and verified the new RfC.

The ORD also has developed an exposure assessment, taking advantage of the new data from EOHSI, IT Corporation, and several other groups. Shortly, we will be developing a new report that evaluates the potential health risks of MTBE oxyfuels.

We need to keep our expectations reasonable. Looking at the nature of the research program, without knowing what the results are at this point, we're hoping the new as well as the older data will enable us to determine what are the likely exposures to MTBE and oxyfuels and whether acute controlled exposures to MTBE can cause health symptoms, affect neurobehavioral functions, or cause eye or nose irritation. We also hope to be able to understand whether acute health symptoms are associated with acute ambient exposures to the whole of MTBE oxyfuels. Hopefully, we're also going to have some estimate of the likelihood of MTBE causing cancer, something we didn't have for the February report. In addition, we should have more information on the effects of MTBE on CO tailpipe emissions at lower temperatures.

To make sure we have some balance here and keep our expectations reasonable, I'd like to give some counterpoint, that is, some questions that we think will remain. Again, I have to remind you that we have not seen the data, so these are our opinions of what will remain to be understood. If indeed health symptoms are found to be associated with acute exposures, what are the quantitative risks and what are the associated uncertainties? It's necessary to know what the key risk factors might be. For most pollutants there are sensitive subpopulations, and it's important to know sensitive subgroups exist so they can be enumerated and their risks evaluated.

I think we can presume that there will be a lot of uncertainty about the cancer classification. So, what sorts of follow-up studies will be needed to decrease the uncertainties? If we do have concerns for chronic noncancer risks—and again, I don't know whether we will or we won't because we haven't seen the data yet—but if we do have concern for chronic noncancer risk, then what follow-up studies would be most appropriate and necessary?

Finally, the comparative risk is a very important question. Even if we knew everything we ever wanted to know about MTBE, it would still be important to know what are the risks that might result from exposure to other oxygenates, such as ethanol and ETBE.

Discussion

It was noted that animal testing of MTBE actually began as early as 1969 and that data from a 28-day study of MTBE in blended gasoline as well as reproductive subchronic studies and oncogenicity studies of MTBE alone were available prior to the beginning of the oxyfuels program in 1992.

In response to a question regarding whether EPA/ORD assessments were being done or considered for other oxygenates, the answer was no, because not enough information is available to support such assessments at present.

Determining the balance between the health benefits of reduced CO and the potential health risks of oxygenated fuels themselves was suggested as another objective for the conference or for future research. This point raised the issue of performing a relative risk comparison of gasoline versus MTBE-oxygenated gasoline. It was noted that orders of magnitude more information exists for CO health effects than for MTBE or MTBE oxyfuels.

Historical Perspective on the Use of Ethers in Fuels[1]

William J. Piel
Manager of Business Development of Oxygenated Fuels, ARCO Chemical Company and Head of the Technical Committee for the Oxygenated Fuels Association

ARCO Chemical has been involved in commercial production of fuel oxygenates since 1969, and so we'd like to share some of that experience of how we got to where we are today. Here's what I'm going to try to cover. I'll discuss how fuel alcohols were developed as low-cost gasoline extenders for more expensive crude oil in the days when we went through the oil embargoes. Then I'll address how ethers were developed as lead-octane replacements. I'll show worldwide MTBE production growth for the past two decades, and talk about some of the pre-Clean Air Act oxygenated fuel programs that were conducted by some of the states. I will then tell you a little about MTBE use in European gasolines and talk about some of the vehicle emission benefits we've learned from reformulated gasoline studies.

Fuel oxygenate development was started to develop an alternative to gasoline derived from high-cost petroleum, particularly during the oil embargoes of 1973 and 1979, though it in fact did start slightly before that. As I mentioned, ARCO Chemical has been involved in this since 1969, when we were producing tertiary butyl alcohol (TBA) as a gasoline blending component, both for gasoline as well as for some octane. We call that GTBA, for gasoline-grade TBA. Then we saw where the U.S. Government subsidized, and EPA granted a waiver for, 10% bio-ethanol in gasoline in 1978.

Soon after that, we saw methanol and co-solvent blends commercialized in 1981. The incentive there was methanol, which was derived from natural gas at roughly $2 per million BTU. Crude then was equivalent to about $6 per million BTU. So there was an economic incentive to look for a lower cost gasoline blending component such as methanol. In that case, GTBA and other alcohols were used as co-solvents to help blend the methanol into gasoline.

But then soon thereafter, crude collapsed, down to about $15 a barrel, and with that was a loss of incentive for a lot of the alcohol blending. So, many of the alcohol blends were discontinued in 1986. But at the same time, MTBE was being expanded and developed as an octane alternative to lead in gasoline, and that was really promoted when EPA decided to accelerate the phaseout of lead compounds in gasoline in the mid-1980s. It also was helped by the growth in premium gasoline in that same time period.

I'll talk a little about what MTBE is. As I mentioned, it was developed as an octane enhancer; it was a high-octane alternative to lead compounds or aromatics in gasoline. It was first commercially used in Europe in 1973 where it was first developed in Italy and then shortly thereafter was developed, produced, and used in Germany for gasoline blending.

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[1]Copies of the slides for this presentation may be found in Appendix A.

The U.S. production began in 1979 after the EPA provided approval through a waiver process. Originally it was allowed at seven volume percent in gasoline. That limit was raised to 11% in 1981 under the "substantially similar" ruling, and then was raised to 15% in 1988 after going through a major waiver review sought by Sun Oil Company.

The European Economic Community set a standard of 15% MTBE in 1985, before the United States did. In Europe, MTBE also was used as a replacement for lead and aromatic compounds used in gasoline. In actuality, MTBE is generally used throughout the world for octane in gasoline, both in the Far East as well as Europe and here in the United States.

Recent interest in MTBE has been more from an environmental viewpoint, because of its use to modify gasoline composition to reduce emissions associated with vehicles. The largest benefit is reducing CO emissions and that's due to the oxygenate effect or improved combustion processes, as mentioned already by Mary Smith. But it also helps reduce other mobile source pollutants such as volatile organic compounds (VOCs), nitrogen oxides (NO_x), particulate matter ≤ 10 μm, and toxics such as benzene. Because the oxygenates do not include sulfur, generally when you use the oxygenate, it helps dilute the gasoline's sulfur content from crude; so generally it also contributes to reduction in sulfur oxides (SO_x) as well as all the other things I just mentioned.

I'll talk a little bit about the production of MTBE and other ethers. All the ethers I'm going to address were actually considered as early as the 1930s, when Shell Oil Company was looking at them. The production technology that's in place today was essentially developed in the late 1950s and patented around 1960, and it's essentially the same reaction process and reactor configuration that have been used since then.

The reaction is fairly simple; it's made by combining isobutylene (from a number of sources) and methanol. The isobutylene has a very active tertiary carbon for adding hydroxyl groups such as methanol. The reaction is highly selective, with very minimal by-products. The few that are produced are preliminary products such as di-isobutylene, tri-isobutylene and TBA, which is produced from the small amount of water that gets in the feed stocks and combines with the isobutylene to make TBA. All these contaminants have generally been found in gasoline for a long time.

At present, the three main sources of isobutylene, which is usually the commercially limiting factor for producing MTBE, are a by-product of the refinery fluid catalytic cracking process for making gasoline. Isobutylene also is produced by isobutane dehydrogenation (where the hydrogen is removed to make the isobutylene) and dehydration of TBA, which is made from the isobutane oxidation. Recently there have been some commercial processes for making isobutylene called skeletal isomerization, where normal chain olefins are reconfigured or reshaped to make the preferred tertiary carbon. We can probably expect to see a few of the latter production processes in the future.

Ethyl tertiary butyl ether is an alternative to MTBE. It's made by combining bio-ethanol and isobutylene. It has been in a semi-commercial state for the past two years, and has been made both in Europe and in the United States in existing MTBE processes. It's fairly simple to switch over from MTBE to ETBE; the reaction kinetics are similar as well as

the process operation. So a few refiners and others have switched from MTBE to ETBE for trial production purposes.

Tertiary amyl methyl ether is a commercial ether that has been produced in refineries for a number of years. In Europe it has been in production since the mid-1980s. It's made by combining refinery isoamylene with methanol. Isoamylene is another active olefin that has tertiary carbon for combining alcohols or hydroxyl groups. Isoamylene is a very volatile product that's made by the fluid catalyst cracking process as well and normally goes directly into gasoline blending.

These latter two ethers, ETBE and TAME, generally have much lower volatility than MTBE. That's one of their major advantages and why they're being considered and developed today. Methyl tertiary butyl ether generally has a vapor pressure of about 8 psi at 100 °F, whereas ETBE is about around 4 psi, and TAME is around 2 psi. They're considerably less volatile than MTBE.

I show a simple diagram of the process flow unit (see Appendix A). For refinery MTBE production, the isobutylene is usually found in the mixture with other butylenes and butanes coming from the fluid catalyst cracker, but the isobutylene selectively reacts with methanol using an acid type catalyst in very mild reactor conditions. So the mixed four-carbon chain compounds (C_4s) from the fluid cat cracker are fed to the reactor along with methanol. In the reaction, the methanol almost completely reacts with isobutylene with a high conversion, 96 to 97% or higher. The unreactive C_4s will then vaporize off the separation tower where the higher boiling MTBE is then removed off the bottom of the fractionating tower. In the refinery, this would go directly to gasoline blending.

A lot of MTBE capacity has been developed based on butane plants for commercial sales, generally to refiners. In the first step, the isobutane—and this could be directly from liquified petroleum gas (LPG) or from normal butane, again from LPGs—is dehydrogenated to make isobutylene, which is combined with methanol to make MTBE in a very conventional MTBE unit. These would be large-scale units, generally on the order of 500,000 metric tons per year or larger. Today, roughly about two-thirds of the MTBE produced in the world is derived from butane, versus that made from the fluid catalyst cracker, C_4s, that I mentioned earlier.

The MTBE is then usually shipped in large commercial movements, such as barges, and moved into industry storage for the oxyfuel program. The production is all year around, but the demand is very seasonal. During the wintertime, the MTBE is removed from storage and shipped to the refinery where it will be stored or blended into gasoline to make the oxygenated gasoline.

The MTBE production increased quickly from the mid-1980s. In 1980, there were only four process units. (I report the capacity in two different ways: for refiners, that's 19,000 barrels a day; for other people, it's in millions of gallons per year, in this case about 290 million gallons per year.) In 1985, the number of plants started to grow and when we get to 1990, we're up to 78 plants throughout the world for roughly 230,000 barrels of capacity or about 3.5 billion gallons per year production capacity of MTBE.

There were 117 plants by the end of 1992 for a total capacity of roughly 360,000 barrels per day or almost 6 billion gallons per year of production capacity throughout the world. We've made estimates of how many plants and how much production capacity will be in place. Right now it looks like about 186 plants will be in place by 1995 for about 600,000 barrels per day of capacity or a little over 9 billion gallons per year of MTBE throughout the world. This doesn't include any TAME plants or ETBE plants that might be in place by then as well. In 1995, roughly two-thirds of that MTBE will be needed in the United States, assuming follow through with the Clean Air Act requirements.

Our oxyfuel experience really started back in Colorado, where they introduced the first oxygenated fuels program for reducing CO. They started off with a large demonstration fleet test that they conducted there in late 1987 and then instituted their first oxyfuel program of 1.5 weight percent oxygen. Just for convention, the 2.0 weight percent oxygen is about 11% MTBE and 2.7% oxygen is about 15 volume percent MTBE, which right now is required for most oxyfuel areas. Colorado increased their oxygen number to 2.0% in the 1988-1989 winter and to 2.6% in the 1989-1990 winter. Also that same winter season, three other areas introduced an oxyfuel program: one in Arizona and two in Nevada. So there's actually a number of years of experience before the Clean Air Act started oxyfuel programs for controlling CO emissions.

Since that time, a number of these areas have moved up their oxygenate level, and for this past winter we're up to 2.7% in all these areas, except for Tucson, which was not a CO nonattainment area before introducing their oxyfuel program. That roughly describes our oxyfuel experience in the United States now. As I mentioned earlier, MTBE was actually around much longer, where it was used mostly in premium gasoline in concentrations on the order of 5 to 11%, although with the use of the Sun Oil Company waiver in 1988. they used it as high as 15% in their premium gasolines.

In Europe, it has also been widely used, actually before the United States. A similar oxygenated gasoline in Europe, introduced by Neste Oy Company, is called "city gasoline." It was introduced in Finland, where the company is actually headquartered. This program started in May 1991; it requires two weight percent oxygen using 11% MTBE. The gasoline now represents about 80% of the gasoline sold in Finland, where it's promoted as an emission reduction gasoline.

Methyl tertiary butyl ether in Europe is mostly used in premium gasolines as an alternative to using lead and aromatics for octane. Lead is now being phased out in Europe. Much of the gasoline now has reduced lead content or no lead. Also, in Europe only about 15% of the cars have catalyst and vapor recovery systems, so they're not quite up to where the United States is on emission reduction technology on their cars. As a result, their car emissions of unburned gasoline are generally five to ten times greater than for the U.S. cars that we have today. So the absolute emissions are higher. But when using MTBE and getting the element benefits, and the combustion improvements, the absolute reduction benefits are much greater there because they have much higher emissions from their cars on a grams per mile basis.

Some of the emission reduction benefits of reformulated gasoline using 15% MTBE and blending that to the refinery are based on EPA's "complex model", which is the most recent version that just came out about two weeks ago. This model takes all the emissions data and tries to determine the relative impact of all the different fuel parameters, working toward the reformulated gasoline program goal of 15% reduction of VOCs and toxics, starting January 1995. That requirement then jumps to a 25% reduction of VOCs and toxics in the year 2000. The estimates show CO down 17%, VOCs generally reduced by 6%, NO_x down by 3%, SO_x (due to dilution of the sulfur) down about 15%, and total toxics down about 18%. Of the individual toxic pollutant contributions in milligrams per mile, benzene is the largest, and you generally see almost a 20% reduction of benzene with MTBE. Of all the toxics mentioned here, the only one that really goes up is formaldehyde. To some degree that's offset when you look at the VOC reduction, because much of the unburned hydrocarbon coming out of the tailpipe generally will eventually go through a formaldehyde stage and be oxidized in the atmosphere, and there's less VOCs coming out of the tailpipe. -So when you look at the total inventory, there's somewhat of an offsetting effect from just the VOC reduction.

So where does this leave us now? We went through the history of using oxygenates and looked at the emission reduction benefits for the Clean Air Act and reformulated gasoline. Today, MTBE and bio-ethanol are the main oxygenate options. Future options include TAME and ETBE, which are much less volatile ethers than MTBE. Volatile organic compound reductions will be more important as well as lower volatility, so these ethers will take on more importance.

Methyl tertiary butyl ether is one of the most widely produced petrochemicals in the world. It ranks with petrochemicals such as toluene, benzene, and others. It has now been in commercial use for over 20 years, so there's been a lot of experience with it, and it has been used just about everywhere (i.e., all the major gasoline markets in the world). Also, the oxyfuel programs were demonstrated in the United States for 3 years prior to the Clean Air Act being developed.

Based on all the emission testing that's available, the use of MTBE helps reduce major air toxic pollutants and generally contributes to reductions in the six criteria pollutants. As a replacement for lead, MTBE helps reduce CO, helps reduce ozone by reducing VOC and NO_x, as well as reduces the NO_x directly, along with SO_x and particulates. So generally, the use of MTBE is viewed as helpful and beneficial in reducing the mobile source pollutants.

Discussion

In response to one question, the speaker clarified that the model showing emission reductions was the EPA complex model, not the Mobile 5 model. One person asked whether there would be an overall reduction of pollutants in view of the reduction in fuel efficiency and consequently greater consumption of gasoline. The response was that EPA measures emissions in terms of grams of pollutants per mile driven, not per gallon consumed. Thus, any increase in emissions associated with a reduction in fuel efficiency would be captured by that measure.

Session Two

EMISSIONS AND AIR QUALITY UNDER WINTER CONDITIONS[2]

Chair: Steven Cadle, General Motors Corporation

Discussant's Summary

Robert Sawyer, University of California, Berkeley

It is estimated that by the mid-1990s, approximately 6 billion gallons of MTBE per year will be used in the United States. This estimate is significant and requires that scientists and the public understand the consequences of using MTBE in fuels.

During Session Two, three speakers provided experimental data on the effects of MTBE use on emissions under cold conditions. Ken Knapp of the EPA/ORD reported the emission results, using standardized Federal testing procedures at temperatures from −20 to 75 °F. These data showed that CO emissions increase as temperature decreases and that CO is reduced when MTBE is added to fuels. However, the effect of MTBE addition on CO emissions is not consistent, which suggests vehicle-to-vehicle differences and the need for more data to establish a statistically significant trend for the effect of MTBE on CO emission at low temperatures. Chandra Prakash of Environment Canada provided data on two vehicles tested at temperatures from −20 to 70 F°; the data showed no significant MTBE effects on CO emissions. Finally, David Veazy of the University of Alaska-Fairbanks reported on vehicle emissions data observed in Fairbanks, Alaska, under actual use conditions (rather than FTP conditions). He noted that cold weather cold starts there are often followed by approximately 15 to 30 min of cold idle to allow the vehicle to warm up. These operational conditions are quite different from the FTP. The CO emissions during this Fairbanks cold start sequence dominate. He concluded that adding MTBE had little effect on cold-start emissions but reduced on-road CO emissions. Increased use of electric engine heaters would be a more effective means of reducing CO emissions. These data are not sufficient to establish that adding MTBE reduces CO emissions under cold-weather, cold-start conditions.

The next three speakers reported on ambient air quality measurements. Gerry Guay of the Alaska Department of Environmental Conservation noted that extreme winter conditions in Fairbanks—very cold temperatures, very little sunshine, and stable, very low inversions—cause relatively low CO emissions (estimated at 50 tons per day) to produce ambient CO levels that exceed air quality standards. He outlined measurement methods and difficulties. Roy Zweidinger of EPA/ORD reported on air quality in outdoor and indoor environments and on fuel composition measurements in Fairbanks, Stamford, and Albany.

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[2]Copies of the slides for the presentations in this session may be found in Appendix B.

High concentrations of MTBE and other hydrocarbons were found in motor vehicle repair service bays. Measurements taken from a Fairbanks home having an attached garage also showed high levels of gasoline vapors, including MTBE. Larry Anderson, of the University of Colorado-Denver, analyzed the effect of the Colorado fuel oxygenates program on air quality over the past 6 years. He attempted to determine the relation between CO levels, which decreased strongly during the 6-year period, and oxygenate use. He concluded that adding oxygenate had no statistically significant effect on CO emissions.

Both emissions and ambient measurement data raise concerns related to wintertime CO emissions: "Is MTBE doing any good?"

Discussion

In response to a question, the source of the 6 billion gallons per year figure for MTBE use in the United States was attributed to an estimate that worldwide use would be about 9 million gallons of MTBE and that two-thirds of this amount would be used in the United States. What fraction of the MTBE use would be independent of the wintertime oxygenate program would depend on several factors. If the data were based on the difference between year-round-reformulated gasoline with 2.0% oxygen and winter gasoline with 2.7% oxygen, then 10 to 20% MTBE would be used strictly for the wintertime oxygenate program. If all of the oxygenate (in addition to that which would be used for octane improvement) were there for wintertime CO, then approximately 40% of the oxygenate would be used in the CO program.

Another questioner asked if there were no regulatory requirements for oxygenated fuels, what fraction of the MTBE would be used? It was noted that MTBE is added to fuels for a number of reasons, including reducing vapor pressure requirements, which has pushed displaced butanes into MTBE production.

One commentator noted the difficulty of determining the effect of adding oxygenate on Denver's CO levels because of the number of Denver's CO-related control measures. He noted that early analysis of the effect of the wintertime oxygenate program on CO emissions during the first year showed decreases of 15% in New Jersey, 11% in Connecticut, 15% in Washington, 17% in Oregon, and 10% in California. He suggested that Larry Anderson apply his analyses to these new data. In response, Larry Anderson said that his analysis would work well in other areas, but that these same areas, as in the case of Denver, also were experiencing CO reduction from other programs.

It was noted that the relatively high vapor pressures of the cold weather fuels suggested a need to measure cold weather evaporative emissions (as they might be important for indoor emissions). The response was that these measurements, although difficult, would be made, and that the expectation is to see the increased vapor pressure increasing low molecular weight hydrocarbons more than increasing MTBE emissions.

An inconsistency was pointed out between vehicle emissions measurements that showed little effect of MTBE on formaldehyde emissions and data for Denver that showed significant increases in ambient aldehydes. One respondent noted that secondary aldehydes (formed in

atmospheric reactions) could dominate atmospheric measurements, whereas another person indicated that ambient increases were from direct emissions.

A member of the audience questioned the statistical significance of the Denver data. There was no statistically significant effect of MTBE on CO at the 95% confidence level; whereas a 10% change at some locations may have been missed, this would not have occurred at the downtown Denver site. Another person questioned whether meteorological changes were adequately addressed. The response was that using data from six winters should account for meteorological changes.

The potential beneficial effects of diluting gasoline with MTBE and thereby reducing gasoline toxicity were pointed out. However, it also was stated that such a dilution effect would accompany any nontoxic additive and was not peculiar to MTBE. Another beneficial effect of MTBE, other than CO reduction, is as an octane improver compared to other toxic compounds, such as benzene.

Session Three

HUMAN EXPOSURES[3]

Chair: Charles Powers, Health Effects Institute

Discussant's Summary

Steve Colome, Integrated Environmental Services

Given the extremely rapid turnaround of the research presented in this session on human exposures, there was not enough time for the authors to write papers; therefore, this meeting is the first presentation of findings. As a result, this summary was extemporaneous.

The quality of this research and the speed with which it has been refined and presented is admirable. The interval between initial complaints associated with using MTBE last winter and the decision to address the issue was extremely short. Sponsors and contractors quickly assembled the funding and equipment, developed the field protocols, and conducted measurements and analyses. A few months later, there was evidence of fairly clear data results—this is indeed impressive, if not unprecedented. The funders and the researchers who were involved in this project are to be congratulated for their wisdom, skill, and effort in completing such an extraordinary set of studies.

The picture presented by these investigators is relatively coherent. With this new work, there is substantially more information available now than there was before measurements were taken. The exposure values that have been generated by this project may even have sufficient certainty at this stage to frame the exposure element of an initial assessment of acute health effects.

Despite the clear picture presented by this research, there are some areas of concern that need to be addressed. There was a serious lack of information that was available prior to this meeting on human exposures to, and health effects that may result from, MTBE. The experience of this meeting should reemphasize the value of collecting at least a modest amount of exposure data for MTBE and the other alternative fuels that are under consideration. The following is a summary of the presentations.

Ted Johnson discussed a sampling program designed to gain insight on MTBE exposures that the public would experience at service stations during refueling operations. The measurements that he presented were made during late winter and early spring in the northeastern United States. Results from the survey indicate the concentration ranges that occur during vehicle refueling. The concentrations are less than 10 ppm in all cases and less than a couple of parts per million in almost all circumstances. The data also provide some

[3]Copies of the slides for the presentations in this session may be found in Appendix C.

evidence that stage-two vapor recovery further reduces exposures, as compared to uncontrolled releases of tank vapors. Based on the median values presented by Ted Johnson, it appears from this preliminary data that vapor recovery may provide almost an order of magnitude of exposure reduction.

Jack Hinton reviewed over 2,000 occupational exposure measurements that have been conducted on workers in the fuels industry. The vast majority of work-shift exposures were less than 10 ppm, and in a majority of the labor categories, the maximum short-term exposures were around 100 ppm. Isolated concentrations up to 1,000 ppm were observed in barge-related tasks in the transportation sector. These were the highest concentrations observed, and they were for nonroutine activities. One important point is that the measurement sets reported by Dr. Hinton were not collected for the purpose of developing exposure distributions. These measurements represent an assembly of exposure values and a useful compilation of the data.

Paul Lioy discussed commuting exposures in the same area of the country that Ted Johnson's work was conducted. Most of these concentrations—note the change in measurement units—were less than about 30 ppb, with averages generally below around 10 ppb. As is often found in exposure assessments, there was a wide distribution of concentrations with some evidence of higher outliers. The highest concentrations were measured inside a vehicle cabin, presumably from exposure to the car's own exhaust.

Alan Huber tried to put these data together and make some sense of the compilation of exposures. He considered activities and time spent in those activities using microenvironmental concentrations that were, in most cases, less than 1/100th of a ppm, according to some of the data collected in Alaska. He considered an approach to modeling MTBE for long-term exposure assessment. This would have a primary focus on cancer risk assessment. However, the more difficult challenge, and the focus of most of the health research presented at this meeting, is to understand and model short-term exposures to MTBE. That should be the direction for future exposure modeling.

Discussion

It was pointed out that EPA now has a method for MTBE analysis that has no interference from hydrocarbons and that the method is specific for MTBE. Another commentator noted that even though ambient measurements were initiated in rapid response to the Alaska situation, intentional efforts were made to get measurements over a range of different types of exposures to support the exposure modeling.

It also was noted that Dr. Huber used the upper limit for his microenvironmental exposure assessment, and, thus, the estimates were conservative. However, because Dr. Huber's exposure ranges were developed in part from Alaska data, one should be aware that Alaska, unlike most other areas in the United States, has exceedingly high levels of CO on the neighborhood scale, not just at street-side. Thus, if CO and MTBE are correlated, then MTBE estimates in Alaska neighborhoods would be much higher. However, it would probably be inappropriate to extrapolate Fairbanks' background levels to other cities, because during the winter there are strong inversions and Fairbanks is in a "bowl" in which

concentrations build up. In other cities, weather systems come through clearing CO out of the air. So it would be expected that background levels in other places would be considerably lower than the background in Fairbanks.

A commentator noted that CO is emitted from the tailpipe, whereas MTBE is an evaporative emission either from refueling or evaporation from the car. Indeed, the data are not adequate to support a one-to-one correspondence between CO and MTBE. Another person added that in the average car about 10 to 40 g/mile of CO is emitted and only up to about 10 mg/mile of MTBE is released through the tailpipe.

It was observed that eventually, as one attempts to relate the exposure analyses in microenvironments to other acute or chronic effects information, it will be important to sort out which people it is that the law is asking us to protect in this particular case, which will finally turn out to be a risk management question.

Session Four

ACUTE HEALTH EFFECTS OF MTBE EXPOSURE[4]

Chair: Lawrence Reiter, Office of Research and Development, U.S. Environmental Protection Agency

Discussant's Summary

Roger O. McClellan, Chemical Industries Institute of Toxicology

This session included ten papers that addressed potential acute health risks from MTBE exposure. The topics included measuring blood levels of MTBE and, in some cases, its metabolite (TBA) under both field and controlled exposure conditions. Other topics included assessing various health indicators in individuals exposed to MTBE under environmental conditions or in controlled exposure studies. These papers provide substantial information for assessing the potential human acute health risks of MTBE exposure.

Figure 1 is a paradigm linking sources of MTBE with exposure, dose, and response data. It is necessary to understand the quantitative relationship between these data.

The data presented in Session Four, and in other sessions at this conference, considered a range of MTBE sources resulting in exposure of people in their occupational, consumer, and environmental settings. Occupational exposures include those occurring during the manufacturing, blending, transportation, and distribution of MTBE or MTBE-containing fuels, as well as exposures of service station, garage, and taxicab personnel. Consumer exposures can occur during refueling or during vehicle use; environmental exposures can occur anywhere in the locale where MTBE is being used as a fuel additive. These exposures occur principally when oxygenated fuel use is mandated, although MTBE is routinely used as an octane enhancer for premium fuels.

Exposure

Summary data on MTBE exposures from various microenvironments are shown in Table 1. These data are presented as background for the discussion that will follow. The exposure values are typically well below 1 ppm (3.6 mg/m^3), the exception being refueling values. Other values of special interest are those for automotive shops (0.1 to 0.5 ppm or 0.36 to 1.8 mg/m^3).

Several sets of field data on acute health effects of MTBE exposure are of special value. These are the data from Fairbanks, AK, and Stamford, CT, in which

[4]Copies of the slides for the presentations in this session may be found in Appendix D.

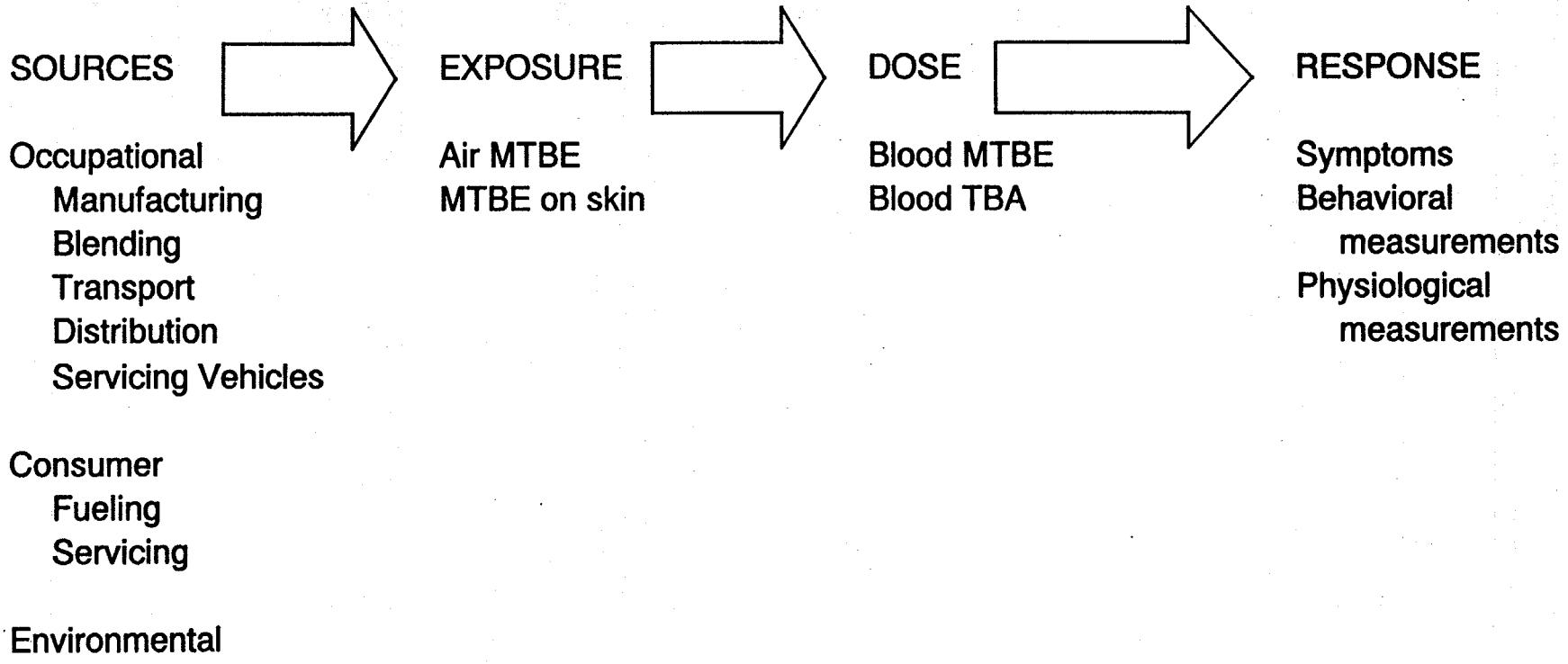

Figure 1. Paradigm for evaluating potential human health risks of exposure to methyl tertiary butyl ether (MTBE) and other oxygenates.

TABLE 1. Summary Data on Microenvironmental Exposure to Methyl Tertiary Butyl Ether

Source	Microenvironment Concentrations	EPA Estimate ppm (mg/m^3)
Gas refueling	Pump	1-10 (36)
	Other	0.1-1 (3.6)
Commute/in vehicle		0.005-0.1 (0.36)
Automotive shop		0.1-0.5 (1.8)
Public garage		0.1-0.5 (1.8)
Residential garage	High	0.1-1 (3.6)
	Low	0.001-0.005 (0.018)
Residence	High	0.005-0.01 (0.036)
	Low	0.001-0.005 (0.018)
Office		0.001-0.01 (0.036)
School/public buildings		0.001-0.01 (0.036)
Outdoors	High	0.01-0.1 (0.36)
	Low	0.001-0.01 (0.036)

measurements were made of both air and blood concentrations of MTBE. In Fairbanks, during MTBE fuel use, measurements of MTBE in the garage workplace were made along with measurements of MTBE in the blood of 18 garage workers. The median value for the garage was 370 $\mu g/m^3$ (range of 40 to 2,930 $\mu g/m^3$), which decreased to 130 $\mu g/m^3$ (ranging from nondetectable to 510 $\mu g/m^3$) following the cessation of the distribution and sale of MTBE fuel. Similar MTBE air data were developed for Stamford along with data on MTBE in blood. The blood and air measurements were not collected simultaneously. The air concentration of MTBE was measured in four garages: 10 samples yielded values from 5 to 1,549 $\mu g/m^3$.

In addition to the above data on occupational and environmental exposures, exposure data were available from two controlled human MTBE exposure studies. One study was conducted at Yale University and involved a 1-h exposure to MTBE at 1.7 ppm (6.0 mg/m^3) MTBE. Blood measurements of MTBE were made on some subjects. A second study was done at the EPA/University of North Carolina-Chapel Hill facility and involved a 1-h exposure to 1.4 ppm (5.0 mg/m^3) of MTBE.

Dose (Blood Methyl Tertiary Butyl Ether and Tertiary Butyl Alcohol)

A major strength of the present data set is the availability of information on dose, in this case, blood MTBE and blood TBA, which complements the exposure data and provides

a linkage between exposure and response data (Figure 2). Blood TBA levels are available for Stamford and for several individuals exposed under controlled exposure conditions.

In Fairbanks, the median blood MTBE levels in workers (mechanics, service station attendants, and garbage collectors) were slightly above 1 mg/L (preshift) and were further elevated (postshift) to approximately 2 μg/L. Individual values ranged up to slightly more than 30 μg/L. As a group, the values for gasoline pump attendants were highest, followed closely by mechanics, with the lowest MTBE blood concentrations being observed in taxicab drivers. Blood MTBE measurements also were made on commuters, who had MTBE blood concentrations from 0.18 μg/L (precommute) to 0.83 μg/L (postcommute) when MTBE fuel was being sold in Fairbanks. A good correlation was observed between workplace exposure concentration of MTBE and blood MTBE levels; a 10-fold increase in workplace air concentration (from 30 to 300 $\mu g/m^3$) resulted in approximately a 10-fold increase in blood MTBE over the preworkshift value (from 0.5 μg/L to 5 μg/L). These data may be normalized as follows: 1,000 $\mu g/m^3$ (0.28 ppm) MTBE exposure yields a 17-μg/L increase in MTBE (or restated, 0.10 ppm [360 $\mu g/m^3$] MTBE exposure yields a 6.0-μg/L increase in MTBE). These values have been calculated by assuming an equilibratory relationship between air MTBE and blood MTBE over a range of exposure concentrations from environmental levels to the high concentrations measured in occupational settings (and those used in the controlled chamber studies). Blood TBA values were not reported for Fairbanks.

In Stamford, Connecticut, blood MTBE and TBA measurements were obtained from gas pump attendants, car repairmen, and commuters. The MTBE measurements ranged from just over 30 μg/L (car repairmen) to less than the detection limit of 0.05 μg/L. The median value was highest for three gas pump attendants (about 15 μg/L), intermediate for 21 car repairmen (about 1.5 μg/L), and lowest for 14 commuters (about 0.1 μg/L). The median blood TBA values were similar in ranking: 75 μg/L, 15 μg/L, and 2 μg/L, respectively.

The MTBE blood values for garage workers in Stamford were generally similar to those found in Fairbanks, whereas the commuter blood MTBE levels appeared to be slightly lower. Because the air and blood concentrations of MTBE were measured on samples collected at different times, it is not possible to directly correlate them. However, using the normalized relationship developed earlier from the Fairbanks data, the normalized relationship between air-to-blood MTBE developed earlier from the Fairbanks data appear to fit with the Stamford data. Stamford air data yielded estimates of MTBE in blood that are consistent with the measured values.

The relationship between blood MTBE and blood TBA is of interest. The extent to which the TBA blood levels exceeded those of MTBE is in accord with the MTBE clearing rapidly from blood and being distributed to tissues, such as fat, where it is slowly released and metabolized to TBA, which has a long residence time in blood and tissue before being metabolized and/or excreted.

In controlled human exposure study at Yale University, four subjects (two males and two females) provided blood samples before, during, and up to 1.5 h after a 1-h exposure to 1.7 ppm MTBE (approximately 6.0 mg/m^3). The peak blood MTBE concentration was 17 μg/L at the end of the 1-h exposure and decreased to 7 μg/L 1 h after exposure was

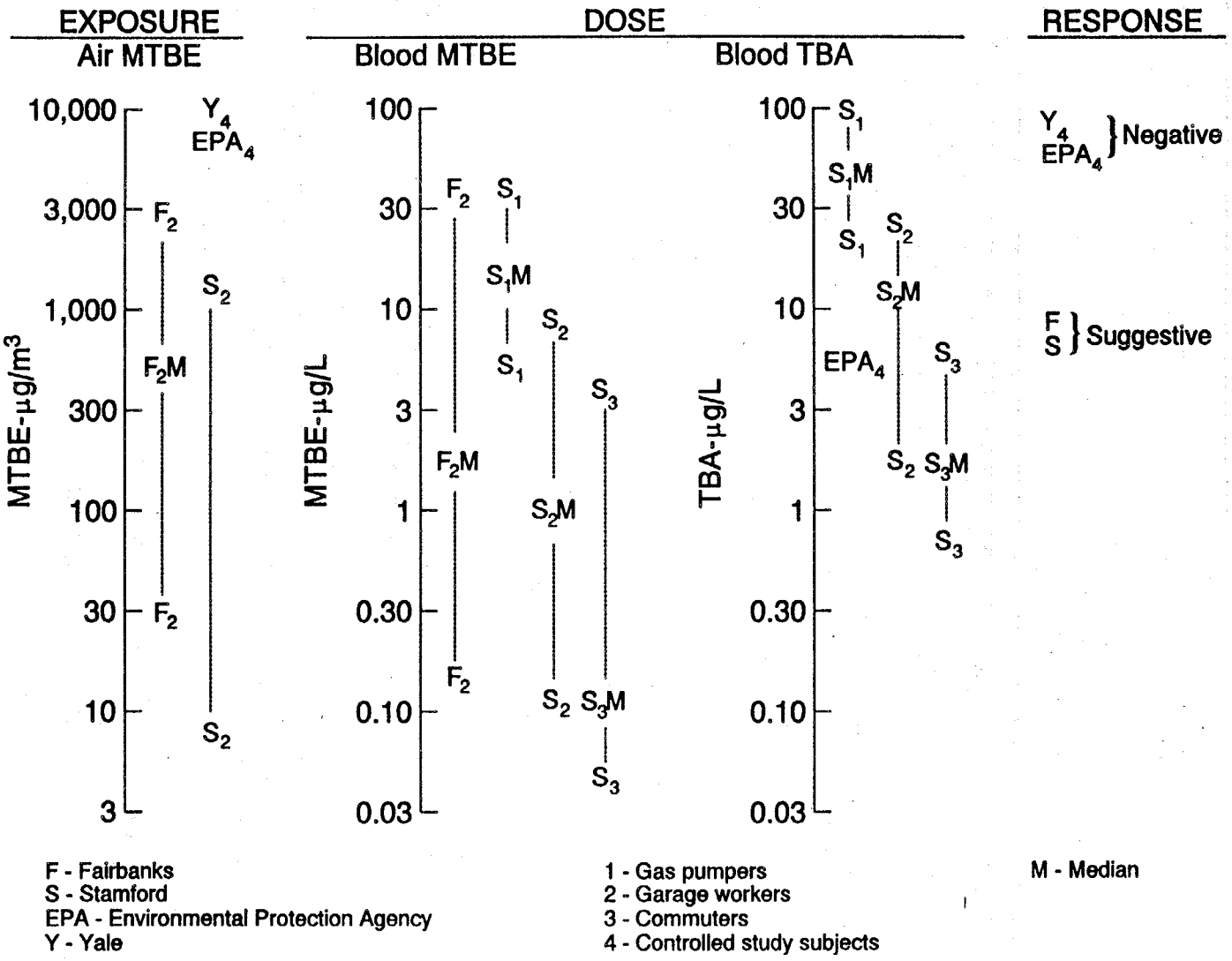

Figure 2. Synthesis of Exposure-Dose-Response Paradigm for methyl tertiary butyl ether (MTBE).

terminated. Data were not reported on blood TBA levels, but would be of interest if they could be obtained.

In the Yale study, it appeared that the blood MTBE levels were still increasing at the end of the 1-h exposure period. Using the air-to-blood relationship normalized from the Fairbanks data, the MTBE blood level might be approximately 100 μg/L for exposure to 1.7 ppm (or 6 mg/m^3) of MTBE, contrasted to the 17 μg/L of MTBE that was measured. These differences may relate, in part, to the differences in exposure duration (1 h for the controlled exposure and longer for the worker exposures) and equilibrium time for MTBE blood levels of exposure concentrations exceeding 1 h. An additional factor may be the ventilation (exercise) levels of the controlled exposure subjects versus the exposed workers. It is possible also that the Fairbanks study systematically underestimated the air concentrations of MTBE to which the workers were exposed, thus overestimating the blood MTBE to air MTBE relationship. Or there may be unidentified factors that are influencing the relationship.

In EPA's controlled human exposure study, two individuals who were exposed for 1 h to 1.4 ppm of MTBE had blood concentrations of 15 and 27 μg/L, respectively. These concentrations decreased with exposures of 15 min, reaching 1 to 2 μg/L at 4 h postexposure. Blood TBA levels rose steadily during the 1-h exposure and maintained a steady concentration of 7 to 10 μg/L up to 7 h postexposure. Using the values from the Fairbanks study, it is estimated that the 1.4 ppm (5.0 mg/m^3) exposure to MTBE would have yielded blood MTBE concentrations of about 85 μg/L, as compared to the 15 and 27 μg/L MTBE measured, respectively. With the Yale study, the apparent discrepancy may be from the exposure duration, exercise levels, or other unidentified factors. The apparent half-time of blood TBA associated with the 1-h exposure to MTBE suggests that if the duration of the MTBE exposure had increased, the blood TBA levels would have increased further from both MTBE exposure concentration and duration.

Health Responses

The range of health effect responses evaluated for individuals who were exposed to MTBE is impressive. The field studies conducted in Fairbanks and Stamford used questionnaires to ascertain health complaints, which included headaches, eye irritation, burning sensations in the nose or throat, cough, nausea or vomiting, dizziness, spaciness or disorientation, as well as other health complaints not thought to be associated with MTBE exposure. In Fairbanks, the questionnaires were administered both during the period when MTBE-oxygenated fuels were used (Phase I) and after their use had ceased (Phase II). Between Phase I and Phase II, the complaints decreased.

Of special note are the analyses conducted using postshift blood levels of MTBE as exposure measures. Even with the small study population of 18 individuals, there was a high correlation between blood levels of MTBE and the health complaints (headaches, eye irritation, burning of nose or throat, cough, nausea, dizziness, and spaciness) attributed to MTBE exposure. There was no similar association for health complaints, such as muscle aches and fatigue, not relatable to MTBE exposure. The authors emphasized the limitations of the study related to possible bias and the limitations of the sample size.

The Stamford study was similar to that conducted in Fairbanks although it was conducted later and in a community whereas health officials were not aware of any health complaints or public concerns related to MTBE use. The questionnaires asked about the prevalence of 15 symptoms over the previous month that were unrelated to the cold or flu. The data from occupationally exposed individuals were analyzed by grouping the population into two groups based on blood MTBE levels (over 3.8 μg/L [top quartile] and under 3.8 μg/L). This analysis suggested an association between blood MTBE and key symptoms, such as was seen in Fairbanks. The toxicokinetic data now available suggest that it may be useful to perform a similar analysis using TBA, because it may be a better surrogate internal dose measure for MTBE exposures.

The investigators who conducted the Stamford study offered recommendations for conducting future epidemiological studies with MTBE-exposed populations. These included:

- The location and timing of a study of the general population should be chosen to maximize potential exposure to MTBE and to minimize bias in reporting.
- Occupational studies should focus on persons with exposure to gasoline.
- Studies should focus on measuring symptoms that are present at the time MTBE exposure is measured.
- Comparison groups should have comparable exposures to gasoline fumes, but not to MTBE exposures.
- The contribution of exposure routes (other than inhalation) to the body should be examined.
- Follow-up studies should be planned for more definitive evaluation.

The two controlled human exposure studies represent substantial undertakings. The Yale University study involved 43 persons, ages 18 to 34 years, and the EPA study involved 37 persons, ages 18 to 35 years, with about equal numbers of males and females in each study. The Yale study involved three exposures: a control exposure to air, a 1-h exposure to 1.7 ppm MTBE, and a 1-h exposure to a 17-component mixture of volatile organic compounds. The EPA study involved a control exposure to air and a 1-h exposure to 1.4 ppm MTBE.

Both studies used a range of behavioral and physiological indicators that might be altered in response to exposure to low levels of organic solvents. For the EPA study, these included:

- Indicators of symptomatic responses, including headaches, nasal irritation, throat irritation, cough, eye irritation, odor quality, and dizziness. These were measured before and during exposure using questionnaire responses.
- Indicators of neurobehavioral responses measured before and at the end of exposure.
- Indicators of upper airway inflammation measured before, immediately after, and 18 h after exposure. This included nasal lavage to assess cytological and biochemical indicators of response.
- Indicators of ocular response, before and after exposure. These included hyperemia, noninvasive tear film breakup, and impression cytology.

The assessments conducted in the Yale University study were quite similar. When considering the results of both the EPA and Yale studies, it is important to keep in mind that

the data-gathering phase of both studies has only very recently been concluded, that a tremendous amount of data was generated, and that only preliminary analyses had been completed at the time of the MTBE conference. Based on their preliminary analyses, the investigators concluded that there were no symptomatic responses or findings suggestive of ocular or nasal inflammation, cell damage, or irritation in normal, healthy, young people exposed for 1 h to 1.4 or 1.7 ppm MTBE.

Synthesis

The information on acute health effects of MTBE in humans can be assessed within the framework of an exposure-dose-response paradigm. The controlled exposure studies involving 80 individuals exposed to either 1.4 ppm (5.0 mg/m^3) or 1.7 ppm (6.0 mg/m^3) for 1 h with rigorous evaluation of health responses yielded no symptomatic responses, nor any findings suggestive of ocular or nasal inflammation, cell damage, or irritation. These negative findings, with exposure concentrations at the level of the highest values seen in occupational settings and several orders of magnitude above typical environmental levels, are reassuring, especially regarding exposures of up to 1 h. The results of the controlled studies are even more reassuring when the blood MTBE levels in the controlled exposure studies are compared to those observed in the field studies. The peak MTBE blood levels observed in the controlled exposure studies are typically greater than those observed in the field studies. However, it is important to note that the blood MTBE levels were still increasing at the end of the 1-h exposures and, if the exposures had been continued, even higher blood MTBE levels would have been realized.

The results of the field epidemiological studies in Fairbanks and Stamford appear to contradict the results of the controlled exposure studies. The studies, launched on short notice, were basically exploratory. The conduct and analysis of the studies were handicapped by the potential for bias, confounding, and small sample size. The suggestive effects at exposure concentrations typically lower than those of the controlled exposure studies are difficult to reconcile with the clearly negative results of the controlled exposure studies. One possibility might be confounding, which is related to the low odor threshold for MTBE. It is possible, particularly in the Fairbanks study, that the suggestive effects observed were linked to the odor of the new MTBE fuel. This may have been compounded by the publicity and controversy over the mandated oxygenates program and the 14¢/gallon increase in prices. However, the data analysis was strengthened in both field studies in which small populations were stratified by blood MTBE level.

An additional factor that needs to be considered is the disposition of the TBA metabolite of MTBE. As may be seen in Figure 2, the blood TBA levels observed in the field studies were greater than the blood MTBE levels by factors of about 5 (TBA to MTBE) for the highest exposed individuals, about 10 for the intermediate exposures, and about 20 for the lowest exposures. The highest TBA levels observed in Stamford (over 50 $\mu g/L$) exceeded those observed in the controlled exposure study (5 to 10 $\mu g/L$). This reflects both concentration and duration of MTBE exposure, with MTBE clearing rapidly from blood, and TBA clearing relatively slowly. These data suggest that TBA may be a useful internal dose surrogate for MTBE, perhaps better than measurements of blood MTBE. It would be

very useful to reanalyze the epidemiological data, stratifying the subjects by blood TBA levels, as a marker for cumulative MTBE exposure.

To strengthen the present impressive data set on the potential acute health effects of MTBE exposure, additional targeted research studies would be advantageous. This should include additional pharmacokinetic studies to allow more adequate modeling of blood MTBE and TBA levels for various exposure scenarios. This will aid in linking the results of controlled human exposure studies to data from field epidemiological studies. The results of modeling of MTBE pharmacokinetics can then be used in designing additional controlled exposure studies directed at validating the pharmacokinetic models through variations in exposure concentration and duration and the level of exercise (ventilation) of the subjects. The controlled exposure studies can use a more targeted set of response indicators than the earlier studies to assess the potential for responses from longer duration exposures.

The present database clearly indicates a lack of response to the short-term exposures typically encountered by the general population. However, additional epidemiological studies focusing on occupationally exposed populations with measurements of both blood MTBE and TBA as indicators of internal dose would be useful in ascertaining any potential effects of longer term exposures to MTBE and in differentiating responses to MTBE from those arising from other fuel components found in the same environment. A key element of any future studies is to use an exposure-dose-response paradigm orientation with blood levels of MTBE and TBA serving to document the internal (or effective) dose for various exposure scenarios and to provide a mechanistic link to any possible MTBE-exposure related responses. Further, it should be noted that the experience gained with MTBE provides a "blueprint" for investigating exposure-dose-response relationships for other oxygenates, such as ETBE and TAME.

Session Five

CHRONIC HEALTH EFFECTS OF MTBE EXPOSURE[5]

Chair: Robert Drew, American Petroleum Institute

Discussant's Summary

John Doull, University of Kansas

Session Five focused on the chronic health effects of MTBE exposure and included presentations by Larry Andrews of ARCO Chemical on the chronic inhalation studies, Jeff Gift of EPA on RfCs, and Charlie Hiremath of EPA on cancer assessment for MTBE.

Dr. Andrews discussed the results of the cooperative oncogenicity study in rats and mice, and he presented preliminary data from a follow-on, 28-day study in male rats. The major finding was an increase in kidney tumors in the male rats, and there was considerable discussion within the presentation and in the subsequent discussion as to whether this MTBE effect met all of the EPA-recommended criteria for an alpha-2μ-globulin mechanism. Methyl tertiary butyl ether clearly meets most of the criteria, and some of the other agents that are thought to act through the alpha-2μ-globulin mechanism do not meet all of the EPA recommended criteria. Although there also was a dose-related increase in interstitial adenomas of the rat testis, the incidence range of these tumors was within the range of historical controls. Methyl tertiary butyl ether produced an increased incidence of hepatocellular tumors in mice, and there also was a dose-related increase in endometrial cell hyperplasia, but these effects occurred only at dosage levels that exceeded the maximum tolerated dose for MTBE. In his discussion of how the EPA might view this data, Dr. Hiremath stressed the need for a weight-of-evidence approach involving all tumor types in deciding whether a linearized multistage analysis and potency estimation should be made for MTBE. Dr. Doull urged the agency to use the actual incidence data from the Bushy Run study to calculate potency rather than the slope provided by a model that has multiple uncertainties and is hypothetical at best.

In describing the methodology used to establish the RfC for MTBE, Dr. Gift discussed neurologic/behavioral, reproductive, kidney nephropathy, and other noncancer endpoints that were considered by the EPA RfC Workgroup. The workgroup determined that the no-observed-adverse-effect level (NOAEL) was 403 ppm for increased liver and kidney weights and increased severity of spontaneous renal lesions in female rats and for prostration in female rats, along with swollen periocular tissue in both male and female rats. The lowest-observed-adverse-effect level for these effects was 3,023 ppm. After adjusting this value for the exposure duration, the NOAEL was divided by safety factors of 10 (for sensitive subpopulation), 3 (for interspecies extrapolation), and 3 (for database deficiencies)

[5]Copies of the slides for the presentations in this session may be found in Appendix E.

to obtain an RfC for MTBE of 1 ppm. This value can be compared to a threshold limit value (TLV) of 40 ppm that has been recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) and 100 ppm that has been adopted by the "WEEL" committee of the American Industrial Health Association, recognizing that these occupational levels are for an 8-h/5-day week, whereas the RfC is for a continuous life-time exposure.

During the discussion in response to a question about MTBE-induced endocrine effects, it was suggested that such effects may be from the tumors seen in the MTBE rats and mice, and it was pointed out that TBA (a metabolite of MTBE) has produced thyroid tumors in an National Toxicology Program study.

One of the most stimulating aspects of the discussion for this session was the dialogue between the public health officials who were asking for advice on what to tell their constituents and the scientists both within and outside the Agency who were challenged to assess the public health significance of their studies. The EPA scientists indicated that their evaluation of MTBE carcinogenicity is still in progress, but that it appears there is limited evidence in animals for this effect, and if MTBE is a possible human carcinogen, it is likely to have a very low potency.

In his opening remarks for this session, Dr. Drew pointed out the importance of this type of cooperative research effort to both industry and the Agency and his hope that this cooperative effort will serve as a model for similar ventures between industry, the regulatory bodies, and academia.

Session Six

NEW FINDINGS FOR OTHER FUEL OXYGENATES[6]

Chair: Randy Roth, ARCO

Discussant's Summary

Bernard Goldstein, Environmental and Occupational Health Sciences Institute

Session Six began with a reminder from Judith Graham of EPA that MTBE is only one of a large number of oxygenates that have been proposed for meeting the mandates of the Clean Air Act. Next, Randy Roth of ARCO Chemical provided information about U.S. oxygenated fuel production capacity. As of January 1, 1993, there are about 170,000 barrels per day of MTBE produced in the United States. For methanol, 120,000 barrels per day of MTBE are produced; and for fuel-grade ethanol, the number of barrels produced is approximately 90,000. There is far less TBA, ETBE, and TAME produced, the latter being produced in quantities of about 5,000 barrels per day. Among the physical characteristics, vapor pressure is critical: MTBE is about 7.8 to 8, ETBE is 4, TAME is 2.5 to 2, and ethanol is 2.3. The octane ranges from about 110 to 115.

Ethyl Tertiary Butyl Ether

Michael Wells, a toxicologist with Amoco, reviewed the existing data on ETBE. After briefly outlining acute toxicity studies that show ETBE's low toxicity, Dr. Wells presented the results of a subchronic study in Fischer rats sponsored by Amoco.

Ten rats of each sex per group were exposed to ETBE for 6 h/day for 5 days a week for a total of 4 weeks. Target exposure concentrations were 0 (for control), 500, 2,000, and 4,000 ppm ETBE. The parameters were mortality, body weights, and physical and clinical observations. There was a neurotoxicity assessment with a functional observation battery. Necropsies were performed on all the animals, and histopathology was performed on the controls as well as on the high exposure group.

None of the rats died during the study, and there were no treatment-related effects observed on body weights. In terms of clinical observations, animals exposed to 500 and 2,000 ppm generally showed no different signs than the control animals. However, during the exposure, the 4,000-ppm ETBE group did display treatment-related effects, which were primarily central nervous system (CNS) suppression, including general sedation, reduced motor activity, and mild-to-moderate ataxia. Within 15 min following termination of the exposure, the high exposure group appeared to return to normal, suggesting that ETBE is eliminated very rapidly.

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[6]Copies of the slides for the presentations in this session may be found in Appendix F.

Among the many endpoints of the functional observation battery performed for the neurotoxicity assessment, only high limb splay showed a significant difference from control. This occurred only in the 4,000-ppm group and was notable on Day 20. Also observed in the 4,000-ppm group, but this time on Day 5, was a significant decrease in body temperature in male animals. Other observations included an increase in white blood cell counts in female rats at 2,000 and 4,000 ppm, and some increase in organ weights at the higher exposure levels, which were not correlated with any specific histopathology.

Tertiary Amyl Methyl Ether

Health and ecological effect data on TAME were presented by Russell White, a toxicologist at Chevron who also chairs the API Air Fuels Health Effects Work Group. Dr. White pointed out the similarities and differences between TAME and MTBE. The same fluid catalytic cracking unit in a refinery that produces the equivalent of 2,000-barrels per day of MTBE could be used to produce about 2,500 to 3,000 barrels per day of TAME. The lower vapor pressure of TAME has advantages over MTBE in terms of the drive to lower the vapor pressure of gasoline to meet requirements related to the ozone standard.

The toxicological information available includes a pre-manufacturing test battery performed by Exxon Chemical, a 28-day inhalation toxicity study with neurotoxicity assessment by Amoco (identical to the study done on ETBE), and from API, some ecotoxicology studies, dermal sensitization studies, and odor and taste threshold studies.

Review of the single-dose acute study, the median lethal dose (LD_{50}) study, revealed that the signs and symptoms that are observed—ataxia hyperactivity, dyspnea, and the LD_{50} values—are comparable for both ETBE and MTBE. There is not a significant difference between males and females. There was no indication of dermal irritation or sensitization by TAME. Both an Ames test and a micronucleus study were negative.

A repeated-dose oral study was performed in which the animals were dosed 7 days a week for 29 consecutive days with doses up to 1g/kg. Food consumption and body weights were reduced in the high-dose males only. There were no effects in the female animals. In the males, though, two animals out of the 10 died, apparently in relation to exposure to the compound. The hematology and clinical chemistry were fairly unremarkable. There were no treatment-related histopathological findings in any of the tissues.

The repeated-dose study of TAME by inhalation used an identical test design to that reported earlier by Dr. Wells for ETBE, including identical measurement endpoints. There was mortality in the high-dose group: about 28% of the test animals at 4,000 ppm died. The clinical signs, including sedation, ataxia, hypoactivity, and hypothermia, were very similar to those observed with ETBE. Central nervous system effects that were observed immediately after exposure were transient, with the animals essentially back to normal the next morning. There was a decrease in body weight in high-dose males, whereas there was no effect with ETBE. Again, no histopathological findings were observed in the high-dose tissues. A small but significant increase in cholesterol levels was observed at the highest dose in both males and females.

The API has initiated some preliminary ecotoxicology studies in common test strains evaluating the effects of TAME on aquatic organisms. Using *Daphnea magnio*, a fresh water invertebrate, the no-observed-effect level (NOEL) for the test was 83 mg/L, with the actual interpolated EC_{50} as 100 mg/L, which can be considered essentially nontoxic. Preliminary results in the rainbow trout suggest a NOEL over 300 mg/L, indicating that TAME does not appear to be a particular problem in the fresh water vertebrate species. Biodegradation studies suggest that under anaerobic conditions, little biodegradation occurs, which is probably related to TAME being both an ether and a tertiary structure.

Based on a review of the physical characteristics and reactivity of TAME, Dr. White suggested that it was unlikely that human exposure levels would be higher than those observed for MTBE. He further suggested that the current evaluation of MTBE would be a useful base for formulating hypotheses to study TAME's potential toxicity.

Specific studies that were proposed included some 90-day repeat-dose studies focusing on the rat kidney and mouse liver. Pharmacokinetics and metabolism studies would particularly be of interest in understanding the extent to which the oxygenates persist in blood and how they are metabolized. A third suggested approach would be a combined reproductive/developmental study. Finally, based on other presentations at the meeting, Dr. White suggested that human studies would be lowest on his list, but would not be ignored. The smell of TAME is very similar to MTBE and some people find it even more objectionable. Although TAME has a lower vapor pressure, more of it must be used in gasoline to reach the same oxygen content. In addition, Dr. White remarked that it is unlikely TAME will be the only oxygenate in the gasoline. A blend of MTBE and TAME, or even with ETBE mixed in, would be more likely. Dr. White did not recommend a 2-year animal study of TAME.

Health Effects of Inhaled Ethanol

The health effects of inhaled ethanol were reviewed by Robert MacPhail, Chief of the Neurobehavioral Toxicology Group at EPA's HERL, and research professor at the University of North Carolina. There is a rich database on ethanol, although there is relatively much less information on inhalation than on ingestion. The targets of concern for ethanol are the CNS for acute and chronic effects, the developing fetus, and the liver.

In his review of the literature, Dr. MacPhail found 26 papers related to inhalation toxicology of ethanol in animals and humans. In humans, there are some old reports that include numbness and drowsiness following exposure to 3,000 to 9,000 ppm ethanol, and sensory irritation at 10,000 ppm ethanol, with 20,000 ppm ethanol considered to be intolerable by human volunteers. The acute CNS effects of ethanol begin with CNS stimulation, including excitement and hyperactivity, at low concentrations. At higher concentrations, depression is seen, accompanied by muscle relaxation, incoordination, and narcosis, which could lead to death by respiratory failure.

There are a variety of studies on hyperactivity and hypoactivity, reflex deficits, and performance impairments in animals exposed to ethanol. Recovery is ordinarily rapid and complete. Concentrations generally range from about 10,000 to 40,000 ppm, and durations

are generally several minutes to a few hours. There is evidence from studies of a variety of alcohols that the lipid-water partition coefficient is an important determinant of acute toxicity, further suggesting that it is a membrane effect of ethanol that is responsible for toxicity, at least in the nervous system.

Tolerance to a number of the acute CNS effects has been reported for ethanol, as well as cross-tolerance with other alcohols and with anesthetic agents. Most of the so-called chronic animal studies in the literature are relatively short term and have the goal of developing an animal model of ethanol dependency.

In humans, chronic ethanol use can produce severe central and peripheral nervous system effects, including the Wernicke-Korsakoff syndrome. Among the many other effects reported in humans is an increased susceptibility to a number of infections. The cancers that are associated with chronic ethanol exposure are usually limited to the oral cavity, to the pharynx, larynx, and esophagus.

Dr. MacPhail reviewed a long and useful compilation of individual studies showing the effects of chronic ethanol administration in a variety of organ systems. There is evidence that the acetaldehyde metabolite of ethanol may be important, particularly in chronic CNS toxicity.

There are good animal models of the fetal alcohol syndrome, which is characterized by growth retardation, by a small brain at birth, hypotonia, generally decreased body tone, cranial facial dysmorphology, and mental retardation. Initially, the fetal alcohol syndrome was considered to be a high-dose phenomenon, but as more was learned about the syndrome, it has become apparent that effects on the fetus can be seen in moderate-to-mild alcohol consumers during pregnancy.

Dr. MacPhail reviewed the work of B.K. Nelson, of the National Institute for Occupational Safety and Health, who evaluated occupational exposures to ethanol inhaled by rats for 7 h daily. No prominent developmental effects have been observed. There are data indicating some neurochemical changes in the offspring of rats exposed prenatally to inhaled ethanol, but the pattern of effects is that they are generally small and inconsistent.

Discussion

It was noted that the amount of information on MTBE is of an order of magnitude greater than that of ETBE or TAME, and the information on CO is of many orders greater than that of MTBE. The increase in oxygenate use this past winter, which resulted in health complaints leading to this meeting, was required by Congress to meet the CO standard. However, in almost all areas of the country that exceeded the CO standard, the only adverse effect of CO that can be considered to be scientifically demonstrable would be a shortening of time to angina attacks among the population of individuals with arteriosclerotic heart disease (i.e., angina syndrome) who have been shown to be at risk from this reversible effect. There is a comparative risk issue in determining whether it is appropriate to cause acute symptoms in one population, if this is in fact occurring, to protect another population. It is possible that no angina attacks were avoided in Alaska by MTBE, in view of the

relatively young population and the 8- to 12-h time to equilibration of CO levels with human hemoglobin. It is unlikely that many people with angina would be outdoors exerting themselves for 8 h during an Alaskan winter.

The almost complete lack of mixture studies also was pointed out, particularly the mixture of an oxygenate in gasoline to which humans would be exposed. Additionally, studies should address what the addition of an oxygenate to gasoline might do to dermal absorption of benzene. There was a call for more basic studies of mechanism of action as a necessary approach to introducing oxygenates to gasoline. Commentators from the floor provided additional information about the potential distribution of TAME, supported the call for pharmacokinetic studies and mixture studies, and emphasized that the database on human exposure was confined to healthy individuals rather than to those who were potentially susceptible.

Session Seven

CONFERENCE SUMMARY

Discussant's Summary

Gareth Green, Harvard School of Public Health

The risk assessment paradigm for analyzing problems in this very complex interdisciplinary field is well reflected in the organization of this conference. Science defined by this conference and other research work will provide a rational basis for managing risks posed by MTBE and other fuel oxygenates in the future. The purpose and goals of the workshop were to answer the following questions:

- What are the population exposures to MTBE?
- What are the health effects of acute exposures?
- Are reported symptoms due to ambient MTBE exposures?
- Is MTBE a cause of cancer?
- Does MTBE decrease CO at very low temperatures?
- What are the quantitative risks?
- What are the key risk factors (cold temperature, age, etc.)?
- Are follow-up studies needed?
- What are the risks of alternative oxygenates?

In her charge to the conferees, Dr. Graham focused on the relationship among epidemiological studies, clinical studies, and animal toxicology in the health effect analysis. There was much discussion on effects of acute exposures to MTBE from epidemiological studies and from clinical test exposures. Also discussed was the biological activity of MTBE in vitro. There was little information on structure—activity relations, a useful focus for exploring and analyzing greater or lesser risks of alternative oxygenates. There were extensive data on human exposure, particularly as to concentration and, to a lesser degree, on time of exposure; there were few data on the potential number of people exposed. Most of the focus was on recent experimental findings.

Adding MTBE to gasoline reduced CO concentration in proportion to the percentage concentration of MTBE, indicating a diluent effect rather than a chemical interaction. However, there is a variation in emissions, depending on engine design, vehicle age, engine size, operating conditions, and temperature effects, as shown by the cold-soak effect on increased CO emissions.

Several pieces of data showed rather striking progress in reducing CO in several communities over the last decade, primarily related to improvement in engine design and combustion technology. This decline in the community CO levels suggests that other approaches to CO control may be effective and may diminish the need for oxygenate additives; conversely, use of MTBE correlated with the reduction of CO exceedances in some communities, notably in Denver. Methyl tertiary butyl ether was noted to increase

carbonyls, aldehydes, and formaldehyde, which might account for some of the irritant symptomatology that has been reported. The Alaskan studies also pointed to alternate strategies for CO control—for example, the potential for engine preheating to reduce the cold-soak effect on CO emissions. Another possibility for CO control is to eliminate the 10% of vehicles responsible for 70% of pollutant emissions.

The exposure parameters from indoor/outdoor to occupational settings, in auto shops, and garages were laid out quite clearly (see Table 2). There appears to be a higher risk for significant MTBE exposure in closed spaces, compared with ambient levels. The data show that the pollutant levels of MTBE are worse in closed environments, such as residential garages, work places, service stations, and microenvironments in quasi-occupational settings. A higher proportion of time may be spent indoors in the winter months in Alaska than in cities in the lower 48 states. This time factor for exposure needs to be factored in to quantify chronic exposure values.

TABLE 2. Estimated Exposures to Methyl Tertiary Butyl Ether

	ppm
Indoor	0.001 - 0.01
Outdoor	0.001 - 0.1
Auto shop	0.1 - 0.5
Garage	0.1 - 1.0
Chambers	1.4 - 1.7
Gas fill-up	0.1 - 10.0 (Stage II↓)
Occupational	1.0 - 1000.0
	ppm × hours
Residence	20-41
Commute	52
Gas fill-up	13-26
Public garage	30
Outdoors	10
Auto shop	0.5

The studies using experimental chambers show where the human experimental exposure model fits into this scale. It is very difficult to quantify the range of the gas fill-up exposure, due to high variation. For example, instances of gasoline spillage at the pump may increase the risk of dermal, as well as respiratory tract, absorption. There has been much progress in controlling vapor release at the pump, as shown by the data on vapor concentration reduction

at pumps employing Stage II vapor recovery. However, there are still huge variations in MTBE exposure concentrations that occur in specialized occupational settings. Despite the proposed reduction of the ACGIH TLV, there still are opportunities for massive exposures over short periods of time, which should be examined more carefully to understand the potential toxicity of this or related substances.

Introduction of the time factor into the exposure equation almost reverses the rank order of total exposure to MTBE in comparative settings, raising many questions about the relative significance of peak exposures versus chronic low-level exposures. We need to know how well humans metabolize and excrete MTBE at low levels of exposure and whether there may be an exceedance of a threshold in a short-term, high-concentration exposure.

The epidemiologic studies and the clinical tests do not document a risk for serious illness with acute short-term exposure. The availability of a blood biomarker that correlates with exposure concentration allows the epidemiologic studies to minimize the exposure/dose variable. Future studies of this and related agents ought to include biomarker measures where available. Two of the epidemiological studies reported a significant correlation of some key symptoms at the high end of exposure to MTBE, one study in the cold climates of Alaska, and the other in the milder temperatures of Connecticut. In contrast was the study that failed to find differences in symptoms in comparative populations in neighboring New Jersey. A third study showed no effect of MTBE exposure on health insurance claims, as may be seen in air pollutant episodes. However, this indicator may be neither highly sensitive nor highly specific.

The clinical experimental exposures showed no symptomatic effects of 1 h of MTBE exposure at 1.4 and 1.7 ppm, yielding 16 to 20 μg MTBE/L of blood. The strengths of the clinical studies were in using controlled exposures, using a dose biomarker, and using both subjective and objective measures of effect (a significant contrast to some of the epidemiological studies). In addition, the findings were reproduced in two different exposure studies with consistent results.

Despite all their strengths, both types of human studies have limitations. There were design flaws in the epidemiological studies, difficulty with sensitivity and specificity of the symptomatic indicators of effect, lack of simultaneous exposure measurements, the bias of self-selection, and psychological and economic confounders. Limitations in the clinical studies include a lack of a dose range, a relative lack of an age range in comparison with the community epidemiological studies, and lack of simultaneous co-exposures. The epidemiological studies took place in complex work environments with people working hard and exposed to other stresses and agents with similar symptomatic effects. The clinical studies comprised a single brief exposure of 1 h to the agent in question.

Chronic health effects of MTBE are unknown for humans. In animals, the pathologic potency of MTBE is relatively low, with increased mortality and nephro-pathology only at very high ranges (3,000 to 8,000 ppm) in rats and mice. Testicular, liver, and kidney tumors, as well as the other pathologic findings, seemed to reflect exacerbations of endemic disease rather than the production of new types of cancer.

In a variety of in vitro tests, MTBE is nongenotoxic and nonclastogenic. The RfC for continuous human exposure is 3 $\mu g/m^3$. The limit value for the workplace exposure is currently being modified. Human carcinogenicity at this point is indeterminant, although an evaluation is in process.

Other fuel oxygenates (e.g., TAME) are under development. Their lower vapor pressure values may bring the benefit of lower exposures to tank evaporations and evaporations in the course of pumping gasoline.

Conclusions

1. The association of reported symptomatology with MTBE use in the community was documented in some epidemiological studies but not in others reported at this meeting. A precise exposure-response relation sufficient to invoke causality was not demonstrated.
2. Methyl tertiary butyl ether does not cause symptoms or objective changes at the dose and durations tested in the human experimental studies. The challenging task facing the assessment of risk from MTBE exposure is how to resolve the differences among the several epidemiological studies and between the clinical and the epidemiological findings. Although not conclusive, the data bear sufficient validity to accept both sets of findings at this point and consider how to come to terms with those conflicts.
3. Co-factors may influence the symptomatic responses in the field studies. In Alaska, the economic cost of increased fuel prices, the negative attitude toward government intervention, and general anxiety in the community, suggest that significant co-factors influenced the response in some of those field studies.
4. Methods are available to measure exposure, dose, and response in systematic studies. Any future studies should be required to incorporate those methodologies for assessment of these exposures.
5. Chronic health effects have not been demonstrated by the data. From a synthesis of the animal data and the kinds of findings and lack of findings in the acute exposures, one can reasonably conclude that chronic effects are unlikely at ambient exposures.
6. Future initiatives, to assess health risks of alternate oxygenates or other additives, are to pursue preventive strategies by using the understanding and methodology that now exist.

Unanswered Questions

1. What accounts for the differences in the conclusions between the clinical tests and the epidemiological studies?
2. What is the human dose response?
3. What are the net health benefits of the oxygenates?
4. Are there susceptibility factors such as age, working conditions, work stress, etc., to explain the difference in the epidemiological studies and the clinical studies?
5. What are the risks of other oxygenates?
6. What are the mechanisms of the noncarcinogenic, biological, and health effects?
7. Are the emissions and ambient data adequate?
8. What is the influence of psychological factors on health effects in humans?
9. What is the effect of mixed exposures on the response to MTBE?

10. Finally, what is the comparative risk of MTBE and CO at the measured levels of exposure?

Discussion

A member of the audience from the State of Colorado stated that Colorado believes that oxygenated gasolines are a very effective method of reducing CO pollution. This last winter, the Colorado Department of Health believes that CO tailpipe emissions were reduced by approximately 25%, which translates into a reduction of approximately 5 days this last winter that the City of Denver did not violate the CO standard. It is believed that this one program gave an incremental benefit such that 50% of CO exceedance days were prevented. It also is believed that CO is a health threat, even at 9 ppm, for some groups of people, and that there is a health benefit even going below 9 ppm. Although Colorado advocates the use of a variety of clean gasolines, MTBE is just one of those gasolines. It is felt that giving the consumer a choice of fuel diversification played a large role in the major public acceptance of the Colorado program. Gasoline is composed of hundreds of different components, 90% of which have not undergone the same scrutiny as MTBE; and it is suggested that not only MTBE be subject to this battery of testing, but there are many other components in gasoline that need to be subjected to the same level of scrutiny.

Another speaker noted that the big issue in Fairbanks is the cold temperature effects and that none of the experimental health studies were done at the temperatures of Fairbanks. Cold start emissions are a large source of CO; during the first 1 to 2 min of the operation, CO can be as much as 8 to 10%. This indicates that a lot of uncombusted fuel is getting through. The question is how much MTBE gets through in those first 1 to 2 min in Fairbanks when people start their cars. A calculation assuming an air to fuel ratio of about four to one, which is reasonable for the first 1 or 2 min of operation during a cold start, and assuming that none of the MTBE was combusted, indicates there would be 5,000 ppm coming out of the tailpipe. This raises the question of what would be the effects on somebody at a gas station breathing 5,000 ppm for maybe even two or three breaths at −40 °F, especially if they are breathing 8% CO at the same time. Also, what are the toxicity and cancer effects of just fuel alone compared to that of MTBE?

In response to the last question, a speaker noted that unleaded gasoline has been tested in similar studies in rats and mice, and the rat kidney tumor and the mouse liver tumor are issues in exposures to unleaded gasoline also. Furthermore, it was noted that the Chemical Industries Institute of Toxicology has done a lot of work on those findings and has come up with a lot of information on the cancer mechanisms. In addition, there has been an extensive 10-year sequence of animal studies and several large epidemiology studies of both distribution workers and refinery workers associated with the manufacture of gasoline. The carcinogenic risk was considered essentially minimal, with the exception of aromatics and, specifically, benzene. This speaker also asserted that it was premature to draw a conclusion that MTBE is associated with symptoms at high doses based on the epidemiologic findings, for although there is some suggestive evidence of effects in a few studies, the MTBE biomarker could be equally correlated with total hydrocarbon exposures associated with sitting next to vehicles or refueling vehicles.

It was noted that the negative findings of the New Jersey study should be viewed in light of the difficulty of assuring an effective partition of automobiles by north and south due to the north/south traffic in New Jersey. On the other hand, air and personal monitor samples were collected and a subset of those people who had the highest exposure were compared to the people who had the lowest exposure, with no statistical difference in symptoms.

One commentator encouraged the EPA, perhaps in conjunction with the National Institute for Occupational Saftey and Health, to establish a round-robin testing program for MTBE and other oxygenated fuels, because of the analytical problems associated with MTBE or other oxygenated fuels in complex hydrocarbon environments. It also was recommended that concurrent monitoring be available for additional aromatics, such as benzene, when these studies take place.

A speaker noted that comparative risk assessments are needed to develop intelligent, useful, and good public policies. The information provided at this meeting was helpful, but there are many important areas that were not addressed and therefore cannot be used to draw conclusions about the public policies related to use of MTBE. For example, little was presented on the potential increase in emissions of aldehydes from the use of MTBE, which could be related to some of the symptoms seen in Alaska. The possibility that aldehydes are increased might provide the kind of exposure that produces a secondary effect from the use of MTBE as opposed to an effect of MTBE itself. Also, there were very few data on the potential levels of exposure in the microenvironment of the motor vehicle itself. Previously, studies on CO in Anchorage, where individuals drove through traffic for short periods of time, showed excursions of CO levels 50 times higher within the vehicle than in ambient air at an intersection. So, very high levels of CO could be transiently experienced.

In response to a question about the regulatory use of the RfC and its relationship to the recommended TLV, an EPA representative responded that EPA believes that exposure of people for a lifetime to MTBE at the level of the RfC will not have a significant risk of noncancer adverse effects. This form of a dose-response assessment needs to be interpreted as part of a risk characterization, which in turn is used to create policy. In the risk assessment of MTBE, the RfC is used to characterize the risks of chronic noncancer health effects, but is interpreted in light of an exposure assessment. The RfC is very different from the TLV because TLVs are intended to protect workers specifically, whereas RfCs are intended to protect the entire population. The primary difference is the TLVs deal with a 40-h work week, whereas RfCs deal with a continuous 24-h/day, 7-day/week community exposure. The RfC is also intended to protect sensitive subpopulations and adds another uncertainty factor to account for those populations.

Another speaker noted a need for vehicle test protocols appropriate to local conditions—not just with respect to temperature, but also in terms of the way the vehicles are actually used and driven. Also, from a public health standpoint, no one has yet addressed the effects on the very young, the very old or, in some way, the very sick, in addition to very cold temperatures and some of the other climatic differences that occur in Alaska. Such susceptibility factors remain an unknown at this time.

A commentator noted that EPA's Total Exposure Assessment Methodology (TEAM) studies routinely found that aldehyde levels—formaldehyde and acetaldehyde—are higher indoors than outdoors, as is benzene. This raises the question of why carboxyhemoglobin levels are higher in some residents of Fairbanks and the possibility there is an indoor source of CO, such as kerosene heaters or attached garages. Another speaker added that 40 ppm for the CO TLV is a recommended value that is still at the committee level; it is not an adopted value.

Some discussion was devoted to Dr. Green's conclusion about a correlation of symptom reports with the high exposure groups in occupational settings. A CDC scientist addressed this issue by noting that "there was a small association[7] between being in the upper quartile [of blood MTBE levels]..... and being more likely to report symptoms."

It also was noted that, starting in 1995, reformulated gasoline will be required in O_3 nonattainment areas, and there is a congressional mandate to have an oxygen content of 2.0% in that gasoline. So the issue of oxygenates will not go away.

[7]A subsequent published report of the CDC/Alaska study by Moolenaar et al. (1994) states that there was "a relationship between the highest quartile of blood MTBE concentrations and key health complaints on the day of testing, but this finding was not statistically significant." A similar analysis of data from workers in the CDC/Stamford, CT, study indicated a statistically significant association.

APPENDIX A

SESSION ONE: SPEAKER ABSTRACTS AND PRESENTATIONS

AUTHOR(S): William Piel (ARCO Chemicals)

TITLE: HISTORICAL PERSPECTIVE ON USE OF ETHERS IN FUELS

NO ABSTRACT SUBMITTED

OVERVIEW OF

FUEL OXYGENATE DEVELOPMENT

BY
WILLIAM J. PIEL

ARCO CHEMICAL COMPANY

PRESENTED AT
WORKSHOP ON MTBE AND OTHER OXYGENATES
AN UPDATE OF HEALTH RISK RESEARCH
FALLS CHURCH, VA.
JULY 26-28, 1993

OVERVIEW OF FUEL OXYGENATE DEVELOPMENT

ALCOHOLS AS LOW COST GASOLINE EXTENDERS

ETHERS AS LEAD-OCTANE REPLACEMENT

WORLD-WIDE MTBE PRODUCTION GROWTH

PRE-CAA OXYGENATED FUELS PROGRAMS

MTBE IN EUROPEAN GASOLINES

VEHICLE EMISSION BENEFITS

ARCO CHEMICAL COMPANY, JULY 1993

FUEL OXYGENATE DEVELOPMENT

ORIGINALLY DEVELOPED AS ALTERNATIVE TO $30/BBL CRUDE

T-BUTYL ALCOHOL COMMERCIALIZED IN 1969
SOLD AS GASOLINE COMPONENT (GTBA)

US GOVERNMENT SUBSIDY FOR 10% BIO-ETHANOL IN 1978

METHANOL / COSOLVENT BLENDS COMMERCIALIZED IN 1981

MANY ALCOHOL BLENDS DISCONTINUED IN 1986 WITH $15 CRUDE

MTBE EXPANDED WITH U.S. LEAD PHASEDOWN IN 1985-87

ARCO CHEMICAL COMPANY, JULY 1993

WHAT IS MTBE ?

