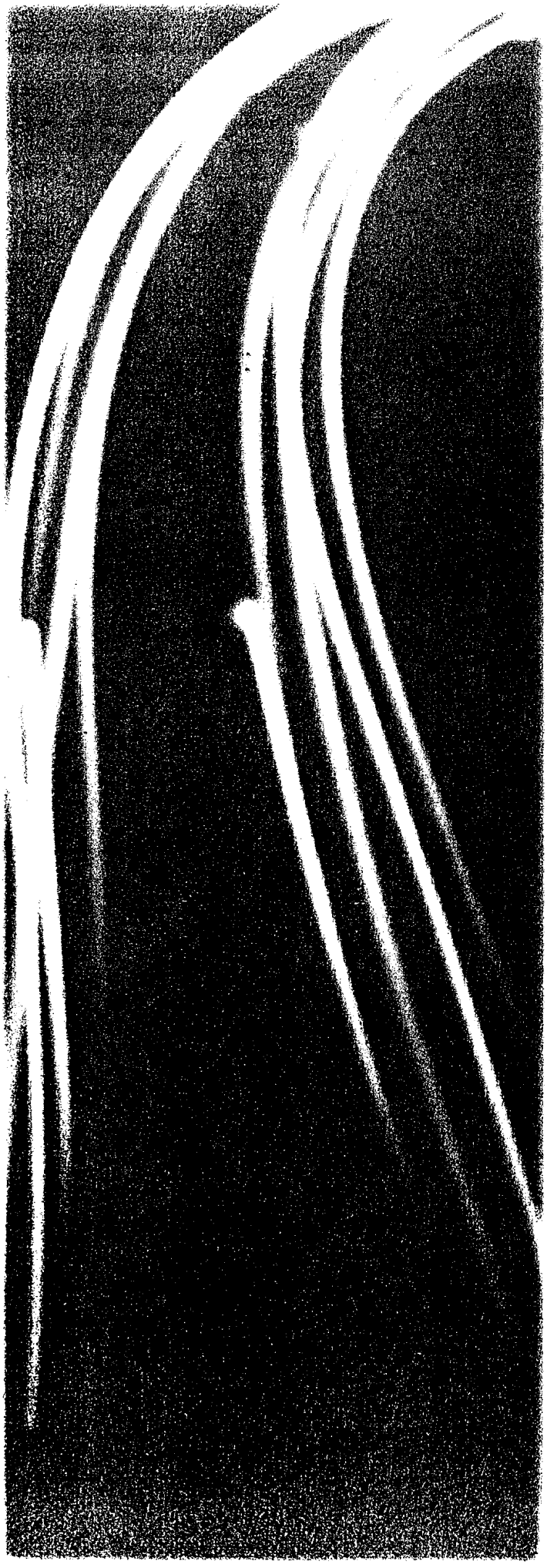

1 Air Quality Effects of the Winter Oxyfuel Program

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CONTENTS

SCOPE OF THE CHAPTER

The effects of the winter oxyfuel program on air quality are assessed in this chapter. The focus of the program is on carbon monoxide (CO) but other pollutants including volatile organic compounds (VOC), nitrogen oxides (NO and NO_2 designated as NO_x), particulate matter, and the toxic air pollutants (TAP), benzene, 1,3-butadiene, formaldehyde, and acetaldehyde are also affected to varying degrees. Data from vehicle emission studies, model predictions, and ambient air quality measurements are reviewed for this assessment.

BACKGROUND OF THE WINTER OXYFUEL PROGRAM

Carbon monoxide is a colorless, odorless, and poisonous gas produced by the incomplete combustion of carbon-containing fuels. Elevated levels of ambient CO have been shown to be a human health hazard (Morris *et al.*, 1995). The EPA has set National Ambient Air Quality Standards (NAAQS) for CO that specify upper limits of 35 ppm for a one-hour period and 9 ppm for an eight-hour period. Generally the eight-hour limit is the more restrictive and virtually all recorded exceedances in recent years involve violation of this limit. Monitoring stations are allowed one exceedance of the air quality standard per year. A second exceedance constitutes a violation. For this reason the second maximum value of CO has been adopted as an important indicator in air quality trend studies. In cities during the winter, on-road vehicles account for a large fraction of the emissions, up to 95% (USEPA, 1995a).

A network of air pollutant monitoring stations has found a persistent pattern of high levels of carbon monoxide (CO) during winter months in many U.S. urban locations. The winter peak values occur during months when temperature inversions trap pollutants near the ground and inhibit dispersion and dilution. The buildup of CO is aggravated in cold climates by increased CO emissions from cold vehicles. Figure 1.1 shows the monthly average CO concentrations over the last 14 years recorded at a monitoring site in downtown Denver, Colorado. At this highly polluted site the peak values occur typically during the months November through February, corresponding to the period of frequent inversions and low temperatures. The average winter CO concentrations at this site are about twice as large as the average summer values, which are indicated by the minima in the data.

Gasoline-fueled engines are a major source of carbon monoxide (CO) and other pollutants. Under ideal conditions, the complete combustion of a hydrocarbon fuel results in a product mixture of mainly carbon dioxide (CO_2) and water vapor in the exhaust stream. The effect of the combustion air/fuel (A/F) ratio on the exhaust composition can be understood with reference to Figure 1.2. This figure is a representative example of the effect of the air/fuel ratio on exhaust pollutant formation in a 1980 vintage engine. It should be noted that the figure gives the engine emissions, called engine out emissions, not the tailpipe emissions, which are considerably lower when a properly functioning catalyst system is used. The dashed line represents the air/fuel ratio with equivalent amounts of oxygen and fuel required for complete combustion. But even at this point 5 - 10% of the fuel carbon is emitted as CO.

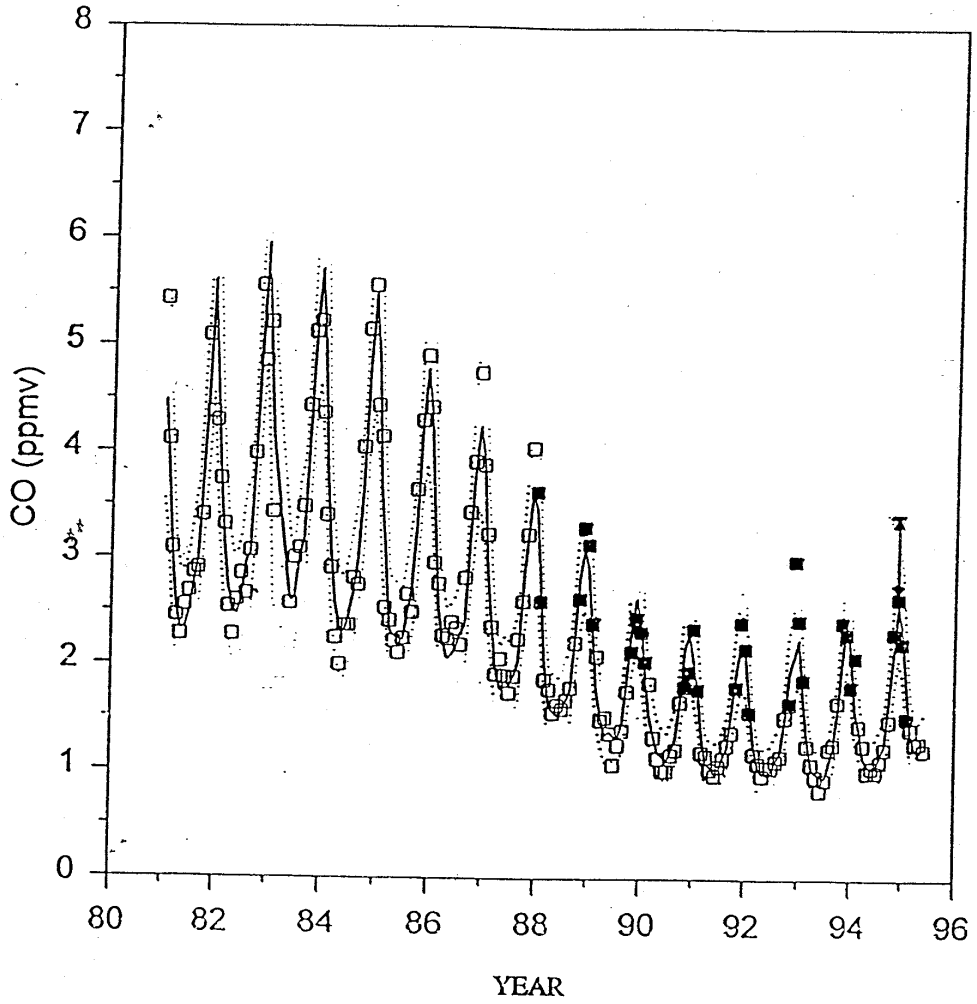

Figure 1.1 A 14-year record showing monthly average values of hourly average CO concentrations at the CAMP air quality monitoring site in Denver, Colorado. The filled symbols indicate the months during which oxyfuels have been used. The bar above the point at 95 shows what the ambient CO concentration would be if one assumes the measured value corresponds to a 24% reduction due to oxyfuels. (Figure courtesy of Larry Anderson)

Some fuel is not completely oxidized, because of limitations of combustion kinetics and quenching of the combustion by the cool metal surfaces of the engine cylinder. The result is incomplete oxidation of the fuel and the emission of CO and some residual organic compounds. About half of the emitted organic material is unburned fuel and half is partially oxidized fuel products. The engine operates in a fuel rich condition when started (cold start) and at an A/F ratio of about 13 for maximum power during a hard acceleration. Under the latter condition about 25% of the fuel carbon is emitted as CO. The nitric oxide (NO) pollutant (generally referred to here as NO_x) has an interesting inverse relationship with the CO and hydrocarbon (HC) pollutants. The NO increases under high A/F ratio (lean) conditions because it is made by the reactions of excess oxygen and nitrogen at high temperatures. Frequently the NO_x emissions are low when the CO and HC emissions are high.

Several actions have been taken to reduce vehicle emissions. The EPA has promulgated emission standards for gasoline fueled vehicles since 1968. A summary of these standards for selected years is given in Table 1.1. In addition to CO, the emissions of hydrocarbons (HCs) and NO_x are regulated, because they contribute to photochemical smog and ozone production. During the past 30 years vehicle manufacturers have responded to the emission regulations by installing emission control devices. Current technology includes a computer-controlled feedback system incorporating oxygen sensors, three-way catalysts, and fuel injection into closed loop and adaptive learning strategies. The concept of the closed loop technology is to measure the oxygen concentration in the exhaust system and to control the vehicle A/F ratio near the stoichiometric point to minimize pollutant emissions. Improved catalysts have also helped reduce emissions. The reduction in exhaust emissions, indicated by comparing the emission levels in the top line of Table 1.1 with the current standards in the bottom line is a factor of 10 for NO_x and about 25 for CO and HC.

Table 1.1 Vehicle exhaust emission standards in grams per mile (U.S. passenger cars, excluding California).

Model Year	Hydrocarbons	CO	NO_x
Pre-1968 (no standards)	11.0	80	4
1973/4	3.4	39	3.0
1977	1.5	15	2.0
1981	0.41	3.4	1.0
1996	0.41	3.4	0.4

Although the introduction and improvement of vehicle emission control devices has led to a decline in urban CO levels, many areas continued to exceed the NAAQS into the late 1980's. Beginning in January 1988, a program of adding an oxygenated organic compound to gasoline was instituted in the Denver, Colorado, area. In subsequent years many other regions in the U.S. that continued to exceed the NAAQS, called nonattainment areas, were required by EPA to adopt similar programs to reduce ambient CO levels. The concept behind the EPA oxyfuel program is to introduce additional oxygen into the combustion mixture by adding an oxygen-containing compound to the fuel. This is equivalent to shifting the A/F ratio in Figure 1.2 toward the right. The added oxygen has been shown to reduce

the amount of CO in the engine exhaust in many studies. The additives are called oxygenates and the most common ones are an alcohol: ethyl alcohol (ethanol) or *tertiary*-butyl alcohol (TBA) or an ether: methyl *tertiary*-butyl ether (MTBE), ethyl *tertiary*-butyl ether (ETBE), *tertiary*-amyl methyl ether (TAME), or *tertiary*-amyl ethyl ether (TAEE).

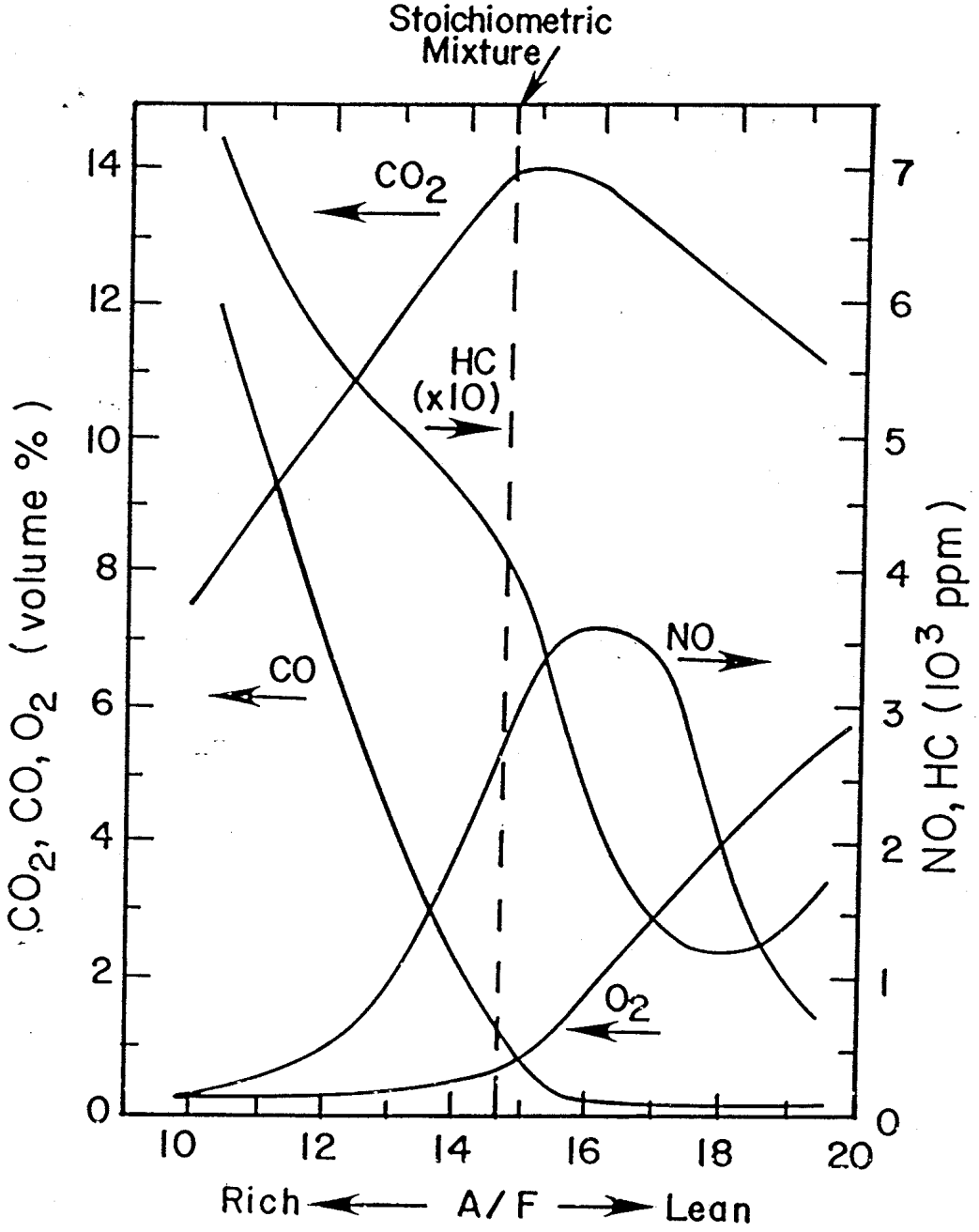

Figure 1.2 Typical gasoline engine pollutant emissions as a function of the intake air to fuel ratio (A/F). The ratio values are based upon mass. The stoichiometric point is a theoretical value at which the amounts of air and fuel are equivalent for complete oxidation of the fuel. Note the different scale for hydrocarbons (HCs) which is 10 times the value for nitric oxide (NO). Adapted from Kummer (1980).

Currently, ethanol and MTBE dominate the market. Adding about 15% by volume MTBE or about 7.8% by volume ethyl alcohol to a standard gasoline achieves a 2.7% by weight oxygen fuel. The amount of oxygen added to a fuel is relatively small, typically 2 to 3.5% by weight.

In this report, emission measurements are distinguished from ambient air quality measurements. Emission measurements are those which sample and measure gases and particles at the tailpipe. The emissions are the gases emitted by the vehicle after passing through any pollution control devices and may also include gases from fuel evaporation. Ambient measurements are those made in the atmosphere. These are characteristic of the gases we breathe in an urban environment. Some air quality measurements are made that are neither an emission measurement nor an ambient measurement, but are somewhere in between. For example, measurements made in a restricted environment such as a tunnel or parking garage are not strictly emission measurements or ambient measurements, although some information about both can be deduced from them.

EFFECTS OF OXYFUELS ON VEHICLE EMISSIONS

Introduction

An assessment of the effects of oxyfuels on vehicle emissions must take into account a complex array of variables affecting emissions. Firstly, the vehicle fleet itself is undergoing a continual change-over. In general the newer models emit less pollution because of improved emission control devices and the use of fuel injection, which makes it possible to provide tight control of A/F stoichiometry. In addition to significant model year changes, the emissions vary from vehicle to vehicle depending upon how it is maintained and operated and the quality of the fuel used.

Secondly, emission studies must be performed on a wide variety of fuel compositions. One of the most extensive studies of fuel effects on automobile emissions is the Auto/Oil Air Quality Improvement Research Program (AQIRP). In this program three domestic automobile manufacturers and 14 oil refining companies cooperated to test the effects of vehicle technology and fuel composition on vehicle emissions. The study has developed an extensive database for a matrix of fuels, vehicles, and operating conditions. Although the program is not specifically directed at studying oxyfuel effects, it provides a valuable database of carefully documented measurements.

