

Ethanol fuelled motor vehicle emissions: A literature review

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AIR HEALTH EFFECTS DIVISION
Health Canada

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EXECUTIVE SUMMARY

This literature review has been prepared in response to a request from the Air Health Effects Division of Health Canada to provide input for the possible updating of a 1999 human health impact evaluation related to the large-scale introduction of motor vehicle fuel containing 10% ethanol. The Health Canada study of 1999 that had been made available by the Air Health Effects Division was first reviewed. The literature search and review was then undertaken via a computerized search from the Compendex® interdisciplinary engineering database and a review of research and development programs and related publications from a number of institutions with direct relevance to the study.

Interest in emissions from motor vehicles derives from their direct human health impacts, their contribution to secondary pollutant formation, and their contribution to greenhouse gas emissions. The Health Canada study estimated the percentage change in baseline commuter exposure to six compounds in the summer and winter in the Lower Fraser River Valley resulting from the complete market introduction of E10. The impact of large scale introduction of E10 was also the focus of a California Air Resources Board report entitled *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline*. The study was undertaken following the decision to phase out MTBE from California reformulated gasoline and looked at the ambient air quality impacts of alternative scenarios, including the substitution of ethanol for MTBE in reformulated gasoline.

Environment Canada is currently working on Phase 2 of a project on emissions from vehicles fuelled with ethanol-gasoline blends. The Phase 1 report, *The Evaluation of Ethanol – Gasoline Blends on Vehicle Exhaust and Evaporative Emissions, Phase 1* reports on the exhaust emissions and fuel economy of three ethanol blended fuels in five late model vehicles, including a hybrid electric-gasoline vehicle. Phase 2 of the project will focus on a more detailed speciation of the exhaust emissions, as well as those emitted through fuel evaporation.

The results of experimental studies and the overall representation of those results in emission models such as MOBILE6 suggest that the use of E10 would lead to lower emissions of CO, HC, and air toxic emissions with the exception of acetaldehyde which increases in the exhaust of vehicles using ethanol.

It is recommended that detailed emission modeling be undertaken for the GVRD and Southern Ontario regions, using Canadian vehicle fleet data, and the appropriate ambient and fuel mix conditions in each region by making use the new modeling capabilities that have become available recently in the MOBILE6.2 model. Such modeling would provide a good comparison for the effect of E10 on regulated and non-regulated emissions estimated in the Health Canada study of 1999.

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1. Introduction

This literature review has been prepared in response to a request from the Air Health Effects Division of Health Canada to provide input for the possible updating of a 1999 human health impact evaluation related to the large-scale introduction of motor vehicle fuel containing 10% ethanol. This review on motor vehicle emissions is only one aspect of the overall effort organized as a panel of experts on different aspects. Other members of the panel are carrying out similar studies on other aspects that can be integrated into a comprehensive human health risk assessment. The findings are also being presented in a workshop bringing together all the panel members.

Following a brief orientation to the issues related to the use of ethanol as a transportation fuel the report will review and summarize the key elements of the 1999 study before the recent literature is discussed to ensure that the discussion is presented in this specific context.

1.1 Ethanol as a transportation fuel

Ethanol has been a potential fuel for internal combustion engines right from the end of the 19th century when Henry Ford designed a car that used ethanol as fuel. Gasoline later gained prominence for spark ignition engines although ethanol was used at various times and for specific purposes, for example in high performance racecars. With the air pollution effects of motor vehicle emissions becoming serious, ethanol started receiving attention as a cleaner burning alternative fuel. However, once the emission control technology developed for gasoline vehicles matured, emissions of CO, NO_x and unburned hydrocarbons (HC) were reduced so significantly by this technology that the relative advantage of ethanol as a cleaner fuel was largely diminished. On the other hand, there is still significant interest in ethanol as an oxygenate blend for gasoline, particularly after the elimination of methyl tertiary butyl ether (MTBE) as a source of oxygen in reformulated gasoline in California.

More recently, concerns with the accumulation of greenhouse gases in the atmosphere focused attention on ethanol once again, this time as a potentially renewable transportation fuel. The CO₂ emitted when ethanol is burned in an engine can be re-captured from the atmosphere by growing corn that is then used to produce the ethanol, thus completing the cycle. This cycle needs to be looked at carefully to quantify the emissions associated with each stage and the net reduction compared to alternative energy sources but it is clear that at least part of the CO₂ emissions can be avoided by using such a renewable cycle. There is also interest in developing processes that can produce ethanol from biological feedstocks other than corn, although corn is currently the dominant source.

Although the emission control technology developed for gasoline engines is very successful in reducing emissions of CO, NO_x and HC per distance driven, the increasing number of vehicles and the distances traveled by these vehicles eliminate a significant

part of these benefits with the result that motor vehicle emissions continue to be of concern from a human health perspective. With increased scientific understanding about these emissions the detailed analysis of the unburned hydrocarbons has become important. Different species of hydrocarbons can have different direct human health effects as well as different roles in the formation of ground level ozone that then becomes a human health stressor. The quantification of the emission rates of individual species from motor vehicles and the difference in these emission rates with different fuels has therefore become a key objective in dealing with motor vehicle emissions.

Ethanol is currently used as a transportation fuel typically not in pure form but blended with gasoline in different proportions. A mixture of 90% gasoline, 10% ethanol is referred to as E10 and is the most common form since it can be used interchangeably with gasoline by vehicles without any special arrangement of the fuel/air system on the vehicle. E85 (85% ethanol, 15% gasoline) does require adjustment of the fuel/air system and is used by flexible fuel vehicles (FFVs) that are equipped to sense the alcohol content of the fuel and make the necessary adjustment.

Brazil has the highest proportion of ethanol in the transportation fuel supply. It is estimated that in Sao Paulo, a metropolitan center of 17 million people, 40% of the total fuel volume is ethanol (Colon et al, 2001). Approximately 40% of the cars in Brazil operate on 100% ethanol. The remaining cars run on a blend of 22% ethanol (78% gasoline). The U.S., by comparison, uses ethanol in 12% of its fuel, mostly at a blend of 10% ethanol, (90% gasoline) (RFA, 2003). In Canada, although the industry is still in its infancy ethanol-blended gasoline (E10) is now available at over 700 gas bars across the country (CRFA, 2003) and E85 is now available in select locations.