METHYL TERTIARY BUTYL ETHER - OCTANE ENHANCER

HI-OCTANE ALTERNATIVE TO LEAD AND AROMATICS

MTBE FIRST COMMERCIALLY USED IN EUROPE (1973)

US PRODUCTION IN 1979 AFTER EPA WAIVER APPROVAL

ORIGINALLY ALLOWED AT 7 VOL % IN GASOLINE

LIMIT RAISED TO 11% IN 1981, THEN 15% IN 1988

EUROPE SET EEC STANDARD OF 15% IN 1985

RECENT INTEREST HAS BEEN ENVIRONMENTAL

LARGEST BENEFIT IS REDUCING "CO" EMISSIONS

HELPS REDUCE MOBILE SOURCE VOCs, NOX, TOXICS & PM-10

DILUTES GASOLINE SULFUR CONTENT FOR LOWER SOX

ARCO CHEMICAL COMPANY, JULY 1993

MTBE AND OTHER ETHER PRODUCTION

MADE BY COMBINING ISOBUTYLENE AND METHANOL

- REACTION IS HIGHLY SELECTIVE, MINIMAL BY-PRODUCTS
- DI-ISOBUTYLENE, TRI-ISOBUTYLENE & T-BUTYL ALCOHOL

THREE MAIN SOURCES OF ISOBUTYLENE

- BY-PRODUCT OF REFINERY FLUID CATALYTIC CRACKERS
- ISOBUTANE DEHYDROGENATION
- DEHYDRATION OF T-BUYTL ALCOHOL FROM ISOBUTANE OXIDATION

ETBE : ETHER ALTERNATIVE TO MTBE

- COMBINE BIO-ETHANOL AND ISOBUTYLENE

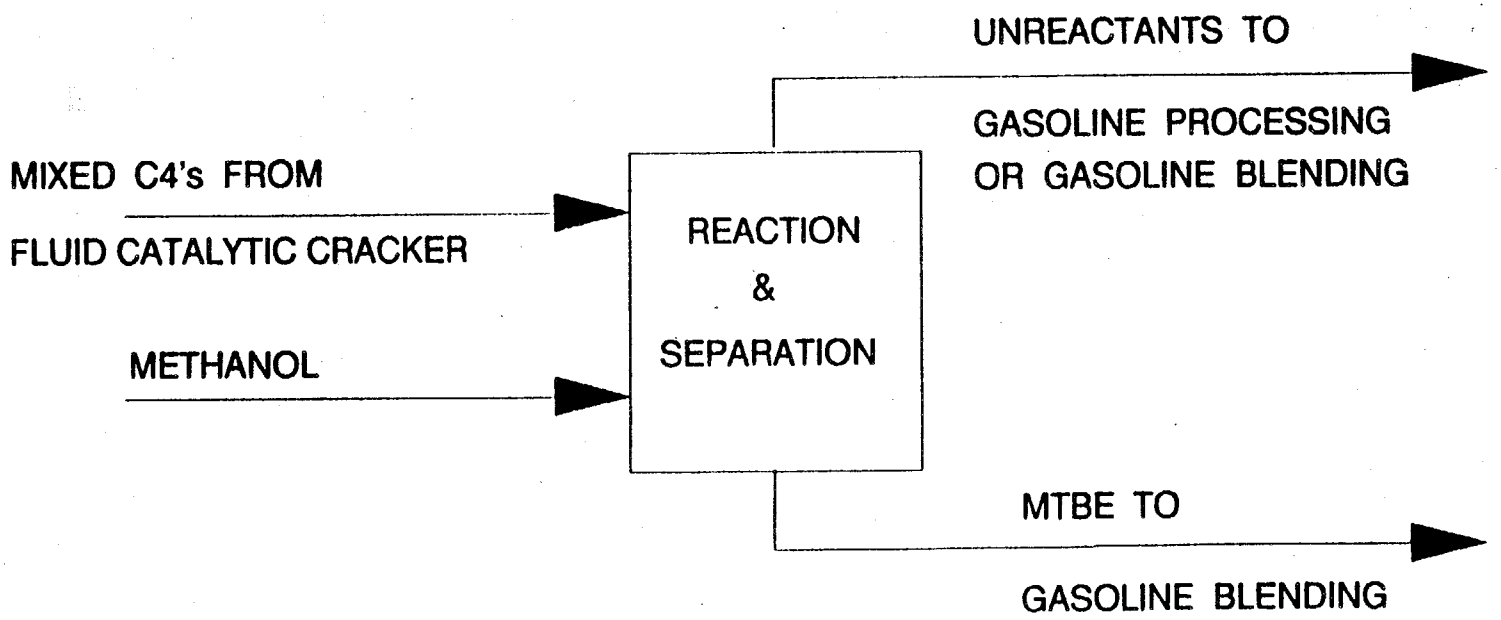
TAME : COMMERCIAL ETHER PRODUCED IN REFINERIES

- COMBINE REFINERY ISOAMYLENE WITH METHANOL

ARCO CHEMICAL COMPANY, JULY 1993

REFINERY MTBE PRODUCTION

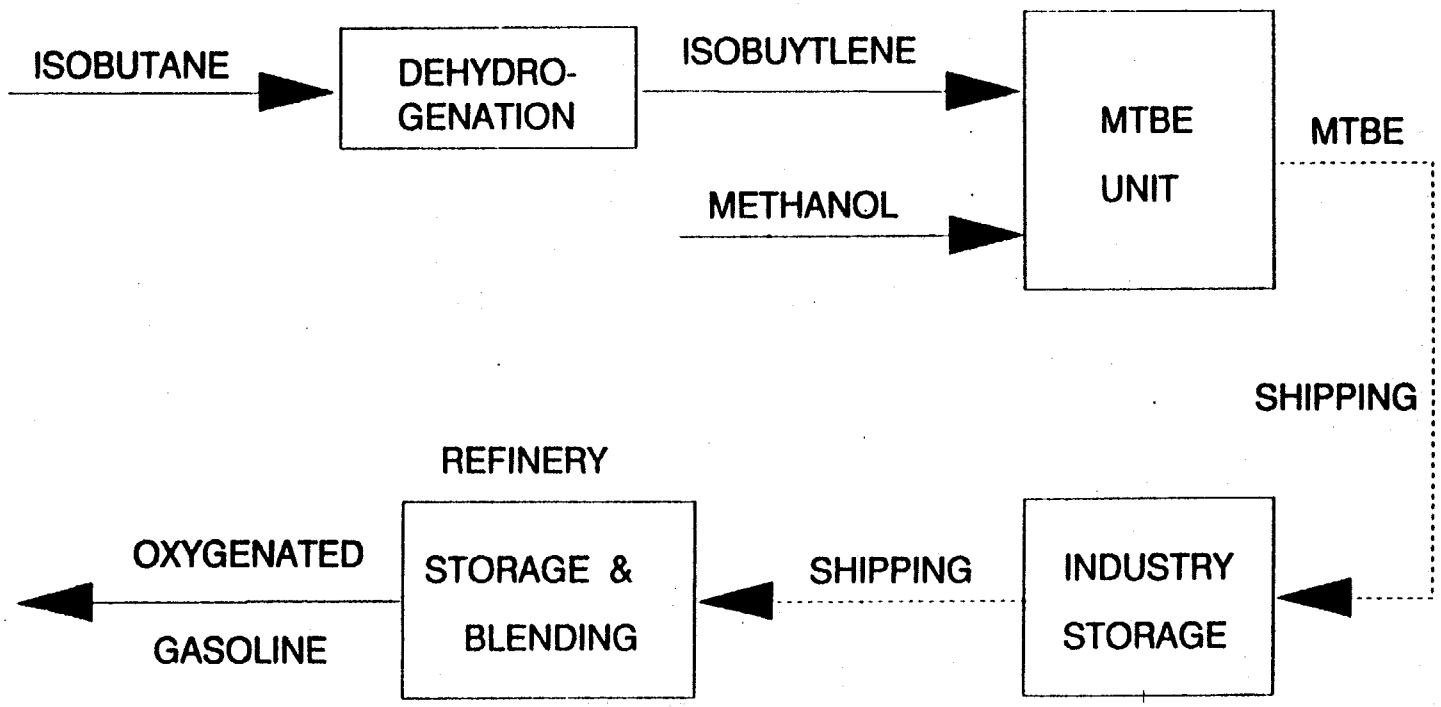
ISOBUTYLENE SELECTIVELY REACTED FROM C4 HYDROCARBON MIXTURE



ARCO CHEMICAL COMPANY, JULY 1993

BUTANE BASED MTBE PRODUCTION

FOR COMMERCIAL SALES



ARCO CHEMICAL COMPANY, JULY 1993

WORLD MTBE EXPANDED GREATLY SINCE MID 1980'S

	NUMBER OF PLANTS	YEAR END CAPACITY M BBLS/DAY	YEAR END CAPACITY MM GAL/YR
1980	5	19	290
1985	19	49	750
1990	78	232	3500
1992	117	367	5600
1995 ESTIMATED	186	600	9200

ARCO CHEMICAL COMPANY, JULY 1993

YEARS OF EXPERIENCE WITH OXYGENATED FUEL PROGRAMS

WINTER-TIME MINIMUM OXYGEN STANDARDS - WT % OXYGEN *

WINTER SEASON	COLORADO	ARIZONA		NEVADA	
		PHOENIX	TUCSON	LAS VEGAS	RENO
87/88	1.5				
88/89	2.0				
89/90	2.6	2.3		2.5	2.0
90/91	2.6	2.3	1.8	2.6	2.0
91/92	2.6	2.7	1.8	2.7	2.7
92/93	2.7	2.7	1.8	2.7	2.7

* 2.7 % OXYGEN EQUAL TO 15 VOL % MTBE

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MTBE USE IN EUROPEAN GASOLINES

"CITY" GASOLINE INTRODUCED IN FINLAND

- STARTED MAY 1991 BY NESTE OY
- 2 WT % OXYGEN USING 11% MTBE
- REPRESENTS 80% OF GASOLINE IN FINLAND

MTBE IN MOST PREMIUM GASOLINES THROUGHOUT EUROPE

- OCTANE ALTERNATIVE TO LEAD & AROMATICS

ONLY 15% OF CARS HAVE CATALYST & VAPOR RECOVERY

- CAR EMISSIONS 5 TO 10 TIMES GREATER THAN U.S. CARS
- ABSOLUTE EMISSIONS REDUCTIONS EVEN GREATER WITH MTBE

ARCO CHEMICAL COMPANY, JULY 1993

MTBE'S NET IMPACT ON VEHICLE EMISSIONS *

FTP EMISSIONS			% CHANGE
CO			(17)
VOC s			(6)
NOx			(3)
SOx			(15)
TOXICS (mg/mile)	BASE	+MTBE	(18)
BENZENE	57	47	
BUTADIENE	6.7	5.7	
FORMALDEHYDE	7.7	9.2	
ACETALDEHYDE	4.2	3.7	
POM (PM-10)	3.1	2.8	

* EPA'S COMPLEX PREDICTIVE MODEL FOR REFINERY BLENDING OF 15% MTBE

ARCO CHEMICAL COMPANY, JULY 1993

SUMMARY

MTBE AND BIO-ETHANOL ARE TODAY'S MAIN OXYGEN OPTIONS

FUTURE OPTIONS LIKELY INCLUDE TAME & ETBE

ONE OF THE MOST WIDELY PRODUCED PETROCHEMICALS

MTBE NOW IN COMMERCIAL USE FOR 20 YEARS

OXY FUEL PROGRAMS DEMONSTRATED FOR 3 YEARS PRIOR TO CAA

USE OF MTBE HELPS REDUCE MAJOR AIR POLLUTANTS

CONTRIBUTES TO REDUCTIONS IN SIX CRITERIA POLLUTANTS

LEAD, CO, OZONE, NOx, SOx & PARTICULATES

ARCO CHEMICAL COMPANY, JULY 1993

APPENDIX B

SESSION TWO: SPEAKER ABSTRACTS AND PRESENTATIONS

AUTHOR(S): Kenneth T. Knapp

TITLE: COLD TEMPERATURE MTBE DYNAMOMETER STUDY

ABSTRACT

Several research questions have emerged while implementing the wintertime oxygenated fuel program in Alaska. These questions are: (1) does the cold temperature increase CO emissions; (2) does MTBE decrease CO emissions; and (3) is MTBE safe? This paper addresses the first two questions.

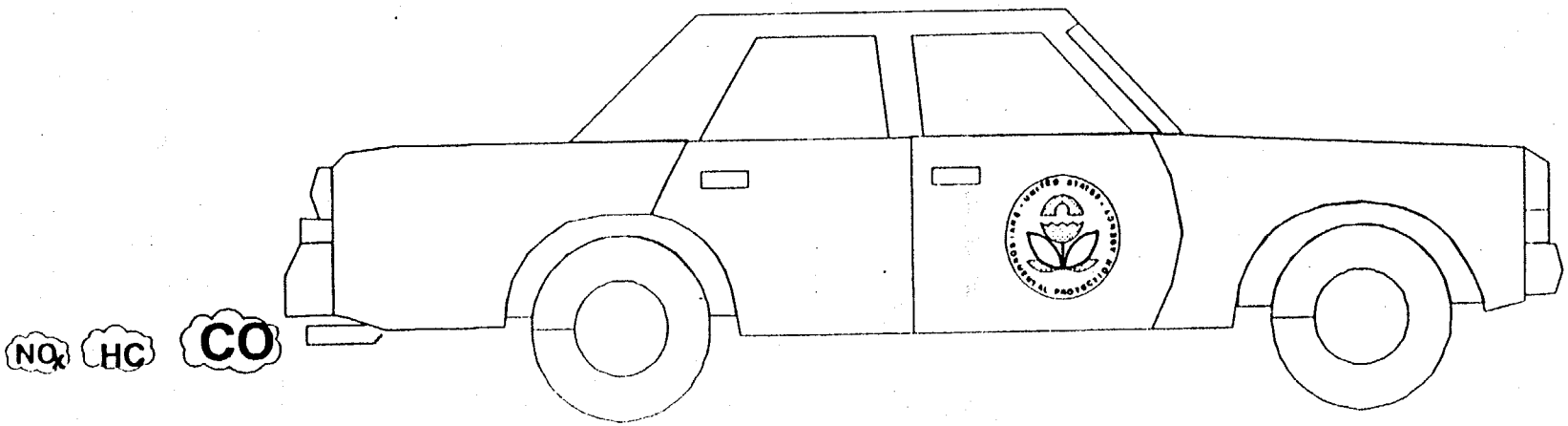
Little or no data existed on the effects of temperature and MTBE on CO emissions at very low, or subzero, temperatures. The Mobile Sources Emissions Research Branch (MSERB) of the Atmospheric Research and Exposure Assessment Laboratory (AREAL) had studied effects at temperatures down to 40°F. To assist in evaluating these problems, MSERB ran Federal Test Procedures (FTP) on a 1984 Buick Century V-6 carburetored car with two fuels: (1) a base fuel and (2) a base fuel with 15% MTBE added (the vapor pressure and octane of the MTBE fuel were adjusted to that of the base fuel) at temperatures of 75, 40, 20, and 0°F. This vehicle had been tested with other MTBE fuels at temperatures down to 40°F. The results of these tests indicated that there was a major increase in CO emissions when temperatures decreased: MTBE reduced the increases of CO emissions. However, at 0°F, the CO emissions with MTBE fuel were still 3.5 times higher than that at 75°F for either fuels. Fuels with lower levels of MTBE gave smaller decreases in CO emissions. Thus, the decrease in CO emissions appears to be MTBE-concentration-dependent.

The next phase of the study was to develop a test program for testing a fleet of vehicles at low temperatures. A protocol was developed including a fleet of test vehicles that is similar to the vehicle distribution in Fairbanks, Alaska. The fleet consisted of 10 vehicles: five cars and five light duty trucks (including a four-by-four truck). The vehicles are currently being tested at 75, 20, 0, and -20°F, with the FTP in the MSERB cold cell dynamometer and in the Environment Canada cold cell. Half of the vehicles are fueled with carburetors and half with fuel injection. Two of the vehicles are identical, one pair is fueled by carburetors, and the other pair by fuel injection. One set is being tested at MSERB and the other set is being tested at Environment Canada. Two fuels are being tested, one base fuel having specifications of those used in Fairbanks, and the second with about 15% MTBE added. The MTBE content turned out to be only 12.5%. The vapor pressure and octane were adjusted for the MTBE fuel to match that of the base fuel. MSERB provided Environment Canada with the two fuels. Emissions analyses included regulated emissions, CO, NO_x, HC, and CO_2, both real time and integrated, and speciated organics including over 250 HC, aldehydes, ketones, and MTBE. Both real-time monitors and FTIR are being used. Temperatures of the cell and vehicle oil, coolant, and catalyst are also being continuously measured during the FTP.

Results to date indicate there is a strong dependence of CO emissions on temperature, with the CO emissions increasing when temperatures decrease. With some vehicles, there are advantages in using MTBE while others show no differences. The data show that the change in CO emissions are dependent on several other factors including fuel composition, full vapor pressure, and vehicle type. These results of multi-dependency agree with those found in the Auto/Oil Air Quality Improvement Research Program sponsored by the auto and oil industries.

MOBILE SOURCE EMISSIONS RESEARCH

COLD TEMPERATURE MTBE DYNAMOMETER STUDY



by Kenneth T. Knapp

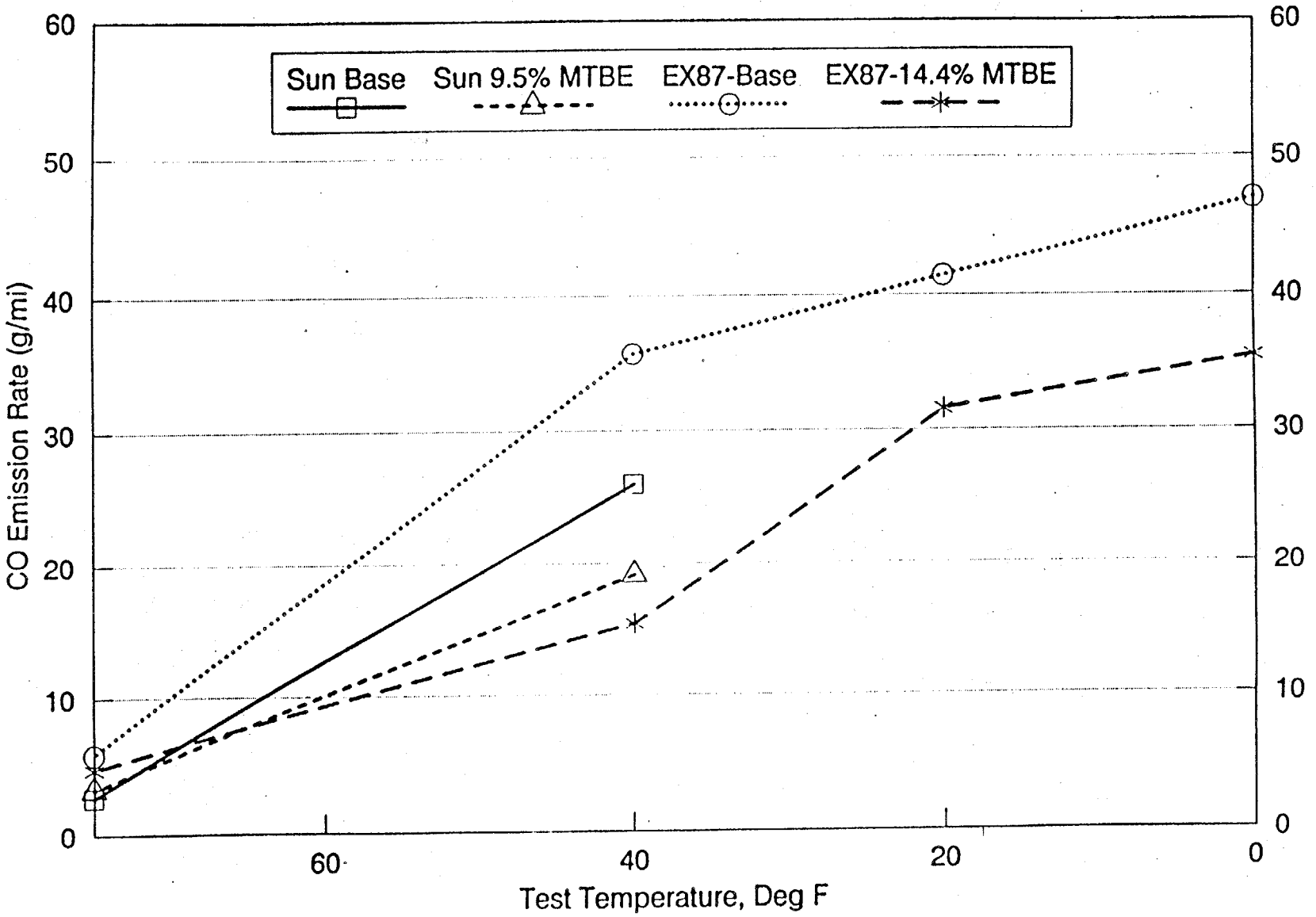
TEST CONDITIONS

STUDY	TEST VEHICLES	FUELS	TEMPERATURES °F	TEST CYCLES
Phase I	Buick Century	Exxon 87 Base	75,40,20,0	FTP, I/M240
		Exxon 87 MTBE	75,40,20,0	FTP, I/M240
		Sun Base	75,40	FTP
		Sun MTBE	75,40	FTP
Phase II	Fleet	Alaska II Base	75,20,0,-20	FTP, I/M240
		Alaska II MTBE	75,20,0,-20	FTP, I/M240

Table I

Proposed Low Temperature MTBE Test Fleet

Year	Make	Model	Engine Type	Engine Size	Fueling Sys	Drive wt	HP	Dyno Set
84	Buick	Century	V-6	3.0L	Carb 2V	FWD	3280	11.9
86	Chev	Monte C	V-8	5.0L	Carb 4V	RWD	3750	9.6
87	Chev	Caprice	V-8	5.0L	Carb 4V	RWD	4000	9.7
92	Chev	Corsica	V-6	3.1L	MPFI	FWD	3250	6.5
92	Chev	Corsica	V-6	3.1L	MPFI	FWD	3250	6.5
90-2	Toyota	Corolla	I-4	1.6L	MPFI	FWD	2750	8.3
91	Dodge	Pick-up	V-6	3.9L	TBI	RWD	4750	16.5
87	Chev*	Blazer	V-6	2.8L	TBI	4x4	3875	12.0
84	Chev*	S-10 LDT	V-6	4.3L	Carb 2V	RWD	3500	11.7
84	Mazd*	pick-up	I-4	2.2L	Carb 2V	RWD	3000	11.4



1984 Buick Century operated on fuels with varying levels of MTBE

FUEL SPECIFICATIONS

FUELS	Ex87 Base	Ex87 M	Sun B	Sun M	Alaska II B	Alaska II M
OCTANE	87	87	87.8	88.8	87.0	88.6
RVP	13.3	10.8	9.0	8.9	14.5	15.5
T90	343	367	346	294	321	298
COMP vol %						
MTBE	1.1	14.4	0	9.5	0	12.1
Benzene	1.0	0.9	1.4	1.5	1.4	0.9
Aromatics	31.1	30.1	38.0	23.8	25.6	19.7
Olefins	12.5	10.1	9.5	11.3	15.4	9.6
Paraffins	53.1	41.4	51.4	54.6	57.1	59.8

MEASUREMENTS IN MTBE STUDY

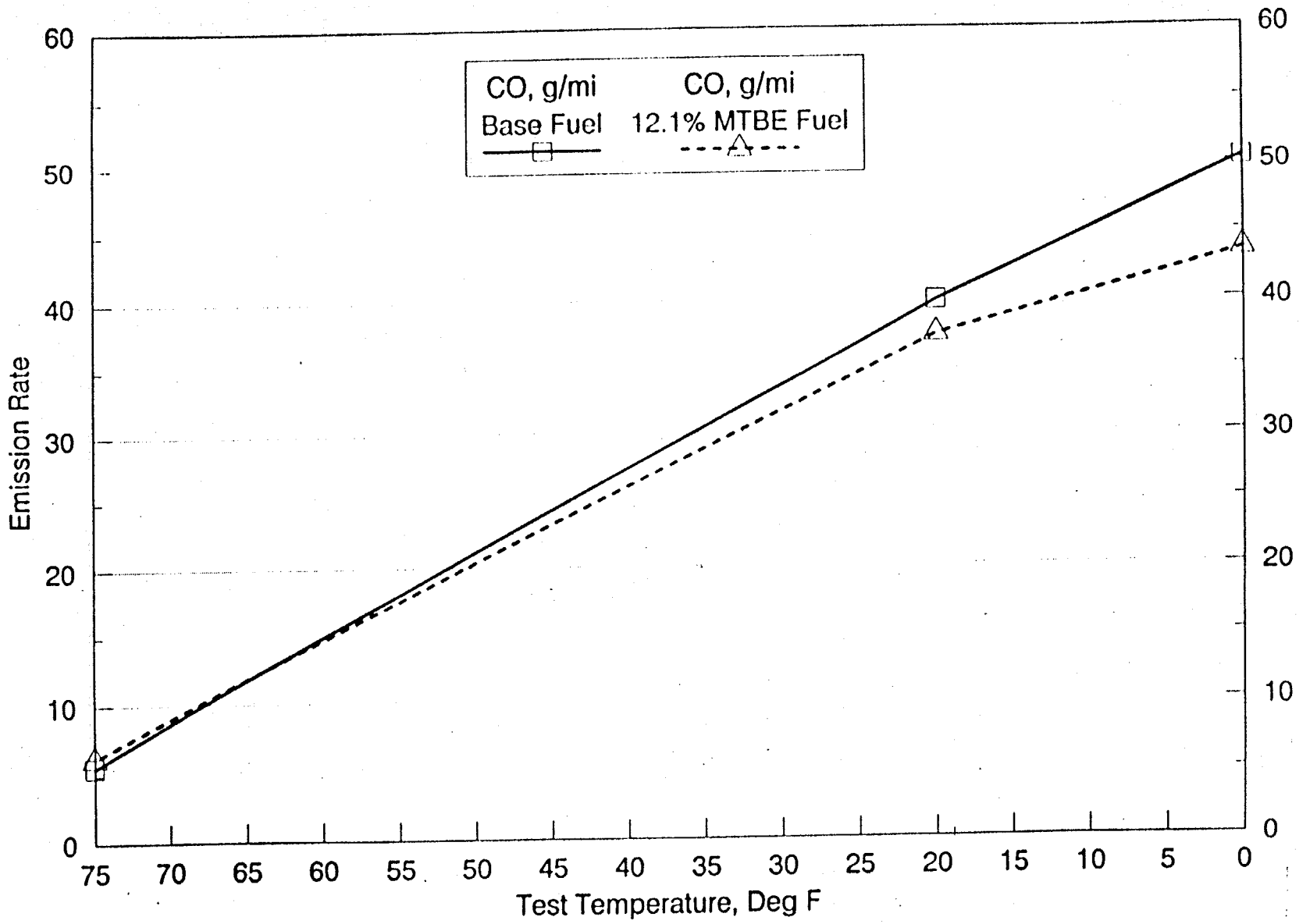
TEMPERATURES

- Vehicle Oil
- Vehicle Coolant
- Dynamometer Cell
- Catalyst, before and after

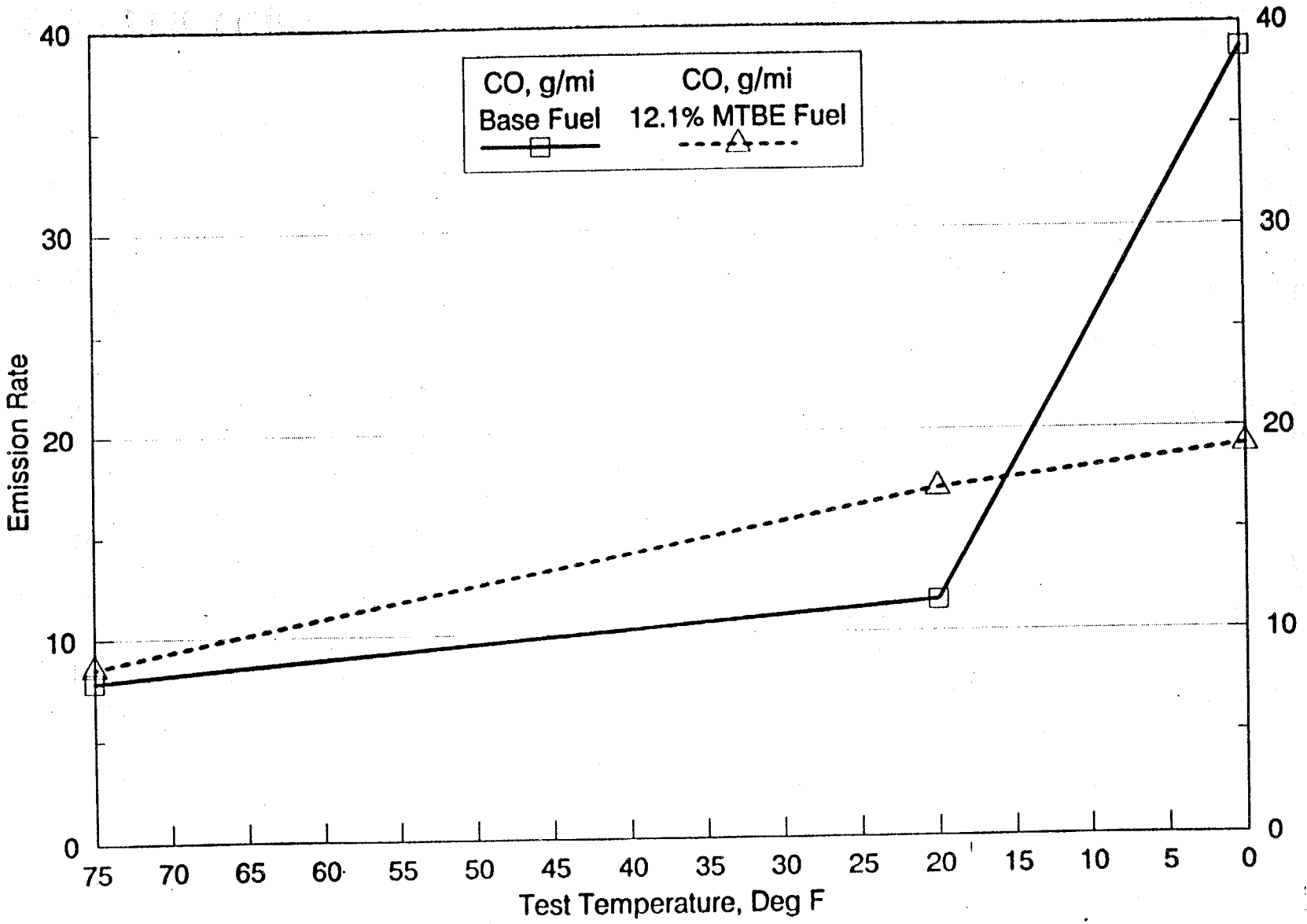
CHEMICAL ANALYSES

- Regulated emissions (CO, NOx, Total Hydrocarbons, and CO_2)
  - Real Time - Bench Monitors and FTIR
  - Integrated Bag Samples (Bags 1, 2, 3, and 124)

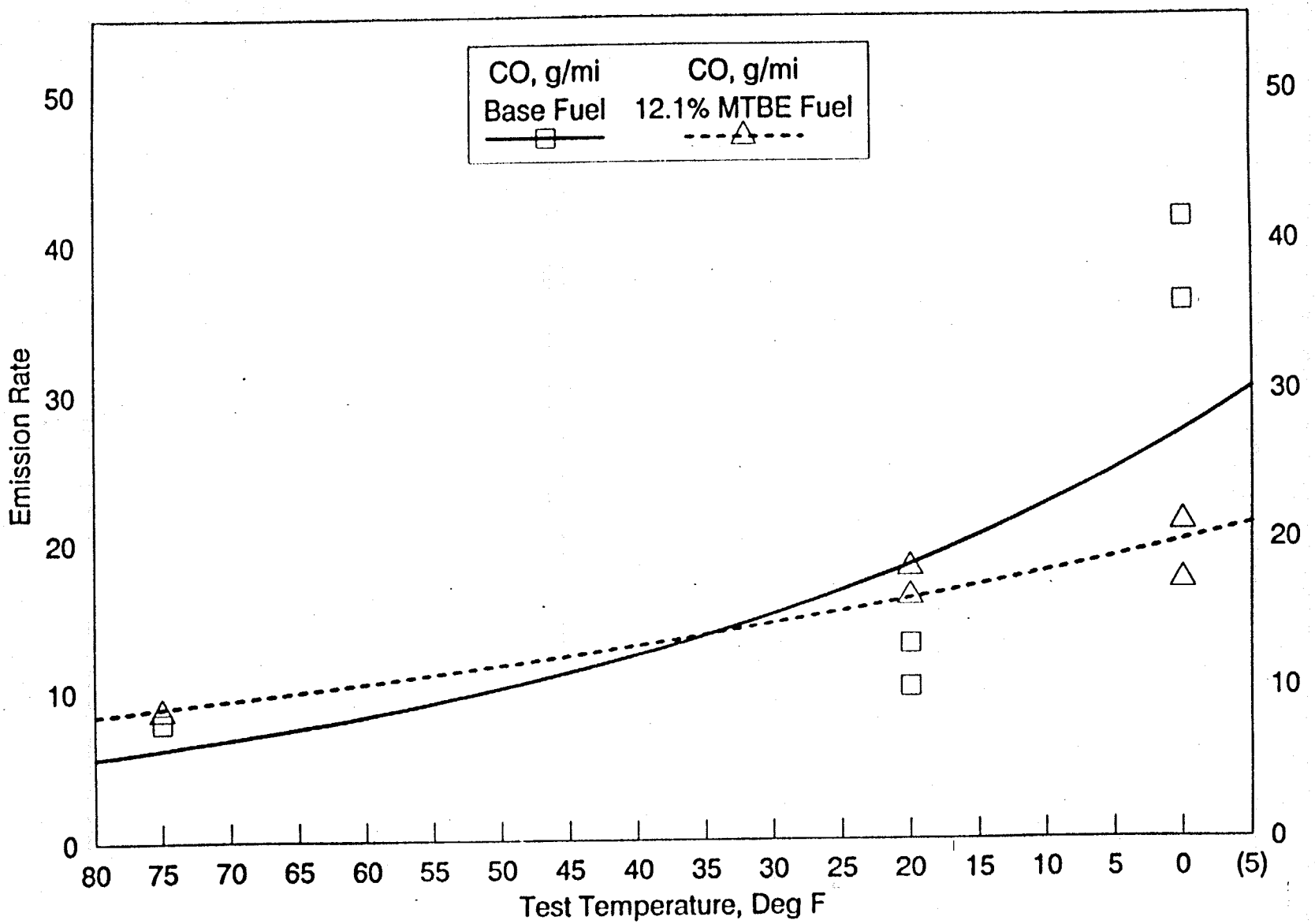
- Speciation
  - VOC's - >250 components (benzene, 1,3-butadiene, etc.)
  - Carbonyls - 12+ (formaldehyde, etc.)
  - Oxygenates - 10+ (MTBE, methanol, etc.)



1984 Buick Century



1992 Chevrolet Corsica



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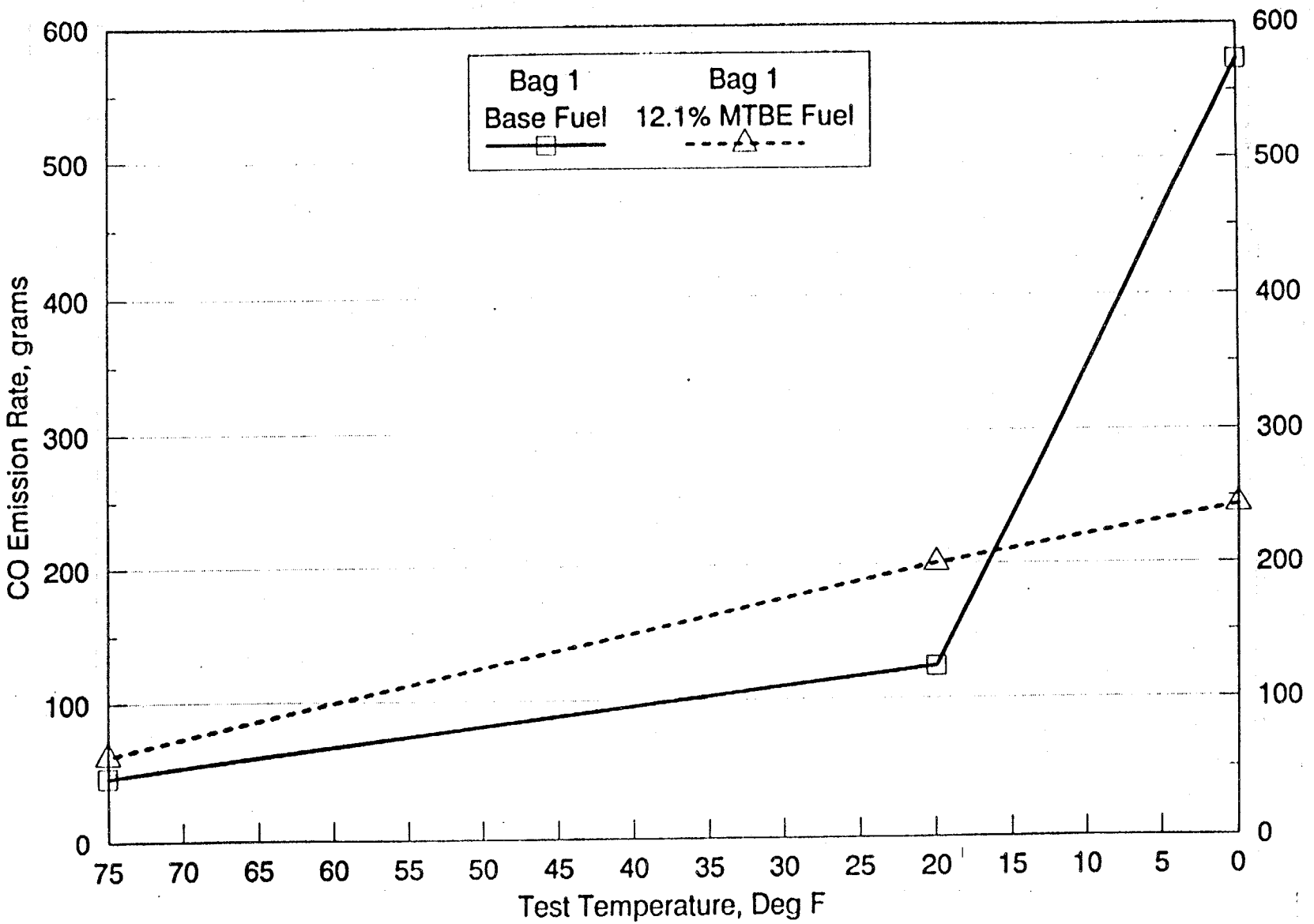
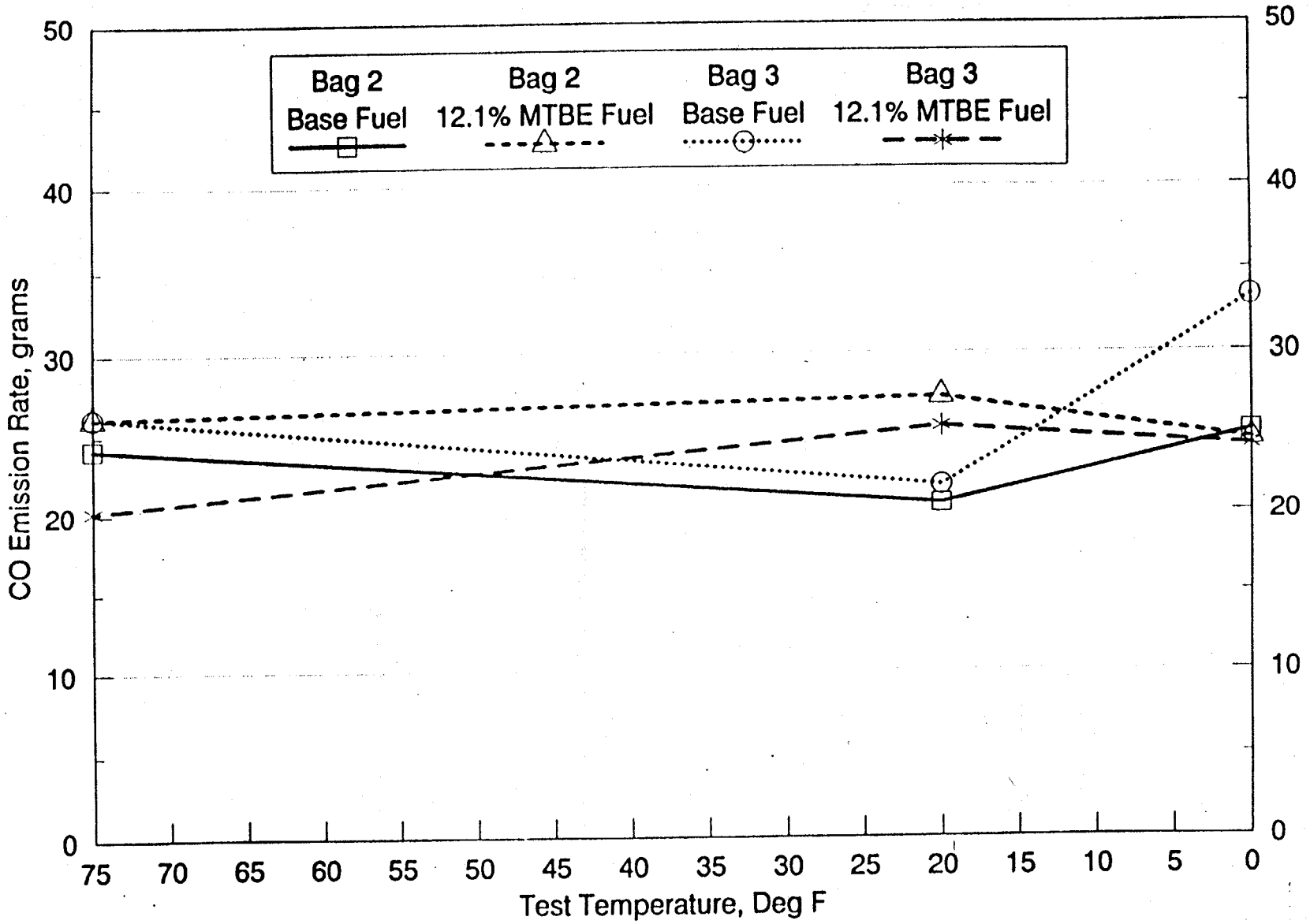
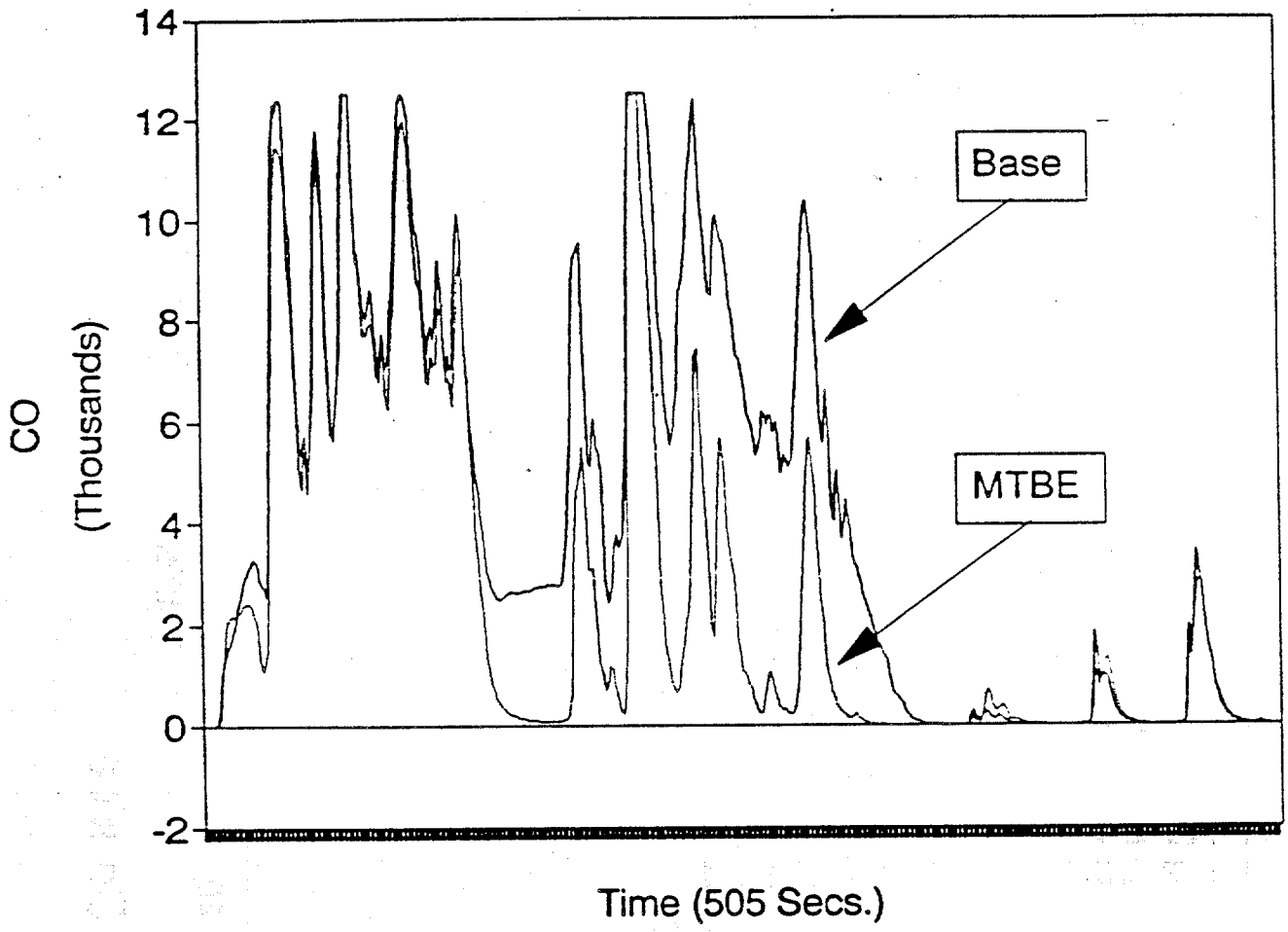


1992 Chevrolet Corsica

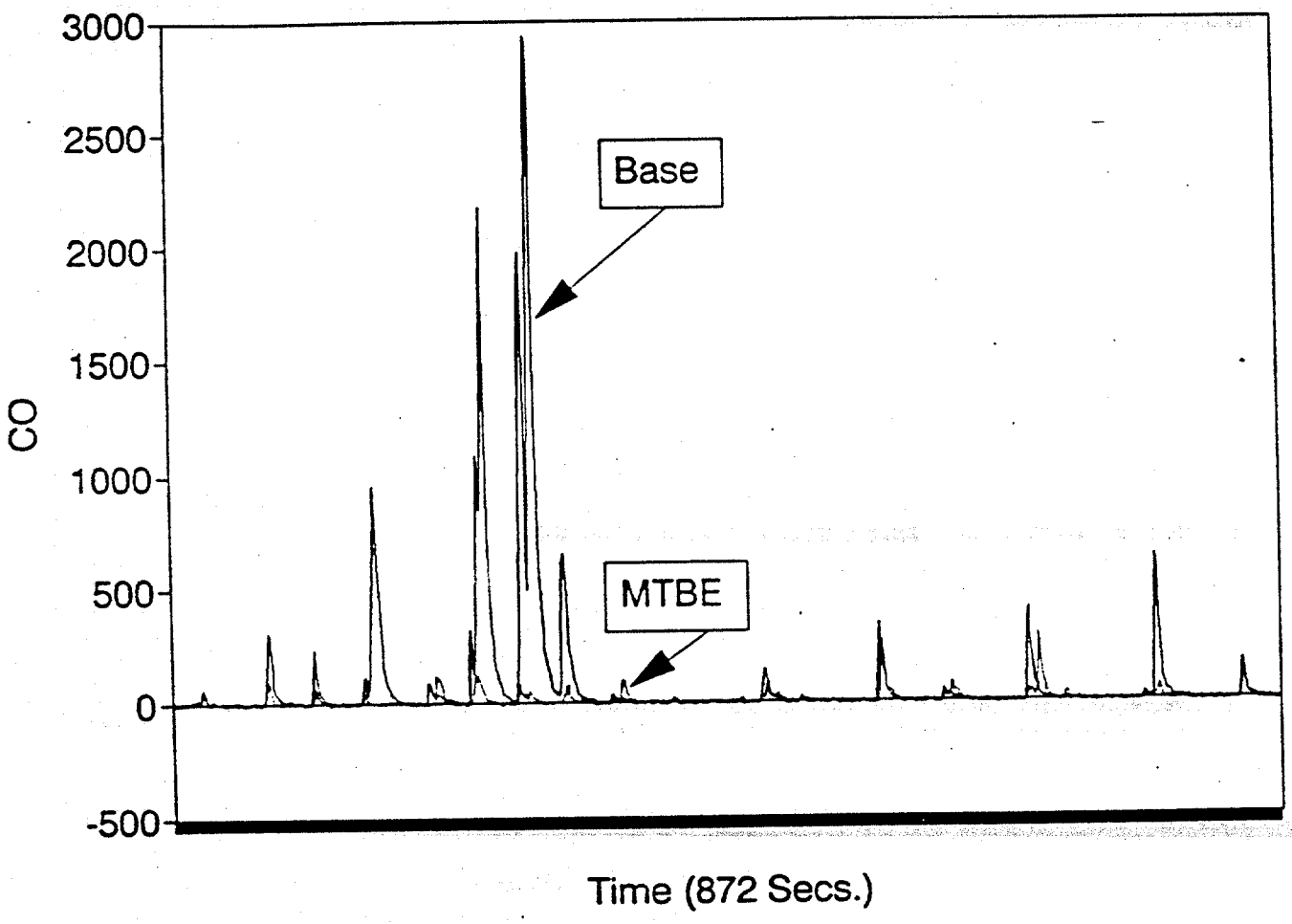


1992 Chevrolet Corsica

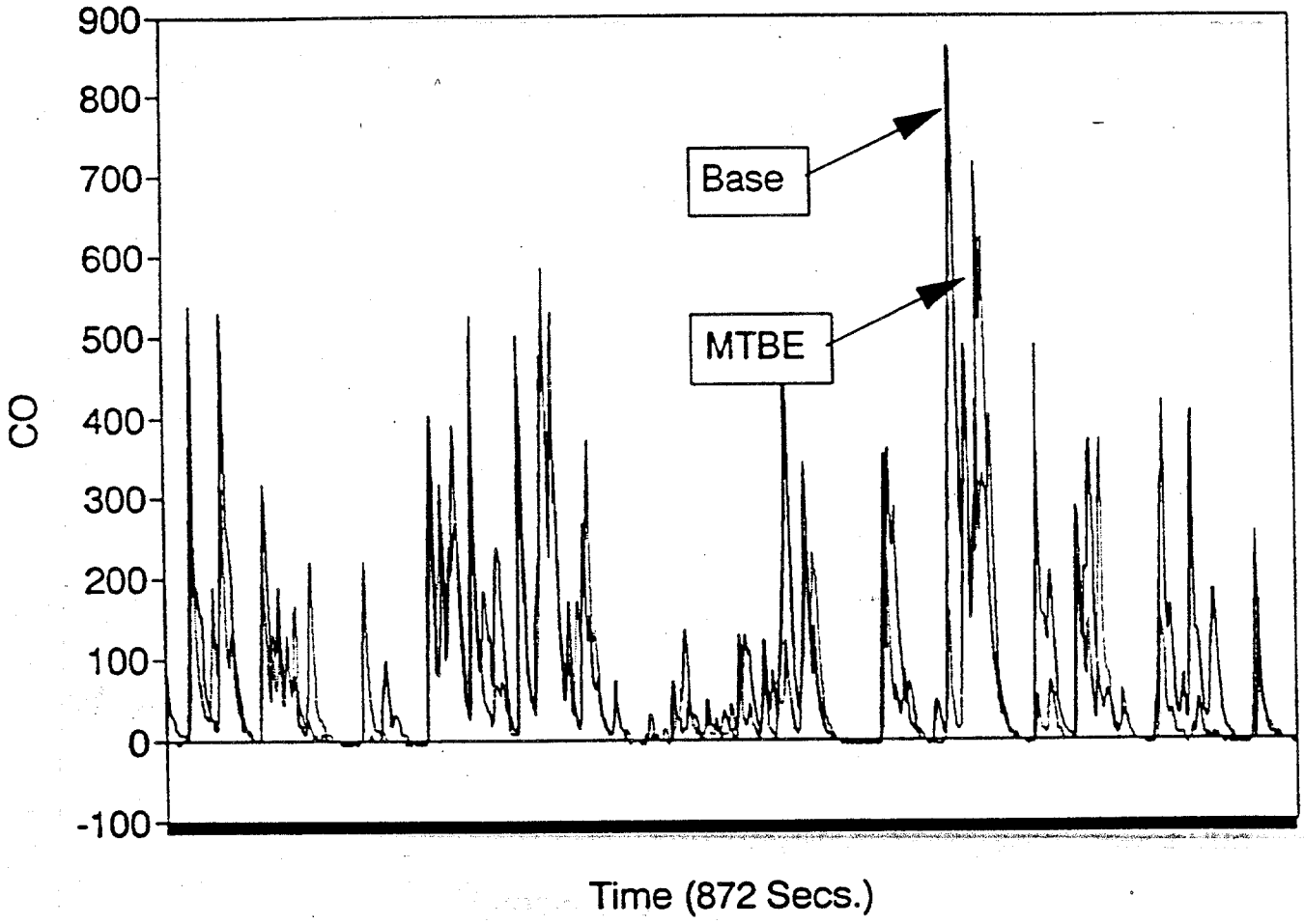
Buick Bag 1, 0 Degrees F

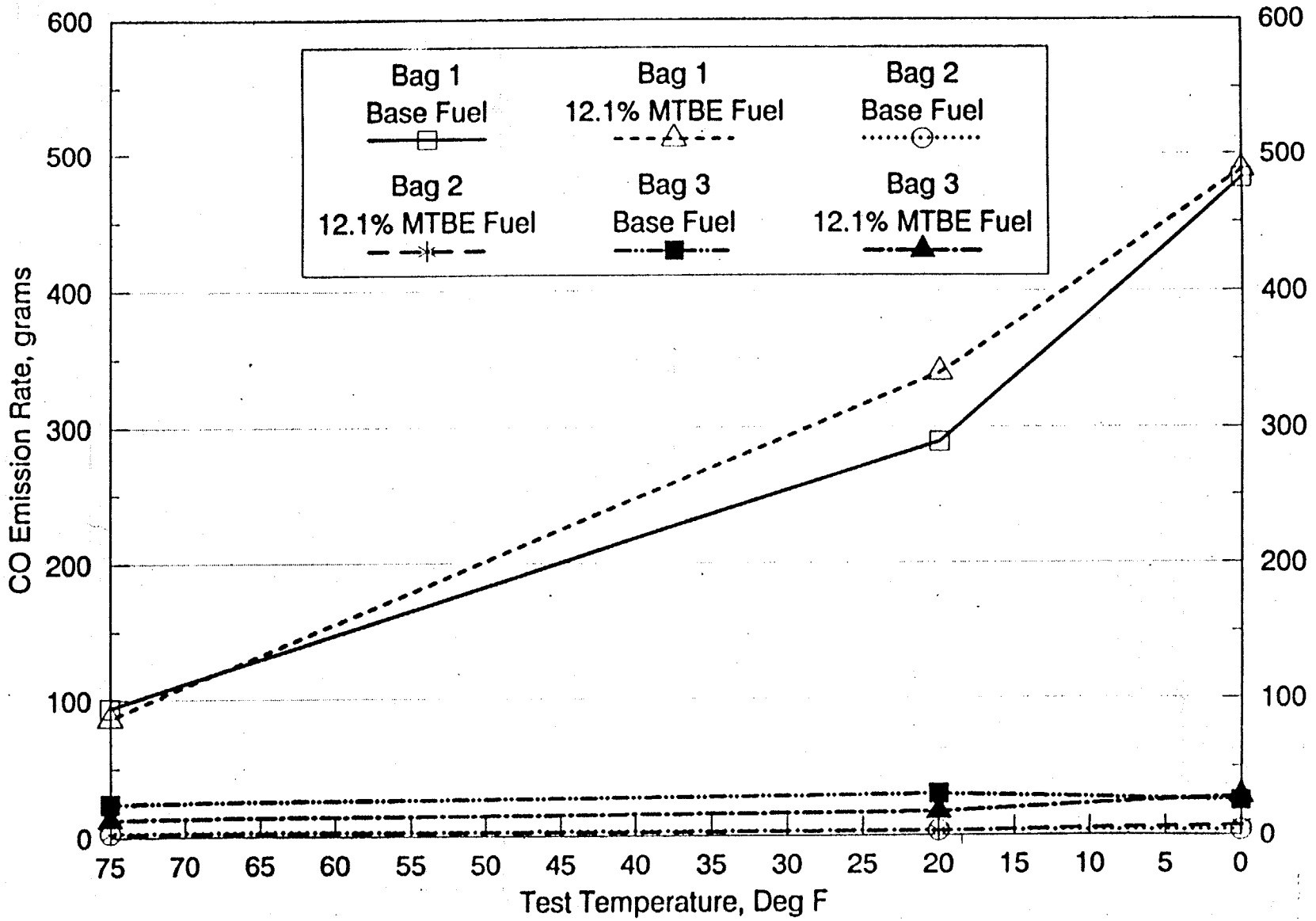


Buick Bag 2, 0 Degrees F

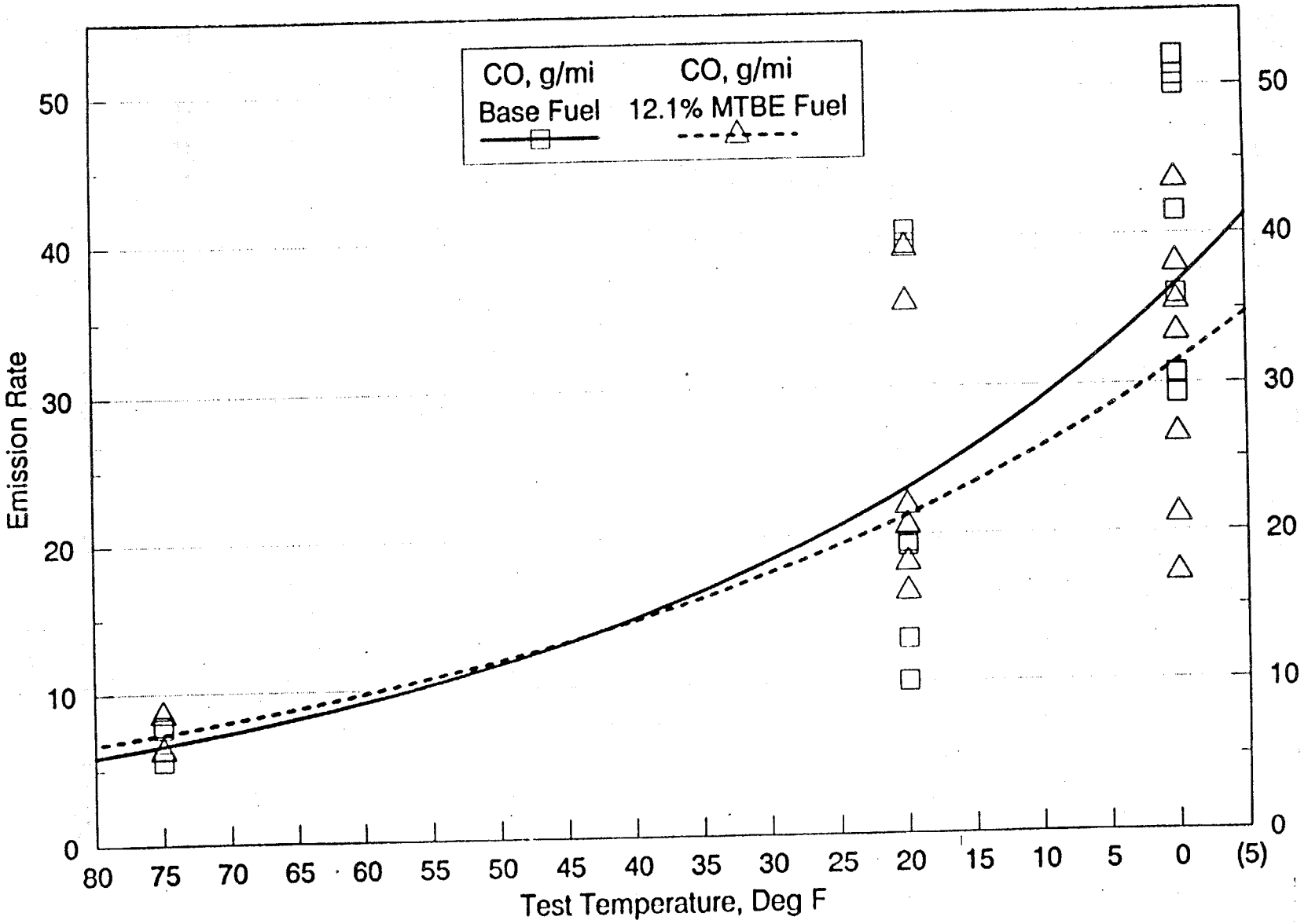


Corsica Bag 2, 0 Degrees F

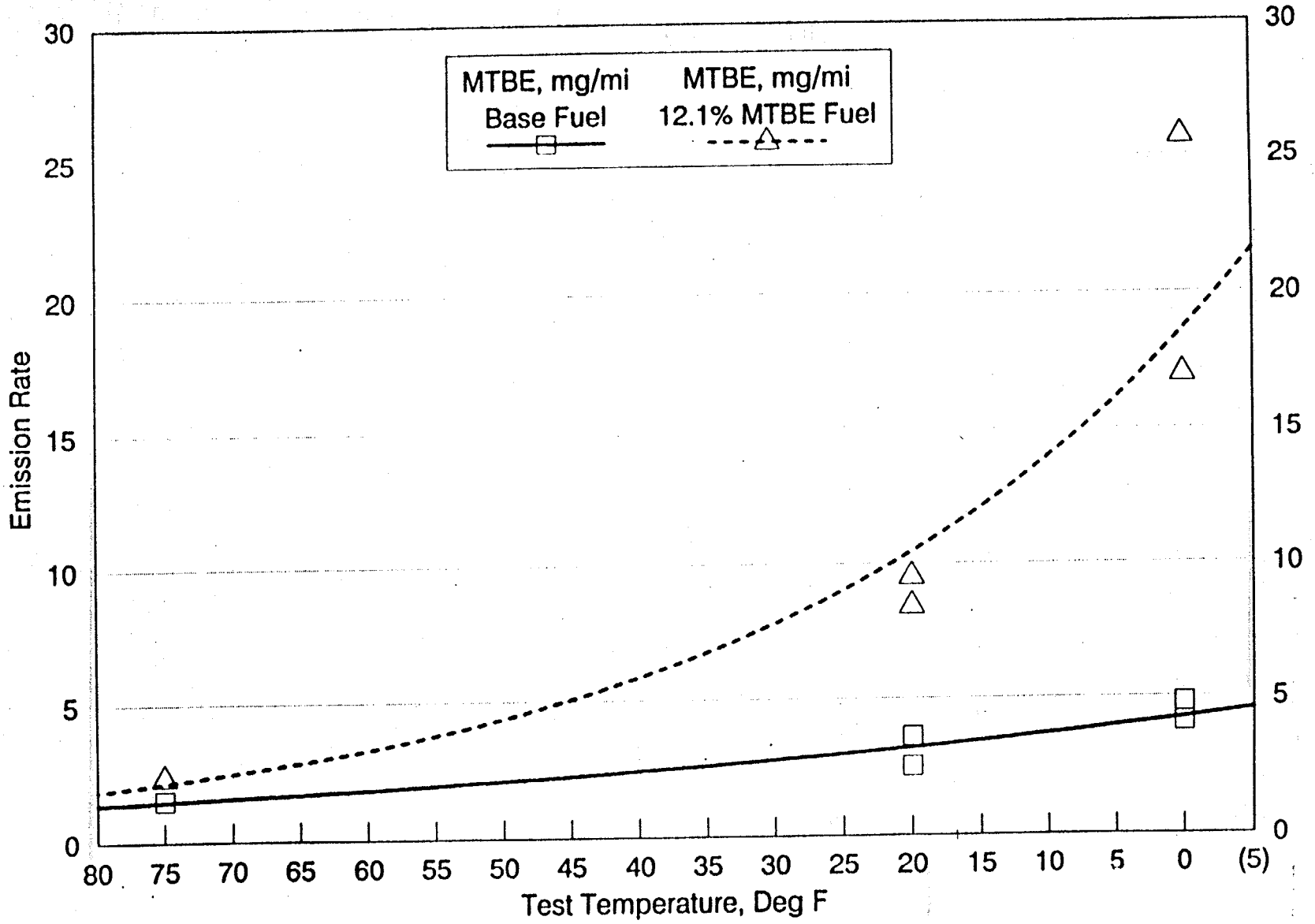




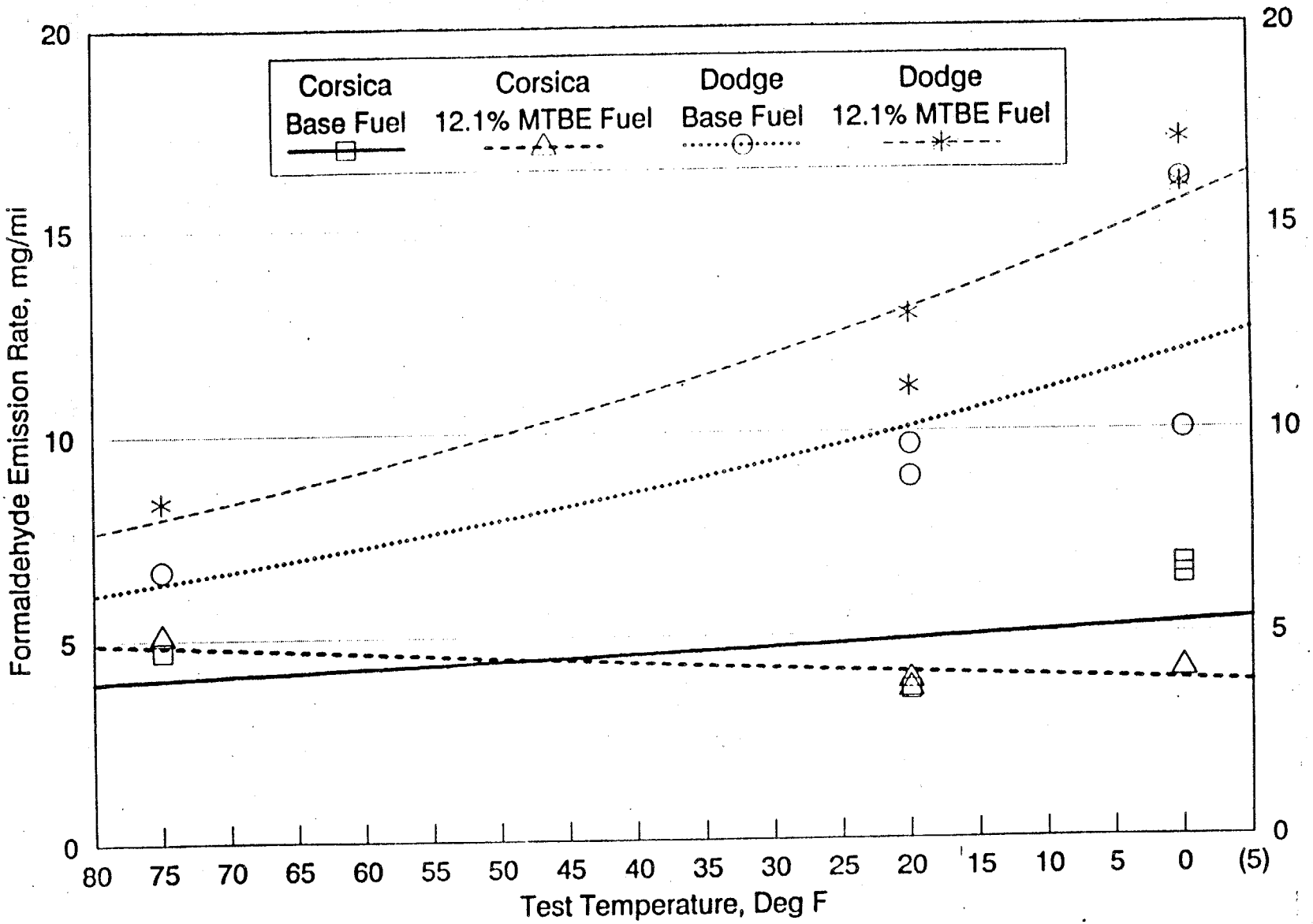
1991 Dodge Truck



Dodge/Buick/Corsica/Monte Carlo



1992 Chevrolet Corsica



Dodge and Corsica Formaldehyde Emissions

CONCLUSIONS

1. CO emissions increase with a decrease in operating temperature.

2. The CO increase with temperature is less with MTBE in the fuel under certain conditions.

3. The emissions data spread increases with a decrease in temperature.

4. The data suggest additional variables affect the CO emissions.

AUTHOR(S): Chandra B. Prakash

TITLE: EMISSIONS UNDER COLD CONDITIONS

(1) Test fuels: Baseline gasoline
15% MTBE (oxygenated gasoline)

(2) Test vehicles: 1992 Chevrolet Corsica
1987 Chevrolet Caprice
1991 Toyota Corolla

Fuels and vehicles were provided by EPA-RTP, except for the Toyota Corolla, which came from the Environmental Canada fleet.

(3) Test temperature range: -20°F to 75°F

FUEL EFFECT

The emissions results were analyzed using the student t-test to determine 95% confidence intervals. The results indicate that there was no statistically significant difference in regulated emissions or carbon dioxide (CO_2) emissions between fuels over the ambient temperature range of 75°F to -20°F.

The difference in formaldehyde and total carbonyl (aldehyde and ketone) emissions for the two fuels were also found to be statistically insignificant. However, vehicle-to-vehicle differences were noticeable. The Corsica and Caprice gave higher formaldehyde and carbonyl emissions compared to baseline gasoline, while the trend was reversed with the Corolla. This finding is based on two runs at each fuel-temperature combination over the 20°F to -20°F temperature range and a single run at 75°F for either fuel.

It is generally recognized that the use of oxygenated gasolines compared to base gasoline reduces CO emissions, while it increases NO_x and formaldehyde emissions. However, the present data on two test vehicles as well as the recent emissions test results at Environment Canada on eight new technology vehicles (3-way catalyst with a closed loop system) using oxygenated and baseline gasolines suggest that the fuel effect on these vehicles is rather small and is, in most cases, insignificant.

Therefore, the wintertime oxygenated fuels program should be expected to offer diminishing CO benefits (reductions) as older vehicles are gradually replaced with new technology vehicles.

The MTBE in the vehicle exhaust, while using MTBE containing fuel, was present only in bag 1 and ranged between 0.3 to 0.9 ppm.

TEMPERATURE EFFECT

Regulated emissions increase with decreasing temperature. The increase in HC and CO emissions can be attributed to a reduction in combustion and catalyst efficiency. Immediately following start-up, particularly at lower ambient temperatures, the engine operates in a fuel-rich mode so as to sustain combustion. Excess fuel is required to ensure that sufficient fuel remains vaporized within the cylinder during intake and compressions strokes. These conditions result in higher HC and CO emissions. In addition, the engine out HC and CO are not converted efficiently in the catalyst. The catalyst efficiency remains poor immediately following engine start-up until the catalyst reaches its operating temperature ("light-off" point).

Nitrogen oxide emissions are a thermal phenomena that would not be expected to be affected by a reduction in ambient operating temperatures. Rather, the increased NO_x emissions trend can be explained by the overall reduction in catalyst conversion efficiency. Due to the low catalyst temperature and low A/F ratio (rich) following engine start-up, the NO_x reduction capability of the catalyst is extremely limited. Of interest is the apparent plateau in NO_x emission from the Corsica model at temperatures of 20°F or less. This may be the result of the engine electronic control system.

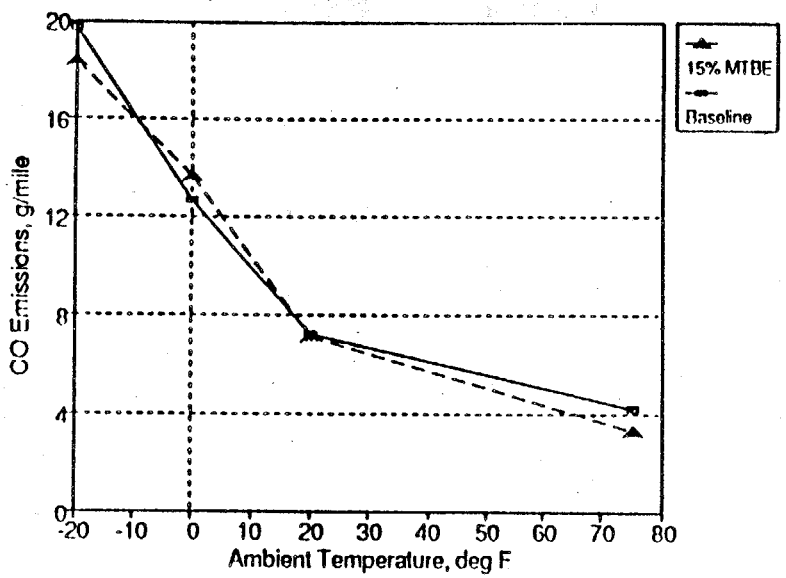
Carbon dioxide emissions are vehicle specific and can be attributed to the increased fuel consumption due to reduced combustion efficiency and increased engine/vehicle friction until the vehicle has warmed up.

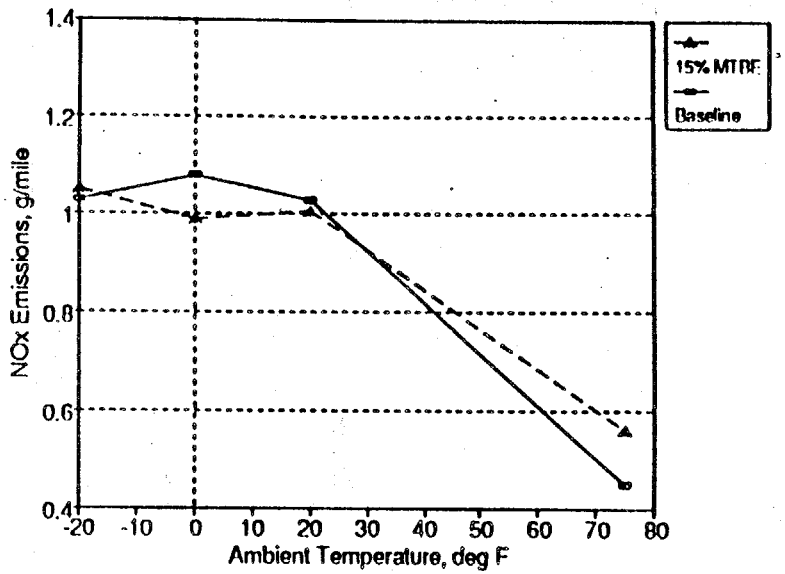
The formaldehyde and carbonyl emissions followed the general trend of HC emissions and increased with decreasing ambient temperature. Typically, formaldehyde emissions at -20°F were about twice as compared to emissions at 75°F.

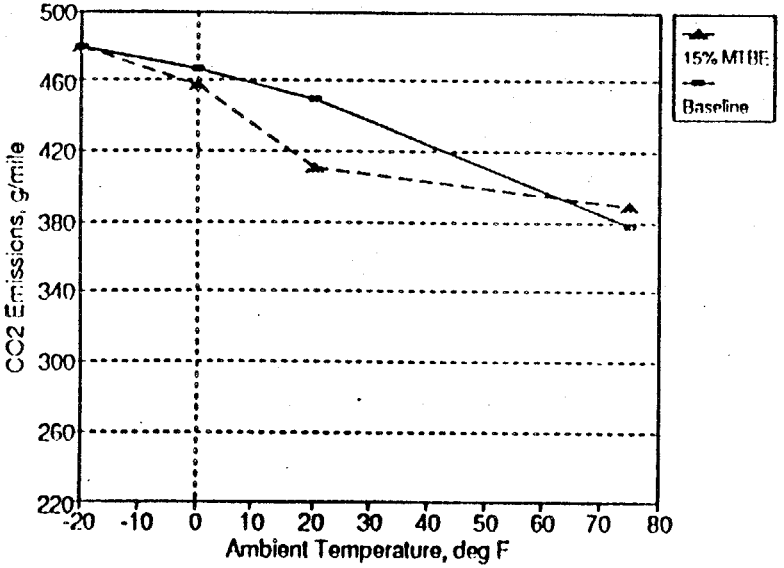
GENERAL OBSERVATIONS

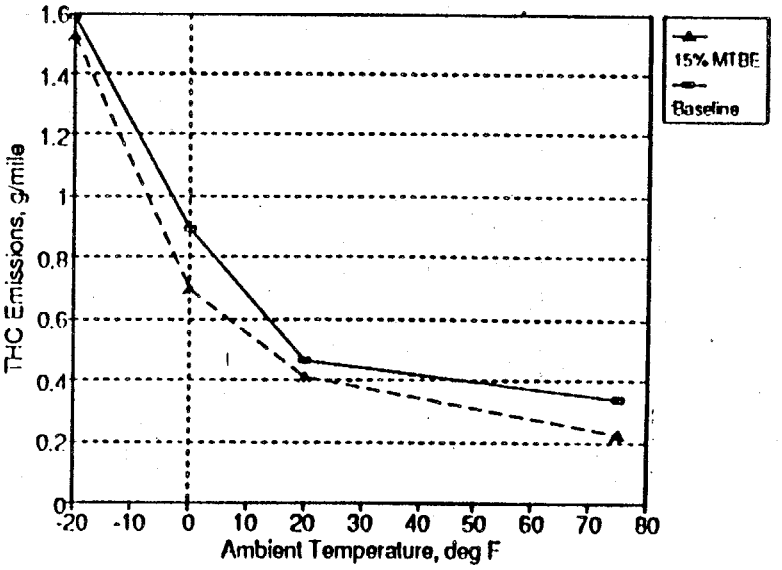
The Caprice (equipped with a carburetored fueling system) showed an unusual behavior by giving higher CO and HC, while lower NO_x emissions with MTBE fuel compared to baseline gasoline. Although the differences in exhaust emissions between the two fuels were not statistically significant, it should be mentioned that this car also gave very high evaporative emissions during tests at EPA. It is likely that the abnormal behavior of the Caprice gave a much larger variation in exhaust emissions and the unusual trend of CO emissions.

The data supports the general belief that vehicles and their control systems are designed for optimum emissions performance at certification conditions, and, in most cases, the emissions are much higher during off-cycle and low ambient temperature conditions. Finally, the data also indicate that there is considerable variation in regulated emissions from one vehicle to another.