Gasoline is a mixture of numerous different hydrocarbons, including alkanes, alkenes and aromatic compounds, which can be blended in many different combinations. Into these combinations oxygenates are added. In some cases oxygenated fuels are prepared by adding the oxygenate to a standard gasoline. This technique is referred to as splash blending. In other cases, the fuels are blended, usually at a refinery, to obtain certain properties, for example, the addition of oxygenates to increase a fuel's octane rating or to achieve important parameters, such as overall vapor pressure or to minimize emissions of certain pollutants. [Fuel vapor pressure is reported as Reid vapor pressure (RVP), the vapor pressure at 100 °F.] This technique is referred to as match blending.

Finally the ambient conditions of vehicle operation in oxyfuel areas cover a broad range. Elevation varies from sea level to one mile (Denver, Colorado) corresponding to pressures from 1 to 0.8 atmosphere. Temperatures also vary from around +80 ° to -40 °F (27 ° to

-40 °C). It is not surprising that no individual study has covered the broad range of variables required to characterize completely vehicle emission effects.

This report covers two types of studies used to obtain information on vehicle emissions: (1) dynamometer studies and (2) field studies. The dynamometer studies are usually conducted in a controlled laboratory environment at 75 °F, usually on a well maintained vehicle and under a standard format called the Federal Test Procedure (FTP). During the FTP, exhaust gas is sampled and analyzed during three phases of vehicle operation. The first phase (called Bag 1) represents cold start emissions, the second phase (called Bag 2) represents emissions under stable vehicle temperatures, and the third phase (called Bag 3) represents hot start emissions. Thus the effects of fuel composition on emissions can be quantified for each phase of operation and a standard driving cycle. Dynamometer studies have the advantage that many variables affecting emissions can be controlled and characterized and that the composition of the exhaust can be accurately quantified by a variety of laboratory instruments. A limitation of dynamometer studies is that it is practical to perform only representative tests and that tests are not made over the full spectrum of driving conditions. These limitations contribute to the uncertainty of predicting the emissions of the on-road vehicle fleet.

Field studies include both remote sensing and tunnel studies. The remote sensing studies employ a roadside detector that optically analyzes the exhaust of individual vehicles, typically for CO, HC, and CO_2. The CO_2 serves as a tracer for the exhaust plume and the pollutant concentrations are determined relative to the total amount of gaseous carbon species which is mainly CO_2. A camera can be synchronized with the exhaust analysis to identify the vehicle and subsequently to provide details of the engine and pollution control devices. The remote sensor has the advantage that a large number, on the order of 100,000, of on-road vehicles can be tested and characterized. It has a disadvantage that the range of vehicle operating conditions is limited, typically, to a hot stable mode and only a couple of emission constituents are measured. The tunnel studies involve the analysis of air sampled within a tunnel. This confined space allows the exhaust emissions of many vehicles to be analyzed collectively. Many exhaust components can be quantified. This measurement represents a population of on-road vehicles under real operating conditions. The disadvantages are that individual vehicles are not characterized and that the emissions represent a limited range of operating conditions, typically, the hot stable mode.

It is not possible, within the scope of this assessment, to evaluate the numerous studies of the effects of oxygenates on vehicle emissions. A few examples are cited here to illustrate representative studies and important issues.

Dynamometer Studies

CO Emissions. The Auto/Oil AQIRP study by Reuter *et al.* (1992) reports the effects of oxygenated gasolines and RVP on emissions from twenty 1989 model year vehicles. The test vehicles represented a broad range of engine sizes from 2 to 5.7 liter displacements and had between 10,000 and 29,000 miles on their odometers. The fuel inlet systems included two with carburetors, four with throttle body injection, ten with port fuel injection, and four with sequential fuel injection. All of the vehicles employed three-way catalyst systems and two vehicles also had oxidation catalysts. The fleet can be characterized as a relatively new, low emission group of vehicles. Eleven fuels were studied including four 3.7 wt % oxygen ethanol fuels, two 2.7 wt % oxygen MTBE fuels, and one 2.7 wt % ETBE fuel.

The tests were conducted according to the FTP. Some of the results are summarized in Table 1.2. The oxyfuel effects on the emissions are given as a percent change observed with the oxyfuels normalized to the oxygen content of the test fuel, that is, divided by the wt % oxygen content of the fuel.

Table 1.2 Summary of results from Auto/Oil AQIRP study (Reuter *et al.*, 1992) of oxyfuel effects on twenty 1989 model year vehicles exhaust emissions. This fleet is a relatively new, low emission group.

		% Change with Oxyfuel per wt % Oxygen[c]		
Emission[a]	**Mass Emission[b] (g/mi)**	**3.7% O_x EtOH**	**2.7% O_x MTBE**	**2.7% O_x ETBE**
CO	2.5	-3.6 ± 1.3	-3.4 ± 2.4	-5.4 ± 2.7
HC	0.21	-1.3 ± 0.7	-2.4 ± 1.3	-1.9 ± 1.4
NO_x	0.6	+1.4 ± 1.1	+1.3 ± 2.0	+2.0 ± 2.3
Benzene	9×10^{-3}	-3.1 ± 1.6	-4.1 ± 3.0	-3.5 ± 3.0
1,3-Butadiene	9×10^{-4}	-1.6 ± 1.5	-0.6 ± 2.9	-1.0 ± 3.1
Formaldehyde	1.5×10^{-3}	+5.2 ± 8.4	+5.9 ± 15.3	+6.3 ± 26.6
Acetaldehyde	1.4×10^{-3}	+43 ± 12	-0.3 ± 13	+95 ± 25

[a]HC = Total hydrocarbons

[b]Mass emissions are approximate average values for test fuels.

[c]The oxyfuel effects have been normalized to 1 wt % oxygen. The oxygen wt % of the test fuel is noted: 3.7% O_x means 3.7 wt % oxygen. The uncertainties represent 95% confidence limits.

Reuter *et al.* found a statistically significant reduction in CO, total HC and benzene emissions with all three fuel oxygenates compared to the non-oxygenated fuels. The NO_x emissions increased for all of the oxygenates, but the result was statistically significant for only the ethanol fuels, the fuel set with the highest oxygen content. The average effect for the complete fuel set was also found to be significant, about (+1.6 ± 1)% NO_x per wt % oxygen. Acetaldehyde emissions increased greatly for ethanol and ETBE fuels. The fleet average CO benefit for the 7 test oxygenate fuels is -3.8% per wt % oxygen. The effect of reducing the fuel RVP by 1 psi did not have a statistically significant effect for the oxygenate fuel set, although it did reduce the CO emissions by 10.4 ± 8.0% in the non-oxygenated fuel set. In general HC and CO emissions are reduced when fuels with lower RVP are used. An important result from a comparison of effects of the different oxygenates is that they all have quite similar benefits, when normalized to the wt % oxygen content. It is generally assumed that the oxygenates' effects are indistinguishable except for the special effects on aldehyde emissions as discussed later.

Another Auto/Oil study (Hochhauser *et al.*, 1991) compared the emission benefits of a 15% MTBE fuel in current and older vehicles. The current vehicles were the same 1989 model year group described by Reuter *et al.* (1992). The older vehicle group consisted of fourteen 1983-1985 model year vehicles with 42,000 to 79,000 odometer miles and 1.8 to 5.7 liter displacement engines. Twelve of these older vehicles had carburetors and two had throttle body injection. Four of the vehicles had three-way catalysts (TWC), four had oxidation catalysts (OC) and six had both TWC and OC. The older group of vehicles also had relatively low emission levels. The results of the study are summarized in Table 1.3. The

mass emissions from the older group are from 2 to 2.4 times larger than the current fleet. The oxyfuel benefits are also larger for the older higher emitting vehicles. The effects of the oxyfuel on the current fleet are similar to the results reported in Table 1.2, as expected.

Table 1.3 Summary of results from Hochhauser *et al.* (1991) on the effects of a 15% MTBE fuel (2.7 wt % oxygen) on a current group of 1989 model year vehicles and a group of older 1983-1985 model year vehicles. Both groups included cars and light duty trucks and represent relatively low emitting vehicles.

Emission [a]	Mass emission[b] (g/mi)	% Change with oxyfuel per wt % oxygen[c]
CO		
Current Fleet	2.8	-4.1 ± 1.3
Older Fleet	6.2	-5.2 ± 1.4
HC		
Current Fleet	0.22	-2.2 ± 0.9
Older Fleet	0.53	-3.4 ± 1.1
NO_x		
Current Fleet	0.6	+0.5 ± 0.7
Older Fleet	1.2	+0.5 ± 0.7

[a]HC = Total hydrocarbons.

[b]Mass emissions are average values for test fuels.

[c]Note that the oxyfuel effects have been normalized to 1 wt % oxygen.
The uncertainties represent 95% confidence limits.

A study was carried out as a part of the Auto/Oil AQIRP series to examine fuel effects on high emitting vehicles (Knepper *et al.*, 1993). The effects of oxyfuels on high emitting vehicles are particularly important because there is evidence that, although they represent a small fraction of the on-road fleet, they are responsible for a disproportionately large amount of urban CO as discussed in the section on "Model Predictions." A group of seven 1986-1987 model year vehicles were selected for their high emission characteristics. The vehicles were diagnosed to have various problems that caused them to run fuel rich. The Federal Test Procedure CO emissions ranged from 17 g/mi to 216 g/mi. The HC emissions were also quite high, ranging from 1.5 g/mi to 15 g/mi. The NO_x emissions tended to be low as expected for vehicles running in a fuel rich condition, averaging about 0.5 g/mi. The oxyfuel effects were tested with a 3.65 wt % oxygen ethanol fuel and 2.76 and 2.54 wt % oxygen MTBE fuels. The results are summarized in Table 1.4. Knepper *et al.* reported that the emission levels varied greatly due to unstable maintenance of the air/fuel ratio. The values given in Table 1.4 for percent changes were obtained from bar charts. In general the measurements had greater variability and much larger confidence limits than results from stable vehicles. The CO benefits are larger than observed in normally operating vehicles, averaging about -9.7% per wt % oxygen. The HC emissions were similarly reduced, averaging about -9.4% per wt % oxygen. The NO_x emissions increased,

averaging about +9%, although the mass emission for NO_x remained generally low.

Table 1.4 Summary of results of Auto/Oil AQIRP study of oxyfuel effects on high emitting vehicles (Knepper *et al.*, 1993). This group of vehicles had mechanical defects causing them to run in a fuel rich condition.

Emission[a]	Mass Emission[b] (g/mi)	% Change with Oxyfuel per wt % Oxygen[c] 3.65% O_x EtOH	2.7% O_x MTBE
CO	149, 124	-7.4 ± 7.4	-12 ± 7
HC	12.0, 9.2	-6.8 ± 6.3	-12 ± 4
NO_x	0.39, 0.55	+5.8 ± 3	+12 ± 3

[a] HC = Total hydrocarbons.

[b] Mass emissions are fleet average for reference fuels. The first number is for the ethanol and 2.76 wt % oxygen MTBE fuels. The second number is for the 2.54 wt % oxygen MTBE fuel.

[c] The oxyfuel effects have been normalized to 1 wt % oxygen. The uncertainties represent 95% confidence limits.

A series of tests were conducted by EPA (Mayotte *et al.* 1994 a,b) to determine the effects of oxygenates and other fuel parameters on normal and high emitting vehicles characteristic of the general population. The vehicles were grouped according to the HC emission, where vehicles emitting <0.82 g/mi represent the normal emitter group. Although high HC emission levels often correlate with high CO emission levels, they do not always correlate, so the high HC emitting fleet may not be a high CO emitting fleet. In Phase I of the program (Mayotte *et al.*, 1994a) a fleet of twenty 1987-90 model year (MY) normal emitters and sixteen 1987-90 MY high emitters were studied using eight fuels, five of which were 2 wt % oxygen MTBE fuels and one of which was a 3.7 wt % oxygen ethanol fuel. In the Phase II study (Mayotte *et al.*, 1994b) twelve fuels were tested in thirty-nine vehicles, twenty-seven 1986-91 MY normal emitters and twelve 1986-89 MY high emitters. Ten of the fuels were reformulated blends containing 2.0% by weight oxygen MTBE and one was a 2.5% by weight oxygen MTBE/ethanol blend. The results are summarized in Table 1.5. In Phase I of the study the high emitters had significantly larger reductions in CO and HC emissions with oxygenate fuel than the normal emitters. In Phase II the normal and high emitters showed similar CO and HC emission effects with the oxygenated fuels. The fleet benefits are estimated to be in the range of 4 to 5% reduction in CO per wt % oxygen in these studies. The oxyfuel effects on NO_x emissions are small in all cases. The only statistically significant result was the highest oxygen content fuel produced an increase in NO_x emission in the Phase I normal emitter group.

Although the primary objective of the oxyfuel program is the reduction of winter CO emissions, relatively little is known about the effects of oxygenates on emissions at low operating temperatures. Vehicle testing at low temperatures poses special problems. A gasoline engine generates a large amount of heat, so a large cooling capacity is required in

a test laboratory to simulate the operating conditions of a cold environment. The rate at which the engine and the catalytic converters of vehicle warm to obtain efficient operation is critically important for a test to represent realistic operating conditions.

Table 1.5 Summary of results of EPA study of normal and higher emitting vehicles (Mayotte *et al.* 1994a, b).

	% Change with Oxyfuel per wt % Oxygen			
	Phase I			
	Normal Emitters		High Emitters	
Emission[a]	2% O_x MTBE	3.7% O_x EtOH	2% O_x MTBE	3.7% O_x EtOH
CO	-2.4 ± 4.0	-2.3 ± 2.0	-8.0 ± 2.3	-6.8 ± 2.1
HC	-4.2 ± 2.8	-2.0 ± 1.5	-5.1 ± 1.8	-5.2 ± 1.5
NO_x	+1.0 ± 2.1	+1.5 ± 1.2	0 ± 5.2	-0.5 ± 3.3
	Phase II			
	Normal Emitters		High Emitters	
Emission	2% O_x MTBE	2.5% O_x MTBE/EtOH	2% O_x MTBE	2.5% O_x MTBE/EtOH
CO	-4.4 ± 2.7	-2.9 ± 1.9	-3.9 ± 2.1	-4.8 ± 2.4
HC	-4.4 ± 1.7	-1.4 ± 1.6	-3.3 ± 1.5	-1.5 ± 2.5
NO_x	-0.7 ± 1.5	-0.1 ± 1.2	-0.4 ± 1.6	-0.7 ± 3.6

[a]HC = Total hydrocarbons

[b]Oxyfuel effects have been normalized to 1 wt % oxygen. The uncertainties represent 90% confidence limits.

Hood and Farina (1995) have reviewed studies of oxyfuel effects on emissions from light duty vehicles at low ambient temperatures. One of the studies they reviewed was reported by Most (1989) and conducted under the auspices of the Coordinating Research Council. The test fleet consisted of sixteen vehicles representing a range of fuel inlet and emission control technologies: four 1979-1980 MY carbureted vehicles with OC; six 1983-1986 MY vehicles of which four were carbureted and two were fuel injected and all had TWC; and six 1986-1988 MY vehicles with fuel injection and adaptive learning, closed-loop TWC systems. The test fleet did not include any high emitters. The test fuels included 11.5 and 13 psi RVP fuels and oxygenate mixtures that were an 11% MTBE blend, and two 10% ethanol blends. The emission tests were conducted at sea level and 5000 ft altitude and at temperatures at 35 °, 50 ° and 75 °F. The emission test results are summarized in Table 1.6. The oxyfuel benefits have been normalized to 1 wt % oxygen. The oldest technology group, the carbureted OC vehicles, had the largest and most consistent reduction in CO emissions at all temperatures, typically about 9% reduction in CO per wt % oxygen. The middle technology group, the closed-loop, three-way catalyst vehicles, had reduced benefits from oxyfuels, typically about 3.4% CO reduction per wt % oxygen. The highest technology group, the adaptive learning vehicles, had mixed effects from oxyfuels, and in some cases showed small enhanced CO emissions with fuel oxygenates. The oxygenate effects on this group at 5000 ft were negative, where half of the test set indicated an increase in CO emissions with fuel oxygenate.

Table 1.6 Percent changes in average CO emissions from oxyfuels (13 PSI Fuel Set) under different ambient conditions of temperature and altitude. Reported by Most (1989). [Taken from Hood and Farina (1995)]

Fleet[a] Technology	Temp. (°F)	CO % Change with Oxyfuel per wt % Oxygen[b] 11% MTBE 2% O_x	10% EtOH (Splash) 3.66% O_x	10% EtOH (Matched) 3.75% O_x
		Sea level		
CL/AL/TWC	35	-2.8	-0.14	-4.0
CL/AL/TWC	50	-5.1	-3.2	-1.4
CL/AL/TWC	75	-4.1	-4.0	-0.21
CL/TWC	35	-1.8	-4.3	-3.8
CL/TWC	50	+1.4	-3.2	-3.5
CL/TWC	75	-3.8	-4.4	-1.5
		5000 ft altitude		
CL/AL/TWC	35	+1.3	+1.9	
CL/AL/TWC	50	-2.5	-5.9	
CL/AL/TWC	75	+6.1	-4.5	
CL/TWC	35	-5.9	-3.7	
CL/TWC	50	-9.4	-4.3	
CL/TWC	75	-0.3	-2.6	
COC	35	-13.2	-7.2	
COC	50	-6.5	-8.4	
COC	75	-9.8	-9.9	

[a]CL = closed loop, AL = adaptive learning, TWC = three-way catalyst, COC = carbureted with oxidation catalyst.
[b]The oxyfuel effects are normalized to 1 wt % oxygen.