1.2 Health and Environmental issues associated with fuel ethanol

The CO, NO_x, HC, and particulate matter (PM) emissions in the exhaust of internal combustion engines are of direct concern from a human health perspective. In addition, evaporative emissions of hydrocarbons and other volatile components of fuels have gained in relative importance as the exhaust emissions have been reduced by emission control technology. While these emissions are present with all fuels used in vehicles, the relative emission rates and their composition can change significantly from one fuel to another. Ethanol's introduction as a clean alternative fuel is mostly related to the reductions in CO and exhaust HC that can be realized. Ethanol has higher volatility than gasoline so that it will tend to increase evaporative emissions when blended with gasoline unless the composition of the gasoline itself is changed to counteract this increase in volatility. This can be done by reducing the fraction of lighter hydrocarbons like butane in the gasoline. On the other hand evaporative emissions of ethanol itself are not of particular concern at the ambient concentration that are encountered.

In terms of individual HC and other volatile compounds, attention has focused on the following list of compounds in the "Air Toxics" group, so named because they are known or suspected to be hazardous to human health.

benzene
1,3 butadiene
formaldehyde
acetaldehyde
acrolein
MTBE (methyl tertiary butyl ether)

Formaldehyde and acetaldehyde are of particular interest from an alcohol fuel perspective as these compounds form directly from the combustion of the alcohol (formaldehyde from methanol, acetaldehyde from ethanol), resulting in higher emissions, while the emissions of the others are generally reduced relative to gasoline.

The CO₂ emitted from the combustion of ethanol fuel is not a direct human health hazard but like all other emissions of CO₂, contribute to global climate change effects. As indicated above, the use of ethanol from biomass (e.g. corn) can reduce the amount of CO₂ emitted per unit energy derived from the fuel.

1.3 Objectives and methodology

The objectives of the study and the tasks related to it are:

1. To review and evaluate the available literature on emissions from motor vehicles using ethanol-blend gasoline.
2. Prepare a written summary of the information, with an analysis of the possible consequences of widespread introduction of ethanol-blend gasoline in Canada.
3. Prepare an oral slide presentation with slides summarizing the contents of the written report and present it at the workshop.
4. Participate in a workshop with other panel members plus other invited participants to be held in Ottawa.
5. Assist in the preparation of a final report comprising the findings of all panel members plus other workshop participants as a result of the workshop discussion

The draft risk assessment document (HC, 1999) that had been made available by the Air Health Effects Division was first reviewed. This is a comprehensive document that arrives at human health risk assessments due to the large-scale introduction of E10 fuel in the Greater Vancouver Regional District and Canada. It was therefore important to understand the context and methodology within which the information from an updated literature review might be utilized.

The literature search and review was then undertaken via two parallel paths:

- a) A computerized search from the Compendex® interdisciplinary engineering database for the years 1997-2003 using “ethanol” and “emissions” as keywords.
- b) A review of research and development programs and related publications from a number of institutions with direct relevance to the study:

California Air Resources Board

<http://www.arb.ca.gov/>

CONCAWE (Conservation of Clean Air and Water in Europe)

<http://www.concawe.be/>

Coordinating Research Council

<http://www.crao.com/>

Environment Canada, Emissions Research and Measurement Division

<http://www.etcentre.org/>

Health Effects Institute

<http://www.healtheffects.org/index.html>

NRC Institute for Chemical Process and Environmental Technology

<http://icpet-itpce.nrc-cnrc.gc.ca/research.html>

U.S. EPA Office of Transportation and Air Quality

<http://www.epa.gov/otaq/>

U.S. DOE Alternative Fuels Data Center

<http://www.afdc.doe.gov/>

The risk assessment document of 1999 included a comprehensive review of literature until 1997. Considering the increased pace of research and publication activity on motor vehicle emission modeling and air toxics risk assessment in the late 1990's it was felt that starting in 1997 would be justified and efficient for journal articles. In the case of the institutional literature, earlier dates have been included where appropriate.

Although the immediate focus of this paper are emissions from ethanol fuelled vehicles, some references that were encountered during the search and that were of relevance to other aspects of the overall risk assessment study have also been included. These are presented in the literature review list under appropriate headings although they will not be discussed in any detail. It is envisaged that these may serve to complement the work of other panel members in some instances.

2.0 Health Canada Draft Risk Assessment Study, 1999

Health Impact Evaluation of the Complete Market Introduction of a Fuel Containing 10% Ethanol for the Greater Vancouver Regional District and Canada

The objective of this study was primarily to estimate the relative changes in the ambient and microenvironment concentrations of vehicle-related compounds resulting from the utilization of E10 reformulated fuel. This was followed with an estimation of the public

health outcomes due to these changes and the economic value of avoided health impacts due to these changes. The compounds considered were:

- benzene
- 1,3 butadiene
- formaldehyde
- acetaldehyde
- CO
- NO_x
- Ozone
- PAN (peroxy acetyl nitrate)

The study arrives at ambient concentration estimates through the following steps:

- 1) Quantification of tailpipe and evaporative emissions
- 2) Estimation of the relative contribution of vehicle emissions to the overall emission inventory
- 3) Estimation of baseline ambient air concentrations
- 4) Estimation of secondary formation of ozone and organic species resulting from the introduction of E10
- 5) Modeling of the relative changes in ambient concentrations under E10 use.