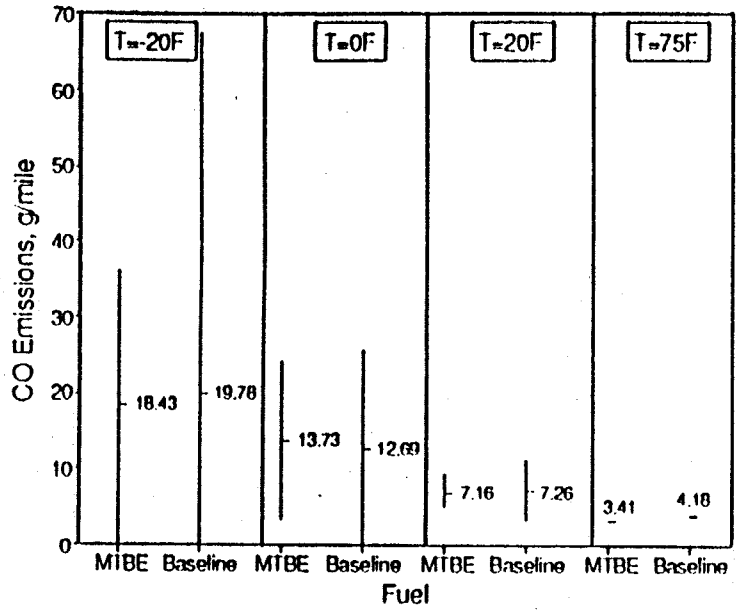


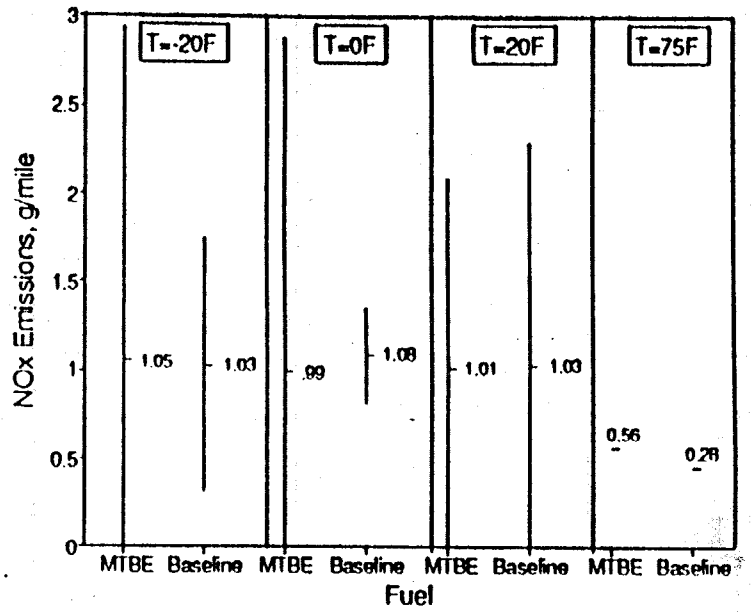


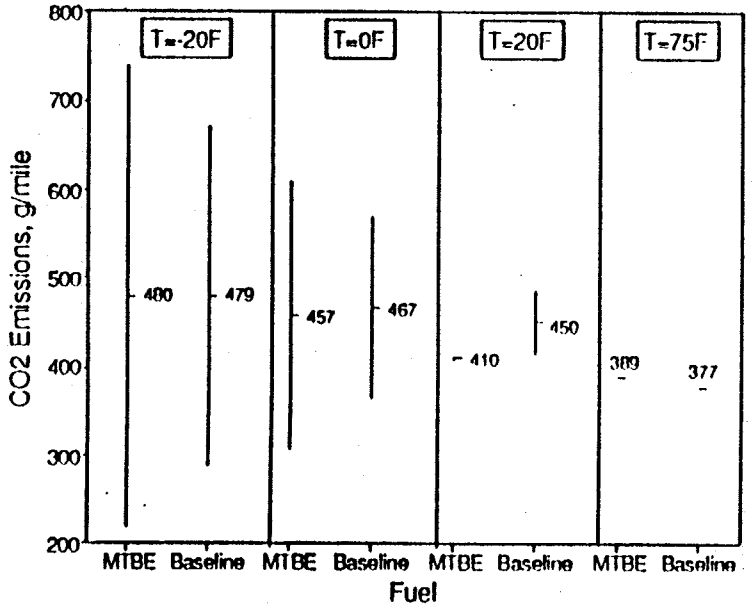


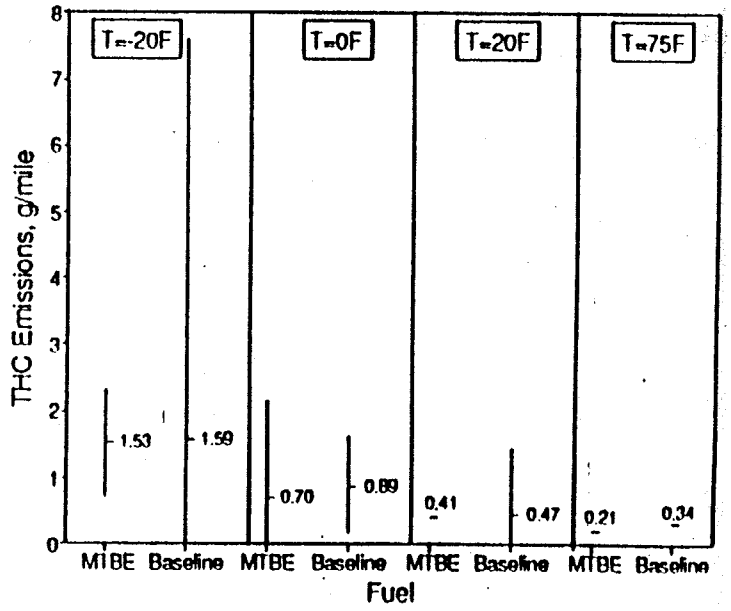


Composite emissions as a function of temperature for Corsica using FTP drive cycle

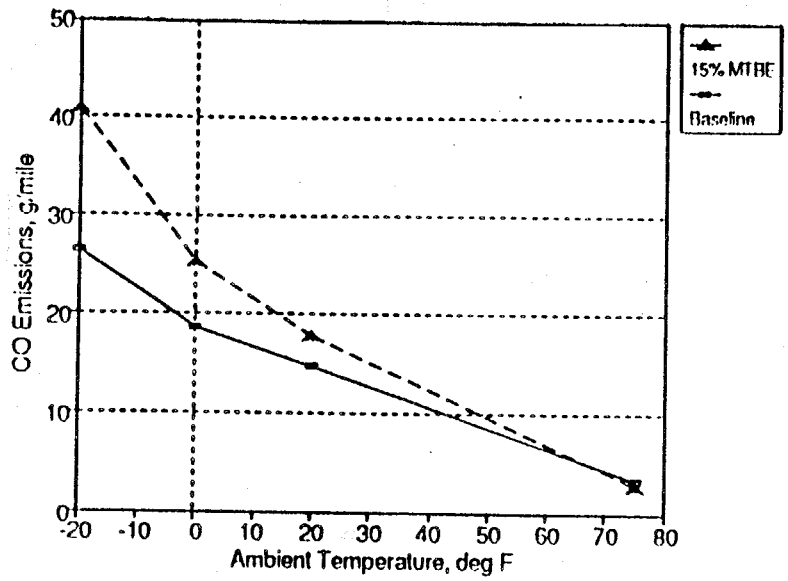


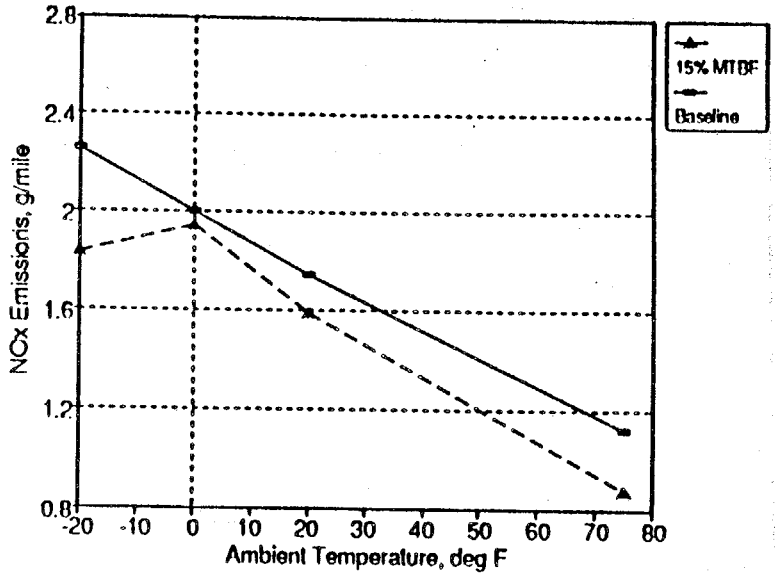


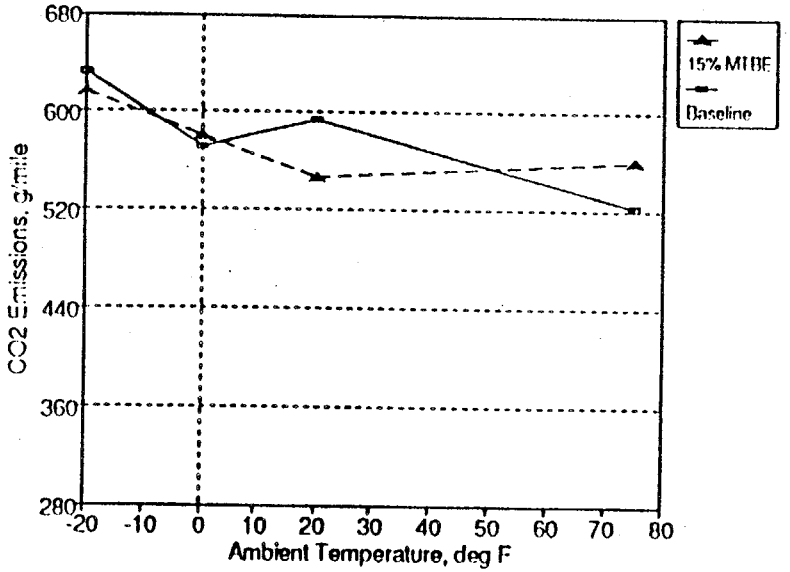


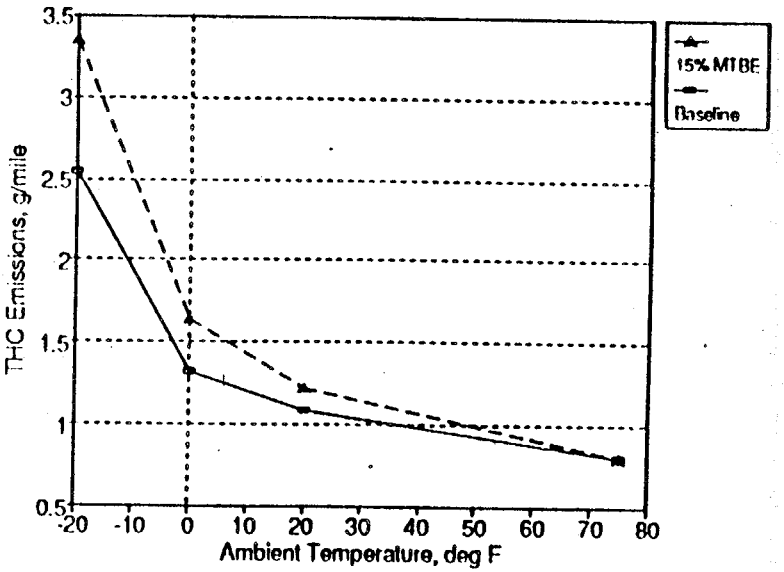


Fuel effect on composite emissions for Corsica, showing 95% confidence intervals

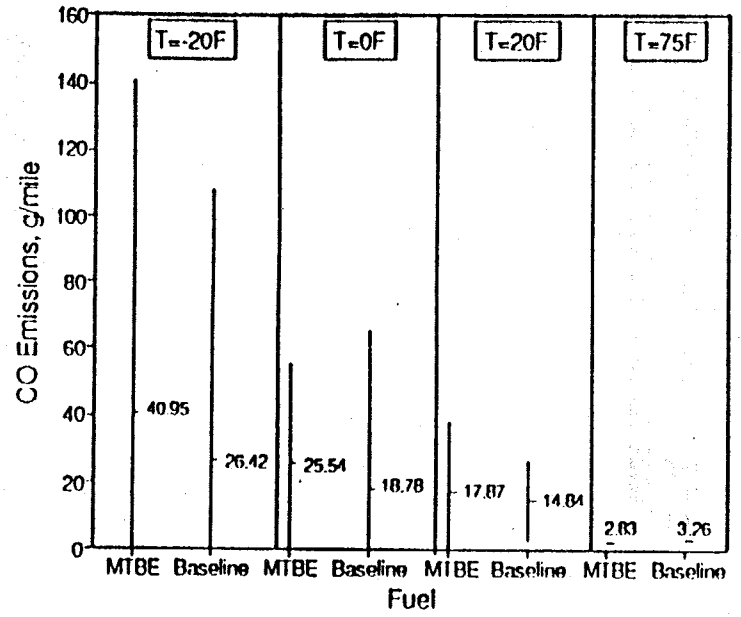


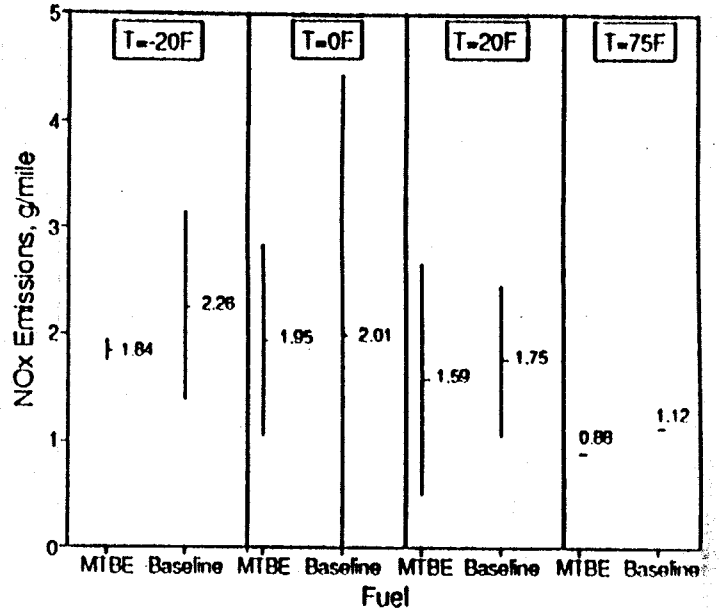


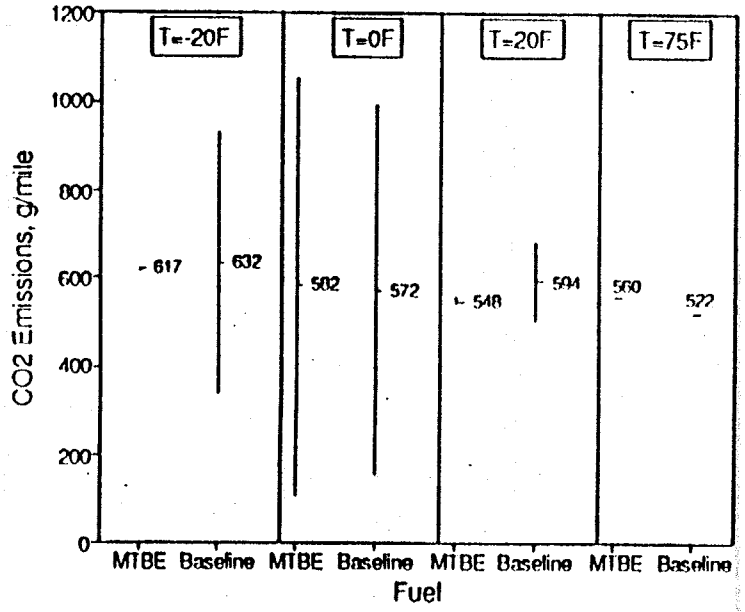


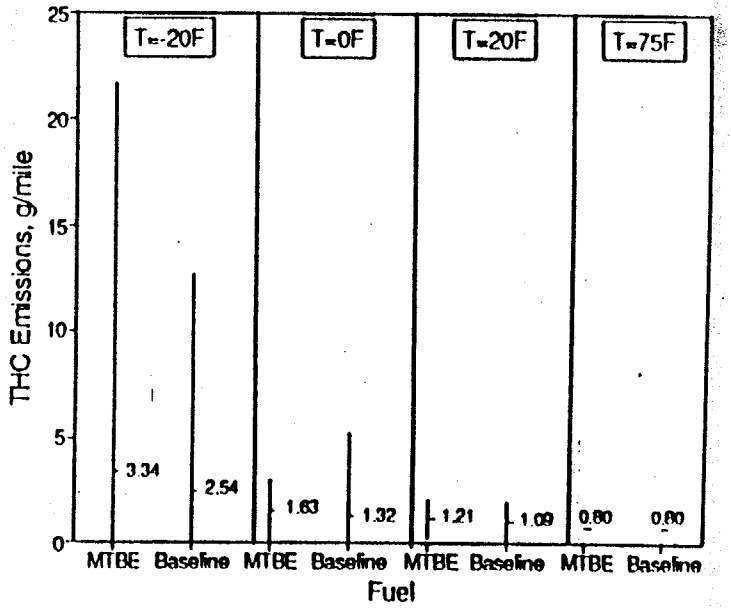


Composite emissions as a function of temperature for Caprice using FTP drive cycle

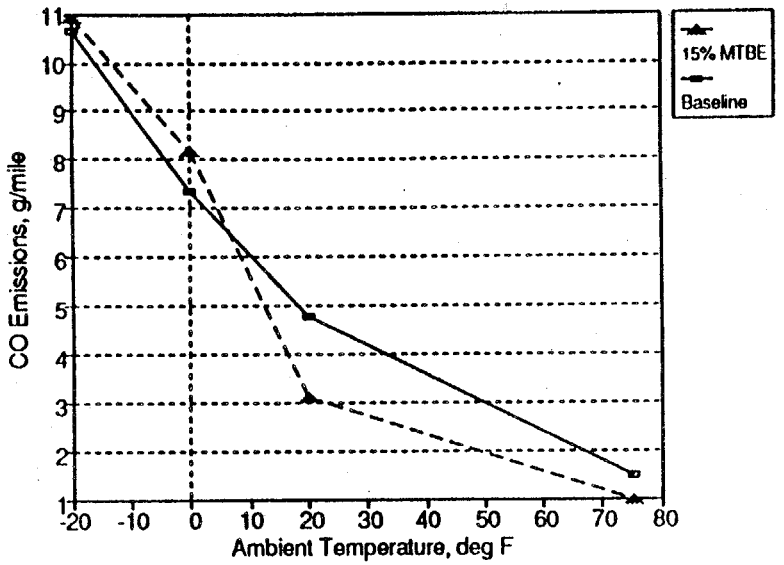


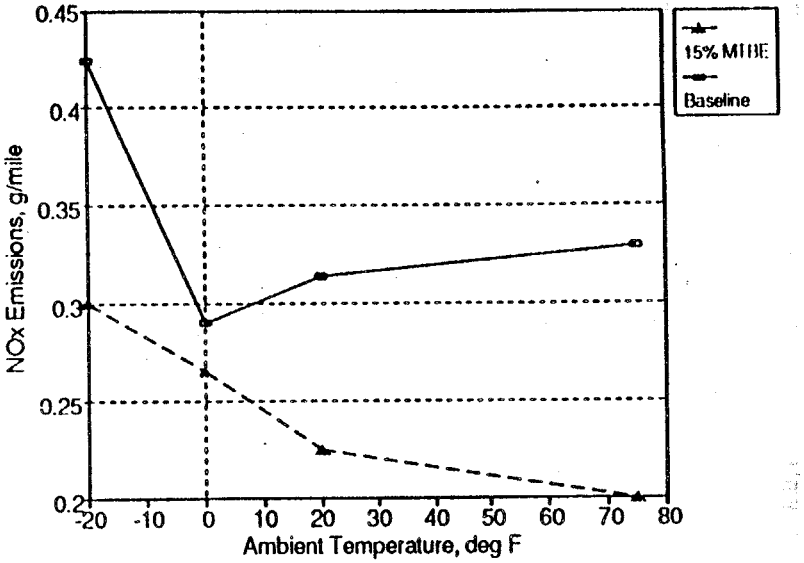


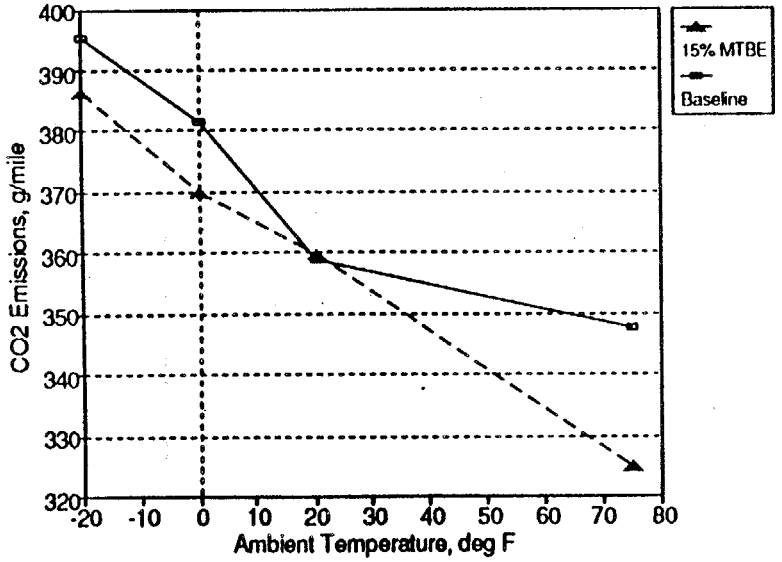


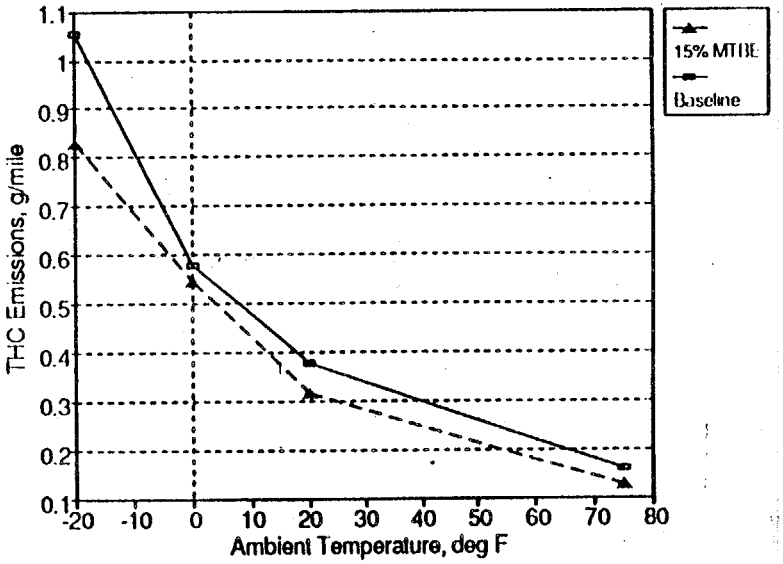


Fuel effect on composite emissions for Caprice, showing 95% confidence intervals

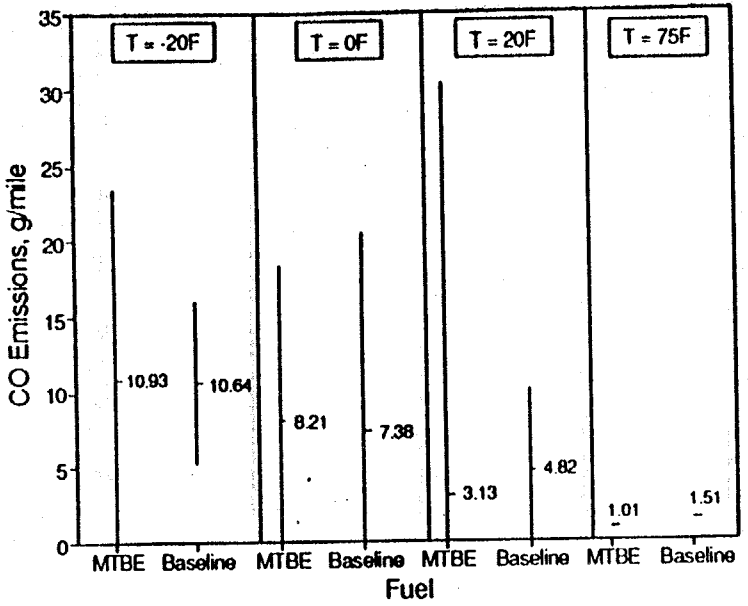


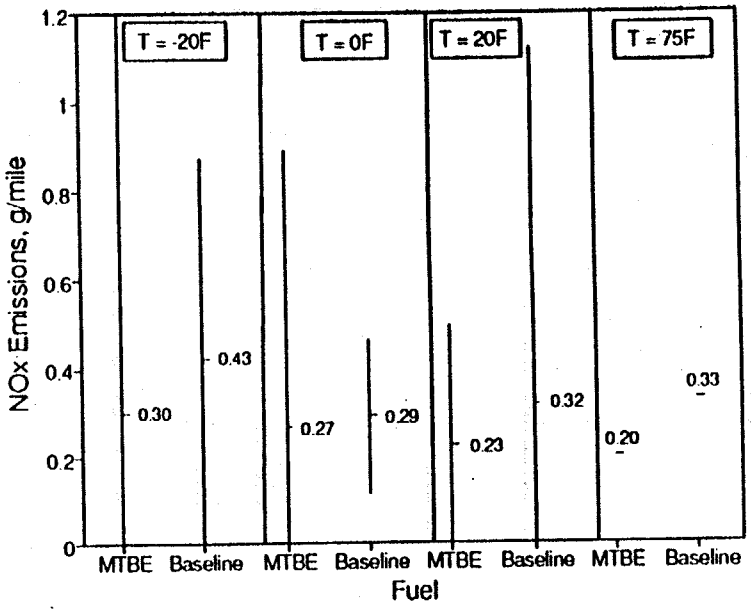


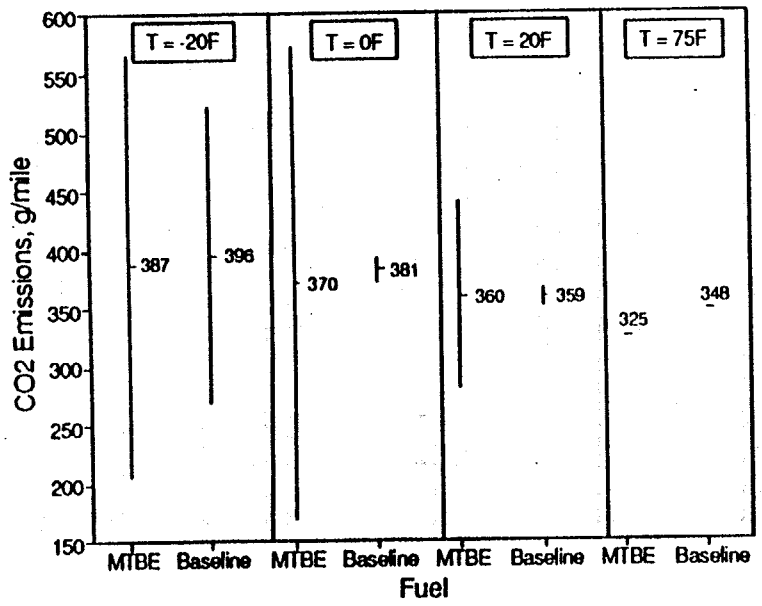


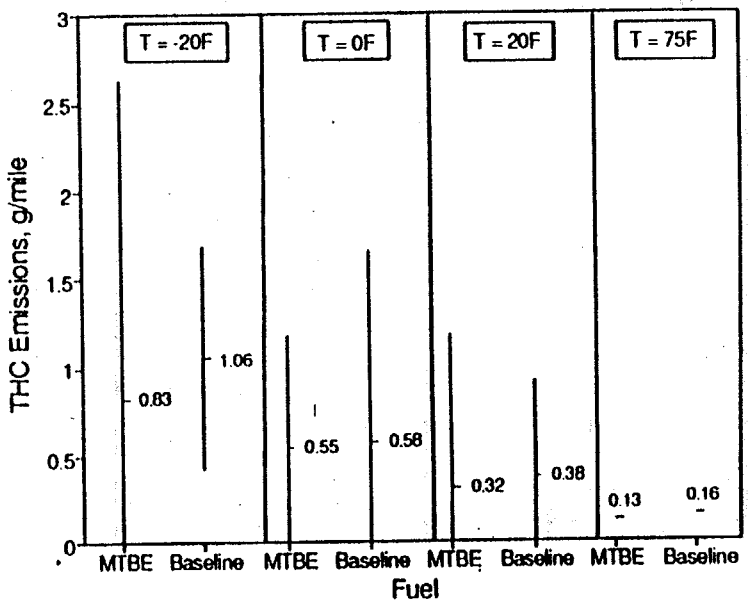


Composite emissions as a function of temperature for Toyota using FTP drive cycle

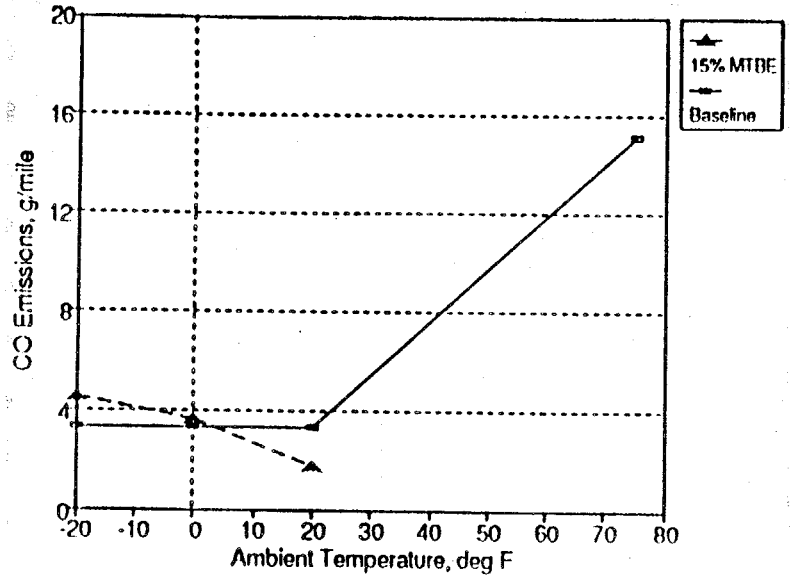


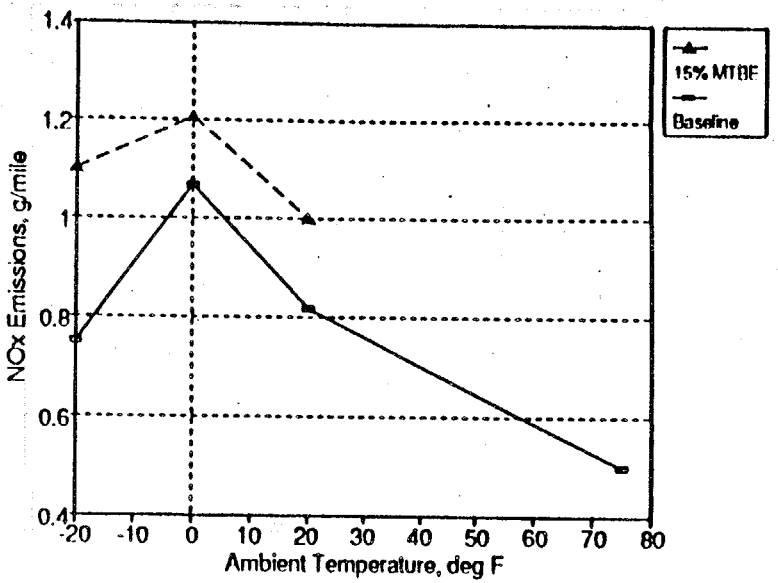


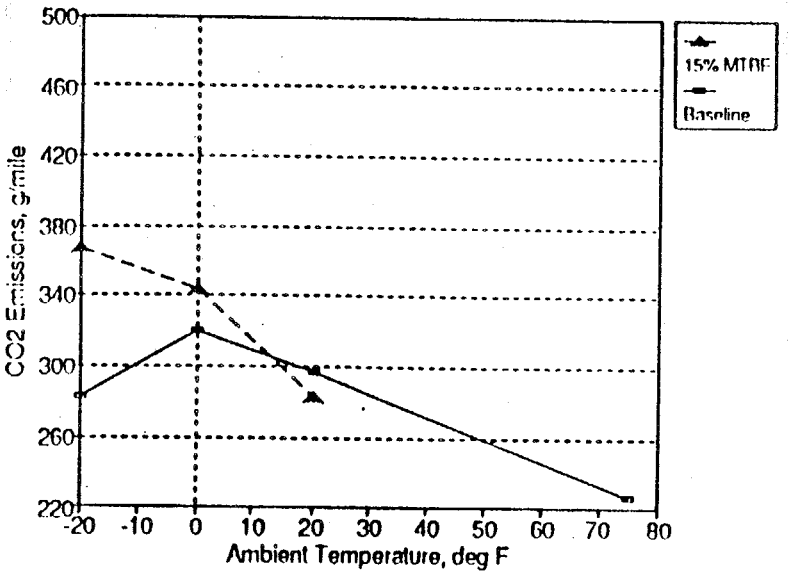


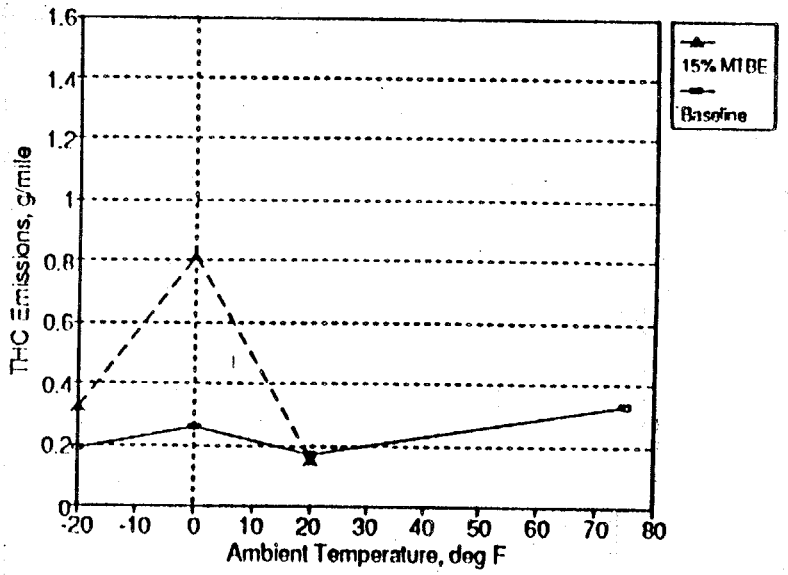


Fuel effect on composite emissions for Toyota, showing 95% confidence intervals

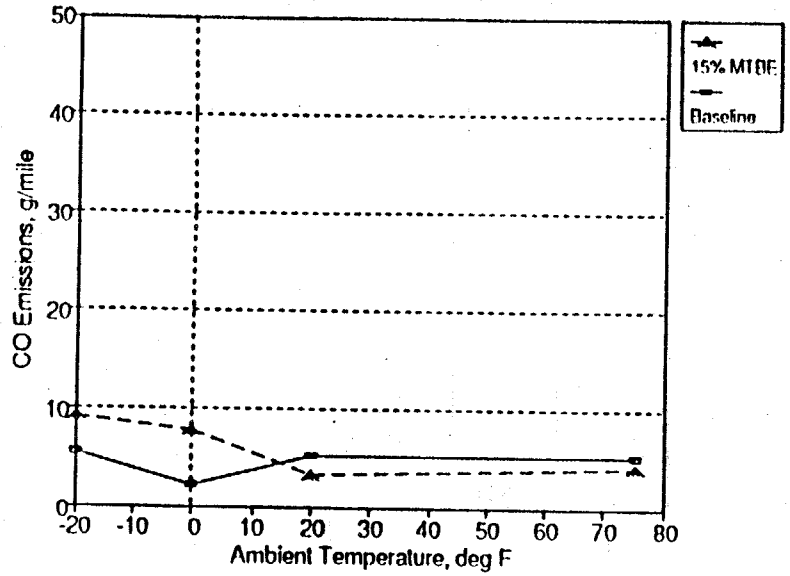


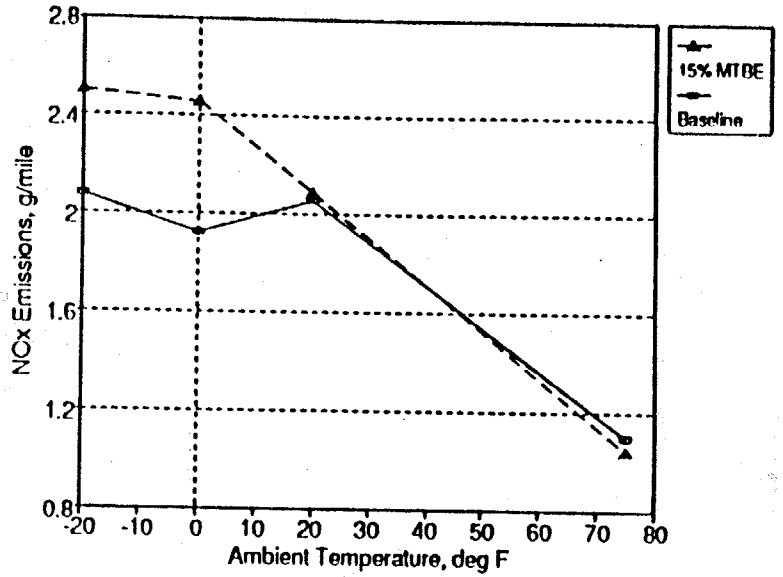


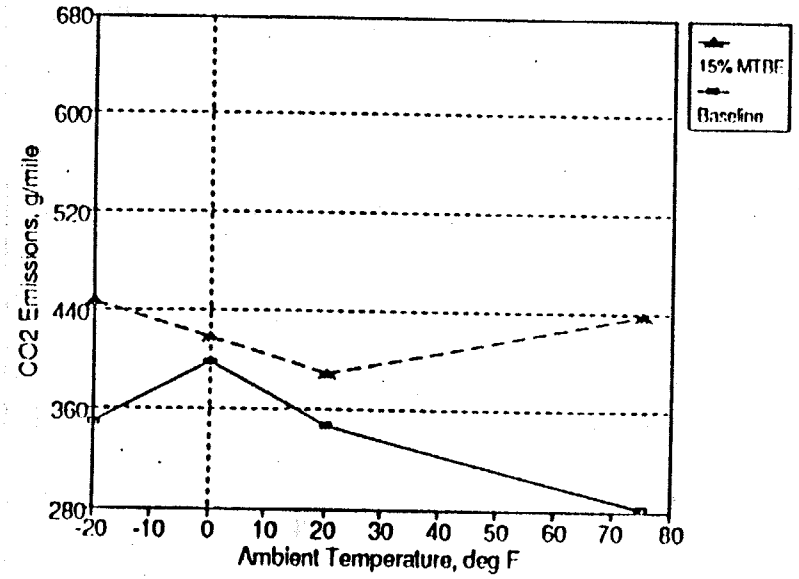


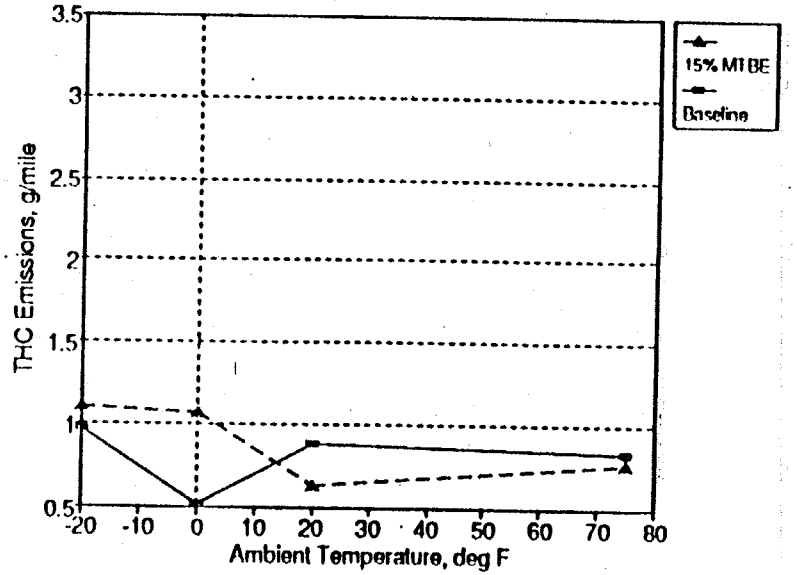


Composite emissions as a function of temperature for Corsica using IM240 drive cycle

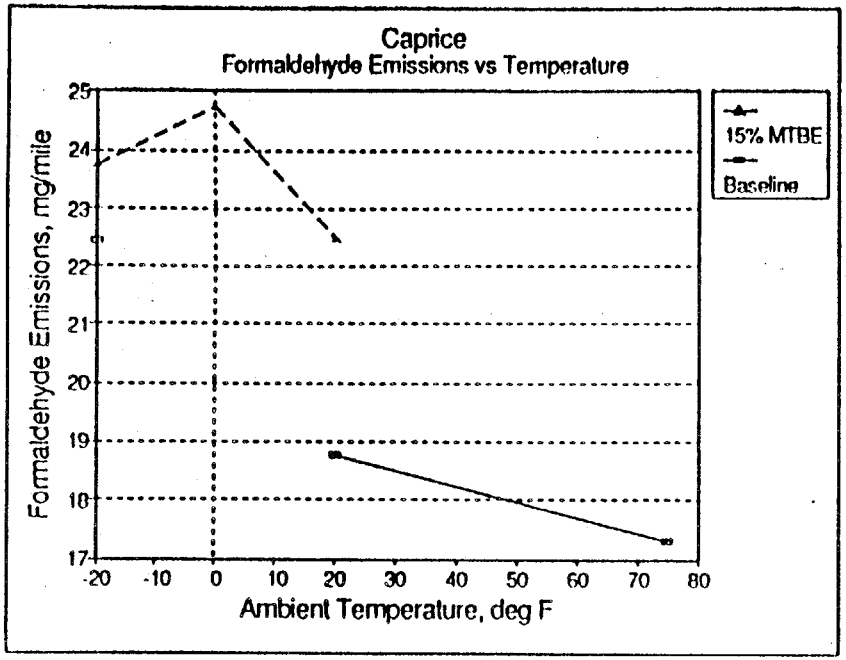


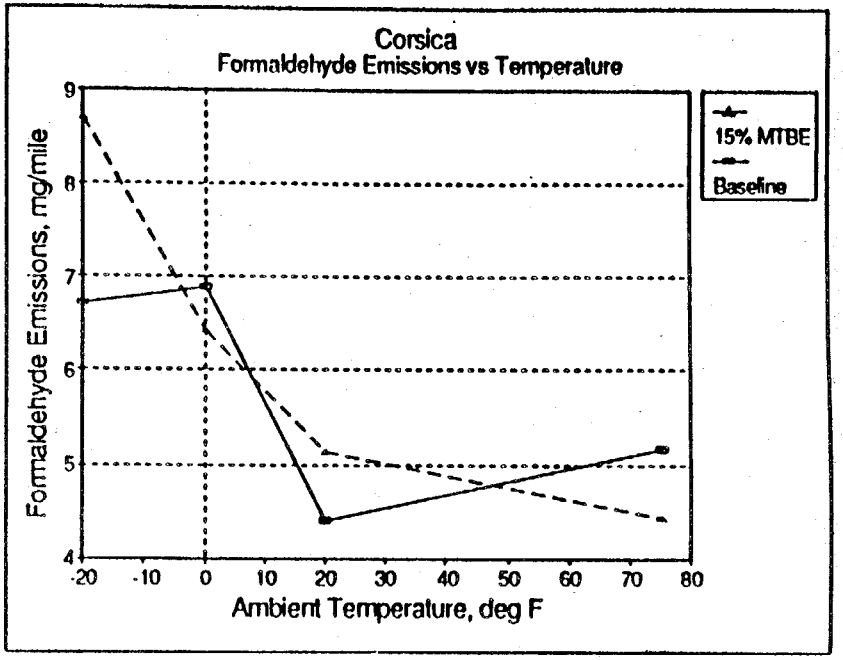


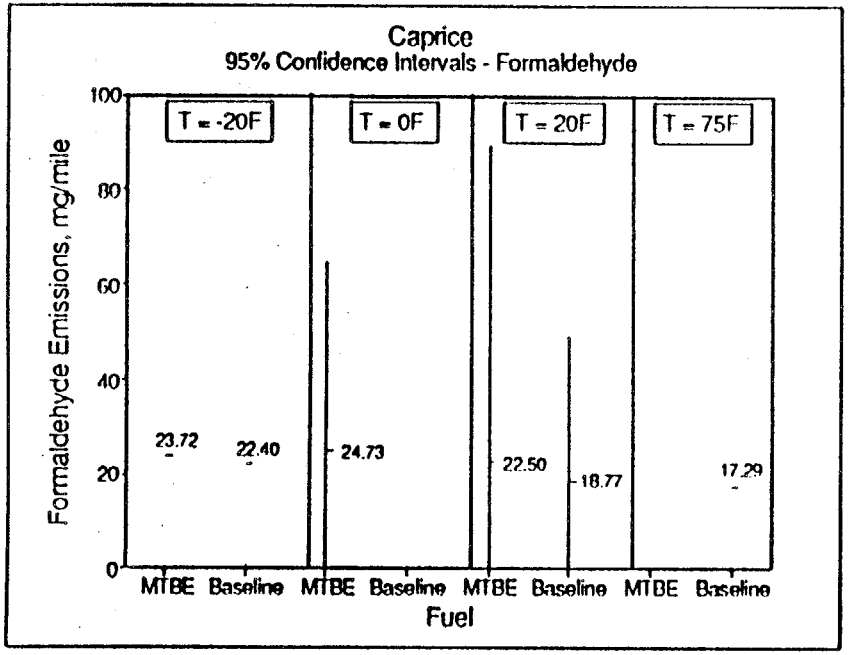


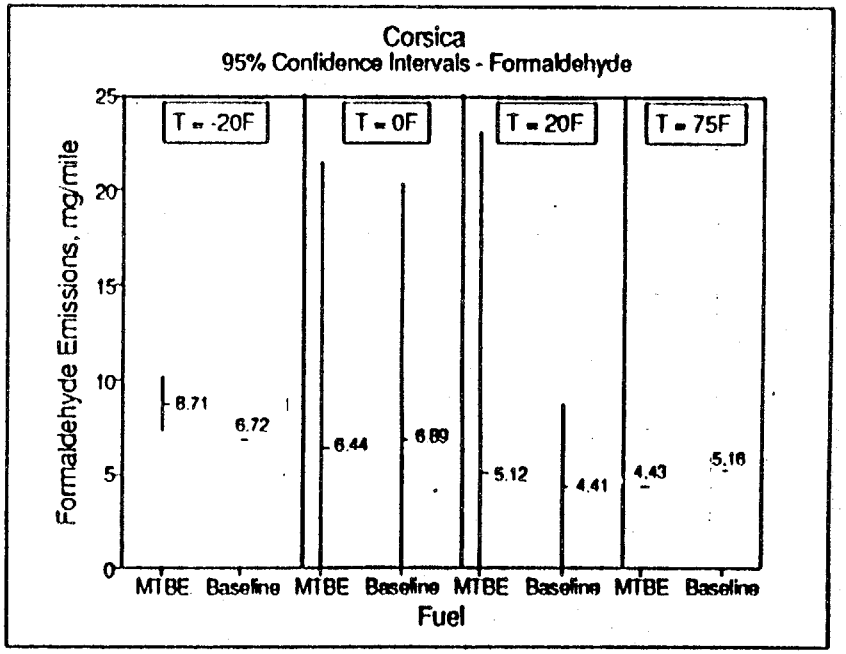


Composite emissions as a function of temperature for Caprice using IM240 drive cycle

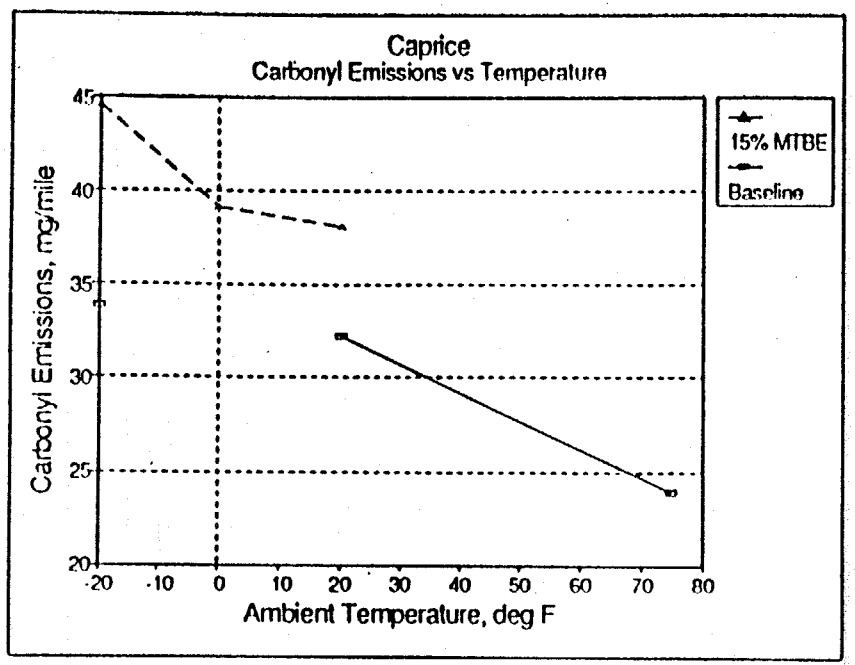


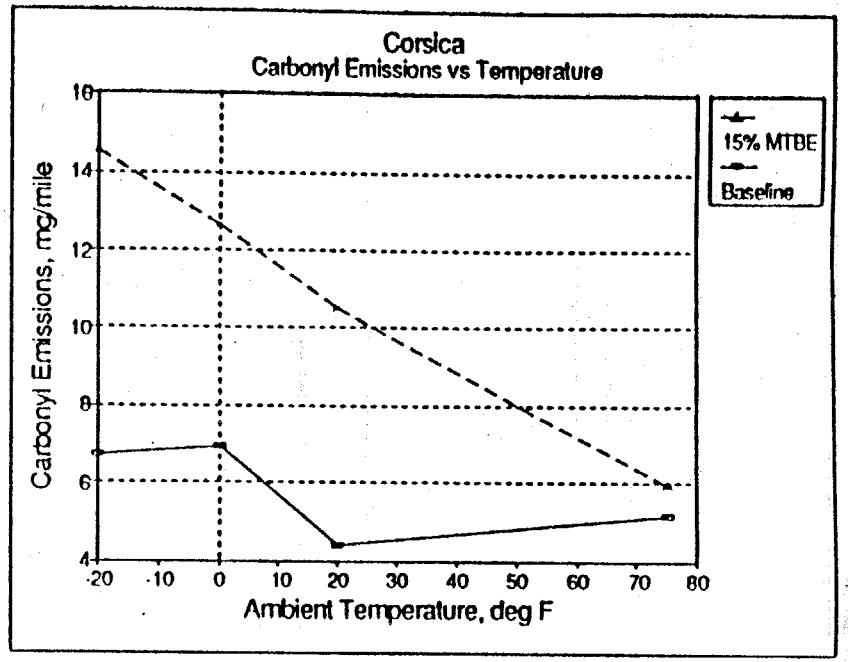


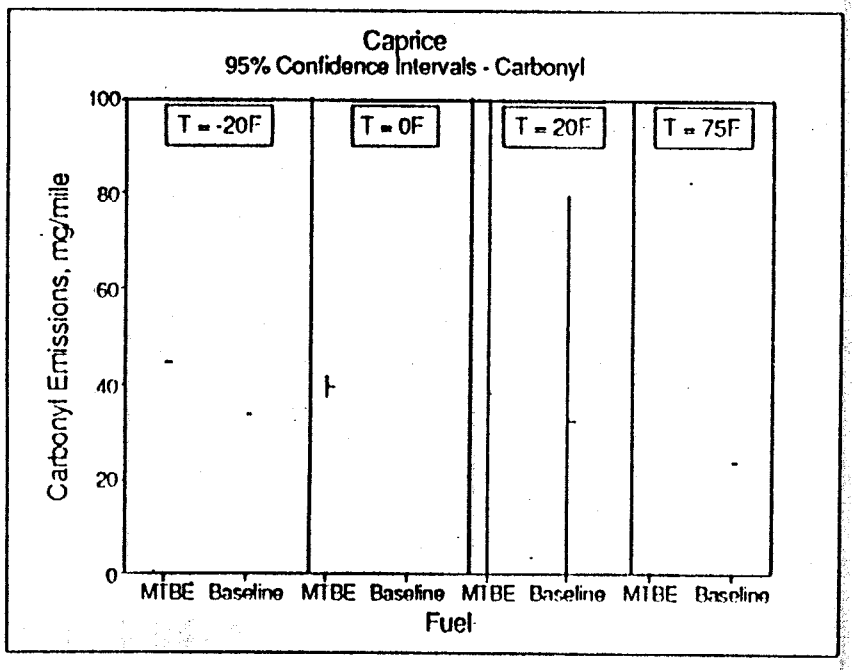


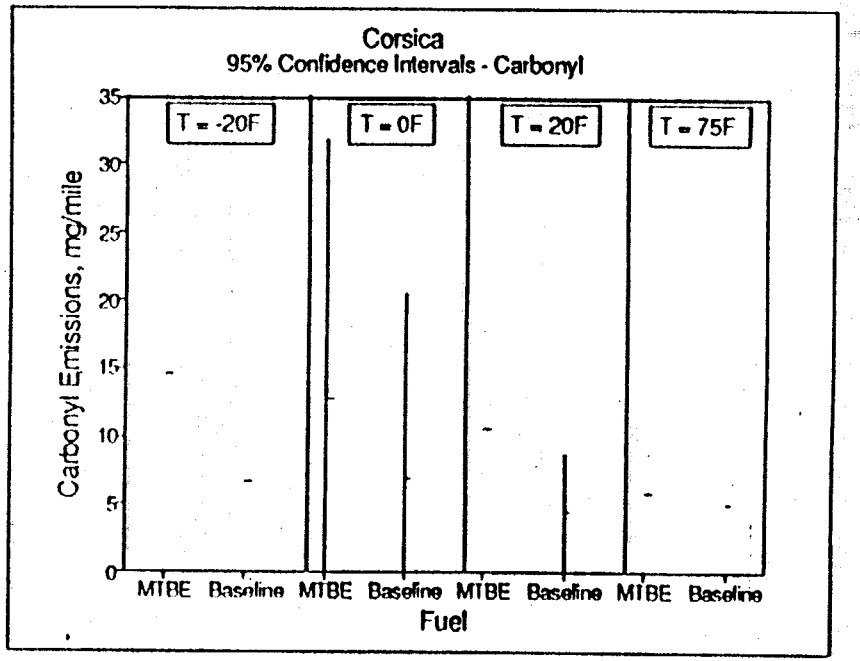


Temperature and fuel effect on composite formaldehyde emissions for both Caprice and Corsica









Temperature and fuel effect on composite carbonyl emissions for both Caprice and Corsica

AUTHOR(S): Dave Veazey, Marcus Martin, Perry Klein, & Dr. Richard Benner

TITLE: CARBON MONOXIDE EMISSIONS IN FAIRBANKS, ALASKA

Vehicles at Fairbanks' wintertime temperatures were tested for exhaust emissions both for cold start and on-road operation. For cold start emissions, engine pre-heating reduced CO emissions by as much as 70%, while oxygenated fuel had no detectable effect. On-road emissions of CO were reduced by an average 28% from using oxygenated fuel. From the results, a CO inventory was revised for Fairbanks, which estimated a total burden of 49.2 tons per day (a 54% decrease from a previous inventory).

Cold start CO emissions appeared to be independent of temperature from +20°F to -40°F. The amount of cold soak time was the primary factor responsible for increased emissions. Due to the inherent chaotic behavior of such a transient mode, cold start emissions contained variability that would not allow serious statistical analyses. One hundred and twenty of the 166 cold start tests conducted were instead combined into a normalized data set such that trends in emissions behavior could be examined. The calculation method used to convert from %CO to grams of CO was found to over-estimate emissions by 10-20%. Fortunately, the results are based on the magnitude of the relative difference between tests on each particular vehicle, and the validity of the results should not be affected. Not all cold start tests comparing pre-heating and fuel type were conducted at identical temperatures. Clear fuel tests were conducted from -40°F to +30°F, while oxygenated fuel tests were conducted from -18°F to +30°F. As a result, if the oxygenated fuels tests had significantly decreased emissions, it would have been difficult to determine any effect from oxygenated fuels. Because there appeared to be no change in CO emissions from either oxygenated fuels or ambient temperatures, it might be surmised that using oxygenated fuels is not effective in reducing cold start emissions.

Four vehicles were tested for on-road emissions. As discussed previously, the calculation from %CO to grams of CO introduces error that is not taken into account. This creates even more error for on-road emissions as the volumetric exhaust flow may change considerably during operation. It is the magnitude of the difference between clear and oxy fuels that is of interest. Run-to-run repeatability is crucial to believing these results. The relative standard deviation ranged from 5-40%. In all cases except one, CO emissions were reduced with oxygenated fuel. Only one vehicle, the high emitter, gave results that indicated a statistical difference between clear and oxygenated fuel. Although not all of the results were statistically significant, they were used to estimate the reduction in CO emissions from oxygenated fuel use. Carbon monoxide was reduced by 22% for highway driving and 32% for city driving.

A remote sensor was used to measure 462 vehicles over 2 days. It was found that 14.5 tons, over 70% of the CO from on-road emissions, came from the dirtiest 10% of the Fairbanks vehicle fleet. The total CO from on-road emissions was 20.3 tons/day.

Based on these results, and the fact that the prior CO inventory was done without benefit of any vehicle measurements, a revised CO inventory estimated only the CO emissions that directly affected attainment of the CO air quality limit. Our results conclude that 49.2 tons CO/day are emitted into Fairbanks. This is a 54% decrease from the prior estimate of 105 tons/day. This represents an upper limit to emissions in Fairbanks. A worst case scenario was used for cold start emissions (with 40% of the vehicles being pre-heated) in which 475 grams/vehicle was emitted by half the registered vehicles each day. All of the fuel purchased each day was attributed to on-road emissions (none to cold starts), providing a high estimate for on-road emissions. Although the numbers used for this inventory are speculative, it was felt that a CO

inventory based on real numbers with some uncertainty would benefit policy-makers who were at the time consulting a CO inventory which was done with no measurements at all. Although this study was not conducted following federal guidelines and procedures, the assumptions made and the conclusions drawn are reasonable, and further study should be initiated to investigate our findings.

From our revised inventory, it was estimated that ambient CO would be reduced by 11% from an oxygenated fuels program. If drivers pre-heated their vehicles all the time, the reduction would be estimated at 8.2 tons, or 17%. By fixing the dirtiest 10% of the vehicles on the road a benefit of 27%, or 13.2 tons could be realized (this estimate changes gross polluters into moderate polluters). If all vehicles were pre-heated and the dirtiest 10% of the vehicles were repaired, there would be a 43% reduction in ambient CO. In the last 4 years, the highest exceedance was 11.9 ppm. A 25% reduction in ambient CO would be required to reach compliance. Neither an oxygenated fuels program or increasing the use of engine pre-heaters will provide this reduction. Only fixing the dirtiest 10% of the vehicles or combining gross polluter repairs with increased pre-heater use would accomplish this according to our results.

FAIRBANKS CO EMISSIONS STUDY

1- COLD STARTS

2- ON-ROAD EMISSIONS

3- CO INVENTORY & CONTROL STRATEGIES

FAIRBANKS 1990 CARBON MONOXIDE INVENTORY

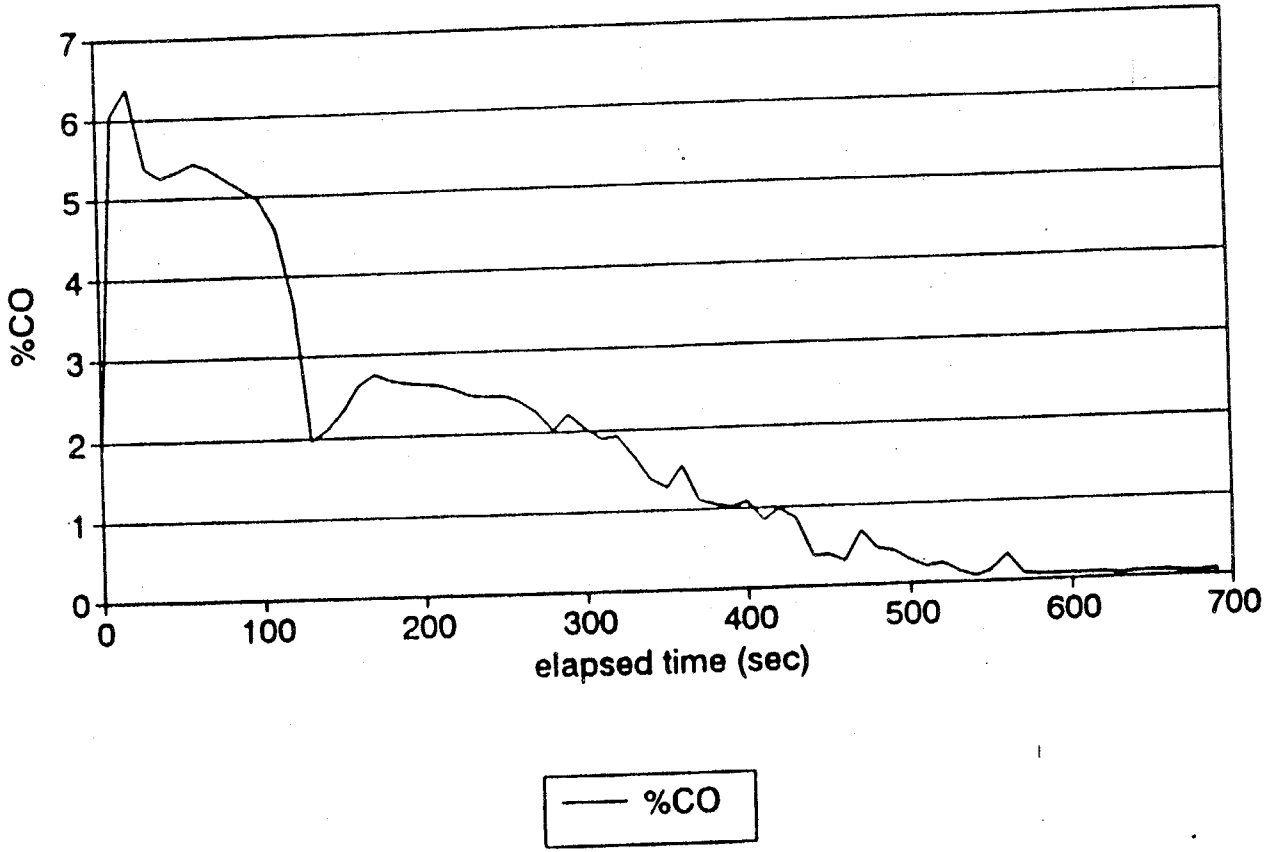
SIERRA RESEARCH, 1992

VEHICLE EMISSIONS	96 TONS
WOOD BURNIING	9 TONS
OTHER	~~12 TONS~~
TOTAL	105 TONS

*91% OF CO EMISSIONS ARE FROM VEHICLES

COLD START EMISSIONS CO% VS. TIME

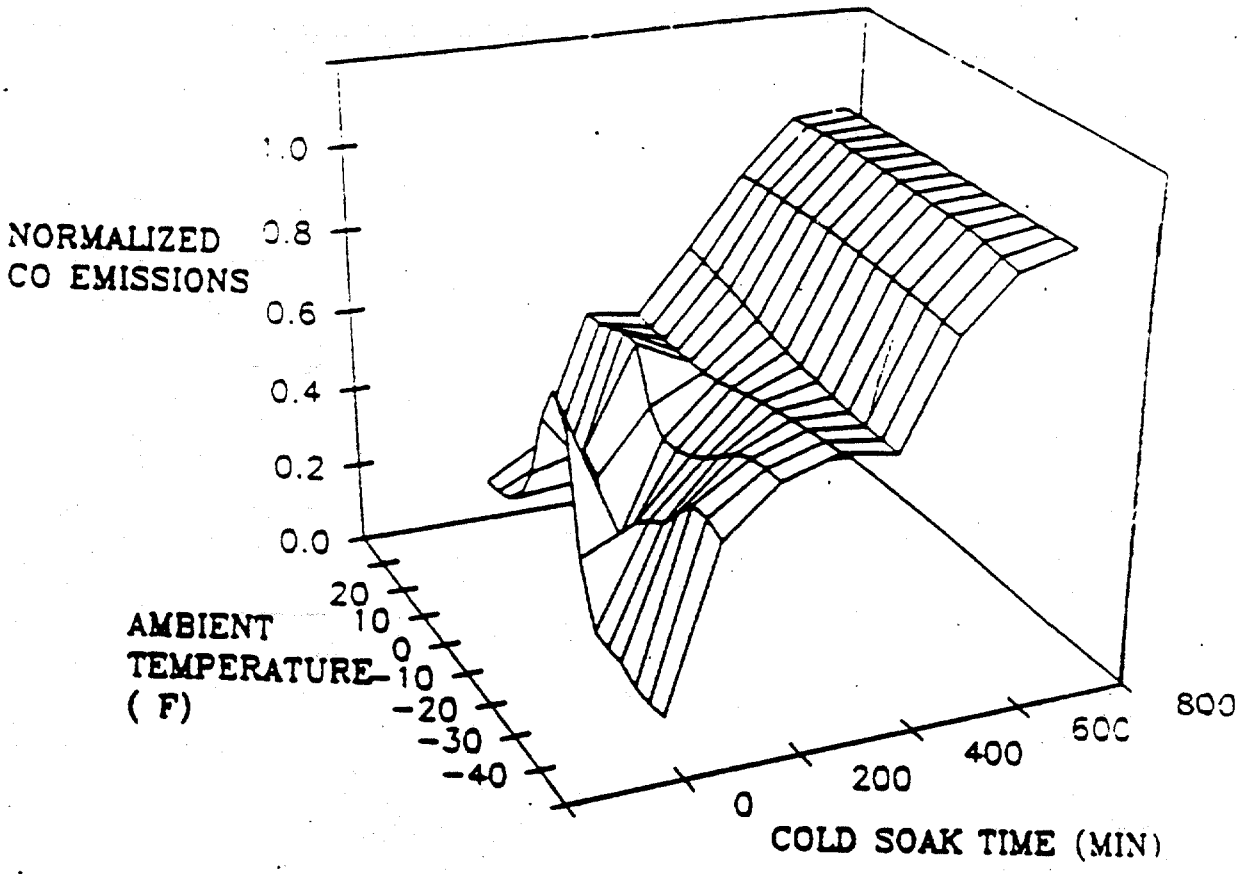
170 MIN COLD SOAK -40 F (MI-005)



NORMALIZED CO EMISSIONS

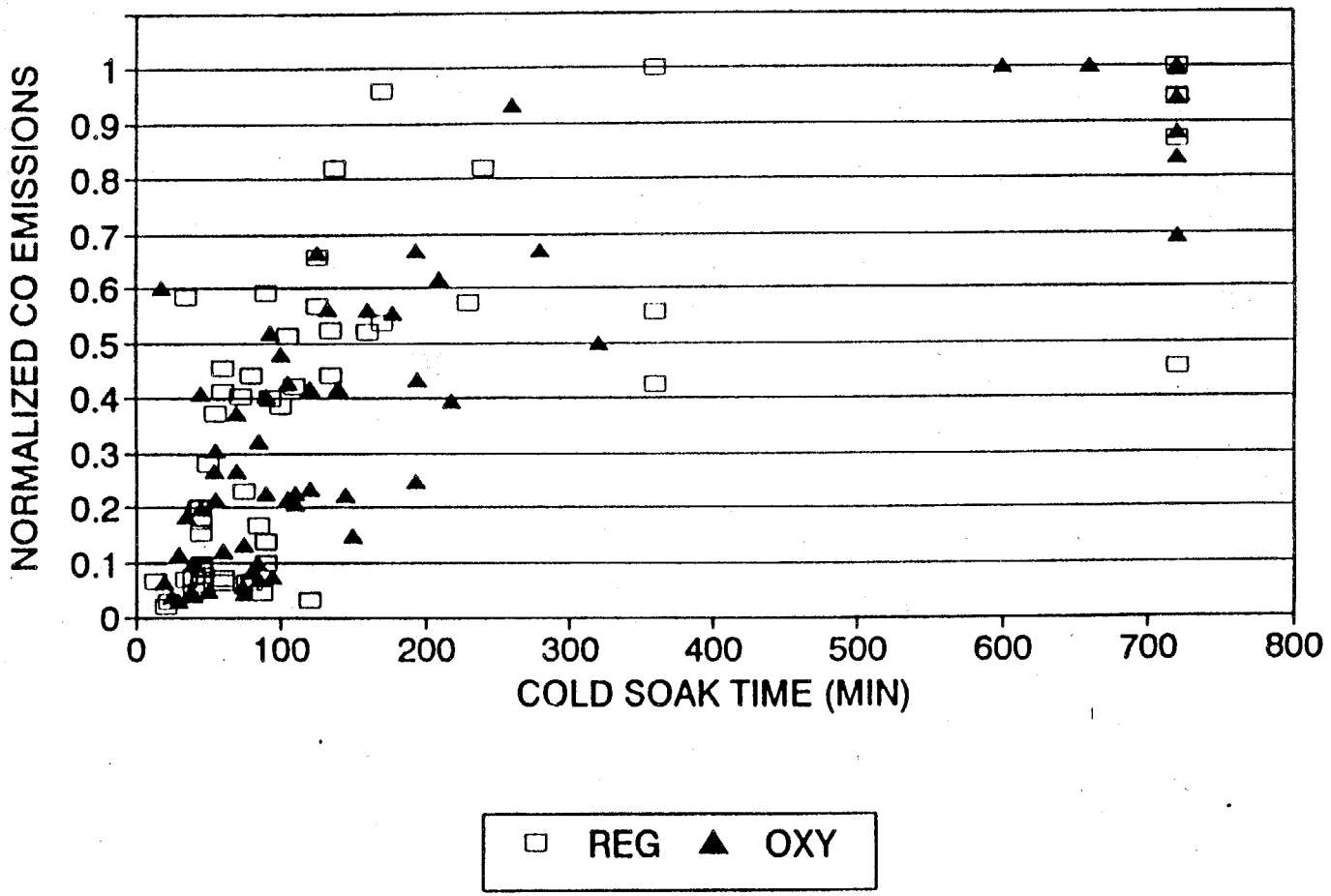
AS A FUNCTION OF TEMPERATURE AND SOAK TIME

(COMBINED DATA SET)



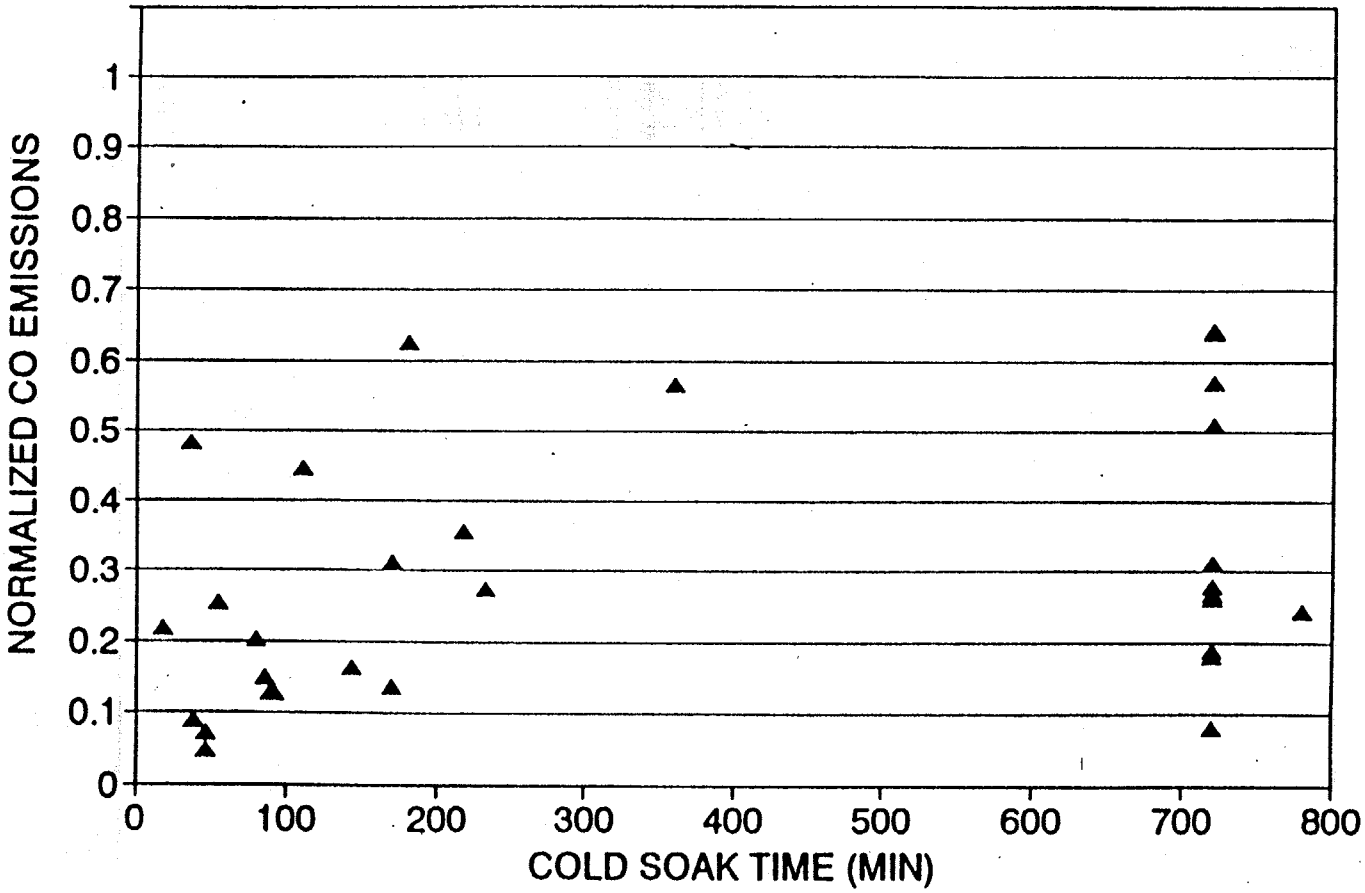
CO EMISSIONS VS COLD SOAK TIME

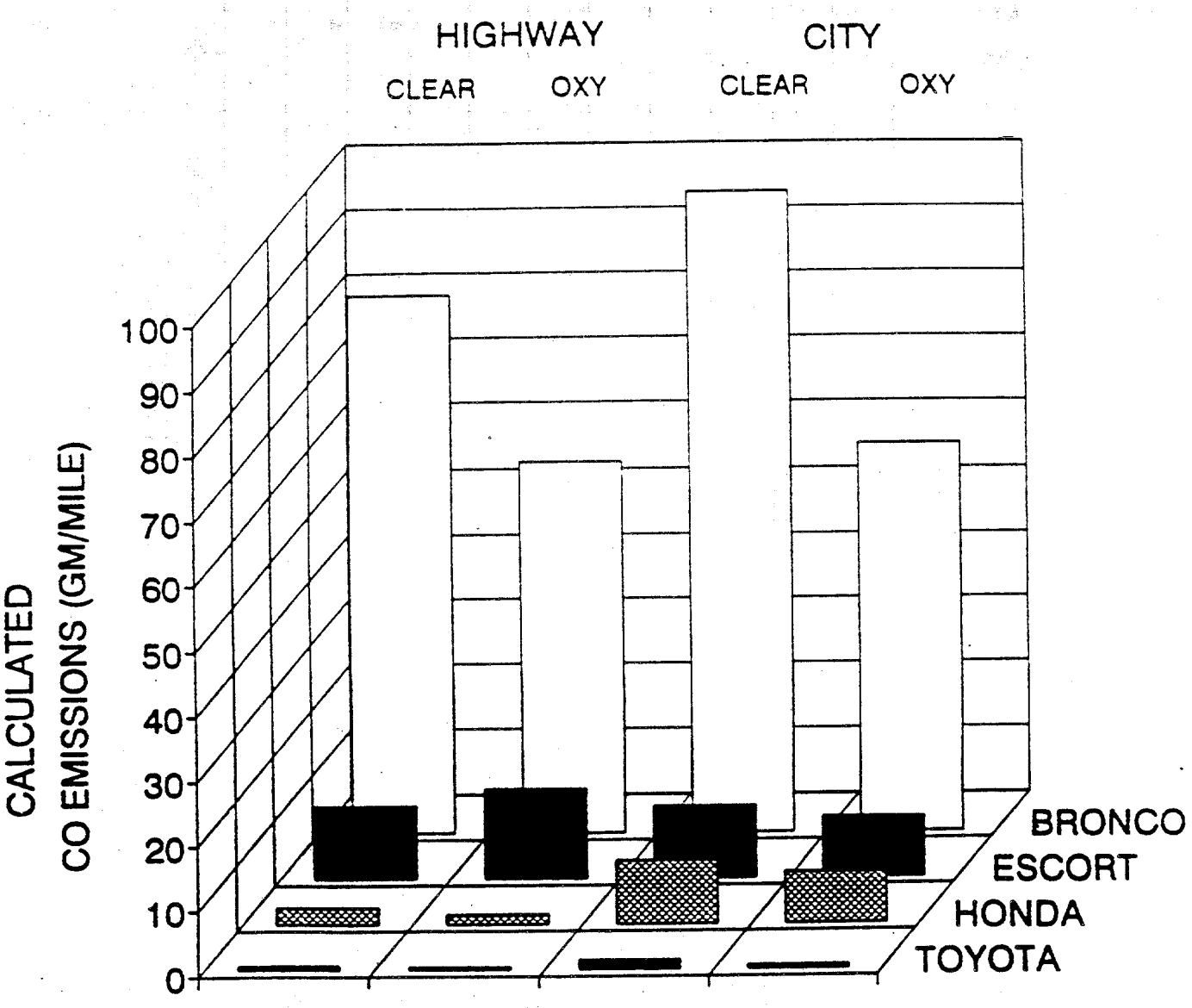
NORMALIZED, COMBINED DATA SET



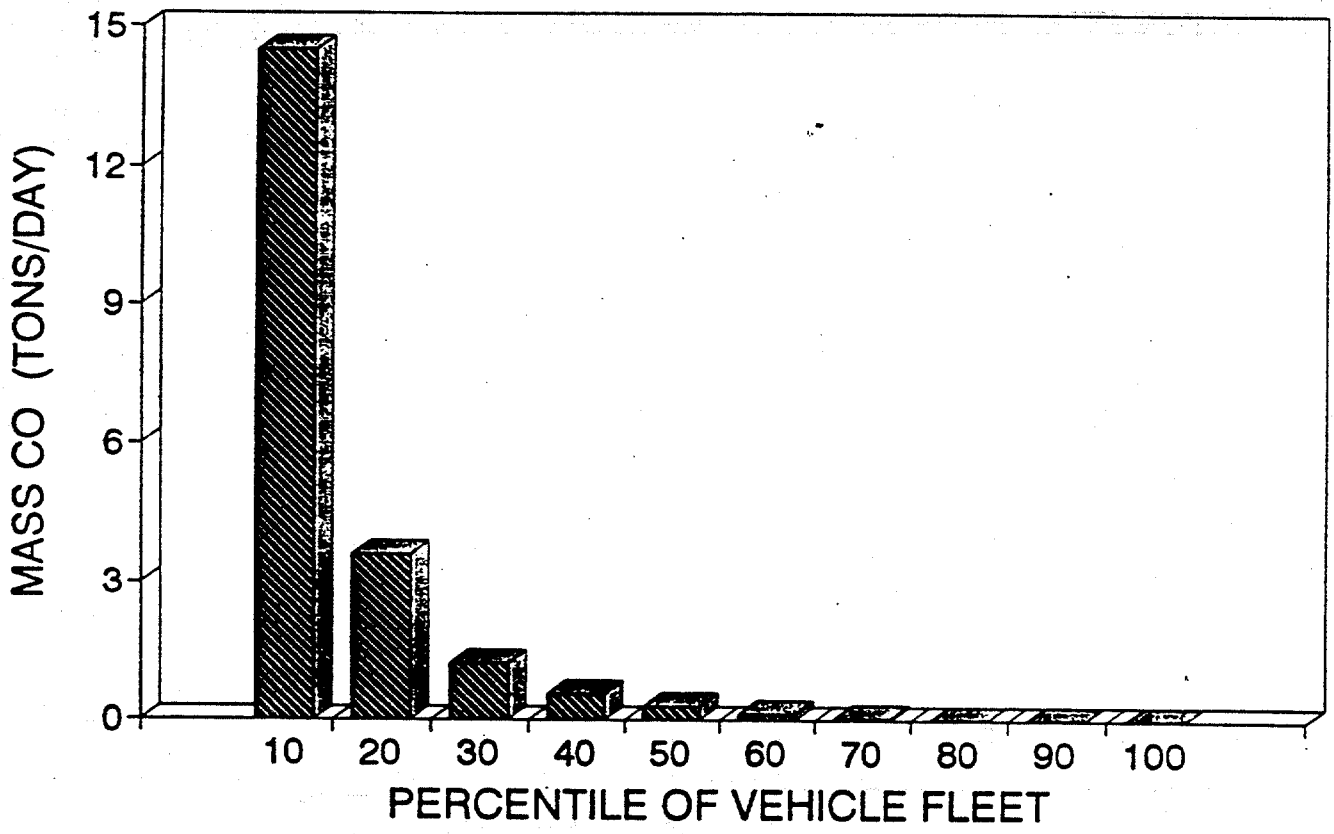
CO EMISSIONS VS COLD SOAK TIME

PLUGGED IN ALL TEMPS



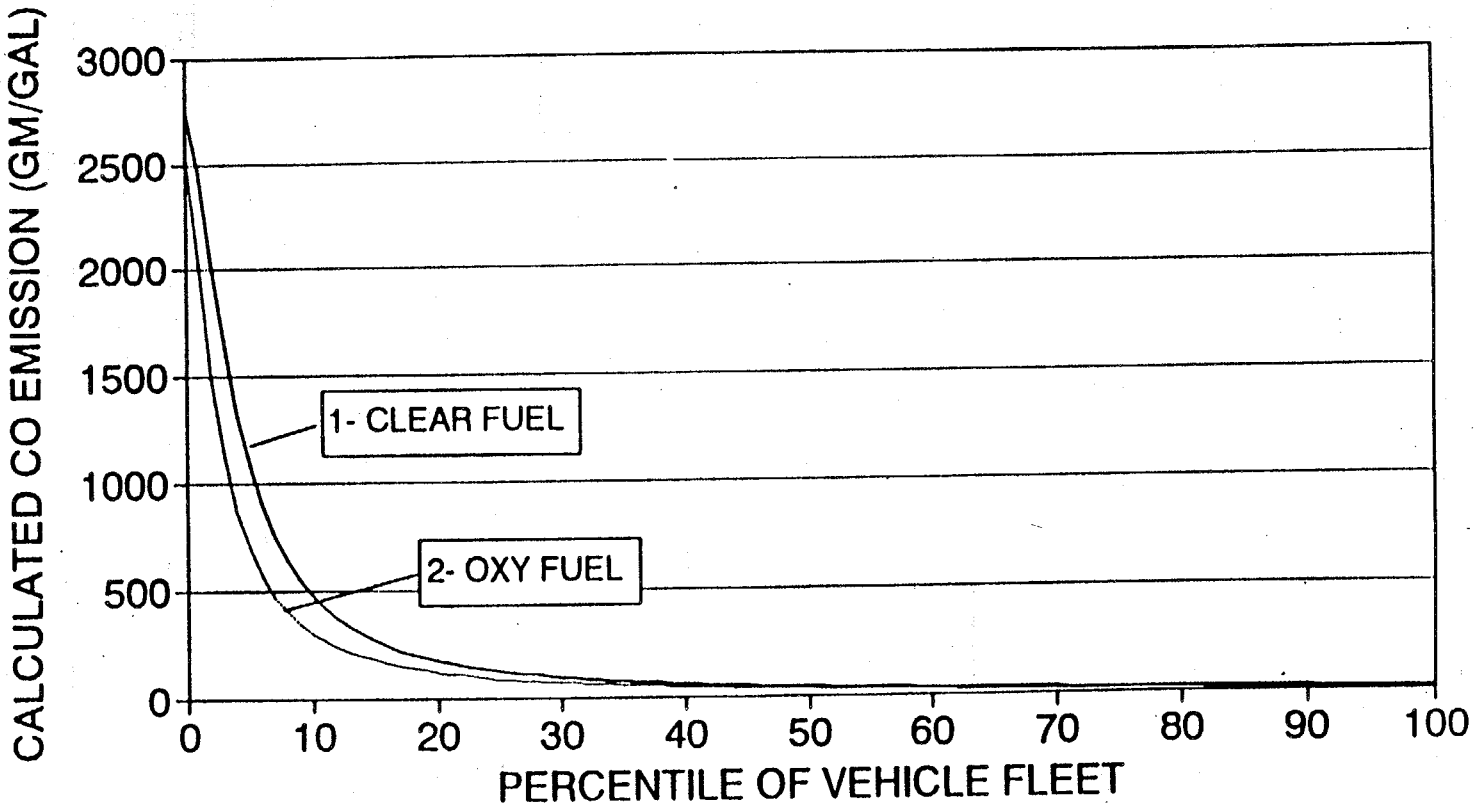

HIGHWAY
CITY
CLEAR
OXY
CLEAR
OXY
CALCULATED
CO EMISSIONS (GM/MILE)
100
90
80
70
60
50
40
30
20
10
0
BRONCO
ESCORT
HONDA
TOYOTA

MASS CO EMISSIONS (TONS/DAY)
ON-ROAD OPERATION



CO EMISSIONS DISTRIBUTION

FAIRBANKS VEHICLE FLEET



COLD START EMISSIONS INVENTORY

COLD START WORST CASE SCENARIO = 475 g/vehicle

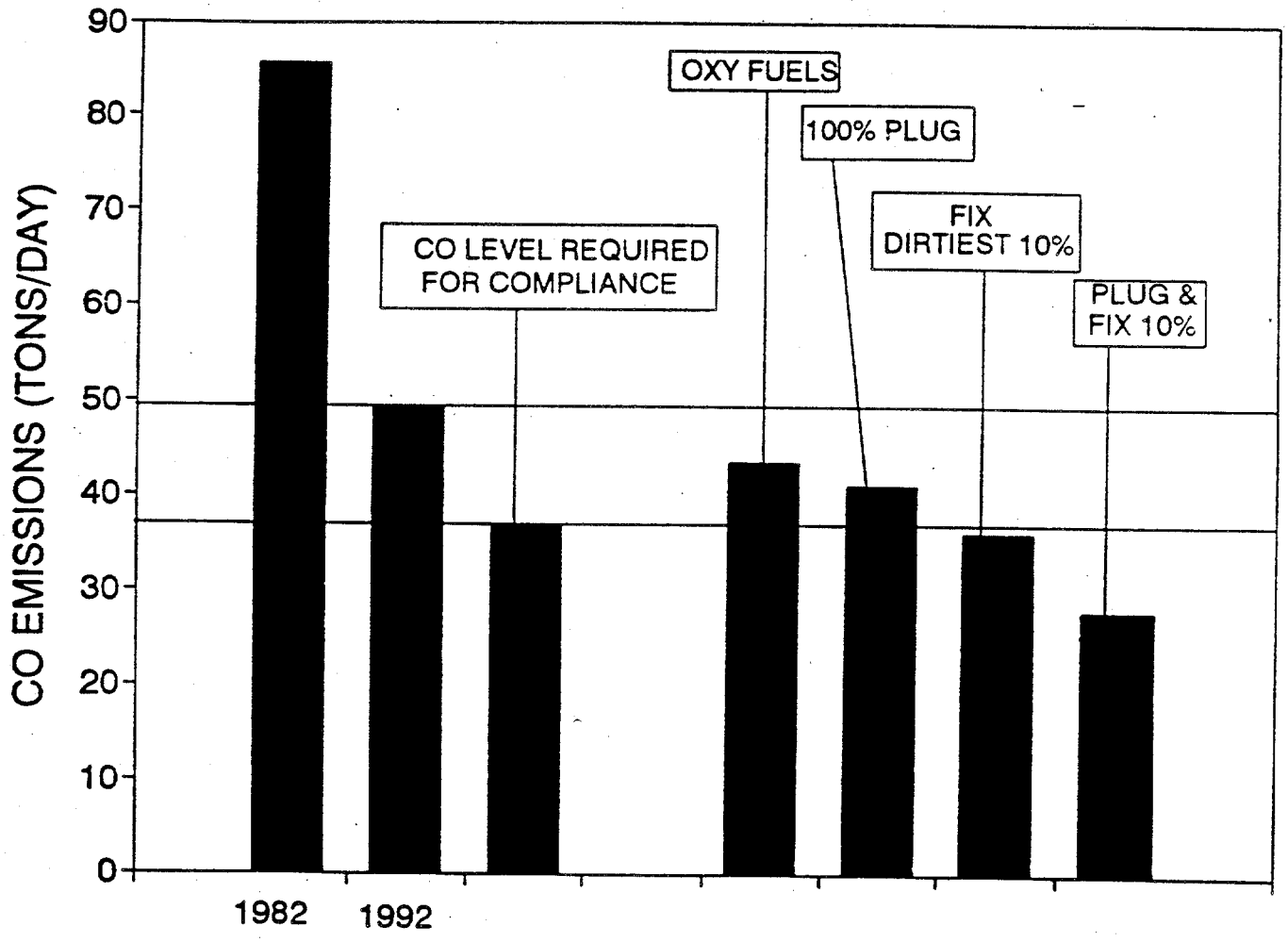
48,140 VEHICLES = 25.2 tons/day

COLD START CO EMISSIONS AT VARYING PLUG-IN RATES

	COLD START CO EMISSIONS (tons/day)
0% PLUG IN	25.2
20% PLUG IN	22.4
40% PLUG IN	19.7
60% PLUG IN	17
80% PLUG IN	14.2
100% PLUG IN	11.5

*The above data represents an upper limit to CO emissions from cold starts in the FNSB.