Hood and Farina (1995) reviewed results from a study sponsored by the American Petroleum Institute (Lax, 1994). The study examined the effects of oxygenate and RVP onemissions from an eleven vehicle fleet at 35 °, 55 ° and 80 °F. The 1981 to 1989 MY test fleet was divided into six categories: one - OL/CARB/OC; one - CL/MPFI/OC; two - OL/CARB/TWC; one - CL/CARB/TWC; two - CL/TBI/TWC; and four - CL/MPFI/TWC, where OL = open loop, CARB = carbureted, OC = oxidation catalyst, CL = closed loop, MPFI = multi-port fuel injection, TWC = three way catalyst, and TBI = throttle body fuel injection. The fuel oxygenates included 10% ethanol (3.5 wt % oxygen), 15% MTBE (2.7 wt % oxygen) and 17.1% ETBE (2.7 wt % oxygen). The fleet average CO emission levels were about 5, 7, and 15 g/mi at 80 °, 55 °, and 35 °F, respectively. The fleet fuel effects are summarized in Table 1.7. For CO emissions, the oxyfuel benefits decreased by about a factor of 3 at the lowest temperature, 35 °F, compared to the effects at 55 ° and 80 °F. The HC emissions were consistently reduced by fuel oxygenate by about 3.5% per wt % oxygen at all temperatures except for the high oxygen fuel at 35 °F. The NO_x emissions were generally increased by the addition of fuel oxygenate. No distinct emission benefit of one oxygenate over the others was identified.

Table 1.7 Summary of oxyfuel effects from American Petroleum Institute (Lax, 1994) study [taken from Hood and Farina (1995)].

Temperature (°F)	Oxyfuel Effect per weight % Oxygen[a]					
	2.7 wt % O_x fuels			3.5 wt % O_x fuels		
	CO	HC	NO_x	CO	HC	No_x
35	-1.9	-3.7	-1.4	-1.8	-2.1	+0.9
55	-6.4	-3.4	+2.7	-6.3	-3.4	+2.7
80	-5.7	-3.8	+1.5	-5.6	-3.7	+1.5

[a] These data represent the 13 PSI fuel set.

Hood and Farina (1995) summarize the effects of oxygenates at low ambient temperature as follows: (Note the % benefits have been calculated assuming an average 3.1 wt % oxygen fuel.)

(1) At temperatures of 80 ° to 55 °F there are only small changes in vehicle exhaust emission levels. Vehicles with closed-loop controls experience CO and HC reductions in the ranges 1 to 4.5% per wt % oxygen and 1 to 4.8% per wt % oxygen, respectively. The CO reductions in open-loop control vehicles were greater, from 3.2 to 10% per wt % oxygen.

(2) At temperatures of 55 ° to 20 °F the CO and HC emissions generally increase relative to their levels at 75 °F. The oxygenates reduce CO and HC emissions but the effect on CO (on a percentage basis) is smaller than at 75 °F. Vehicles with closed-loop controls experience CO and HC emission reductions in the ranges 0.6 to 6.5% per wt % oxygen and 0.6 to 3.9%, respectively. Vehicles with open-loop controls experienced CO and HC emission reductions of 0.6 to 8.4% per wt % oxygen and 0.3 to 2.6% per wt % oxygen, respectively.

At temperatures below 20 °F very few data are available. The HC and CO emission rates show large increases of 2 to 6 times higher than at 75 °F. The available data fail to show consistent reductions with added oxygenate.

The reason for the low and sometimes negative oxygenate effects on CO emissions observed at low temperatures has not been identified. This is in contrast to most fuel-emission effects which can be understood in terms of chemical and engineering principles. Doyon *et al.* (1993) have discussed the effects of fuel volatility on vehicle CO and HC emission levels at low temperatures. Generally higher vapor pressure fuels are used during the winter season to compensate for the effect of low ambient temperatures decreasing fuel vapor pressure. It is possible that the oxygen present in the oxygenate is consumed by the excess hydrocarbon in the cooler fuel rich environment encountered at low temperatures. Thus the fuel oxygen oxidizes hydrocarbons to CO rather than oxidizing CO to CO_2. Therefore the oxygenate may enhance CO emissions.

Fuel vapor pressure and fuel sulfur content affect the CO and HC emission levels of vehicles. Mayotte *et al.* (1994a) reported an 11.3% reduction in CO emissions in the ombined normal and high emitting fleet, when the fuel RVP was reduced from 8.3 to 7.6

psi. A large effect of sulfur content on CO emissions was noted by Mayotte *et al.* (1994a) who found a 13.8% reduction in CO emissions in the combined normal and high emitting fleet, when fuel sulfur was decreased from 324 ppm to 112 ppm by weight. An Auto/Oil AQIRP study (Benson *et al.*, 1991) reported 13% CO, 16% HC and 9% NO_x reductions from a ten vehicle, 1989 MY, low emitting fleet, when the fuel sulfur content was decreased from 466 ppm by weight to 49 ppm. Sulfur is known to poison the catalyst thereby reducing its efficiency. Although RVP and sulfur influence the CO emissions of vehicles, their levels are not controlled in most winter oxyfuel areas. Fuel sulfur and RVP are controlled in California.

Other Emissions. Most dynamometer studies report the effects of oxyfuels on pollutant emissions other than CO. An important effect of all oxygenate fuels is achieved through dilution. For example, adding 8 to 15% by volume oxygenate to a base gasoline or blend lowers the benzene concentration proportionately. In some fuels, oxygenates have been used to replace benzene and other aromatics as octane enhancers. Since some emissions are unburned fuel components, the dilution effect directly lowers their levels. On the other hand the unburned oxygenates are found in the exhaust too. Sulfur emissions are also reduced by dilution. Sulfur dioxide can decrease catalyst performance and is a source of secondary atmospheric particles via oxidation to sulfuric acid.

Table 1.2 shows some representative effects of three standard oxygenates on total hydrocarbons and several critical pollutants at 75 °F for a fleet of twenty relatively clean 1989 vehicles. These results can be summarized as follows: The HC emissions generally decrease with added fuel oxygenate. The NO_x emissions increase with fuel oxygenate. Benzene emissions are reduced by fuel oxygenate. The 1,3-butadiene emissions are reduced but not significantly except for the ethanol fuel with the highest oxygenate content. The formaldehyde emission did not change significantly, although most studies find MTBE increases formaldehyde emissions (Hood and Farina, 1995). Acetaldehyde emissions increase greatly with ethanol and ETBE fuels. The data in Table 1.3 show that the effects of oxygenates on HC and NO_x emissions from older, higher emitting vehicles are similar to the effects observed on the clean fleet (Table 1.2).

In general one would expect NO_x emissions to increase with the addition of oxygenate to a fuel. The addition of oxygenate is equivalent to increasing the air/fuel ratio in Figure 1.2. NO_x emissions are found to be less affected by oxygenates at low temperatures (Hood and Farina, 1995). This may be related to the increased HC emissions at lower temperatures. The effects of low temperatures on toxics and other emissions are not well characterized.

In developing the California wintertime oxygenates program, the California Air Resources Board staff evaluated the available data on the effect of fuel oxygen on motor vehicle emissions and concluded that adding levels of oxygen higher than 1.8 to 2.2 wt % to gasoline would lead to NO_x emission increases. They estimated that implementing a wintertime oxygenate program with 2.7 wt % oxygen as specified in the Clean Air Act could increase NO_x emissions by about 4 to 8% (CARB, 1992). The effect of oxygenates on NO_x emissions appears to be nonlinear and is discussed further in the section on "Model Predictions."

Ambient particulate matter concentrations are affected by both direct emissions and by secondary products formed by the atmospheric oxidation of VOC, SO_2, and NQ

emissions. Direct particle emissions from gasoline-fueled vehicles are small and the effect of oxyfuels is not known. The effects of NO_x, VOC and SO_2 on particle formation in the winter urban environment are not well known.

Field Studies

Bishop and Stedman (1989, 1990) used remote sensing to evaluate the effects of oxyfuels on vehicle emissions in Denver, Colorado. At the time of their initial study (Bishop and Stedman, 1989) a 1.5 wt % oxygen fuel was required and the Colorado Department of Health predicted a vehicle CO emission reduction of (11.7 ± 2.5)% using the EPA MOBILE 3 Model. Bishop and Stedman analyzed CO emissions from about 60,000 vehicles at a freeway on-ramp during and after the oxyfuel season. They found a (6 ± 2.5)% reduction in emitted CO that could be attributed to oxyfuel. The vehicles sampled for this result were probably in the hot stable operating mode.

In a second study Bishop and Stedman (1990) analyzed emissions from Denver vehicles at two locations, a freeway on-ramp and an off-ramp before, during, and after the Colorado oxyfuel season, 1 November 1988 through 28 February 1989. During this period Colorado required a 2.0 wt % oxygen fuel. The Colorado Department of Health used the EPA MOBILE 3 Model to estimate a 15.3% reduction in vehicle CO emissions. Bishop and Stedman analyzed more than 117,000 individual measurements of which about 4,900 vehicles were identified by make and model. They reported a decrease in average CO emissions of (16 ± 3)%. They also found that between 7 and 10% of the vehicles were responsible for 50% of the CO emissions. Their results showed that newer vehicles tended to have much lower CO emission levels than older vehicles but the emission levels seemed to level off for pre-1976 vehicles. The CO reduction corresponds to (8 ± 1.5)% per wt % oxygen.

An even more comprehensive remote sensing study in Denver was reported by PRC (1992). In this study the following factors were accounted for: gasoline composition, ambient temperature and pressure, vehicle speed, vehicle age, vehicle emission control technology, and the vehicle operating mode, e.g., cold start vs. hot running modes. A total of about 80,000 measurements were made at three locations, a freeway exit ramp and two parking garages. The study was conducted between October 1991 and April 1992. The fuel from selected in-use vehicles was sampled and analyzed. The Colorado oxyfuel program at this time required 2.0 wt % oxygen in November and 2.6 wt % oxygen in December through February. The study found an average 0.3% oxygen one month before the program, 2.64% oxygen during the program, and 0.4% oxygen about 35 days after the program.

The PRC study found that there was about a 25% reduction in CO emissions and a 14% reduction in HC emissions that could be attributed to oxyfuels at the off-ramp site. The CO reduction corresponds to about -10% CO per wt % oxygen. These vehicles are probably operating in a hot stable mode. When broken down into MY groups, the report concluded that each group receives approximately the same percentage benefit from oxyfuels. The newer vehicles have, on average, lower emissions, so the average reduction in CO mass emission decreases as the average age decreases. Vehicles emitting more than 3.5% CO (3.5% of the total gaseous carbon emissions are CO) were classified as high emitting vehicles. It was found that high emitting vehicles were 3.2% of the 1983 (MY) and newer population and they contribute 33.4% of the CO outside of the oxyfuel program. It was concluded that the 50% of the vehicles emitting the least CO realize very little CO

reduction due to oxyfuel usage and that the 10% of the vehicles that emit the most CO contribute more than half of the total CO and account for most of the reduction realized by oxyfuel use. No significant effect of ambient temperature on emissions from hot stable vehicles was found.

A remote sensing study in Raleigh, NC, was reported by Rhudy *et al.* (1995). The study was made before, during, and after the 1994-95 winter oxyfuel program which requires 2.7 wt % oxygen fuels. Carbon monoxide emission measurements were made on approximately 180,000 vehicles with more than 2,000 individual vehicles measured at least once during each of the three measurement periods. The study found no significant reduction in CO that could be attributed to the oxyfuel program. This finding may be flawed because of the lack of control over important variables, notably the ambient and vehicle operating temperatures. Nevertheless, the conclusion contradicts the findings of all other similar studies. This measurement program is to be continued with improved controls.

A recent field study of oxyfuel emission effects was conducted by Kirchstetter *et al.* (1996) in the Caldecott tunnel in the San Francisco Bay area in August and October, 1994. In this area a 2.0 wt % oxygen fuel is required from 1 October to 31 January. The oxygenates in use were 80% MTBE and 20% ethanol. The pollutant concentrations were measured in August, when the average oxygen content of the fuel was only 0.3 wt % (due to the use of oxygenates as octane boosters), and in October. The vehicles sampled were operating in the hot stabilized mode. The vehicles passing through the tunnel had the following populations: 70% passenger cars, 30% pickup trucks and small vans, and 0.2% heavy duty trucks and buses, during both sampling periods. The typical speeds were 40 to 50 mph on a 4.2% uphill grade. Two potential complications of this study are that the CO emissions were not measured after the winter oxyfuel season and that the slight uphill grade could cause some vehicles to run in a power demand mode with a rich air/fuel ratio. The latter condition would result in an enhanced oxyfuel benefit.

Kirchstetter *et al.* report that during the oxyfuel period, CO emissions were reduced by (21 ± 7)%, VOC emissions were reduced by (18 ± 10)%, benzene emissions were reduced by (25 ± 17)%, NO_x emissions and acetaldehyde emissions did not change significantly, and formaldehyde emissions increased by (13 ± 6)%. The acetaldehyde and formaldehyde effects are consistent with the use of primarily MTBE oxygenate. Speciated profiles are reported for a large number of VOCs. This study reports a substantial CO reduction of 14 to 28% that can be attributed to a 1.7 wt % oxygen fuel or about -(12 ± 4)% CO per wt % oxygen. A study in August 1995 (R. Harley, personal communication, 1996) found the CO emission factor during the non-oxyfuel period was reduced by about 14% compared to the previous August. Based on this the reported CO decrease should be adjusted to about (19 ± 7)%.

The remote sensing and tunnel studies find larger oxyfuel benefits than the dynamometer FTP studies. The reason for this difference may be related to the fact that the remote sensing and tunnel measurements test emissions during the hot stable mode of vehicle operation. Rapp *et al.* (1993) analyzed the effects of certain fuel properties, including oxygenate, on emissions during specific modes of vehicle operation for the same twenty vehicle fleet described in the Auto/Oil AQIRP study by Reuter *et al.* (1992). The HC, CO, and NO_x emissions were measured during nine different operating modes, which are part of the FTP. The results from this analysis could be useful in comparing data from tunnels

and remote sensing, which observe vehicles operating generally in a single mode, with data from the standard emission test, the FTP. The tunnel study by Kirchstetter *et al.* (1996) states that the vehicles travel at steady speeds of 40-50 mph. This range can be compared to results for 30 mph and 55 mph cruise modes, for which oxyfuel benefits of 9.6% and 0.9% CO reduction per wt % oxygen, respectively, were reported by Rapp *et al.* These figures represent the largest and smallest CO benefits found in the study, which is surprising considering the two cruise modes are rather similar. The average effect for the two modes is a 5.4% CO reduction per wt % oxygen, which is 59% larger than 3.4% CO reduction per wt % oxygen reported for the FTP. The 30 mph cruise result of -9.6% CO per wt % oxygen is possibly representative of the urban freeway on/off ramp traffic and is nearly 3 times larger than the FTP benefit. This analysis indicates that the tunnel study (Kirchstetter *et al.*, 1996) and the remote sensing studies (Bishop and Stedman, 1989, 1990; PRC, 1992) may overestimate the oxyfuel benefit compared to the FTP result. However, it should be noted that in the study of Rapp *et al.* (1993), the fleet was a relatively clean and low emitting group of vehicles. It is not reasonable to attempt to quantitatively apply the factors from the vehicle mode study to an on-road fleet.

A comparison also can be made between the tunnel and remote sensing results with the Bag 2 emissions from the hot stable phase of the FTP. Data reported by Hochhauser *et al.* (1991) for the Auto/Oil AQIRP 1989 MY current (low emitting) and older fleets give the ratios of the Bag 2 to the composite (FTP) oxyfuel benefits as 2.10 and 1.14, respectively. These ratios also indicate that the hot stable phase emissions have larger oxyfuel CO reductions than the FTP results shown in Table 1.3. They are increased by 110% for the current fleet and 14% for the older fleet. These factors cannot be applied directly to the tunnel and remote sensing results, but they further indicate that those types of measurements are likely to overestimate the overall oxyfuel benefits.

Summary of Vehicle Emissions Studies

The emission studies reported here are presented as representative examples of efforts to quantify the effects of fuel oxygenates on vehicle emissions. For the purpose of predicting the effect of oxygenate usage on urban air quality, the FTP dynamometer studies provide the most useful available data. These studies measure the emission effects over a range of vehicle operating conditions. Unfortunately these studies have some very important limitations: (1) A relatively small number of vehicles are studied and these are not necessarily representative of the on-road fleet and specifically the fraction that emits the largest amount of pollution. (2) The studies with the best controls on fuel composition, such as the Auto/Oil AQIRP studies, do not necessarily represent the effects of the fuels sold to the consumers in winter oxyfuel areas. Most FTP emission studies seek to isolate the effects of specific fuel parameters known to influence vehicle emissions, such as the concentrations of sulfur, aromatics, oxygenates, olefins, and paraffins as well as volatility factors. In the real world these factors are not controlled individually. In most winter oxyfuel program areas the only significant specification for the fuel is the wt % oxygen. It is known that RVP as well as the concentrations of sulfur and aromatics also strongly influence CO emissions, for example. Therefore the applicability of the fuel parameters derived from the carefully controlled studies reported above to the fuels sold in winter oxyfuel program areas is unproven. (3) The FTP test cycle does not necessarily represent real urban driving conditions. Although the FTP cycle does provide a valuable standard for comparing fuel and vehicle effects, it is not possible that any single standard is appropriate to driving in all cities and conditions. For example, there is tremendous variability possible in factors such as terrain, traffic patterns, traffic speed, traffic

congestion, and travel distance which complicate any attempt to devise a representative driving urban cycle. An extremely important factor that has not been investigated adequately is the effect of low temperatures on oxygenated fuel performance. It is known that the amounts of CO and HC pollutant emissions rise dramatically with decreasing temperature. The few low temperature studies reported indicate that the effectiveness of fuel oxygenate at reducing CO emissions decreases dramatically at low temperatures. Improvements in vehicle technology, specifically air/fuel ratio control and catalyst efficiency, have led to recent generations of vehicles that emit much less pollution. These cleaner cars not only emit much less CO per mile traveled but also have a lower percentage reduction in emissions in response to the use of fuel oxygenate. Therefore these clean vehicles account for a relatively small improvement in air quality, when using oxygenated fuel (PRC, 1992). In a vehicle with a properly functioning oxygen sensor, the feedback control of the air/fuel ratio acts to defeat the purpose of adding oxygenate to the fuel. The vehicles that will benefit the most from oxyfuels are high emitters, generally older vehicles or newer vehicles with broken emission control systems (PRC, 1992).