In addition to outdoor ambient concentrations, the concentrations in the following microenvironments are also estimated:

- In-vehicle
- Underground parking garages
- Gas station and refueling
- Indoors

The quantification of tailpipe and evaporative emissions from E10 fuelled vehicles is done in relative terms to a base case of gasoline fuelled vehicle emissions by analyzing data from the Auto/Oil Air Quality Improvement Program (CRC, 1991, 1993, 1997). The results of emission tests from 20 light duty vehicles equipped with three way catalyst and adaptive learning emissions control technology for two fuels (U.S. “industry average” gasoline, and tailor blended E10) were analyzed to obtain E_{10}/E_{base} mass emission rate and evaporative emission rate ratios. Although this approach is based on a specific set of vehicles and conditions which may not represent all the diverse conditions experienced by the entire vehicle fleet it was felt that a number of factors justified projection of the results to the scenario under study:

- a) While the absolute emission rates of different vehicles with different fuels may show significant variation under different driving conditions, the ratios of emissions with two different fuels is less sensitive to other factors.
- b) The tests results were with two fuels similar to those that would be in use for the region considered by the modeling

- c) The vehicles used were equipped with recent emission control technology that is representative of the vehicle fleet for the time period considered by the modeling

The results are presented in summary form in the Table 2.1 below. While this table presents the key ratio as an average for the vehicles tested, regression analysis of the emission results provides additional insight for interpreting and using these figures. For example, 1,3-butadiene, benzene, CO and NOx emissions related strongly ($r^2 > 0.8$) with the vehicle indicating that a high emitting vehicle with conventional gasoline will also have high emissions with E10. Formaldehyde and acetaldehyde emission on the other hand correlated weakly ($r^2 \sim 0.1 - 0.22$) with vehicles indicating that a high emitter with conventional gasoline will not necessarily be a high emitter with E10 and vice versa. An even more important result of the regression analysis is that the ratios indicated in Table 2.1 are not statistically significant for formaldehyde and only marginally statistically significant ($p=0.07$) for acetaldehyde. The absence of a significant correlation between fuel composition and aldehyde emissions is later reflected in modeling results.

Table 2.1 The average ratio of emissions from alternative fuel (E10) vehicles to emissions from gasoline vehicles, E10/E_{base}. (condensed from HC, 1999, Table 5)

Exhaust emissions	E10/E _{base}
NOx	1.03±0.20
CO	0.82±0.18
Formaldehyde	1.43±1.05
Acetaldehyde	2.43±1.27
1,3-butadiene	0.92±0.12
Benzene	0.87±0.19
Evaporative emissions	
Benzene	1.18±0.55

Benzene is emitted both from the tailpipe and as part of evaporative emissions. The Auto/Oil program data provides for the quantification of “hot soak” and “diurnal” emissions, i.e. those emitted from a vehicle when it is parked after a trip, and those emitted due to daily changes in temperature. The data reported are grams of hydrocarbon emitted per test simulating these situations. These are then converted to equivalent grams per distance driven by considering the number of trips (3.05) and total distance (31.1 miles) driven per day by the average light duty vehicle to arrive at the expression: $\text{Evap. g/mi} = (3.05 \times \text{g}_{\text{hot soak}} + \text{g}_{\text{diurnal}})/31.1$.

The relative quantities of exhaust and evaporative emissions under driving conditions were estimated in an Environment Canada study carried out in the Cassiar Tunnel in Vancouver (McLaren et al 1996). Using chemical mass balance receptor modeling this study estimated that 83.3% of non-methane hydrocarbon (NMHC) emissions were from the tailpipe while the rest were evaporative. This ratio was applied directly to benzene in the Health Canada study (HC, 1999) although it should be possible to extract the specific result for benzene from the results of the receptor model. On the other hand, the absolute

emission rates from the tunnel study are the important input to the next steps in the modeling rather than the ratio of exhaust to evaporative under driving conditions.

All of the compounds being studied here are emitted by other sources in addition to motor vehicles. It is therefore important to estimate the contribution of motor vehicles to the total burden when trying to determine the overall impact on ambient air quality of changes in the motor vehicle contribution. The chemical mass balance receptor modeling used for estimating tailpipe vs. evaporative emissions in the tunnel study mentioned above can also be used to estimate the contribution of different types of motor vehicle emissions in the outdoor, underground garage, indoor, in-vehicle, and gas-station microenvironments. Table 2.2 reproduces the contribution of light duty gasoline vehicles (LDGV) to total emissions of the mentioned compounds in the Lower Fraser River Valley (LFV) from Table 7 of the Health Canada study (HC, 1999).

Table 2.2 Estimation of light duty gasoline vehicle contributions to total emissions in the Lower Fraser River Valley in 1990. (condensed from HC, 1999, Table 7)

	LDGV contribution, %
1,3-butadiene	76.92
benzene	67.58
acetaldehyde	40.57
formaldehyde	30.35
CO	88.11
NO _x	33.82
VOC	40.38

The compounds emitted by vehicles undergo complex chemical and photochemical reactions in the atmosphere, at rates that depend on the compound and the prevailing atmospheric conditions. Some of the compounds emitted by vehicles (e.g. formaldehyde, acetaldehyde) can also be produced in the atmosphere through photochemical reactions. Modeling the overall impact of a change in motor vehicle emissions therefore requires knowledge of the primary (directly emitted) and secondary (formed in the atmosphere) contributions to the total burden. This in itself is a challenging task since it depends on meteorological conditions as well as the emissions of other compounds that may effect the secondary formation in the atmosphere. The quantification of the effect requires complex regional air quality models that attempt to simulate hundreds of photochemical reactions taking place in the atmosphere over the course of several days (Singleton et al, 1997).

The Health Canada study ultimately arrives at estimates of the percentage change in baseline commuter exposure to six compounds in the summer and winter in the Lower Fraser River Valley resulting from the complete market introduction of E10. The results are furthermore broken down by seven microenvironments where commuters may be exposed to these pollutants. The results are summarized in Table 2.3

Table 2.3 Average percentage changes in baseline commuter exposure following the introduction of E10 in the Lower Fraser River Valley. (condensed from HC, 1999, Tables 33 and 34)

	Benzene	1,3-butadiene	Acetaldehyde	Formaldehyde	CO	NOx
Summer	3.5%	-2.02%	6.96%	1.69%	-13.87%	1.6%
Winter	0.29%	-6.65%	9.82%	2.64%	-13.41%	1.81%

3.0 Update on literature related to emissions from motor vehicles using fuel ethanol

As outlined under Objectives and Methodology, the objective of this literature review is primarily to review sources that may contribute to the quantification of emissions from ethanol fuelled vehicles. The Compendex search of scientific literature has identified many documents in the 1997-2003 period that are of direct relevance to this objective. These have been documented in Section 5.1. The methodology also included a review of activities at a number of institutions with direct relevance to the study. The results of these reviews will first be summarized before a critical examination of the emission data contained in the literature is undertaken with a view to identifying how the new data since 1997 may contribute to the methodology employed in the Health Canada study of the impacts of increased use of E10.