FAIRBANKS CO EMISSIONS ESTIMATES



SUMMARY

COLD STARTS:

- COLD START EMISSIONS ARE DEPENDENT ON SOAK TIME, NOT TEMPERATURE FROM +20 °F TO -40 °F.
- CO EMISSIONS FROM COLD STARTS ARE NOT REDUCED WITH OXYGENATED FUEL.
- ENGINE PRE-HEATING CAN REDUCE COLD START EMISSIONS BY 70%.

ON-ROAD EMISSIONS:

- ON-ROAD EMISSIONS OF CO ARE REDUCED BY 28% WITH OXYGENATED FUEL.

CO INVENTORY:

- A REVISED CO BUDGET INDICATES THERE IS ~~38%~~ 54% LESS CO THAN PREVIOUSLY ESTIMATED.

AUTHOR(S): Gerry Guay

TITLE: AIR QUALITY MONITORING - OXYGENATED FUELS

The introduction of oxygenated fuels into the gasoline supply in Fairbanks, Alaska, during October 1992 resulted in numerous health-related complaints. In response, Alaska's Department of Environmental Conservation's (ADEC) Ambient Analysis Group initiated a fast-track program to procure, install, and operate a monitoring network capable of quantifying ambient concentrations of hydrocarbon emissions, fuel additives, and aldehydes.

While experience has demonstrated that it is not uncommon to experience an influx of public apprehension and concern over the introduction of oxygenated fuels (gasoline with an additional 2.7% oxygen by weight - MTBE) into CO non-attainment areas, the number, type, and apparent severity of complaints took the Departments of Environmental Conservation and Health and Social Services by surprise. As the number of complaints increased, a request for assistance was made by the State Epidemiologist to the National Centers for Disease Control and Prevention (CDC) to help evaluate the severity and cause of the reported health effects. Simultaneously, ADEC was in the process of identifying a source of hydrocarbon and aldehyde monitoring instrumentation that could be made available to Alaska within 2 weeks. The Oregon Graduate Institute (OGI) was selected to provide hydrocarbon sampling systems, and the U.S. Environmental Protection Agency's (EPA) Region 10 and Desert Research Institute (DRI) supplied the aldehyde monitors. Although the original target date of Thanksgiving was missed by a day or two, the response of all agencies was exceptional.

The original monitoring project was designed to evaluate ambient exposures in Fairbanks, Alaska. Monitoring sites were selected to survey locations in industrial, urban, residential, traffic corridors, and background areas of the city. As coordination between the CDC and ADEC improved, the state realized that an emphasis on ambient air monitoring would not support CDC's objectives. In a last minute change, the monitoring project was redesigned to focus on worker exposure. The majority of the monitoring effort was conducted in automotive garages and fleet vehicles that routinely travel the Fairbanks area.

Monitoring was conducted in three phases. The first phase ran December 1-15 and was established to identify the level of hydrocarbon and aldehyde emissions in Fairbanks from the use of oxygenated fuels. Air sampling for volatile organic hydrocarbons (VOC) was conducted using OGI volatile organic hydrocarbon samplers. Monitoring and analytical protocols followed Method 14 of EPA's Compendium of Methods for the Determination of Toxic Organics in Ambient Air. Sampling for aldehydes was performed using Method 11 and portable aldehyde samplers. After the decision was made to remove MTBE from the fuel supply, a second phase of monitoring was conducted between December 17-22 (the phase-out period). Because no baseline data existed on emission characteristics from fuel in Fairbanks, a third phase of monitoring was conducted from February 17 through March 3. Phase 1-3 monitoring dates and locations are attached.

AUTHOR(S): Roy B. Zweidinger

TITLE: AIR QUALITY MEASUREMENTS IN FAIRBANKS, STAMFORD, AND ALBANY

The introduction of oxygenated fuels (15% MTBE) in Fairbanks, Alaska, in 1992 resulted in many health complaints from consumers. The Governor of Alaska suspended sale of these fuels on December 11, 1992. Air samples were collected prior to the suspension (phase 1), during the phase-out period (phase 2), and after about 2 months after suspension, at which time the MTBE fuels were expected to be at nominal levels (phase 3). For comparison, air samples were also collected from Stamford, Connecticut, which also sold 15% MTBE oxygenated gasoline (but had no consumer health complaints) and Albany, New York, where MTBE was only present in gasoline at nominal levels to enhance octane (Table I). Fuel samples collected from gas stations in Fairbanks during phase 2 and 3 indicated the average wt % MTBE in unleaded regular gasoline decreased from 8.46% to 1.00%, while the average for premium gasoline decreased from 14.66% to 5.56% (Table II).

A limited number of samples were collected from several types of microenvironments in all three cities. The samples were 8-hour averages with start times varying between 7:30 am and 1:00 pm. Volatile organic compounds (VOCs), including MTBE, were collected in evacuated 6-L stainless steel canisters that used either positive pressure pump-type samplers or controlled vacuum-bleed samplers. Aldehydes were collected using 2,4-dinitrophenylhydrazine (DNPH), coated C-18 (Alaska phase 1 only), or silica gel cartridges. The VOCs were analyzed by gas chromatograph (GC) with flame ionization detection (FID), while the aldehydes were analyzed by high-performance liquid chromatography (HPLC). These data are not suitable for short-term exposure assessment. While the data provide approximate ranges of MTBE and other VOC concentrations in the air, they do not accurately quantify air concentrations in cities over a particular period. It should also be noted that ambient temperatures and other meteorological conditions varied greatly among the cities.

For comparison purposes, the sampling sites were divided into seven groups (Table III): auto traffic (ambient, near roadways); residential (ambient, not adjacent to a major roadway or intersection); gas station (ambient, near pump island); background (ambient, outside city limits); garage service area (indoor, cars, gasoline, and other solvents present); parking garage (ambient, Stamford only); and indoor (inside offices and homes).

Figures 1-4 are logarithm plots of the average concentration of MTBE, benzene, total non-methane organic carbon (NMOC), and 1,1,1-trichloroethane (methylchloroform) observed at sites in the three cities. Figure 5 is a normal plot for formaldehyde. (Note: Concentrations are in parts per billion carbon (ppbC), for all compounds except formaldehyde, which are in ppbV. (To convert MTBE ppbC to ppbV, divide by 4 and not 5 to correct for FID detector response calibrated to propane.) The highest average concentrations of MTBE (679 ppbC), benzene (1181 ppbC), total NMOC (80.5 ppmC), and formaldehyde (30.8 ppbV) were found in garage service bays. Concentrations of 1,1,1-trichloroethane exceeded 14,000 ppbC (Fairbanks, phase 3). Aside from the service bays, MTBE concentrations were next highest at gas stations (149 ppbC Fairbanks, phase 2; decreasing to 22.6 ppbC, phase 3). The Stamford gas station MTBE concentrations were the lowest (15 ppbC) but were likely the result of sampler location (Albany average = 96.1 ppbC). Gas station sampling in Stamford was about 15 feet away from the pumps, while sampling in the other cities was at the pump island. Benzene levels were higher in Fairbanks (average roadside 49 ppbC, phase 2; 79 ppbC, phase 3) than in the other cities (Stamford, 5.6 ppbC; Albany, 2.6 ppbC) and increased slightly with the reduction of MTBE in gasoline.

The indoor and outdoor (residential) MTBE concentrations averaged about 28 ppbC in Fairbanks, with residential outdoor levels falling to 4.1 ppbC in phase 3. Similar concentrations were also noted indoors, but the overall indoor average concentration was high because of one home (Hamilton Acres) where concentrations of 80 ppbC were observed (figures 6 and 7). This home had an attached garage and also had elevated levels of benzene (260 ppbC) and other compounds associated with gasoline (figures 8 and 10). Formaldehyde concentrations were higher indoors (10-28 ppbV) than outdoors (2-20 ppbV), which is generally the case, and appeared typical of those seen in indoor air studies (Figure 9).

Figures 10-12 are simulated chromatograms for several indoor versus ambient samples that were collected concurrently in Fairbanks. Figure 10 shows the home with an attached garage mentioned above and indicates the presence of gasoline vapors indoors. Figure 11 shows a situation where most compounds had similar concentrations inside and outside and lacked an indoor source. Methylchloroform (ME-CHLOROFORM) and hexane are hard to explain and are likely contaminants. Toluene, however, may have an indoor source. Figure 12 is a location near a major intersection; concentrations are slightly higher outside than inside. A compound found indoors in high concentrations and having a retention time similar to pentane was identified as 2-propanol. Figure 13 shows an attempt to indicate the increased evaporative emissions at a Fairbanks gas station compared to roadside ambient measurements. Concentrations of VOCs observed at the 2nd and Cushman sites were normalized to the observed concentration of benzene, and these factors were used to predict concentrations at the gas station. The observed concentrations of light hydrocarbons are much higher than predicted concentrations; this indicates increasing evaporative emissions from refueling.

Disclaimer: The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

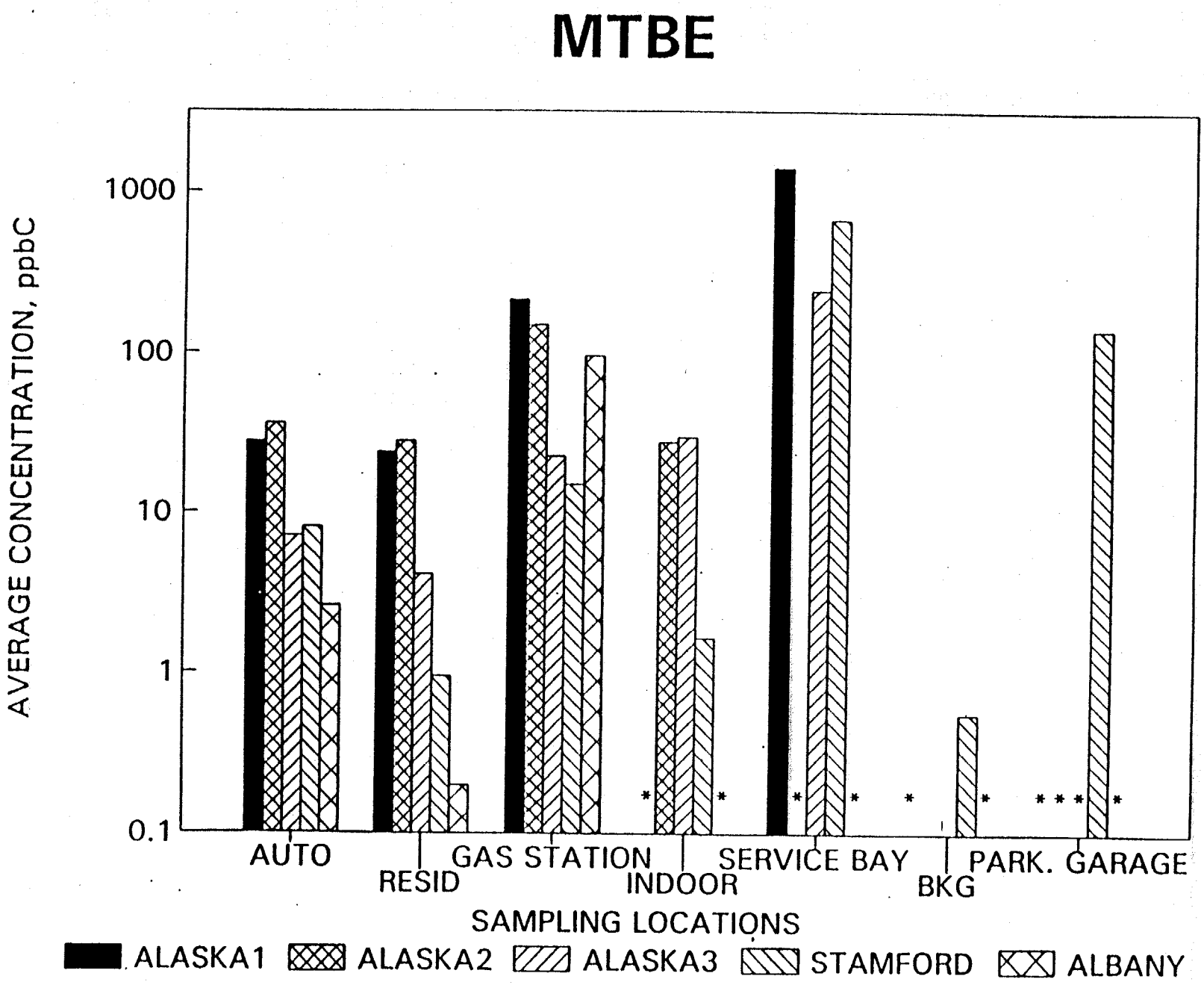

MTBE
AVERAGE CONCENTRATION, ppbC
1000
100
10
1
0.1
AUTO
RESID
GAS STATION
INDOOR
SERVICE BAY
BKG
PARK. GARAGE
SAMPLING LOCATIONS
ALASKA1
ALASKA2
ALASKA3
STAMFORD
ALBANY

FIGURE 1

BENZENE

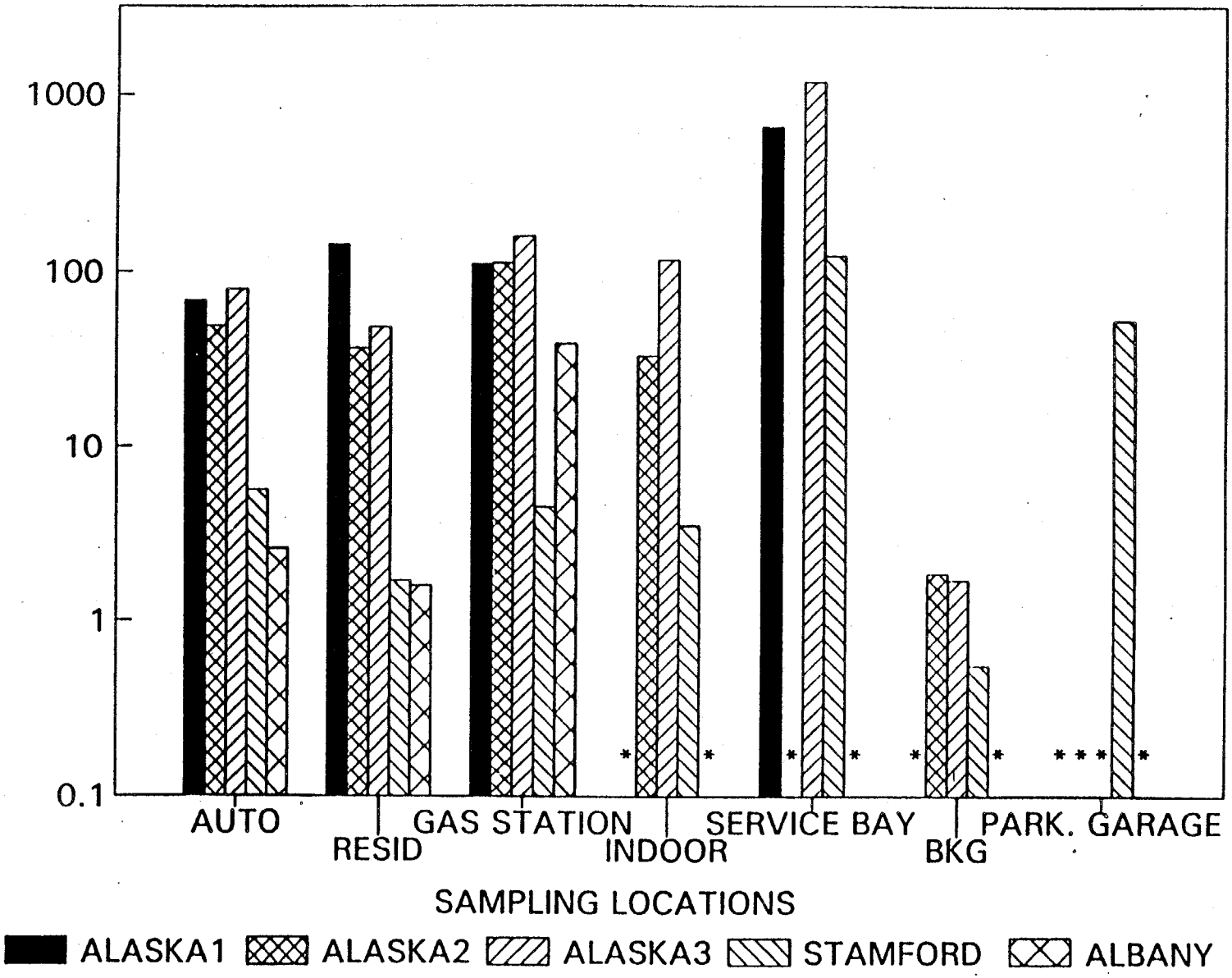


FIGURE 2

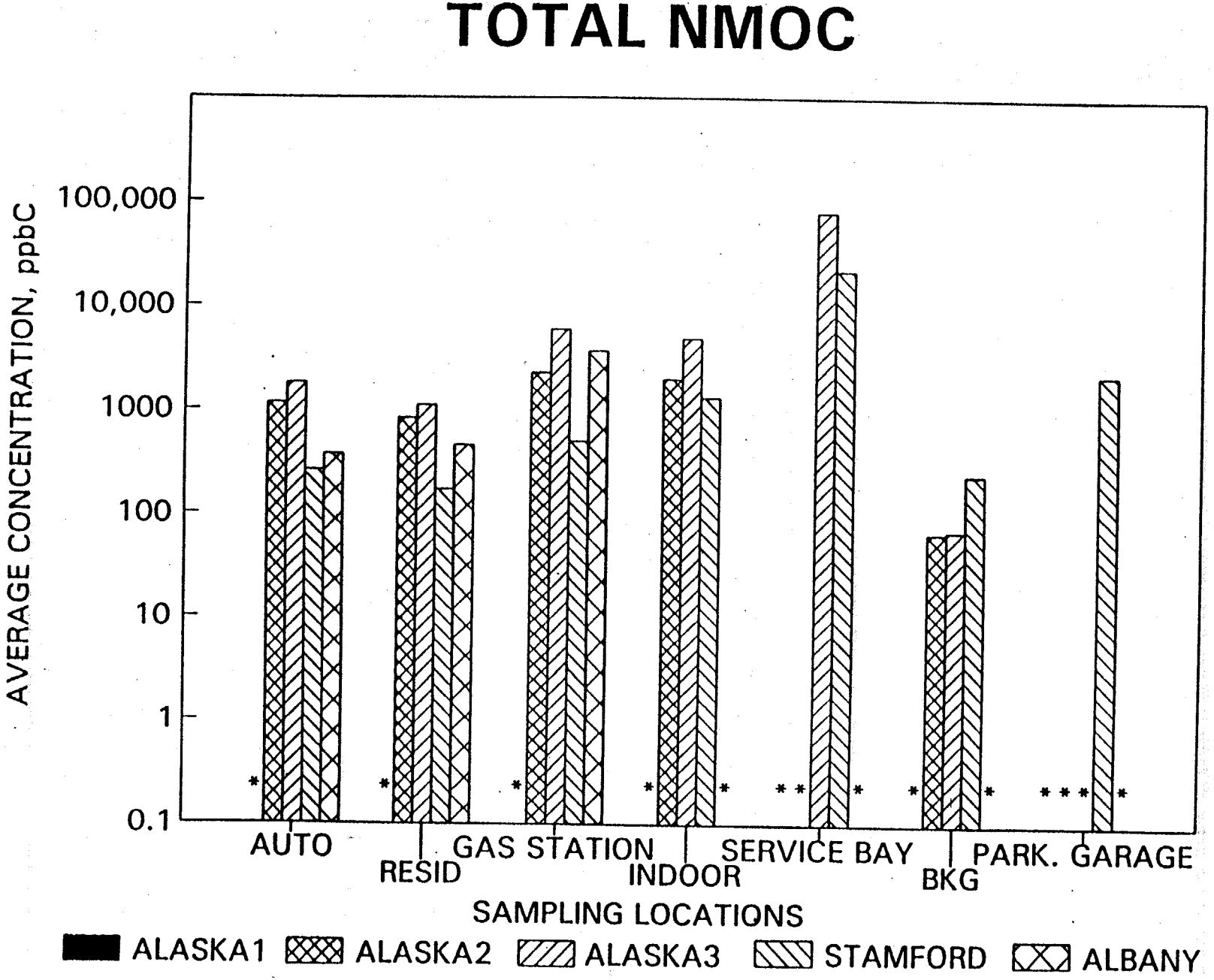

TOTAL NMOC
AVERAGE CONCENTRATION, ppbC
100,000
10,000
1000
100
10
1
0.1
AUTO
RESID
GAS STATION
INDOOR
SERVICE BAY
BKG
PARK. GARAGE
SAMPLING LOCATIONS
ALASKA1
ALASKA2
ALASKA3
STAMFORD
ALBANY

FIGURE 3

1,1,1-TRICHLOROETHANE

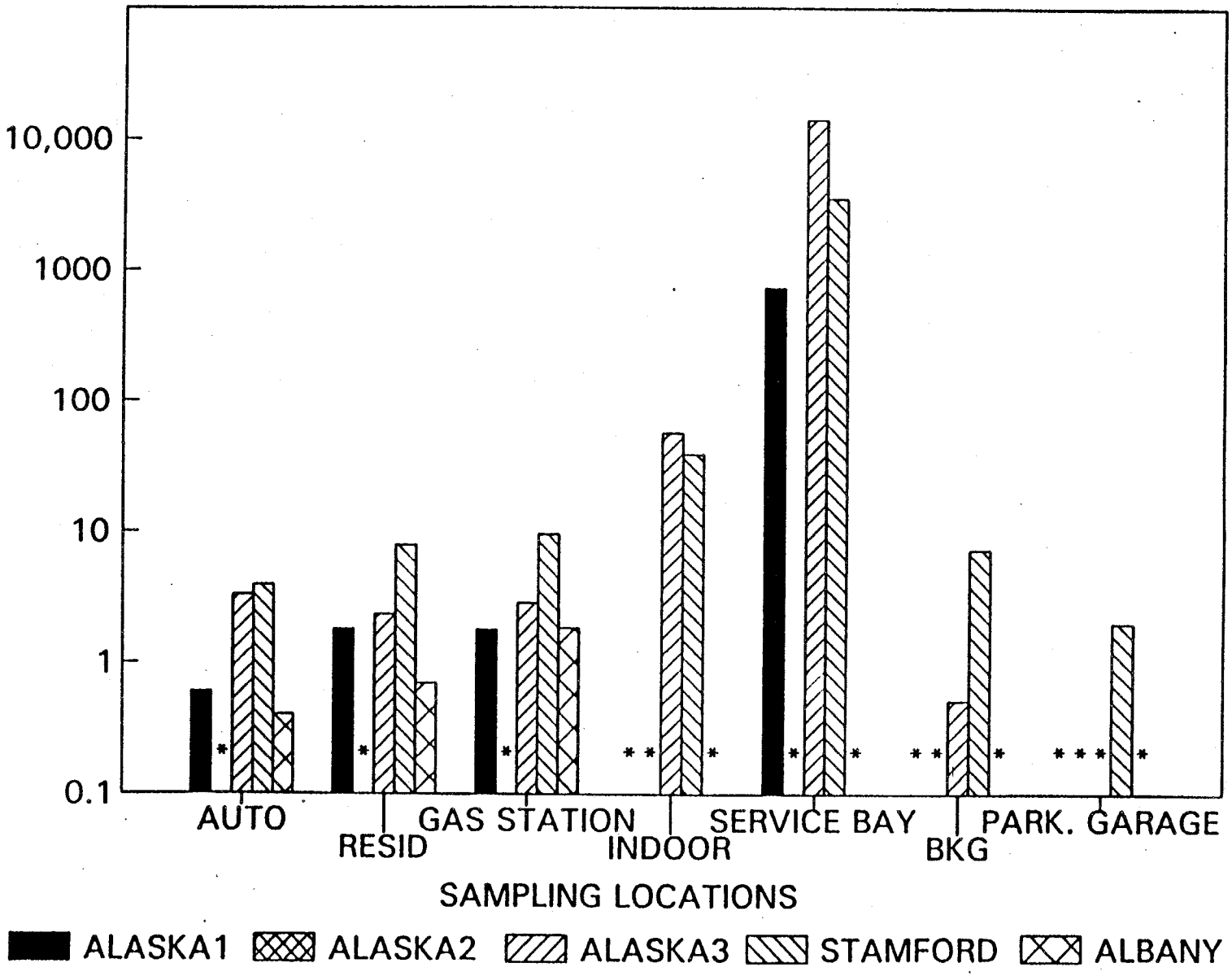
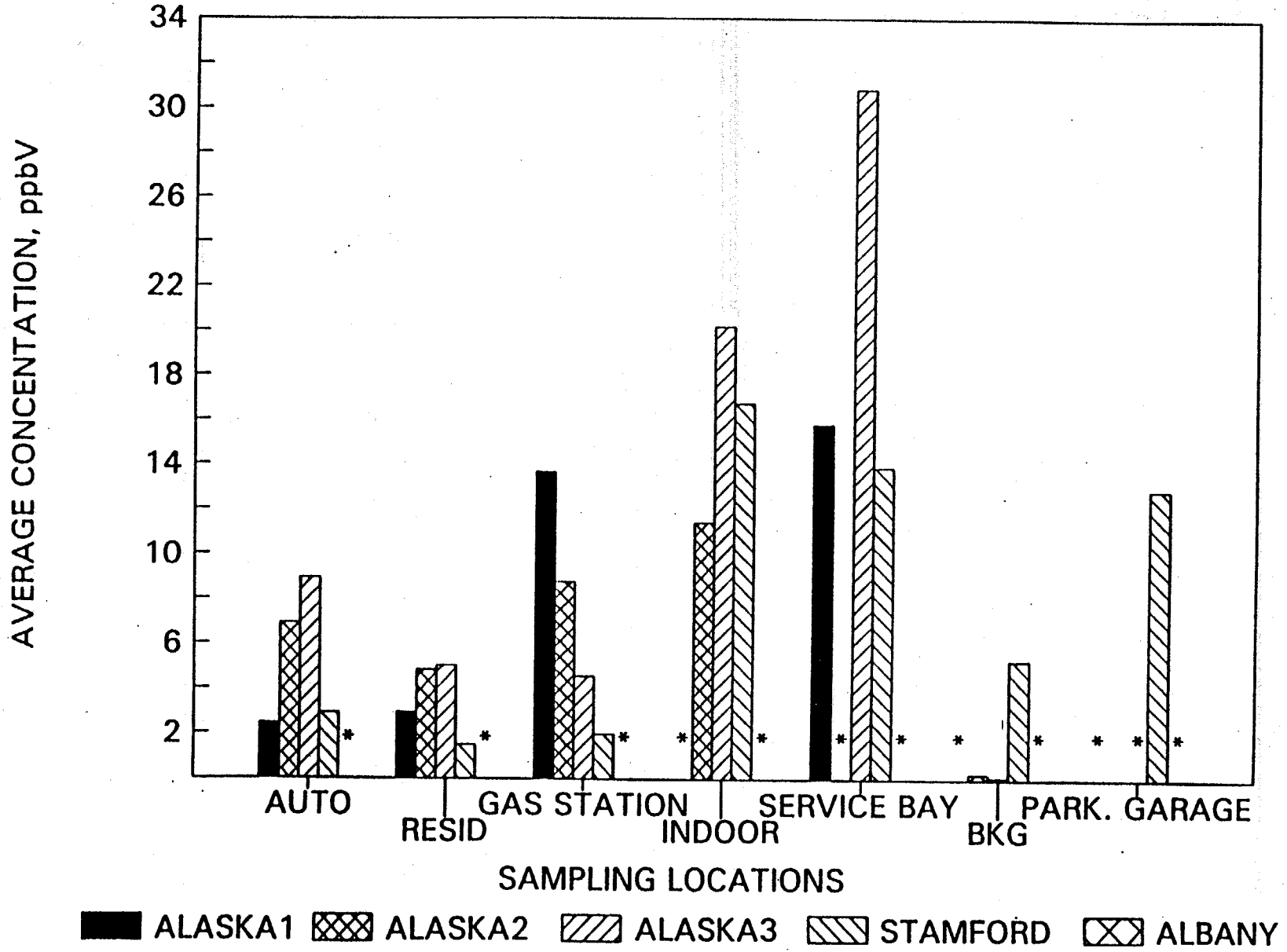


FIGURE 4

FORMALDEHYDE



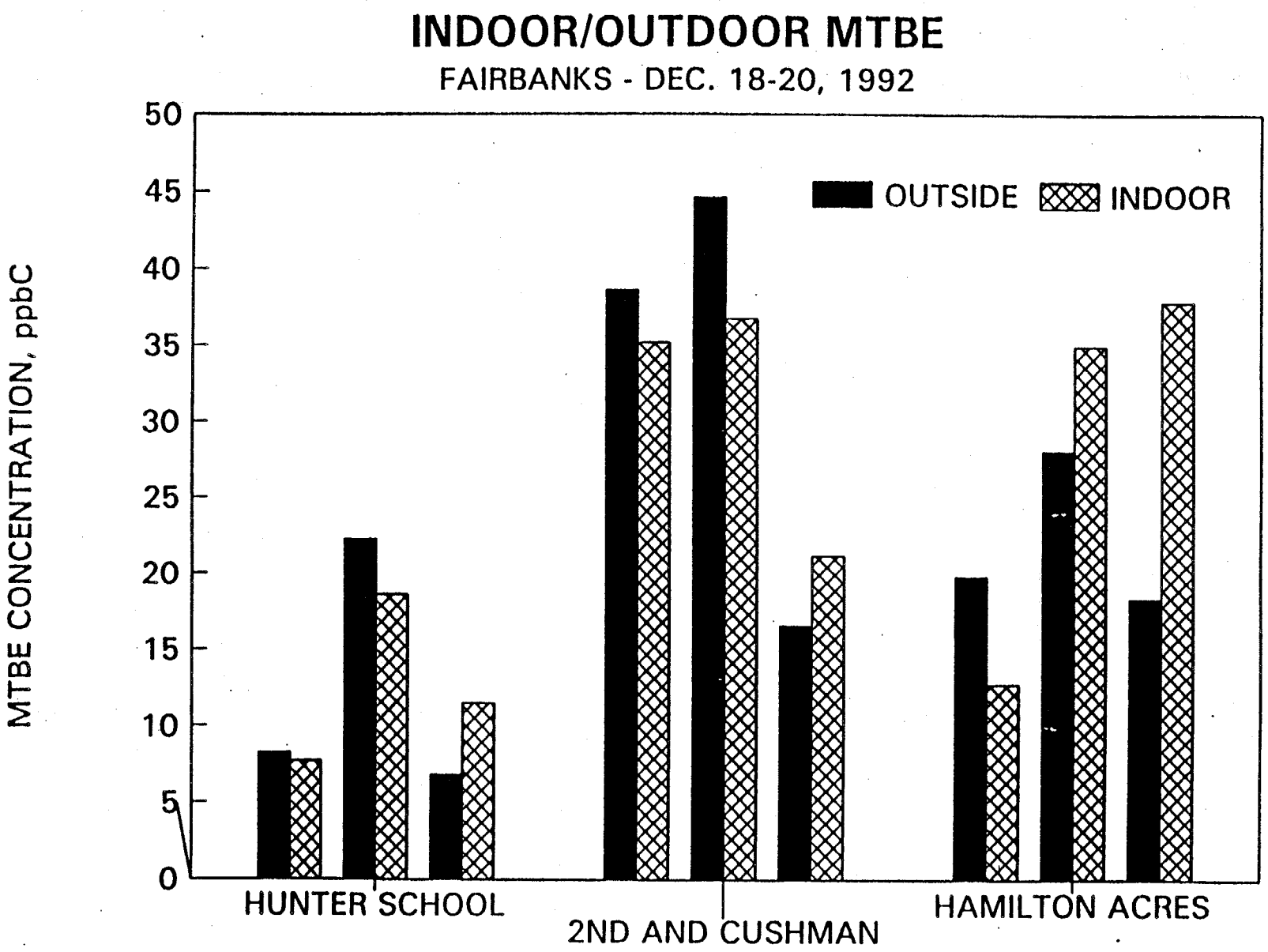

INDOOR/OUTDOOR MTBE
FAIRBANKS - DEC. 18-20, 1992
MTBE CONCENTRATION, ppbC
50
45
40
35
30
25
20
15
10
5
0
OUTSIDE
INDOOR
HUNTER SCHOOL
2ND AND CUSHMAN
HAMILTON ACRES

FIGURE 6

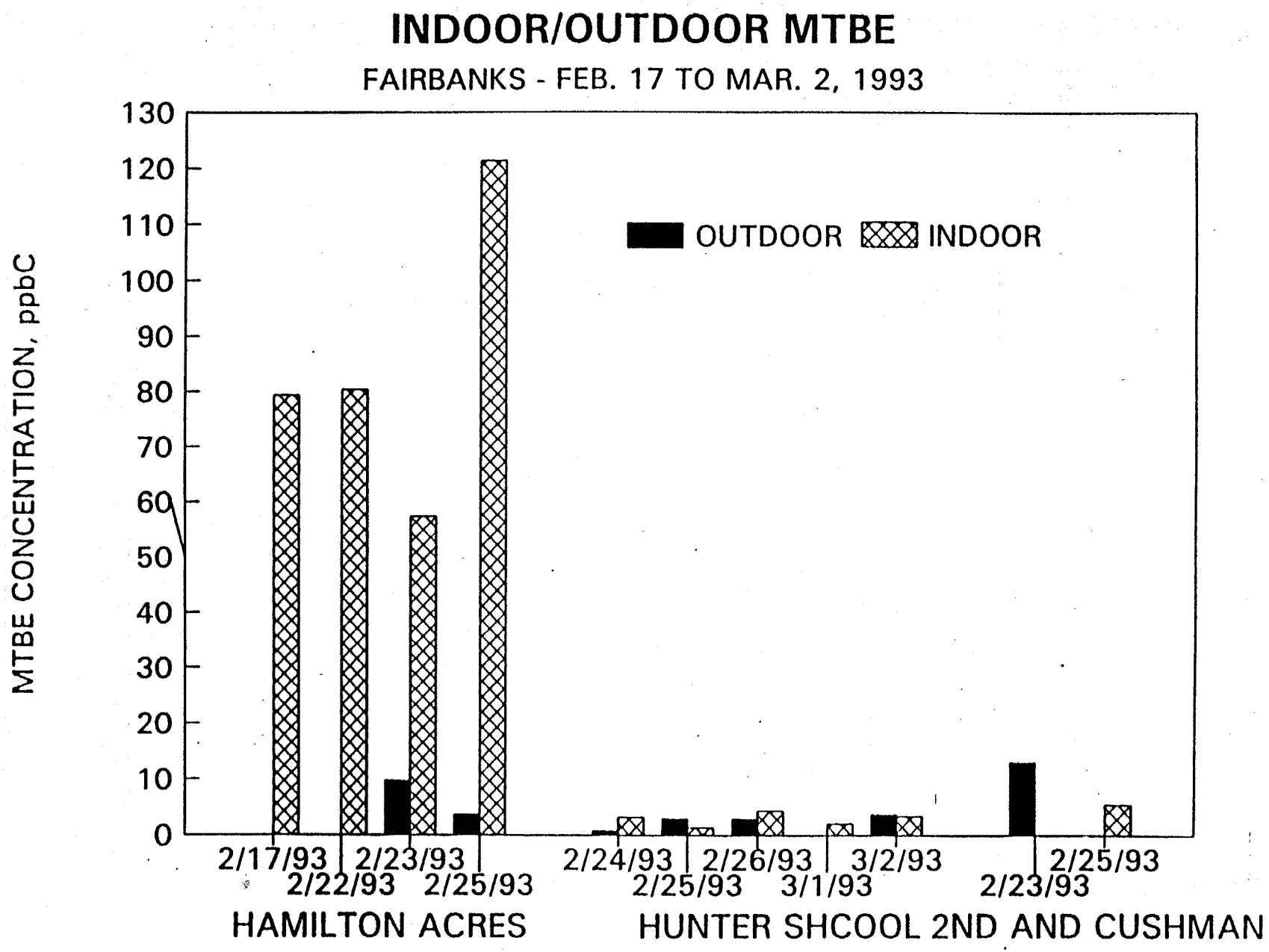

INDOOR/OUTDOOR MTBE
FAIRBANKS - FEB. 17 TO MAR. 2, 1993
MTBE CONCENTRATION, ppbC
130
120
110
100
90
80
70
60
50
40
30
20
10
0
OUTDOOR
INDOOR
2/17/93
2/22/93
2/23/93
2/25/93
2/24/93
2/25/93
2/26/93
3/1/93
3/2/93
2/23/93
2/25/93
HAMILTON ACRES
HUNTER SHCOOL 2ND AND CUSHMAN

FIGURE 7

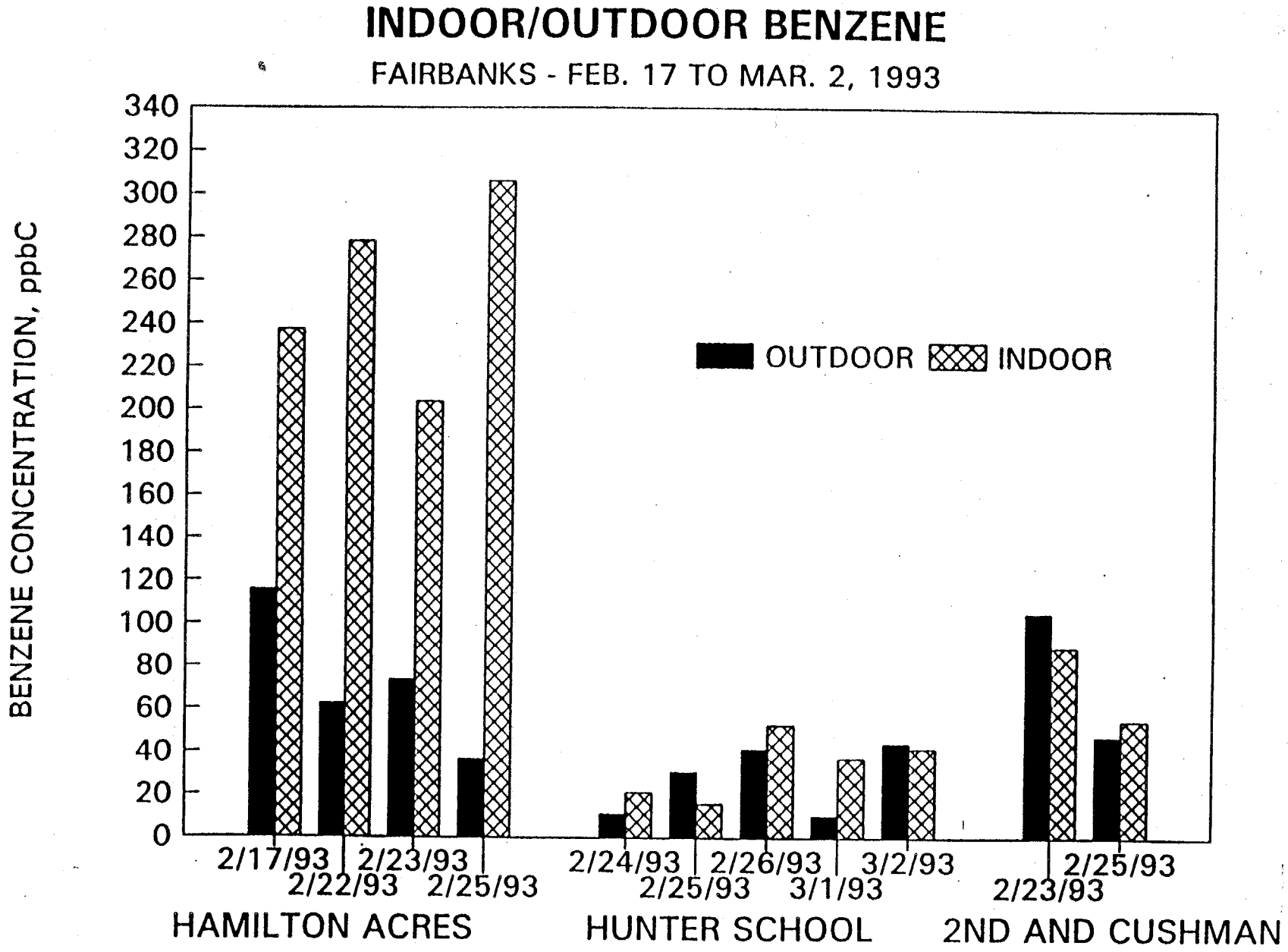

INDOOR/OUTDOOR BENZENE
FAIRBANKS - FEB. 17 TO MAR. 2, 1993
BENZENE CONCENTRATION, ppbC
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
OUTDOOR
INDOOR
2/17/93
2/22/93
2/23/93
2/25/93
2/24/93
2/25/93
2/26/93
3/1/93
3/2/93
2/23/93
2/25/93
HAMILTON ACRES
HUNTER SCHOOL
2ND AND CUSHMAN

FIGURE 8

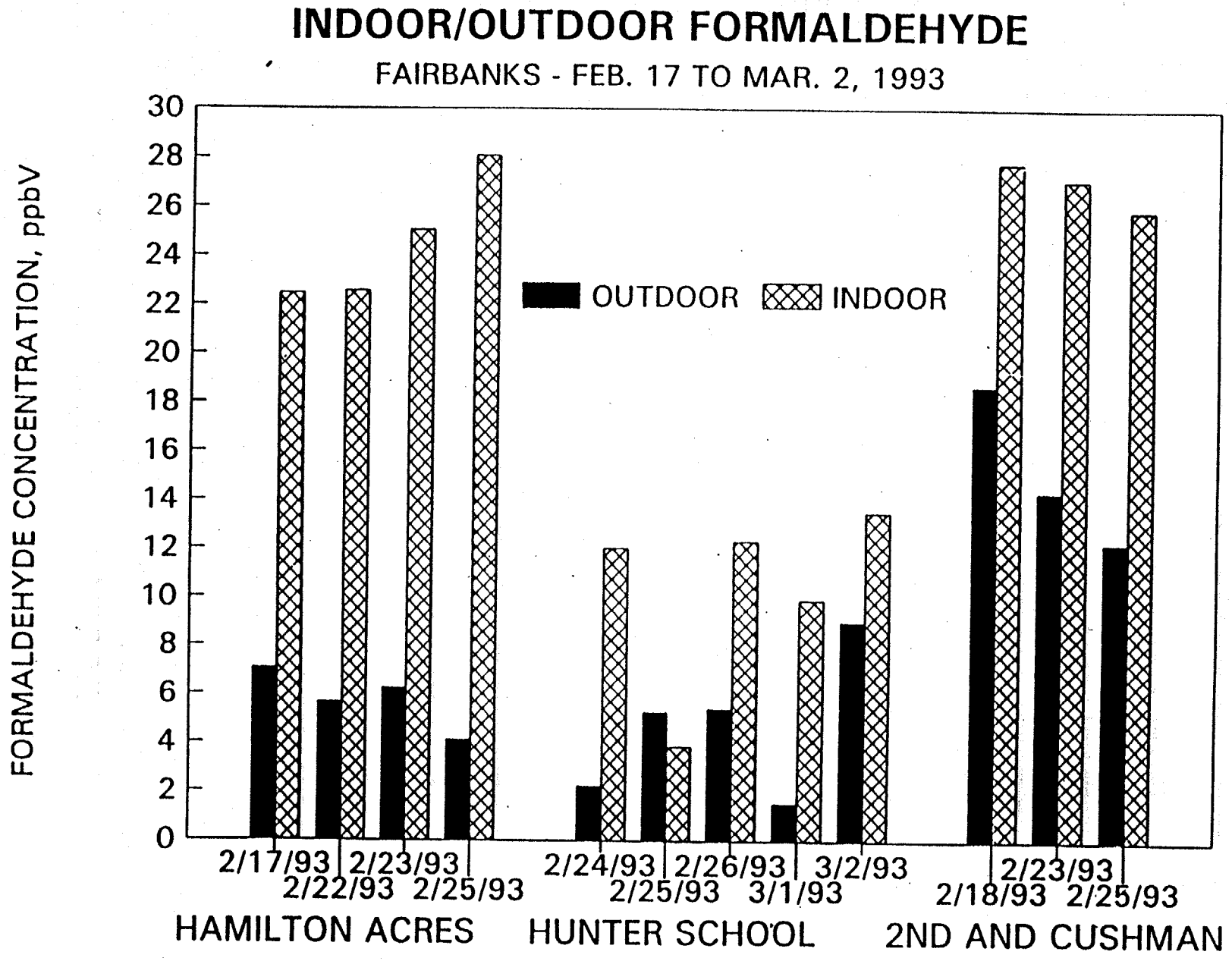

INDOOR/OUTDOOR FORMALDEHYDE
FAIRBANKS - FEB. 17 TO MAR. 2, 1993
FORMALDEHYDE CONCENTRATION, ppbV
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
OUTDOOR
INDOOR
2/17/93
2/22/93
2/23/93
2/25/93
2/24/93
2/25/93
2/26/93
3/1/93
3/2/93
2/18/93
2/23/93
2/25/93
HAMILTON ACRES
HUNTER SCHOOL
2ND AND CUSHMAN

FIGURE 9

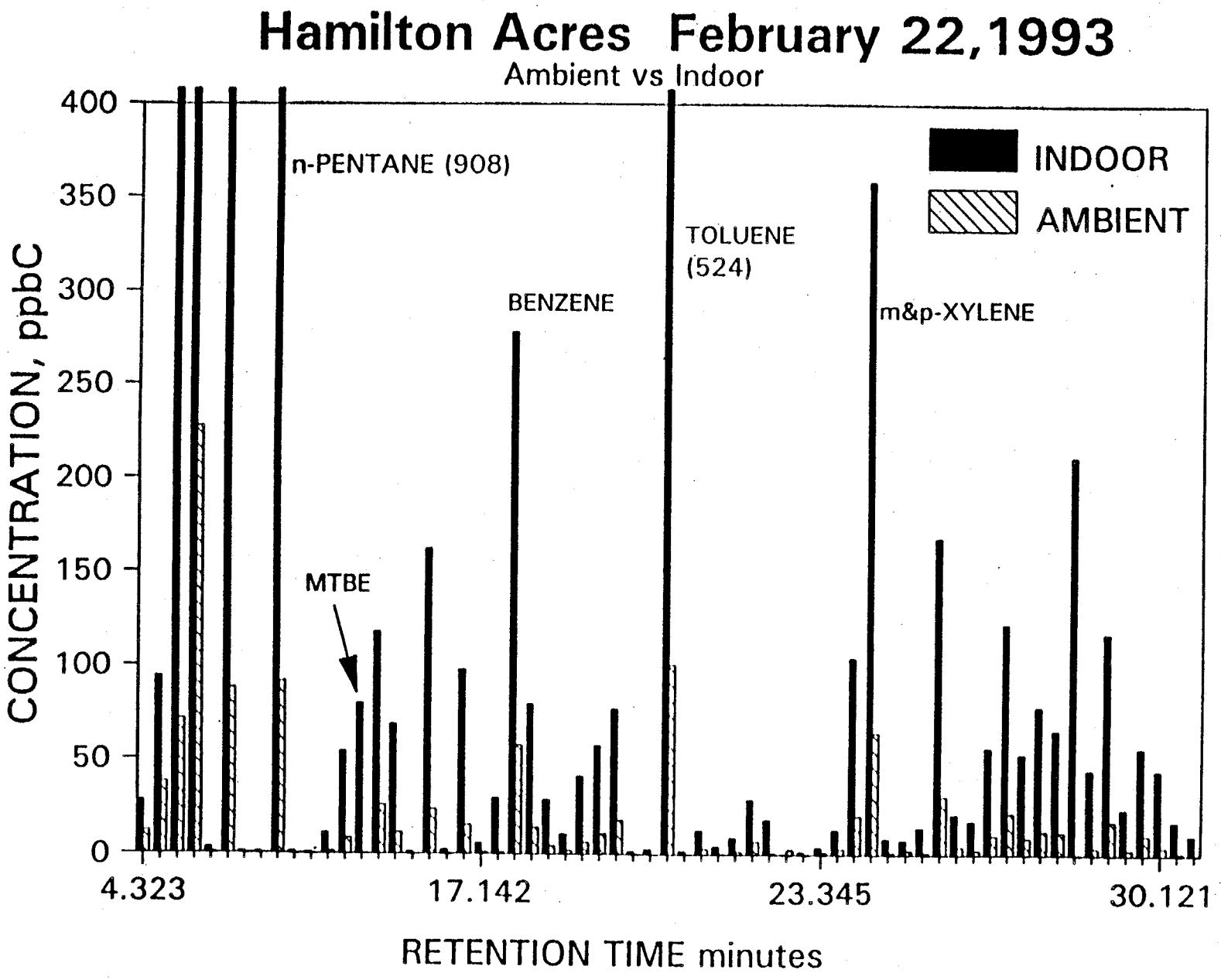
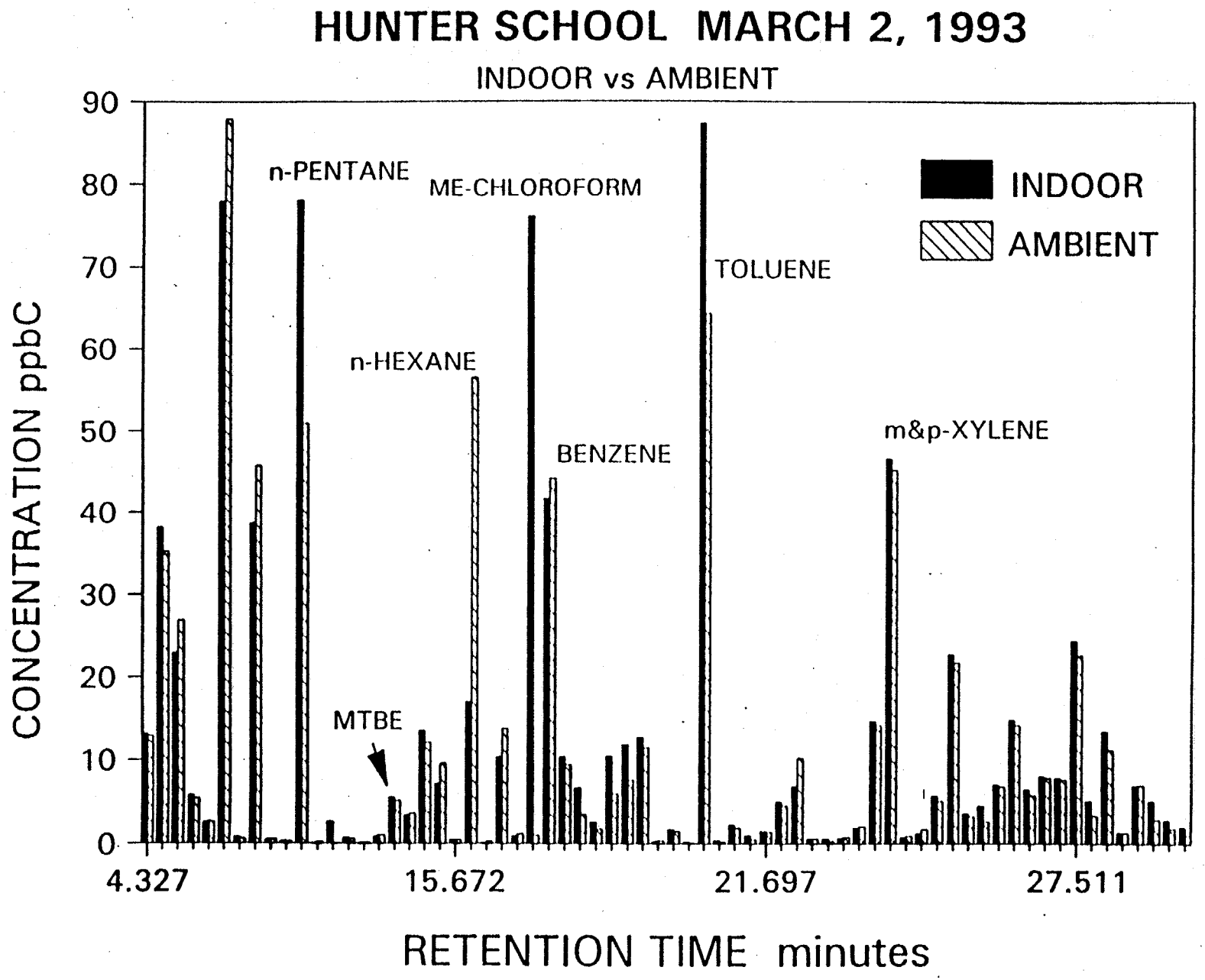

Hamilton Acres February 22,1993
Ambient vs Indoor
INDOOR
AMBIENT
n-PENTANE (908)
TOLUENE
(524)
BENZENE
m&p-XYLENE
MTBE
CONCENTRATION, ppbC
400
350
300
250
200
150
100
50
0
4.323
17.142
23.345
30.121
RETENTION TIME minutes

FIGURE 10


HUNTER SCHOOL MARCH 2, 1993
INDOOR vs AMBIENT
CONCENTRATION ppbC
90
80
70
60
50
40
30
20
10
0
n-PENTANE
ME-CHLOROFORM
n-HEXANE
BENZENE
TOLUENE
m&p-XYLENE
MTBE
INDOOR
AMBIENT
4.327
15.672
21.697
27.511
RETENTION TIME minutes

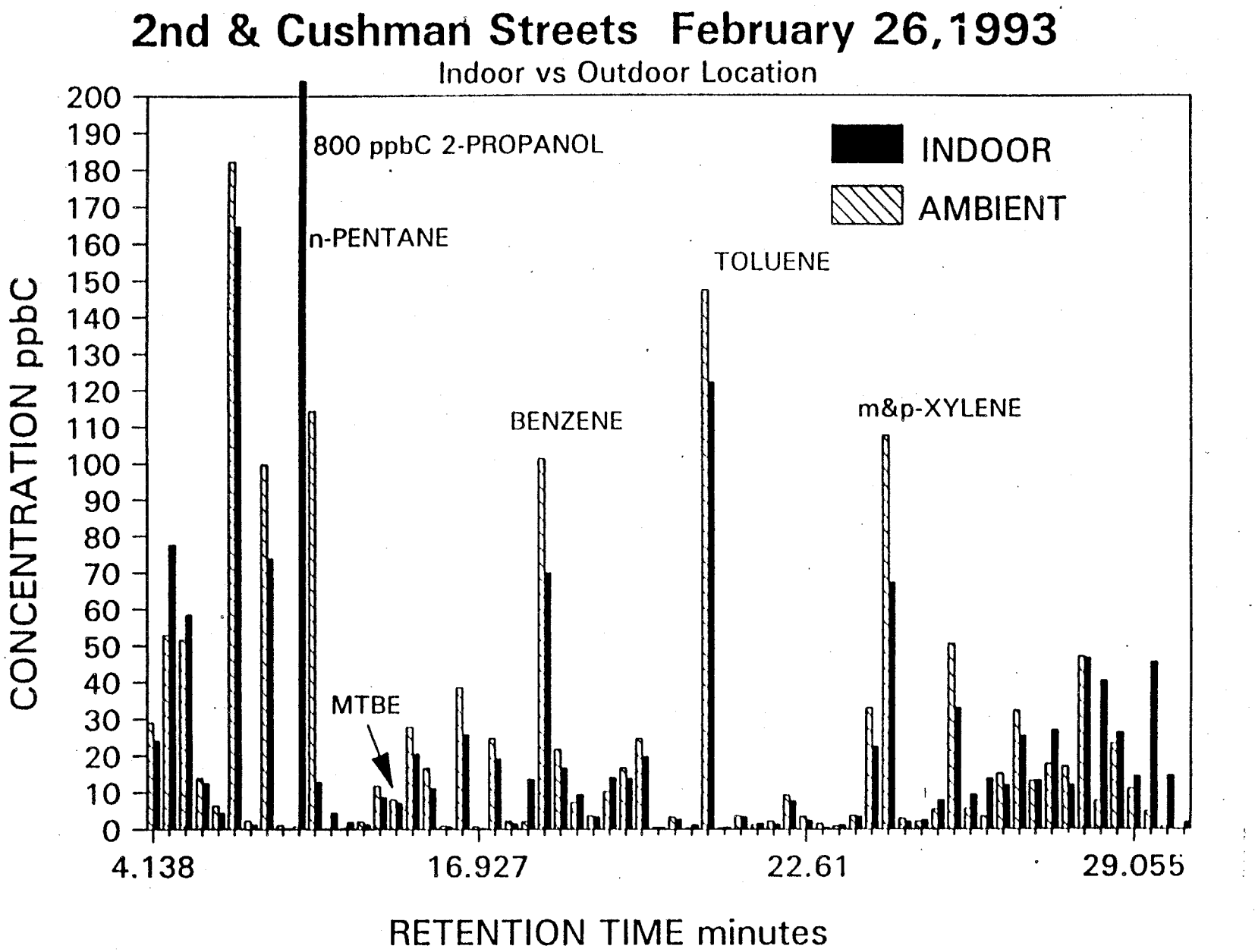

2nd & Cushman Streets February 26,1993
Indoor vs Outdoor Location
CONCENTRATION ppbC
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
800 ppbC 2-PROPANOL
n-PENTANE
MTBE
BENZENE
TOLUENE
m&p-XYLENE
INDOOR
AMBIENT
4.138
16.927
22.61
29.055
RETENTION TIME minutes

FIGURE 12

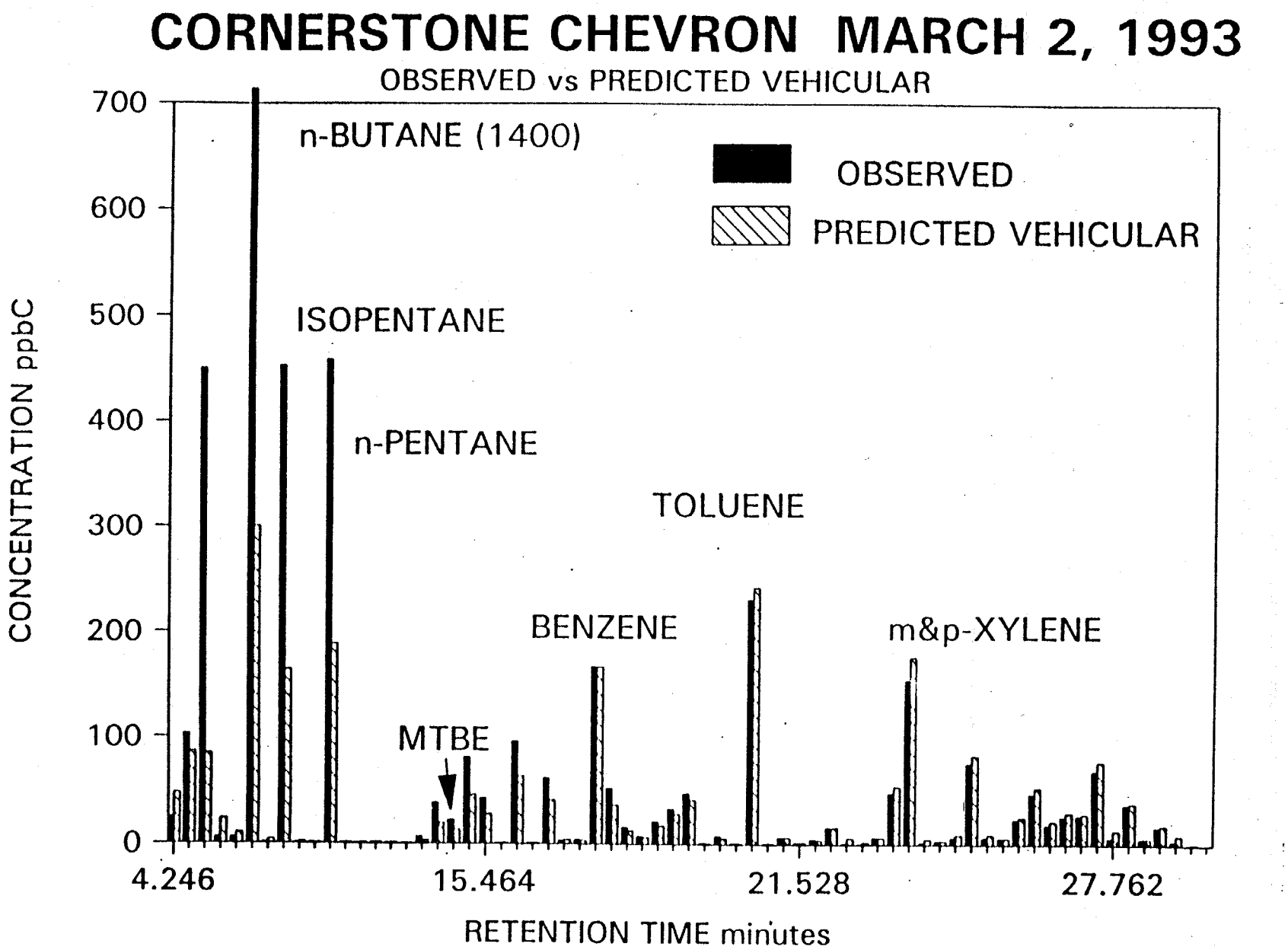

CORNERSTONE CHEVRON MARCH 2, 1993
OBSERVED vs PREDICTED VEHICULAR
700
600
500
400
300
200
100
0
n-BUTANE (1400)
OBSERVED
PREDICTED VEHICULAR
ISOPENTANE
n-PENTANE
TOLUENE
BENZENE
m&p-XYLENE
MTBE
CONCENTRATION ppbC
4.246
15.464
21.528
27.762
RETENTION TIME minutes

FIGURE 13

TABLE I

SAMPLING CONDITIONS

CITY		DATES	AMBIENT TEMP. °C
FAIRBANKS	PHASE 1	DEC. 01-12, 1992	-30 to +1.7
	PHASE 2	DEC. 17-22, 1992	-33 to -12
	PHASE 3	FEB. 02-MAR. 5, 1993	-19 to -2
STAMFORD		APRIL 14-15, 1993	+6 to +20
ALBANY		MAY 05-15, 1993	+5 to +21
		MAY 26-27, 1993	

TABLE II

WT.% MTBE IN FAIRBANKS, ALASKA FUEL SAMPLES

	COLLECTED DEC. 1992		COLLECTED FEB. 1993	
	UNLEAD REGULAR	PREMIUM	UNLEAD REGULAR	PREMIUM
MINIMUM	1.86	14.16	0.00	0.83
MAXIMUM	15.41	14.93	8.36	8.77
AVERAGE	8.46	14.66	1.00	5.56
FUELS TESTED	6	6	35	34

TABLE III

MTBE SAMPLING SITES

TYPE\LOCATION	FAIRBANKS	STAMFORD	ALBANY
AUTO TRAFFIC	2ND /CUSHMAN[a] ; UNIV./AIRPORT	LIBRARY	NEAR PARKING LOT AT NYDOH (UNIV. PLACE)
RESIDENTIAL	HAMILTON ACRES[a] HUNTER SCHOOL[a]	STARK SCHOOL PLAYGROUND	CMT SITE IN SCHENECTADY
GAS STATION	CONNERSTONE CHEVRON	MOBILE; DPW PUMPS	MOBILE; GETTY GAS
BACKGROUND	OLD NENANA HWY[b]	SHIPPAN POINT	NONE
GARAGE SERVICE AREAS	AURORA MOTORS; FAIRBKS MOTORS; SEEKINS FORD; TUNDRA TOURS; GABE'S AUTO; RAE'S GARAGE	DPW; SUBURBAN CADILLAC; DEMOTT'S GARAGE	NONE
PARKING GARAGE	NONE	GOVT. CENTER	NONE
INDOOR	HAMILTON ACRES; HUNTER SCHOOL; OLD POST OFFICE	PUBLIC HEALTH DEPT.; ST. JOHNS RECTORY	NONE
VEHICLE INTERIORS	SEVERAL CARS AND TRUCKS	NONE	NONE

[a]CONCURRENT SAMPLING INDOOR AND OUTDOOR SOME DAYS.
[b]12 HOUR SAMPLING

AUTHOR(S): Larry G. Anderson, Pamela Wolfe, and John A. Lanning

TITLE: THE EFFECTS OF OXYGENATED FUELS ON CARBON MONOXIDE AND ALDEHYDES IN DENVER'S AMBIENT AIR

INTRODUCTION

We began studying the effects of oxygenated fuels in Denver in December 1987, a few weeks before oxygenated fuels were used along the Colorado Front Range. Our initial work attempted to determine the effects of oxygenated fuel use on concentrations of formaldehyde and acetaldehyde in Denver's atmosphere. This work has continued with a 4-hour average monitoring of formaldehyde and acetaldehyde, 24 hours a day, seven days a week, from roughly October through April of the first few years, and year-round through the past 3 years (see T13) and up to the present.

After the first year of the program, we learned that the state agency was evaluating the effectiveness of oxygenated fuel use for reducing atmospheric CO concentrations. Emissions test data and emissions and air quality modeling were used to calculate the expected reduction of atmospheric CO concentration. We began looking for and are still researching ways of analyzing the ambient concentration data to assess the effectiveness of oxygenated fuel use.

CARBON MONOXIDE EFFECTS

The techniques used in this work will not be discussed because detailed presentation appears in Wolfe et al. (1993). In our analyses, we use a structural time series approach, which requires a long data series. We have completed analyses using these techniques for five air monitoring stations along Colorado's front range. These include the CAMP site in downtown Denver, Carriage west of downtown in a residential area, National Jewish Hospital (NJH) east of downtown in a residential/commercial area, and two sites outside Denver, one in Boulder and the other in Colorado Springs. The data analyzed began in 1981 or as late as mid-1983 (depending on the site) and extends through January or February 1993. These data sets include six complete oxygenated fuel seasons in Denver.

The analyses to be discussed here are for either monthly average CO concentration data, which is most appropriate for assessing the normal or average behavior, and the monthly maximum 8-hour average CO, which include only the extreme values, representing only the extreme 8-hour period of the month. The analysis technique is intended to deal with lognormally distributed data with serial correlations and to extract information about the seasonal, long-term trend and oxygenated fuel effects on CO ambient concentrations. The model results for the monthly averaged CO data and the monthly maximum 8-hour average CO data for the five sites are graphically shown in the attached figures (T4 - T8).

Figure T9 summarizes the analyses results of the monthly averaged CO data. A polynomial trend is allowed in the model; the highest order term that is significant is listed for each data set. For all sites except CAMP there are significant downward trends that are either linear or quadratic. At CAMP the cubic term is significant, which suggests that there has been a significant slowing in the downward trend in CO. The oxygenated fuel parameter in the model is not significant at the $\alpha = 0.05$ level for any of the five sets. Although the oxygenated fuels parameters are not significant, they do provide a valuable indication of the change observed. For CAMP the oxygenated fuel parameter suggests that there was essentially no change in the

monthly average CO concentration, while at Carriage, National Jewish Hospital, and Boulder there are indications of a 4-7% decrease in CO attributable to oxygenated fuels. The analysis for Colorado Springs requires further work to interpret, and will not be discussed. A summary of the results of the analysis for the monthly maximum 8-hour average CO is shown in Figure T10, a 2% reduction for CAMP and a 10-11% reduction for Carriage, National Jewish and Boulder.

We have continued our analysis to try to determine the reasons for the differences between CAMP and the other air monitoring sites. The CAMP site is in downtown Denver, and subject to considerable commuter traffic. The other monitors are not in areas that are at the beginning or end of many peoples journey. The morning CO is largely affected by emissions from warm vehicles entering the downtown area, while the evening CO is affected by cold vehicles starting and beginning their commute home. We investigated the trend in the 1-hour average CO for the most common hour of the wintertime morning and evening CO peaks, 8-9 a.m. and 6-7 p.m., respectively. Figure T11 shows the results of the analyses of the monthly average of all hours, the morning and evening hour. It is clear that during the winter, the evening CO peak is much larger than the morning peak, while during the summer, the morning peak is larger. From our analysis of this data (see T12), the oxygenated fuels effect on the morning CO data was a reduction of CO by about 2% when the area was most affected by the emissions from relatively warm vehicles. The effect of oxygenated fuel on the evening CO data was to increase CO by about 6.5% when the area was most affected by emissions from relatively cold vehicles. We believe that the cold start emissions have not been adequately dealt with in the models used to assess the effectiveness of oxygenated fuels.

In downtown Denver, where CO is highest, the effect of using oxygenated fuels on CO concentrations is a 0-2% reduction; for Carriage, National Jewish Hospital, and Boulder the decrease is 5-11%. All these effects are much smaller than the about 20% reductions in CO concentrations being predicted by the modeling for the more recent years. Cold start CO emissions may explain the reasons CO reductions are smaller in downtown Denver than at the other sites.

ALDEHYDE EFFECTS

A summary of the techniques used and the data collected has been presented by Anderson et al. (1993) and will not be repeated here. We have found very strong correlations between formaldehyde and CO measured at the same site in downtown Denver, particularly during the winter (see T14). This suggests that both formaldehyde and CO have the same source. In Denver 80-90% of the CO emissions are from motor vehicles, which suggests that motor vehicles are a major source of formaldehyde. Since we do not have CO data from the same site as our aldehyde data for the entire time period, we have not looked at trends in the formaldehyde to CO ratio. Figure T15 shows the observed trend in formaldehyde, acetaldehyde and the correlation coefficient between formaldehyde and acetaldehyde over the 6 years of these measurements. Figure T16 shows the trend in the formaldehyde-to-acetaldehyde (F/A) ratio for this period. The formaldehyde concentration and the F/A ratio were significantly greater for each of the last four winters, when compared to the first two winters. The formaldehyde concentration during the most recent winter (1992-93) was significantly lower than during the previous three winters, but the F/A ratio was not significantly different from that for the previous winter.

Emissions data have shown an increase in the F/A emissions ratio when MTBE blended fuels are used (Hoekman, 1992). Those data show that the F/A emissions ratio for three-way catalyst equipped vehicles increases from 2.3-2.4 for the reference fuel to 2.6-3.1 when 11% by

volume MTBE blended fuels are used. These F/A emissions ratios and their increase are quite similar to the F/A concentration ratios and their increase observed in Denver during the winter. The required oxygen content of the fuel increased from 1.5-2.7% by mass during the six winters of this study. These emissions data also suggest that the F/A emissions ratio should decrease as noncatalyst equipped vehicles are replaced by newer three-way catalyst equipped vehicles.

These data suggest that motor vehicles are a major source of formaldehyde in Denver during the winter, and that there has been a significant increase in the formaldehyde concentration and the formaldehyde-to-acetaldehyde ratio. Fleet turnover effects should lead to decreases in both quantities. Increased vehicle miles traveled should increase formaldehyde, but not affect the F/A ratio. But the use of MTBE blended fuels is expected to increase both the formaldehyde concentration and the F/A ratio. This is what we have observed over the 6 years of oxygenated fuel use in Denver.

REFERENCES

Anderson, L.G. et al., 1993. Effects of using oxygenated fuels on the concentrations of aldehydes in Denver. Paper 93-TP-50.04, 86th Annual Meeting of the Air & Waste Management Association, Denver, Colorado.

Hoekman, S.K. 1992. Speciated measurements and calculated reactivities of vehicle exhaust emissions from conventional and reformulated gasolines. *Environ. Sci. Technol.* 26: 1206-1216.

Wolfe, P., L. G. Anderson, and J. A. Lanning. 1993. A structural time series assessment of the effectiveness of the oxygenated fuel program in reducing carbon monoxide concentrations in downtown Denver. Paper 93-T-41B.03, 86th Annual Meeting of the Air & Waste Management Association, Denver, Colorado.