Some of the important conclusions from vehicle emission studies are as follows:

- Carbon monoxide exhaust emissions from vehicles operating at temperatures of 50 °F and higher are reduced by oxyfuels by about 2 to 10% per wt % oxygen in FTP tests. For most vehicles the reductions are about 3 to 6%. The CO emission reduction is generally smaller in vehicles with newer technology: fuel injected, adaptive learning, closed loop, three-way catalysts; and larger in vehicles with older technology: carbureted, oxidation catalysts. Malfunctioning, high CO emitting vehicles operating fuel rich also experience larger CO reduction benefits from oxyfuels.

- The vehicle emission database at low temperatures is inadequate. Oxyfuel effects on vehicle CO emissions are uncertain at temperatures below 50 °F. Low temperature studies show some benefits down to 20 °F in some vehicles, but generally the results are not conclusive. Some studies report an increase in CO emission with oxyfuels at low temperatures. It has not been demonstrated that oxyfuels will significantly improve air quality at low temperatures.

- Hydrocarbon exhaust emissions from vehicles are reduced by 1 to 7% per wt % oxygen by oxyfuels. Generally the benefits are lower in new technology vehicles and larger in older and higher emitting vehicles.

- Nitrogen oxide exhaust emissions are not changed significantly by low concentrations of oxygenates but some studies show an increase in NO_x emissions with oxygenate concentrations higher than about 2 wt % oxygen.

- Fuel oxygenates decrease vehicle emissions of the toxics, benzene and 1,3-butadiene.

- Fuel oxygenates increase emissions of toxic aldehydes. Ethanol and ETBE increase acetaldehyde emissions by large amounts. MTBE increases formaldehyde emissions.

- Some but not all remote sensing and tunnel studies find a large reduction in CO emissions attributable to oxyfuel use in on-road vehicles. The reported CO benefits are about 10% per wt % oxygen. Since the sampled vehicles are operating in a hot stable mode, this benefit is likely to be larger than the FTP benefit.

- Fuel vapor pressure and sulfur content have been shown to strongly influence CO emissions, but these variables are not employed as a part of the CO emission control strategy in most areas.

MODEL PREDICTIONS

Introduction

The data collected from emission studies are used to develop computer models for predicting pollutant emission levels. The major EPA models for evaluating vehicle emissions and fuels are the MOBILE Model and the Complex Model. The California Air Resources Board (CARB) has developed the CARB EMFAC and Predictive models for similar purposes. The models are used to predict emissions for studies of photochemical ozone and oxidant production, for particle concentrations, and for other ambient air quality issues. An advantage of the models is that they can be used to predict effects such as the changes in vehicle emissions from using an oxyfuel. They give the user a number. The disadvantages are that one has very little sense of the uncertainty in the number or of the most important parameters defining the uncertainty. The parameters that affect the CO emissions from vehicles have been found to be many and complex. The varying effects of vehicle emission control technology, vehicle age and condition, fuel composition, and ambient temperature defy generalization. The ability of any present model to predict reliable emission levels at low temperatures is doubtful, because comprehensive emission data do not exist.

Kirchstetter *et al.* (1996) compared their measured emission rates with some values predicted by the CARB EMFAC7F Model. They compared the mass ratios for CO/NO_x and VOC/NO_x and found that the model agreed well with the observed VOC/NO_x ratio but was low by nearly a factor of two in predicting the CO/NO_x ratio. Unfortunately, few such detailed data sets which examine oxyfuel effects exist for testing the model predictions.

EPA Models

The MOBILE Model is designed by EPA specifically for use by the states in the preparation of the highway mobile source portion of emission inventories required under the Clean Air Act. The MOBILE 5a Model is the standard tool currently available to make fleetwide estimates of the effects of oxygenated fuels for purposes of area-wide inventories. It estimates emission levels in grams of pollutant per vehicle mile (g/mi) under a wide variety of conditions, such as altitude, ambient temperature, average travel speed, operating modes, fuel volatility, mileage accrual rates, and different fleet compositions. It also takes into account the impact of numerous emission control regulations and in-use vehicle emission reduction programs. The model can predict emissions for calendar years 1960 through 2020. Because the model takes into account such a wide variety of conditions and programs over an extended period of time, it accounts for their effects with varying levels of sophistication and accuracy.

The basis for the MOBILE Model series is the on-going Emission Factor testing program conducted by EPA since the early 1970's. In this program, in-use vehicles are solicited from their owners and the emissions of these vehicles are measured in contractor and EPA laboratories. Since 1990, data have also been collected at state run Inspection and

Maintenance (I/M) stations, where vehicles arrive for mandatory, periodic emission inspections. The database derived from these testing programs has been used by EPA to develop estimates of the in-use performance of highway vehicles for use in the MOBILE Models. Some of this analysis has appeared in journals and technical papers (Barth, 1984; Bruetsch, 1981; Becker and Rutherford, 1979; Darlington, 1981; Glover and Brzezinski, 1989; Harvey and Michael, 1985; Lorang, 1984; Lorang *et al.* 1982; Michael, 1981, 1982, 1983, 1984; Montalvo and Hare, 1985; Pidgeon, 1984; Shelton, 1983, 1984; USEPA, 1983, 1984, 1985, 1988).

The adjustments to the basic emission levels estimated in the MOBILE Model to account for oxygenated fuels are fairly simple. These adjustments account for differences in the technologies in the vehicle fleet and the changes in the composition of the fleet in different areas and different calendar years. The model assumes a linear relationship between fuel oxygen level and percent emission benefit for vehicles of any particular baseline (non-oxy) emission level. The linearity constant depends on baseline emission level and vehicle fuel delivery technology. For example, for 1981 and later model years, there are a series of oxygenate benefit/emission level parameters derived from studies of oxyfuel benefits on a fleet of 273 vehicles. These parameters are integrated into MOBILE 5a. A representative series of parameters is given in Figure 1.3. Pre-1981 vehicles have parameters accounting for vehicle age, technology, and CO emission level. The technology factor accounts for the fuel inlet system but does not explicitly identify the exhaust emission control system. The figure shows that the magnitude of the emission benefit per fuel weight % oxygen increases with vehicle emission level reflecting the EPA test programs which found higher benefits on higher emitters and leveling off at the highest emission levels. In general the CO reduction factors are quite large, rising to almost 10% per wt % oxygen at an emission level of about 15 g CO/mi. Few of the emission studies in the previous section indicated a benefit as large as 10% per wt % oxygen.

Since the largest CO reduction benefit is realized by the vehicles with the highest emission levels (g CO/mi), the predicted reduction in fleet CO emissions from oxyfuel usage is weighted heavily toward the high emitter benefit. For example, a "fleet" of 10 vehicles consisting of 9 relatively clean vehicles with an average CO emission level of 4 g/mi and one high emitting vehicle with an emission level of 60 g/mi has a fleet emission level of 96 g/mi. Assuming an average oxyfuel benefit of 5% CO reduction per wt % oxygen for the 9 clean vehicles and a 10.5% CO reduction per wt % oxygen for the high emitter, a 3.1 wt % oxygen fuel is predicted to reduce the fleet CO emission from 96 g/mi to 70.9 g/mi, or -26.1%. Thus the fleet benefit from oxyfuel use is equivalent to an average of 8.4% CO reduction per wt % oxygen, which is much larger than the individual benefit experienced by 90% of the vehicles in the hypothetical fleet.

Because the model predicted reduction in vehicle fleet CO emissions due to oxyfuels is heavily weighted by the effects on the higher emitting vehicles, the distribution of higher emitting vehicles in the fleet population is a critically important factor. Vehicle emission levels are assessed by EPA using the EPA IM240 test. It should be noted that the IM240 test employed to obtain emission data for the MOBILE 5a Model represents vehicles in warm to hot modes of operation, although the IM240 test is intended to be a FTP surrogate. The tests involve vehicles brought in for inspection. Since inspection is not required of new vehicles during the first two years, unless there is a change of ownership, the effects of new vehicles on the emission distribution is presumably accounted for separately. Figure 1.4 shows representative emission measurement data used in the MOBILE 5a Model giving

the percentage of the total fleet emissions versus the percent of the fleet population as diamonds connected by a line. These data represent a fleet with an Inspection/Maintenance Program. The figure shows that the highest emitting 15% of the fleet accounts for about 50% of the CO emissions.

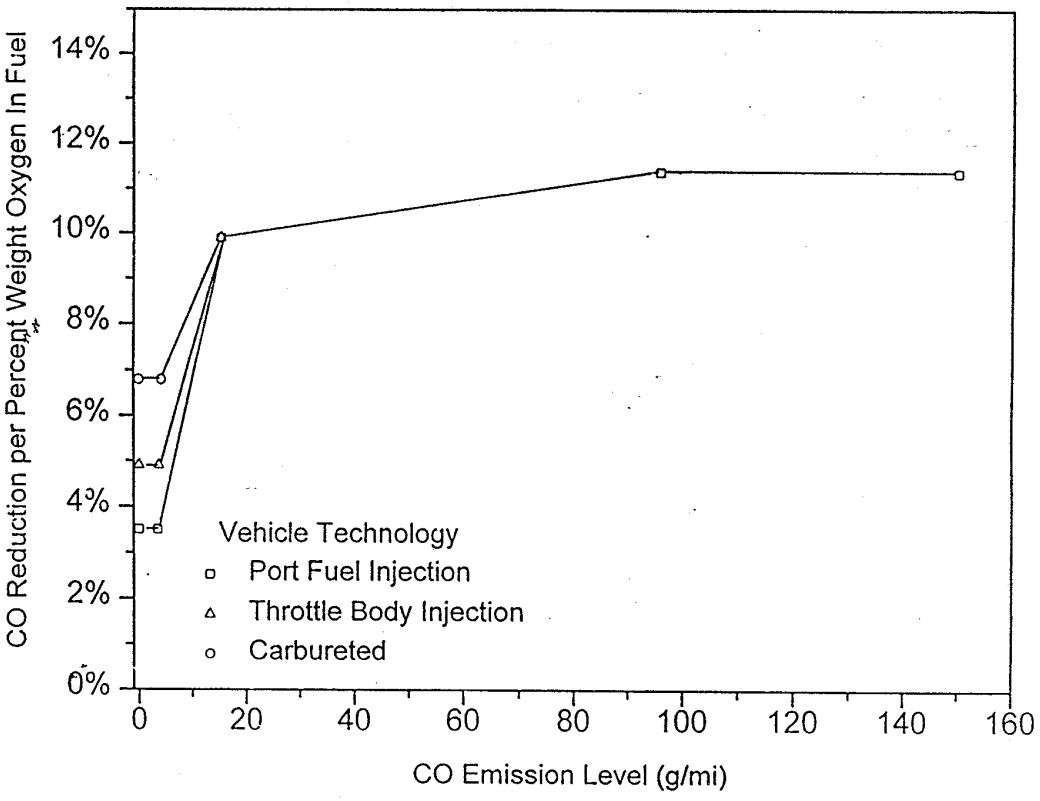

Figure 1.3 This figure shows representative data used as input for the EPA MOBILE 5a Model indicating the percent reduction in CO emissions per percent by weight oxygen fuel versus the vehicle CO emission level. These data are derived from emission studies of 273 1981 and later model year vehicles. At very low emission levels the parameters depend only upon the fuel inlet technology. As the emission levels increase to about 15.3 g CO/mi, the lines merge. The Figure shows that the % CO reduction increases as the emission level increases.

This figure can be compared with results from an analysis of roadside emission tests conducted in California in 1989. Lawson (1993) examined data from low-idle (~1000 rpm) emission measurements of 4,421 vehicles at locations throughout California. The results from his analysis are shown as circles in Figure 1.4. He reports a relatively small fraction of the vehicles, about 10%, accounts for about 62% of the emissions. In general his results show a small fraction of the vehicle population accounts for the bulk of the emissions from vehicles in the idle mode of operation.

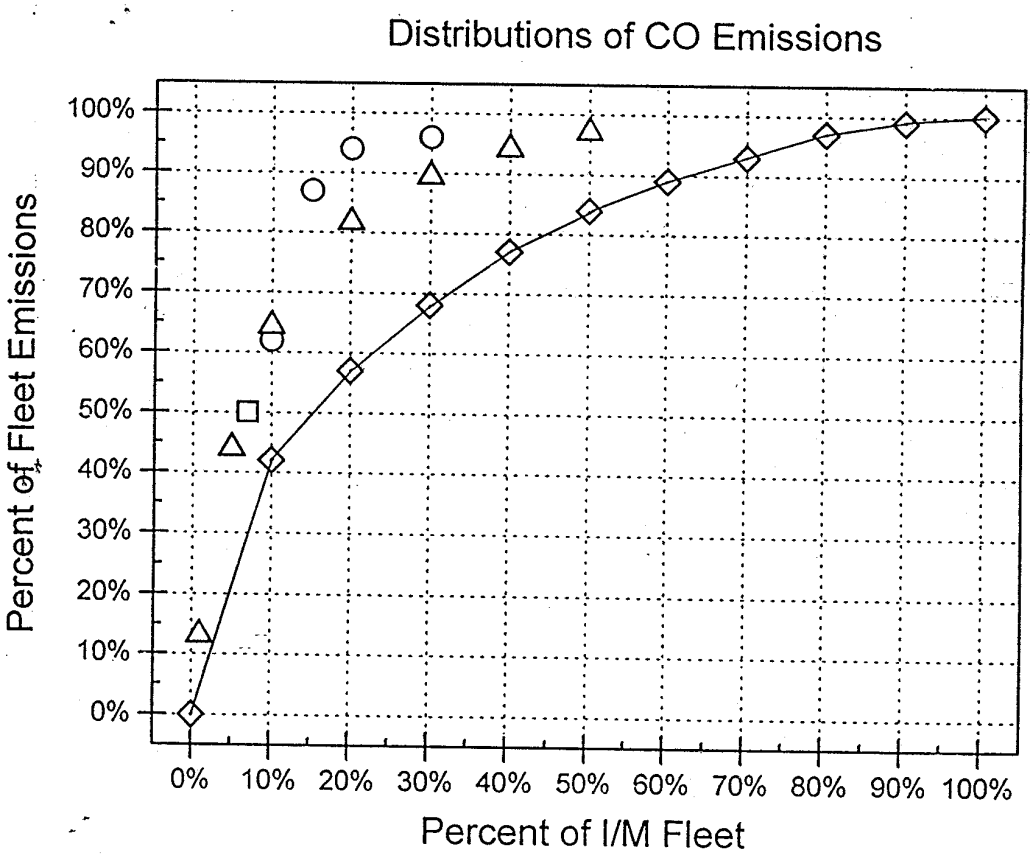

Figure 1.4 The diamonds and line in this figure show a fleet distribution of CO emissions for model years 1976-1993 vehicles. These data represent a fleet with an Inspection/ Maintenance Program. The distribution is based on EPA testing of in use vehicle fleets in Phoenix, AZ and Hammond, IN using a 4 minute transient emission inspection (IM240) developed from the Federal Test Procedure. The symbols O (open circle) represent data reported by Lawson (1993) for 4,421 vehicles inspected in California. The study was conducted in 1989 on vehicles operating in a low-idle mode. The symbols □ (open square) represent data reported by Zhang *et al.* (1995) from remote sensing measurements of about 87,200 vehicles in the U.S. during 1991-92. The vehicles in this study were measured while operating on the road and leaving or entering an urban freeway. The symbols △ (open triangle) represent data reported by Shepard *et al.* (1995) from 17,182 remote sensing on-road measurements in suburban Detroit. (The EPA data are courtesy of J.R. Cook, EPA.)

A similar result was found in a remote sensing study conducted between June 1991 and June 1992 and reported by Zhang *et al.* (1995). They made on-road measurements of operating vehicles in three U.S. cities, Chicago, IL, Denver, Colorado, and Los Angeles, CA. The measurement sites included slight uphill and flat surfaces that were city streets or freeway on-ramps or off-ramps. The results can be summarized as follows: in Chicago 8,733 vehicle tests show 7.5% of the vehicles account for 50% or more of the CO emissions; in Denver 35,945 vehicle tests show 6.7% of the vehicles account for 50% or more of the CO emissions and in Los Angeles 42,546 vehicle tests show 7% of the vehicles account for 50% or more of the CO emissions. The results of these measurements are indicated by the square symbol on Figure 1.4.

A 1992 study in suburban Detroit by EPA and General Motors (GM) produced 23,979, and 17,182 measurements, respectively, of CO emissions using adjacent remote sensors (Shepard *et al.*, 1995). The analysis excluded unidentified vehicles, diesel-fueled vehicles, and heavy duty trucks. The GM group included vehicles from 1964-1993 model years. The distribution of CO emission rates from the GM data set are plotted as triangles in Figure 1.4 for comparison with the other sets. The EPA sensor produced a distribution similar to the GM results. It should be noted that these results as well as those reported by Lawson (1993) and Zhang *et al.* (1995) represent vehicles operating in the hot stable mode and therefore do not account for emissions over the full range of modes covered in the FTP, the EPA standard for vehicle emissions tests. On the other hand, the IM240 test used to produce the data indicated by the line is conducted on hot stable vehicles as well. The measurements made in Chicago and Denver were made on vehicles traveling on urban freeways, while the California measurements were made on an urban street. The agreement among these data sets indicates similar distributions are found in various locations.