California Air Resources Board

The California Air Resources Board is a part of the California Environmental Protection Agency, an organization that reports directly to the Governor's Office in the Executive Branch of California State Government. To provide safe, clean air to all Californians and to protect the public from exposure to toxic air contaminants are among its major goals. A staff report entitled *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline* (CARB, 1999) has virtually the same objectives and similar methodologies to the Health Canada study (HC 1999), albeit in a different geography. The study was undertaken following the decision to phase out MTBE from California reformulated gasoline and looked at the ambient air quality impacts of alternative scenarios, including the substitution of ethanol for MTBE in reformulated gasoline. Although the study is of the same year as the Health Canada report, it includes some later literature as it was completed late in 1999 with a very concerted effort due to the pressing issue of phasing out of MTBE. It should be considered one of the key items in the current literature review.

Also significant is the release of the latest version of the motor vehicle emission factor model and software, *EMFAC2002* (CARB, 2002). EMFAC has been used by CARB for motor vehicle emission inventories in California and is the starting point for any analysis concerning ambient air quality impacts.

Coordinating Research Council

Much of the research aimed at the effect of reformulated gasoline on emissions and the detailed characterization of these emissions have been completed for the Coordinating Research Council, a consortium of motor vehicle manufacturers and fuel manufacturers. A report entitled *Air Toxics Modeling* (CRC, 2002) while not specific to investigating the effects of ethanol, has many overlapping challenges and methodologies with the Health Canada study (HC, 1999).

CONCAWE (Conservation of Clean Air and Water in Europe)

CONCAWE is the European oil companies' organization for environment, health and safety. The emphasis of its work lies on technical and economic studies relevant to oil refining, distribution and marketing in Europe. Three recent reports address greenhouse gas as well as air pollution and health issues: *Energy and greenhouse gas balance of biofuels for Europe - an update* (CONCAWE 2002), *Alternative fuels in the automotive market* (CONCAWE 2002), *Overview and critique of the air pollution and health: a European approach (APHEA) project* (CONCAWE, 1999)

Emissions Research and Measurement Division – Environment Canada

ERMD is Environment Canada's national laboratory for motor vehicle emission testing and characterization, including the monitoring of compliance of new vehicles with emission regulations as well as research projects aimed at various topics. ERMD is currently working on Phase 2 of a project on emissions from vehicles fuelled with ethanol-gasoline blends. The Phase 1 report, *The Evaluation of Ethanol – Gasoline Blends on Vehicle Exhaust and Evaporative Emissions, Phase 1* (ERMD, 2002) reports on the exhaust emissions and fuel economy of three ethanol blended fuels in five late model vehicles, including a hybrid electric-gasoline vehicle. The fuels that were evaluated included a summer grade gasoline and splash blends of this gasoline with 10, 15, and 20 percent ethanol by volume. Phase 2 of the project will focus on a more detailed speciation of the exhaust emissions, particularly during engine start-up, as well as those emitted through fuel evaporation. The effect of commingling – mixing different fuels in the fuel tank will also be investigated.

Health Effects Institute

The Health Effects Institute (HEI) is an independent, nonprofit corporation supported jointly by the U.S. Environmental Protection Agency (EPA) and industry, with a mandate to provide high quality, impartial, and relevant science on the health effects of pollutants from motor vehicles and from other sources in the environment. A report from the Health Effects Institute's Oxygenates Evaluation Committee (HEI, 1996) focuses primarily on MTBE. A more recent report (HEI, 2002) has data on emission measurements in highway tunnel studies, aimed primarily at quantifying diesel versus

gasoline vehicle emissions but including data on formaldehyde and acetaldehyde (among other carbonyl compounds) that are of interest from the viewpoint of ethanol fuelled vehicles.

NRC Institute for Chemical Process and Environmental Technology

Collaborating with Environment Canada's Meteorological Service and the federal interdepartmental Program of Energy Research and Development (PERD), ICPET develops modeling technology to analyze the role of traffic and alternative fuel technologies (reformulated gasoline, diesel fuels, etc.) on the formation of airborne particulates. This research aims at developing tools and knowledge to evaluate fuel and transportation codes to meet future air quality standards. ICPET's modeling activities (Singleton et al, 1997; McLaren et al, 1995; McLaren et al, 1993) have already formed a critical component of the Health Canada study (HC, 1999) and any updating of emission data will need to be reviewed/used by the Air Quality Modeling group to assess its significance in terms of ambient air quality impacts.

U.S. EPA Office of Transportation and Air Quality

OTAQ is a very important source of information for motor vehicle emissions in the U.S. and Canada, given the harmonization of motor vehicle emission control technology and regulations. *Motor Vehicle Related Air Toxics Study* (EPA, 1993) is a comprehensive study of motor vehicle related air toxics emissions and their impact on ambient air and exposure to individuals in different microenvironments. *Fuel Oxygen Effects on Exhaust CO Emissions* (EPA, 2001) has data specific to ethanol blends in gasoline. *User's Guide to MOBILE 6.1 and MOBILE6.2: Mobile Source Emission Factor Model* (EPA, 2002a), **and** *Technical Description of the Toxics Module for MOBILE6.2 and Guidance on Its Use for Emission Inventory Preparation* (EPA, 2002b) incorporate the results of much of the research of fuel composition effects on emissions carried out in the late 1980's and 1990's. The MOBILE6.2 emission factor model now estimates the emission rates of benzene, 1,3 butadiene, formaldehyde, acetaldehyde, acrolein, and MTBE from the in-use vehicle fleet as a function of the transportation fuel mix in a particular region. Environment Canada has commissioned work for a Canadian version of MOBILE6 to be developed but this has not yet been released. Despite the differences in the emissions of the U.S. and Canadian fleet vehicles of 1980's vintage, the modeling incorporated in MOBILE6 will most likely be widely used to estimate motor vehicle emissions and the effects of different fuels in Canada. The effect of the differences from the 1980's will diminish in future years as the U.S. and Canadian fleets come to be dominated by vehicles produced to the same emission standards.