The Effects of Oxygenated Fuels on Carbon Monoxide and Aldehydes in Ambient Air of Denver

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Pamela Wolfe[2]
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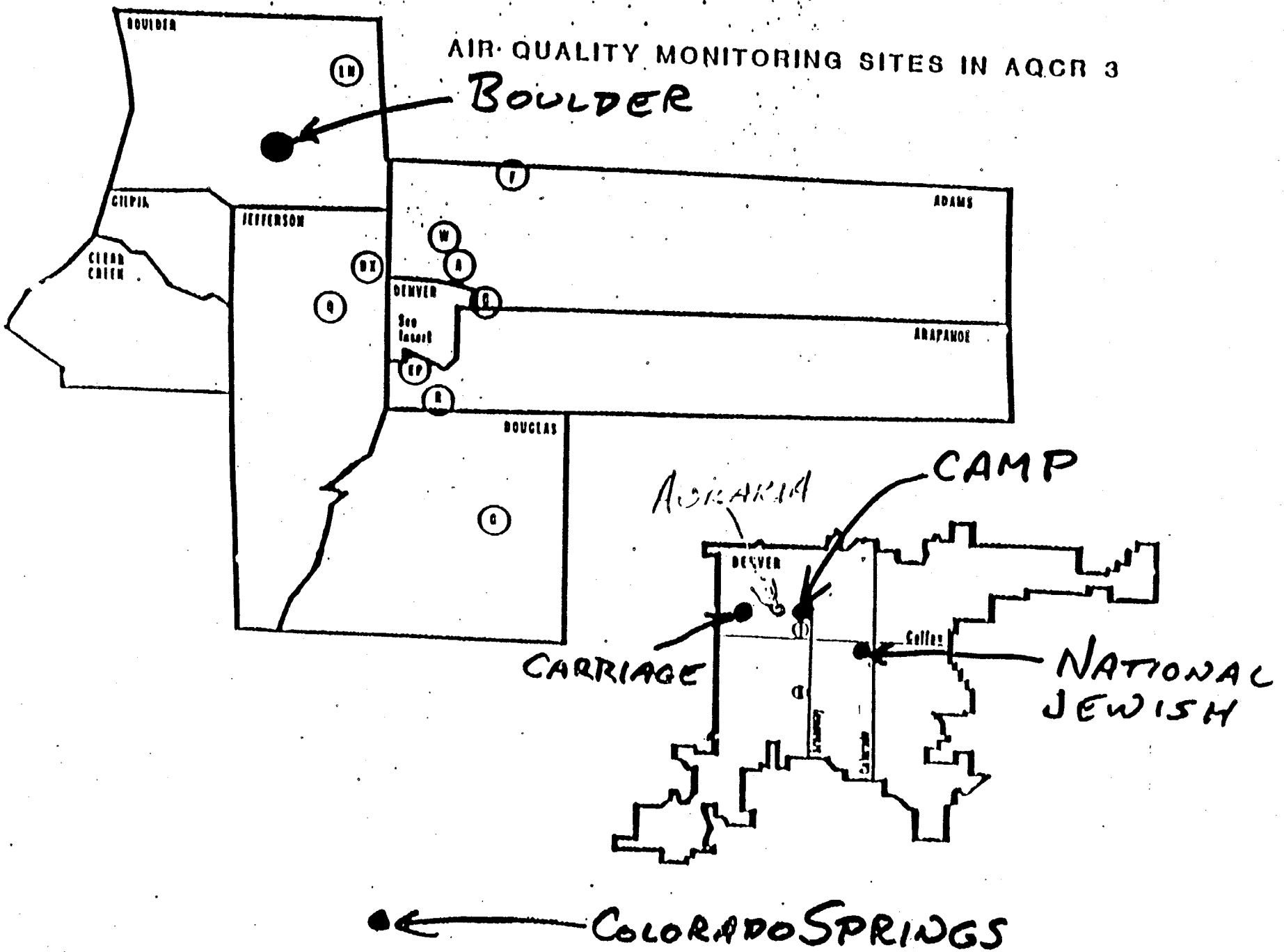
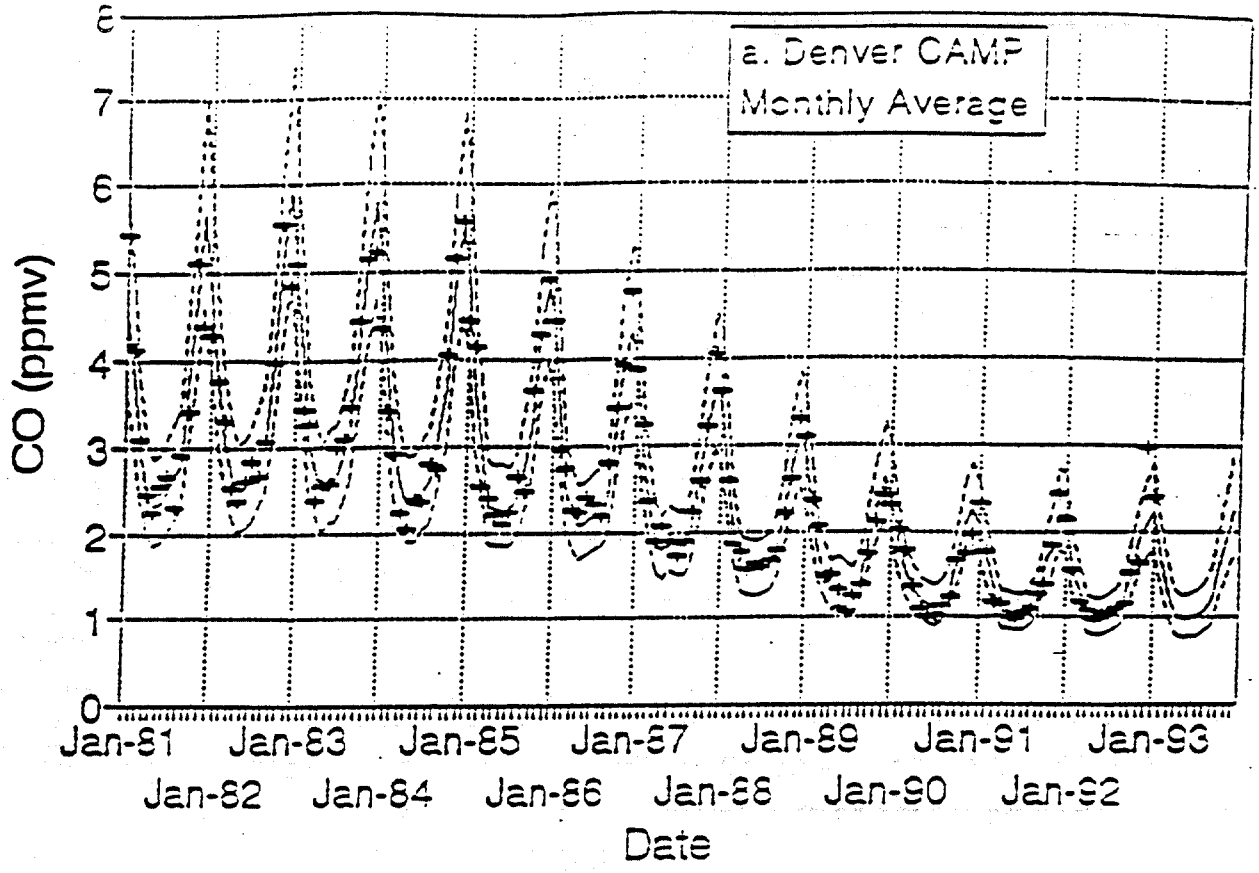
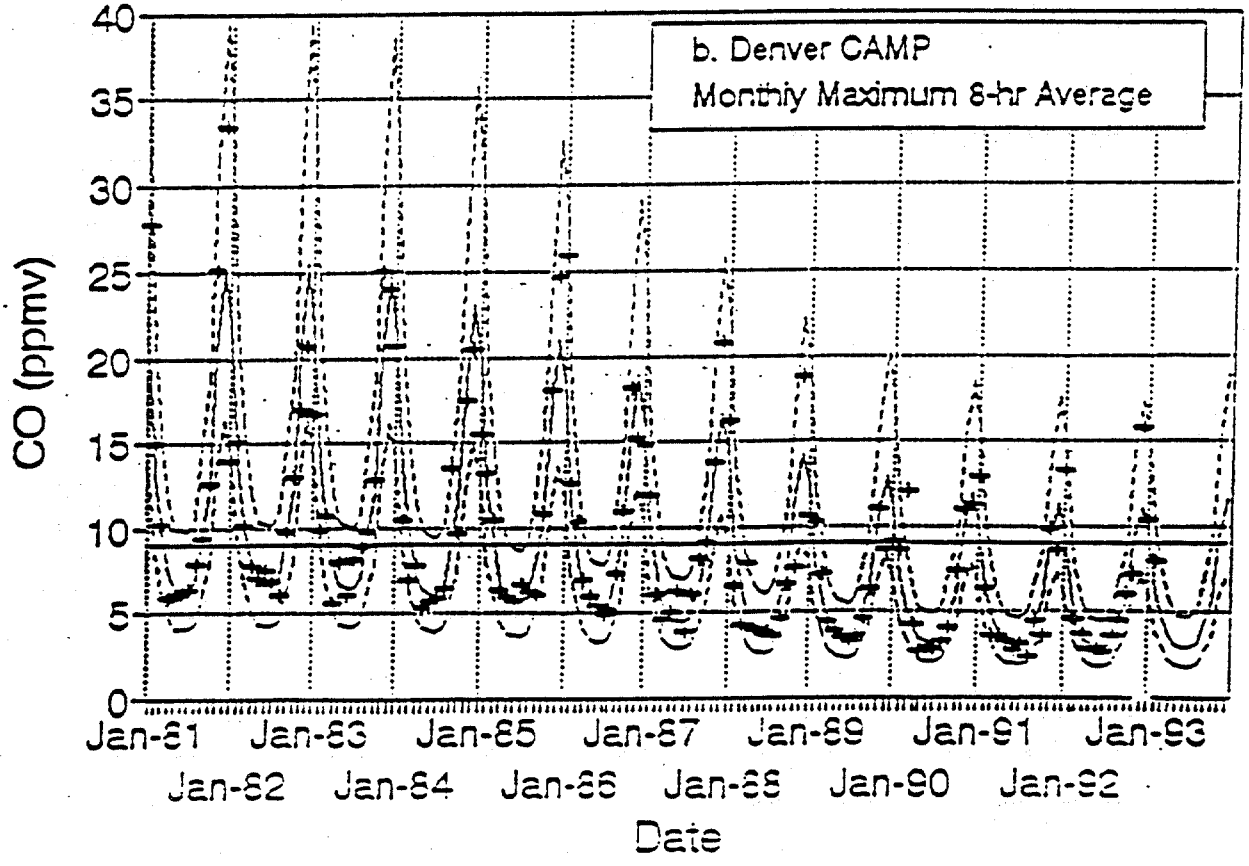
Purpose of this Project

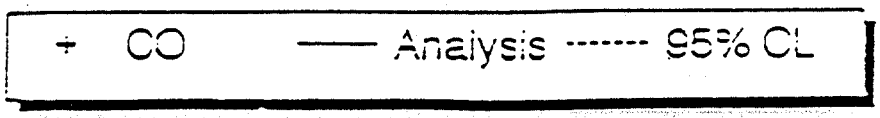
1. To develop techniques using ambient concentration data that are suitable for assessing the effectiveness of oxygenated fuels for reducing atmospheric concentrations of carbon monoxide.

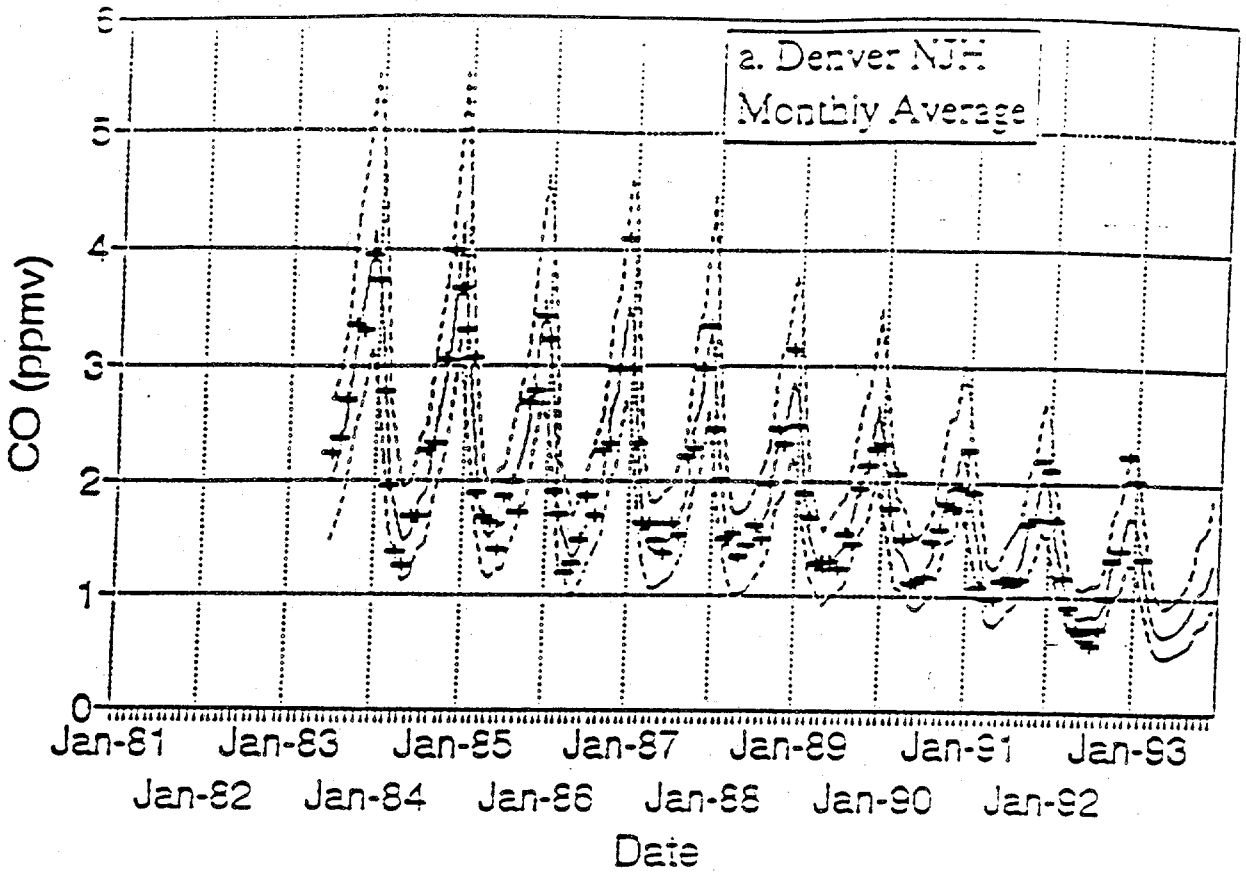
2. To collect and analyze the data necessary to assess the effect of oxygenated fuels use on the atmospheric concentrations of formaldehyde and acetaldehyde.

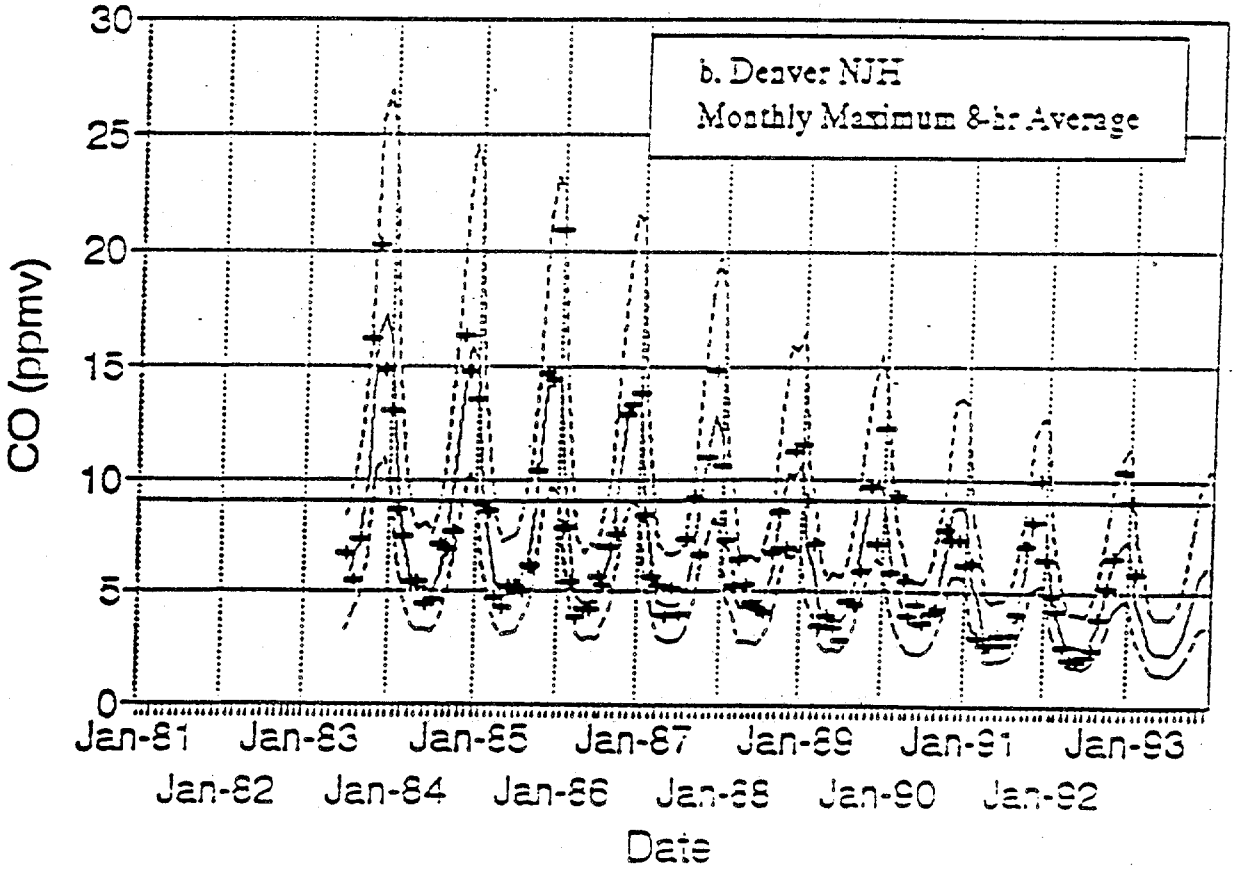

AIR QUALITY MONITORING SITES IN AQCR 3
BOULDER
BOULDER
GILPIN
JEFFERSON
CLEAR CREEK
DENVER
ADAMS
ARAPAHOE
DOUGLAS
AURARIA
CAMP
CARRIAGE
NATIONAL JEWISH
COLORADO SPRINGS

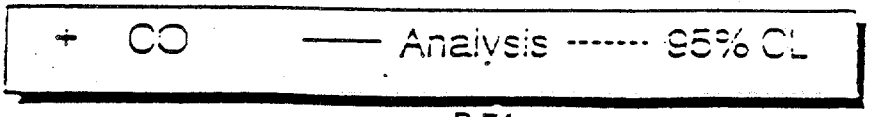

a. Denver CAMP
Monthly Average
CO (ppmv)
0
1
2
3
4
5
6
7
8
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date

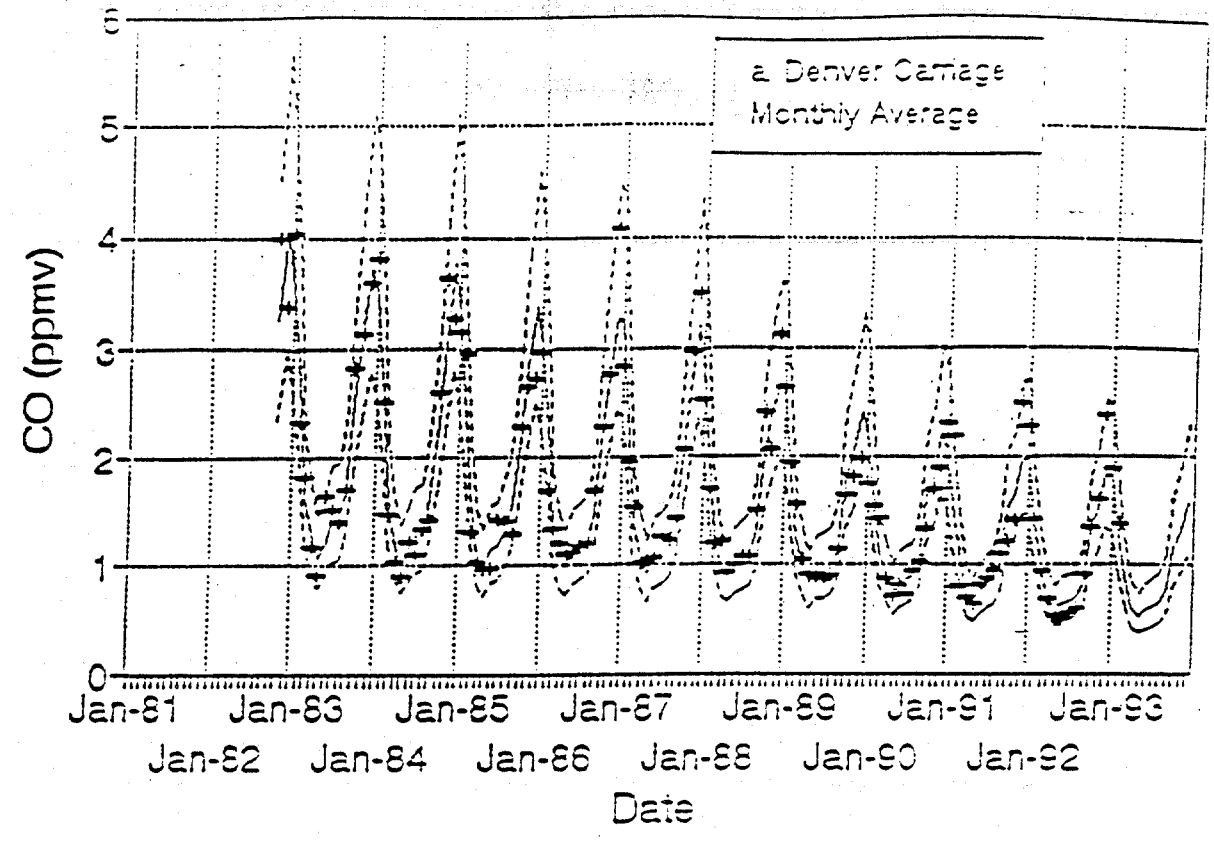

b. Denver CAMP
Monthly Maximum 8-hr Average
CO (ppmv)
0
5
10
15
20
25
30
35
40
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date

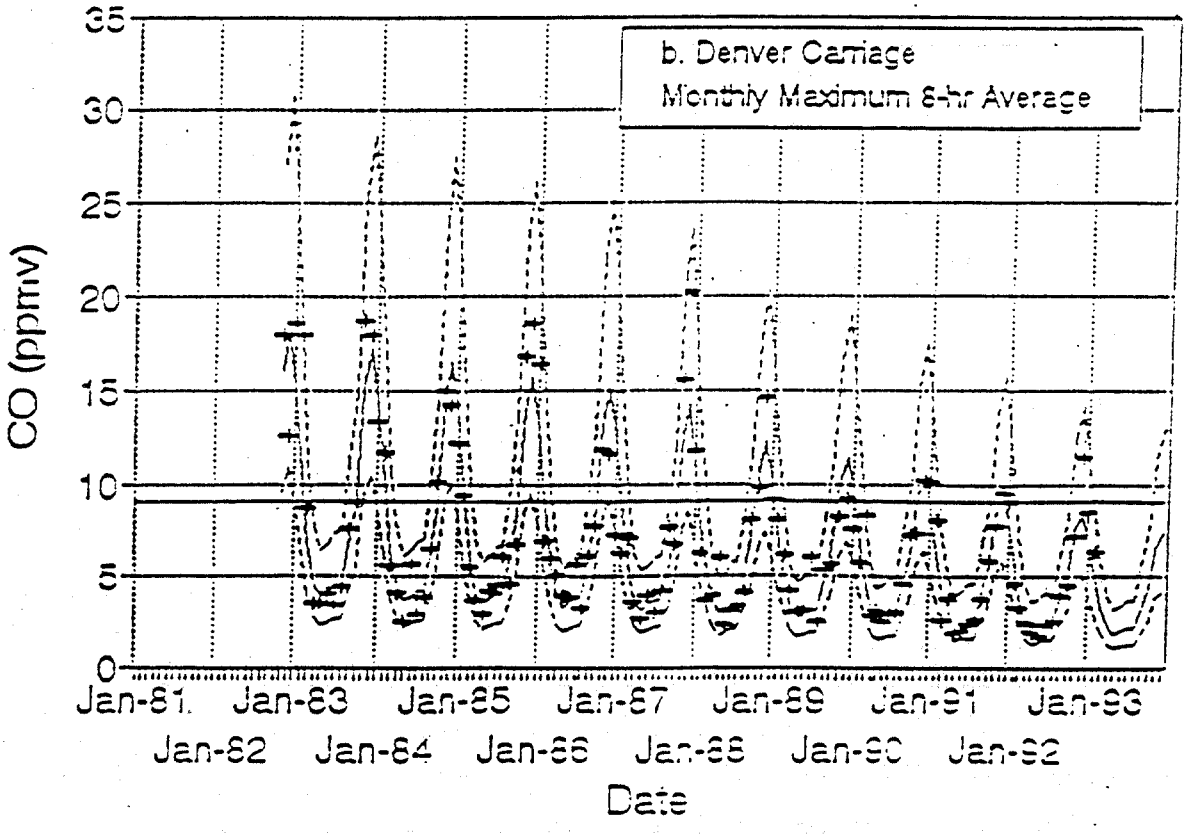

+ CO
Analysis
95% CL

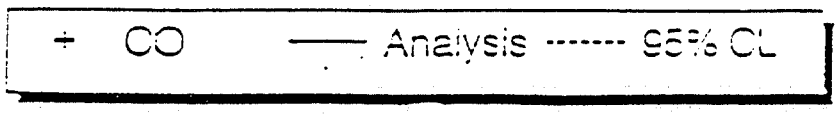

a. Denver NJH
Monthly Average
CO (ppmv)
0
1
2
3
4
5
6
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


b. Denver NJH
Monthly Maximum &-hr Average
CO (ppmv)
0
5
10
15
20
25
30
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


+ CO
Analysis
95% CL


a. Denver Carriage
Monthly Average
CO (ppmv)
0
1
2
3
4
5
6
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


b. Denver Carriage
Monthly Maximum 8-hr Average
CO (ppmv)
0
5
10
15
20
25
30
35
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date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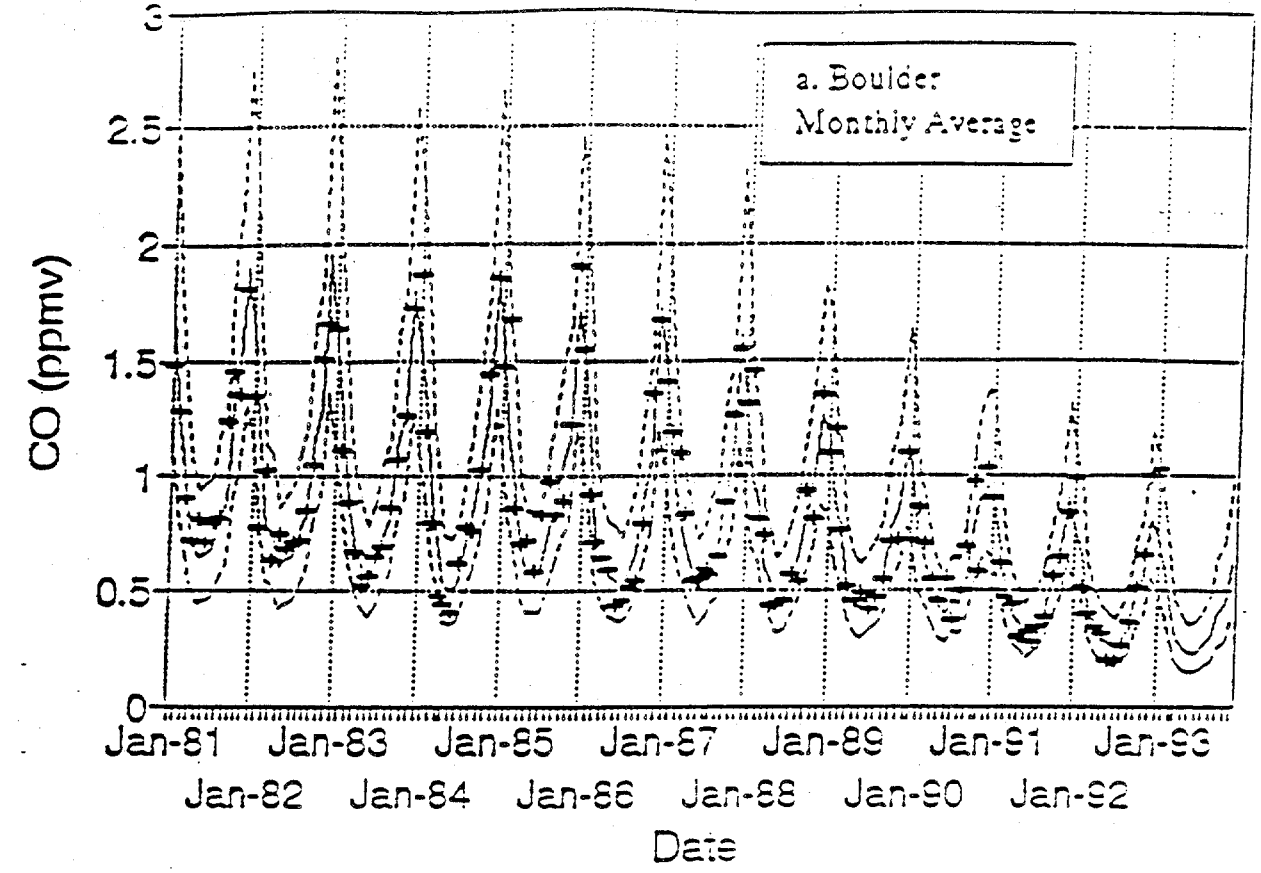
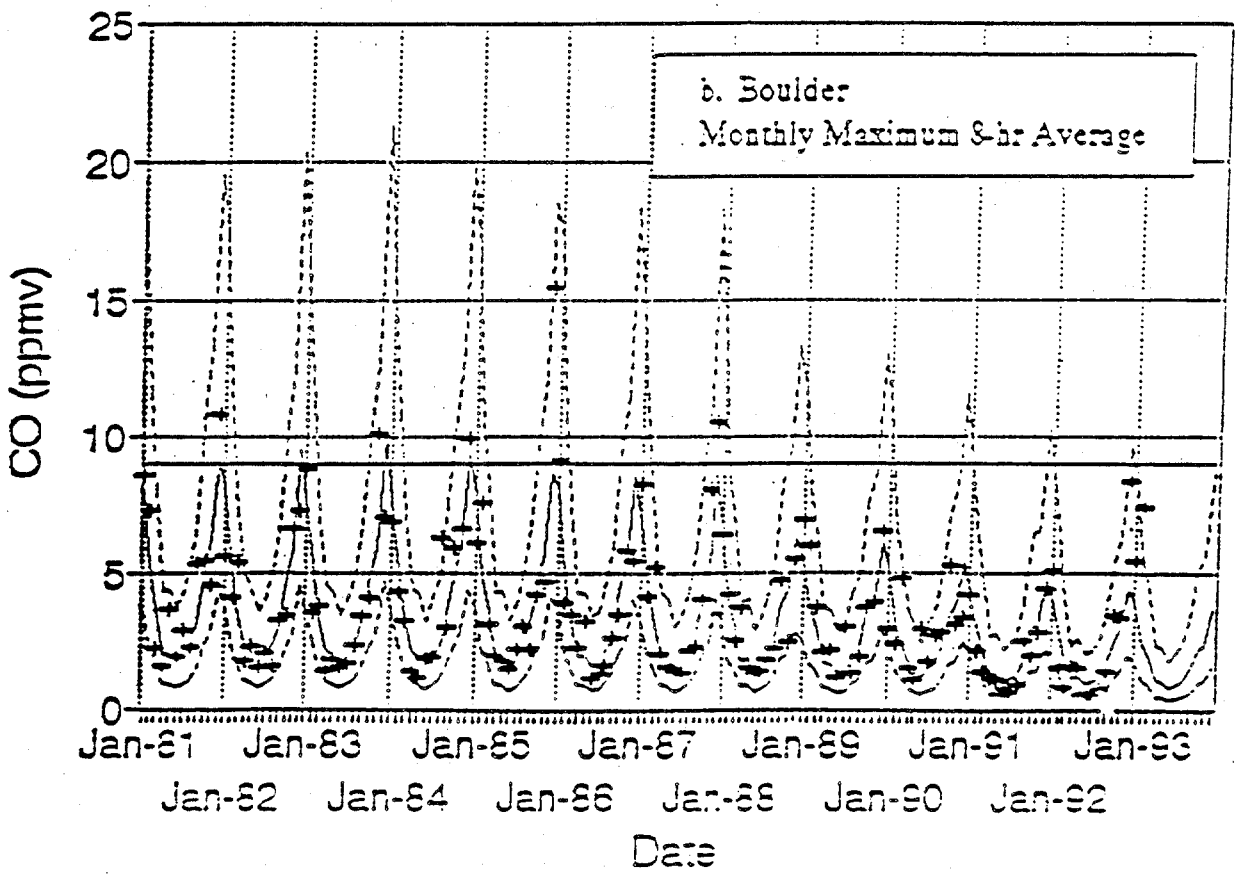
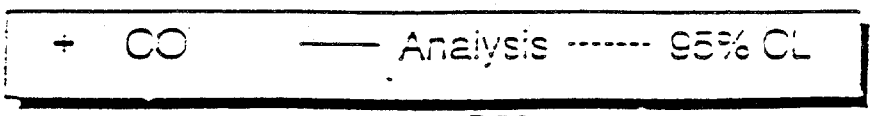
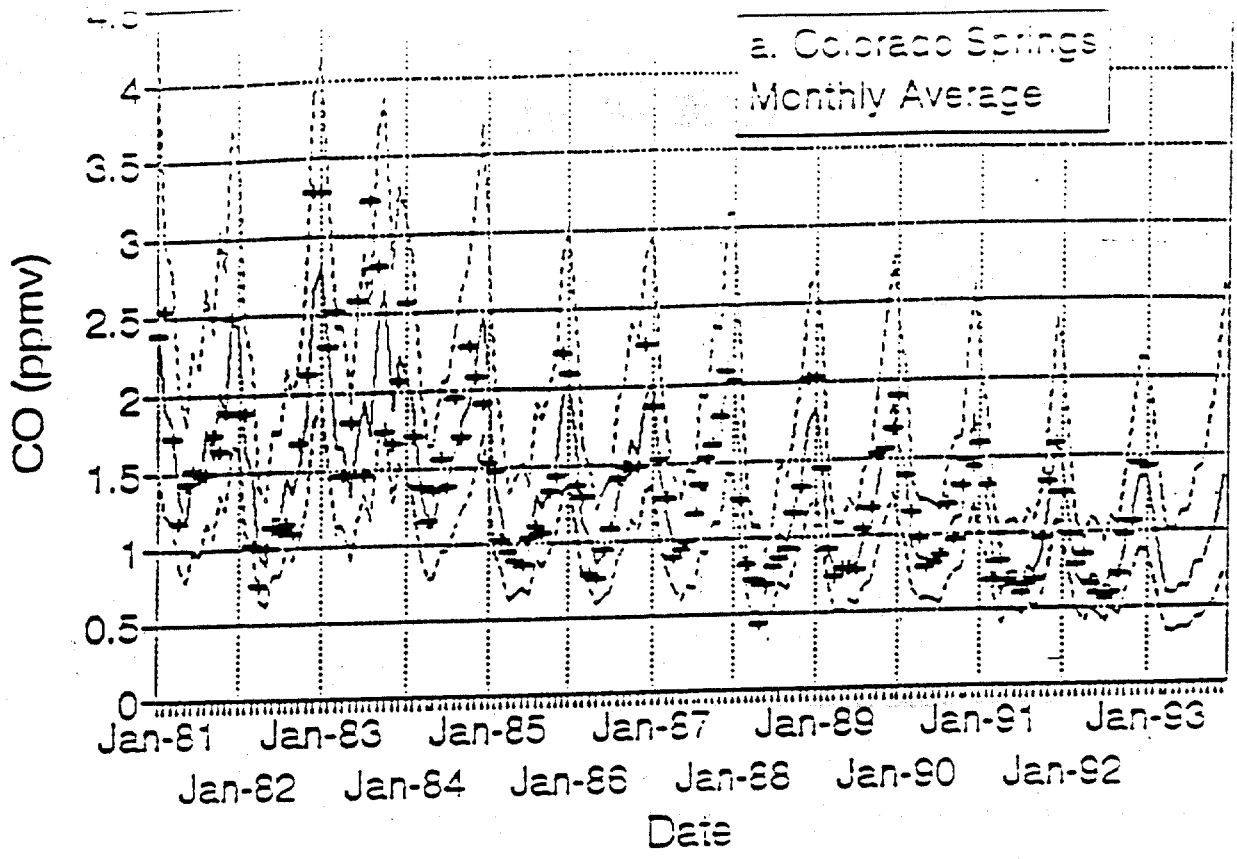
Analysis
95% CL


a. Boulder
Monthly Average
CO (ppmv)
3
2.5
2
1.5
1
0.5
0
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


b. Boulder
Monthly Maximum 8-hr Average
CO (ppmv)
25
20
15
10
5
0
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


+ CO
Analysis
95% CL


a. Colorado Springs
Monthly Average
CO (ppmv)
4
3.5
3
2.5
2
1.5
1
0.5
0
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
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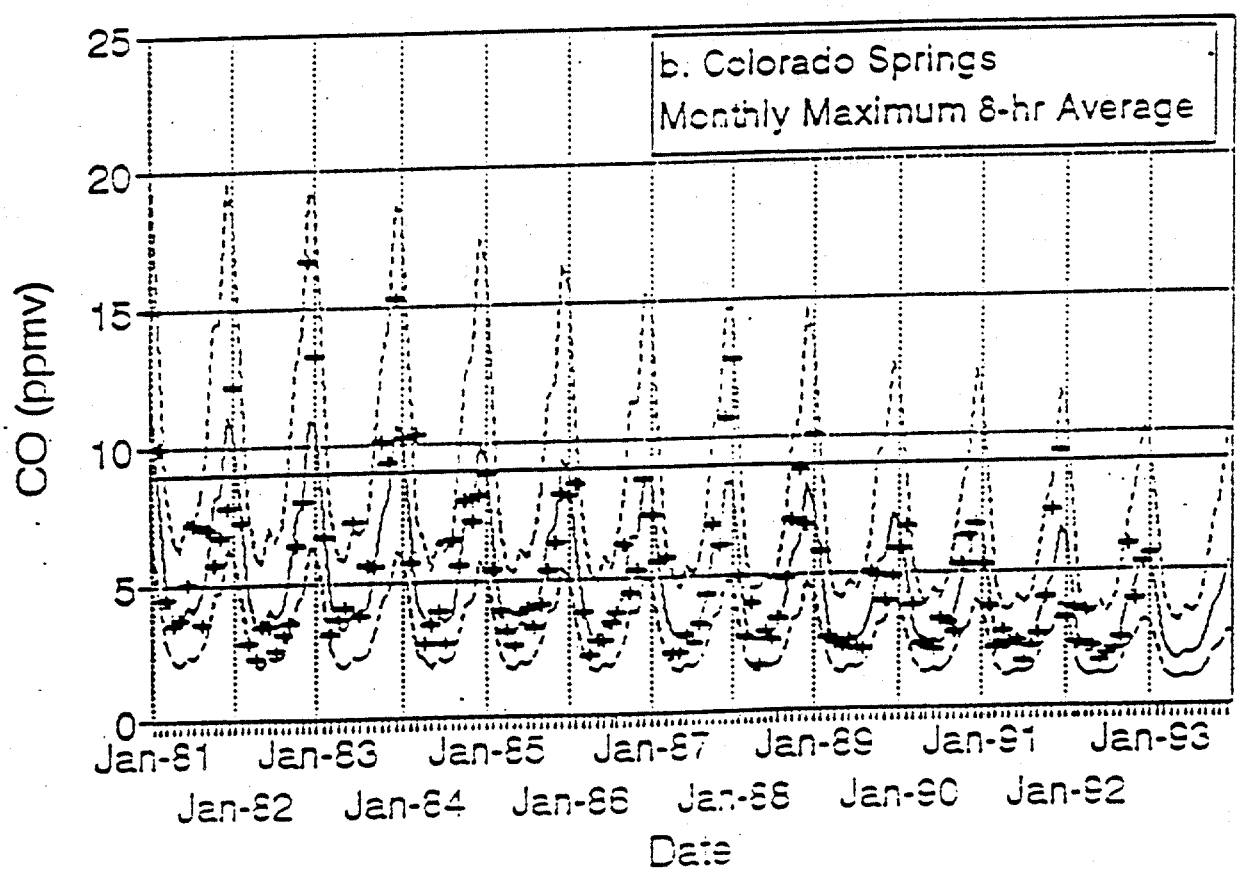
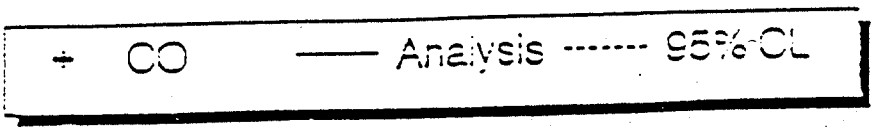
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


b. Colorado Springs
Monthly Maximum 8-hr Average
CO (ppmv)
25
20
15
10
5
0
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date


CO
Analysis
95%-CL

CAMP (avg)

- Trend: cubic
- Oxy Parameter: not significant (+ 0.5%)
- Power of the Test: .83

Carriage (avg)

- Trend: linear (downward)
- Oxy Parameter: not significant (- 6%)
- Power of the Test: .55

National Jewish Hospital (avg)

- Trend: quadratic (downward)
- Oxy Parameter: not significant (-7%)
- Power of the Test: .58

Boulder (avg)

- Trend: quadratic (downward)
- Oxy Parameter: not significant (-4%)
- Power of the Test: .44

Colorado Springs (avg)

- Trend: linear (downward)
- Oxy Parameter: not significant (+ 12%)
- Power of the Test: .39

CAMP (max)

- Trend: cubic
- Oxy Parameter: not significant (- 2%)
- Power of the Test: .43
- Continued Exceedances Likely

Carriage (max)

- Trend: linear (downward)
- Oxy Parameter: not significant (- 10%)
- Power of the Test: .33
- Continued Exceedances Likely

National Jewish Hospital (max)

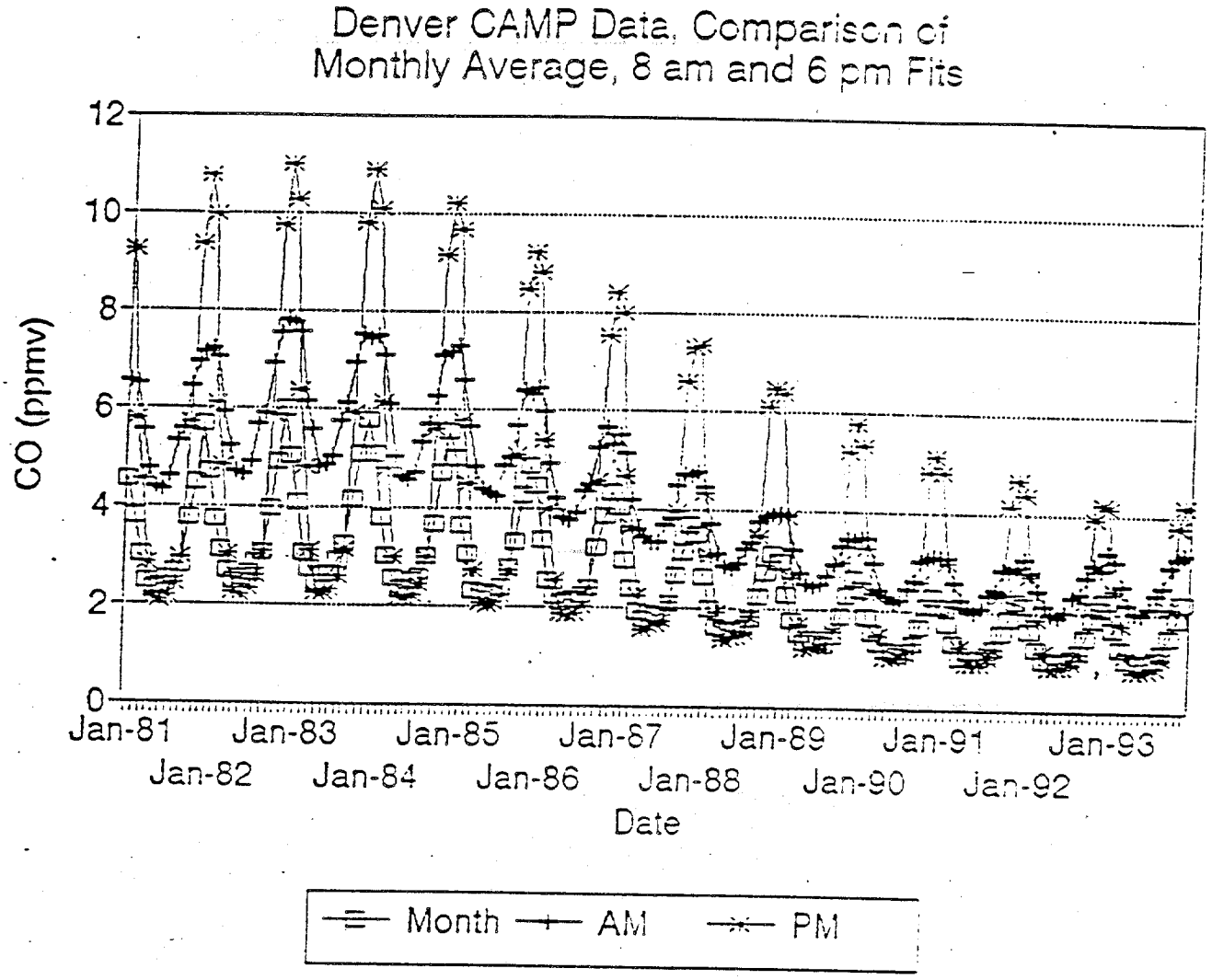
- Trend: linear (downward)
- Oxy Parameter: not significant (-10%)
- Power of the Test: .33

Boulder (max)

- Trend: linear (downward)
- Oxy Parameter: not significant (- 11%)
- Power of the Test: .21

Colorado Springs (max)

- Trend: linear (downward)
- Oxy Parameter: not significant (+ 1.5%)
- Power of the Test: .31


Denver CAMP Data, Comparison of
Monthly Average, 8 am and 6 pm Fits
CO (ppmv)
12
10
8
6
4
2
0
Jan-81
Jan-82
Jan-83
Jan-84
Jan-85
Jan-86
Jan-87
Jan-88
Jan-89
Jan-90
Jan-91
Jan-92
Jan-93
Date
Month
AM
PM

Diurnal Effects on the Results of Oxygenated Fuels
CAMP Data - Monthly Averaged Carbon Monoxide

	Oxy Fuels Effect	R^2
All Hours	+ 0.5 %	.90
8 - 9 am	- 2.0 %	.87
6 - 7 pm	+ 6.5 %	.95

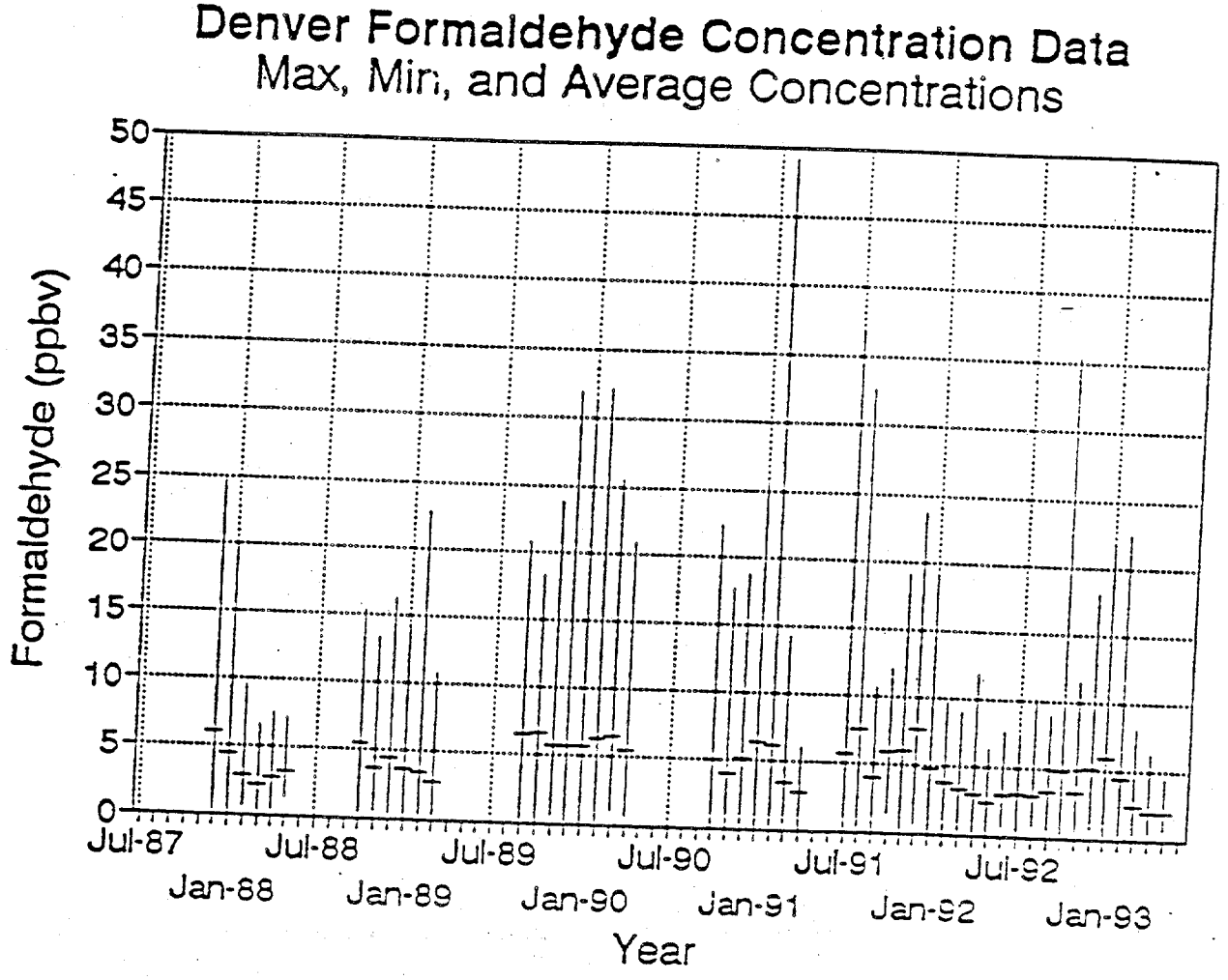
Morning period - more warm vehicle emissions

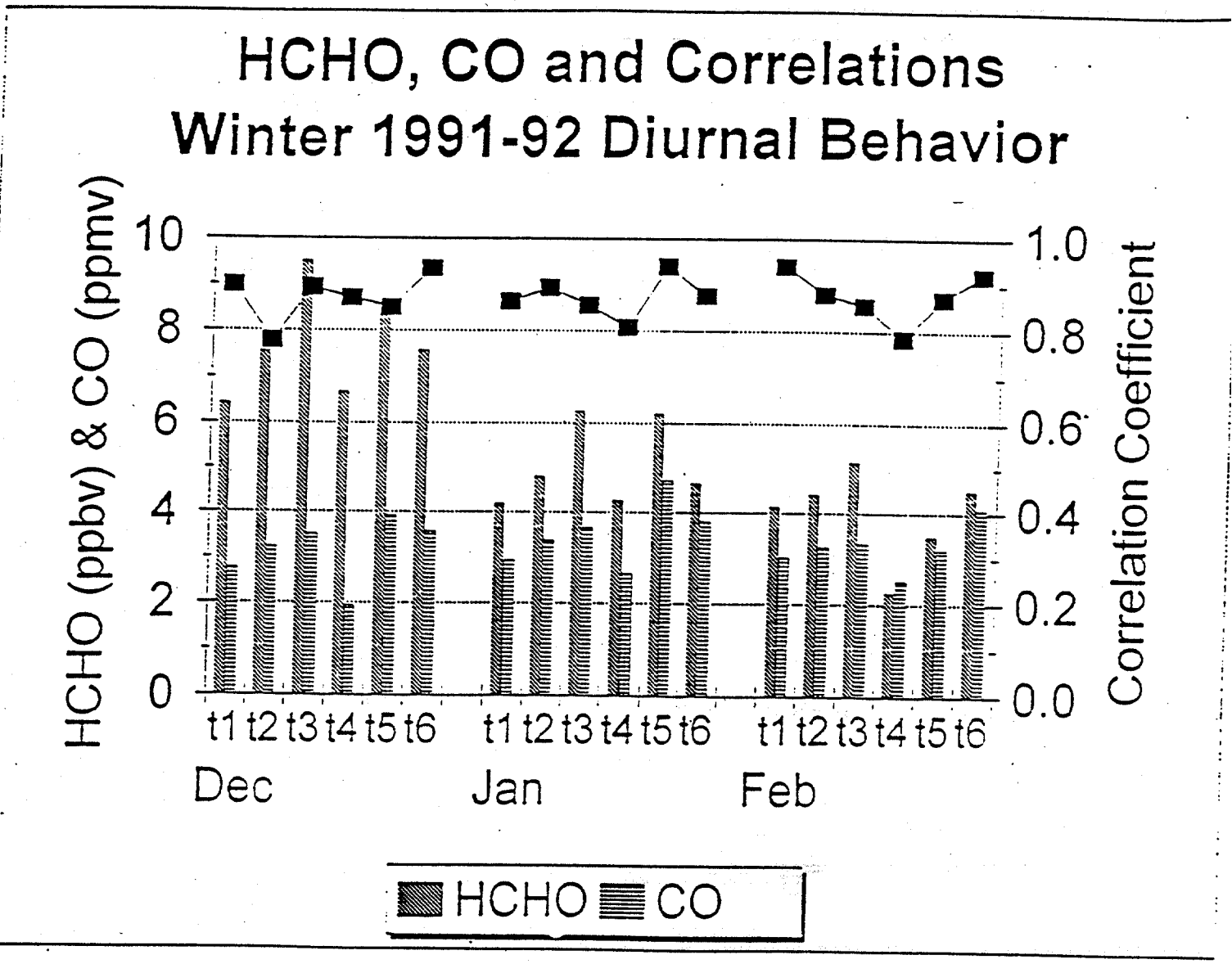
CO decrease attributable to oxygenated fuels

Evening period - more cold start vehicle emissions

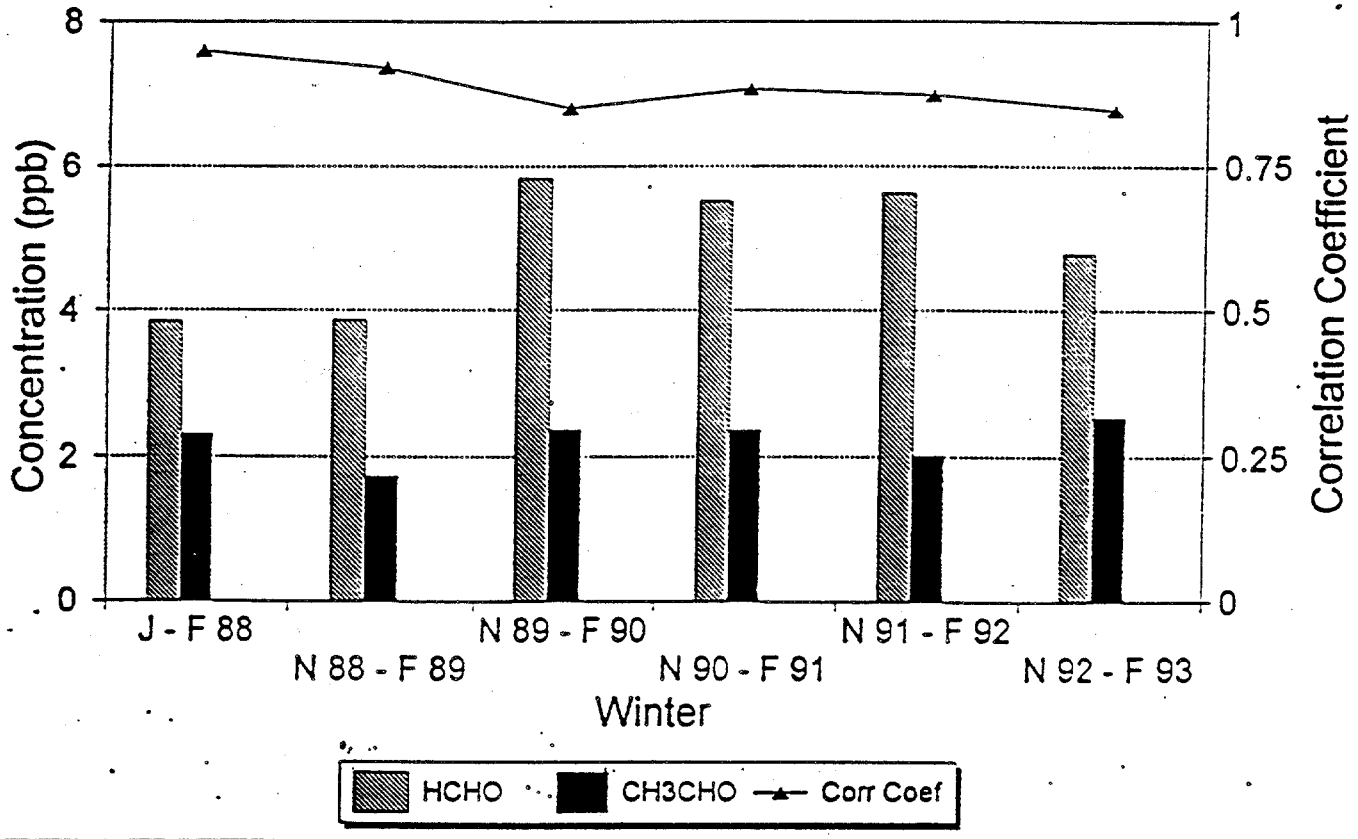
CO increase attributable to oxygenated fuels

We believe that CAMP shows less benefit from oxygenated fuels use because a larger fraction of its CO emissions are due to cold starts, as compared to the other sites studied.

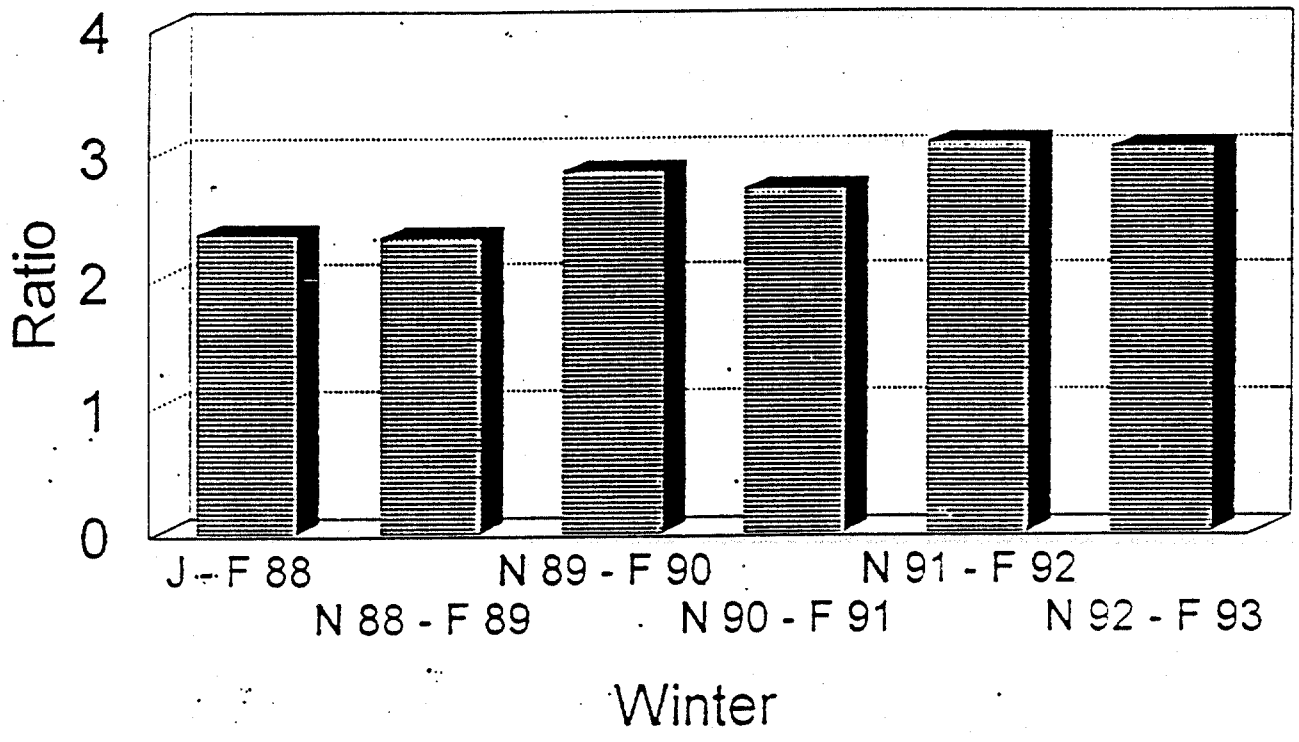

Denver Formaldehyde Concentration Data
Max, Min, and Average Concentrations
Formaldehyde (ppbv)
50
45
40
35
30
25
20
15
10
5
0
Jul-87
Jan-88
Jul-88
Jan-89
Jul-89
Jan-90
Jul-90
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Year


HCHO, CO and Correlations
Winter 1991-92 Diurnal Behavior
HCHO (ppbv) & CO (ppmv)
Correlation Coefficient
10
8
6
4
2
0
1.0
0.8
0.6
0.4
0.2
0.0
t1 t2 t3 t4 t5 t6 t1 t2 t3 t4 t5 t6 t1 t2 t3 t4 t5 t6
Dec
Jan
Feb
HCHO
CO

Trend in winter HCHO, CH3CHO and correlation coefficient



Trend in winter formaldehyde to acetaldehyde ratio



CONCLUSIONS

1. There is a strong downward trend in CO at all Colorado monitoring sites studied.

2. This downward trend is site dependent.

3. Oxygenated fuels have had no significant effect on the ambient CO at any of the five Colorado monitoring sites studied.

4. The effect of oxygenated fuels on ambient CO was found to be a reduction of 5 - 11% at three of these sites. At the downtown Denver site the effect was even smaller.

5. We believe that the benefits of oxygenated fuels use are reduced in downtown Denver due to the greater importance of cold-start emissions, as compared to the other monitoring locations studied.

6. During the winter motor vehicles are a major source of HCHO in the Denver metropolitan area.

7. There has been a significant increase in both formaldehyde and the formaldehyde-to-acetaldehyde ratio since the beginning of oxygenated fuels use (as the oxygen content of the fuel increased).

8. Based upon emissions data, both formaldehyde and the formaldehyde-to-acetaldehyde ratio are expected to increase with oxygenated fuel use.

9. But the effect of oxygenated fuels use on ambient HCHO has not yet been firmly established.

Acknowledgements

Faculty Associates:

Jeffrey Boon
James Koehler
Robert R. Meglen

Students:

Charles M. Machovec
Philip Anderson
Andrea Lewis
Neil Anderson
Kerry Grant
Heather Spurgeon
John Koeppe
Eugene Gorman
Zahra Nadji
Regina A. Barrell
Joyce Miyagishima

Financial Assistance:

University of Colorado at Denver
Auraria Higher Education Center
Global Change and Environmental Quality
Program, University of Colorado

APPENDIX C

SESSION THREE: SPEAKER ABSTRACTS AND PRESENTATIONS

AUTHOR(S): Ted Johnson (IT Corp.)

TITLE: SERVICE STATION EXPOSURES

ABSTRACT

The compound methyl tertiary butyl ether (MTBE) is routinely added to gasoline during the winter driving season to reduce carbon monoxide (CO) emissions from motor vehicles in CO non-attainment areas. MTBE is also added to gasoline during other seasons to increase octane rating. In 1992, the U.S. Environmental Protection Agency (EPA) began receiving complaints of headaches, nausea, and other symptoms following alleged wintertime exposures to MTBE. In early 1993, EPA began planning a series of clinical research studies to investigate the validity of these claims. To properly design these studies, EPA required estimates of typical air concentrations of MTBE that motorists and attendants may experience during refueling at service stations that dispense gasoline containing MTBE. EPA also expressed interest in determining typical MTBE concentrations at the property boundaries of these service stations.

In response to these needs, the American Petroleum Institute (API) funded a field study in which IT Air Quality Services (ITAQS) measured ambient MTBE concentrations at 10 service stations in the New York metropolitan area. The stations included:

1. Two full-service stations with Stage II vapor recovery controls on a commuting route near East Brunswick, New Jersey;

2. Three self-service stations with Stage II vapor recovery controls in Westchester County, New York; and

3. Five self-service stations without Stage II vapor recovery controls in Fairfield County, Connecticut.

The selection of full-service stations in New Jersey was mandatory, as self-service stations are not permitted in that state.

Each station was monitored on a different day between April 7, 1993, and April 23, 1993. The monitoring activities at each station were conducted during two 4-hour periods, nominally 8 a.m. to 12 a.m. and 2 p.m. to 6 p.m. Four-hour canister and impinger samples were collected at four perimeter locations (north, east, south, and west) and one pump location at each station, in customer breathing zones at the New York and Connecticut stations, and in attendant breathing zones at the New Jersey stations. In addition, 4-hour charcoal tube samples were collected in the breathing zones of all stations. These samples were analyzed for MTBE, BTEX (benzene, toluene, ethylbenzene, xylene), and formaldehyde.

Continuous CO measurements were made in the pump area of each station using a Metrosonics pm-7700 monitor. Organic vapor analyzers (OVA) were used to continuously monitor total hydrocarbon (THC) concentrations in the pump areas and breathing zones. These measurements were made to identify individual refueling events that could not be distinguished in the 4-hour samples collected by the canister samplers.

Field personnel monitored meteorological parameters, gasoline composition (oxygenate content, Reid vapor pressure, BTEX), and gasoline sales and deliveries during each sampling period. Personnel also noted the time each vehicle was refueled and conducted regular counts

of traffic on nearby roadways. Gasoline pumping activities were continuously recorded by a stationary video camera.

Research findings presented on July 27, 1993, at the MTBE Workshop were limited to the results of analyzing (1) MTBE data collected by canisters and (2) continuous THC data collected by OVA. The principal findings are summarized below.

1. Mean and maximum 4-hour average MTBE concentrations generally decrease from breathing zone to pump island to perimeter, suggesting that refueling activities are the principal source of MTBE that is measured at service stations.

2. MTBE concentrations are generally lower at stations with State II vapor controls.

3. Mean 4-hour MTBE concentrations are below 1 ppm at breathing zone and pump island locations and below 0.02 ppm at the station perimeters.

4. Maximum 4-hour MTBE concentrations are below 2.6 ppm at breathing zone and pump island locations and below 0.2 ppm at station perimeters.

5. The canister breathing zone measurements may underestimate actual breathing zone concentrations during fuel dispensing by station-specific factors ranging from 1 to 3. Most factors fall between 1.0 and 1.4.

During the ITAQS service station study, a research team headed by Dr. Paul Lioy collected air samples in the passenger compartments of automobiles during the typical home-to-work commutes. Automobiles in this companion study were refueled at stations included in the service station study. Breathing zone MTBE concentrations measured by Lioy's team during these refueling events were generally comparable to breathing zone measurements made by the ITAQS team.

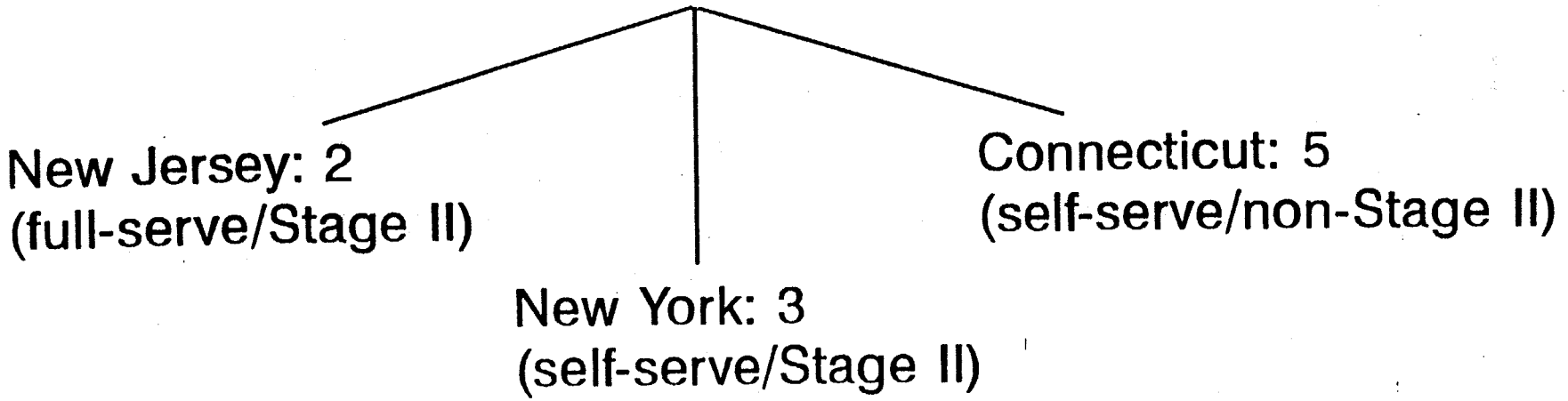
American Petroleum Institute
Service Station Monitoring Study

Ted Johnson, IT Corp

July 27, 1993

Service Station Monitoring Study

- Designed to characterize MTBE air concentrations at typical stations dispensing gasoline containing MTBE
- Monitoring Period: mid-April, 1993
- 10 stations monitored:



Service Station Exposure Monitoring

Sampled:

- breathing zone
- pump island
- station perimeter

Analyzed:

- air
  - MTBE, BTEX
  - formaldehyde
  - CO, total hydrocarbons
- fuel
  - oxygenate content
  - RVP
  - BTEX

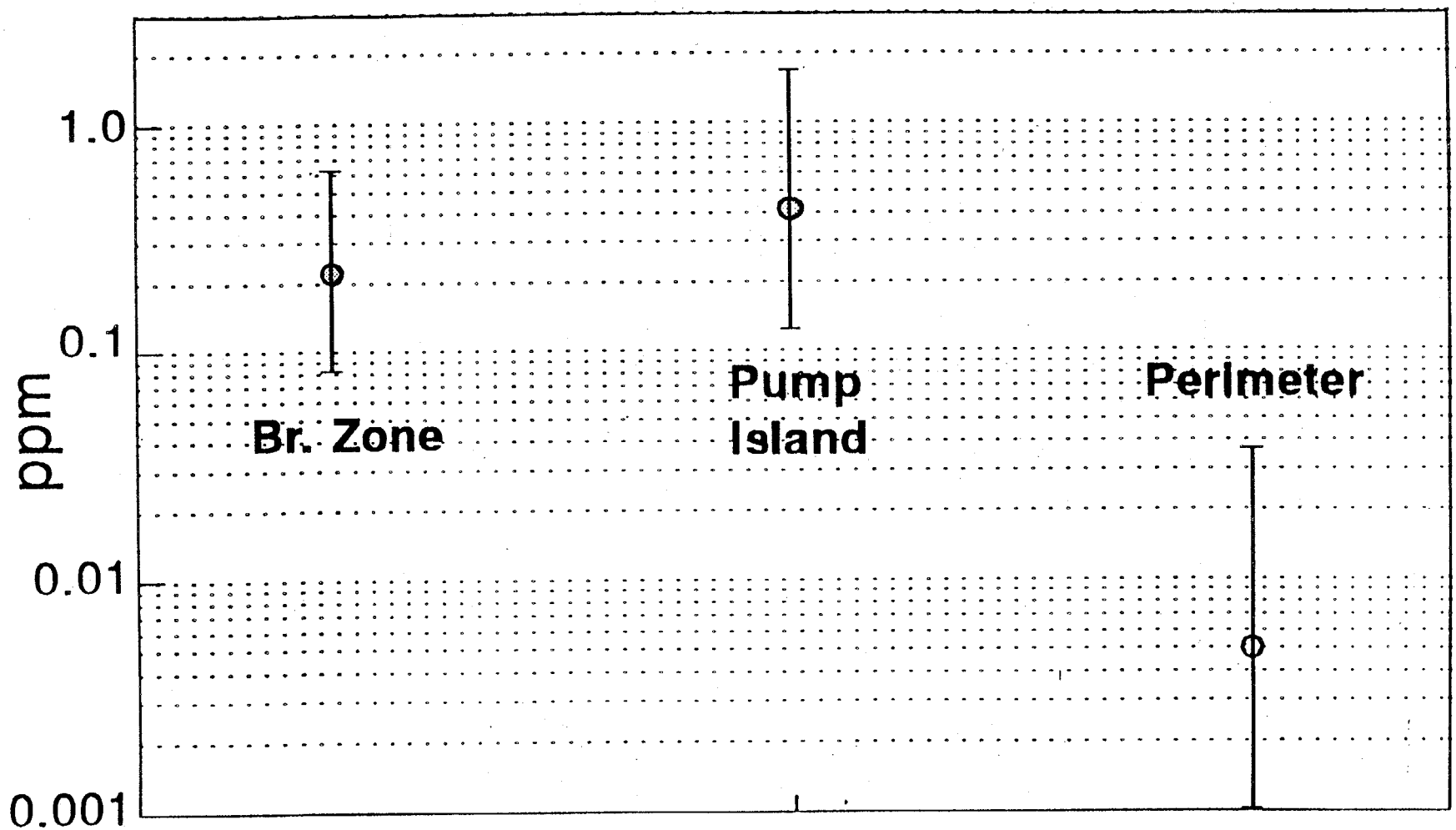
Conditions:

- am/pm rush hour (4 hr samples)

Service Station MTBE Concentrations
Stage II/Full - Serve

Location	No. Values		Concentration, ppm				
	All	N.D.	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Br. Zone	4	0	0.084	0.520	0.245	0.224	2.15
Pump Island	4	0	0.120	1.600	0.440	0.409	3.16
Perimeter	16	1	0.001	0.036	0.003	0.005	3.48

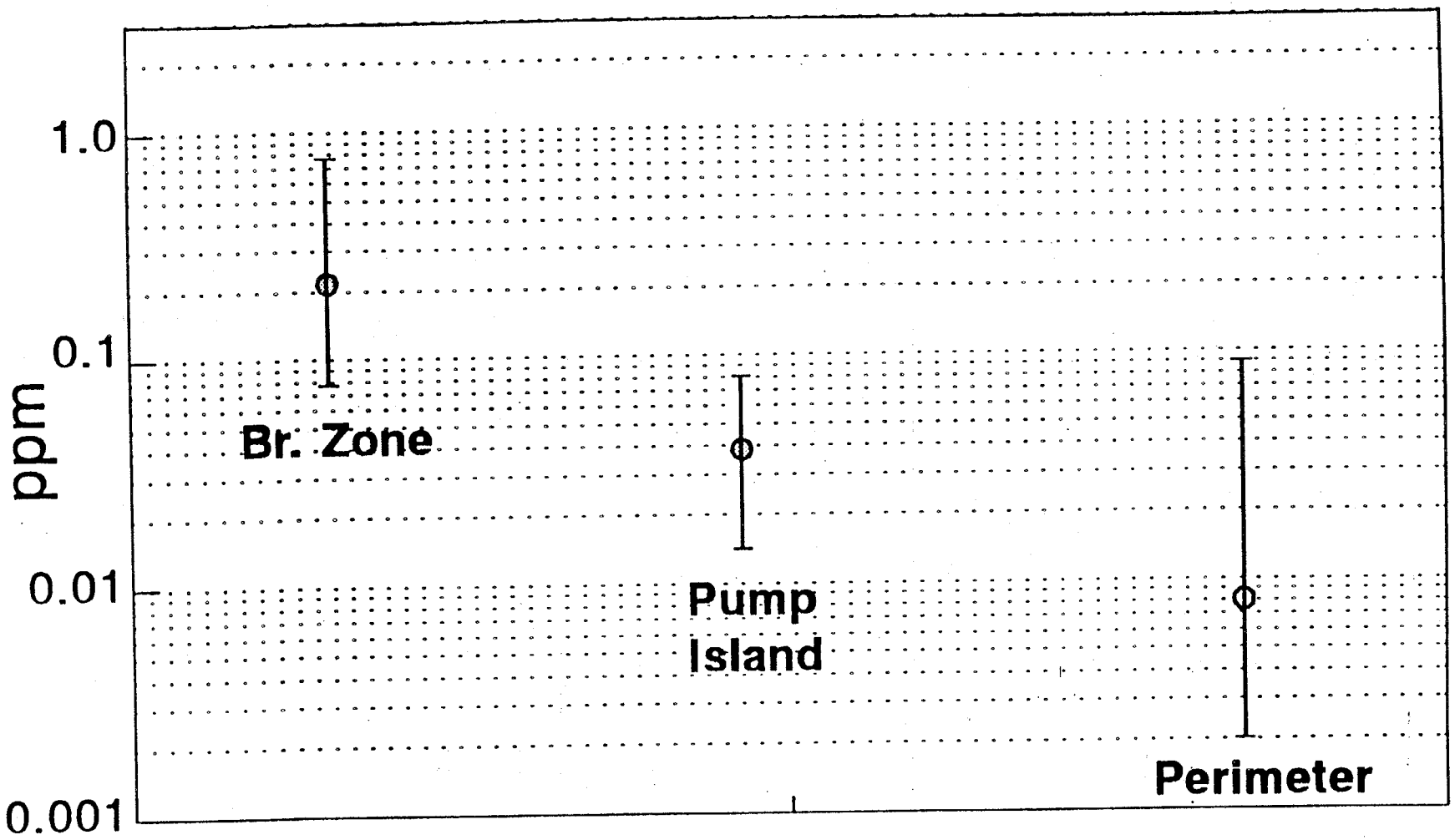
Service Station MTBE Concentrations
Stage II/Full - Serve



Service Station MTBE Concentrations
Stage II/Self - Serve

Location	No. Values		Concentration, ppm				
	All	N.D.	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Br. Zone	6	0	0.077	0.780	0.205	0.204	2.31
Pump Island	6	0	0.014	0.080	0.048	0.038	2.18
Perimeter	24	0	0.002	0.083	0.007	0.008	3.03

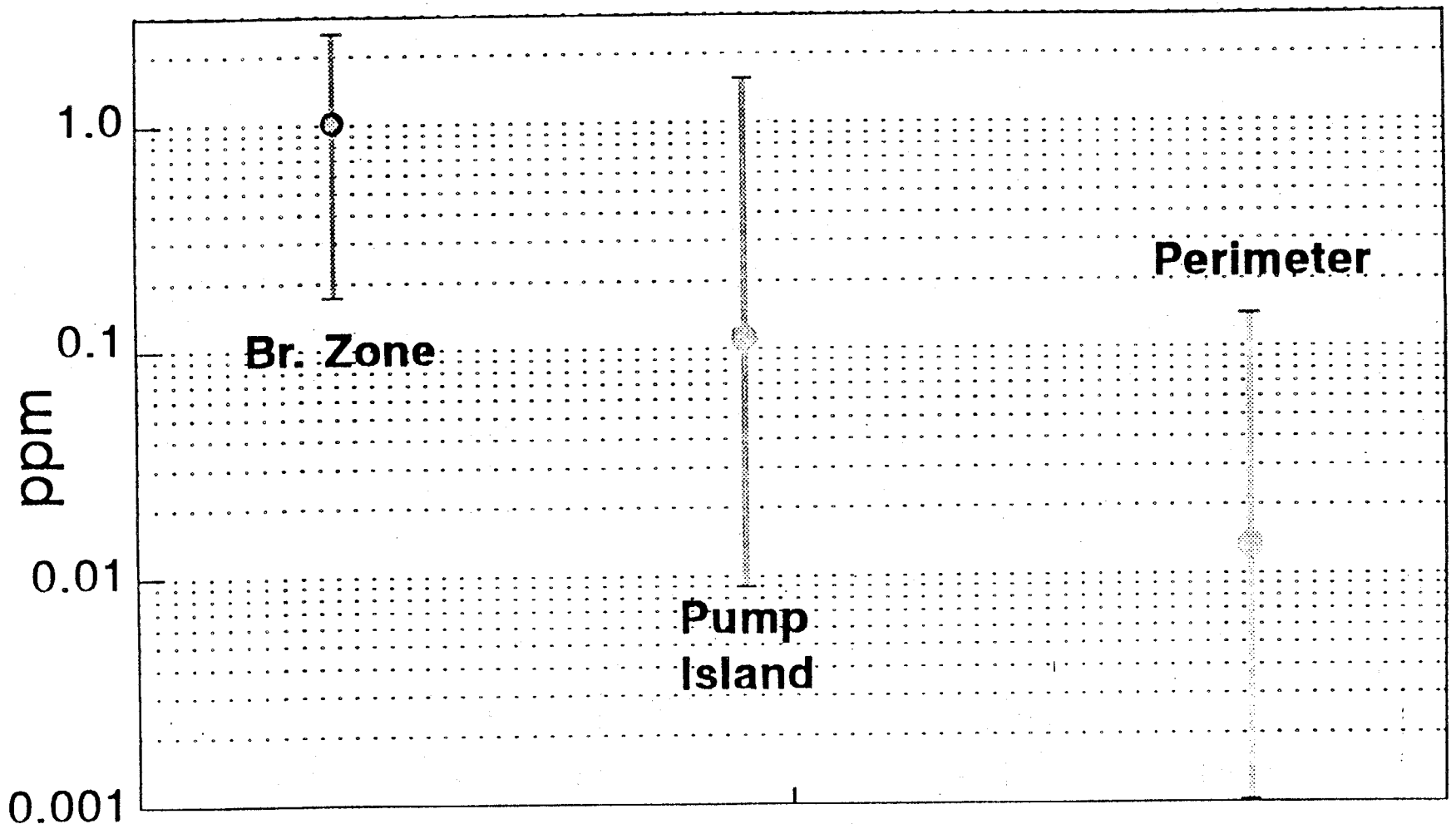
Service Station MTBE Concentrations
Stage II/Self - Serve