Because the remote sensing method employed by Zhang *et al.* (1995) and Shepard *et al.* (1995) is a transient test of a vehicle's emissions, they may not detect some vehicles with high emission levels during other parts of the driving cycle. It is likely that some vehicles emit large amounts of CO in an erratic manner or during certain operating conditions such as a hard acceleration. To the extent that these vehicles qualify as high emitters, they may not be identified as such by the remote sensing technique. This is a weakness of any method that samples emissions for only a single mode of vehicle operation. The effect of this limitation will be to under-represent the population of high emitters in the fleet distribution.

Although the studies by Lawson (1993), Zhang *et al.* (1995), and Shepard *et al.* (1995) do not represent FTP tests, they find similar results for two different modes of operation. The idle and remote sensing distributions indicate a population with a very large fraction of the total CO emissions, about 50%, coming from a small fraction, about 7%, of the vehicles. Because the highest emitting fraction of the fleet tends to receive the greatest benefit from oxyfuels, this distribution indicates a small benefit in terms of grams of CO per mile for most of the vehicle fleet and a large benefit for a small fraction of the fleet. This concept is examined quantitatively in the PRC (1992) report. The EPA emission distribution in Figure 1.4 indicates a population in which about 15% of the vehicles account for about 50% of the emissions. A distribution with too many high emitters will result in an overestimate of the oxyfuel CO reduction benefit when coupled to the emission level data in Figure 1.3. The MOBILE 5a data indicate that the cleanest 50% of the fleet accounts for about 16% of the CO emissions. By contrast the idle and remote sensing studies

indicate that about 50% of the fleet emits less than 5% of the total CO. The difference between the two sets of distributions is significant.

The effect of ambient temperature on vehicle emissions can be predicted with the MOBILE 5a Model. Emission studies have shown that the amount of CO and HC emissions increase with decreasing temperature, particularly the amount contributed by the cold start mode. After a vehicle has warmed up, the fuel inlet and pollution control systems are expected to function nearly the same as at 75 °F, the emission test standard temperature. As the ambient temperature decreases, the time required to reach standard temperature operation increases. At very low temperatures standard operation may not be obtained during the vehicle operation. The MOBILE 5a Model does not include a correction for the effect of temperature on the oxyfuel benefit, because the quantity and quality of low temperature emission data are judged to be inadequate to derive low temperature parameters for the oxyfuel benefits. Therefore, the 75 °F series of oxyfuel parameters, such as those shown in Figure 1.3, are applied to the low ambient temperature emissions levels. The available low temperature data indicate that those parameters will greatly overestimate the CO reduction at low temperatures.

Sample runs were performed with the MOBILE 5a Model for a variety of scenarios to illustrate the predicted benefits of a 3.1 wt % oxygen oxyfuel on vehicle CO emissions. These results are shown in Table 1.8. All of the model runs are representative of the FTP, the EPA standard operating cycle for vehicle emission testing. The emission levels indicate the total amount of CO emission per FTP cycle per vehicle divided by the effective number of miles the vehicle traveled. The predicted oxyfuel benefits are given as the total % reduction and the % reduction per wt % oxygen. The predicted benefits are large, about -28%, and vary little for the different scenarios. The baseline calculations show that the emission levels decrease greatly from 1980 to 1994, but the oxyfuel benefit increases slightly during that period. One might expect an opposite trend, a decreasing benefit with the newer fleets, because the newer technology vehicles generally show less benefit from oxyfuels. The effect of an I/M Program on the CO emission factor is predicted to be substantial, reducing emissions by about 30%, but the oxyfuel benefit on the I/M fleet is still large – 27.8%. The benefits of I/M programs are not the focus of this assessment, but a study by Lawson (1993) was not able to observe an effect of California's I/M Program on reducing tampering or emissions as measured by the idle test. The 35 °F prediction indicates an increased CO emission level as expected. The predicted oxyfuel benefit is not significantly changed, because the MOBILE 5a Model uses 75 °F data for predicting oxyfuel effects at all temperatures.

The 1994 baseline CO emission rate given in Table 1.8, 21 g/mi, is the predicted fleet average. Using this average value, the EPA distribution in Figure 1.4 indicates that more than 50% of the fleet has an emission level of about 14 g/mi or larger. The data in Figure 1.3 show that this corresponds to a predicted oxyfuel benefit of about 10% reduction in CO emission per wt % oxygen. The minimum CO reductions shown in Figure 1.3 are experienced by only about 10% of the MOBILE 5a fleet. The emission distributions indicated by the remote sensing and low idle distributions in Figure 1.3, on the other hand, indicate that about 75% of the fleet is relatively clean, with an average emission level of about 2.8 g/mi, assuming a fleet average CO emission level of 21 g/mi. This emission level is comparable to the Auto/Oil AQIRP 20 vehicle clean fleet the evaluated in Table 1.2. The dirtiest 7% or so of the remote sensing and low idle groups account for about half of the total CO emissions and average about 150 g CO per mile, assuming a fleet average

Table 1.8 MOBILE 5a Model predictions of the effects of 3.1 wt % oxygen oxyfuel on light duty gasoline vehicle CO emissions. (Courtesy of D. Brzezinski, EPA.)

	Emission Level (g/mi)		% Change	
Run Description[a]	**no oxyfuel**	**with oxyfuel**	**Total**	**per wt % oxygen**
1980 Baseline	55.3	40.4	-26.9	-8.7
1990 Baseline	25.4	18.3	-28.0	-9.0
1994 Baseline	21.3	15.2	-29.0	-9.4
1994 with I/M[b]	14.8	10.7	-27.8	-9.0
1994 35 °F[c]	42.8	30.6	-28.6	-9.2
1994 5500 Feet[d]	23.4	16.6	-29.0	-9.4

[a]Unless noted otherwise, the predictions correspond to vehicle operation at 75 °F at sea level and under the Federal Test Procedure.

[b]I/M indicates the effects of a state Inspection/Maintenance Program.

[c]Calculations indicate performance at 35°F.

[d]Calculations indicate performance at an altitude of 5500 feet.

emission rate of 21 g/mi as estimated by the MOBILE 5a Model. The large MOBILE 5a Model predicted CO reduction, 9.4% per wt % oxygen, implies a fleet with a large fraction of vehicles in the high emitting category. This result is not consistent with the fleet emission distributions indicated by the field data (Lawson, 1993; Zhang *et al.*, 1995; Shepard *et al.*, 1995).

The EPA Complex Model for Reformulated Gasoline (RFG) was originally developed in conjunction with Federal reformulated gasoline regulations to elucidate the relationships among individual fuel parameters and pollutant emissions. This model is a compliance model and was developed specifically to identify fuels that would meet the RFG rule requirements for VOC, NO_x, and toxic emission reductions. The VOC and NO_x emissions relate to photochemical air pollution problems, which peak during the summer season. Most of the data on which the Complex Model is based were collected since 1990 on a sample of vehicles selected to be representative of the 1990 model year (mostly fuel-injected) passenger vehicles [Auto/Oil AQIRP 1, 1990; Auto/Oil AQIRP 2, 1991; Auto/Oil AQIRP 6, 1991; Auto/Oil AQIRP 8, 1992; Auto/Oil AQIRP 9, 1992; Mayotte et al, 1994a,b]. These emissions data were collected at typical summertime conditions. The number of high emitting vehicles and the ratio of exhaust and non-exhaust emissions for 1990 model year passenger cars were derived from the MOBILE Model.

The application of the Complex Model to estimating oxyfuel emission effects for the on-road fleet is limited by several factors: (a) The Complex Model is constrained by statute to vehicle technologies which are representative of 1990 model year. (b) The Complex Model emissions data base is for summertime conditions. (c) Carbon monoxide emissions were not a focus of the original Complex Model development. Nevertheless, EPA believes that the Complex Model is a useful tool for estimating the on-road fleet emission effects of oxyfuels for the following reasons (D. Korotney, personal communication, 1996): (1) The Complex Model is based on much of the same data that are considered the most reliable for up-to-date emissions estimates, a sampling of which is described in the above section "CO Emissions." (2) Despite the fact that the Complex Model is constrained to

1990 MY technologies, model years 1986-1991 are represented in its database. EPA estimates that this selection of technologies represents 30 to 50% of the current on-road fleet. (3) The MOBILE 5a Model does not provide estimates of the effects of fuel oxygenate on fleetwide NO_x emissions. EPA believes that the Complex Model is a reliable alternative as discussed below. (4) The Complex Model uses a weighting of the emission effects of normal and high emitting vehicles as a means of representing the emitter class distribution of the in-use fleet. EPA believes this approach allows the very limited data on high emitters to be properly accounted for in the fleet emissions inventory. (5) A carbon monoxide supplement to the Complex Model was developed in 1995 using the same database and statistical regression procedure that was used for the VOC, NO_x, and toxics portion of the model. Thus the Complex Model for CO can be used as a check on the MOBILE Model estimates for CO. (6) Since the Complex Model was built upon a large data set comprised of a wide variety of fuel compositions and vehicles, EPA believes its usefulness for estimating the effect of fuel parameter changes on emission is not limited to RFG.

Table 1.9 summarizes Complex Model predictions of fleetwide exhaust emissions effects for five different oxygenated fuels compared to a base fuel. The fuel parameters for the six fuels are given in the top of the table. The predicted percent changes in emissions normalized to 1 wt % oxygen are given in the bottom part of the table. The mass emissions for the base fuel are also given. There are two notable differences between the MOBILE 5a Model and the Complex Model predictions for CO. The fleet average CO emission, 11.9 g/mi, is about half of that predicted by the MOBILE 5a Model. The Complex Model predicted reductions in CO for the various oxygenate blends are much smaller than those predicted by the MOBILE Model, ranging from about 2 to 4 times smaller. These dramatic differences reflect the effects of improved vehicle technology and the fact that the 1990 technology vehicles do not emit as much CO and do not respond as much to fuel oxygenate as most of the earlier vehicles. In general the fuel effects predicted by the Complex Model are comparable to those reported by Reuter *et al.* (1992) for the 1989 model year group and summarized in Table 1.2. The average CO emission level from the Complex Model is almost five times larger than the Reuter *et al.* study level but the effects of fuel oxygenate are comparable.

The most striking difference between the effects found in Table 1.2 and in some of the other emission studies reviewed here compared to the Complex Model results concerns NO_x, where the emission studies indicate an increase in NO_x emission with fuel oxygenate and the model predicts no effect or a small decrease in NO_x emission. This discrepancy is not as important to the winter oxyfuel program as it is to the Reformulated Gasoline Program, as the latter requires by statute that the NO_x emission can not be increased by RFG. The limited emission studies reviewed here indicate an increase in NO_x emissions when fuel oxygenate is used. This observation is consistent with the expected effect of fuel enleanment as shown in Figure 1.2. The EPA stands behind the accuracy of the Complex Model prediction that fuel oxygen increases do not increase NO_x emissions for this in-use fleet, even for oxygen levels above 2.7 wt % (D. Korotney, private communication). It should be noted that the analysis upon which the Complex Model is based involves a more detailed review of a larger data base. If the addition of oxygenate does not increase fleetwide NO_x emissions, it suggests some effect other than enleanment is influencing the emission. For example, if the oxygenate reduces the combustion temperature or improves the catalyst performance, the simple enleanment effect may not account for the NO_x emission.

A CO emissions model developed by Rao (1996) reports the effects of various fuel parameters on CO exhaust emissions. The database used to develop this model is identical to the database used to develop EPA's Complex Model. Rao's model gives emission effects for both normal and high emitting vehicles, where the high emitters are classified based on total HC emissions. He notes that 29 of the 32 high HC emitters studied would be classified as high CO emitters. The average CO emission for the 32 vehicle high emission group is 31.5 g/mi. For a 3.5 wt % oxygen fuel he finds a 3.3% reduction in CO

Table 1.9 Complex Model predictions of the effects of MTBE and ethanol oxygenated fuels on on-road fleet exhaust emissions. (Courtesy of D. Korotney, EPA.)

	Fuel Parameters					
		A	B	C	D	E
Fuel	**Base**	**15% MTBE**	**15% MTBE + d[a]**	**10% EtOH + R[a]**	**10% EtOH + R + d[a]**	**10% EtOH + d[a]**
Wt % O_x	0.0	2.7	2.7	3.5	3.5	3.5
Sulfur (ppm)	324	324	276	324	291	291
RVP (psi)	10.6	10.6	10.6	10.6	10.6	11.6
E200 (%)	47.3	47.3	55.1	47.3	52.6	52.6
E300 (%)	82.3	82.3	84.9	82.3	84.1	84.1
Aromatics (Vol. %)	30.6	30.6	26.6	30.6	27.8	27.8
Olefins (Vol. %)	13.4	13.4	11.7	13.4	12.3	12.2
Benzene (Vol. %)	1.35	1.35	1.18	1.35	1.23	1.23

Fuel	**Base**	**A**	**B**	**C**	**D**	**E**
Emission	**Mass Emissions (g/mi)**	**Percent Changes (Per wt % Oxygen)**				
CO	11.9	-4.4	-2.7	-2.7	-3.6	-2.2
VOC	0.46	-2.6	-0.4	-0.4	-1.6	-0.6
NO_x	0.68	-0.9	-0.004	-0.003	-0.5	-0.3
Benzene	0.024	-8.5	-4.1	-4.0	-6.4	-6.4
1,3-Butadiene	0.0048	-7.1	-2.8	-2.7	-5.0	-5.0
Formaldehyde	0.0046	+6.0	+4.9	0.0	+0.5	+0.5
Acetaldehyde	0.0023	-3.7	-2.9	+40	+39	+40

[a] d = effect includes dilution, R = RVP is controlled.

per wt % oxygen for normal emitters and a 1.8% reduction for high emitters. The reason for the smaller reduction in CO emission found in high emitting vehicles is not identified and is the opposite of the effect shown in the MOBILE 5a Model benefits shown in Figure 1.3. Rao's model also indicates that reducing fuel sulfur from 339 ppm by wt to 139 ppm decreases CO emissions by 9.6% and 8.0% in normal and high emitters, respectively. This effect is comparable to what is predicted for standard levels of fuel oxygenate, 2.7-3.1 wt % oxygen. It should be noted that this model is applicable to nominal 1990 MY technology vehicles.

Summary of Model Predictions

Models are used to provide inventories of urban vehicle emissions and to assess the effects of fuels and vehicles on urban air quality. Studies of on-road vehicle emissions and urban air quality data have identified discrepancies between the model predictions and the observations [Pierson *et al.*, 1990; Fujita *et al.*, 1992; Cadle *et al.*, 1993; Lawson, 1993; Pierson, 1995; Kirchstetter *et al.*, 1996; Pierson *et al.*, 1996; Robinson *et al.*, 1996]. These studies can lead to refinements in the models. Accurate models require vehicle emission data that are representative of the on-road vehicle fleet, of realistic urban driving patterns and conditions, and of the fuels used by consumers. The previous section of this chapter has shown that the data required to predict the temperature effects of the winter oxygenated fuel program are inadequate. Although the models are critically important to air quality programs such as the winter oxygenated fuel program it seems that few critical tests are devised to evaluate the accuracy or reliability of the model predictions.

The predictions of fuel oxygenate effects on fleetwide CO emissions from the MOBILE 5a Model and the Complex Model can be compared. The CO emission reduction predicted by the MOBILE Model is three times larger than the Complex Model prediction, 9.4% per wt % oxygen compared to a 3.1% average for five different oxygenated fuels. The emission data reviewed here indicate that the MOBILE 5a Model significantly overestimates the oxyfuel effect on CO emissions. The differences between the MOBILE and Complex Model predictions can to some extent be attributed to vehicle emission control technology, since the latter model is focused on newer technology vehicles. The MOBILE 5a Model, however, does not show a significant change in predicted oxyfuel effects from 1980 to 1994.

Some of the important conclusions regarding model predictions can be summarized as follows:

- The EPA MOBILE 5a Model appears to significantly overestimate the benefits of oxyfuels on fleetwide CO emissions. The model predicted benefit for high emitters is very large and the fleet distribution has a large population of high emitters.

- The EPA Complex Model estimates a fleetwide reduction in CO emissions that is about one third of the value predicted by the MOBILE 5a Model. The Complex Model is focused on 1990 model year technology representing vehicles with lower CO emission levels and smaller oxyfuel CO reductions than the MOBILE Model.

- The EPA Complex Model estimates a negligible effect of fuel oxygenate on fleetwide NO_x emissions at oxygenate levels up to 3.5 wt % oxygen. This estimate does not agree with the conclusion drawn from the emission studies reviewed in this assessment, but is based upon an analysis of a larger data set.

- No existing EPA model is capable of accurately predicting oxyfuel effects at temperatures below about 50 °F. The emission data available for assessing the effects of low temperature on oxyfuel performance is inadequate and has not been incorporated into the MOBILE 5a or Complex Models.

- Much of the data upon which the EPA MOBILE 5a Model is based have not been published in the peer-reviewed literature.

AMBIENT AIR QUALITY EFFECTS OF OXYFUELS

Introduction

In this section the effects of the winter oxyfuel program on ambient air quality are assessed. Because the oxyfuel program is intended to improve air quality by reducing the ambient concentration of CO, its direct effect on air quality is the most important measure of the program's effectiveness. The EPA MOBILE 5a Model is the instrument used by the states to predict the CO reduction expected from oxyfuel use within the oxyfuel program areas. Recognizing the limitations of the model, it is the standard against which the observed changes in ambient CO concentrations will be compared. The urban areas with oxyfuel programs during the winter of 1995-6 as well as the areas that are considering redesignation or are not continuing the program are listed in Table 1.10. It can be seen that all of the geographical regions of the U.S. are represented. In spite of the fact that many areas are or have been involved in the winter oxygenated fuel program, relatively few studies have been reported that attempt to measure the effect of the program on air quality.

The target pollutant of the program is CO, but it is possible that other air pollutants such as NO_x, VOCs, toxics (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter), particles and ozone are also affected. All of these materials, except ozone, are directly emitted by vehicles. Some particles grow or are formed from primary and secondary pollutants such as SO_2, sulfuric acid, NO_x, nitric acid, and polar organic compounds. In some cases these pollutants are produced by the oxidation of the primary vehicle emissions. Other sources besides motor vehicles also contribute these pollutants to the urban atmosphere.