U.S. DOE Alternative Fuels Data Center

The AFDC is the U.S. Department of Energy central repository of information related to alternative fuels and alternatively fuelled vehicles. The National Renewable Energy

Laboratory (NREL) of the U.S. DOE carries out research on a wide range of issues related to renewable energies. The results of a study on flexible fuel vehicles (FFV) are reported in *Final Results from the State of Ohio Ethanol-Fueled Light-Duty Fleet Deployment Project* (NREL, 1998). While the study was concerned primarily with issues related to the introduction of E85 rather than E10, it does offer in-use data from 10 FFVs and 2 gasoline vehicles over an 18-month period.

4.0 Critical Review of New Literature on Emissions

The literature related to emissions from ethanol blended gasoline vehicles are listed in sections 5.1 and 5.2 of the bibliography. Literature related to ethanol-diesel blends and associated performance/emission issues are listed separately in subsection 5.1.1. Other sections of the bibliography address the ambient air quality modeling and impact studies (Section 5.3), greenhouse gas emissions (Section 5.4) and life-cycle analysis of ethanol blends and other fuels (Section 5.5). A companion study (Durbin 2003) presents additional analysis on studies (both pre- and post 1997) attempting to quantify the effect of ethanol-blended gasoline, particularly E10, on emissions from motor vehicle sources.

Interest in emissions from motor vehicles derives from their direct human health impacts, their contribution to secondary pollutant formation, and their contribution to greenhouse gas emissions. The speciation of hydrocarbon and other VOCs in addition to the quantification of CO and NO_x emissions is a main requirement for data to be useful in the present context of direct human health effects and secondary pollutant formation.

Some of the journal articles listed in Section 5.1 pertain to experimental work with a small number (typically one) of vehicles, and/or a matrix of tests, which aim to elucidate detailed responses from test engines/vehicles. While these compile valuable data they are not immediately usable for the purpose of comparing emissions from E10 vehicles with those from gasoline vehicles. Other journal articles report data that have been compiled from a comprehensive project. In such cases the complete project report generally provides more detail in a context closer to that of the present study.

From the perspective of the Health Canada study (HC 1999) a number of studies should be considered key. These are NREL 1998, CARB 1998, CARB 1999, EPA 2001, ERMD 2002, EPA 2002a, and EPA2002b. These are discussed in some detail below.

NREL 1998, *Final Results from the State of Ohio Ethanol-Fueled Light-Duty Fleet Deployment Project*, (National Renewable Energy Laboratories, U.S. Department of Energy, 1998).

The State of Ohio's demonstration project for the use of E85 as a transportation fuel in flexible-fuel vehicles (FFV) included emissions testing that compared the E85 and gasoline vehicle emissions and is worth including in this review. The term "flexible-fuel" refers to the technology that enables the vehicles to use all gasoline, all E85 fuel, or any combination of the two fuels up to 85% ethanol. Indeed, the FFV vehicles in the study

ended up using E85 anywhere from 33% to 82% of their requirements during project, depending on their normal tasks and the availability of E85 in the course of their normal tasks with the state agencies operating them. The study included ten FFVs and three gasoline vehicles operated by five state agencies over 24 months of data collection between 1996 and 1998. Emissions testing was performed on two ethanol FFVs and two standard gasoline vehicles at the Automotive Testing Laboratories (ATL) in East Liberty, Ohio, during May and June of 1997. The Federal Test Procedure (FTP) was performed twice for each test vehicle on each test fuel. The data in the following table have been condensed from the study report. Because hydrocarbon speciation was not performed as part of this program, 1,3-butadiene and benzene emissions could not be reported. The report does include fuel economy and greenhouse gas emission rates as well as an overall assessment of the operational experience. As expected, acetaldehyde (and to a lesser extent, formaldehyde) emissions were elevated when E85 fuel was used.

Table 14. Average Emissions from 2 FFV and 2 Standard Gasoline Vehicles (NREL 1998)

Vehicle Type	FFV		Std. Gas
	E85	RFG	RFG
Emissions			
NMHC(E) (g/mi)	0.149	0.101	0.114
THC(E) (g/mi)	0.189	0.117	0.132
CO (g/mi)	1.33	1.01	1.39
NOx (g/mi)	0.09	0.08	0.22
Formaldehyde (mg/mi)	2.26	0.99	1.27
Acetaldehyde (mg/mi)	13.02	0.3	0.35

RFG : California Phase 2 Certification gasoline

CARB (California Air Resources Board), 1998, *Comparison of a Fully-Complying Gasoline Blend and a High RVP Ethanol Gasoline Blend on Exhaust and Evaporative Emissions, November 1998.*

Exhaust and evaporative emission data from ethanol fuelled vehicles are reported by the California Air Resources Board from a test program which was designed primarily to compare the emissions benefits from a 10 percent ethanol gasoline blend with an 8.0 psi RVP to those from a summer grade California gasoline with 11% MTBE and an RVP of 7.0 psi. The study with 12 vehicles of 1990-1995 model year with three-way catalysts (TWC) and fuel injection was performed at ARB facilities in El Monte, California, between 1995 and 1998 using the federal test procedure (FTP-75). Six of the vehicles were also tested for evaporative emissions using a modified enhanced evaporative test procedure including a two-day diurnal test and a one hour hot soak test. Since the study compares emissions from two oxygenated fuels with 1.0 psi difference in RVP the results are not immediately comparable to the ethanol effects reported in the Auto/Oil program relative to a baseline gasoline. Nevertheless, both the absolute emission levels with ethanol fuel and the comparisons with another oxygenated fuel can be useful. The

report evaluates exhaust and evaporative emissions test data to compare the two fuels for the following emissions/effects:

CO

NO_x

total hydrocarbons (THC)

nonmethane organic gas species (NMOG)

ozone forming potential from NMOG (OFP)

ozone forming potential from NMOG plus carbon monoxide (OFPCO)

sum of toxics masses (TOX)

potency-weighted toxics (TOXPW)

The four toxic compounds evaluated are benzene, 1,3-butadiene, formaldehyde, and acetaldehyde.

