

Methyl Tertiary Butyl Ether (MTBE) and Clean Gasoline Alternatives

**Report to the
Senate Education, Health, and
Environmental Affairs Committee
and the
House Environmental Matters Committee**

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EXECUTIVE SUMMARY

House Bill 373, signed by Governor Robert L. Ehrlich, Jr. on May 26, 2005, requires the Maryland Department of the Environment (MDE) to develop and submit a report on the viability of alternatives to the use of methyl tertiary-butyl ether (MTBE) in gasoline sold in Maryland to the Senate Education, Health, and Environmental Affairs Committee and the House Environmental Matters Committee. The report is to address five issues:

- The availability of other oxygenates;
- The economic impacts of using other oxygenates;
- The environmental impacts on the State of using other oxygenates;
- The effectiveness and efficiency of the use of bacteria and other microorganisms to clean both isolated and widespread incidences of oil and gasoline contamination of soil and groundwater, a process known as “bioremediation”; and
- The short and long term effectiveness of bioremediation compared to other methods of cleaning soil and groundwater contamination.

This report satisfies this requirement of House Bill 373.

Since 1995, the Clean Air Act Amendments (CAAA) of 1990 have required Maryland and other states that exceed federal air quality standards for ozone to use reformulated gasoline (RFG) year round to reduce motor vehicle emissions. The RFG program has been designed to reduce emissions of ozone precursors, mainly volatile organic compounds (VOCs) and nitrogen oxides (NOx), as well as air toxics emissions, from automobiles. All RFG is required to contain a minimum of 2 percent oxygen by weight. Refiners typically blend the oxygenate MTBE at 11 percent by volume to satisfy this requirement.

In Maryland, RFG is used in the Baltimore and Washington metropolitan areas as well as Cecil, Kent, and Queen Anne’s counties. RFG has made a substantial contribution to improving Maryland’s air quality. Its use has enabled Maryland to remain in attainment of the National Ambient Air Quality Standard for carbon monoxide (CO). The use of RFG in Kent and Queen Anne’s counties enabled them to be redesignated to attainment for the 1-hour ozone standard. In addition, RFG played a key role in enabling the Washington ozone non-attainment area to meet the 1-hour ozone standard this past summer and the Baltimore region to come within one monitor hour of meeting the standard. The air quality benefits of the RFG program achieved so far must be maintained so Maryland can preserve current air quality levels and continue to move toward compliance with the new 8-hour ozone standard.

Notwithstanding the positive air quality benefits provided by RFG, the use of MTBE has been shown to have environmental drawbacks. Beginning in the mid-1990s, states began detecting MTBE contamination in their public drinking water supplies. The main cause of the contamination was leaks in petroleum storage tank systems. RFG with MTBE is more prone to causing groundwater contamination because MTBE is water soluble, has a smaller molecular size as well as a low tendency to adhere to soil, and is less biodegradable than other components of gasoline.

In response to the growing concerns from State and local officials and the public regarding MTBE contamination of drinking water, both the U.S. Environmental Protection Agency (EPA) and the Maryland General Assembly appointed entities (EPA Blue Ribbon Panel and Maryland MTBE Task Force) to investigate air quality benefits and water quality concerns associated with oxygenates in gasoline, and to provide independent advice and recommendations on ways to maintain air quality while protecting water quality. The conclusions of these two investigations were similar: (1) enhance groundwater protections; and, (2) recommend that Congress act to remove the 2 percent oxygenate requirement while ensuring there is no loss of air quality benefits. Since these recommendations were made, key events at both the state and federal levels have occurred that enhance protections on drinking water supplies as well as impact the use of MTBE.

In 2004, MDE found MTBE in groundwater at levels necessitating further action. To address this issue, MDE developed emergency regulations to reduce the risks of MTBE contamination in areas where groundwater is the source of water supply. The regulations, which became effective January 26, 2005 and expire on January 23, 2006, address many of the recommendations previously made by EPA's Blue Ribbon Panel and Maryland's MTBE Task Force. MDE is in the process of adopting the regulations under the normal regulatory process. As a result of the implementation of the emergency regulations, MDE has seen an increase in the discovery of MTBE at active service stations. These discoveries allowed the immediate placement of protections on the supply wells, therefore addressing direct human consumption of MTBE. In addition to this regulation, two other bills were passed in the 2005 Maryland General Assembly Session that greatly reduce the risk to MTBE exposure. House Bill 355 requires the testing of water systems that service nontransient noncommunity water systems. These nontransient noncommunity areas include schools, nursing homes, and daycare facilities. House Bill 374 requires immediate notification of groundwater contaminations in high-risk areas.

On August 8, 2005, President George W. Bush signed the federal Energy Policy Act of 2005, which removes the 2 percent oxygen requirement in RFG and created a Renewable Fuels Standard (RFS) that mandates the increased use of renewable fuels, primarily ethanol and biodiesel. The Renewable Fuels Standard essentially ensures that ethanol will be the replacement for MTBE if refiners choose to use an oxygenate. Once the oxygen requirement is removed in the spring of 2006, refiners will have more flexibility in producing compliant RFG. Ultimately, a refiner's decision will be based on feasibility, economics, and geographic location; however, refiners have hinted that in order to avoid liability issues associated with MTBE they will switch from an RFG with MTBE with either RFG with ethanol or non-oxygenated RFG.