Winter Photochemistry

The approximate lifetimes for the toxics and the oxyfuel components in the urban atmosphere during the winter months are of interest in considerations of the air quality effects. Removal of atmospheric contaminants occurs by several mechanisms including OH-radical attack and direct photodecomposition during the daylight hours, NO_3-radical attack at night, and by dry and wet deposition. For most of the pollutants considered here, the first process, OH-attack, is often the most important (Atkinson, 1994).

Unfortunately, no measurements of urban OH radical concentrations during wintertime are available. For the purpose of estimating an approximate upper limit to the amount of winter photochemistry, a crude analysis is made using the available information. These estimates are intended to represent a reasonable upper limit of winter urban photochemistry and therefore are not intended to be representative of the average level of photochemistry, which is likely to be very low and negligible in areas other than the southern latitudes. It should be noted that the estimates given here are different from the estimates given in the chapter on Water Quality, where lifetimes are calculated based on the global average OH concentration, and not a winter urban scenario.

The rate coefficients for the gas-phase reactions of the OH radical with the pollutants (Atkinson, 1994) can be combined with estimated ambient OH radical concentrations to obtain an estimate of the pollutant lifetimes. It is expected that during wintertime the ambient OH radical concentrations will decrease markedly with increasing latitude because

Table 1.10 Areas with winter oxygenated fuel programs in 1995; Areas considered for redesignation for 1995; and Areas previously redesignated.

Areas with Oxygenated Fuel Programs		
Area	Control Period	Fuel Type
New York/No. NJ./Connecticut	10/1 - 4/30	2.7 RFG
Minneapolis/St. Paul, MN	10/1 - 1/31	2.7±
Albuquerque, NM`	11/1 - 2/28	3.1
El Paso, TX	11/1 - 2/28	2.7
Colorado Springs, CO	11/1 - 2/28	3.1
Denver/Boulder, CO	11/1 - 2/28	3.1
Ft. Collins, CO	11/1 - 2/28	3.1
Missoula, MT	11/1 - 2/28	2.7
Provo/Orem, UT	11/1 - 2/28	2.7
Las Vegas, NV	10/1 - 2/28	3.1
Reno, NV	10/1 - 1/31	2.7
Phoenix, AZ	10/1 - 2/28	3.1
Los Angeles, CA	10/1 - 2/28	2.0 RFG
Chico, CA	10/1 - 1/31	2.0
Modesto, CA	10/1 - 1/31	2.0
San Diego, CA	11/1 - 2/28	2.0 RFG
Sacremento, CA	10/1 - 1/31	2.0
San Francisco, CA	10/1 - 1/31	2.0
Stockton, CA	10/1 - 1/31	2.0
Anchorage, AK	11/1 - 2/28	2.7±
Grant's Pass, OR	11/1 - 2/28	2.7±
Klamath Co., OR	11/1 - 2/28	2.7±
Medford, OR	11/1 - 2/28	2.7±
Portland, OR /Vancouver, WA	11/1 - 2/28	2.7±
Seattle, WA	11/1 - 2/28	2.7±
Spokane, WA	9/1 - 2/28	2.7±

Areas considering redesignation or that will not implement oxygenated fuel programs		
Area	**Control Period**	**Fuel Type**
Baltimore, MD	11/1 - 2/28	2.7% RFG Area
Boston, MA	11/1 - 2/28	2.7% RFG Area
Raleigh-Durham, NC	11/1 - 2/28	2.7% RFG Area
Hartford, CT	11/1 - 2/28	2.7% RFG Area
Philadelphia, PA	11/1 - 2/28	2.7% RFG Area
Washington, DC	11/1 - 2/28	2.7% RFG Area
Fairbanks, AK	11/1 - 2/28	2.7%
Salt Lake City, UT	11/1 - 2/28	2.7%

Oxyfuel areas previously redesignated	
Area	**Date of Redesignation**
Greensboro, NC	Sept. 2, 1994
Raleigh-Durham, NC	Aug. 1, 1995
Syracuse, NY	Sept. 23, 1993
Cleveland, OH	Feb. 5, 1994
Duluth, MN	April 14, 1994
Memphis, TN	July 26, 1994

of the reduced intensity and duration of sunlight. Goldstein *et al.* (1995) deduced a summer/winter ratio for OH concentrations of about 9 ± 2 at northern mid-latitudes. Indirect measurements in the downwind portion of the Los Angeles basin in late October 1994 (Gupta, 1995) suggest a 12-hr average daytime OH radical concentration of approximately 1 x 10^6 molecule cm^{-3} (to within a factor of 2-3). It appears that a 24-hr average OH radical concentration in the Los Angeles air basin of around 5 x 10^5 molecule cm^{-3} is a reasonable wintertime limit. Significantly lower OH concentrations are expected in the winter months of December and January. For comparison this value is a factor of 2 lower than the global average tropospheric OH concentration (diurnally, seasonally and annually averaged) of Prinn *et al.* (1995). The OH radical concentrations for cities at higher latitudes are expected to be lower than this value for Los Angeles. For Denver we estimate the winter average OH is a factor of 2 to 5 times lower than the Los Angeles value. With rate constants (cm^3 $molecule^{-1}$ s^{-1} units) for MTBE (2.9 x 10^{-12}), ETBE (8.8 x 10^{-12}), ethanol (3.3 x 10^{-12}) and TAME (5.5 x 10^{12}) at 298 K (the rate constants are not very temperature dependent), the corresponding lifetimes for a 24-hr average OH radical concentration of 5 x 10^5 molecule cm^{-3} are: 8 days for MTBE, 2.6 days for ETBE, 7 days for ethanol and 4 days for TAME. The lifetimes for Denver are estimated to be 2 to 5 times larger than these values. These lifetimes are sufficiently long that the photochemistry of these fuel oxygenates can to a first approximation be neglected. Their fate will be transport out of the urban region and oxidation in the free troposphere. During a 1-day time period, about 12% of the MTBE will react with OH at a radical concentration of 5 x 10^5 molecule cm^{-3}. At higher latitudes, the lifetimes are longer and the photooxidation even less significant.

The products of the gas-phase oxidation of MTBE, ETBE, ethanol and TAME have been investigated at room temperature and atmospheric pressure (Atkinson, 1994, and references therein; Smith *et al.*, 1995). The reaction of MTBE with the OH radical in the presence of NO leads to the formation of *tertiary*-butyl formate (with a 76% yield), formaldehyde, methyl acetate and acetone (Atkinson, 1994 and references therein), ETBE reacts to form *tertiary*-butyl formate, *tertiary*-butyl acetate, ethyl acetate, acetone, acetaldehyde and formaldehyde (Atkinson, 1994, and references therein). Ethanol reacts to form mainly acetaldehyde plus a small amount of formaldehyde and glycolaldehyde (Atkinson, 1994); and TAME reacts to form *tertiary*-amyl formate, methyl acetate, acetaldehyde, acetone (minor), formaldehyde, and a number of other organics and organic nitrates in low yield (Smith *et al.*, 1995).

These products of the tropospheric degradations of the oxygenates are expected to react with the OH radical and, for formaldehyde, acetaldehyde and acetone, to photolyze (Atkinson, 1994, and references therein; Smith *et al.*, 1995). Rate constants for the gas-phase reactions of the OH radical with these products have been measured (Atkinson, 1989, 1994, and references therein; Smith *et al.*, 1995). Based on these OH radical reaction rate constants, the calculated lifetimes of *tertiary*-butyl formate, methyl acetate and *tertiary*-butyl acetate are >30 days at a 24-hr average OH radical concentration of 5 x 10^5 molecule cm^{-3}; the calculated lifetimes of ethyl acetate and *tertiary*-amyl formate are 14 days and 4 days, respectively, for the same OH radical concentration. Formaldehyde, acetaldehyde and acetone also undergo photolysis (Atkinson *et al.*, 1992), with photolysis being calculated to dominate over the OH radical reaction for formaldehyde, to be of similar importance as the OH radical reaction for acetone, and to be less important than the OH radical reaction for acetaldehyde. The lifetimes of acetone and acetaldehyde are expected to be approximately 50 days for acetone and 1.4 days for acetaldehyde, for a 24-hr average

OH radical concentration of 5 x 10^5 molecule cm^{-3}. For formaldehyde, the photolysis lifetime at zenith solar angles of 40 to 70 degrees range from about 5 to 16 hours (Rogers, 1990). Hence, apart from formaldehyde and acetaldehyde which are also emitted in vehicle exhaust and are photooxidation products of other fuel VOCs (Atkinson, 1994), the reaction products of the oxygenates MTBE, ETBE and TAME are fairly long-lived under wintertime conditions.

Concentrations of MTBE averaging about 4 ppb have been measured in the summer in Los Angeles, CA (B. Zielinska, personal communication). Goldan *et al.* (1995) measured MTBE concentrations in Boulder, Colorado of up to about 10 ppb and averaging around 2 ppb during February 1991. In both cases the ambient MTBE can be attributed to an oxygenated gasoline source. Using the OH radical concentration of 5 x 10^5 molecule cm^{-3} averaged over a 24-hr period, and neglecting losses of the products with the OH radical, the amount of *tertiary*-butyl formate formed from 4 ppb MTBE over a 1-day period is about 0.4 ppb.

The lifetimes of the oxygenates and their atmospheric reaction products depend largely on the ambient OH radical concentration, for which no direct data are available during wintertime months and which can not be accurately estimated. Based on an estimated 24-hr average OH radical concentration of 5 x 10^5 molecule cm^{-3} for the Los Angeles area suggests that the lifetimes of MTBE, ETBE, ethanol and TAME due to chemical reaction range from a few days to a week or so, and that advection out of the urban area will dominate over chemical reaction. In fact, the physical loss processes of wet and dry deposition to the Earth's surface may also be significant for these oxygenates. The atmospheric reactions of these oxygenates are calculated to lead to low concentrations of reaction products in the urban environment. For example, the formation of approximately 0.4 ppbv of *tertiary*-butyl formate is estimated over a 1-day time period from MBTE at previously measured ambient MTBE concentrations of about 4 ppbv. Winter photochemistry is even less significant at northern latitudes, for example, in Denver it is likely to be negligible during the winter oxyfuel season.

Trends in Ambient CO

The EPA reports regularly on the national trends in air quality. The report for 1994 trends (USEPA, 1995b) gives the 20-year record shown in Figure 1.5 which indicates a decline of about 60% in the second 8-hour maximum concentration during the 1975-1994 period. During the past 10 years average CO concentrations have decreased about 28% (USEPA, 1995a).

The decline in ambient CO concentrations has had a remarkable effect on the number of exceedances of the EPA 8-hour 9 ppm standard. Table 1.11 shows a count of the number of exceedances during the period from 1985 to 1994. The drop in the number of exceedances during the past 10 years is even more dramatic than the decrease in CO levels, having decreased by over a factor of 10. It should be noted that this is not a count of all of the recorded CO exceedances of the 8-hour standard. The only selection criterion for this count was that to be included a station must have a full 10-year record of data. Table 1.12 gives an accounting of all of the stations reporting exceedances in 1993 and 1994. During this period the number of exceedances seems to have leveled off. This may be due in part to weather conditions, such as temperature inversions, which can strongly influence the frequency of exceedances. There is also the effect of increasing vehicle miles traveled counteracting the reduction in CO emissions per mile. The data in Figure 1.1 may also indicate this effect of the leveling off of the decline in recent years.

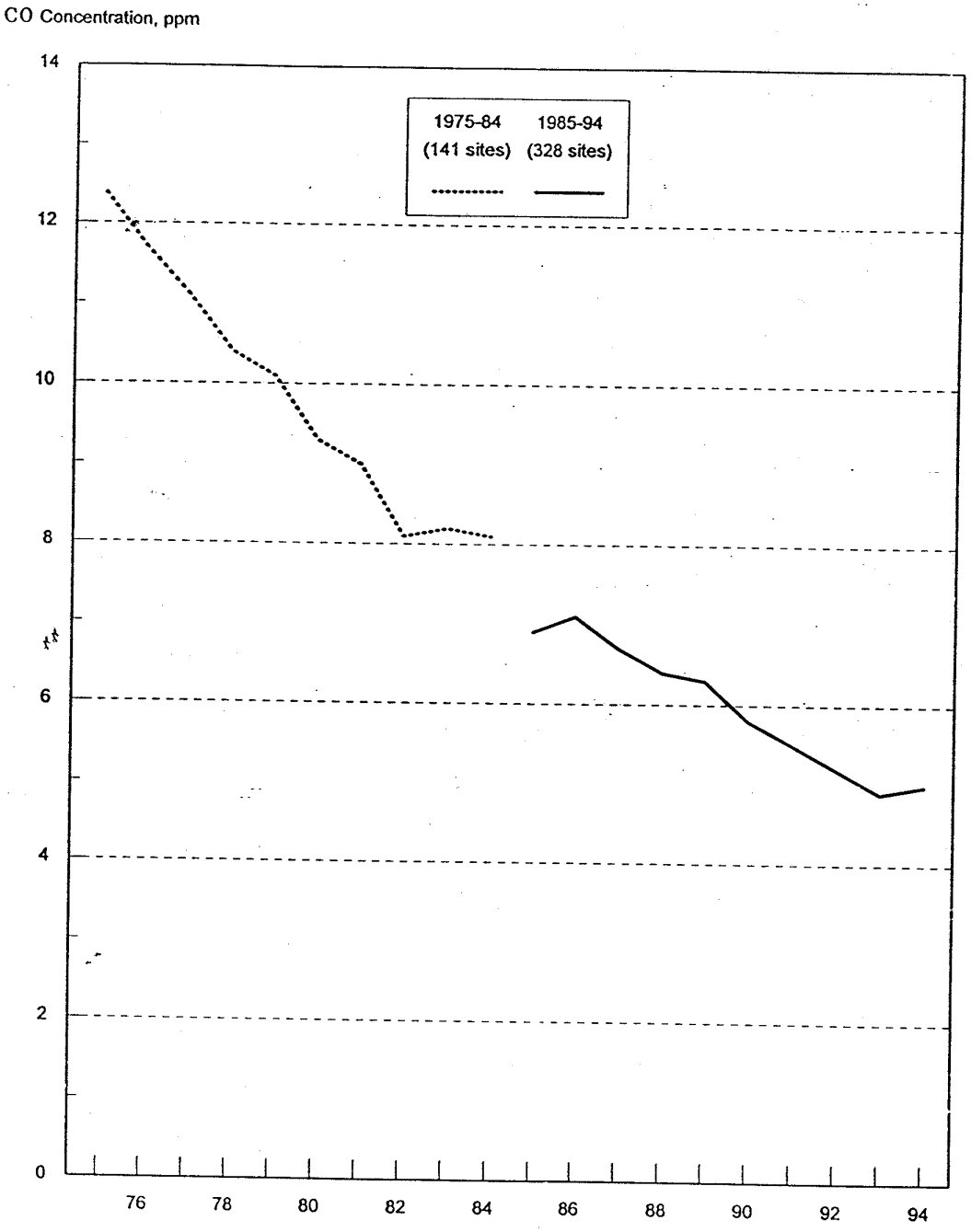

Figure 1.5 Twenty-year trend in CO second maximum 8-hour concentration (USEPA, 1995b). The break in the line around 1984 is due to a change in the number of monitoring sites.

Table 1.11 Count of the total number of exceedances of the 9 ppm 8-hour standard from the 1985-1994 record of all urban stations.*

Year	85	86	87	88	89	90	91	92	93	94
No. of exceedances	778	690	429	359	373	215	125	69	38	60

*Only stations with a full 10-year record (277 stations) are counted. Most urban areas have several stations so it is possible that single exceedance events are counted more than once. The purpose of this table is to show the general 10-year trend.

Since an exceedance involves a 9-ppm concentration threshold, the decline in urban CO concentrations has steadily moved many urban peak values below this limit. EPA data show that the decrease in CO occurred in suburban and rural areas as well (USEPA, 1995b). Because motor vehicles account for most of the CO emissions, it is reasonable to attribute the decline in CO to improvements in vehicle technology in response to the EPA mandated standards in vehicle emissions. The decline started well before the period of oxyfuel usage, which generally began in 1992 and has been limited mostly to winter months.

Table 1.12 Count of all reported exceedances* of the 8-hour 9 ppm standard reported by about 550 urban stations in 1993 and 1994.

Area	**1993**	**1994**
Los Angeles, CA	22	38
Fairbanks, AK	8	7
Imperial, CA	—	10
Steubenville, OH / Weirton, WV	4	7
Las Vegas, NV - AZ	3	5
Anchorage, AK	4	2
Denver, CO	4	4
El Paso, TX	3	1
Phoenix - Mesa, AZ	0	6
Jersey City, NJ	0	3
Newark, NJ	0	2
Detroit, MI	0	2
Provo - Orem, UT	2	1
Miscellaneous	6	8
Total	56	93

*This is not a count of violations, because each area is allowed one exceedance per year and because single events may have been counted by more than one station within an area. Note the Imperial, CA monitor was not in operation in 1993 but accounted for 10 exceedances in 1994.

Since the oxyfuel program was initiated to improve air quality and specifically to reduce winter ambient CO levels, one may expect to find a quantitative improvement in CO air

quality that can be attributed to the use of oxygenated fuels. One way to assess the effects of oxygenate fuel additives on ambient air quality is to compare records of measurements made before, during, and after periods of oxygenate usage. Unfortunately such a straightforward analysis is complicated by a number of factors acting to introduce variations in ambient CO concentrations.