CARB 1999, Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline (CARB, 1999)

CARB conducted further testing in the course of the detailed Air Quality Impacts study (CARB 1999) primarily for the purpose of validating organic gas speciation profiles that were being used in the atmospheric photochemical modeling. In order to determine if the organic gas emission profiles being used were reasonable, a limited emission testing program was conducted at the ARB laboratory in El Monte. This consisted of three fuels and seven vehicles tested on the FTP and the California Unified Cycle:

- MTBE-based Phase 2 regular-grade gasoline.
- ethanol-blended regular-grade gasoline (with oxygen content of 2.05 wt%).
- non-oxygenated regular-grade gasoline.

The seven vehicles were chosen randomly from the Vehicle Surveillance program in California and from State vehicles with the main criteria that 50% of the test vehicles in the program were required to have FTP Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. This criterion was used to ensure that the profiles came from vehicles that represented most of the emissions in California. However, this also meant that the limited vehicle/fuel matrix used had a number of weaknesses including:

- The test vehicles as a group are aged; the mean model year among the vehicles for which the exhaust was speciated is 1981. They do not represent well the emission-control technology that is on the road today, let alone the technology in 2003. Only two have 3-way catalysts, and only three are fuel-injected. Only one is a Japanese brand.
- Several of the vehicles apparently had unstable exhaust emission rates. Many of the differences between gasolines within the same vehicle (up to a factor of five) are too large to be attributed to fuel effects; so, temporal variability in emissions may be assumed
- In only four vehicles were all three test gasolines tested. For some of the vehicles, exhaust aldehydes and isobutene were not reported for some gasolines.

- Only one MTBE-blended, one ethanol-blended, and one non-oxygenated gasoline were tested. Hence, there is no information on the variability of emission measurements within a class of gasoline.
- The test data for the MTBE-free gasolines are from the Unified Cycle, whereas the modeling profiles are based on FTP data.

Perhaps more important than the mass emission rates from the limited emission testing are the emission profile modeling results reported in this study. Using various tools, the study estimates the relative abundance of ethanol, benzene, acetaldehyde, formaldehyde, and 1,3 butadiene (Tables 3.1 – 3.5 respectively in Appendix A of the CARB study respectively) in catalyst and non-catalyst vehicles using four different fuels: RFG using MTBE, non-oxygenate fuel, 2% oxygen with ethanol addition and 3.5% oxygen with ethanol addition.

EPA (United States Environmental Protection Agency), 2001, Fuel Oxygen Effects on Exhaust CO Emissions – Recommendations for MOBILE6, EPA420-R-01-040, July 2001.

This document describes EPA’s effort to estimate simple relationships between fuel oxygen content and exhaust carbon monoxide (CO) emissions for gasoline-powered vehicles. These relationships are then used in MOBILE6 to supplant the MOBILE5 estimates of the effects of oxygen on exhaust CO emissions. A case study with MOBILE6 is presented at the end of this section.

ERMD (Emissions Research and Measurement Division, Environment Canada), 2002, *The Evaluation of Ethanol-Gasoline Blends on Vehicle Exhaust and Evaporative Emissions, Phase 1, Updated November 2002.*

The ERMD study provides new experimental data on the effect of splash blended ethanol-gasoline mixtures (10%, 15%, and 20% ethanol) on exhaust emissions. These data can in principle be compared to and complement the Auto/Oil data used in the Health Canada study (HC, 1999). Relative to the Auto/Oil program the ERMD tests involved fewer vehicles (5 vs. 20) and fuels (4 vs. 11) with different properties but were otherwise similar in methodology and number of repeats (2) per vehicle/fuel combination. However, the two studies were completed with vehicles produced over 10 years apart and there are significant reductions in the absolute emission rates of the vehicles in the latter study, making it very difficult to quantify fuel effects on these emissions. For example, the Health Canada study included Auto/Oil data showing an average emission rate of acetaldehyde with the baseline gasoline (Fuel A) of 1.28 mg/mile vs. 2.31 mg/mile with the use of E10 (Fuel W) from the 1989 model year vehicles. The emission rates of 1999-2001 model year vehicles in the ERMD study were in the 0.16-0.48 mg/mile range with gasoline, increasing to a range of 0.44 – 1.16 mg/mile with 10% ethanol. Thus the ethanol blend emissions of the later vehicles were

generally below the baseline gasoline emissions of the earlier vehicles. Even for the earlier study, the uncertainties associated with the E10/gasoline emission rate ratios meant that the quantification of the fuel effect was not statistically significant for formaldehyde and only marginally significant for acetaldehyde. With the lower emissions rates being quantified in the later study, the percentage changes observed between the base fuel and the ethanol blend are again not statistically significant even though they reach high values. Tables 4.1 and 4.2 demonstrate the case for acetaldehyde and formaldehyde. Similar tables can be generated for other emissions from the data in the ERMD report. The basic message however is the same: the emission rates are not much above the detection limits of the methods available, making small differences in magnitude relatively more important on small measured values than on larger measured values. In terms of the objectives of the Health Canada study, this points out to the need to exercise caution in applying % increase or decrease values used with fuel effects on emissions in various scenarios. Even if one had statistically significant percentage change values from the ERMD study, these would need to be applied to the much lower emissions from the newer model year vehicles and not the entire fleet.

Table 4.1 Acetaldehyde emission results from four vehicles fuelled with E10 and gasoline. (condensed from ERMD, 2002)

FTP-75 composite emissions, mg/mile	Honda Insight	Grand Am	Toyota Echo	Honda Civic
Baseline	0.23±0.10	0.48±0.01	0.42±0.06	0.16±0.07
E10	0.44±0.08	1.05±0.07	0.61±0.86	1.16±0.74
Difference, %	87	119	47	622
Statistically significant?	NO	YES	NO	NO

Table 4.2 Formaldehyde emission results from four vehicles fuelled with E10 and gasoline. (condensed from ERMD, 2002)

FTP-75 composite emissions, mg/mile	Honda Insight	Grand Am	Toyota Echo	Honda Civic
Baseline	0.03±0.08	0.97±0.25	0.86±0.13	0.50±0.09
E10	0.14±0.13	0.99±0.16	0.58±0.62	1.40±0.71
Difference, %	434	1.6	-33	180
Statistically significant?	NO	NO	NO	NO

EPA (United States Environmental Protection Agency), 2002b, Technical Description of the Toxics Module for MOBILE6.2 and Guidance on Its Use for Emission Inventory Preparation , EPA 420-R-02-029, November 2002.