BP recently announced its intent to abandon MTBE blended gasoline and move to an ethanol blended RFG in the Northeast. With this action, BP joins Motiva in making the move to ethanol. ConocoPhillips is expected to switch all of its RFG locations to ethanol-based product this winter. It is also anticipated that a switch to ethanol-blended fuel will occur in the Baltimore and Virginia market later this winter, although no specific plans have been announced. Additionally, the Colonial pipeline, which provides approximately 90% of Maryland's fuel, has started a transition to remove MTBE from conventional gasoline grades. After March 1, 2006, all conventional gasoline transported through the pipeline will contain less than 0.50 percent MTBE by volume. Colonial's timeline for phasing MTBE out of RFG is undefined but will probably be

next year. These are examples of how the industry has already begun to make adjustments based on the removal of the oxygenate requirement.

This report reviews the environmental effects of using either RFG with 10 percent ethanol or non-oxygenated RFG. With either replacement fuel, an increase in ozone precursor emissions (VOC+NO_x) occurs. The analysis concludes that using 10 percent ethanol would increase total ozone precursors from between 11 to 16 tons/day on an average summer day. This is equivalent to a 4 percent increase in VOC and NO_x emissions from the baseline gasoline inventory. The analysis also concluded that using a non-oxygenated RFG would increase total VOC+NO_x emissions by 7 tons/day on an average summertime day, which is equivalent to a 2 percent increase in VOC and NO_x emissions from the baseline gasoline inventory.

This report also looks at the economic impact of changing from the baseline fuel, RFG with MTBE, to either an RFG with 10 percent ethanol or a non-oxygenated RFG fuel. The results indicate that the total recurring cost for continuing use of the baseline fuel, RFG with MTBE, would be \$770,000 annually. If RFG with 10 percent ethanol is used instead of the baseline fuel, the net cost to the state economy would be approximately \$181 million annually. If a non-oxygenated RFG is used instead of the baseline fuel, the total cost to the state economy would be \$174 million annually. A significant portion of the increased cost of using ethanol is involved with its transportation. Local production of ethanol could reduce many of these costs and bring ethanol more in-line with current fuel costs. MDE is working cooperatively with several business interests in developing plans for local ethanol production facilities in the state. MDE will continue to work with these groups and when successful these facilities could dramatically reduce the cost of ethanol in the state. Until that time, transportation costs involved with ethanol will continue to keep ethanol prices high.

Finally, the short and long term effectiveness of bioremediation in cleaning soil and groundwater contamination are presented. The MDE found the use of bioremediation a legitimate remediation tool, both in the short and long term. Some level of natural bioremediation occurs at every remediation site. The ability to augment the natural bioremediation can be limited based on site-specific conditions but has been proven very successful at various sites throughout Maryland and the nation. The ability to use bioremediation will increase with time as the science related to this technology improves. Much of the technology developed to remediate gasoline and MTBE in soil can be expected to work on the remediation of neat ethanol and ethanol blended gasoline. These tools, however, have not been tested on environmental releases; and until they are, determining which methods work best and their effectiveness will remain unknown.

In conclusion, the use of MTBE as an oxygenate will likely remain controversial and will continue to pose a potential threat to the environment should fuel leaks occur. In this regard, recent regulatory enhancements to MDE's underground storage tank program minimize the occurrence of leaks and improve early leak detection capabilities should one occur. These enhancements, as well as other new regulations for testing and notification, are proving to be a successful and cost-effective means of protecting vulnerable drinking water supplies from petroleum contamination whether the product in the tank contains ethanol or MTBE. Ethanol, the main oxygenate substitute, has both environmental and economic advantages and

disadvantages which need to be fully addressed before pursuing this as an MTBE replacement. MDE is working with the ethanol industry to address these concerns, such as local production, and hopes to resolve many of them in the future. The federal removal of the oxygenate requirement in the spring of 2006 will provide the flexibility and options that have long been sought after in meeting the RFG air quality goals while providing the industry the choice of which, if any, oxygenate to use. As a result of this many refiners have begun phasing out the use of MTBE on their own and are expected to continue to do so. Based on this information, it is MDE's recommendation that at this time it would be prudent and both fiscally and environmentally responsible for the state not to pursue any further action regarding the use of MTBE until the full effect of these new policies can be accurately assessed.

BACKGROUND

Since the phase-out of lead from gasoline in the late 1970s, methyl tertiary-butyl ether (MTBE) has been used nationwide at low levels as an octane enhancer or anti-knocking agent. The use of MTBE at higher levels resulted from two fuel programs required by the Clean Air Act Amendments (CAAA) of 1990, the Wintertime Oxygenated, and Reformulated Gasoline Programs.