Meteorology in general is the single most significant variable with which one must contend to measure the effectiveness of the program using ambient data. Temperature inversions are a major contributor to the winter buildup of CO. Therefore the frequency and duration of inversions are important variables affecting winter air quality measurements. Lower temperatures cause a large increase in vehicle emissions. The data in Table 1.8 show that the average CO emission from vehicles doubles when the temperature drops from 75 °F to 35 °F. In evaluating records from urban monitoring stations, other variables may also interfere with the analysis. As described above there is a long-term downward trend in CO over the last decade or so that is attributable to EPA mandated exhaust emission standards, reduced vehicle emissions and a turnover in the vehicle fleet. This trend is being counteracted by a steady increase in vehicle miles traveled, driven by increasing populations and numbers of vehicles. Measurements at specific monitoring sites may be affected by local changes in traffic patterns, by rerouting streets and freeways, and even by changes in traffic light sequencing.

One factor favoring an observable reduction in ambient CO levels is that the predictions indicate a large effect. The MOBILE 5a Model predicts a reduction in CO emissions of about 9.4% per wt % oxygen as shown in Table 1.8. The EPA Air Quality Trends report (USEPA, 1995a) states that in cities automobile exhaust can contribute as much as 95% of all CO emissions and that transportation sources account for 78% of the nation's total CO. The Colorado report on the oxygenated gasoline program (Livo and Miron, 1995) states that mobile source emissions contribute approximately 80% of the total CO emissions in the Colorado Front Range inventories. Thus a factor of (80 ± 10)% seems reasonable for the fraction of winter urban ambient CO contributed by gasoline-fueled vehicles. The MOBILE 5a predicted emission benefit of 9.4% reduction in CO emission per wt % oxygen reduces to an ambient benefit of about 7.5% CO reduction per wt % oxygen. Based on this prediction the 3.3 wt % oxygen fuel used in Colorado would reduce ambient CO by about 24%. To indicate the magnitude of this change, a bar is added to the ambient CO data in Figure 1.1 above the year 95. The top of the bar shows the concentration of CO that would have been experienced without oxyfuel, assuming oxyfuels did reduce ambient CO by 24%. Such a large effect should be readily observable in the ambient CO record, in spite of the confounding effects of meteorology and trends.

California Studies

The state of California has experienced some of the most serious air quality problems due in part to motor vehicle pollution. In the winter of 1992-3 California implemented a modified version of the EPA mandated winter oxyfuel program to reduce ambient CO concentrations. The California oxyfuel program was modified to reduce the required oxygen content from the EPA mandated 2.7 wt % oxygen to 1.8 to 2.2 wt % oxygen, because of possible effects of oxyfuel usage on NO_x emissions (CARB, 1992). Eight metropolitan areas were classified as non-attainment because of CO violations. The winter oxyfuel period for these areas generally fall within the months from October through February.

Dolislager at the California Air Resources Board (CARB) has developed and applied methods of analyzing ambient air quality data to examine the effects of the oxyfuel program on CO concentrations. In his first study (Dolislager, 1993) ambient air quality data in four metropolitan regions, Concord, San Jose, and Vallejo in the San Francisco Bay Area Basin; North Long Beach, Lynwood, and Los Angeles in the South Coast Air Basin; El Cajon in the San Diego Air Basin; and Stockton and Bakersfield in the San Joaquin Valley Air Basin, were analyzed. It was noted that the air quality in the 1992-3 winter, which was the first oxyfuel season, was greatly improved over previous years, for example, CO was reduced over 30% compared to the 1991-2 winter. However it was also noted that the weather in 1992-3 was unusually wet compared to the previous winters and that wet weather is accompanied by greater atmospheric mixing and dispersion. In an effort to eliminate the effects of meteorology, Dolislager developed an analysis in which the ambient concentrations of hydrocarbons (HCs) and nitrogen oxides (NO_x) are used as atmospheric tracers. Like CO, the winter urban HC and NO_x come mainly from vehicle exhaust. By assuming that the HC and NO_x emissions were not significantly changed by the use of oxyfuels, their ambient concentrations provide an independent indication of the effects of meteorology on air quality. Thus changes in ambient CO relative to these tracers give a measure of the effect of oxyfuel usage. Trends in the CO, HC, and NO_x concentrations from the prior winters of 1985-6 through 1991-2 were determined and incorporated into the analysis. The results based upon the HC tracer were somewhat more variable than those based upon the NO_x tracer. Hydrocarbon emissions are found to be reduced by fuel oxygenate in most emission studies, so they are not expected to be a reliable tracer. Some reduction of CO was found in all four air basins studied. The author concluded that the California 1992-3 winter oxyfuel program accounted for a 6 to 10% reduction in ambient CO.

In a subsequent report Dolislager (1996) made a similar analysis of the effect of the winter oxyfuel programs from 1992-3 through 1994-5 based on data from the following monitoring sites: San Jose and Vallejo in the San Francisco Bay Area Basin; Anaheim, Burbank, Costa Mesa, Hawthorne, La Habra, Los Angeles, Lynwood, Pasadena and Reseda in the South Coast Air Basin; Sacramento in the Sacramento Valley Air Basin; Fresno, Modesto and Stockton in the San Joaquin Valley Air Basin. The CO data showed reductions of about 30, 10, and 35%, respectively, for these three oxyfuel winter periods compared to earlier years. NO_x was used as a tracer of the confounding effect of meteorology. From this analysis he concluded that a 5 to 10% reduction in ambient CO could be attributed to the usage of oxyfuel. The accuracy of the analyses reported by Dolislager is heavily dependent upon the assumption that the NO_x emissions are not affected by the 2% by weight oxygen in the fuel. If the fuel oxygenate increases NO_x emissions, he will overestimate the CO effect but if NO_x emissions are decreased he will underestimate the benefit. The tunnel study by Kirchstetter *et al.* (1996) supports this assumption for vehicles operating in the hot stabilized mode. A study by Born *et al.* (1994) also finds the effect of oxyfuels (at the 2 wt % oxygen level) on NO_x emissions is small in California vehicles. On the other hand, there does appear to be a significant change in HC and VOC emissions that can be attributed to the use of oxyfuel (PRC, 1992; Kirchstetter *et al.*, 1996; Born *et al.*, 1994). The 5 to 10% reduction in ambient CO by Dolislager corresponds to an oxyfuel benefit of 2.5 to 5% per wt % oxygen.

CDC Study of 11 Western States

Mannino and Etzel (1996) published a study evaluating ambient CO concentrations in 11 western states. They analyzed data from 62 monitors for the period 1986 through 1992. The data set included five areas with winter oxyfuel programs from two seasons up to five

seasons: Phoenix (3) and Tucson (2), AZ; Las Vegas (3) and Reno (3), NV; and Colorado (5), where the number in parenthesis indicates the number of oxyfuel seasons. The oxyfuels in use in these areas ranged from 1.5 to 2.7 wt % oxygen. The data set also included areas outside of the oxyfuel areas as a control for comparison. Summer (May through August) as well as winter (November through February) periods were analyzed to test for trend effects. Hourly CO concentration data were analyzed to determine the changes in the mean daily CO concentration, the 1-hour maximum daily CO concentration, and the 8-hour maximum daily CO concentration. Analyses for the effects of temperature and wind were also made. The analyses found that the winter season mean daily ambient CO concentration in areas not using oxyfuels was reduced by (10.3 ± 11.5)% in 1989-91 compared to 1986-88. For the same period, the areas with an oxyfuel program showed a decrease in mean daily CO of (20.5 ± 7.9)%, where the uncertainties represent one standard deviation. The net reduction in mean daily CO concentration that can be attributed to oxyfuel usage is about 10%. The amount of oxygenate in the oxyfuels used ranged from 1.5 to 2.7 wt % oxygen, the average being 2.3 wt % oxygen. The observed decrease in ambient CO found in this study is therefore about 4.3% per wt % oxygen.

Colorado, Arizona , New Mexico, and Nevada Studies

The state of Colorado has the longest term oxyfuel program. It started as a two-month program in January 1988 with a 1.5 wt % oxygen additive and an EPA MOBILE Model predicted 12% reduction in ambient CO and has evolved to a current four-month program with a 3.1 to 3.3 wt % oxygen fuel and a model predicted 30% reduction in CO emissions (Livo and Miron, 1995) and an estimated 24% reduction in ambient CO. Anderson and coworkers (Anderson *et al.*, 1994, 1995) have attempted to find evidence of the reported reductions in CO levels by treating the record of ambient CO concentrations since about 1981 with a statistical analysis. The analysis method "a Structural Time Series Analysis" fits a quantity that varies with time, in this case the ambient CO concentrations, with a multi-term expression that accounts for the various independent factors contributing to the variation of CO with time. One term in the expression is associated with the time period during which oxyfuels are in use. The magnitude of this term is a measure of the effect of the oxyfuel program on ambient CO. Two data sets from several different sites in the Colorado oxyfuel program area were subjected to analysis: (1) the monthly average CO and (2) the monthly maximum 8-hour average CO. Figure 1.1 shows a sample of the type of data they analyze. The Colorado oxyfuel seasons are indicated by the filled symbols on the figure. In an analysis of data through 1993, they reported (Wolfe *et al.*, 1994) that they could not find a statistically significant oxyfuel effect. As a further test, they showed that their analysis should detect a 10% CO reduction at about the 80% confidence level. They also analyzed data from four other western cities with winter oxyfuel programs, Albuquerque, NM; Phoenix, AZ; Las Vegas and Reno, NV. In recent years all of these areas have had a winter program using at least a 2.7 wt % oxygen fuel. In general these data showed more variability and scatter. Only data from Phoenix showed a statistically significant reduction in CO due to oxyfuel usage.

A new study from this group (Wolfe *et al.*, 1996) extends and updates their earlier analyses of Denver area data. They analyzed monthly data from three CO monitors for 1981 through June 1995. They combined the results from two different types of statistical analyses, a Structural Time Series Analysis and an ARIMA analysis. They report an oxyfuel reduction in ambient CO of (7 ± 10)%, where the uncertainty represents the 95% confidence limits. This reduction in CO corresponds to about a (2.3 ± 3.3)% CO reduction per wt % oxygen.

Several important factors affecting ambient CO are not explicitly accounted for in their analysis. Meteorology is the most important, because it plays a dominant role in the winter CO maxima. They contend that by averaging over such a large time scale this effect should "average out". A second possible systematic error could come from changes in driving patterns, particularly vehicle miles traveled, during the winter months. More recently they have attempted to assess the role of urban vehicle counts on CO levels (Anderson, 1995, personal communication) and find no significant effect. On the other hand one might expect a small complement to the oxyfuel CO reduction in the Denver area, because during periods of high ambient CO, there are designated no-driving and no-wood burning days. This program discourages driving and prohibits most wood burning, which is a small contributor to ambient CO.

Alaska Study

Anchorage, AK, initiated an oxyfuel program during the winter of 1992-3. The ambient CO concentrations during that period declined by about 20 to 30%, an unusually large amount compared to variations observed in previous years. Heil (1993) developed a model to predict CO concentrations from weather observations, such as wind, temperature, pressure, and cloud cover, from CO emission estimates and from other variables. The idea was to compare the model predictions before and after oxyfuel implementation to determine if there was a residual effect that could be attributed to the oxyfuel. Heil concluded that of the observed 27% reduction in CO during the winter of 1992-3, about 16% was due to the variables in the model, mostly weather. The residual 11% decline in CO could be due to oxyfuel usage, but a propagation of uncertainties in the model and in the input parameters led her to conclude that it was unclear whether or not the oxyfuel program contributed to the decline in CO. If the 11% decline in CO is attributed to the use of a 2.7 wt % oxyfuel, the residual reduction in ambient CO corresponds to 4.1% per wt % oxygen.

North Carolina Studies

Three North Carolina counties (Durham, Forsyth, and Wake), with a history of violating the CO air quality standard, and eight neighboring counties were mandated by EPA to sell only oxygenated fuel during the 1992-3 winter season, November through February. The ambient CO data for selected stations in the oxyfuel program area covering a four-year period including the first oxyfuel season were analyzed by Vogt (1994). As a control these data were compared with ambient CO data from selected urban areas (Fayetteville and Charlotte) outside the oxyfuel program.

A general downward trend in urban CO was reported. The reduction in the observed maximum values was found to be greatest during the 1992-3 oxyfuel season. The study concluded that this change was not statistically significant, although some local improvements may have been realized. It was noted that changes in meteorology introduced a confounding factor in analyzing the air quality data.

A second report by Vogt *et al.* (1994) took a closer look at the weather patterns during the high CO seasons. They analyzed data from two oxyfuel seasons 1992-3 and 1993-4 as well as some prior years. They focused on several parameters including atmospheric stability, wind direction, wind speed, temperature and precipitation. They concluded that any benefit in CO reduction from oxyfuel usage was masked by the influence of meteorological conditions.

A statistical analysis of CO trends from about 1987-9 to 1994 was made by Cornelius (1995) in an effort to find an effect that could be attributed to the North Carolina oxyfuel program. Ambient CO records were analyzed for oxyfuel areas and non-oxyfuel areas including, Raleigh, Durham, Greensboro, Winston-Salem, Charlotte, and Fayetteville. Meteorological data, notably precipitation events, were included in the analyses. The trends in ambient CO were determined for the years prior to the implementation of the oxyfuel program and were extrapolated into the oxyfuel seasons to generate predicted CO levels with which the observed levels were compared. Several areas were exempted from the oxyfuel program beginning with the 1994-5 winter season. All of the sites experienced generally declining CO trends. No quantitative factors were assigned to an oxyfuel effect for any area. In Raleigh, Durham, and Greensboro a reduction of CO during the oxyfuel season beyond the trend was observed, but it was concluded that this could be attributed to either weather or oxyfuel usage. In Winston-Salem the observed ambient CO levels showed no effect that could be attributed to oxyfuel usage.

Utah Study

Keislar *et al.* (1995) made a study of ambient CO concentrations to determine the effects of the oxyfuel program in Provo, Utah. Their approach was to measure CO and CO_2 concentrations at a number of test and control sites before, during, and after the local oxyfuel season, 1 November 1994 to 19 January 1995. The test sites included two street intersections, one mid-block location and one parking garage in Provo. Similar locations in Salt Lake City, which is geographically close but outside the Provo oxyfuel area, were monitored as a control during the test period. In addition the background CO and CO_2 concentrations were monitored. They used five separate numerical techniques to investigate the change in background corrected CO/CO_2 concentration ratios from Provo, after normalization to the Salt Lake City control. They report that their results show that nearly all of the observed CO at the study site can be attributed to mobile sources. Although their measurements are made on whole air samples, their analysis method corrects for the background concentration. Therefore this study is more an analysis of the emission effect of oxyfuels than of the effect on the urban ambient CO level. The test fleet is probably a mix of cold and hot vehicles. The Provo oxyfuel sales indicate that 30 to 35% of the fuel was a 15% by volume MTBE blend and the remainder was a 7.8% by volume ethanol blend. Both contain about 2.7% oxygen by weight.

Although some reduction in CO is observed at the Provo sites during the oxyfuel season, Keisler *et al.* state that no reduction is significant at the 95% confidence level for more than one numerical analysis technique. They report an upper limit of 9-10% mean reduction at the 80% confidence level in the observed CO/CO_2 ratios for morning rush hour samples. Two of the analysis methods found reductions of 15% and 35% in the parking garage at the 82 and 91% confidence levels, respectively. The latter they characterize as cold start data. Keislar *et al.* report that the sensitivity of their method of measuring an oxyfuel effect suffered, because of the use of differences and ratios of individual measurements. Keislar (personal communication, 1995) indicates that some of the background measurements may have been contaminated by local emissions. In that case, their report will underestimate the benefit of the oxyfuel and the reduction would be greater than 10%. The reported 10% upper limit corresponds to the vehicle CO emission benefit. If the ambient concentration benefit is assumed to be 80% of this, the ambient benefit is about 3% per wt % oxygen.

Other Ambient Air Quality Effects

The primary reason for the winter oxyfuel program is to reduce ambient CO concentrations, but emission studies show some effects on other emitted pollutants as well. Unfortunately, there are very few studies of the effects of the winter oxyfuel program on ambient air quality other than the CO studies. Anderson *et al.* (1994, 1995) have reported measurements of formaldehyde (CH_2O) and acetaldehyde (CH_3CHO) in Denver, Colorado, since 1988. They find the winter concentrations of these toxic gases are correlated with ambient CO and conclude that vehicles are an important source of both compounds. Vehicle emission studies find that ethanol gives an enhanced acetaldehyde emission and MTBE gives an enhanced formaldehyde emission. Their data (Anderson *et al.*, 1995) show a steady increase in the formaldehyde to acetaldehyde ratio during the winters from 1988 to 1992-3. During this period the winter oxygenate was changing from about 95% market share MTBE and 5% ethanol to about 55% market share MTBE and 45% ethanol. Thus direct vehicle emission effects are expected to exhibit an opposite trend, i.e., with acetaldehyde concentrations increasing relative to formaldehyde concentrations. The reason for this discrepancy is not understood but may involve unknown factors in the emissions and sources, in atmospheric loss mechanisms (such as heterogeneous reactions), or in the sampling and measurement of the aldehydes. The winter concentrations of these gases are around 4 to 6 ppbv for formaldehyde and 2 ppbv for acetaldehyde in recent years (Anderson *et al.*, 1995).

The Utah Division of Air Quality conducted a study during the 1994-5 winter oxyfuel season in Utah County (Provo) to determine the effect of oxyfuel usage on the concentration of small particles, PM_{10}, in the urban atmosphere (Olson, 1995). PM_{10} refers to particles with diameters of 10 μm or less. These particles are drawn into the lungs and are suggested to be a human health hazard. Particles were sampled and analyzed in both Utah County and in Salt Lake County, which is not an oxyfuel area, as a control during and after the oxyfuel season. Utah County used a 2.7 wt % oxygen fuel during the test period. Unusual meteorology was experienced during the 1994-5 oxyfuel season and there were few atmospheric inversions, which usually account for high levels of small particles. The unusual meteorology also caused some contamination of the Salt Lake County control area with particles from Utah County. An analysis and extrapolation of the data indicated that under extreme conditions of very high particle densities, oxyfuel usage could contribute a small increase in small particle concentration. Cooper *et al.* (1995) have proposed that increases in vehicle NO_x and aldehyde emissions caused by fuel oxygenates may enhance the formation of small particles during winter oxyfuel periods.