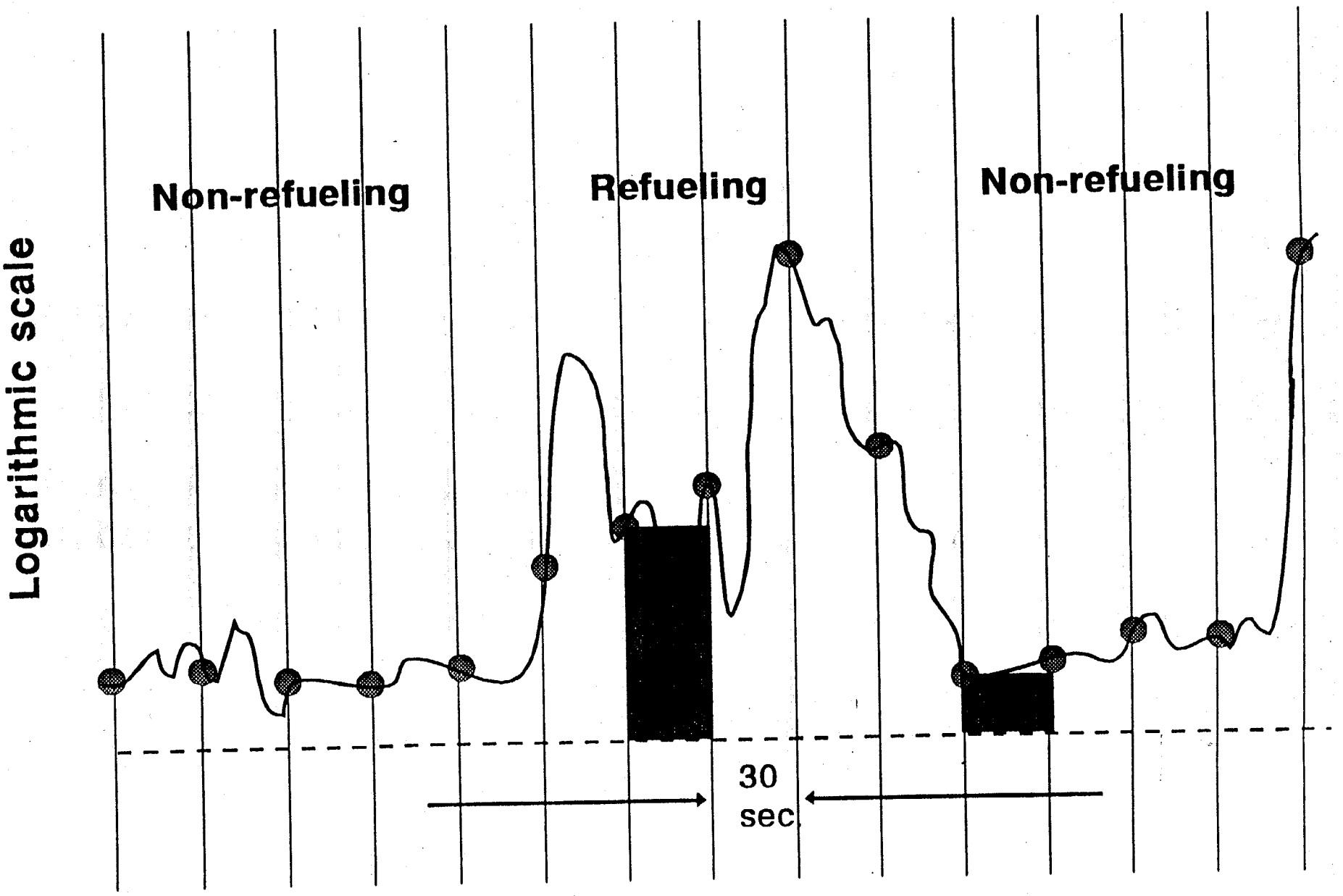
Service Station MTBE Concentrations
Non - Stage II/Self - Serve

Location	No. Values		Concentration, ppm				
	All	N.D.	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Br. Zone	10	0	0.170	2.600	1.500	0.978	2.73
Pump Island	10	1	0.009	1.500	0.170	0.109	5.05
Perimeter	40	2	0.001	0.140	0.014	0.014	3.61

Service Station MTBE Concentrations
Non - Stage II/Self - Serve



Pump Island HC Trace



Estimation of Breathing Zone MTBE Concentrations during Refueling Events Only

- Separate 4 hour mean THC recordings into mean refueling and non-refueling concentrations
- Adjust calculated 4 hour mean THCs to equal canister values
- Breathing zone MTBE concentration during refueling events =

  adjusted mean THC values during refueling
  x canister MTBE/THCs ratios

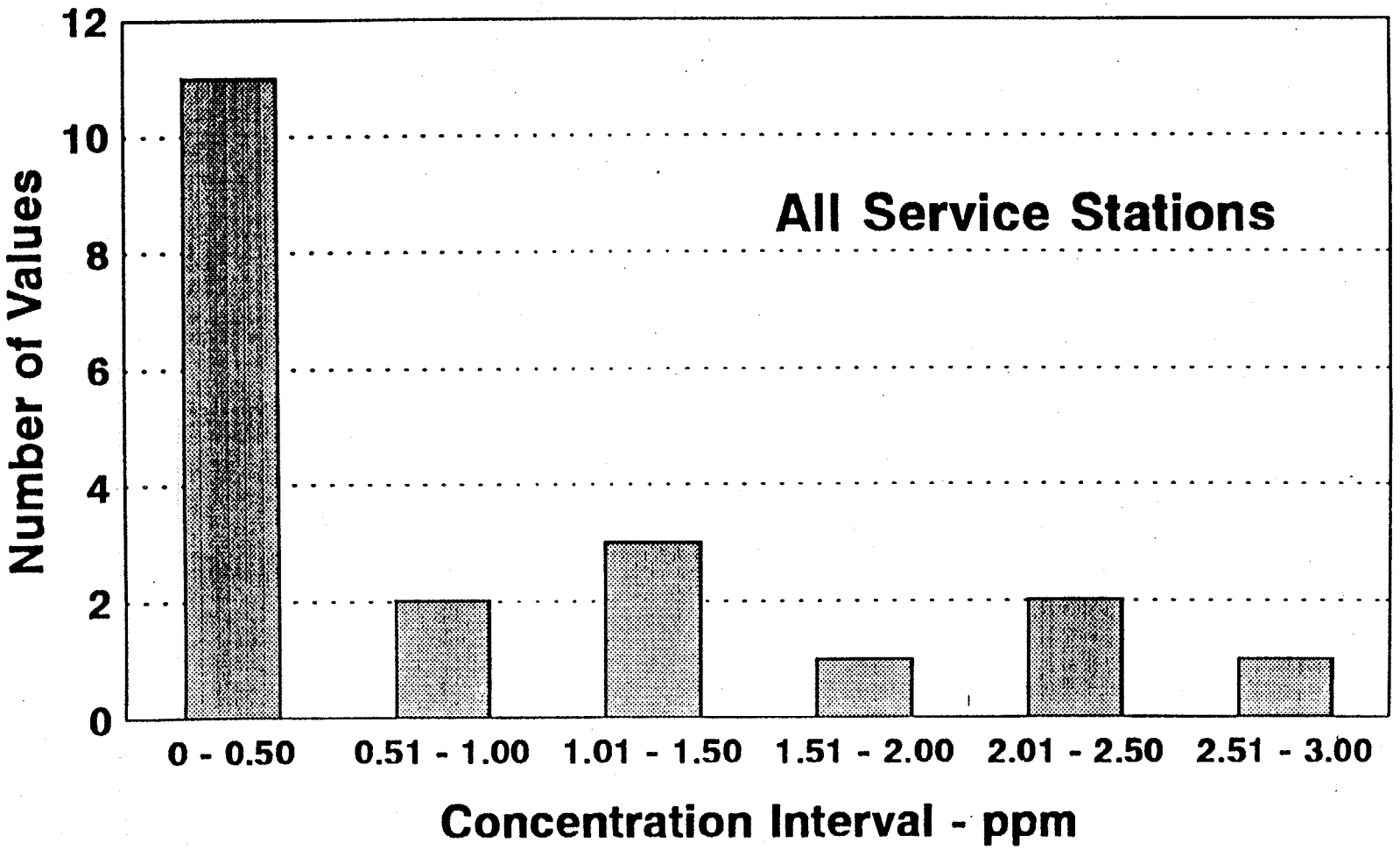
Service Station Breathing Zone Concentrations

Station No. (type)	MTBE - ppm	
	Integrated 4-hr sample	During fuel dispensing only
4 (Stage II/self-serve)	0.10	0.1
5 (non-Stage II/self-serve)	1.20	3.9
6 (non-Stage II/self-serve)	0.17	0.21
7 (" " ")	1.50	2.06
10 (Stage II/self-serve)	0.16	0.15

Individual Service Station Breathing Zone Comparison during Refueling

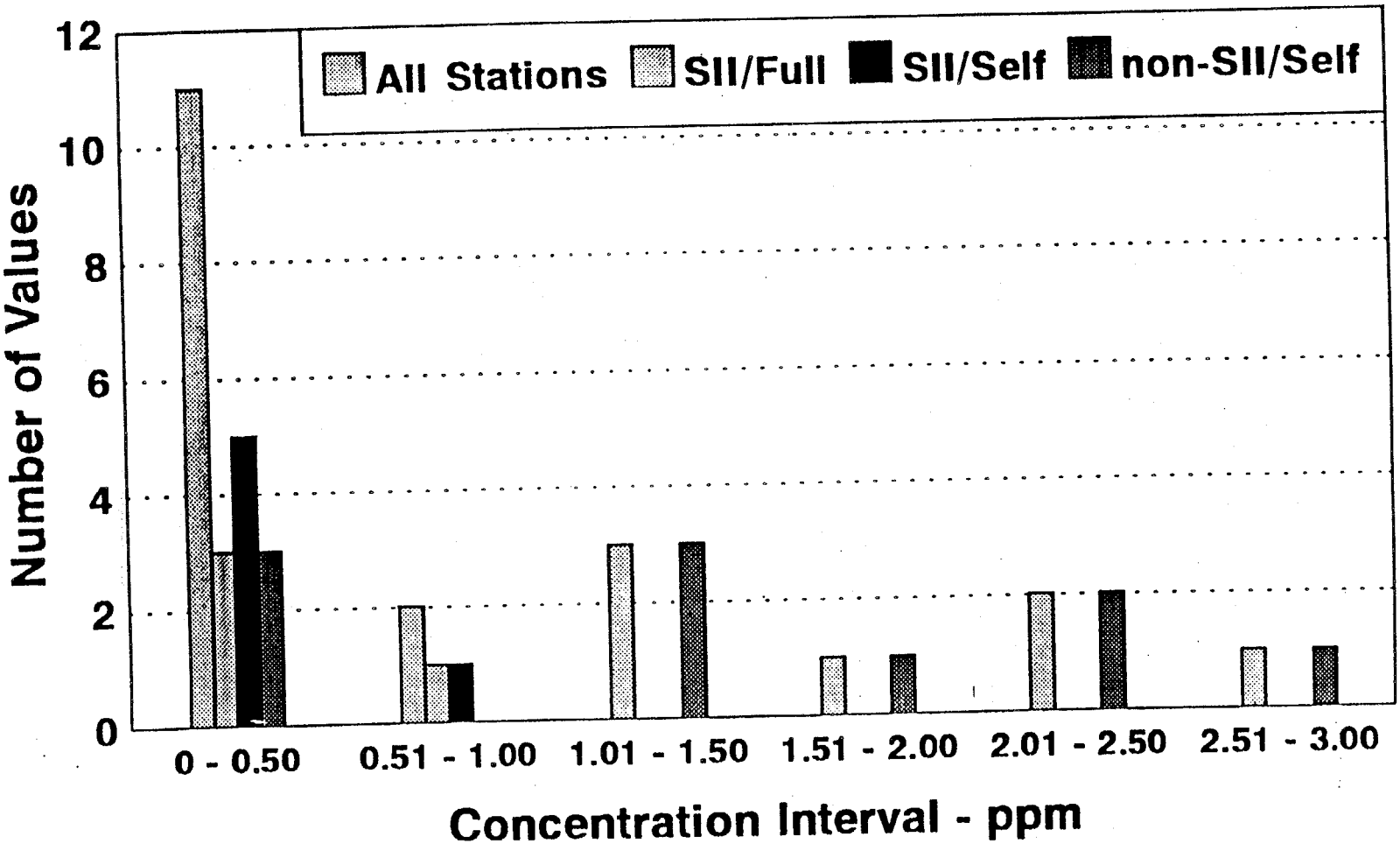
Station No. (type)	MTBE - ppm	
	During EOSHI fuel dispensing	EOSHI Values
4 (Stage II/self-serve)	0.11	0.35
5 (non-Stage II/self-serve)	0.17	0.13
6 (non-Stage II/self-serve)	0.23	--
7 (" ")	?	0.59
10 (Stage II/self-serve)	?	0.09

Distribution of Service Station Breathing Zone Data



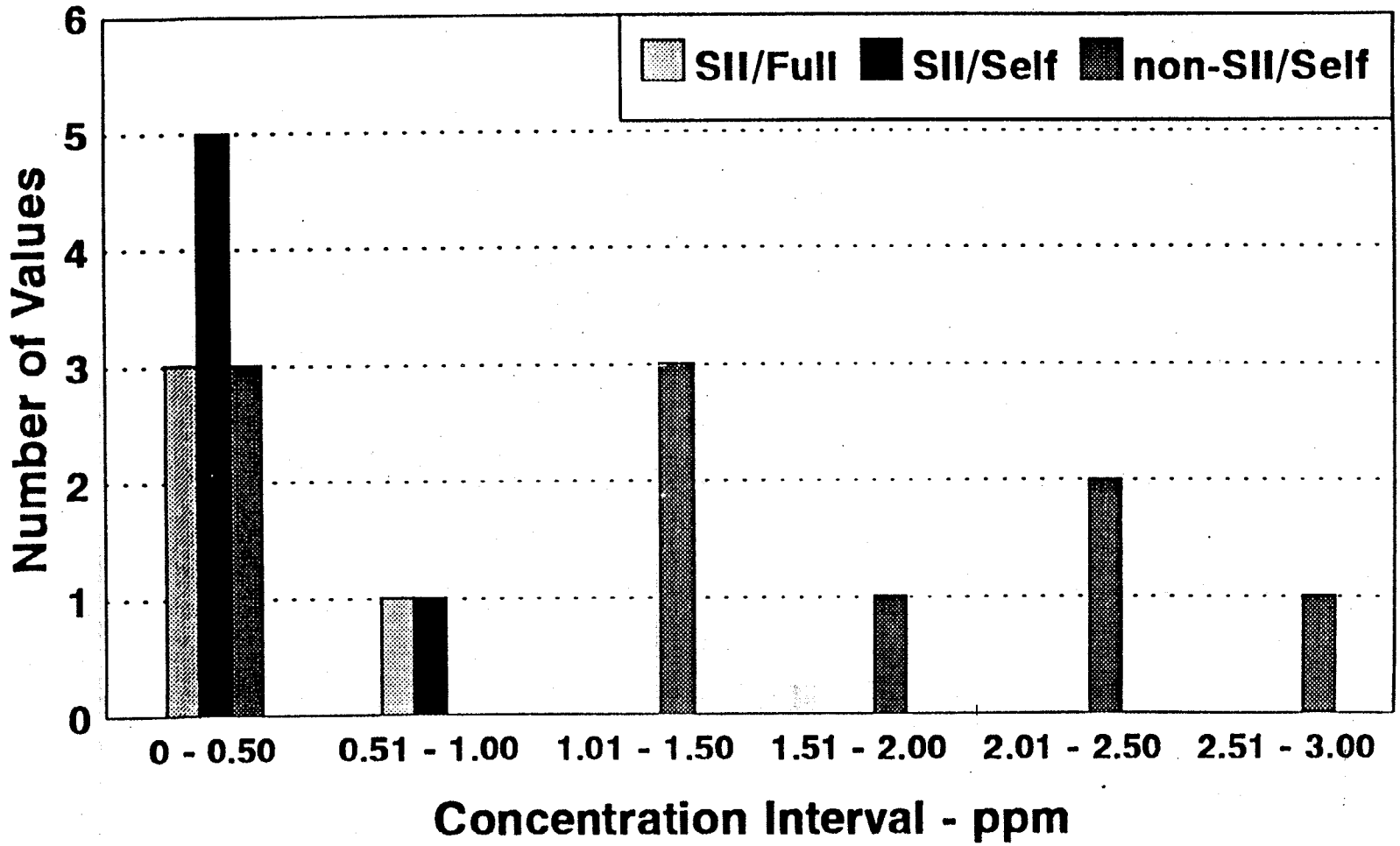
MTBE13

Distribution of Service Station Breathing Zone Data



MTBE14

Distribution of Service Station Breathing Zone Data



MTBE15

Summary

- Maximum and mean 4-hour average MTBE concentrations decrease from breathing zone to pump island to station perimeter and are lower at Stage II controlled stations.
- Mean 4-hour average MTBE concentrations are below 1 ppm at breathing zone and pump island location and are below 0.02 ppm at the station perimeters.
- Maximum 4-hour average MTBE concentrations are below 2.6 ppm at breathing zone and pump island locations and are below 0.2 ppm at station perimeters.
- Breathing zone measurements underestimate actual breathing zone concentrations during fuel dispensing by station-specific factors ranging between 1 and 3 for monitoring periods analyzed to date. Most factors (4 of 5) range between 1 and 1.4.

AUTHOR(S): Jack Hinton, Dr.Ph., CIH

TITLE: OCCUPATIONAL EXPOSURES - MTBE

There are five basic steps in bringing methyl tertiary-butyl ether (MTBE) to market:

- Manufacturing - producing MTBE at both chemical plants and petroleum refinery facilities;
- Blending - introducing MTBE into motor gasolines, which includes handling both neat MTBE and MTBE-blended fuels;
- Transportation - moving MTBE or MTBE-blended fuels via barge, tanker, railcar, truck, or pipeline to points of distribution;
- Distribution - storing and moving MTBE-blended fuels from distribution terminals to service stations; and
- Service Station - storing and dispensing MTBE-blended fuels to the public.

The American Petroleum Institute initiated a survey to collect and aggregate occupational exposure data for MTBE from member companies. The data collected are typical of industry operations are reflective of all the steps listed above, and span 11 years (May 1982 to March 1993). Further, the data are representative of all the major users and manufacturers of MTBE; 92% of the data were gathered in 1990, 50% of the data were collected in the oxyfuel winter months, and 45% of the data were gathered during the 1992/1993 oxyfuel season.

A total of 2,038 exposure measurements were received and distributed as follows:

- 18% area samples
- 7% engineering source samples
- 12% personal samples where employees wore respiratory protection
- 63% personal samples where no respiratory protection was worn

The presentation is based on the data set of 63% personal samples where respiratory protection was not worn. This data set is most representative of potential employee exposure to MTBE. It represents at least the following number of employees per exposure grouping:

Operation	Number of Workers	Number of Exposure Measurements
Manufacturing	881	365
Blending	1,800	523
Transportation	1,489	641
Distribution	7,705	305
Service station	37,753	41
Other	[a]	8
Total	**49,628**	**1,883**

[a]not determined

The data are representative of exposure groupings, with the exception of the service station category. However, the 37,753 employees in the service station category are felt to be an overstatement of the actual number of employees with potential for job activity-related exposure to MTBE. The majority of the 37,753 employees would be store clerks who are responsible for collecting payment for gasoline sales and operating the "food mart" portion of the station. Only a small fraction of this number would be employees whose job description included dispensing fuel and vehicles service and/or repair. The 41 service station exposure measurements are less representative than the other exposure measurement categories listed, but they are not as "out of line" as the comparison of 41 measurements to 37,753 workers implies.

The data are further aggregated for each operation category (manufacturing, blending, transportation, distribution, service station) by sample duration (short-term - less than 30 minutes; task/activity - between 30 minutes and 6 hours; time-weighted-average (TWA) workshift - between 6 hours and 9 hours; and extended workshift - greater than 9 hours) and MTBE source (neat or fuel mixture).

The American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Limit (WEEL) was used to assess exposure exceedances for task/activity, TWA workshift, and extended workshifts. Because no comparable short-term exposure limit exists, the Excursion Limit convention was borrowed from the American Conference of Governmental Industrial Hygienists (ACGIH). This "rule of thumb" convention uses a 3-fold multiplication of the 8-hour exposure limit value to determine an acceptable short-term exposure. This presentation advocates neither the need nor the establishment of a short-term value equal to the 300 ppm value used here (3 x 100 ppm AIHA - WEEL = 300 ppm Excursion Limit). The value of 300 ppm is simply used as a convention to sort and present short-term data.

Personal exposures in the manufacturing category are less than[1] 10 ppm for all sample types for both routine and maintenance operations. A single exposure of 249 ppm was reported for a "bottle-washing" activity in a quality control lab. A review of information associated with this value indicates this to be an atypical exposure, as the automated bottle-wash equipment is usually controlled with exhaust ventilation; and other samples included in this data set, which are representative of this activity, are below the 10 ppm limit reported above.

Personal exposures in the blending category are less than 100 ppm for all sample types for both neat and fuel mixture operations, with the data predominantly being less than 10 ppm.

[1]The term "less than" is used for values below a stated concentration (e.g., <10 ppm) and should not be confused with values below an analytical limit of detection, which are expressed as "below the Limit of Detection".

Personal exposures in the transportation category are generally less than 50 ppm for short-term activities associated with mixed fuel and are generally less than 200 ppm for short-term activities associated with neat MTBE. Short-term exposures for both neat and fuel mixtures can exceed 300 ppm (the highest value being 1050 ppm) and generally reflect barge loading, sampling, and gauging activities or vacuum hosing associated with "pigging" (cleaning) operations in pipelines. Activity/workshift exposures for neat MTBE activities are generally less than 10 ppm, with occasional exposures ranging up to 711 ppm, where barge loading, sampling, gauging, or pigging operations occurred during the shift. Activity/workshift exposures for mixed fuel activities are generally below 10 ppm, with no exposures seen above the 100 ppm WEEL.

Personal exposures in the distribution category are generally less than 10 ppm for the short-term operations and are generally less than 1 ppm for activity/workshift timeframes.

Personal exposures in the service station category are generally less than 100 ppm for short-term activities and are limited to vehicle repair or gasoline dispensing. Activity/workshift exposures are generally less than 10 ppm. Monitored exposures for this category generally represent full-service activities associated with dispensing fuel and garage repairs. Some samples reflect weights and measure inspection activities and fuel dispensing pump repair.

From these data, personal occupation exposures to MTBE are generally well within the AIHA 100 ppm WEEL. The ranges are as follows:

- 26% below the Limit of Detection
- 34% between the Limit of Detection and 1.0 ppm
- 36% between 1.0 ppm and 100 ppm and
- 4% in excess of 100 ppm

Short-term exposures to MTBE are generally well within an excursion value of three times the 100 ppm AIHA WEEL (300 ppm Excursion Limit). The ranges are as follows:

- 19% below the Limit of Detection
- 20% between the Limit of Detection and 1.0 ppm
- 59% between 1.0 ppm and 300 ppm and
- 2% in excess of 300 ppm

The data demonstrate that exposures in excess of 100 ppm TWA or 300 ppm short-term occur infrequently and are generally limited to specific non-routine or "extraordinary" tasks. Once determined, respiratory protection or other ventilation techniques are used to control exposures in these situations.

A relative index based on geometric means (G.M.) of short-term and activity/workshift TWA concentrations can be constructed to rank exposure potential. From this data set, the exposure potential rankings would be:

Operation	MTBE (PPM) G.M. Short-Term	G.M. TWA
Transporting neat MTBE	11.0	0.24
Blending neat MTBE	5.1	0.58
Service station	4.7	0.77
Transporting MTBE/fuel mix	3.3	0.13
Manufacturing-maintenance	1.0	0.14
Distributing	0.85	0.13
Manufacturing-routine	0.84	0.06
Blending MTBE/fuel mix	0.58	0.10

American Petroleum Institute
Occupational Exposures - MTBE

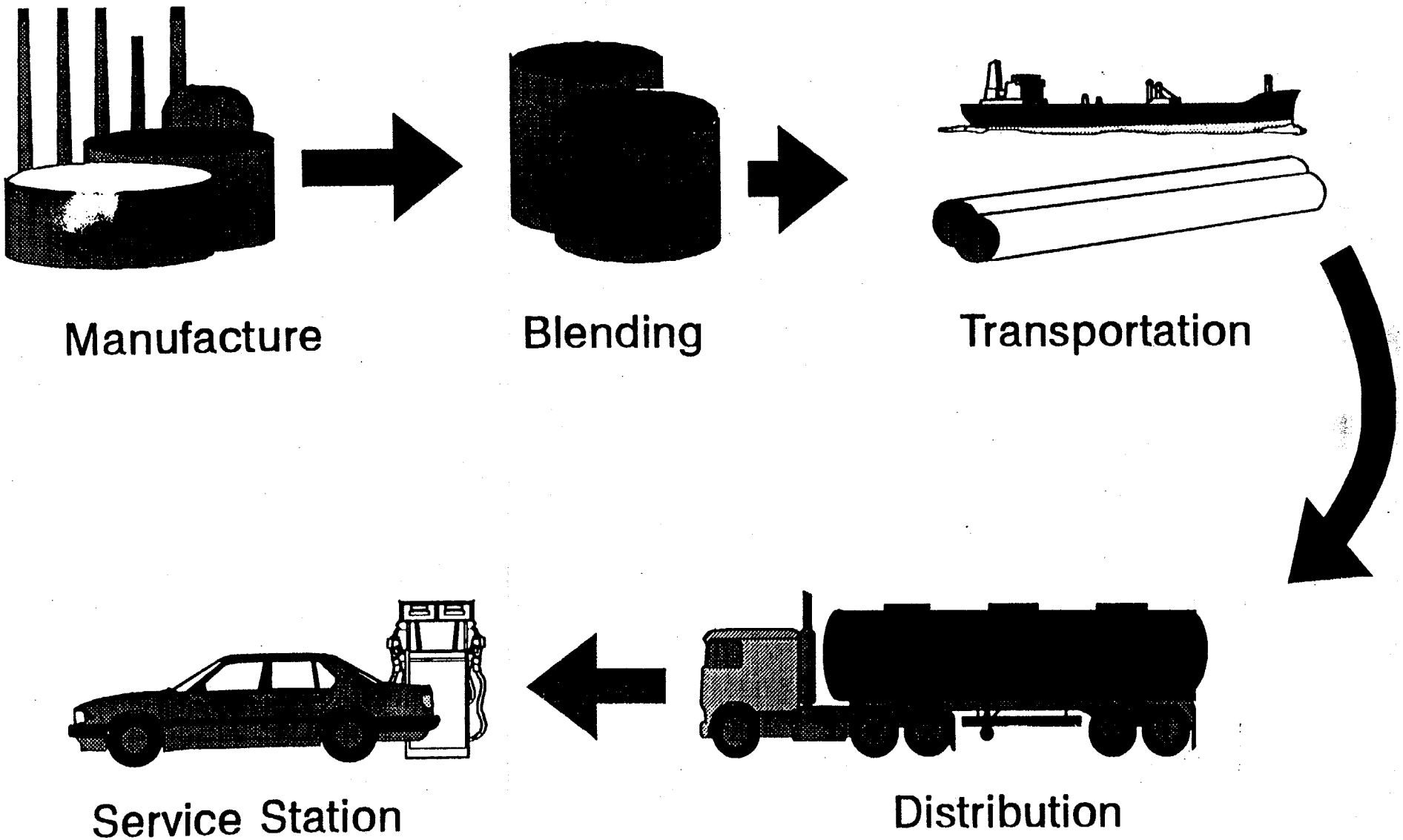
Jack Hinton, Dr PH, CIH

July 27, 1993

Occupational Exposures - MTBE

- Aggregated member company MTBE exposure data
- Timeframe: May, 1982 to March, 1993
- 16 companies responded
  (All major users and manufacturers of MTBE)

The Life Cycle of MTBE



Occupational Exposures - MTBE

Data Variables:

Facility type
State
Measurement locations
MTBE source
Sample type
Job type
Month, Year
Sampling/analytical method
Control information
Operating conditions
MTBE concentrations

Occupational Exposures - MTBE

Operation	# Workers	# Exposure Measurements
Manufacturing	881	365
Blending	1800	523
Transportation	1489	641
Distribution	7705	305
Service Station	37753	41
Other	not determined	8
Total	49628	1883

Occupational Exposures - MTBE

Data distributions: 2038 exposure measurements

18% Area samples

7% Source samples

63% Personal samples w/o resp. protection

12% Personal protection w/resp. protection

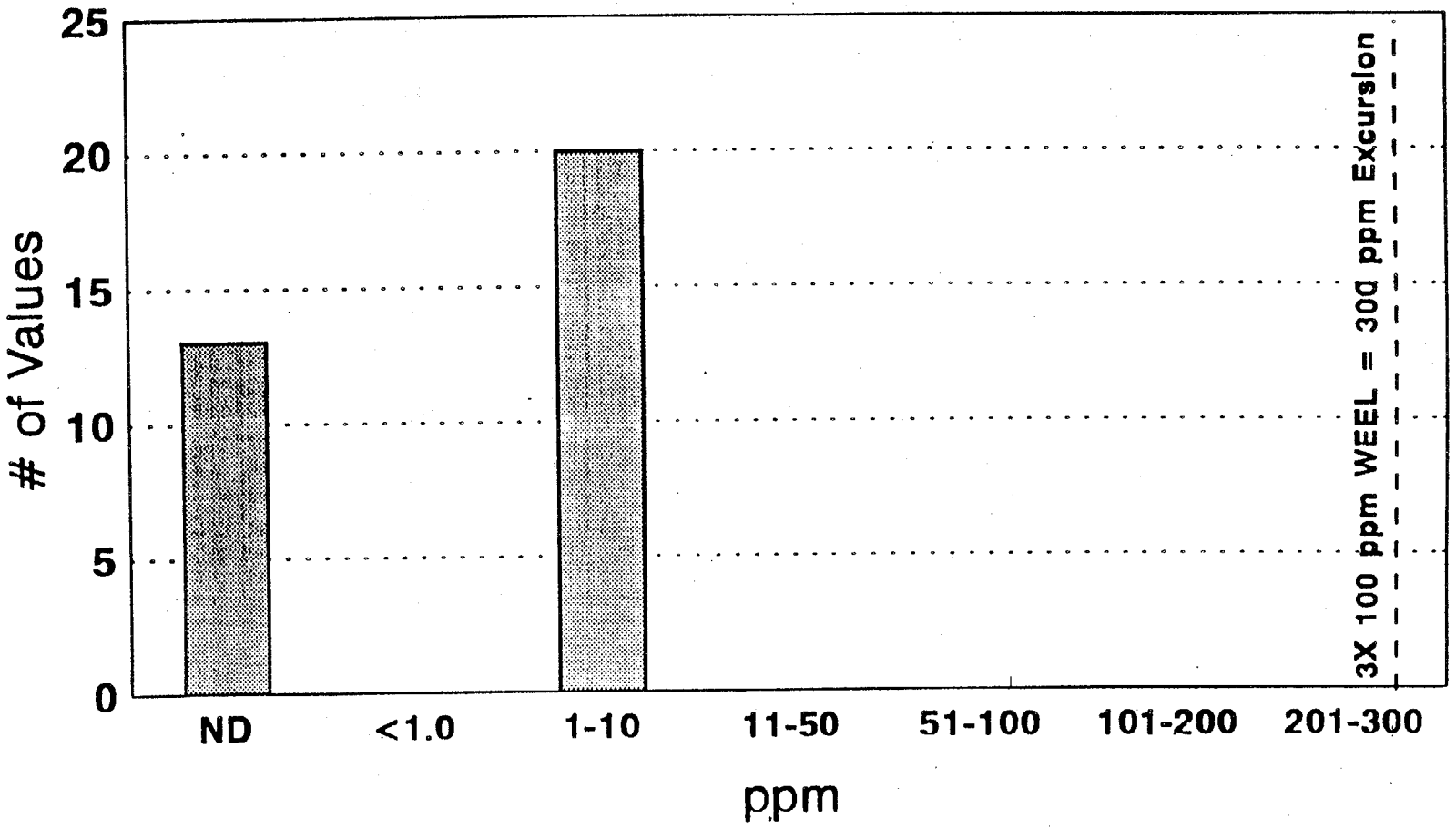
100%

Occupational Exposure - MTBE
Manufacturing - Personal Samples

Operation	Exposure Type	# Values All	# Values ND	Concentration, ppm Min.	Max.	Median	G.M.	G.S.D.
Routine	Short-term	33	13	0.016	7.8	1.0	0.84	3.5
	Task	0	-	-	-	-	-	-
	8-hr TWA	82	38	0.01	249	0.03	0.06	6.0
	Ex Shift	2	0	0.16	0.17	-	-	-
Maintenance/ Turnaround	Short-term	14	1	0.50	7.2	0.70	1.0	2.6
	Task	1	0	0.20	-	-	-	-
	8-hr TWA	12	0	0.04	0.7	0.14	0.14	2.3
	Ex Shift	2	0	0.16	0.2	-	-	-

Occupational Exposures - MTBE

Manufacturing - Personal Samples
Routine Operations - Short-term

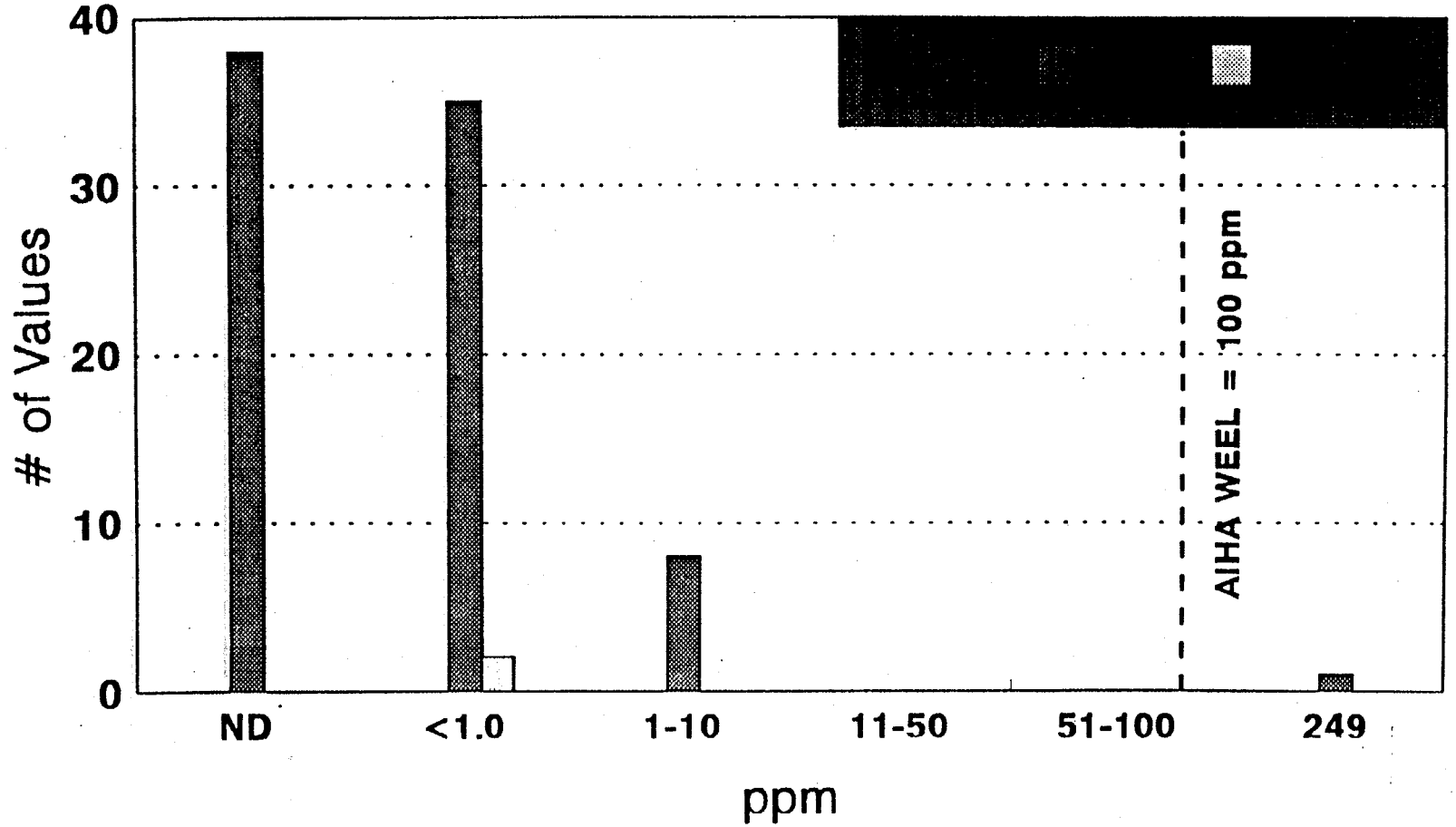


MTBE8

Occupational Exposures - MTBE

Manufacturing - Personal Samples

Routine Operations - Activity/Workshift Exposure

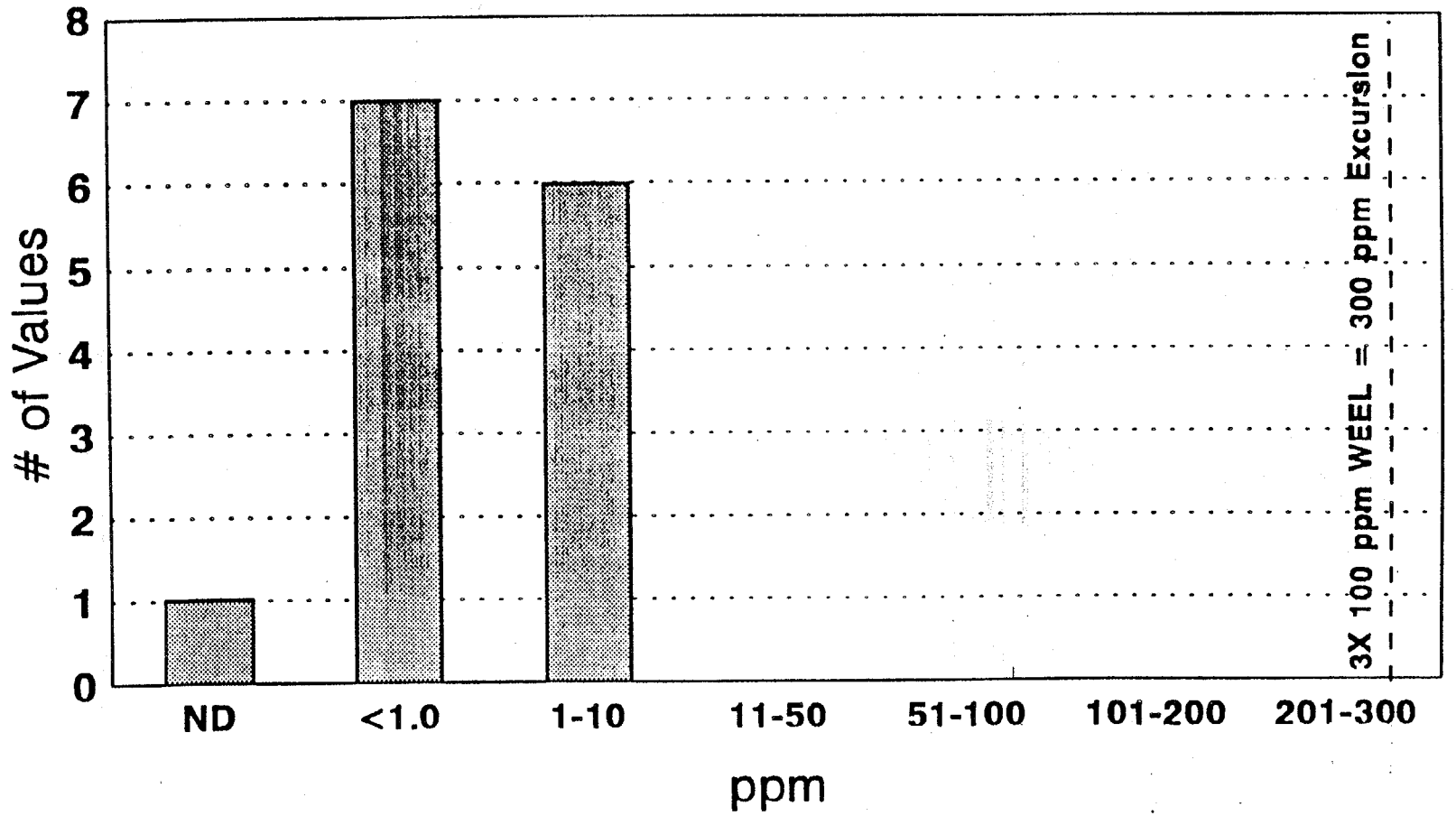


MTBE9

Occupational Exposures - MTBE

Manufacturing - Personal Exposures

Maintenance/Turnaround - Short-term Exposures

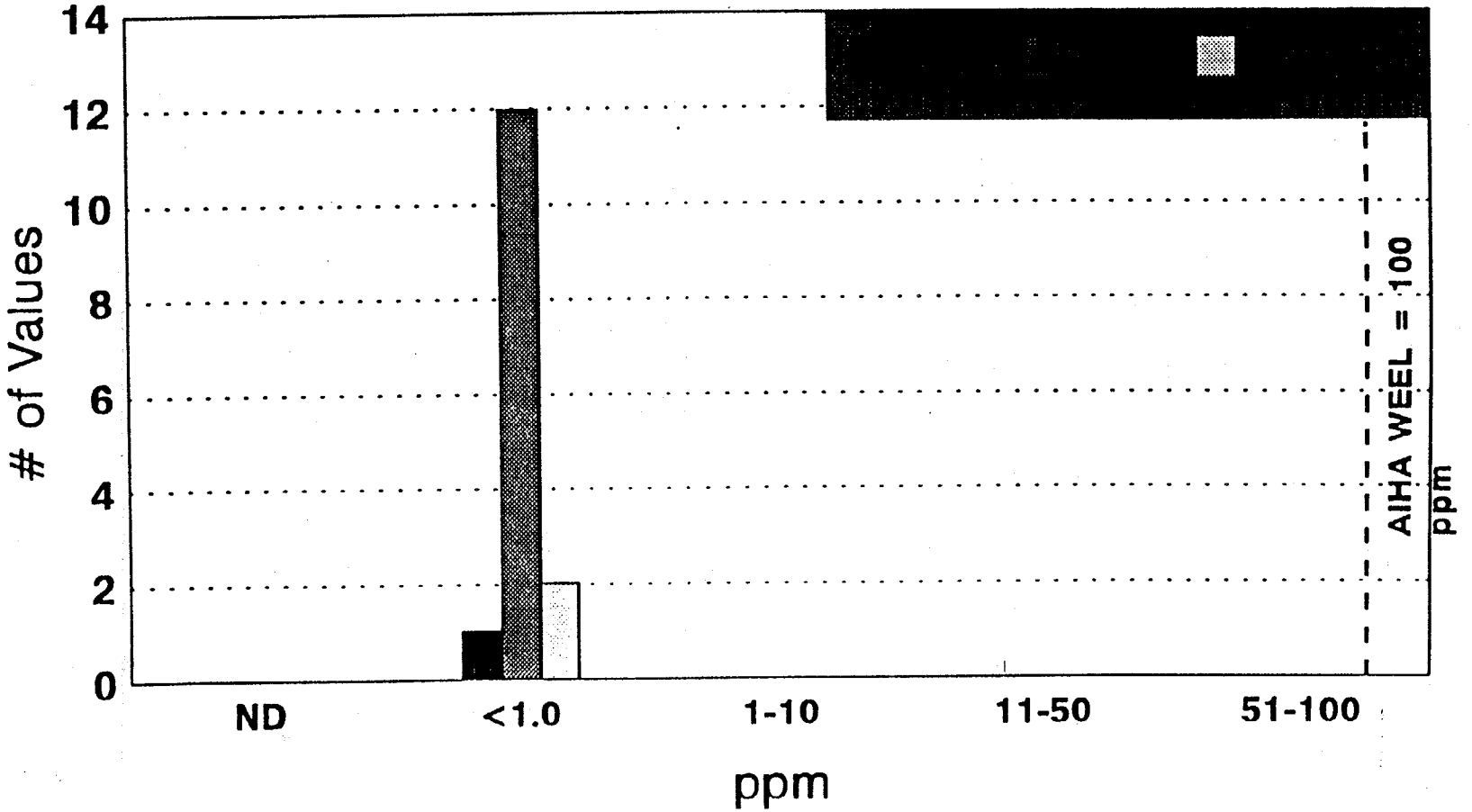


MTBE10

Occupational Exposures - MTBE

Manufacturing - Personal Samples

Maintenance/Turnaround - Activity/Workshift Exposure



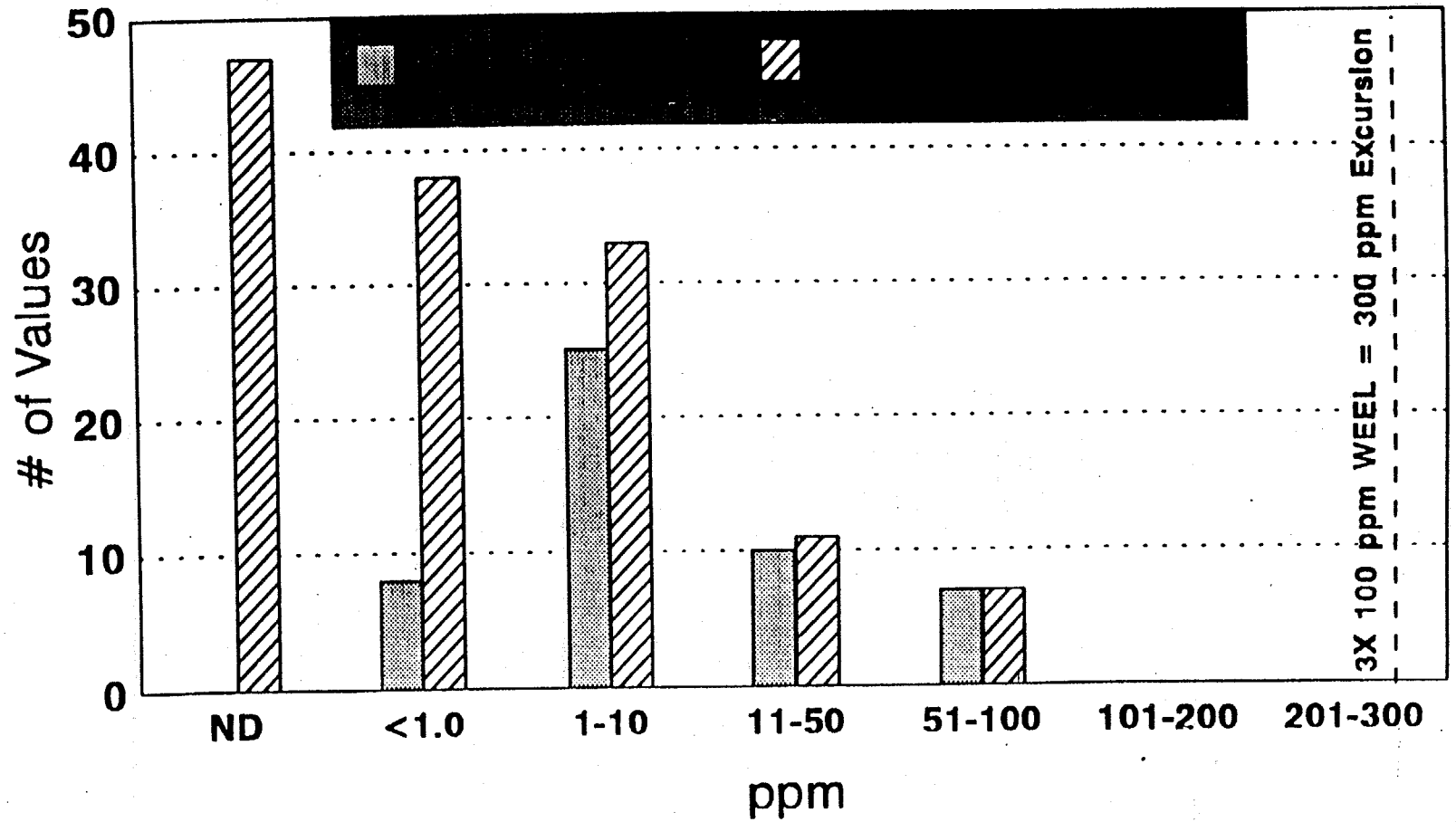
MTBE11

Occupational Exposure - MTBE
Blending - Personal Samples

Operation	Exposure Type	# Values All	# Values ND	Concentration, ppm Min.	Concentration, ppm Max.	Concentration, ppm Median	Concentration, ppm G. M.	Concentration, ppm G.S.D.
Neat	Short-term	50	1	0.01	97	2.3	5.1	5.6
	Task	13	1	0.21	72	1.0	2.1	5.3
	8-hr TWA	13	5	0.04	88	2.6	1.9	9.2
	Ex Shift	9	9	0.23	0.34	0.3	0.3	1.1
Fuel Mix	Short-term	136	47	0.02	100	0.4	0.58	9.4
	Task	19	14	0.03	2	0.05	0.12	3.9
	8-hr TWA	122	78	0.02	14	0.05	0.10	4.1
	Ex Shift	22	13	0.01	0.27	0.02	0.04	2.7

Occupational Exposures - MTBE

Blending - Personal Samples
Short-term Exposure Data

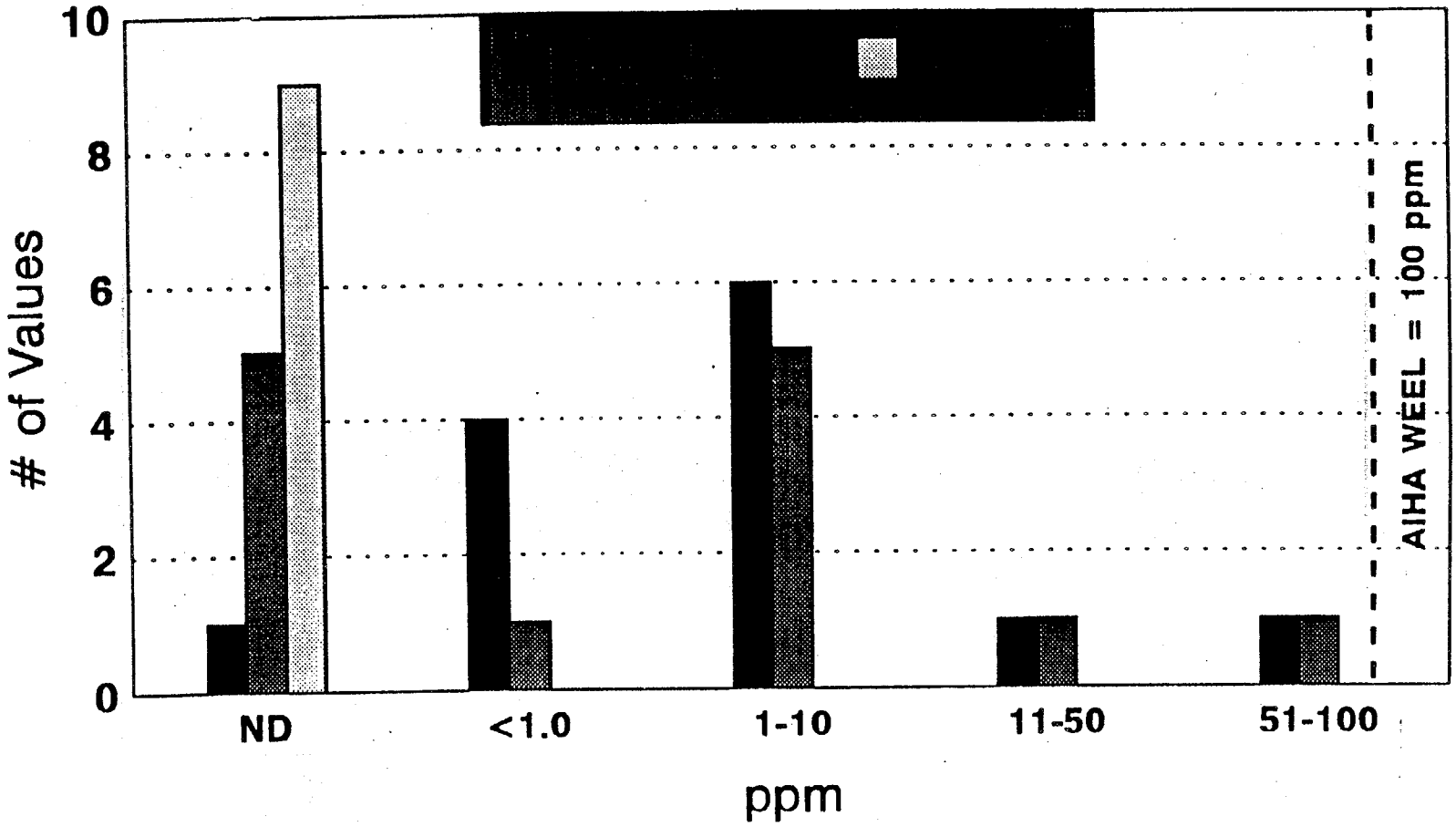


MTBE89

Occupational Exposures - MTBE

Blending - Personal Samples

Neat - Activity/Workshift Exposure

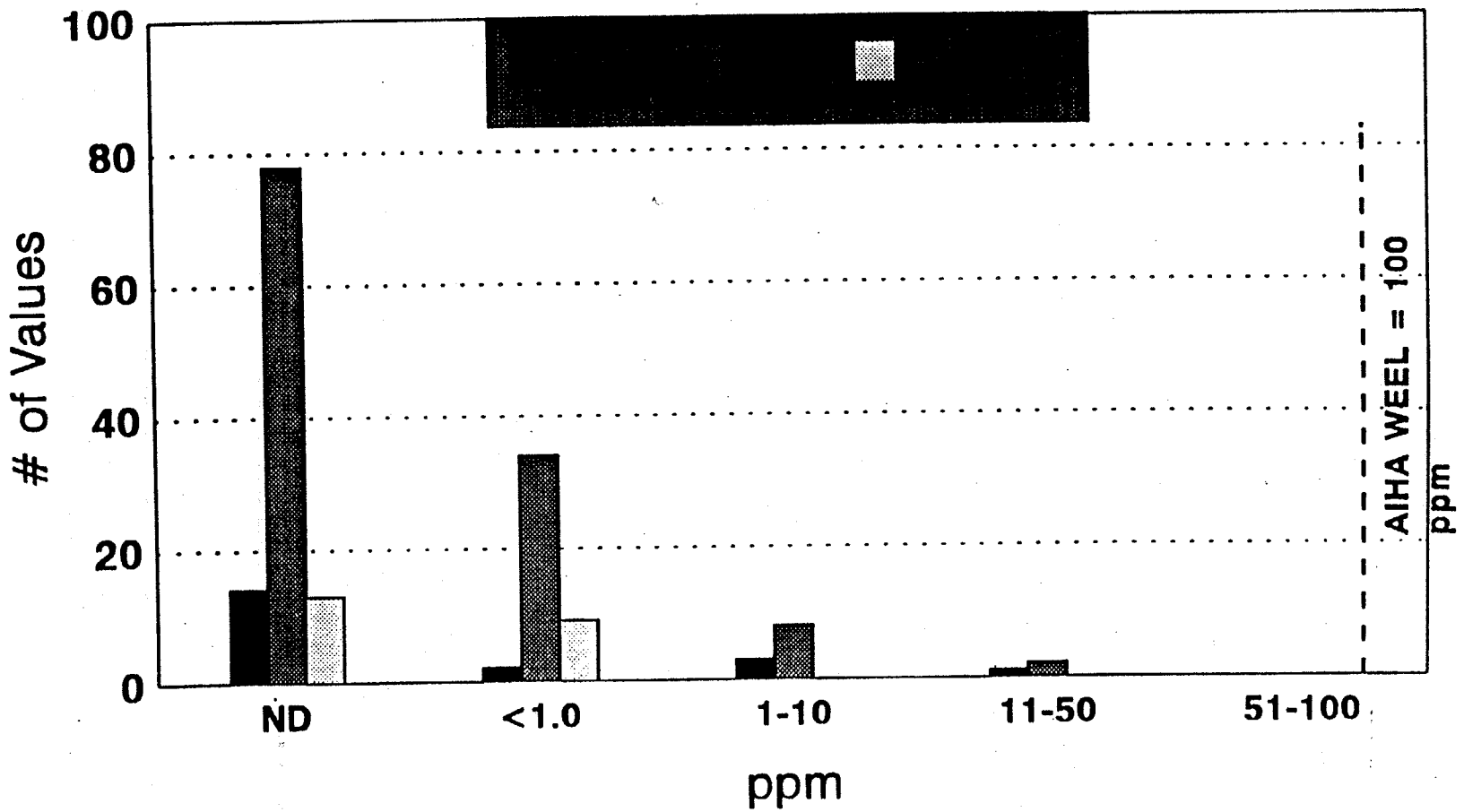


MTBE16A

Occupational Exposures - MTBE

Blending - Personal Samples

Mixed Fuel - Activity/Workshift Exposure



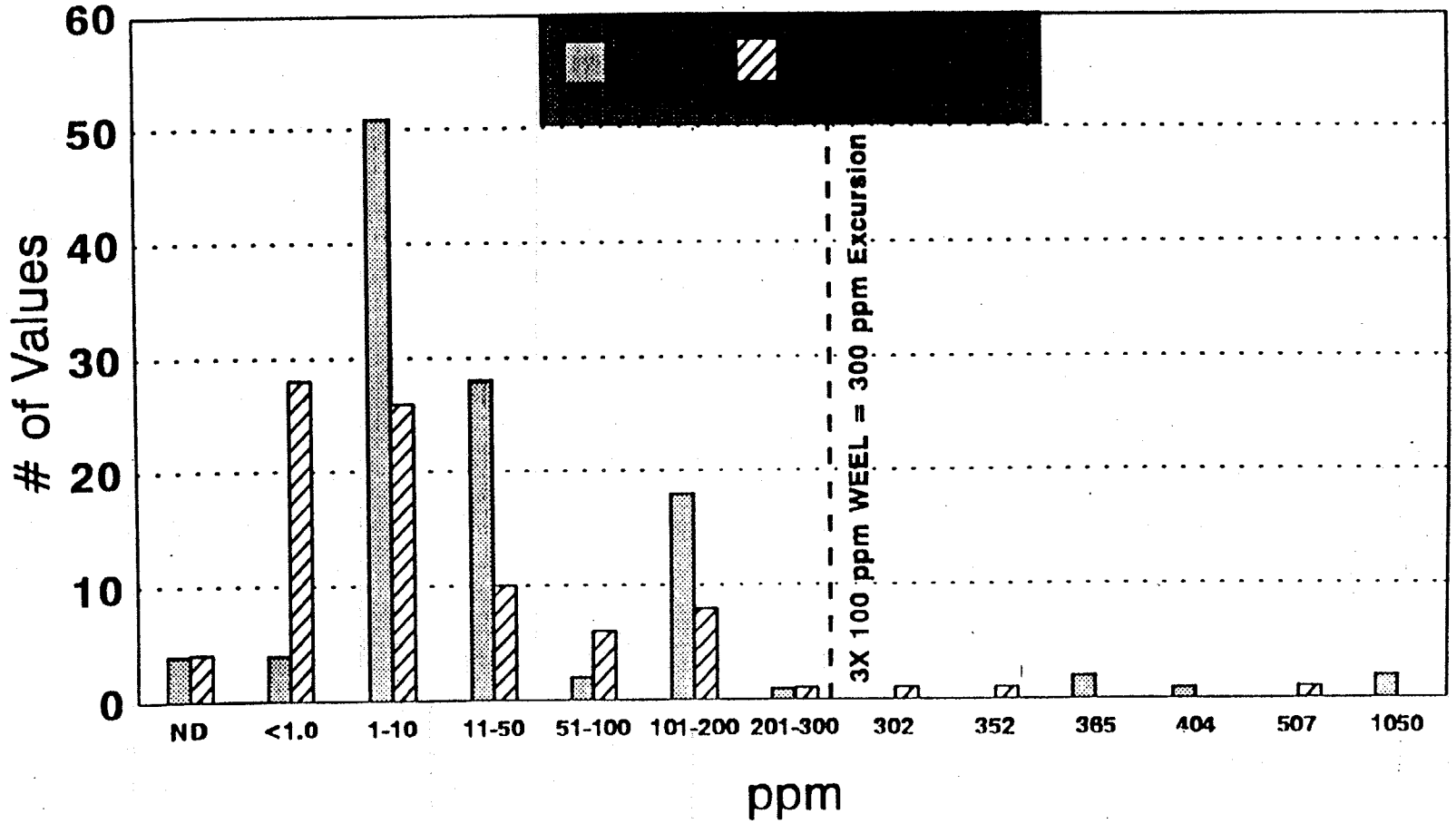
MTBE16B

Occupational Exposure - MTBE
Transport - Personal Samples

Operation	Exposure Type	# Values All	# Values ND	Concentration, ppm Min.	Concentration, ppm Max.	Concentration, ppm Median	Concentration, ppm G. M.	Concentration, ppm G. S.D.
Neat	Short-term	114	4	0.3	1050	9.7	11	7.3
	Task	27	4	0.04	700	2.2	2.3	9.4
	8-TWA	17	1	0.02	712	0.21	0.24	10.6
	Ex Shift	1	0	0.32	-	-	-	-
Fuel Mix	Short-term	86	4	0.01	508	2	3.3	13.2
	Task	92	28	0.02	59	0.42	0.51	14.0
	8-TWA	59	14	0.01	26	0.12	0.13	6.3
	Ex Shift	8	0	0.19	4.5	1.5	1.2	3.0

Occupational Exposures - MTBE

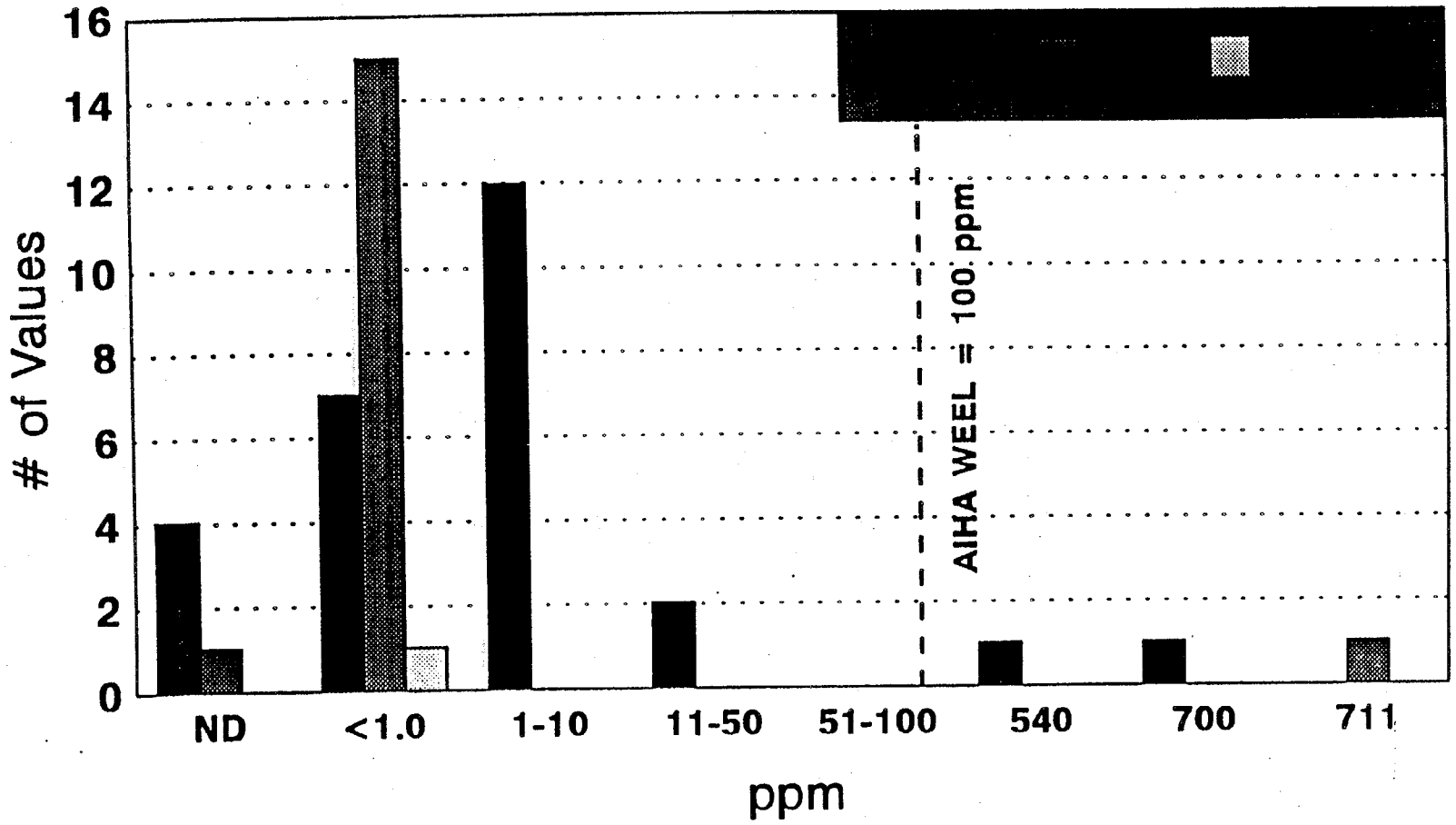
Transport - Personal Samples
Short-term Exposure Data



MTBE18

Occupational Exposures - MTBE

Transport- Personal Samples
Neat - Activity/Workshift Exposures

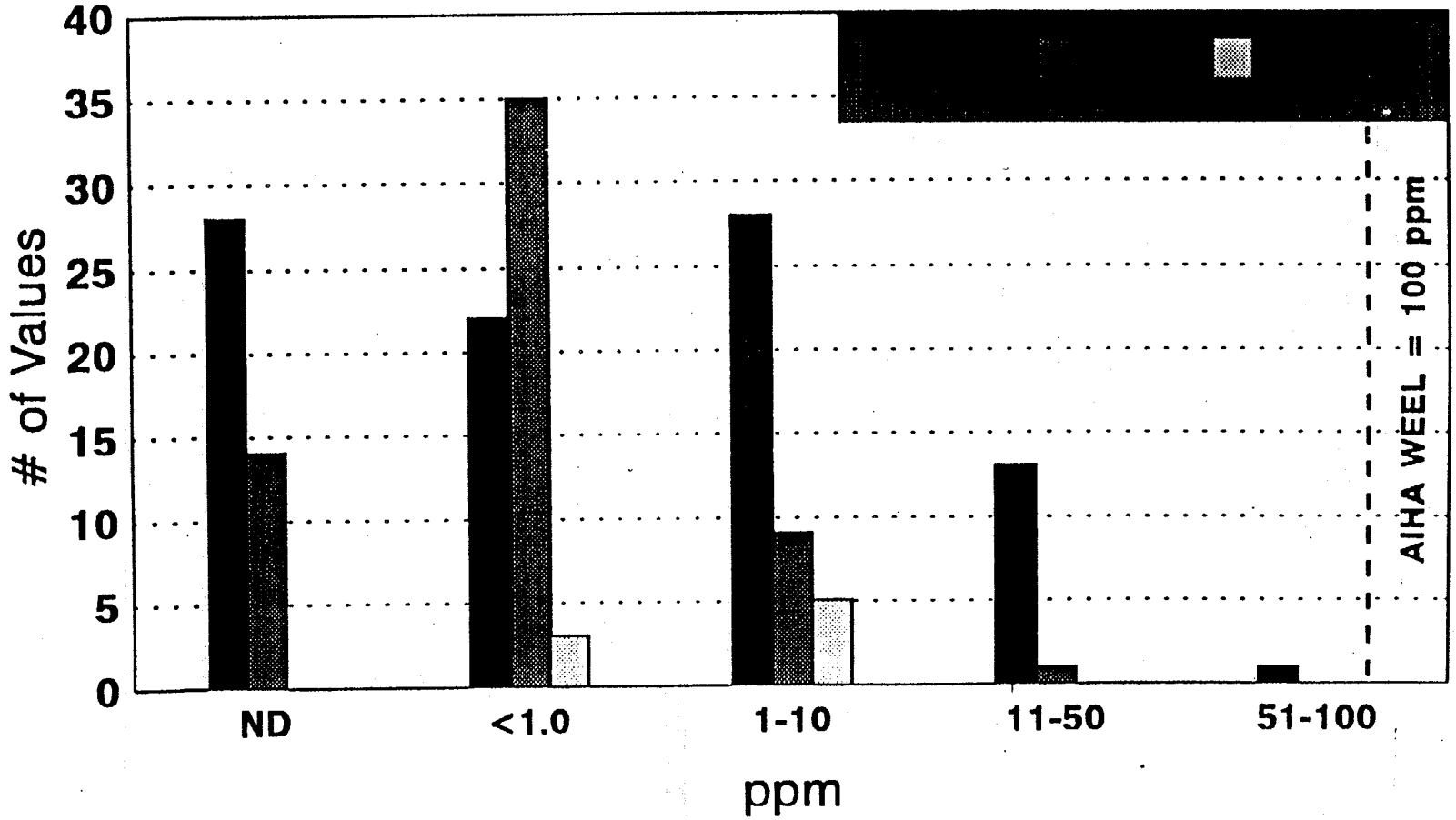


MTBE19A

Occupational Exposures - MTBE

Transport- Personal Samples

Mixed Fuel - Activity/Workshift Exposures



MTBE19B

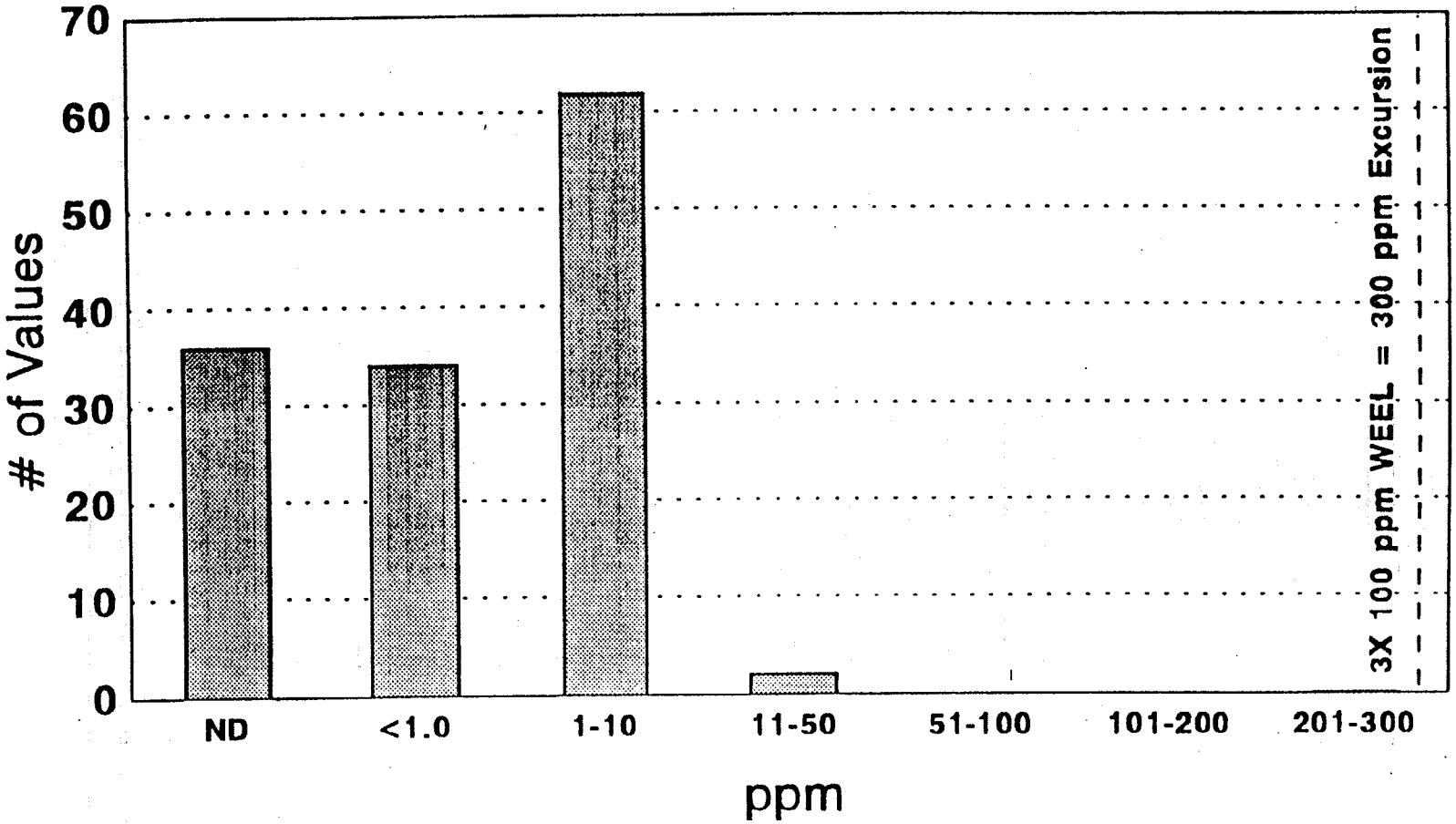
Occupational Exposure - MTBE
Distribution - Personal Samples

Operation	Exposure Type	# Values All	# Values ND	Concentration, ppm Min.	Concentration, ppm Max.	Concentration, ppm Median	Concentration, ppm G.M.	Concentration, ppm G.S.D.
All	Short-term	134	36	0.01	14	0.85	0.49	7.2
	Task	10	1	0.26	4	1.0	1.0	2.4
	8-hr TWA	100	25	0.01	2.2	0.11	0.13	4.0
	Ex Shift	47	1	0.06	6.2	0.71	0.63	2.9

Occupational Exposures - MTBE

Distribution - Personal Samples

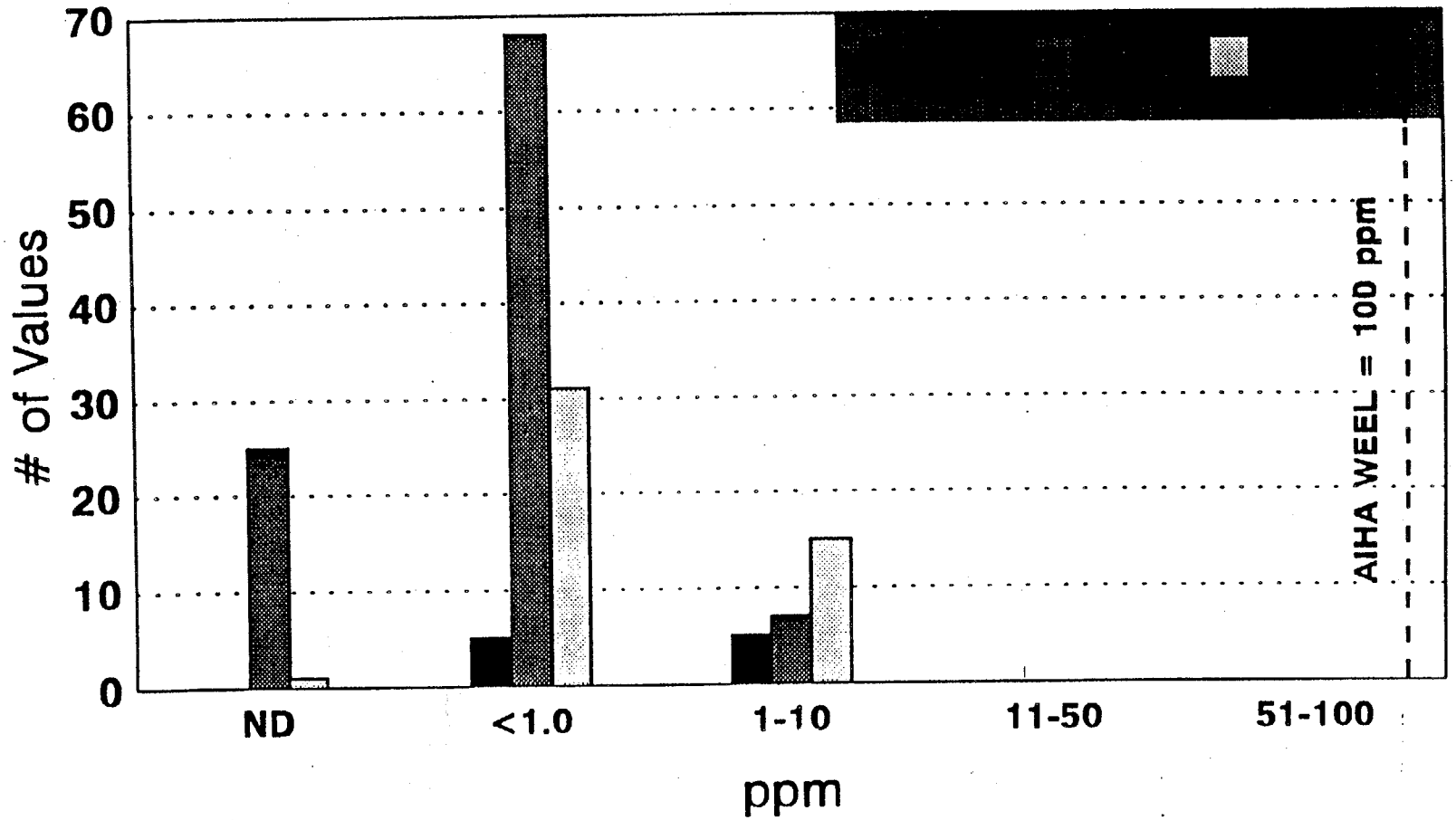
Short-term Exposure Data



MTBE21

Occupational Exposures - MTBE

Distribution - Personal Samples
Activity/Workshift Exposures



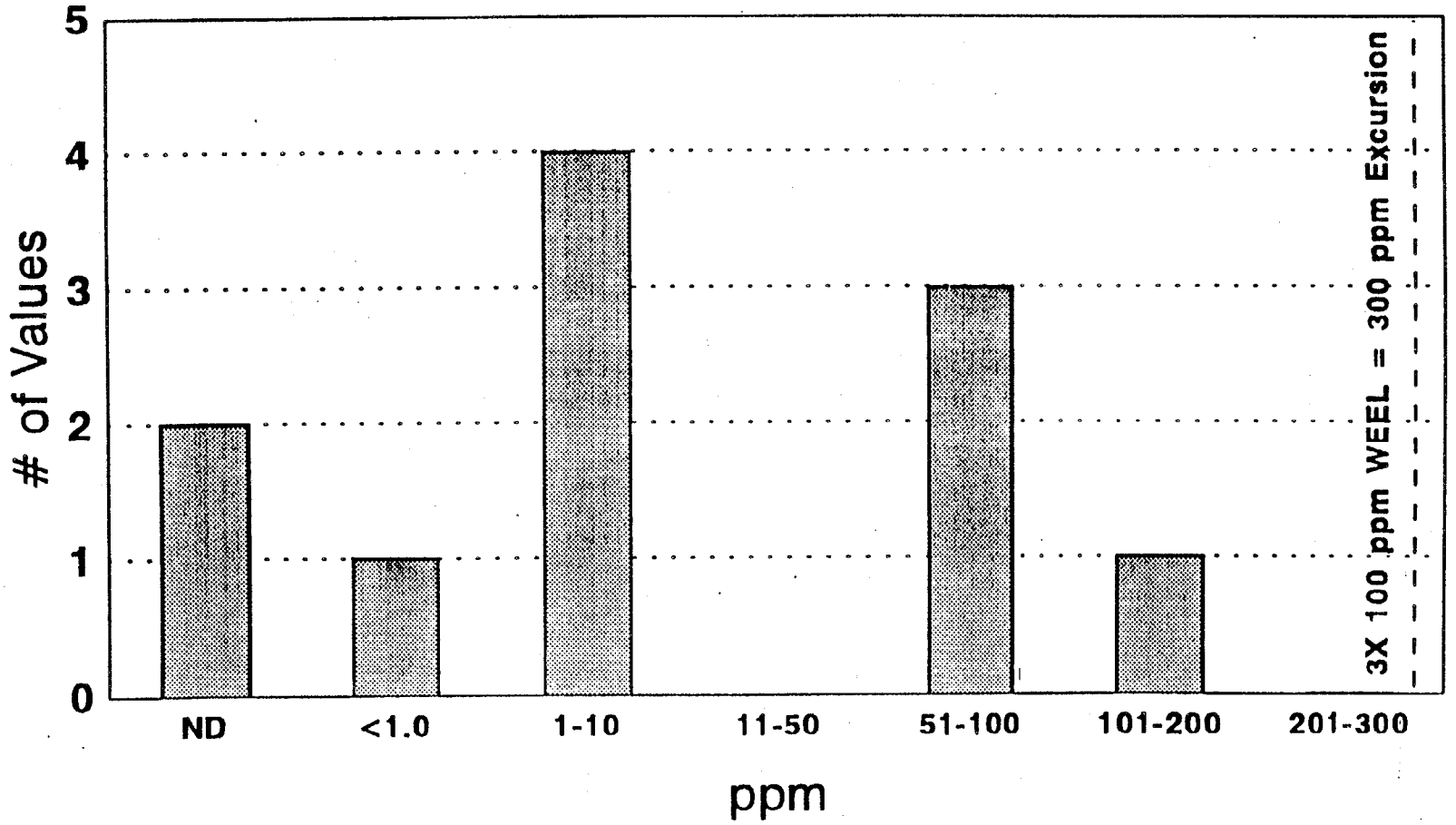
MTBE22

Occupational Exposure - MTBE
Service Station - Personal Samples

Operation	Exposure Type	# Values All	# Values ND	Concentration, ppm Min.	Concentration, ppm Max.	Concentration, ppm Median	Concentration, ppm G.M	Concentration, ppm G.S.D.
Service Station	Short-term	11	2	0.16	136	2.8	4.7	11.5
	Task	5	0	0.01	2.7	0.34	0.75	2.8
	8-hr TWA	13	0	0.09	34	0.59	0.77	4.7
	Ex Shift	11	0	0.01	17	1.1	2.8	4.5

Occupational Exposures - MTBE

Service Station - Personal Samples
Short-term Exposure Data

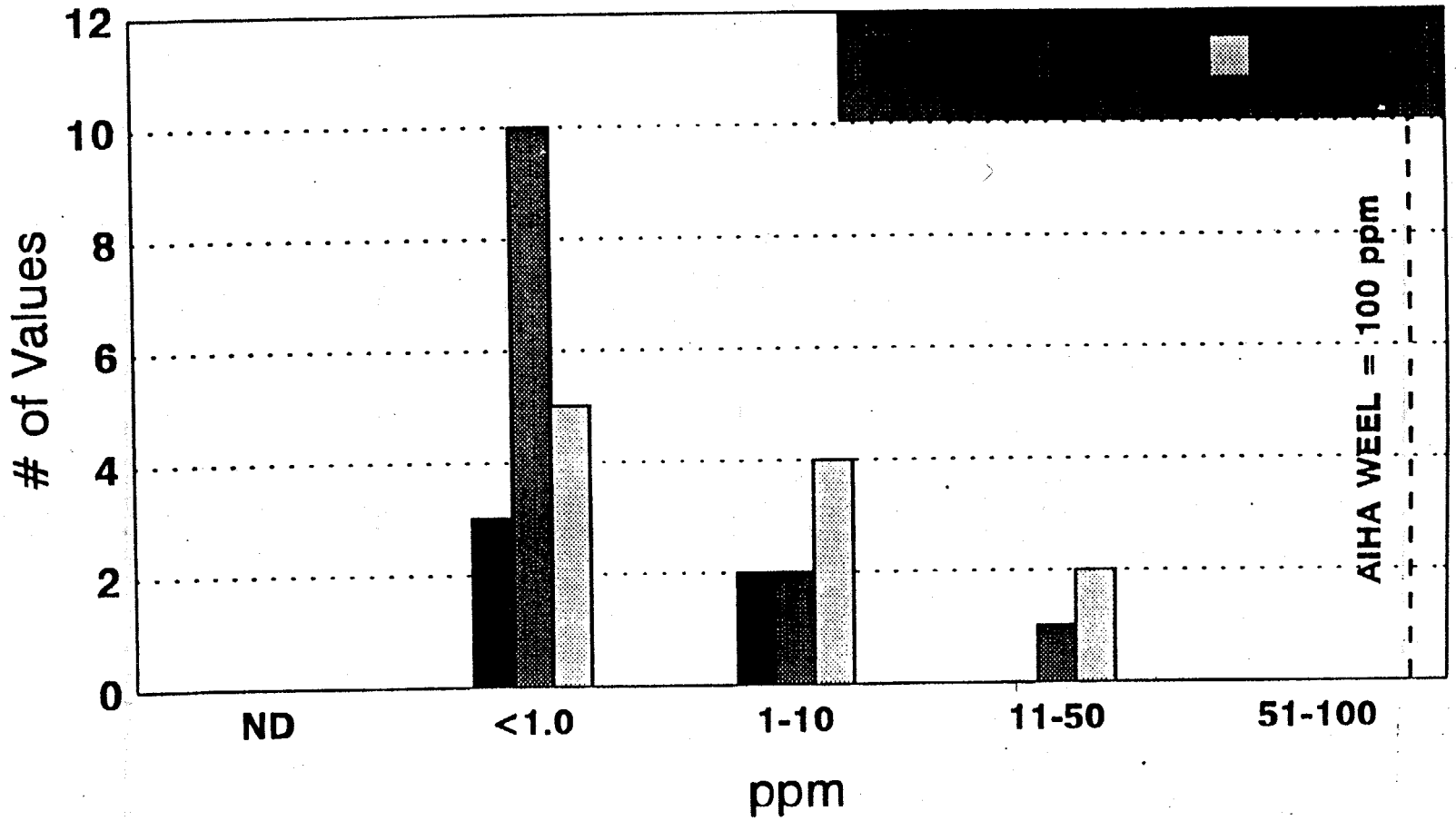


MTBE24

Occupational Exposures - MTBE

Service Station - Personal Samples

Activity/Workshift Exposures



MTBE25

Summary

- The data set is typical of industry operations
- The data set is representative of employee exposures
- The data set spans a 10 year period with the majority of the data post CAA oxyfuel initiation (92% since '90)
- 50% of the data represents oxyfuel winter months, with 45% of all data reflective of the '92 - '93 season

Conclusions

- Personal occupational exposures to MTBE are generally well within the AIHA 100 ppm WEEL, ranging as:

26% below Limit of Detection
34% between LOD & 1 ppm
36% between 1 & 100 ppm
4% in excess of 100 ppm

Conclusions

- Short-term exposures to MTBE are generally well within an excursion value of three times the 100 ppm WEEL (300 ppm).