This report essentially gives the technical and background documentation for the way that air toxics are handled by the MOBILE6 (MOBILE6.2) emission factor program (EPA 2002a). The document also compares some MOBILE6.2 results to results using a previous highway mobile source toxics emission factor model, MOBTOX5b.

EPA has developed two previous toxic emission factor models for highway mobile sources. These models were developed primarily for internal assessment purposes and neither were officially released. However, both were released in draft form for use outside of EPA. The first model, MOBTOX, was developed as part of an assessment of toxic emissions, exposure, and risk, released in 1993 as the Motor Vehicle-Related Air Toxics Study (CRC 1993). This model applied toxic fractions on a technology group basis to total organic gas (TOG) gram per mile emission factors to calculate air toxic emission factors. The TOG emission factors were derived from a version of MOBILE4.1 modified to account for control programs mandated by the Clean Air Act Amendments of 1990. Using MOBTOX, average nationwide in-use toxic emission factors could be estimated for benzene, 1,3-butadiene, formaldehyde, and acetaldehyde, for a number of evaluation years and possible control scenarios.

Several years later, EPA developed a new toxic emission factor model, MOBTOX5b (Cook 1998). MOBTOX5b includes MOBILE6 model enhancements and represents a substantial improvement over the preliminary version used in the 1993 study. The model has the capability to account for differences in exhaust toxic fractions of TOG between normal and high emitting vehicles in calculating emission rates. Moreover, the model accounts for the impacts of aggressive driving and air conditioning usage on toxics. The impacts of fuel reformulation programs and changes in vehicle emission control technology can also be addressed with the model. The model accounts for the impacts of specific fuel parameters included in the Complex Model for reformulated gasoline and a draft fuel effects model for MTBE.

MOBILE6.2 fulfills the need to combine the air toxic and MOBILE models, simplifies the modeling process, and provides a single, consistent interface for modeling vehicle pollutants. The MOBILE6 toxics module fully integrates the calculation of highway vehicle air toxic emission factors for benzene, 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, and MTBE into the modeling framework. It also integrates toxic emissions data and algorithms from EPA's Complex Model for Reformulated Gasoline.

For the purpose of demonstrating the air toxic emission factors in MOBILE6, a hypothetical example has been worked out, with the details presented in Appendix A. Table 4.3 has been compiled from these results and can be compared to the Table 2.1 above that had been compiled from the values used in the Health Canada study (HC 1999) as well as the data from ERMD 2002. The purpose of this comparison is only to

point out the recent availability of these emission factors and the effect of E10 fuel on these emission factors in the most widely used emission factor model. As pointed out in Appendix A, for quantitative comparisons MOBILE6 modelling needs to be undertaken with parameters specific to the time and region in mind. It is noteworthy however that the net effect on formaldehyde emissions is estimated to be a modest decrease, while for acetaldehyde emissions it is a substantial increase.

Table 4.3 The ratio of emissions from alternative fuel (E10) vehicles to emissions from gasoline vehicles, E_{10}/E_{base} estimated by MOBILE6 for a hypothetical case

E10/Ebase ratios	LDGV	LDGT	HDGV	MC	All Veh
VOC :	0.95	0.94	0.98	1.00	0.95
CO :	0.92	0.89	0.75	0.77	0.90
NOX :	1.00	1.00	1.00	1.00	1.00
Benzene:	0.84	0.87	0.93	0.98	0.86
1,3 Butadiene:	0.83	0.82	1.01	1.09	0.85
Formaldehyde:	0.92	1.00	1.11	1.08	0.98
Acetaldehyde:	2.15	2.30	2.33	2.07	1.90
Acrolein:	0.88	0.89	0.96	0.97	0.92

The MOBILE6 output in Appendix A provides the details of the absolute emission rates and it is worth comparing these with the emission rates observed in the ERMD study. It has already been pointed out above in connection with the ERMD study that the vehicles tested were well below their regulated levels of emissions, approaching the detection limits of individual compounds. This makes it difficult to quantify fuel effects in a statistically reliable way. The MOBILE6 emission factors are of the order of several mg/mi for formaldehyde and acetaldehyde whereas the vehicles tested at ERMD had emission rates of a fraction of a mg/mile in general. The good news with this picture is that emission control technology on new vehicles is capable of even more significant reductions than regulated. The bad news is that it is becoming increasingly difficult to estimate the net effects of scenarios like conversion to E10 for the new vehicle fleet.

4.1 Conclusions and Recommendations

The quantification of the net air quality impact of ethanol blended gasoline is a challenging task, starting with the quantification of the emissions from the vehicle fleet, modeling the impact of these emissions on ambient concentrations of many compounds and assessing the exposure risk to individuals. The 1999 Health Canada study entitled *Health Impact Evaluation of the Complete Market Introduction of a Fuel Containing 10% Ethanol for the Greater Vancouver Regional District and Canada* estimates the percentage change in baseline commuter exposure to six compounds in the summer and winter in the Lower Fraser River Valley resulting from the complete market introduction of E10. There are comparable studies, which have looked at similar questions in Brazil where ethanol plays a significant role, and in the U.S. where ethanol use has been increasing.

The quantification of emissions from vehicles using ethanol in the fuel has attracted increasing attention given the complexities involved in modeling the overall air quality impact of changes in fuel. The latest version of the most widely used model for estimating emissions from the vehicle fleet (MOBILE6) incorporates most of the emission data that were obtained in the late 1980's and 1990's, including data on air toxic emission factors. This preliminary review of the updated literature since 1997 suggests that there may be enough new information for a quantitative comparison of the emission data with the estimates used in the 1999 Health Canada study. The experimental studies since 1997 reviewed here and in a companion study (Durbin 2003) point to the difficulties in quantifying the effect of E10 on emissions from a fleet where the newer vehicles have emissions that are much lower than older vehicles. In some cases the emissions are too low to determine the effects of E10 with the required statistical confidence given the relatively small size of the vehicle/fuel study matrix. Nevertheless, the overall body of knowledge that has been incorporated into emission modeling work enables us to draw some conclusions on the effect of E10 on emissions. These will be summarized separately for regulated and non-regulated emissions below.