There are numerous stations making air quality measurements in many urban sites, but no other studies or reports or attempts to assess oxyfuel effects on winter air quality are known. Therefore one must rely upon emission studies and models to estimate the effects of other pollutants on air quality.

Summary of Ambient Air Quality Effects of Oxyfuels

Table 1.13 summarizes the results from studies of the effects of the winter oxygenated fuel program on urban CO concentrations. They are listed in the approximate order in which they are rated to provide a quantitative measurement of the oxygenated fuel effect, with the best studies at the top. The best studies account for the effects of trends and meteorology. The ambient CO analyses are rated as the most significant measurement of the effectiveness of the program, to reduce urban CO concentrations. As described above five analyses were unable to find a statistically significant reduction in CO that could be attributed to the oxyfuel, while four found reductions that generally fall in the range of 5 to 10%. It is not

clear whether or not the studies not finding a measurable oxyfuel effect would be capable of detecting a 5 to 10% reduction in CO. All of the studies report a steady downward trend in CO and problems from the confounding effects of meteorology in extracting an oxyfuel effect. Several of the studies observe that the winter of 1992-3, the first year of the oxyfuel program, was an unusually rainy season and was accompanied by an unusually large drop in CO concentrations. Since the rainy weather is characterized by more than usual dispersion of pollution, a decrease of about 20% in the ambient CO observed that season is attributed to the weather (Heil, 1993 and Dolislager, 1996).

Table 1.13 Summary of studies analyzing ambient CO data to measure the effectiveness of the winter oxyfuel program. The studies are ranked with the ones rated the most quantitative listed first.

Study	Winter Years	Area	Wt % Oxygen	Reported CO Reduction
Dolislager (1996)	1992 to 1995	CA	2	5 to 10%
Mannino and Etzel (1996)	1989 to 1991	AZ CO NV	1.5 to 2.7	~10%
Wolfe *et al.* (1996)	1989 to 1995	CO	2 to 3.1	(7 ± 10)%
Heil (1993)	1992/3	AK	2.7	<11%
Vogt *et al.* (1995)	1992 to 1994	NC	2.7	not detectable
Cornelius (1995)	1992 to 1994	NC	2.7	not detectable

The first column gives the reference for the study.
The second column indicates the years of data analyzed.
The third column indicates the states covered in the analysis.
The fourth column indicates the level of oxygenate used.
The CO reductions reported should be considered an upper limit to the oxyfuel contribution, because other CO reduction programs may also contribute to the reduction as described in the text.

The MOBILE 5a Model predicted reductions in CO emissions range from about 16% in California areas where fuel oxygenate concentration increases by about 1.7 wt % oxygen during the winter oxyfuel season to about 30% in Colorado where a 3.1 to 3.3 wt % oxygen fuel is used. These emission predictions can be adjusted by a factor of 0.8 to account for an estimated 80% (to 95%) of the urban CO coming from gasoline-fueled vehicles. Thus one expects reductions in ambient CO due to oxyfuels of from 13% to 24%. A reduction of 7 to 8% is representative of the effects reported in Table 1.13 and this falls below the predicted reductions by a factor of two to three. It should be noted that the observed reductions in ambient CO are consistent with the predicted oxyfuel effects from the Complex Model. The data in Table 1.9 lead to estimated reductions in ambient CO of about 4 to 8%, which are consistent with the observations summarized in Table 1.13.

The areas with winter oxygenated fuel programs generally have implemented other programs to reduce the winter CO levels. These include Inspection/Maintenance programs, which EPA believes is very effective at reducing CO emissions as indicated by the MOBILE 5a Model prediction of about -27% in Table 1.8. Other programs attempt to reduce urban vehicle traffic by encouraging mass transit, car pool, and van pool commuting. In Colorado wood burning fires are prohibited during periods of high CO and

wood burning fireplaces are forbidden in new construction and remodel projects. These types of programs have the potential of augmenting reductions in CO concentrations in oxyfuel program areas. Therefore the observed reductions in ambient CO reported in Table 1.13 should be viewed as upper limits to the oxyfuel effect as they may overestimate the oxyfuel benefit by neglecting contributions from other CO reduction programs.

Some of the important conclusions regarding ambient air quality studies can be summarized as follows:

- Measurements of urban CO concentrations have been examined by a number of researchers to assess the effects of the winter oxyfuel program. The reported reductions in CO that are attributed to oxyfuels range from undetectably small up to about 10%. Variations in CO concentrations due to meteorology make it difficult to accurately measure small changes. The observed CO reduction is about one half to one third of the effect predicted by the EPA MOBILE 5a Model but is consistent with the effect predicted by the EPA Complex Model. The measured reduction represents an upper limit to the CO effect of oxyfuels because other CO reduction programs may contribute to the observed decrease.

- The effects of oxyfuels on ambient air pollutants other than CO are uncertain. Very little has been done to study ambient air pollutants such as toxics and particles. Most information on oxyfuel effects on other pollutants are derived from vehicle emission studies and models.

- A very small fraction of the ambient CO measurement data available has been analyzed for oxyfuel effects. The benefits of oxyfuels on ambient air quality have not been proven in cold climate areas.

- The fate of the oxygenate vapors in the atmosphere is assessed. During the winter the level of atmospheric chemistry (photochemistry) that normally oxidizes pollutants is very low in most areas. Some of the oxygenate is expected to be scrubbed from the atmosphere by precipitation. The fate for most of the vapors appears to be dispersion and dilution from the urban atmosphere into the free troposphere where it is slowly, on a time scale of weeks and months, photooxidized.

SUMMARY AND CONCLUSIONS

This chapter evaluates vehicle emission data, vehicle emission models, and ambient air quality studies to assess the effects of the winter oxyfuel program on air quality. The focus is upon carbon monoxide, a poisonous gas emitted in gasoline fueled vehicle exhaust. Vehicle emission studies at about 50 °F and higher temperatures find that adding an oxygenate to the fuel reduces CO emissions. For most vehicles the CO reductions fall in the range of about 3 to 6% per wt % oxygen. The standard emission test used to derive these emission effects is conducted at 75 °F. Emission data for winter temperatures below about 50 °F are very limited and inadequate for a reliable prediction of oxyfuel effects. The available data indicate a decreased effectiveness of the fuel oxygenate at low temperatures. Some vehicles at low temperatures have been found to respond to fuel oxygenate with increased CO emissions.

Emission studies show that the pollutant emissions from vehicles have been steadily declining for over two decades. EPA mandated reductions in vehicle emissions and improved emission control technology largely account for the decline. The CO emissions from new 1996 model year vehicles, for example, are about twenty five times less than from new 1970 vintage vehicles. The current generation of vehicles employs oxygen sensors in the exhaust and computer controlled fuel injection to regulate the engine air/fuel ratio. This coupled with high efficiency catalysts greatly reduces the pollutant emissions. The oxygen sensor in the exhaust stream of vehicles decreases the effectiveness of adding fuel oxygenate to reduce CO emissions. Therefore recent generations of vehicles have both lower CO emission levels and lower oxyfuel effectiveness than most older vehicles.

The EPA MOBILE 5a Model is used by states to predict the effects of oxygenate on vehicle emissions and gives predicted reductions of about 9.4% per wt % oxygen. This corresponds to a predicted 25% reduction in CO emissions in areas using a 2.7 wt % oxygen fuel. The model appears to overestimate the effect of oxyfuels on CO emissions by a factor of two or so, in part because it employs very large CO reduction parameters, about 10-11% per wt % oxygen for high emitting vehicles, and an on-road fleet distribution with a large population of high emitting vehicles. The MOBILE Model has no correction for oxyfuel effects at temperatures below 75 °F. The EPA Complex Model was developed to characterize emissions from 1990 model year vehicles, but EPA believes it has some value predicting fuel effects for the present on-road fleet. The Complex Model is also based on 75 °F emission studies. It predicts an oxyfuel reduction in CO that is about one third of the value predicted by the MOBILE 5a Model.

It has not been proven that either the MOBILE 5a Model or the Complex Model is capable of accurately predicting the emissions of the on-road fleet. The standard emission test protocol, the Federal Test Procedure, is unlikely to accurately represent the broad range of conditions that affect vehicle emissions in urban driving. Also the emission levels of the on-road fleet are not known accurately. It is concluded that the most reliable assessment of on-road vehicle emissions is made by examining ambient air quality data.

Relatively few attempts have been made to test the effect of the winter oxyfuel program on urban air quality. The studies that have been conducted, find that the observable reduction in CO that can be attributed to winter oxyfuels ranges from an effect that could not be quantified to a reduction of about 10%. The observed reduction is considered an upper limit because other air quality improvement programs, such as Inspection/Maintenance programs, are conducted parallel to the oxyfuel programs and are likely to contribute some CO reduction. The larger CO reductions are found in warmer climates, California and the southwestern states. Attempts to measure the effectiveness of the program are confounded by meteorology which can cause large year-to-year variations in urban CO concentrations of up to about 20% (Heil, 1993 and Dolislager, 1996). Cold weather and inversions tend to increase ambient CO levels, whereas windy weather and precipitation tend to decrease ambient CO levels. In addition there has been a steady decline in urban CO concentrations for over two decades. This trend is attributed largely to the effects of EPA mandated reductions in vehicle emissions and the resultant developments in vehicle emission control technology.

The studies of ambient CO concentrations with the best accuracy and controls report the oxyfuel effect is in the range of 5 to 10%. If a value of 7 or 8% is taken as representative of the observed reduction in urban CO attributable to winter oxyfuels, this is a factor of two

to three times smaller than the value predicted by the EPA MOBILE 5a Model but is comparable to the prediction of the EPA Complex Model.

The effects of oxyfuels on some other vehicle pollutant emissions have been studied. The emissions of most volatile organic compounds are reduced by fuel oxygenate, notably the toxic compounds 1,3-butadiene and benzene. On the other hand, the emissions of a toxic aldehyde, either formaldehyde or acetaldehyde depending upon the specific oxygenate used, are increased by fuel oxygenate. The emission studies reviewed here indicate that nitrogen oxide emissions increase with oxygenate addition, particularly at levels of oxygenate above about 2 wt % oxygen. Although this observation conforms to the combustion engineering expectation of enleanment, the emission data analysis performed to develop the Complex Model indicates a negligible effect of oxygenate on NO_x emissions.

Two of the major findings of this assessment are that emission data are inadequate to assess the effects of fuel oxygenate at low temperatures, i.e., winter conditions, and that the available analyses of air quality data do not support the large CO reduction predicted by the EPA MOBILE Model. The same issues were identified three years ago at a conference on MTBE and other oxygenates (USEPA, 1995c) sponsored by the Environmental Protection Agency, the American Petroleum Institute and the Oxygenated Fuels Association.

To answer the question of whether the winter oxyfuel program reduces CO in cold weather areas, a carefully designed and conducted analysis of the ambient air quality data is required. Studies that do not account for the effects of the year-to-year trends and meteorology are of limited value. An analysis of data for months within the oxyfuel season and for some months out of the oxyfuel season is required to establish trends before and during the oxyfuel years. As a control for the effects of meteorology, a similar analysis should be made of CO data for adjacent urban areas without an oxyfuel program. Another valuable test of the oxyfuel program could be made on the data from areas that have discontinued the program. In these areas the oxyfuel off-on-off seasons provide a unique data set for examining the ambient air quality effects of oxyfuels. There is a very large volume of data from urban CO monitors that has never been critically analyzed to test for a benefit.

If it is assumed that the winter oxyfuel program reduces urban CO by about 10%, which is a reasonable upper limit from the available studies, the magnitude of the reduction in urban CO concentration can be estimated. EPA data for the areas with winter oxyfuel programs indicate an average CO concentration of about 1.4 ppmv during the last quarter of 1994 and the first quarter of 1995 (J.R. Cook, personal communication). The average CO reduction would be about 0.14 ppmv or less. For comparison the air quality monitors that report urban CO concentrations measure concentration with an accuracy of ±20%, or ±0.28 ppmv at the 1.4 ppmv level. The global (clean air) background CO concentration is about 0.1 ppmv.

The reported reduction in the ambient CO from the winter oxyfuel program could provide some basis for evaluating the program. Because the winter oxyfuel program is intended to reduce the number of exceedances of the CO air quality standard, it would be useful to have a measure of the number of exceedances that have been avoided by the program. And finally the most important issue concerns human health effects. The approximate 10%

reduction in ambient CO found in this assessment could be useful input for evaluating the health benefits of the program.

At the end of each of the previous sections there is a brief summary of the conclusions of that section. The major findings of this assessment are as follows.

Vehicle Emission Effects

- CO exhaust emissions from vehicles operating at temperatures of 50°F and higher are reduced by oxyfuels by about 2 to 10% per wt % oxygen in Federal Test Procedure studies. For most vehicles the reductions are about 3 to 6% per wt % oxygen which corresponds to about 8 to 16% CO reduction for a 2.7 wt % oxygen fuel. The CO emission reduction is generally smaller in vehicles with newer technology: fuel injected, adaptive learning, closed loop, three-way catalysts; and larger in vehicles with older technology: carbureted and oxidation catalysts. Malfunctioning, high CO emitting vehicles operating fuel rich also experience larger CO reduction benefits from oxyfuels.

- The low temperature vehicle emission database is inadequate. Oxyfuel effects on vehicle CO emissions are uncertain at temperatures below 50°F. Low temperature studies show some benefits down to 20 °F in some vehicles, but generally the results are not conclusive. Some studies report an increase in CO emission with oxyfuels at low temperatures. It has not been demonstrated that oxyfuels will significantly improve air quality at low temperatures.

- Hydrocarbon exhaust emissions from vehicles are reduced by 1 to 7% per wt % oxygen by oxyfuels. Generally the benefits are lower in new technology vehicles and larger in older and higher emitting vehicles.

- Nitrogen oxide exhaust emissions are not changed significantly by low concentrations of oxygenates but studies reviewed in this assessment show an increase in NO_x emissions with oxygenate concentrations higher than about 2 wt % oxygen.

- Fuel oxygenates decrease vehicle emissions of the toxics, benzene and 1,3-butadiene.

- Fuel oxygenates increase emissions of toxic aldehydes. Ethanol and ETBE increase acetaldehyde emissions by large amounts. MTBE increases formaldehyde emissions.

- Some but not all remote sensing and tunnel studies find a large reduction in CO emissions attributable to oxyfuel use in on-road vehicles. The reported CO benefits are about 10% per wt % oxygen. Since the sampled vehicles are operating in a hot stable mode, this benefit is likely to be larger than the FTP benefit.

- Fuel vapor pressure and sulfur content have been shown to strongly influence CO emissions, but these variables are not employed as a part of the CO emission control strategy in most areas.

Model Predictions

- The EPA MOBILE 5a Model is used by EPA and the states to predict the effects of the winter oxyfuel programs on urban fleet emissions. It appears to overestimate the benefits of oxyfuels on fleetwide CO emissions by about a factor of two. The model

predicted benefit for high emitters is very large and the fleet distribution has a large population of high emitters. The model predicted CO reduction is much larger when compared to ambient air data.

- The EPA Complex Model is used to assess the effects of fuel composition and vehicle technology on vehicle pollutant emissions. EPA believes it can be used to predict fuel effects on the emissions of the on-road fleet. The Complex Model estimates a fleetwide reduction in CO emissions from oxyfuel that is about one third of the value predicted by the MOBILE 5a Model. The Complex Model is focused on 1990 model year technology representing vehicles with lower CO emission levels and smaller oxyfuel CO reductions than the MOBILE 5a Model.

- The EPA Complex Model estimates a negligible effect of fuel oxygenate on fleetwide NO_x emissions at oxygenate levels up to 3.5 wt % oxygen. This estimate does not agree with the conclusion drawn from the emission studies reviewed in this assessment but is based upon an analysis of a larger data set.

- No existing EPA model is capable of accurately predicting oxyfuel effects at temperatures below about 50 °F. The emission data available for assessing the effects of low temperature on oxyfuel performance is inadequate and has not been incorporated into the MOBILE 5a or Complex Models.

- Much of the data upon which the EPA MOBILE 5a Model is based have not been published in the peer reviewed literature.

Air Quality Effects of Oxyfuels

- Carbon monoxide concentration data for some urban areas have been examined by several researchers to assess the effects of the winter oxyfuel program on ambient air quality. The reported changes in CO that are attributed to oxyfuels range from an effect that could not be quantified up to about a 10% reduction. Variations in CO concentrations due to meteorology make it difficult to accurately measure small changes of the order of 10%. The observed reductions in CO are upper limits and correspond to about one half to one third of the effect predicted by the EPA MOBILE 5a Model but are consistent with the effect predicted by the EPA Complex Model. The measured reduction may represent an upper limit to the CO effect of oxyfuels because other CO reduction programs in winter oxyfuel areas may contribute to the observed decrease.

- Urban concentrations of CO have been declining for about two decades with a rate of about 2.8% per year for the last 10 years. This decrease is attributed largely to stringent EPA mandated vehicle emission standards and to improved vehicle emission control technology, although other air quality programs such as Inspection/Maintenance may also contribute.

- The effects of oxyfuels on ambient air concentrations of pollutants other than CO are uncertain. Very little has been done to assess oxyfuel effects on ambient air concentrations of pollutants such as toxics and particles. Most information on oxyfuel effects on other pollutants is derived from vehicle emission studies and models which may not be directly applicable to the ambient air effects of the on-road fleet.

- A very small fraction of the ambient CO measurement data available has been critically analyzed for oxyfuel effects. The benefits of oxyfuels on ambient air quality have not been proven in cold climate areas.

- The fate of the oxygenate vapors in the atmosphere is assessed here. During the winter the level of atmospheric chemistry (photochemistry) that normally oxidizes pollutants is very low in most areas. Some of the oxygenate is expected to be scrubbed from the atmosphere by precipitation. The fate for most of the vapors appears to be dispersion and dilution from the urban atmosphere into the free troposphere where it is slowly, on a time scale of weeks and months, photooxidized.

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