19% below Limit of Detection
20% between LOD & 1 ppm
59% between 1 & 300 ppm
2% in excess of 300 ppm

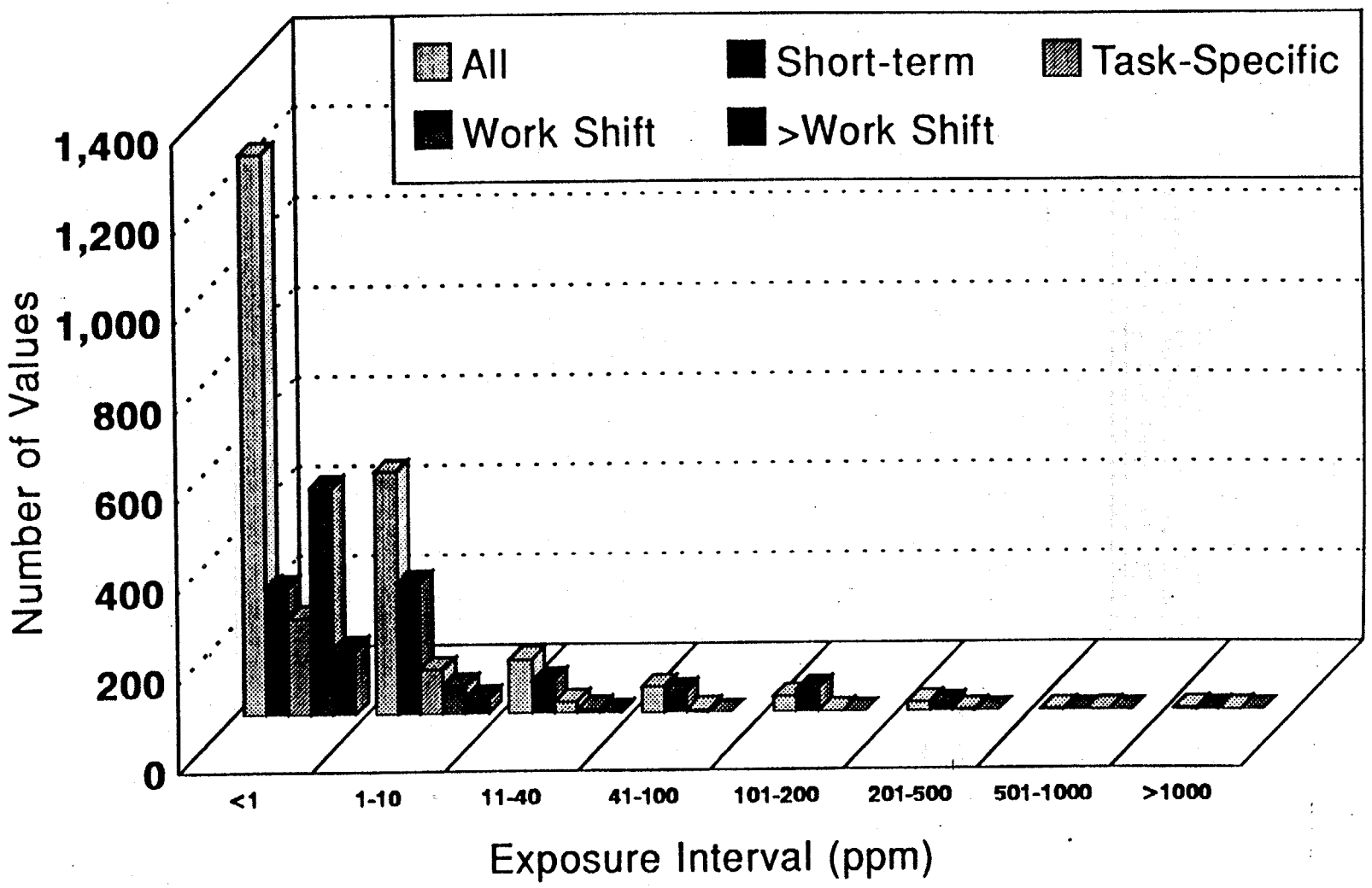
Conclusions

- Data demonstrate exposures in excess of 100 ppm TWA or 300 ppm Short-Term occur infrequently and are generally limited to specific non-routine or extraordinary tasks. Once determined, respiratory protection or other ventilation techniques are used to control exposures in these situations

Occupational settings ranked in order of exposure potential would be:

	ppm	
	G.M. Short-term	G.M. TWA
1. Transporting Neat MTBE	11.0	0.24
2. Blending Neat MTBE	5.1	0.58
3. Service Station	4.7	0.77
4. Transporting MTBE/Fuel Mix	3.3	0.13
5. Manufacturing-Maintenance	1.0	0.14
6. Distributing	0.85	0.13
7. Manufacturing-Routine	0.84	0.06
8. Blending MTBE/Fuel Mix	0.58	0.10

Distribution of Occupational Exposures to MTBE



MTBE301

AUTHOR(S): P.J. Lioy, C. Weisel, E. Pellizzari, J. Raymer

TITLE: VOLATILE ORGANIC COMPOUNDS FROM FUELS OXYGENATED WITH MTBE: CONCENTRATION AND MICROENVIRONMENTAL EXPOSURES TO MTBE IN AUTOMOBILE CABINS

There are two locations where field contact with gasoline and its constituents can lead to a wide range of concentrations and exposure patterns: (1) the interior of an automobile during stop/go commutes, and (2) the activities surrounding refueling practices. These microenvironments were examined during April 1993 in two typical suburban commuting settings: Fairfield County, Connecticut, Westchester County, New York, and Middlesex County, New Jersey. In terms of gasoline dispensing, differences between these locations were that Connecticut and NY had self-service refueling, and a mix of stations with Stage II and non-Stage II vapor recovery controls. New Jersey had Stage II and operator-assisted refueling of vehicles. The experimental design included: (1) selecting a specific commuting route in each area; (2) selecting a specified protocol for refueling samples before, during, and after; (3) selecting four vehicles that represent a mix of present (1992) and older (1986, 1987) automobiles; and (4) collecting interior cabin and personal samples during refueling at self-service stations.

MTBE samples were collected using two methodologies: an active carboxen trap system, and an active canister system. Results from side-by-side sampling with both methods and duplicate analyses of specific canister samples indicated that our data quality objectives were met for both sampling techniques. Both samplers were operated simultaneously in the commuter studies and only trap samples were taken for the personal samples.

The cabin interior results for a 1-hour run from the commuter study yielded a geometric mean concentration of 8.2 ppb and a range of 1.2 to 160 ppb. The Connecticut commuter runs had higher mean concentrations than the New Jersey runs, 23 $\mu g/m^3$ and 16 $\mu g/m^3$, respectively. Comparisons of all paired vehicle hood (outside) and interior cabin (inside) samples indicated that the highest differences were associated with an older vehicle (1987 Caprice). Emission studies conducted on each vehicle appeared to indicate that there is an abnormally high evaporative emissions factor for the Caprice which was between 8-30 times higher than the other three vehicles.

The refueling studies found that the highest levels of MTBE were associated with personal refueling of vehicles at both the Stage II and non-Stage II gasoline stations (range between 13 ppb - 4100 ppb). Elevated but lower levels of MTBE were observed for the interior cabin samples taken during refueling. The pre- and post-refueling levels were lower than the personal and cabin interior samples during refueling. The post-refueling samples, however, were generally higher than the values recorded before a car pulled up to the pump for vehicle refueling.

VOLATILE ORGANIC COMPOUNDS FROM FUELS OXYGENATED WITH MTBE: CONCENTRATIONS AND MICROENVIRONMENTAL EXPOSURES IN AUTOMOBILE CABINS

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ACKNOWLEDGEMENTS

THE RESEARCH WAS SUPPORTED BY:
THE AMERICAN PETROLEUM INSTITUTE
WASHINGTON DC.

THE PROJECT DESIGN WAS DEVELOPED BY EOHSI/R.T.I. IN COLLABORATION WITH:
AN MTBE EXPOSURE WORKGROUP CONSISTING OF MEMBERS OF THE OIL/CHEMICAL INDUSTRIES AND GOVERNMENT

MTBE- OXYGENATED FUEL
MICROENVIRONMENTAL STUDY

HYPOTHESIS:

A MICROENVIRONMENT THAT CAN LEAD TO A RANGE OF EXPOSURES FROM EVAPORATION OF MTBE IN OXYGENATED GASOLINE IS THE AUTOMOBILE INTERIOR DURING PERIODS OF EXTENDED USE IN STOP/GO COMMUTER TRAFFIC AND ACTIVITIES SURROUNDING REFUELING.

MTBE- OXYGENATED FUEL
MICROENVIRONMENTAL STUDY

SPECIFIC AIMS:

A. TO QUANTIFY THE RANGE OF INTEGRATED CABIN CONCENTRATIONS AND MICROENVIRONMENTAL EXPOSURE TO MTBE FOR A REPETITIVE NUMBER OF TRIPS OVER A SPECIFIC COMMUTER ROUTE IN CENTRAL NEW JERSEY

B. TO QUANTIFY THE RANGE OF INTEGRATED CABIN CONCENTRATIONS AND MICROENVIRONMENTAL EXPOSURE TO MTBE FOR A REPETITIVE NUMBER OF TRIPS ON A SPECIFIC COMMUTER ROUTE IN FAIRFIELD COUNTY, CONNECTICUT

C. TO COMPARE THE BREATHING ZONE CONCENTRATION OF DRIVERS WHO RE-FILL THEIR GASOLINE TANK BY SELF-SERVICE vs. THE IN-CABIN MICROENVIRONMENTAL EXPOSURE DURING ATTENDANT ASSISTED REFUELING

MTBE- OXYGENATED FUEL
MICROENVIRONMENTAL STUDY

SPECIFIC AIMS:

D. TO DETERMINE THE INCREMENTAL CABIN CONCENTRATIONS AND MICROENVIRONMENTAL EXPOSURES OBTAINED DURING A COMMUTE DUE TO REFUELING OF THE AUTOMOBILE vs. THE GENERAL OPERATING CONDITIONS OF THE COMMUTE

E. TO COLLABORATE WITH INTERNATIONAL TECHNOLOGIES (IT) CORPORATION FOR THE INTERCOMPARISON OF SAMPLE/ANALYTICAL METHODOLOGIES IN THE COLLECTION AND ANALYSIS OF MTBE: SUMMA CANISTER, CARTRIDGE, CHARCOAL

MTBE- OXYGENATED FUEL

MICROENVIRONMENTAL STUDIES

-TYPES OF SAMPLING SITUATIONS EMPLOYED IN THE FIELD EXPERIMENTS

1. P.M. COMMUTE IN NEW JERSEY
2. A.M. COMMUTE IN NEW JERSEY
3. P.M. COMMUTE IN CONNECTICUT
4. A.M. COMMUTE IN CONNECTICUT
5. CONNECTICUT GAS FULL SERVICE
   - BEFORE
   - DURING ATTENDANT FILLING
   - AFTER
6. NEW JERSEY GAS FULL SERVICE
   - BEFORE
   - DURING ATTENDANT FILLING
   - AFTER
7. CONNECTICUT/NEW YORK SELF SERVICE
   - BEFORE
   - DURING FILLING
   - AFTER
8. CONNECTICUT
   - PRE+POST FULL SERVICE
   - PRE+POST SELF SERVICE

MTBE - OXYGENATED FUEL

MICROENVIRONMENTAL STUDY

- AUTOMOBILES USED IN STUDY
  1. COMMUTER ROUTES
     A. NEW JERSEY
        - 1987 CAPRICE
        - 1992 WHITE CORSICA
     B. CONNECTICUT
        - 1986 MONTE CARLO
        - 1992 GREY CORSICA

- GASOLINE FILL UP STUDIES
  1. FULL SERVICE
     - 1987 CAPRICE
     - 1992 WHITE, GREY CORSICA
     - 1986 MONTE CARLO
  2. SELF SERVICE
     - 1986 MONTE CARLO
     - 1992 GREY CORSICA

EPA EMISSIONS

TESTS FOR COMMUTER VEHICLES

COMPONENT	86 MONTE CARLO	87 CAPRICE	92 CORSICA #C0327W	92 CORSICA #C0563G
HC	0.82 g/mi	0.36 g/mi	0.08 g/mi	0.04 g/mi
NO_x	0.71	0.62	0.24	0.35
CO	29.29	1.54	3.90	1.05
CO_2	431.75	376.60	282.83	286.25
EVAP. (HOT SOAK)	3.63	25.55	0.08	0.16

CAR CHARACTERISTICS

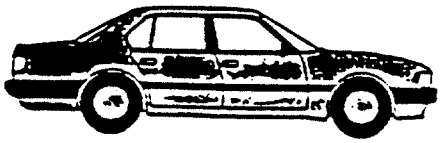
1. Monte Carlo
   5.0 L, V8 Engine - 4 Venturi Carb, Rear Wheel Drive

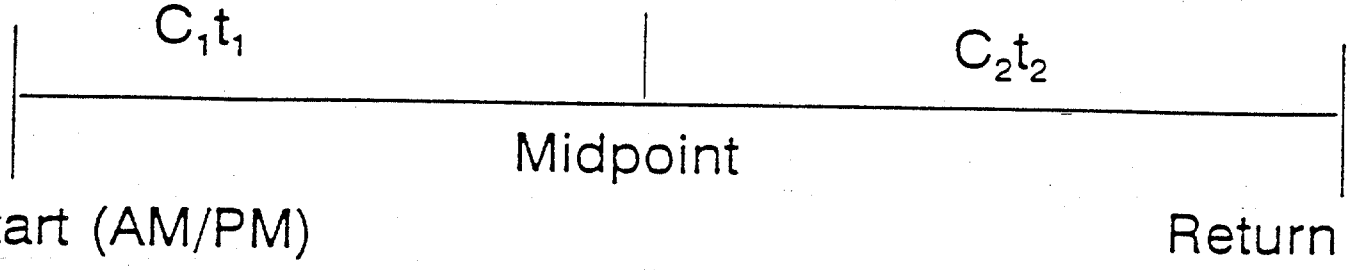
2. Caprice
   5.0 L, V8 Engine - 4 Venturi Carb, Rear Wheel Drive

3. Corsica (Both)
   3.1 L, V6 Engine - Multipoint Fuel Injection, Front Wheel Drive

Design of Automobile Commute and Gasoline Refill Experiments for MTBE Exposure

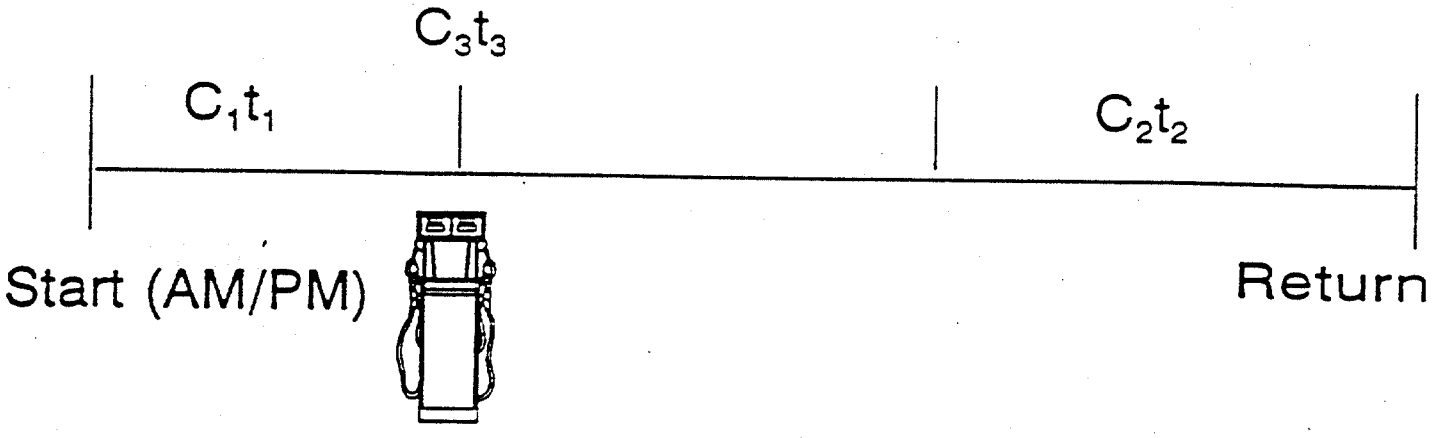
A. New Jersey/Connecticut Commuter Experiments (cm)
All Vehicles





$$E_{cm} = C_1t_1 + C_2t_2$$

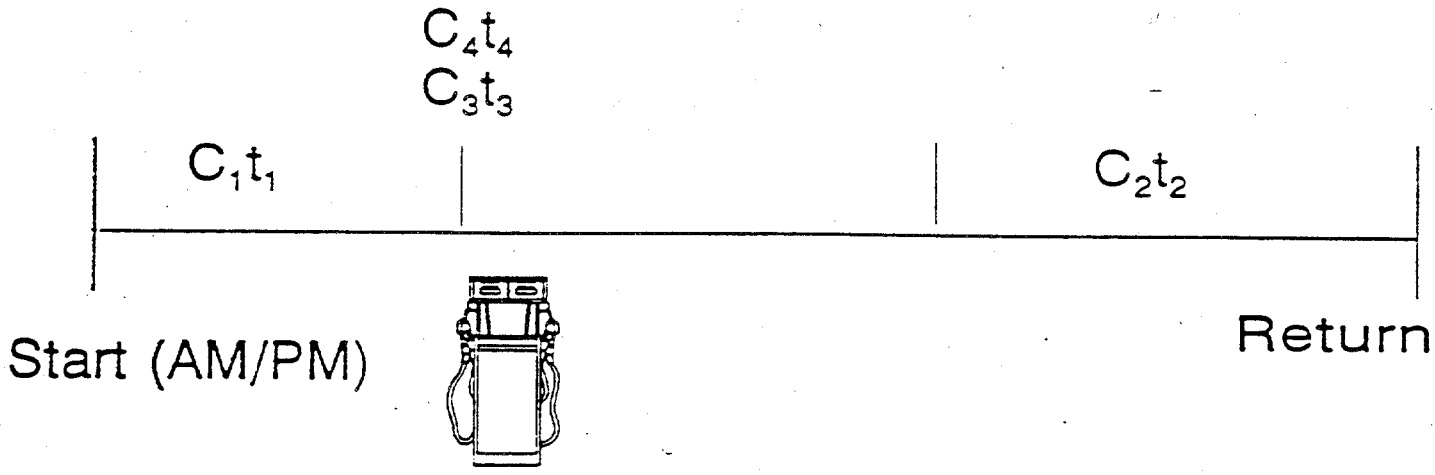
B. Gasoline Refuel Experiments - Attendent Service (GA)



$$E_{gA} = C_1t_1 + C_2t_2 + C_3t_3$$

Design of Automobile Commute and Gasoline Refill Experiments for MTBE Exposure

C. Gasoline Refuel Exeriments - Self Service (gs)



$$E_{gs} = C_1t_1 + C_2t_2 + C_4C_4 \text{ or } C_3t_3$$

Key:

C_i = Concentration in each portion of commute
t_i = Duration of exposure (samples) in each location
E_i = Microenvironmental Exposure
1 = Interior pre-gas or midpoint
2 = Interior post-gas or midpoint
3 = Interior during refuel
4 = Personal during refueling

CUMMULATIVE STREET TRAFFIC

FOR EACH GAS STATION STUDIED IN NY-NJ-CONN

STATE	# OF VEHICLES (8 HRS.)
NJ1	26040
NJ2	36360
NY4	15270
NY9	10410
NY10	15060
C3	12030
C5	8550
C6	11460
C7	12300
C8	13170

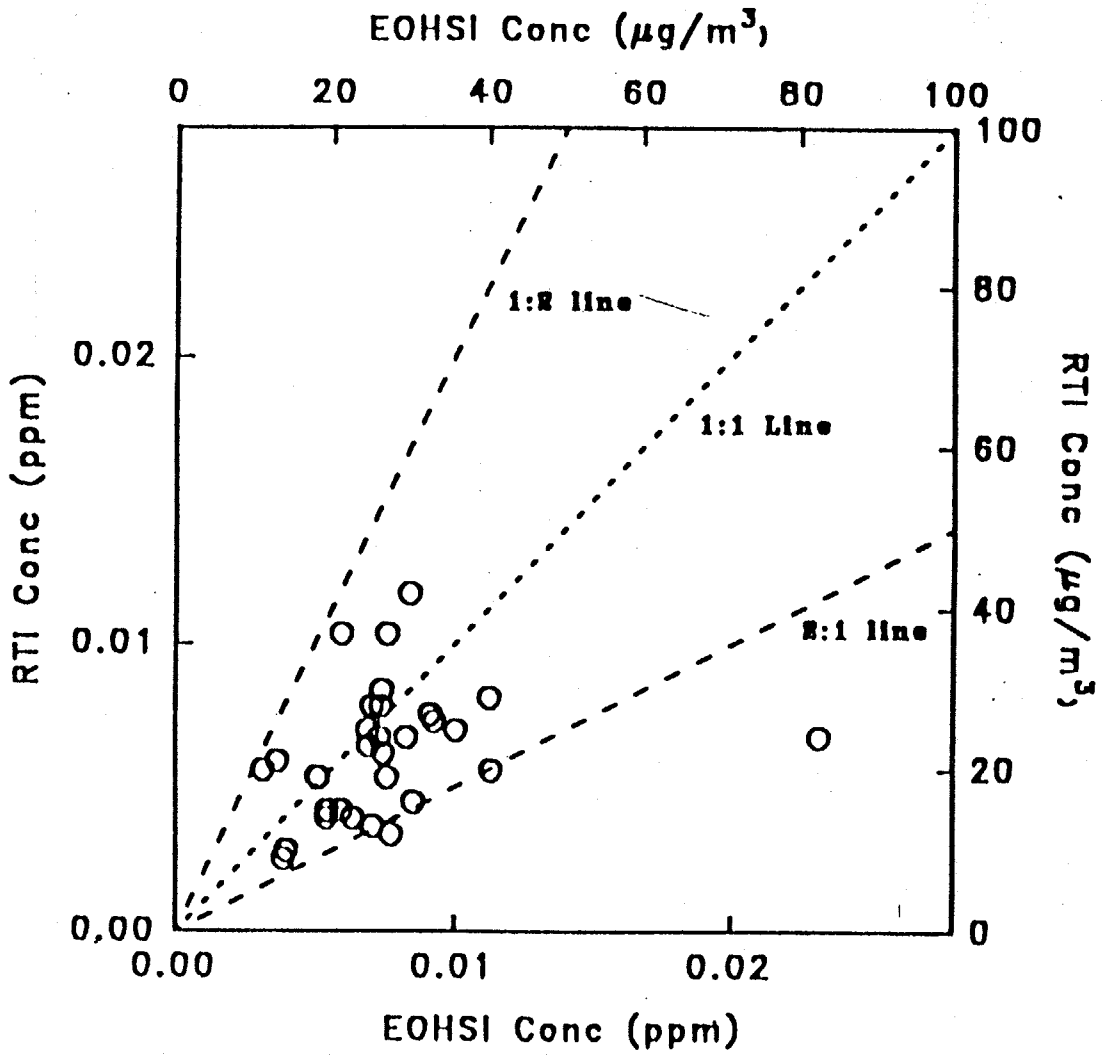
Source: API-IT

MTBE- OXYGENATED FUEL
MICROENVIRONMENTAL STUDY

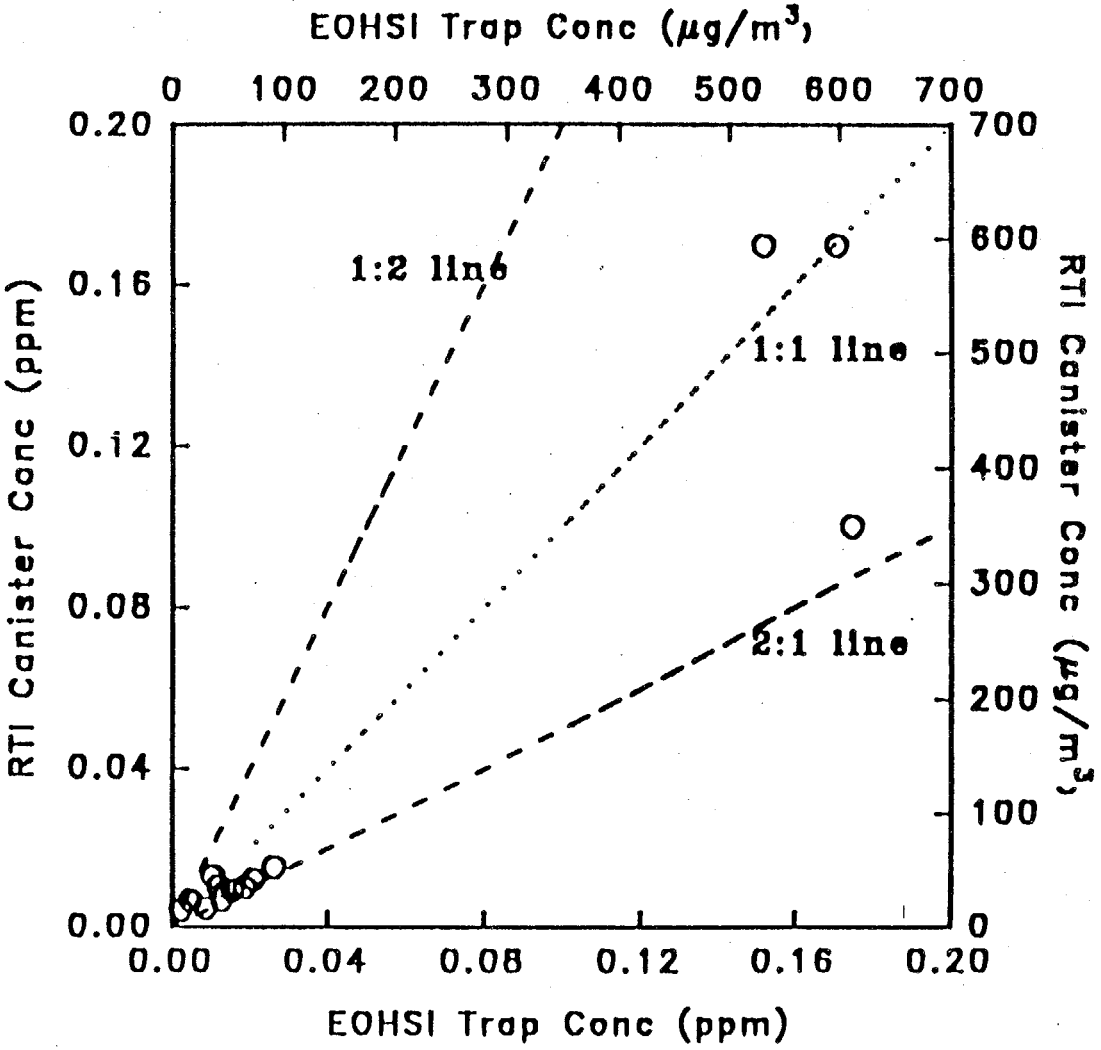
3. QUALITY ASSURANCE STUDIES

A. DUPLICATE SAMPLES
B. INTERCOMPARISON OF ANALYTICAL TECHNIQUES
C. INTERCOMPARISON OF SAMPLING TECHNIQUES- CANISTERS/CARTRIDGES
D. REPLICATE ANALYSIS
E. REPLICATE ANALYSES BETWEEN LABORATORIES
F. QUALITY CONTROL SAMPLES
G. FIELD AUDITS

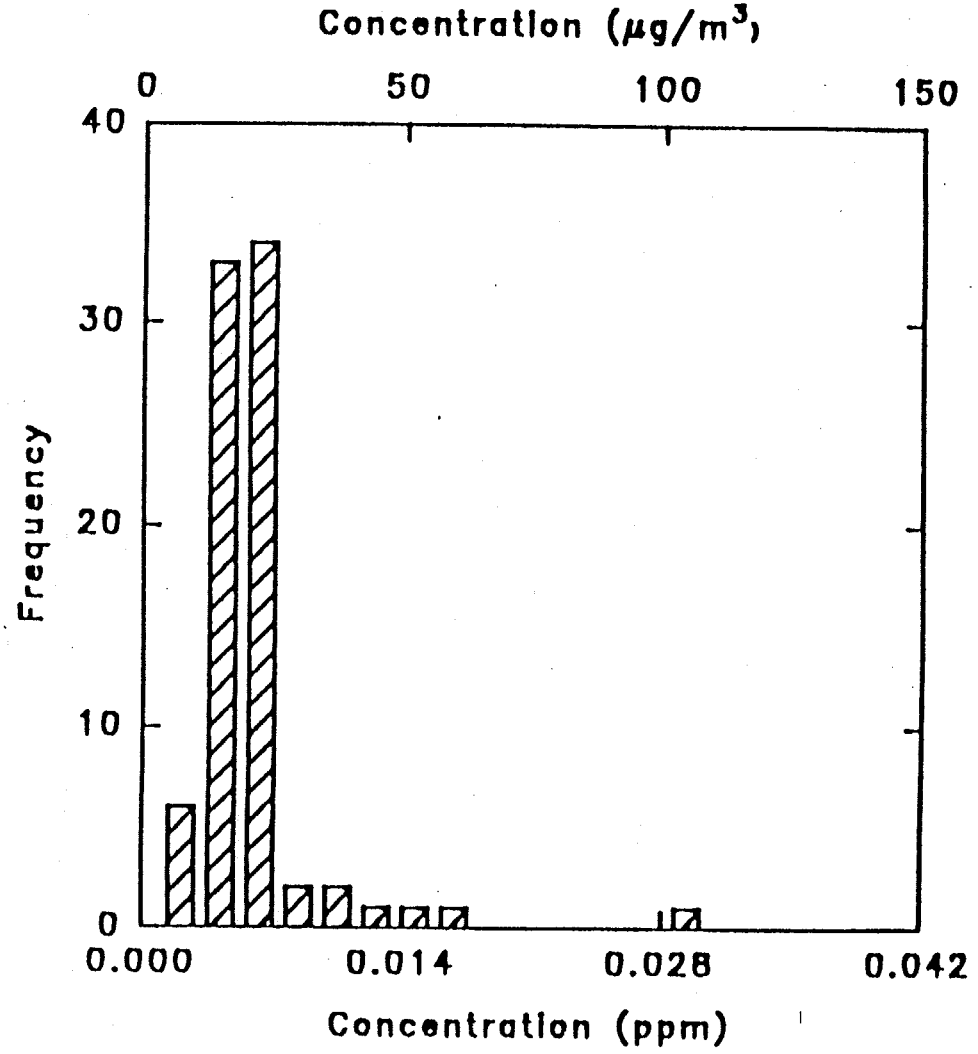
RTI Canister Comparison to EOHSI Adsorbent For Commuting Samples



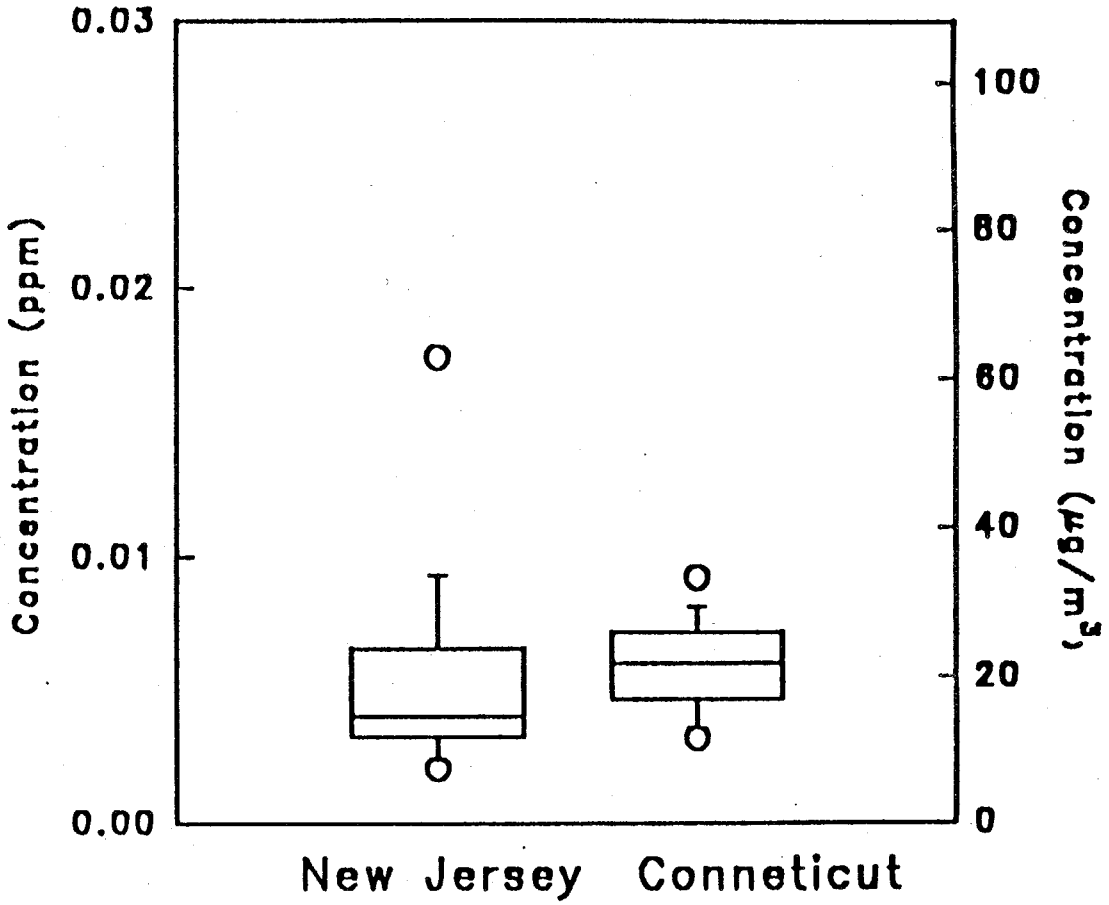
RTI Canister Transferred to EOHSI Traps Comparison for MTBE



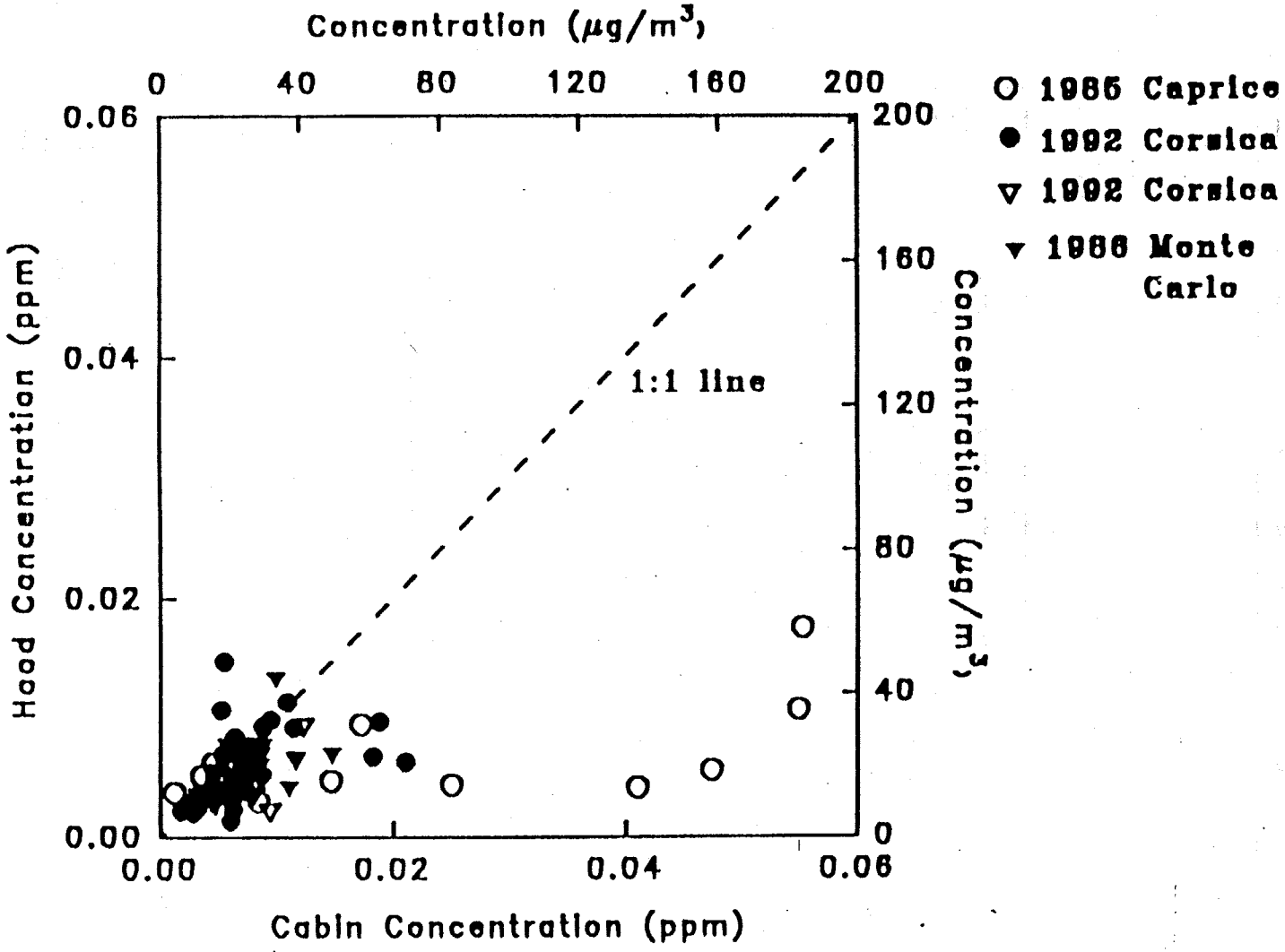
MTBE Frequency Distribution of Commuter Runs



MTBE Concentrations During Commuter Runs



MTBE Concentrations
Cabin vs Hood



Commuter Study
Hood-Cabin
MTBE - PPM

Sample	No. Values	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Hood	104	0.0013	0.090	0.0051	0.0051	1.7
Cabin	156	0.0012	0.16	0.0068	0.0082	2.4

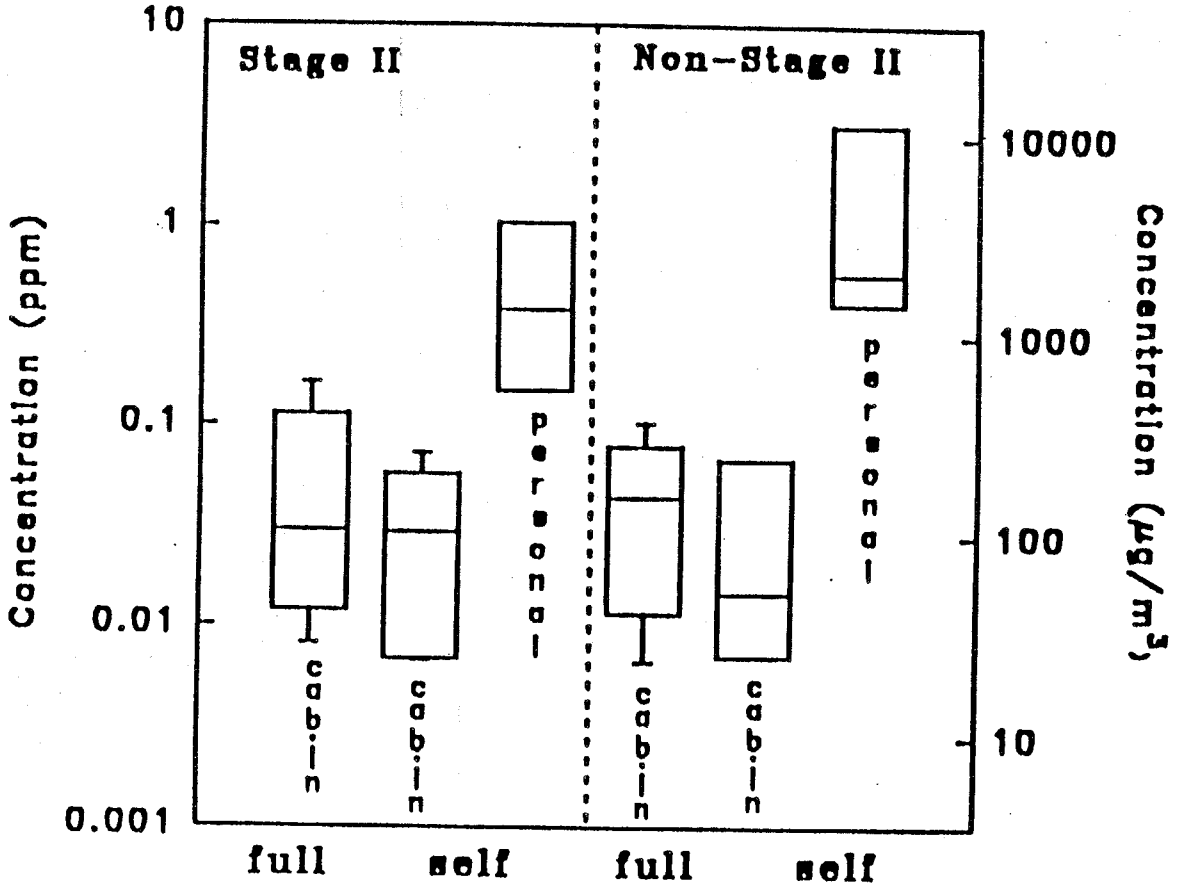
WINTER, 1992-1993

MTBE COMMUTER EXPERIMENTS

DATE	TYPE OF SAMPLE	MTBE ug/m3	MTBE ppm
12/7/92	INTERIOR	70	0.020
12/7/92	HOOD	75	0.021
12/7/92	INTERIOR	360	0.102
12/7/92	HOOD	1000	0.282
12/15/92	INTERIOR	520	0.147
12/15/92	HOOD	213	0.060
12/15/92	INTERIOR	228	0.064
12/15/92	HOOD	142	0.040
12/15/92	INTERIOR	458	0.129
12/15/92	HOOD	279	0.079
12/15/92	INTERIOR	280	0.079
12/15/92	HOOD	189	0.059
12/24/92	INTERIOR	160	0.045
12/24/92	HOOD	139	0.039

USING A 1985 PLYMOUTH

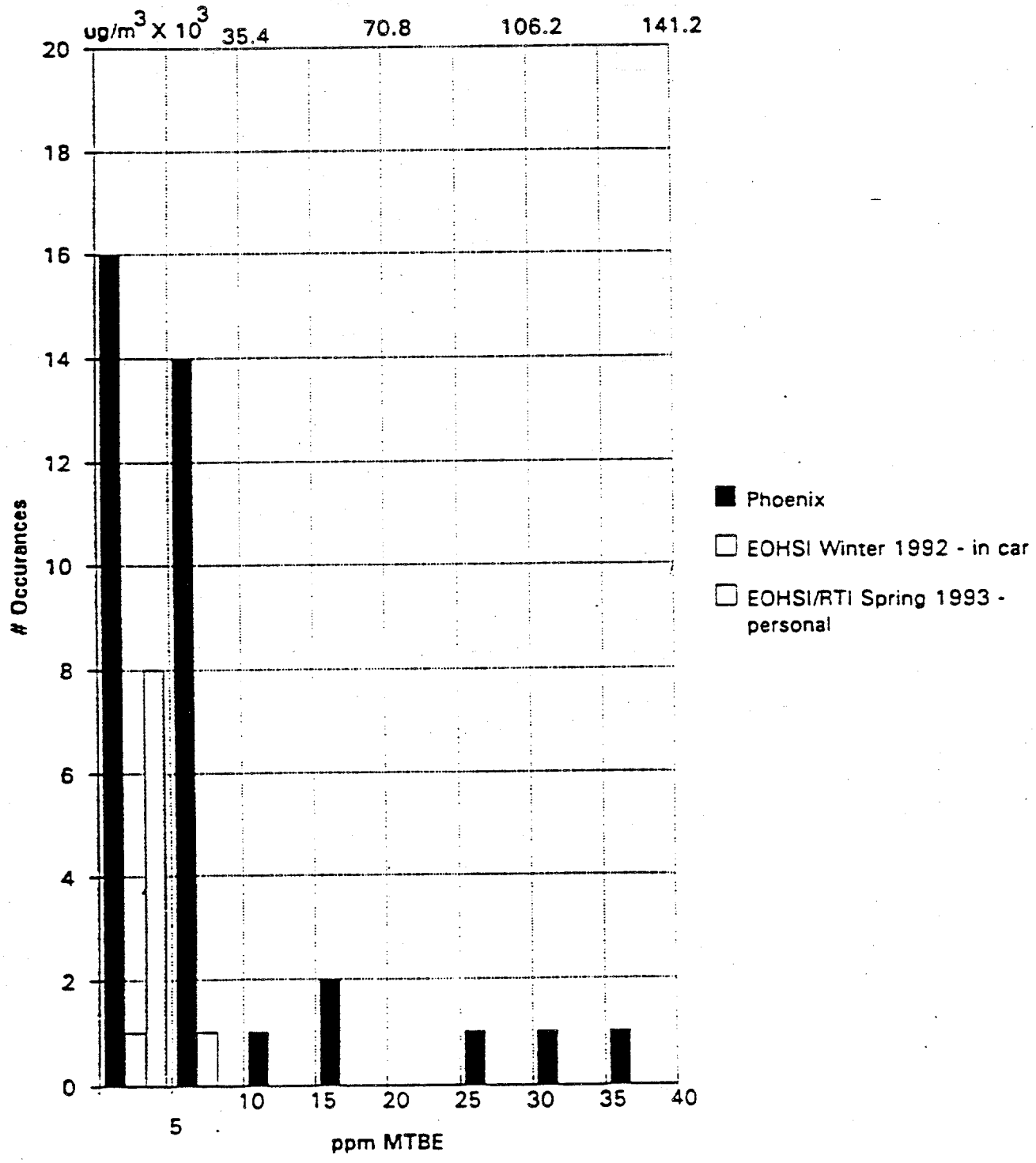
Microenvironmental/Personal Exposure During Refueling Studies NJ/NY/CT



Commuter Study
Personal
MTBE - PPM

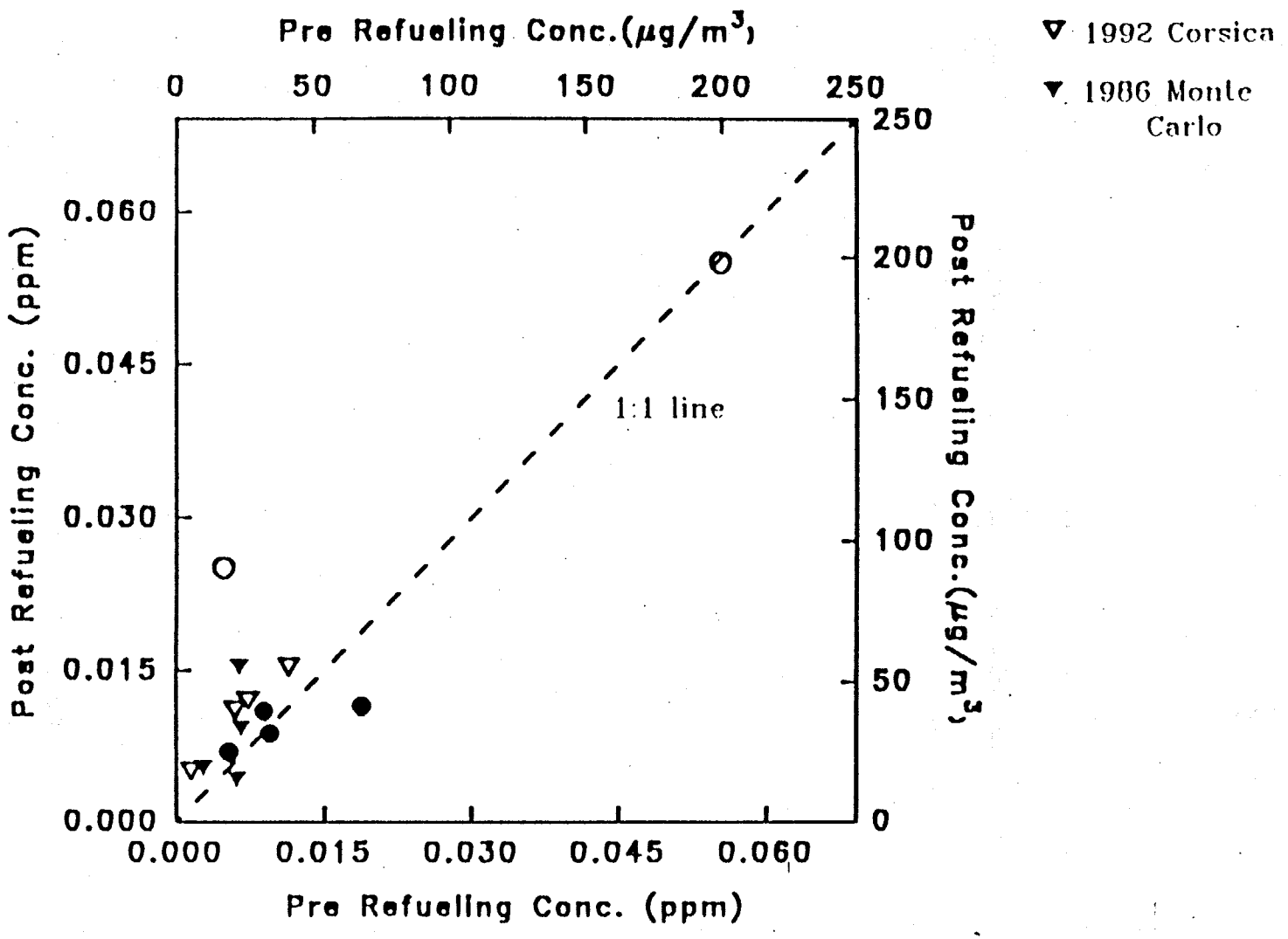
Sample	No. Values	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Stage II Self-Serv.	3	0.35	4.1	0.57	0.93	3.7
NonStage Self-Serv.	4	0.13	1.5	0.38	0.37	3.1

CUSTOMER EXPOSURE DATA TO GASOLINE WITH 12-13% MTBE IN PHOENIX, AZ, 1990



Source: API, Clayton Environ., July 1991

MTBE Concentration Before and After Refueling



Commuter Study
Refueled Runs
MTBE - PPM

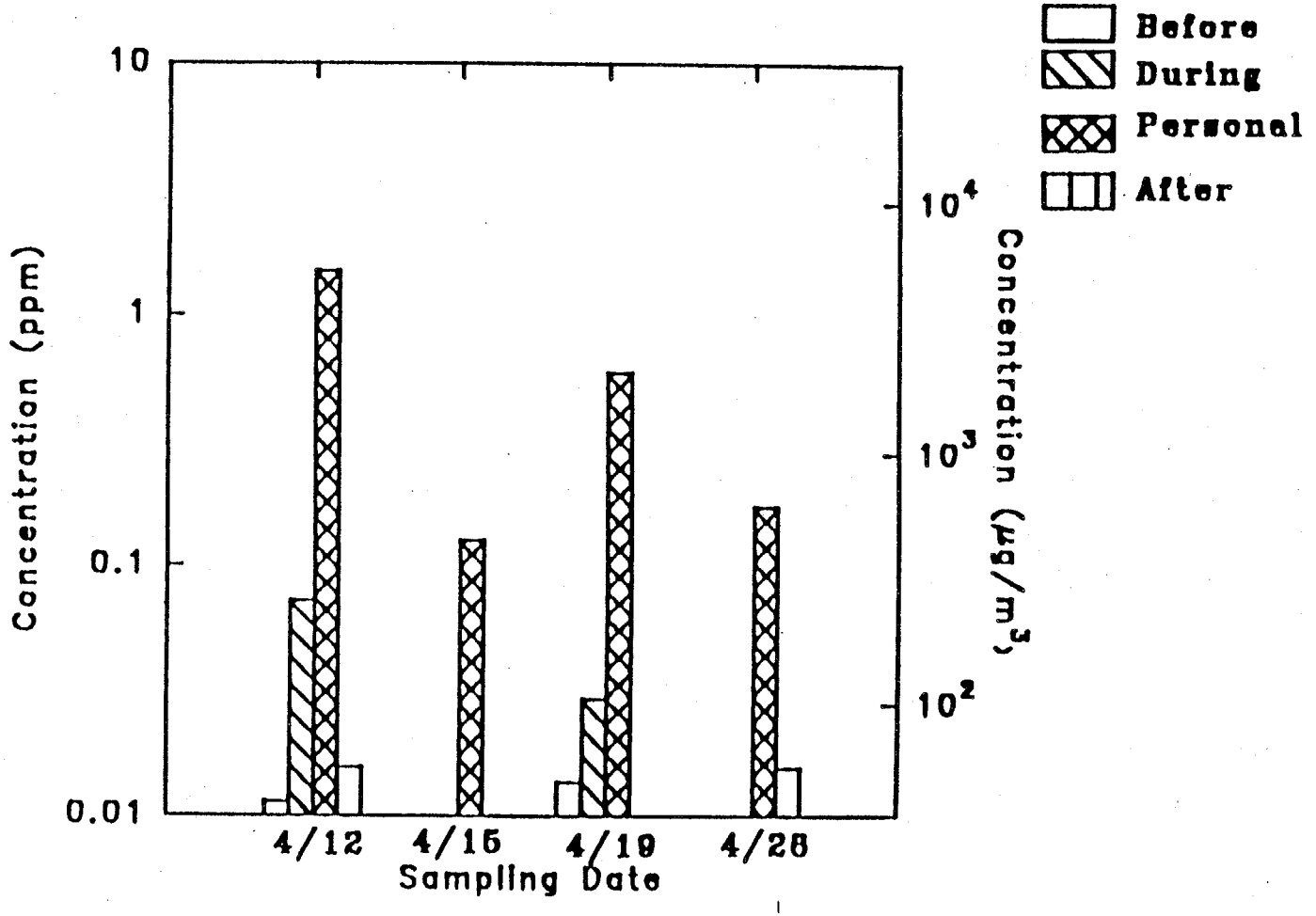
Sample	No. Values	Min.	Max.	Median	Geometric Mean	Geometric Std. Dev.
Before Refuel	27	0.0015	0.090	0.0069	0.0082	2.2
During Refuel(Cab.)	22	0.0033	0.16	0.026	0.026	3.2
After Refuel	27	0.0039	0.055	0.0090	0.0092	1.9

WINTER 1992-1993

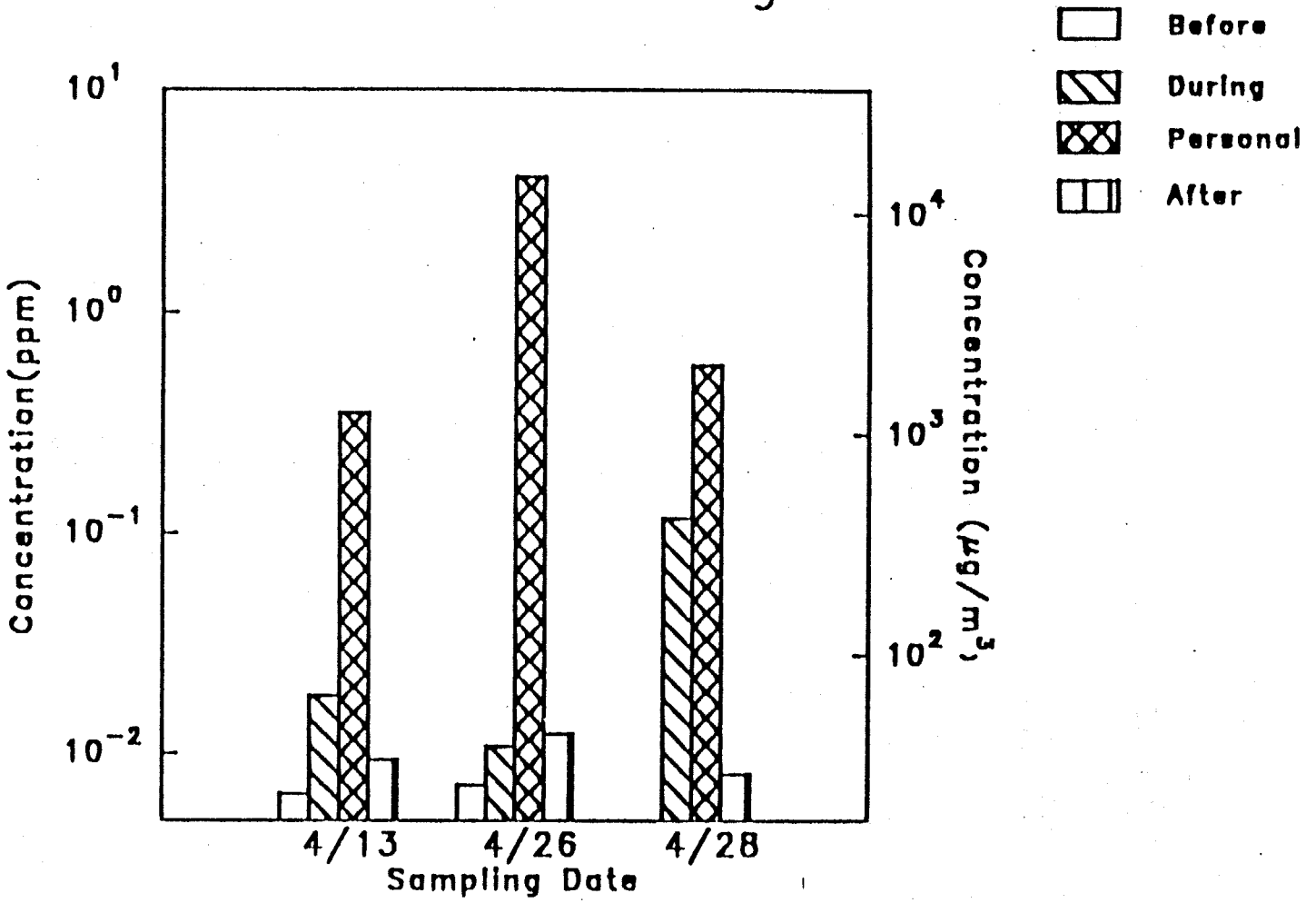
MTBE GASOLINE REFUELING

DATE	TYPE OF SAMPLE	MTBE $\mu g/m^3$	MTBE ppm
1/4/93	PRE-FILLUP	38	0.011
	INTERIOR-DURING FILLUP	21000	5.90
	POST-FILLUP	4600	1.30
1/20/93	PRE-FILLUP	88	0.025
	INTERIOR-DURING FILLUP	2600	0.621
	POST-FILLUP	1150	0.325

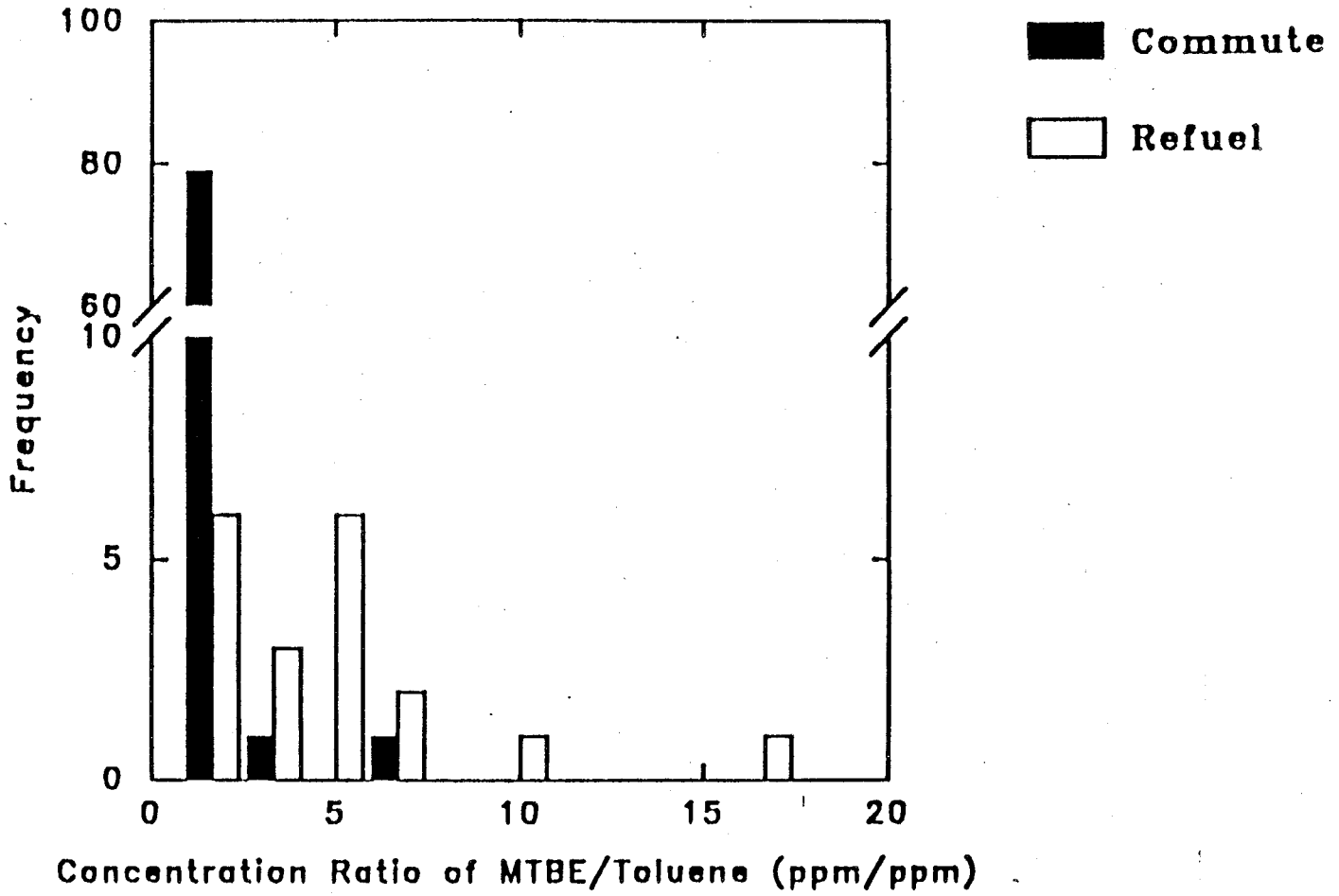
Log MTBE Concentration for CT refueling



Log MTBE Concentration for NY refueling



Frequency Distribution of MTBE to Toluene Concentration Ratio



Preliminary Conclusions & Recommendations

- MTBE was found within the automobile microenvironment at ppb ($\mu g/m^3$) levels during a I hour commute.

- Personal MTBE measurements were found to be at the ppm (mg/m^3) levels during a 5 minute self-service gasoline refueling cycle.

- The 1 hour cabin MTBE levels during a commute exceeded those of roadway air (hood samples) suggesting some retention or evaporation of MTBE into the vehicle.

Preliminary Conclusions & Recommendations

(Continuation)

- The higher levels of MTBE were predominantly found within an automobile that had higher volatilization of VOC from its gasoline tank. This observation should be studied for a larger fleet of these types of vehicles to determine the nature of high-end exposures.

- The in-vehicle MTBE concentrations measured in New Jersey in the Spring, 1993 were generally lower than found in the Winter 1992-1993 experiments. This comparison is not equivalent because the RVP was approximately 20% - 25% lower in the spring and different vehicles were used in each experiment.

- The personal exposures measured in the EOHSI/RTI study were within the range of values measured in Phoenix, Arizona in 1990.

AUTHOR(S): Alan H. Huber

TITLE: HUMAN EXPOSURE ESTIMATES OF METHYL TERTIARY BUTYL ETHER (MTBE)

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 refueling 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 because human exposures are greatest when one is near evaporative emissions. Thus, exposures are greatest when handling gasoline. Figures 2-13 summarize 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 (two stations with full service and phase II vapor recovery), Westchester County, NY (three stations with self service and phase II vapor recovery) and Fairfield County, CT (five 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 Environmental and Occupational Health Sciences Institute (EOHSI)/Research Triangle Institute (RTI) study (Lioy et al., 1993) at the same ten gas stations. All concentrations for the IT study, even those in the intermittent breathing zone, were a 4-hour continuous sample. Because the breathing zone collection was videotaped, 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 National Institute for Occupational Safety and Health (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 refueling period. In the Clayton study, mean MTBE concentrations in the breathing zone for 12-13% 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 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 refueling 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-minute commute and during refueling 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 refueling. The driver's window was completely open during the refueling. The average time to complete a fill-up was about 2 minutes, while the total time at the gas station was approximately 5-10 minutes. 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. Concentrations 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°F. A multi-zonal 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 because 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. Commuting and gasoline refueling environments are clearly the most important, unless one has significant evaporative emissions in the residential garage. The annual estimate uses the Figure 25 values for the 4-month MTBE season and assumes that MTBE concentrations are 10% 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 is difficult to estimate MTBE levels during the non-oxyfuel season because 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), and Kenneth Knapp and Roy Zweidinger (EPA) to share their data files as the data are preliminarily processed. The presented analyses were 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.