Regulated Emissions

Exhaust emissions of CO are lower with E10 than with gasoline. This effect is essentially due to the oxygen in the fuel and is observable with other oxygenate additives. The effect is stronger with older vehicles compared to vehicles with closed-loop control of air/fuel ratio based exhaust oxygen sensors.

Exhaust emissions of NO_x are generally the same with E10 and gasoline although individual studies have shown marginal reductions as well as increases.

Exhaust emissions of hydrocarbons are lower with E10 than with gasoline although the effect is not as strong as for CO. More important than the mass emission rates of

hydrocarbons are the air toxic and ozone forming properties. The air-toxics issue is addressed under non-regulated emissions below. The ozone forming potential of a particular exhaust mix is studied under specific atmospheric conditions by models which incorporate atmospheric chemistry. However, ozone reactivity parameters have been developed to enable comparisons between different exhaust compositions (Carter 1994). The combined changes in mass emission rates and specific ozone reactivities generally result in lower ozone production per distance traveled with E10.

The addition of ethanol to gasoline increases the volatility of gasoline and can result in higher evaporative emissions unless the composition of gasoline is adjusted to reduce volatility. This is of particular concern where E10 and gasoline can commingle in the tanks of vehicles that do not use the same fuel consistently. Evaporative emission from vehicles using ethanol blends have not been studied as much as exhaust emissions and are the subject of the next phase of an Environment Canada study (ERMD 2002).

Non-regulated Emissions

The most notable effect of ethanol addition to gasoline is the increase of acetaldehyde emissions in the exhaust. Although formaldehyde emissions have been observed to increase in some cases as well, the fleet average effect is expected to be a reduction. The emissions of benzene (exhaust + evaporative), 1,3-butadiene, and acrolein are expected to decrease with E10, compared to gasoline.

Emission Modelling

The latest version of the U.S. EPA emission model (MOBILE6.2) is capable of estimating regulated and non-regulated emissions from a fleet of north American vehicles characterized by age distribution and annual mileage accumulation rates, for given fuel properties, and ambient temperature conditions. Environment Canada is presently developing a “Canadian version” of MOBILE6. It is expected that like its predecessor MOBILE5c, it will attempt to quantify emission factor differences characteristic of the Canadian vehicle fleet in the late 1980’s. However, there are no data specific to the Canadian fleet for fuel effects on emissions and the best estimates of such effects will continue to come from MOBILE6 by providing specific Canadian input data wherever possible. It is recommended that detailed MOBILE6 modeling be undertaken for the GVRD and Southern Ontario regions, using Canadian vehicle fleet data, and the appropriate ambient and fuel mix conditions in each region. It is expected that such modeling undertaken in parallel with the development of MOBILE6c will be helpful for both the emission modeling effort of Environment Canada and the quantification of E10 effects that are of interest for Health Canada in the present context.

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APPENDIX A.

MOBILE6 Calculations for the relative emissions from gasoline and E10 fuel in a hypothetical case.

Versions 6.1 and 6.2 of the MOBILE6 emission factor model enable the estimation of particulate matter and air toxics from the motor vehicle fleet with different oxygenate fuels (EPA 2002a, 2002b). To demonstrate this capability and provide a basis for comparison with the estimated effects of E10 on motor vehicle emissions in the Health Canada study (HC, 1999) a hypothetical case has been investigated to look at the difference in fleet wide emission factors for a 1% and 100% conversion of the total fuel supply to E10. The results from this case study have been summarized in the body of the report. The input and output files from these runs are presented here in their entirety. It should be emphasized that this was a hypothetical case for demonstration purposes and any quantitative estimation should only be undertaken by appropriate compilation of the input parameters specific to any case that is being investigated. For example, the specific GVRD fleet, fuel, and ambient air characteristics should be used to estimate the potential effects of various scenarios in GVRD.

Environment Canada is presently developing a “Canadian version” of MOBILE6. It is expected that like its predecessor MOBILE5c, it will attempt to quantify emission factor differences characteristic of the Canadian vehicle fleet in the late 1980’s. However, there are no data specific to the Canadian fleet for fuel effects on emissions and the best estimates of such effects will continue to come from MOBILE6 by providing specific Canadian input data wherever possible.

```

MOBILE6 INPUT FILE :

AIR TOXICS          :
POLLUTANTS         : HC CO NOX
RUN DATA          :

EXPRESS HC AS VOC  :
EXPAND EVAP        :

SCENARIO REC       : Complete market penetration of E10
CALENDAR YEAR      : 2005
MIN/MAX TEMP       : 32. 92.
FUEL RVP           : 7.0
SULFUR CONTENT     : 30.0
GAS AROMATIC%     : 25.0
GAS OLEFIN%       : 15.0
GAS BENZENE%      : 1.5
E200               : 50.0
E300               : 85.0
OXYGENATE          : MTBE 15.1 0.0
                   : ETBE 17.6 0.0
                   : ETOH 10.0 1.0
                   : TAME 6.0 0.00

END OF RUN

```



```

MOBILE6 INPUT FILE :

AIR TOXICS          :
POLLUTANTS         : HC CO NOX
RUN DATA          :

EXPRESS HC AS VOC  :
EXPAND EVAP        :

SCENARIO REC       : Minimal market penetration of E10
CALENDAR YEAR      : 2005
MIN/MAX TEMP       : 32. 92.
FUEL RVP           : 7.0
SULFUR CONTENT     : 30.0
GAS AROMATIC%      : 25.0
GAS OLEFIN%        : 15.0
GAS BENZENE%       : 1.5
E200               : 50.0
E300               : 85.0
OXYGENATE          : MTBE 15.1 0.0
                   : ETBE 17.6 0.0
                   : ETOH 10.0 0.01
                   : TAME 6.0 0.00

END OF RUN

```