National Institute for Occupational Safety and Health (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

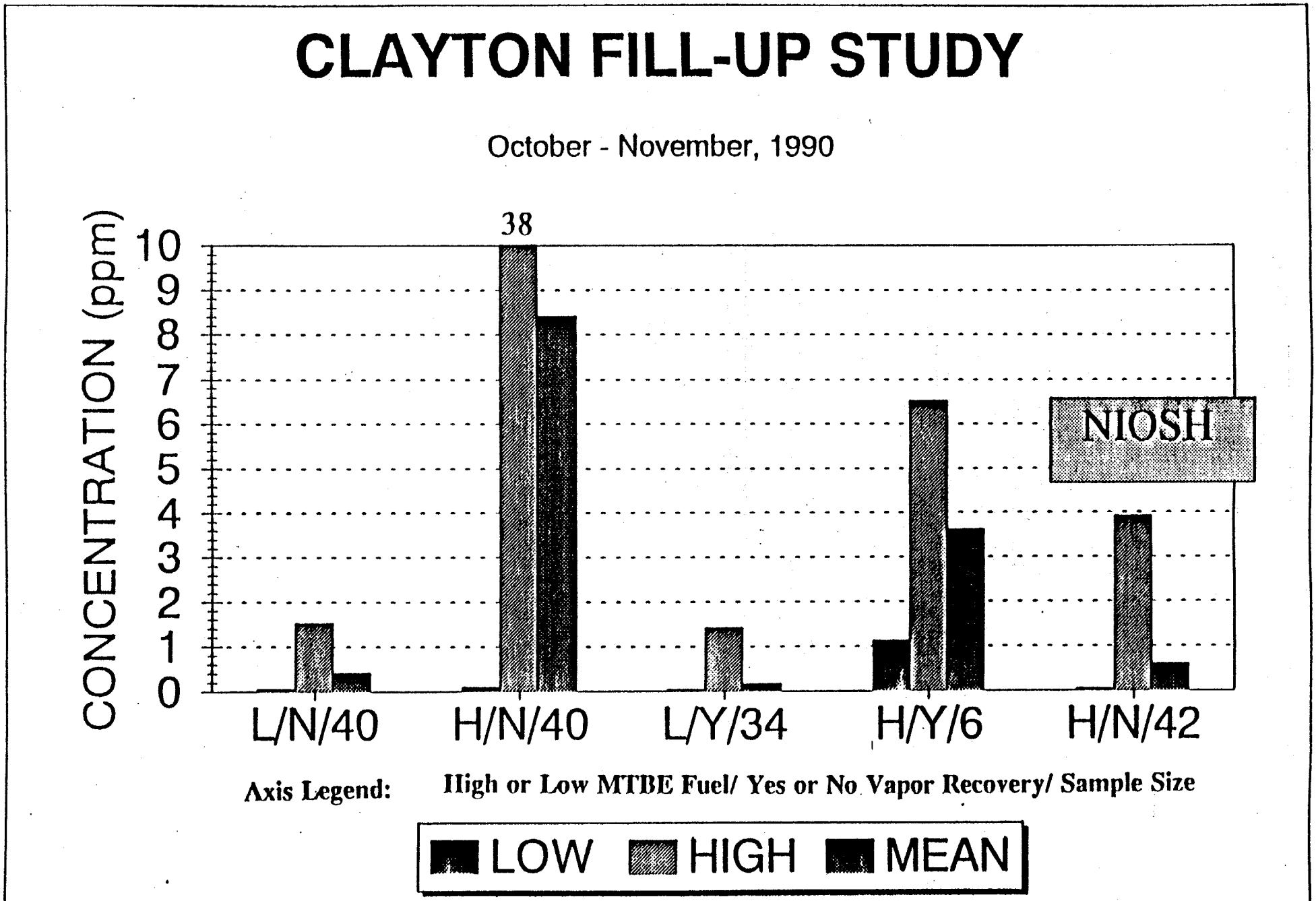
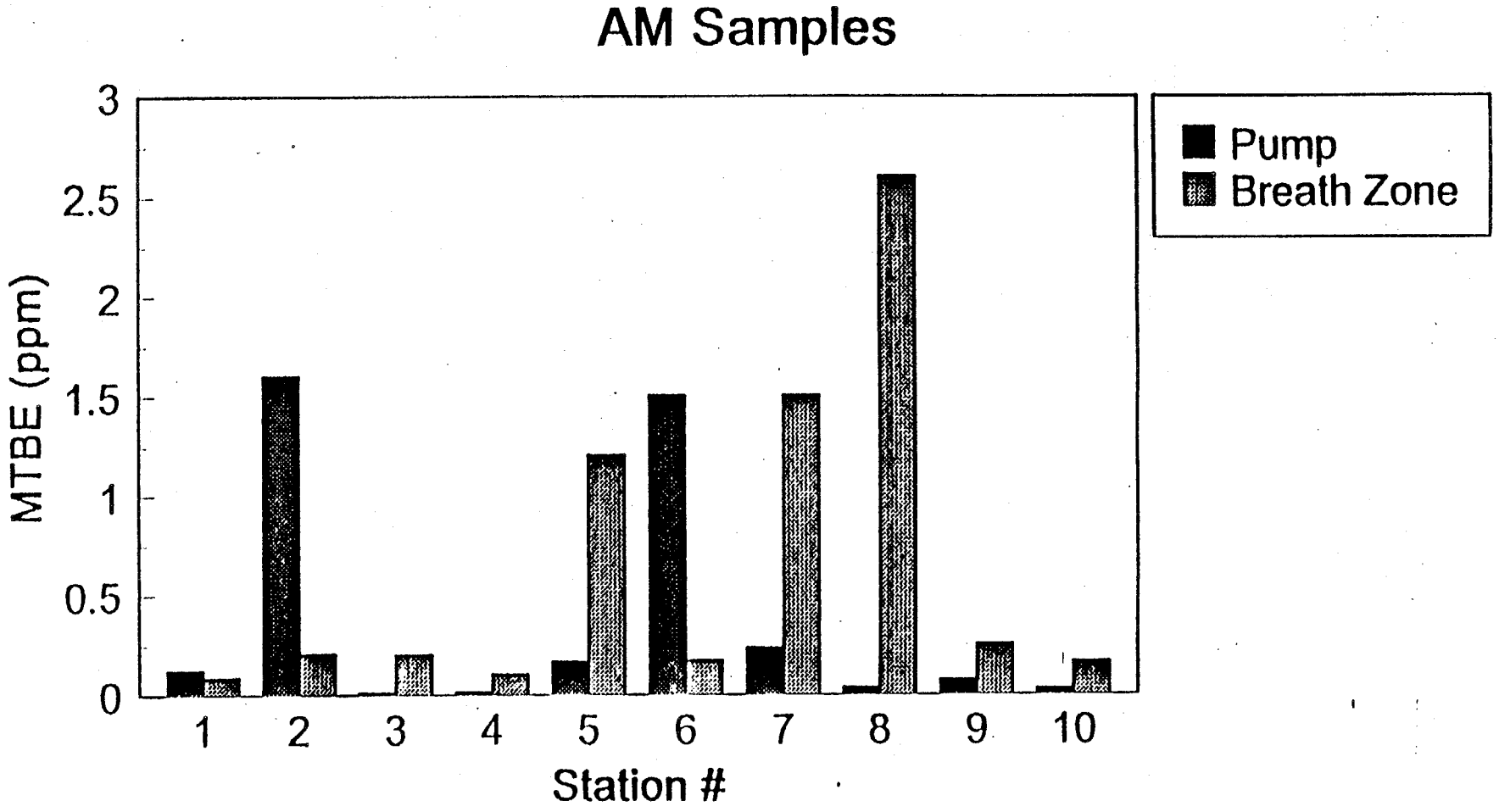

CLAYTON FILL-UP STUDY
October - November, 1990
CONCENTRATION (ppm)
10
9
8
7
6
5
4
3
2
1
0
38
NIOSH
L/N/40
H/N/40
L/Y/34
H/Y/6
H/N/42
Axis Legend:
High or Low MTBE Fuel/ Yes or No Vapor Recovery/ Sample Size
LOW
HIGH
MEAN

Figure 2

Fill-up Stations Data

ITC



4 hr., AM sample

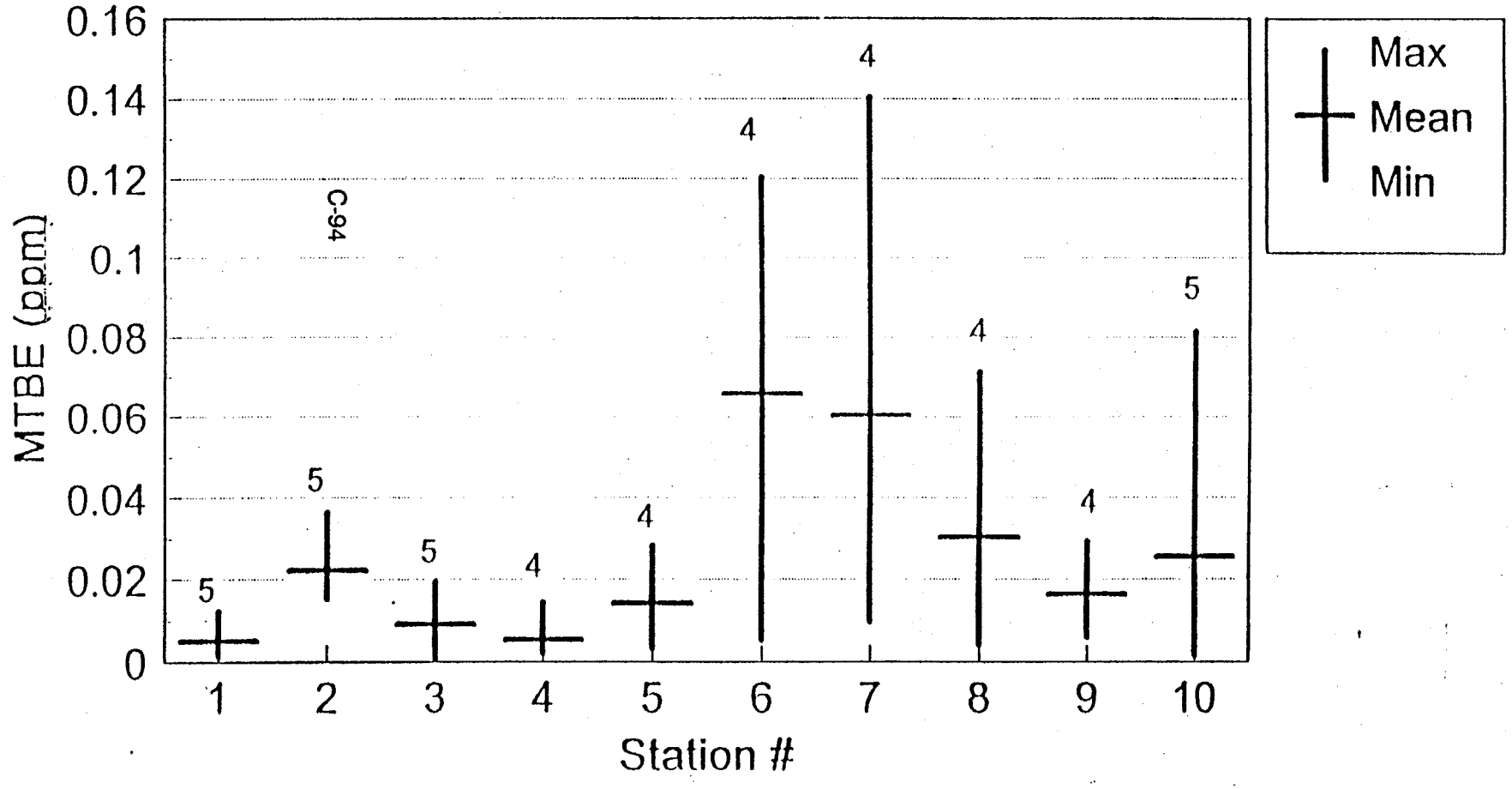
Figure 3

Fill-up Stations Data

fence-line locations

ITC

4 hr., AM Sample



C-94

Locations 1, 2, 3, & 4, combined

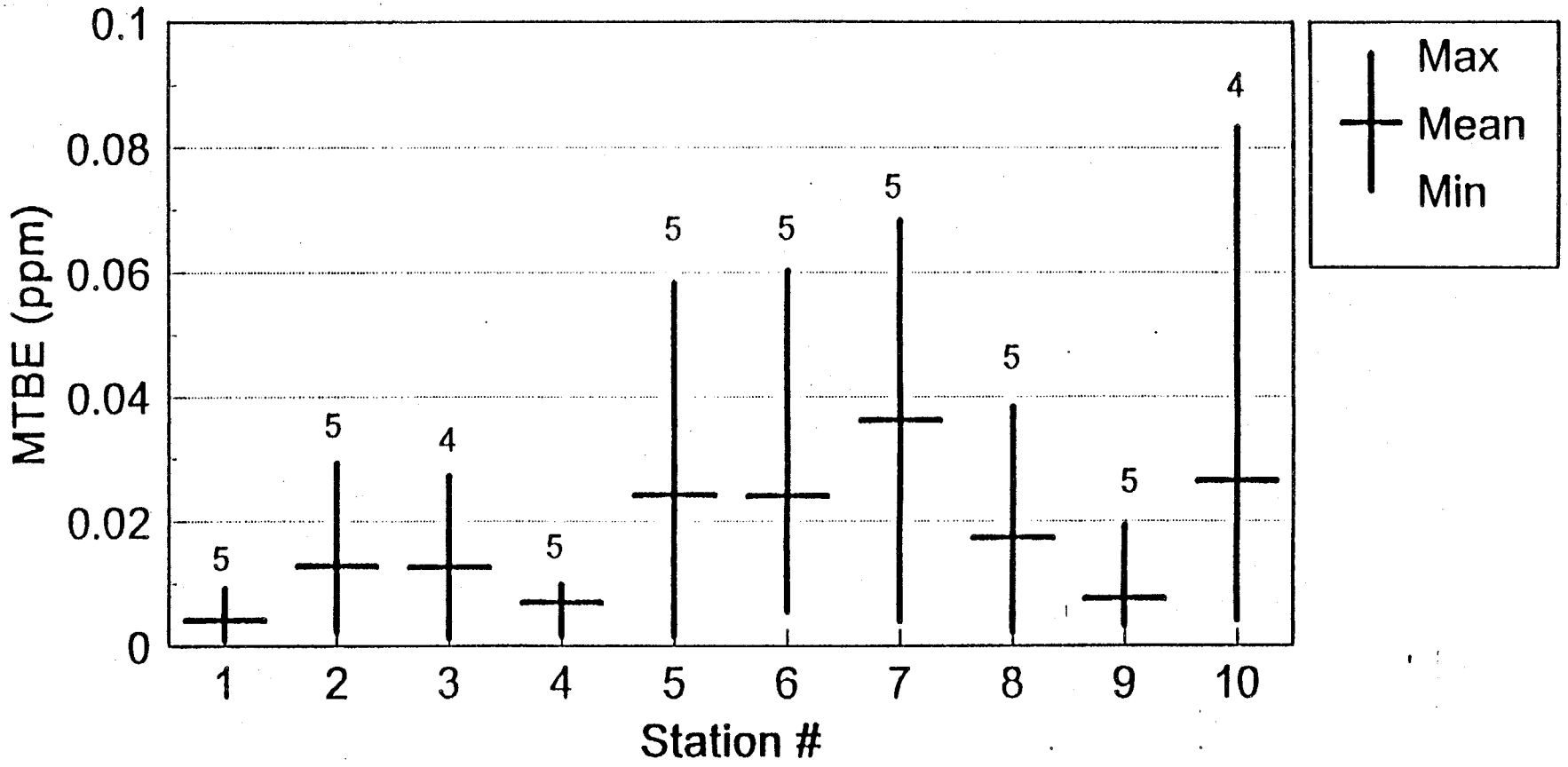
Figure 5

Fill-up Stations Data

fence-line locations

ITC

4 hr., PM Sample



Locations 1, 2, 3, & 4, combined

Figure 6

In-Cabin Concentrations During Refueling
1985 Caprice

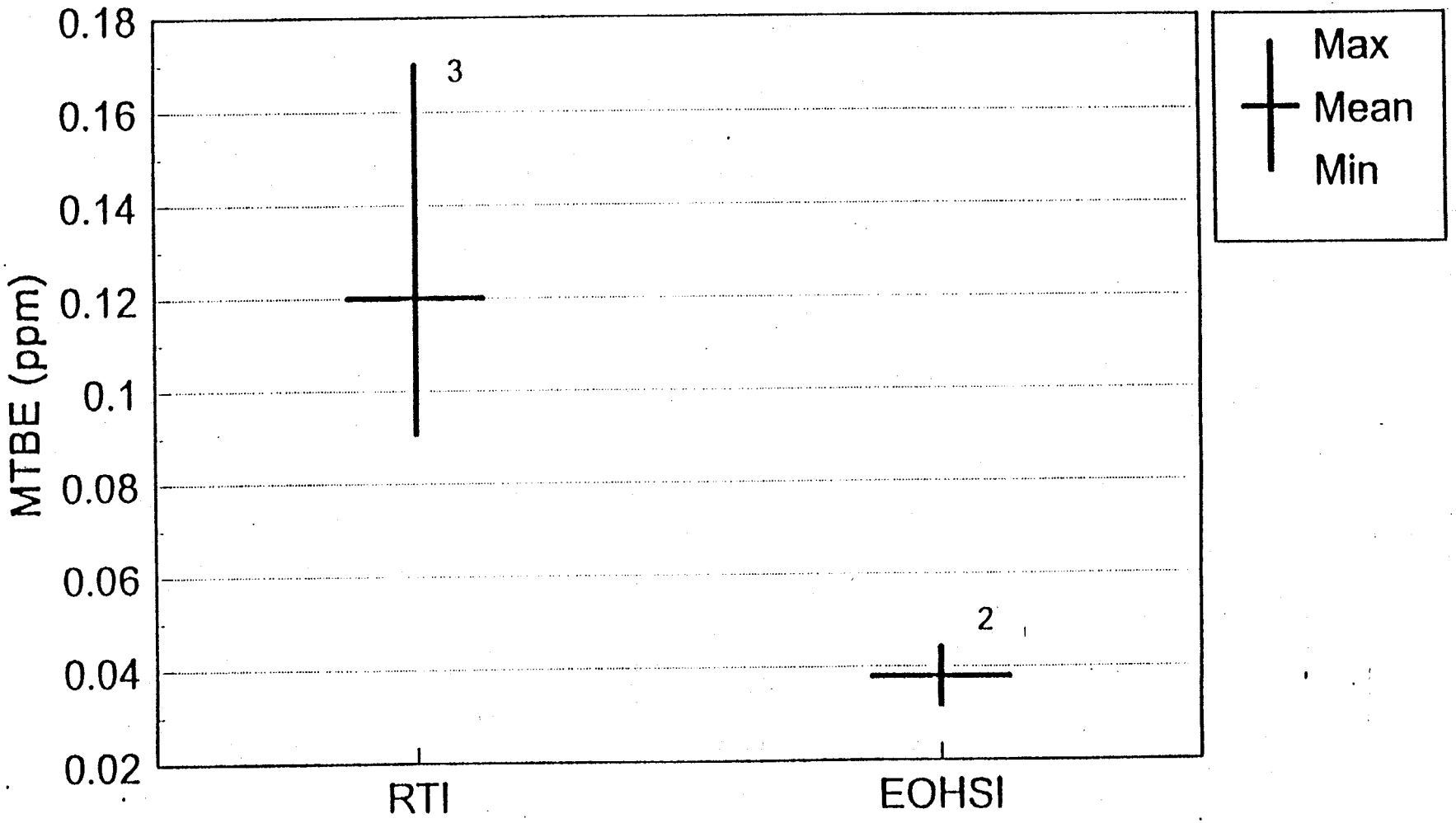


Figure 7

Group 7; NJ during fillup

In-Cabin Concentrations During Refueling
1986 Monte Carlo

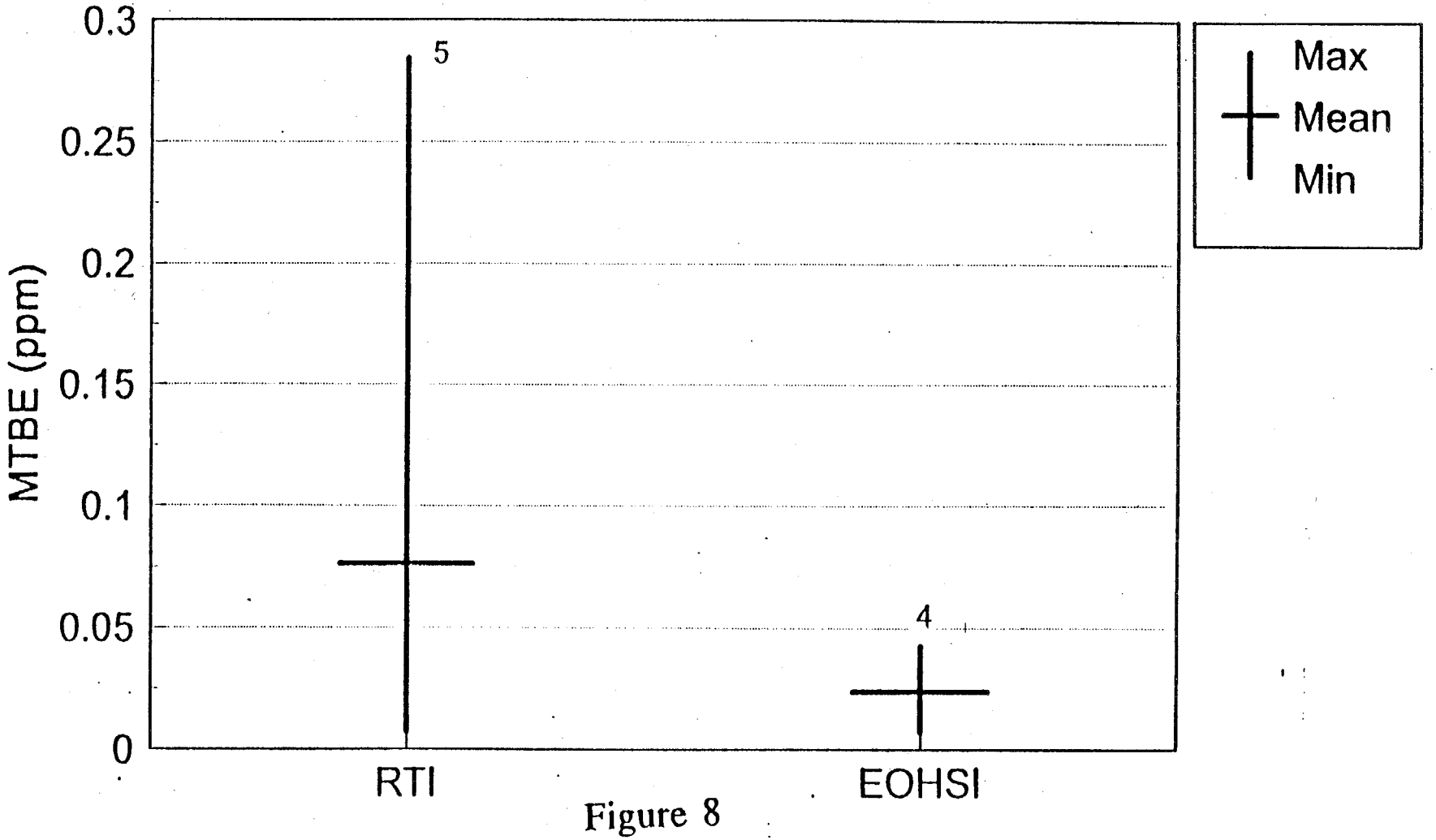


Figure 8

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

In-Cabin Concentrations During Refueling
1992 Corsica (W)

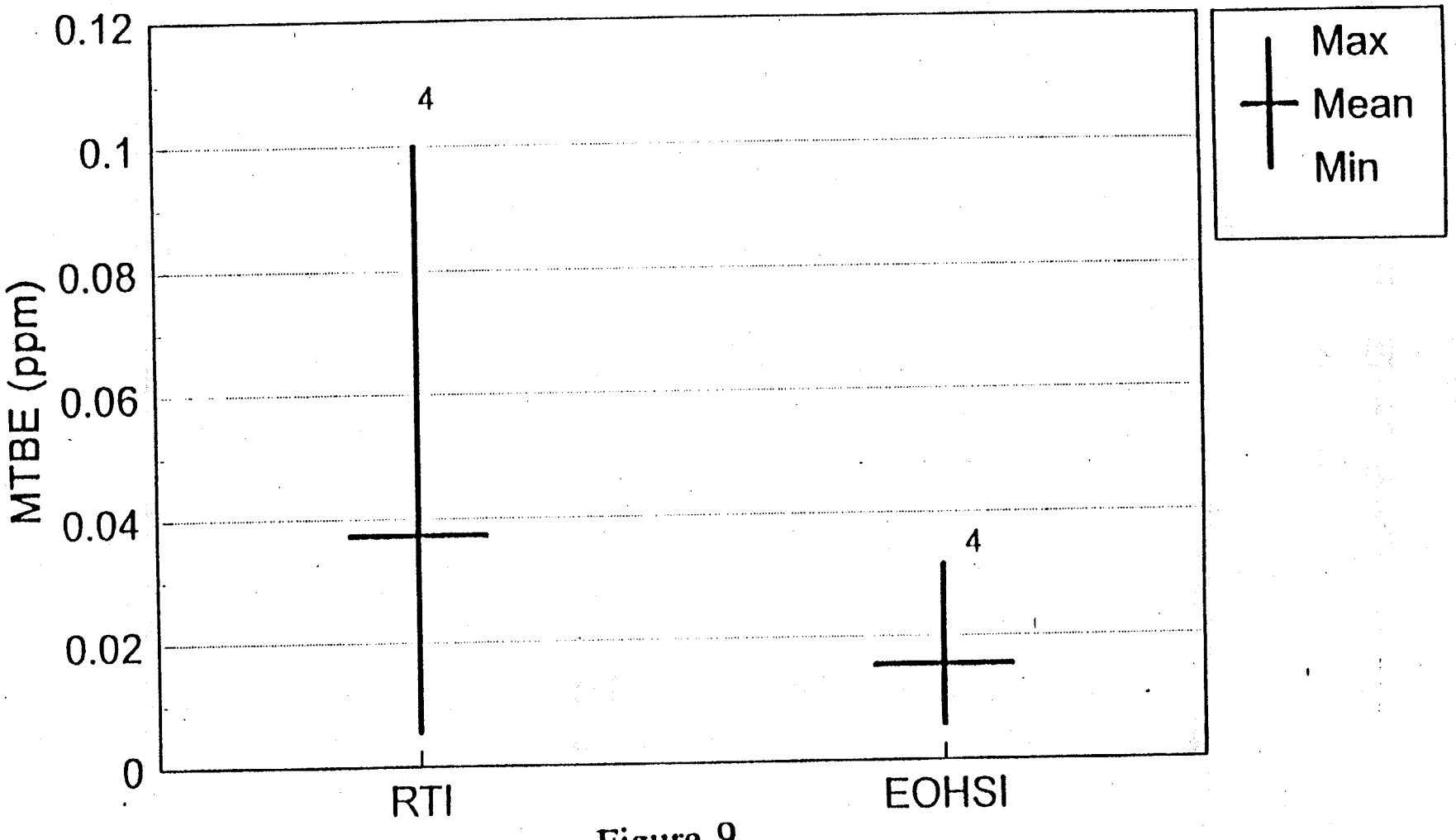


Figure 9

Group 7: N L during fillup

In-Cabin Concentrations During Refueling
1992 Corsica (G)

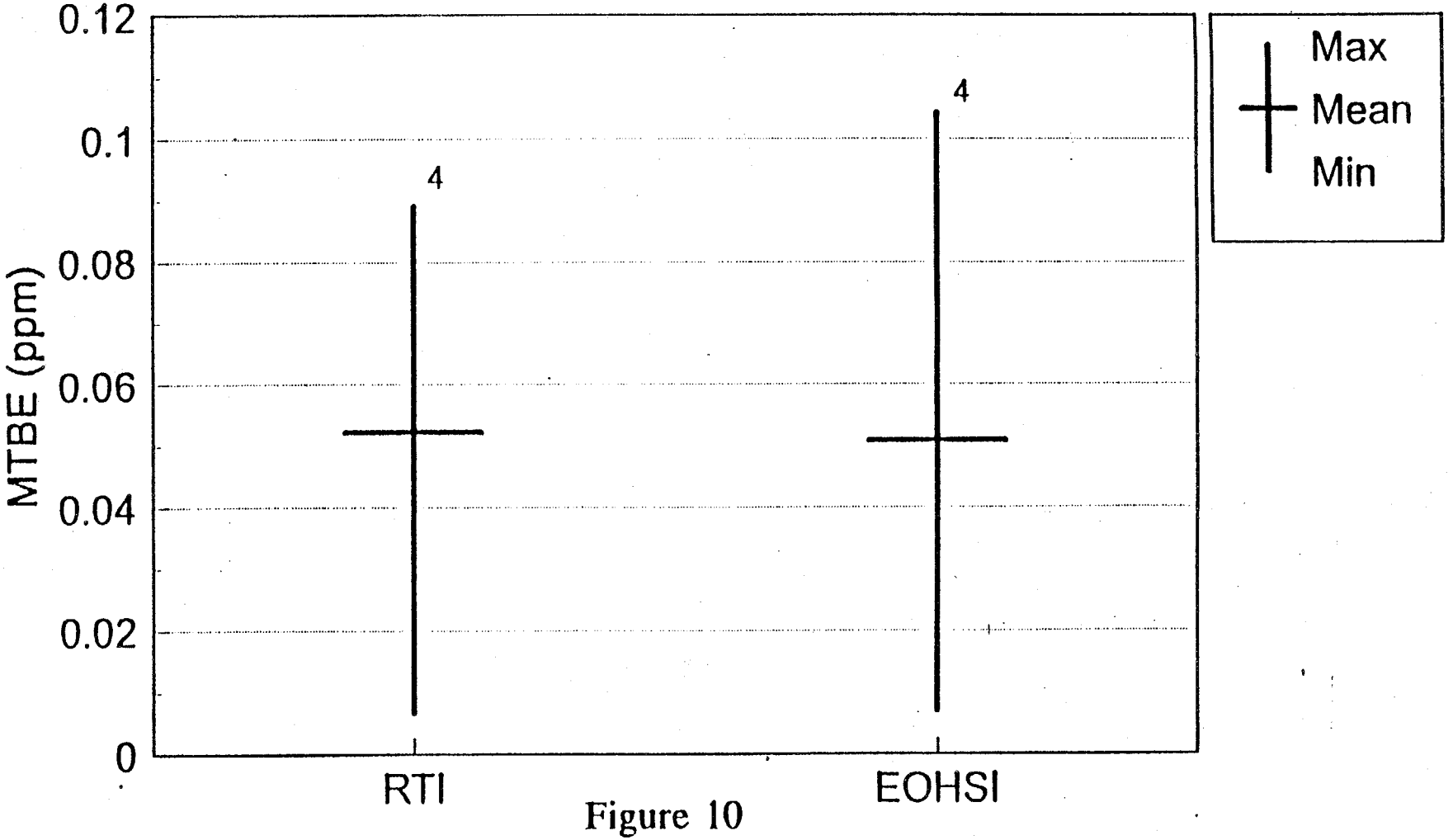


Figure 10

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

In-Cabin Commuting Concentrations
1985 Caprice

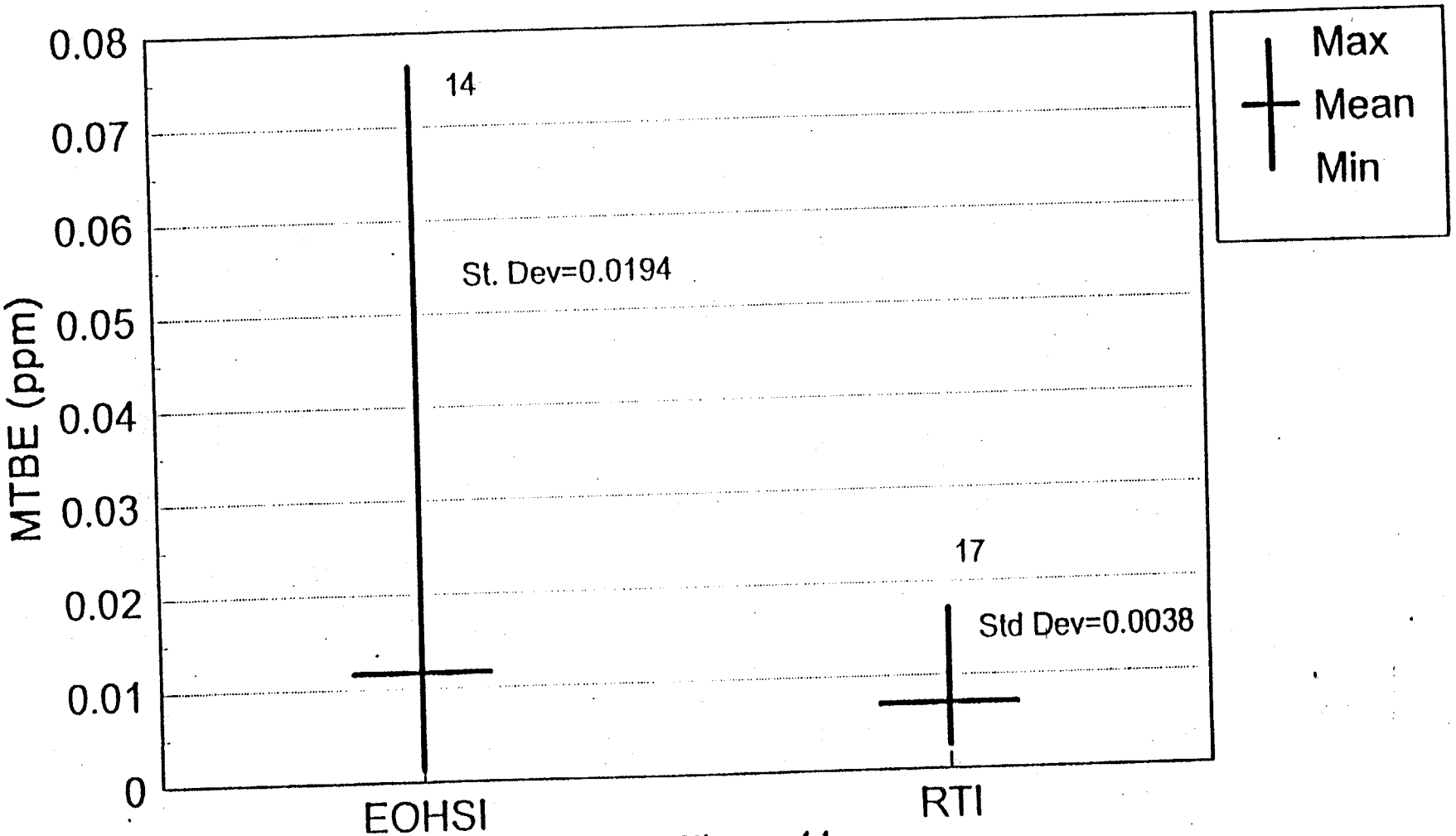


Figure 11

In-Cabin Commuting Concentrations
1986 Monte Carlo

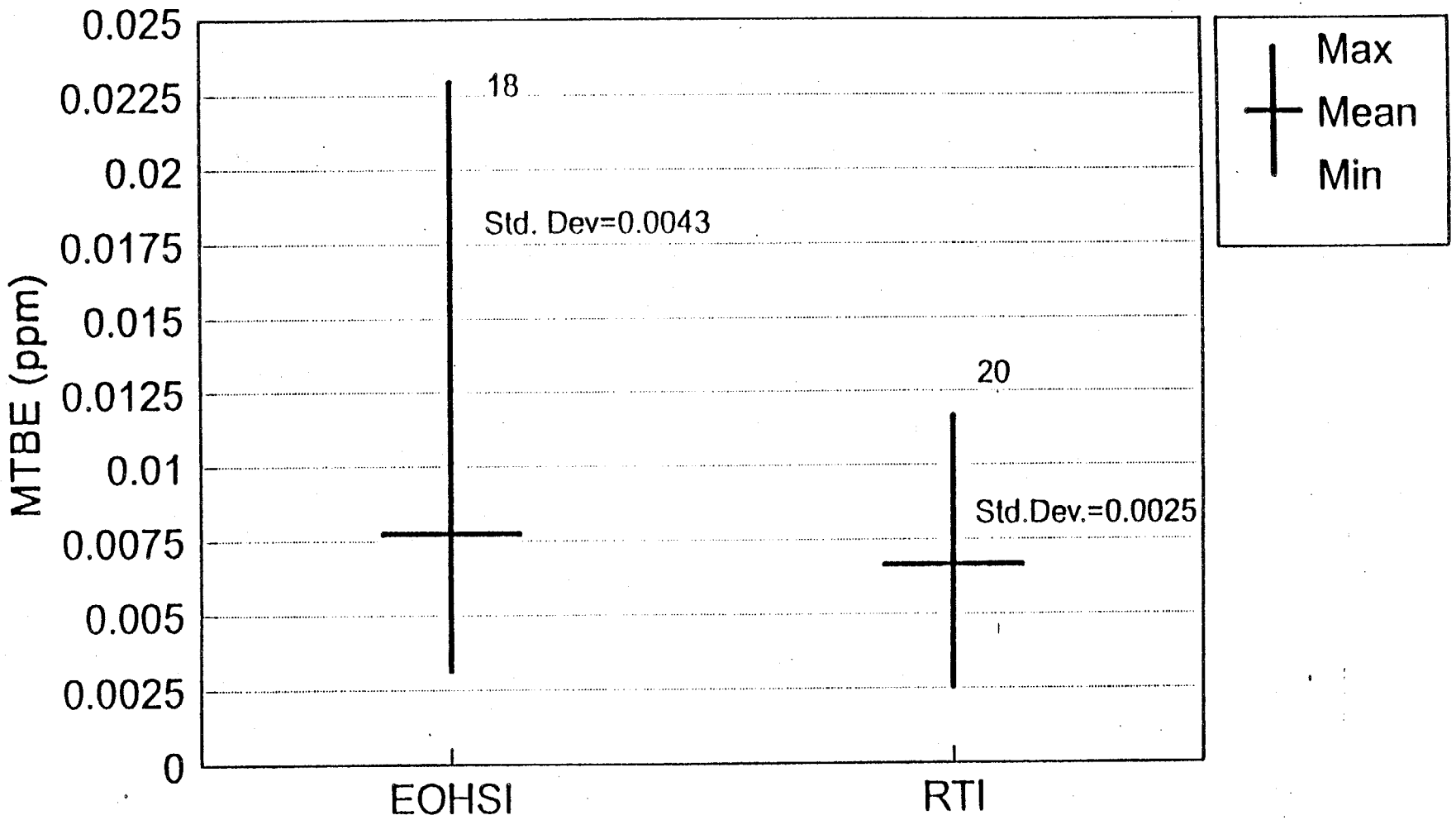


Figure 12

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

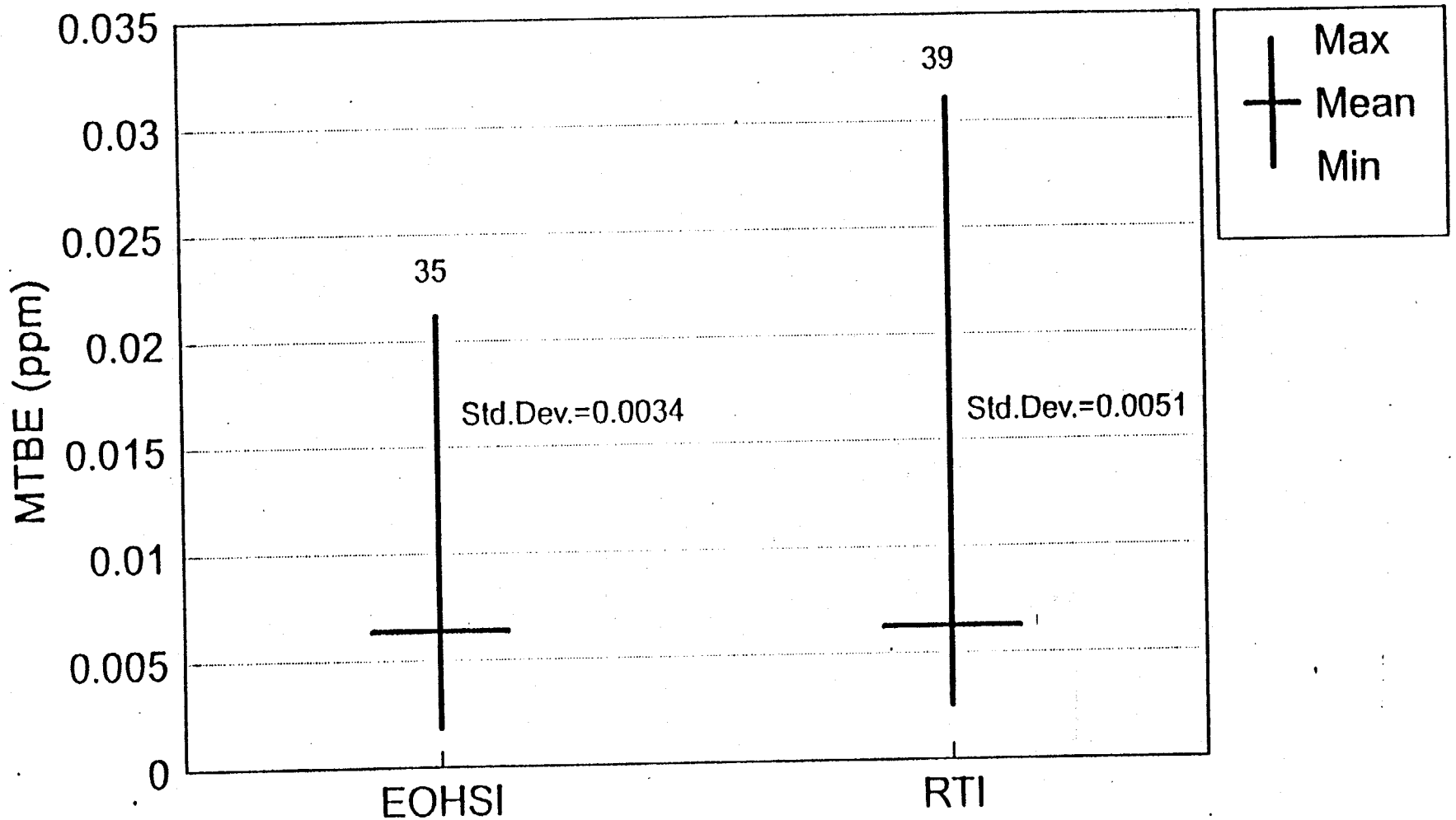


Figure 13

ALASKA MTBE

December 17-22, 1992

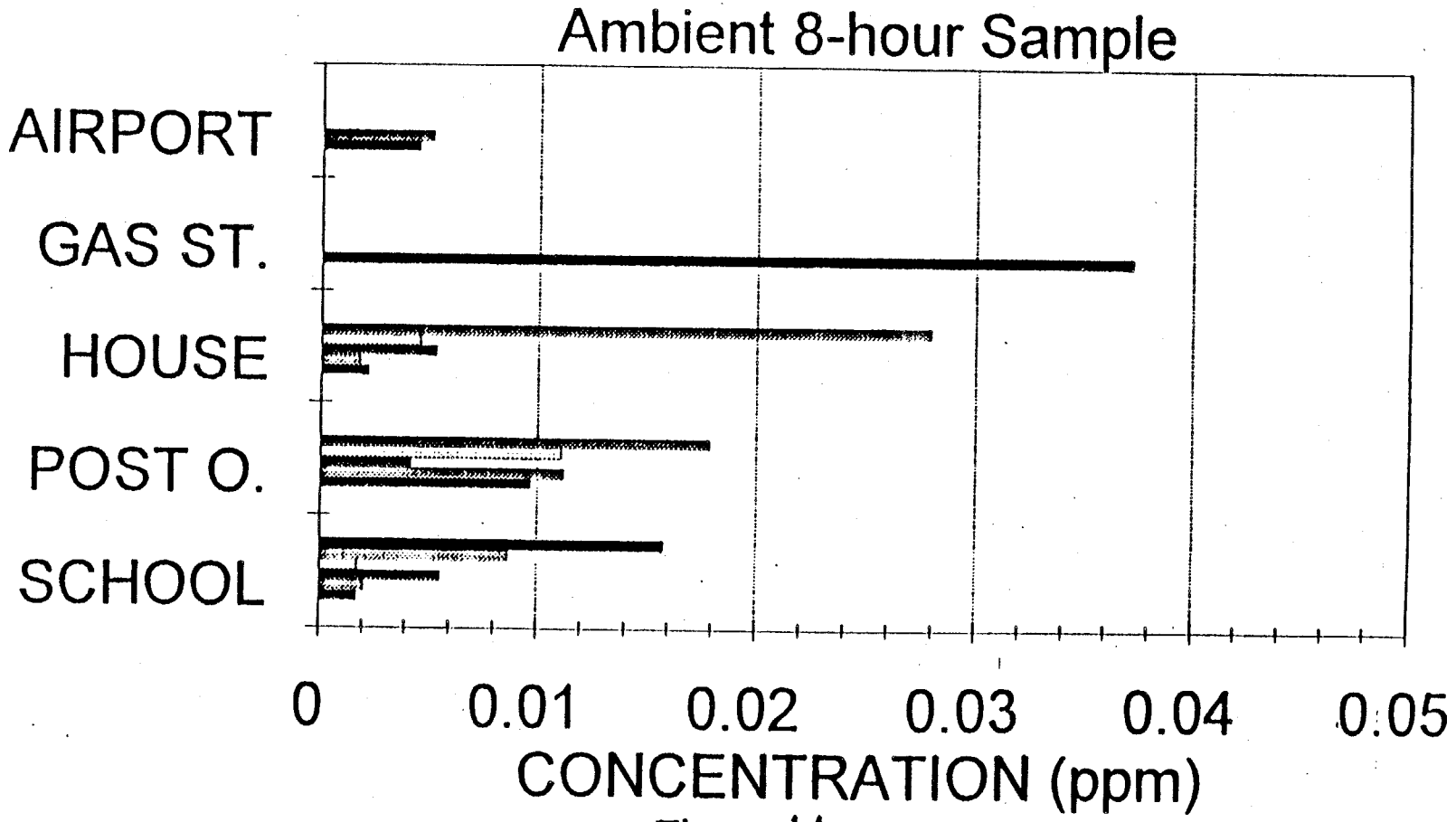


Figure 14

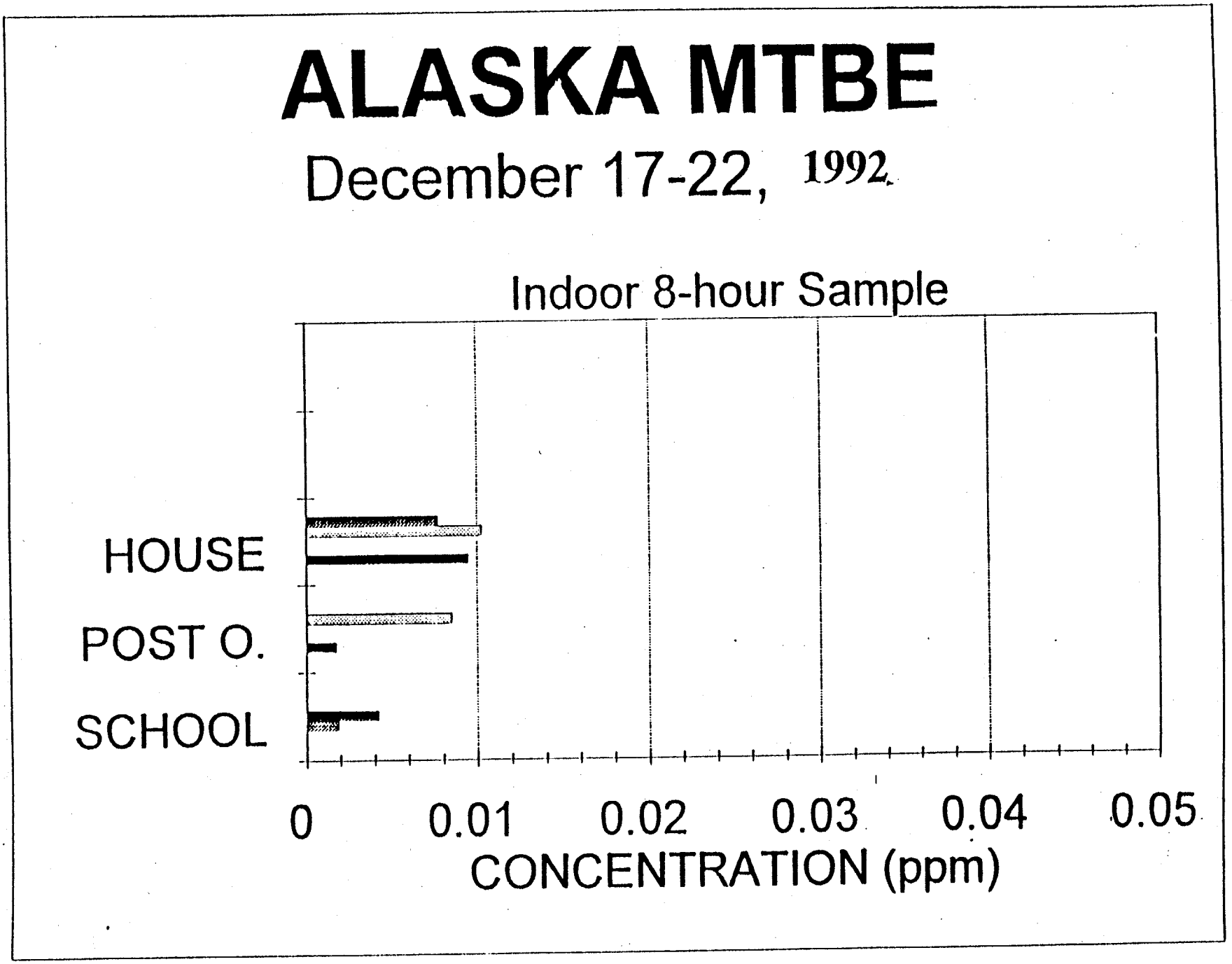

ALASKA MTBE
December 17-22, 1992
Indoor 8-hour Sample
HOUSE
POST O.
SCHOOL
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 15

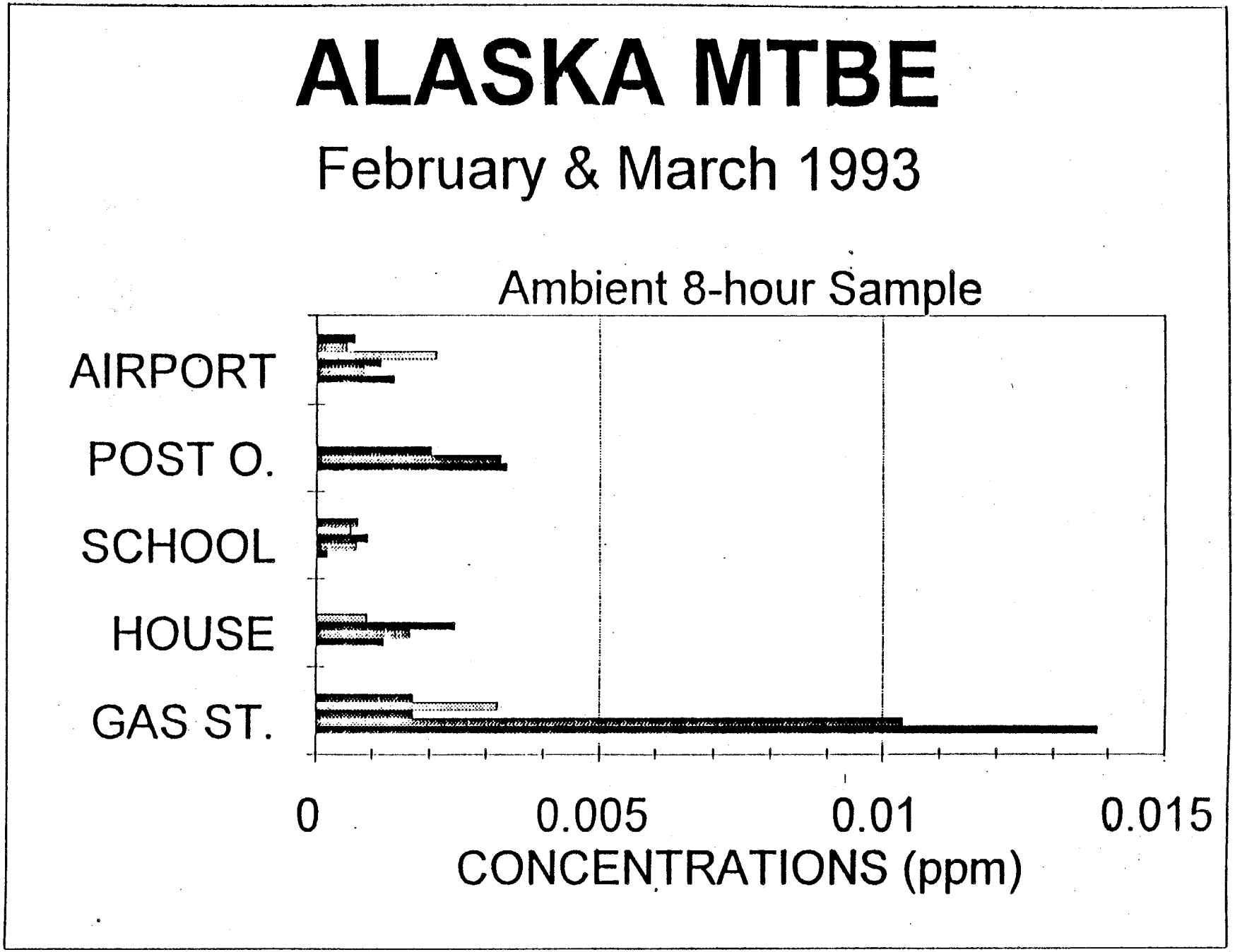

ALASKA MTBE
February & March 1993
Ambient 8-hour Sample
AIRPORT
POST O.
SCHOOL
HOUSE
GAS ST.
0
0.005
0.01
0.015
CONCENTRATIONS (ppm)

Figure 16a

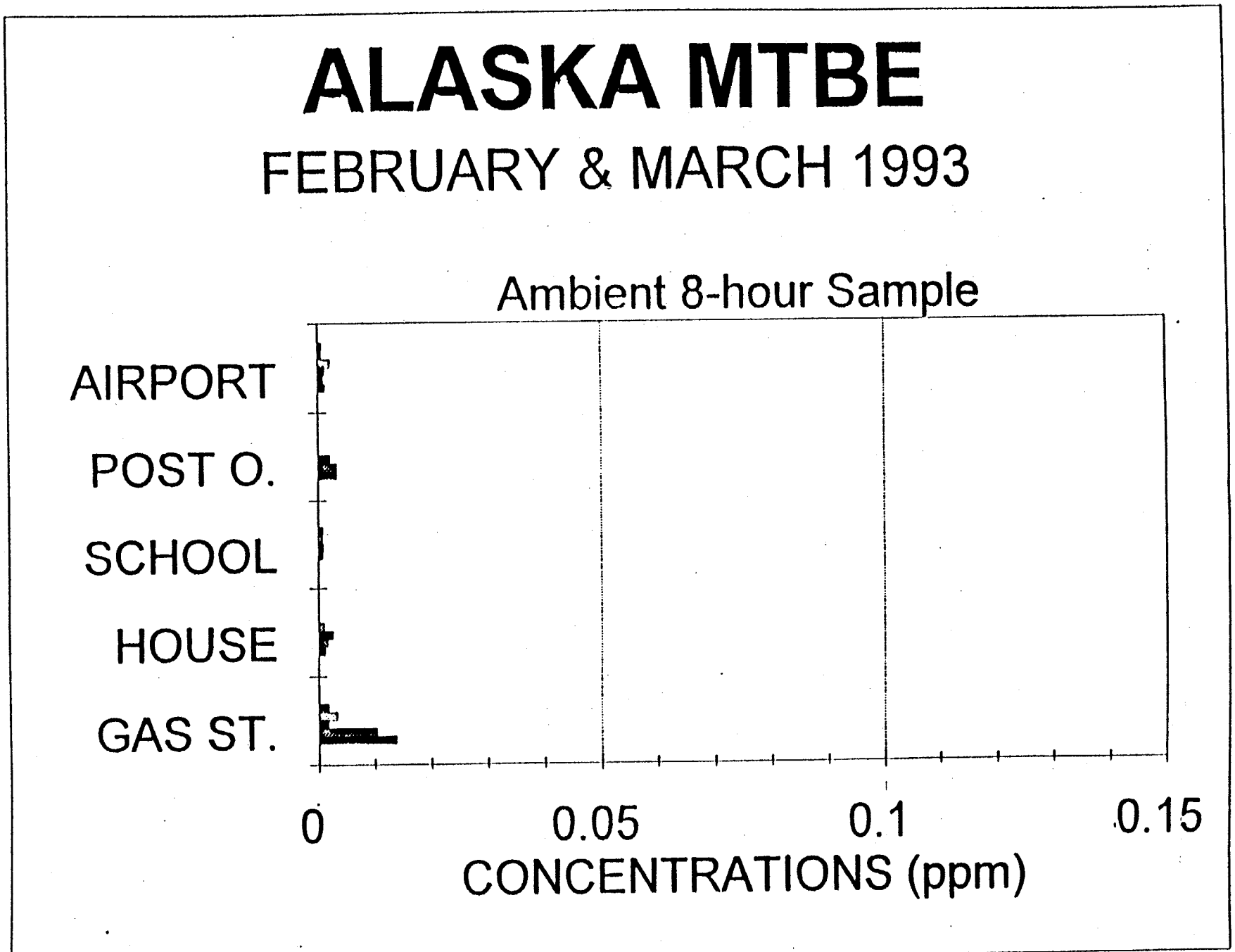

ALASKA MTBE
FEBRUARY & MARCH 1993
Ambient 8-hour Sample
AIRPORT
POST O.
SCHOOL
HOUSE
GAS ST.
0
0.05
0.1
0.15
CONCENTRATIONS (ppm)

Figure 16b

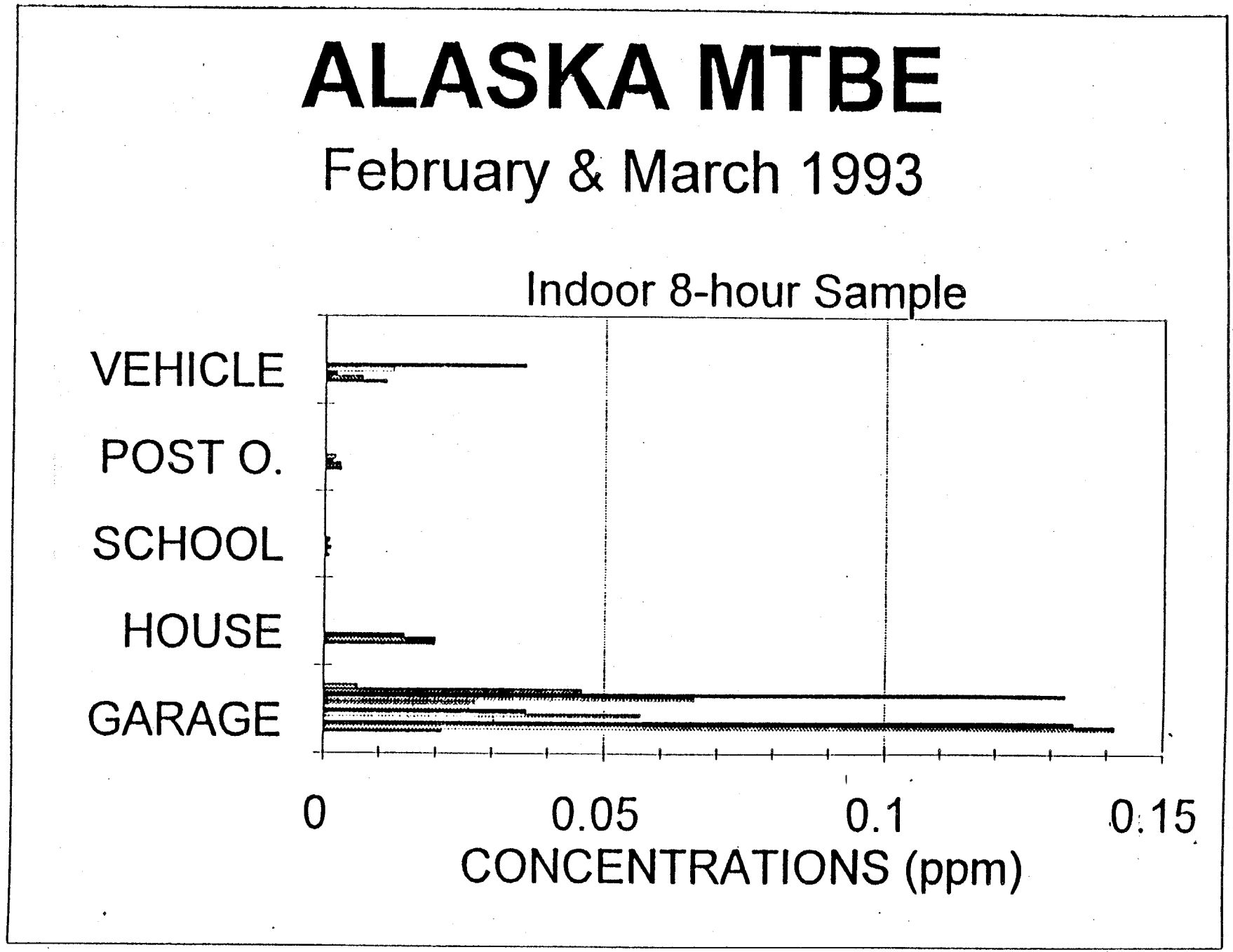

ALASKA MTBE
February & March 1993
Indoor 8-hour Sample
VEHICLE
POST O.
SCHOOL
HOUSE
GARAGE
0
0.05
0.1
0.15
CONCENTRATIONS (ppm)

Figure 17

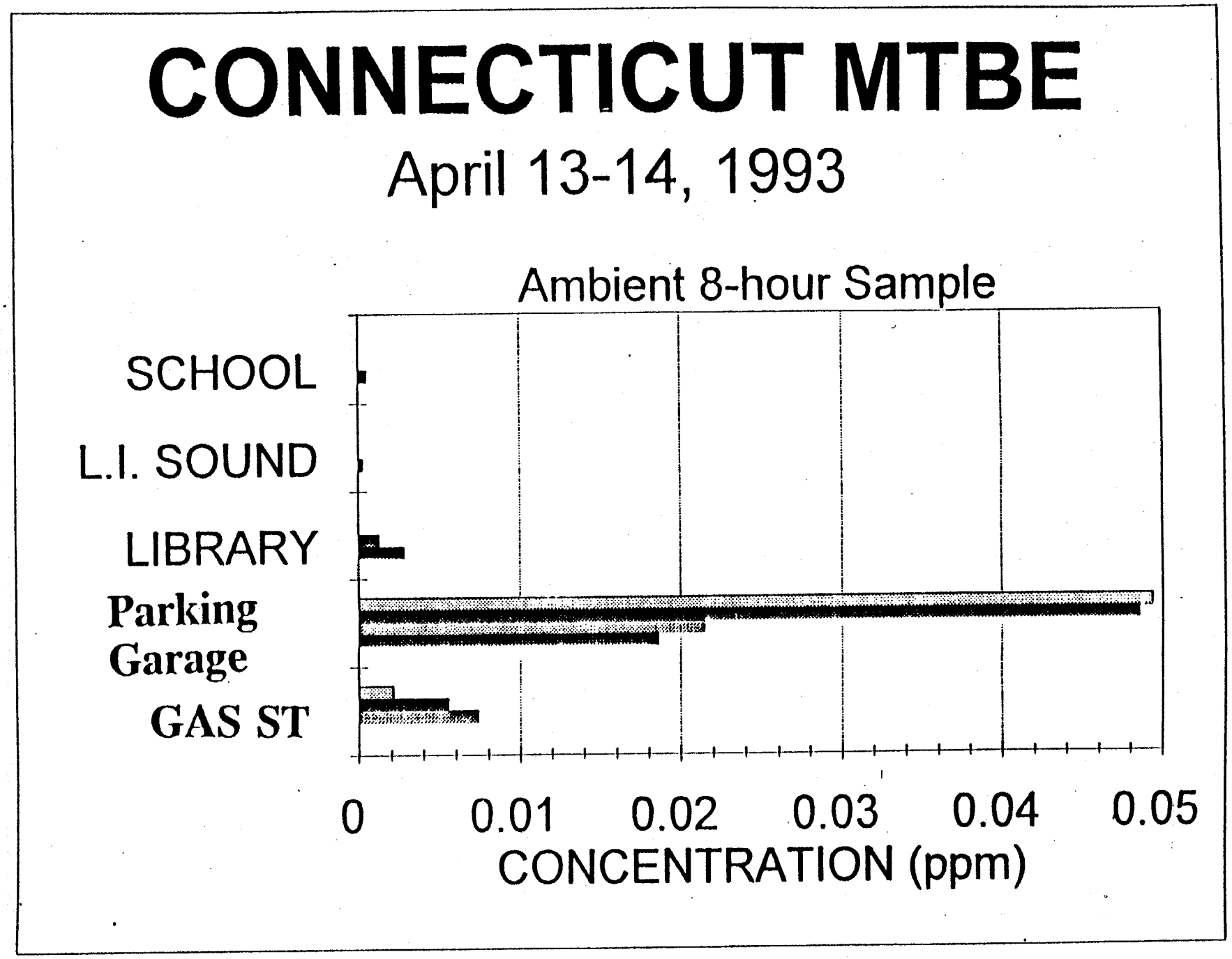

CONNECTICUT MTBE
April 13-14, 1993
Ambient 8-hour Sample
SCHOOL
L.I. SOUND
LIBRARY
Parking Garage
GAS ST
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 18

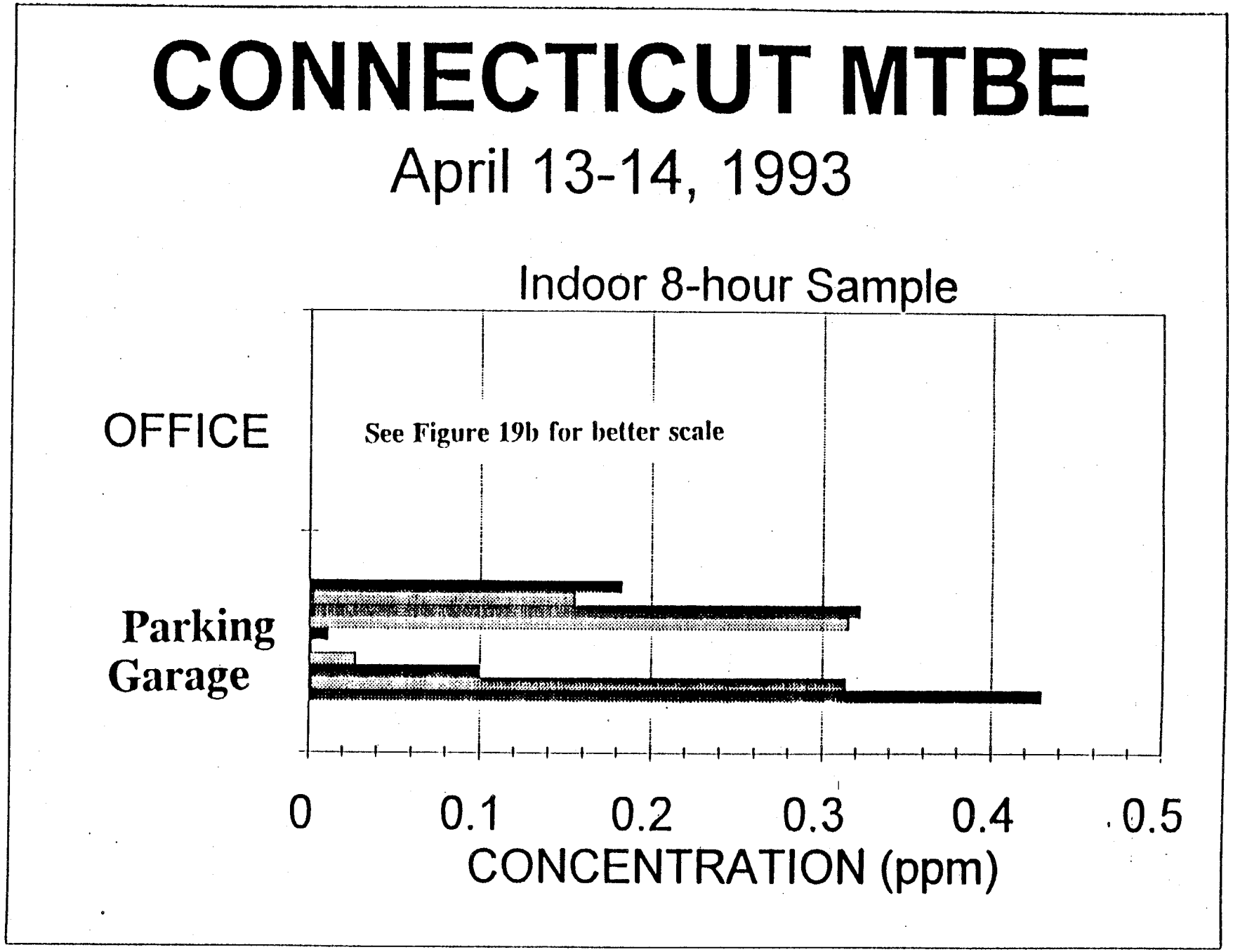

CONNECTICUT MTBE
April 13-14, 1993
Indoor 8-hour Sample
OFFICE
See Figure 19b for better scale
Parking Garage
0
0.1
0.2
0.3
0.4
0.5
CONCENTRATION (ppm)

Figure 19a

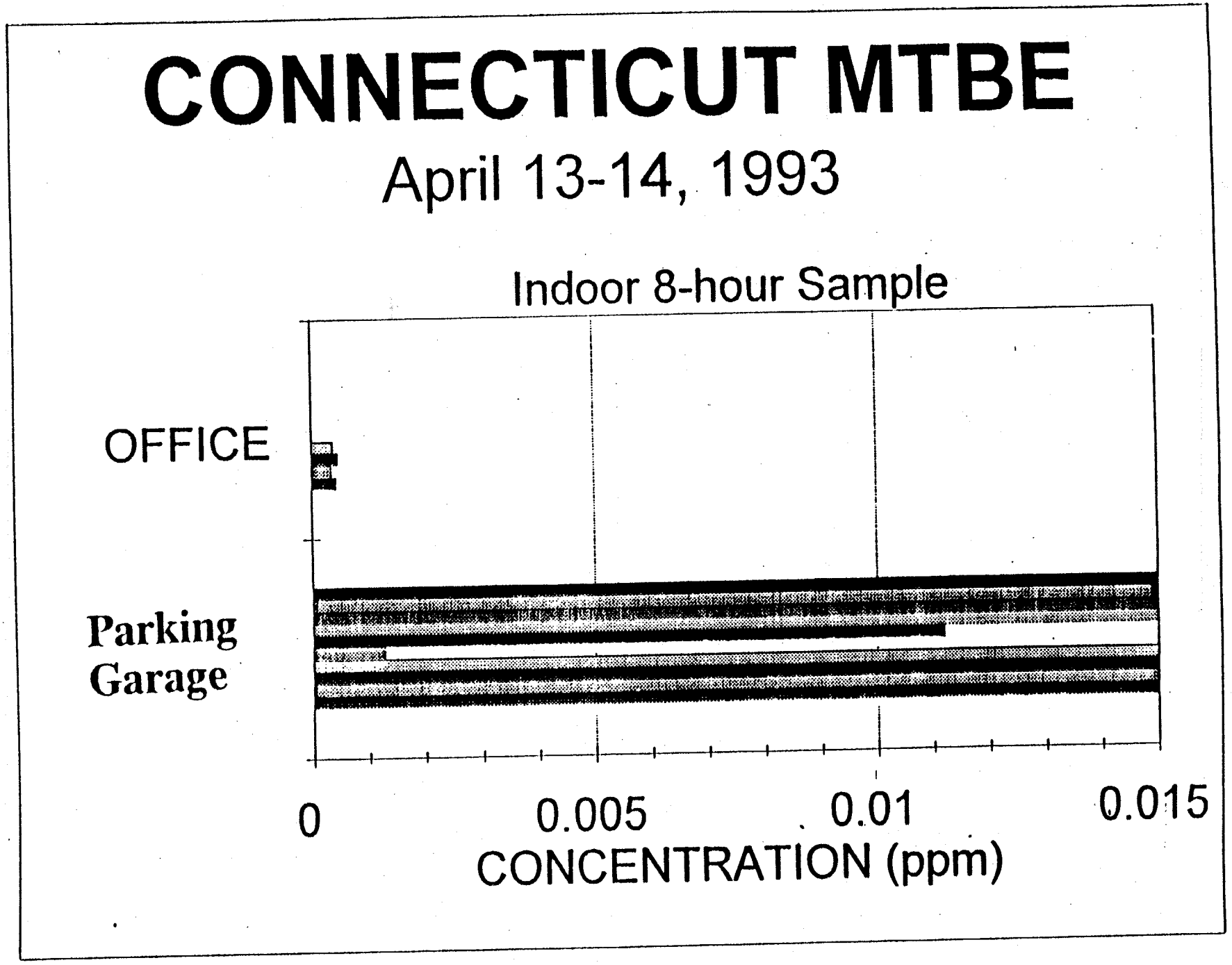

CONNECTICUT MTBE
April 13-14, 1993
Indoor 8-hour Sample
OFFICE
Parking Garage
0
0.005
0.01
0.015
CONCENTRATION (ppm)

Figure 19b

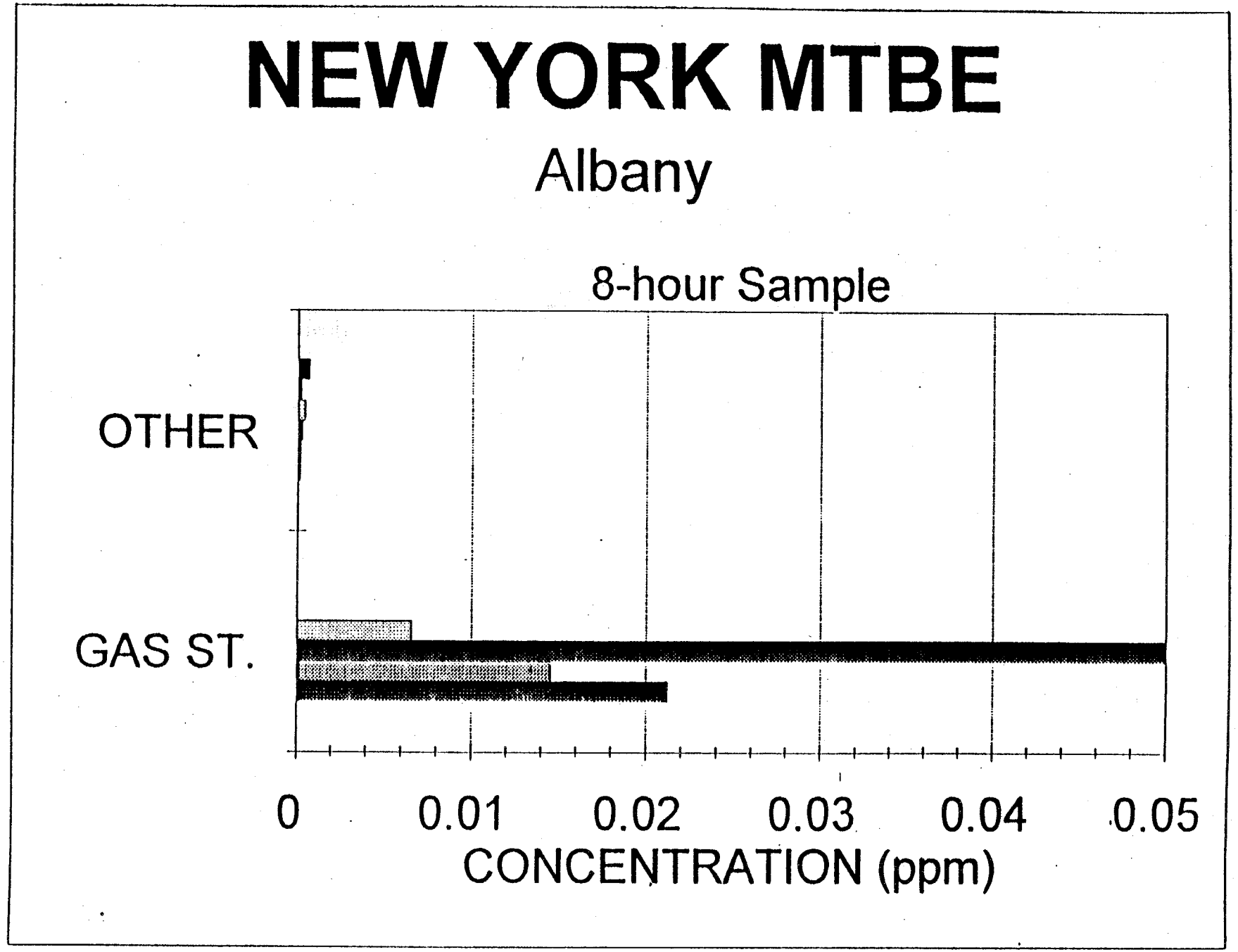

NEW YORK MTBE
Albany
8-hour Sample
OTHER
GAS ST.
0
0.01
0.02
0.03
0.04
0.05
CONCENTRATION (ppm)

Figure 20

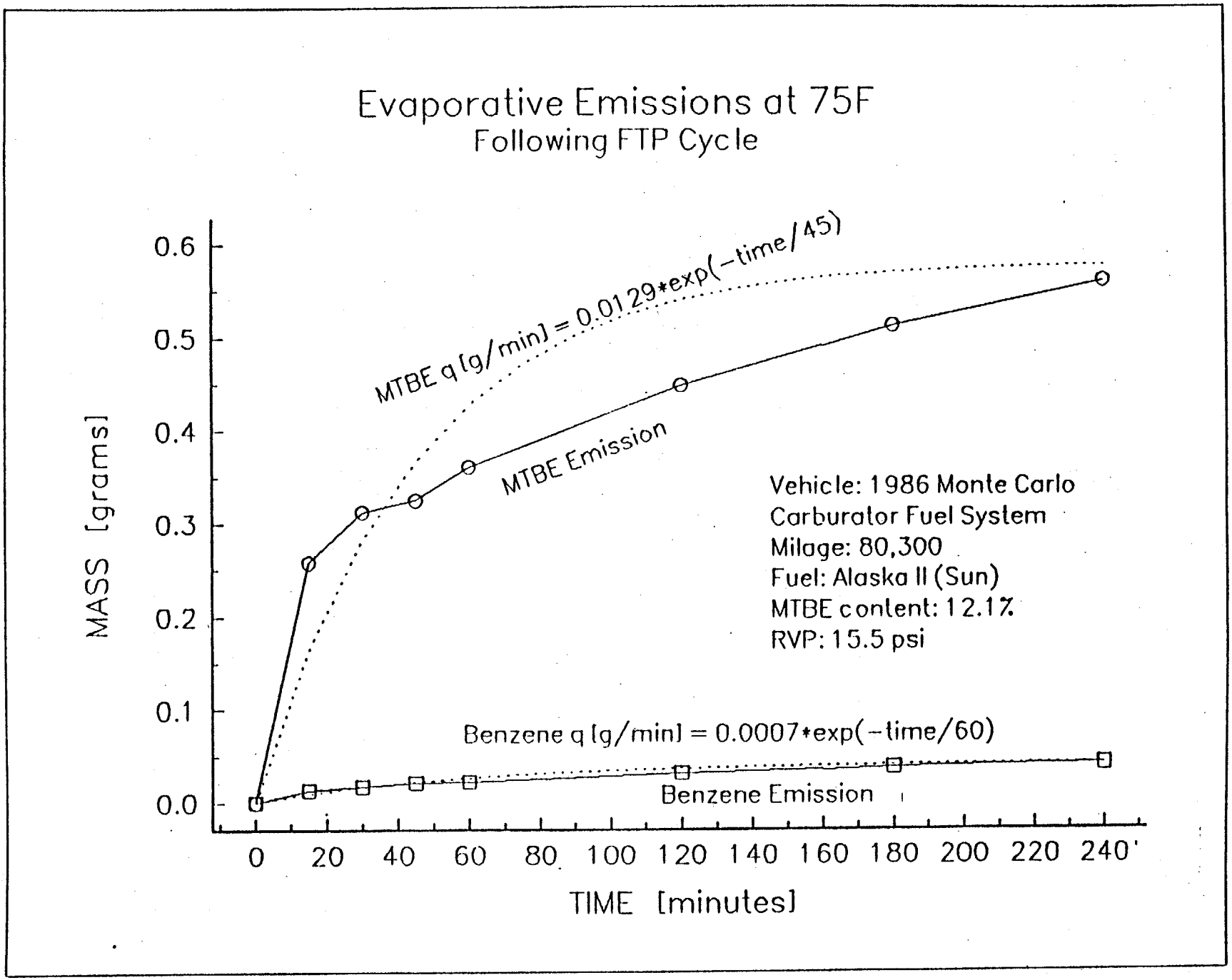

Evaporative Emissions at 75F
Following FTP Cycle
MASS [grams]
0.6
0.5
0.4
0.3
0.2
0.1
0.0
MTBE q [g/min] = 0.0129*exp(-time/45)
MTBE Emission
Vehicle: 1986 Monte Carlo
Carburator Fuel System
Milage: 80,300
Fuel: Alaska II (Sun)
MTBE content: 12.1%
RVP: 15.5 psi
Benzene q [g/min] = 0.0007*exp(-time/60)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

Figure 21

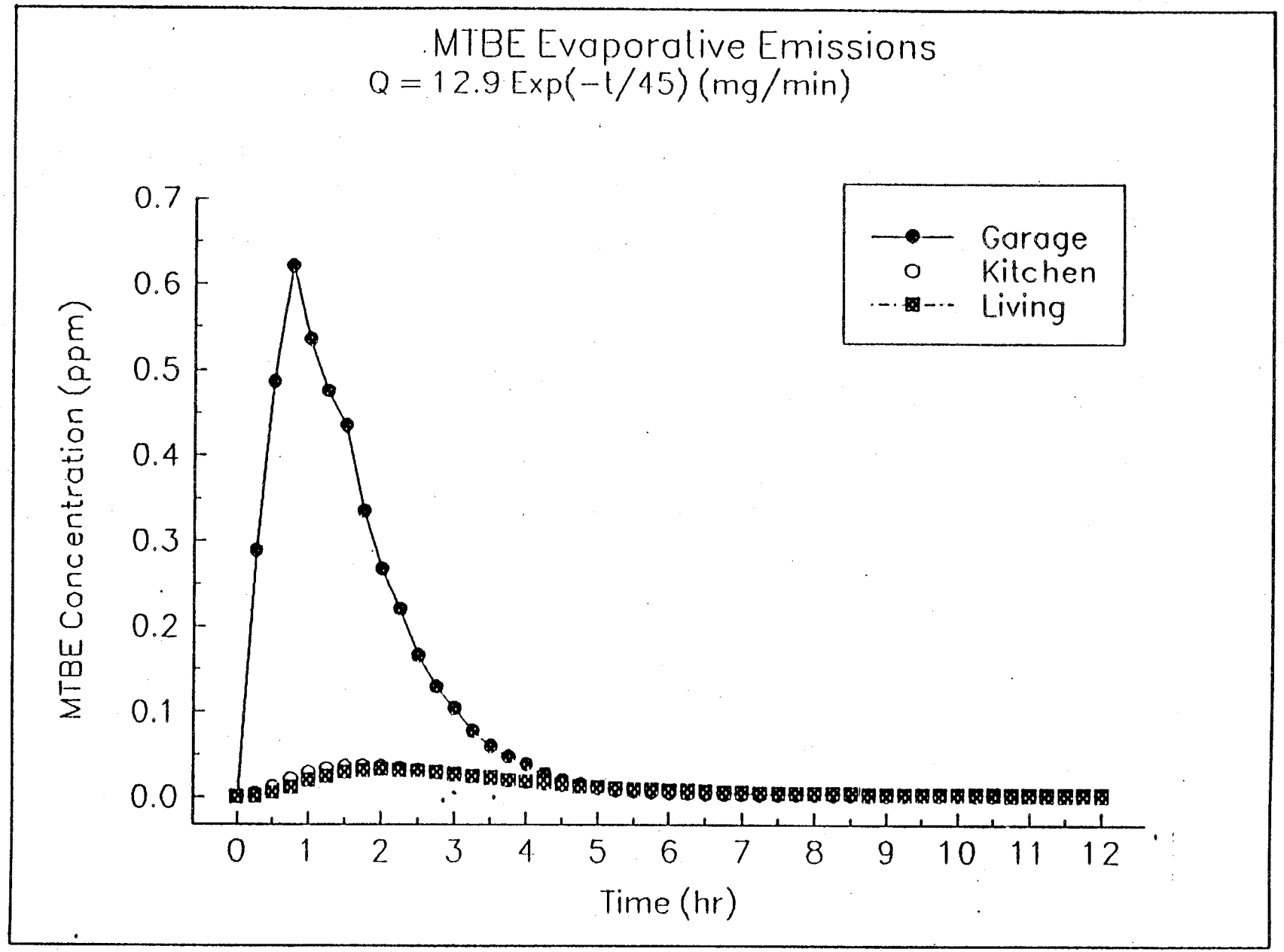

MTBE Evaporative Emissions
Q = 12.9 Exp(−t/45) (mg/min)
MTBE Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0 1 2 3 4 5 6 7 8 9 10 11 12
Time (hr)
Garage
Kitchen
Living

Figure 22

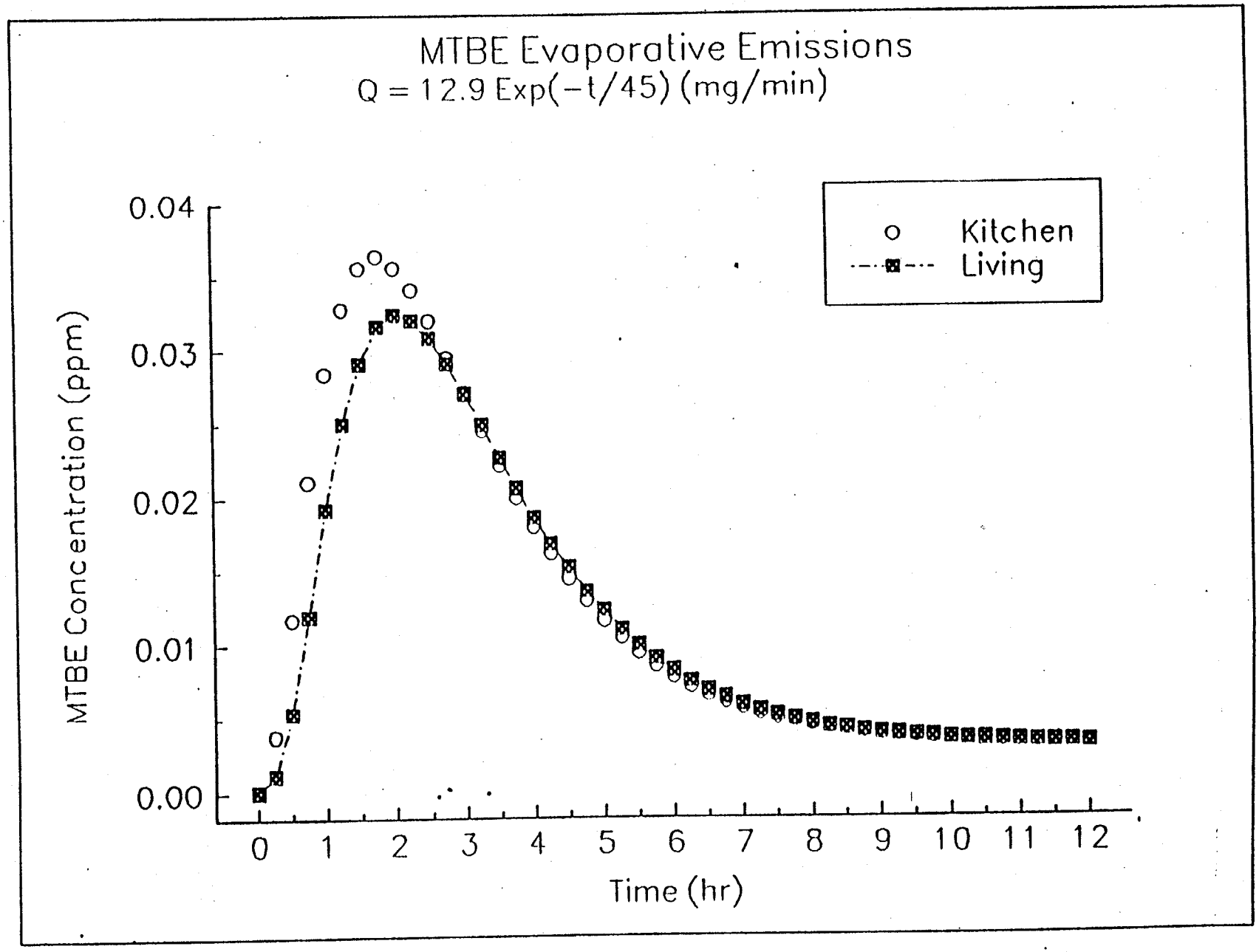

MTBE Evaporative Emissions
Q = 12.9 Exp(−t/45) (mg/min)
Kitchen
Living
MTBE Concentration (ppm)
0.04
0.03
0.02
0.01
0.00
0
1
2
3
4
5
6
7
8
9
10
11
12
Time (hr)

Figure 23