The Wintertime Oxygenated Gasoline Program or “Oxyfuel” program required oxygen-containing chemical compounds, called oxygenates, to be added to winter gasoline to reduce carbon monoxide (CO) emissions that resulted from incomplete combustion during cold weather conditions. For a variety of reasons including cost, availability, and performance properties, MTBE emerged as the primary oxygenate in most parts of the country. The “oxyfuel” requirement applied only to areas in violation of the National Ambient Air Quality Standards (NAAQS) for CO. At the time, Maryland had several CO nonattainment areas, and the Maryland Department of the Environment (MDE) adopted a regulation that required, beginning in November 1992, gasoline sold from November through February to contain 2.7 percent oxygen by weight. The program accomplished its goal of reducing CO emissions so effectively that, by 1995, the State had attained the NAAQS for CO, and the oxyfuel program was terminated. The program is currently a contingency measure in the CO maintenance plan, which has been submitted to and approved by the United States Environmental Protection Agency (EPA).

The second CAAA requirement is the Reformulated Gasoline Program (RFG). Since 1995, the CAAA have required Maryland and other states that exceed federal air quality standards for ozone to use RFG year round to reduce motor vehicle emissions. The primary goal of the RFG program is to reduce emissions of ozone precursors, mainly volatile organic compounds (VOCs) and nitrogen oxides (NOx), as well as air toxics emissions, from automobiles. To meet this goal, all RFG must contain a minimum of 2 percent oxygen by weight, a requirement that petroleum refiners typically satisfy by adding the oxygenate MTBE to gasoline. In order to meet the 2 percent by weight requirement, refiners introduce MTBE into RFG at 11 percent by volume.

RFG is required in the Baltimore ozone non-attainment area, which is comprised of Baltimore City and Baltimore, Anne Arundel, Carroll, Harford, and Howard counties, as well as the Cecil County portion of the Philadelphia ozone non-attainment area. As allowed by the CAAA, Maryland opted-in other ozone non-attainment areas of the State, expanding the geographical areas to include the Washington DC metropolitan counties of Montgomery, Prince George’s, Calvert, Charles, and Frederick, as well as Kent and Queen Anne’s counties on the Eastern Shore. The remaining Maryland counties use conventional gasoline.

In Maryland, over a third of VOC and NOx emissions come from motor vehicles. The MDE estimates that the use of RFG in the specified areas of Maryland reduces VOC emissions from motor vehicles by more than 14 tons per day. RFG also provides substantial reductions of air toxics emissions. In addition, the use of RFG in lawn and garden equipment and other small engines produces further, unquantified emission reductions, which help air quality during our summertime ozone season.

RFG has substantially improved air quality in Maryland. Its use has enabled Maryland to remain in attainment of the NAAQS for CO and it is an important part of the State's CO maintenance plan. Its use in Kent and Queen Anne's counties enabled these counties to be redesignated to attainment for the 1-hour ozone standard and for the MDE to receive approval of those counties' maintenance plans. RFG, along with other programs implemented since 1990, enabled the Washington ozone non-attainment area to meet the 1-hour ozone standard this past summer and the Baltimore region to come within one monitor hour of meeting the standard. The benefits of RFG have also enabled Maryland's former severe, 1-hour non-attainment areas to be classified as moderate non-attainment areas under the new 8-hour ozone standard. The air quality benefits achieved by the RFG program so far must be maintained so Maryland can preserve current air quality levels and continue to move toward compliance with the new 8-hour ozone standard.

The RFG program continues to be a critical component in Maryland's comprehensive air quality plan. Its use has proven to be a very cost-effective control measure for reducing ozone precursors, carbon monoxide and air toxics emissions from motor vehicles.

PREVIOUS RESEARCH ON OXYGENATES

Notwithstanding the positive air quality benefits provided by RFG, the use of MTBE has been shown to have environmental drawbacks. Beginning in the mid-1990s, states began detecting MTBE contamination in their public drinking water supplies. The main cause of the contamination was leaks in many of the country's underground storage tanks, above ground petroleum storage tanks and piping systems. RFG with MTBE is more prone to cause groundwater contamination because MTBE is water soluble, has a smaller molecular size as well as a low tendency to adhere to soil, and is less biodegradable than other components of gasoline. Consequently, MTBE is more mobile in groundwater than other gasoline constituents and may often be present when other components are not. Other sources of contamination include atmospheric deposition, storm water runoff from paved surfaces, watercraft, spills, and improper disposal of fuels. The physical properties of MTBE, combined with the various ways MTBE can be released into the environment, have resulted in the detection of MTBE in drinking water supplies across the country as well as here in Maryland. MTBE has become a contaminant of concern that could, without specific targeted measures, continue to threaten drinking water supplies into the future.

EPA Blue Ribbon Panel

In November 1998, in response to the growing concerns from State and local officials and the public regarding MTBE contamination of drinking water, the EPA appointed a Blue Ribbon Panel to investigate the air quality benefits and water quality concerns associated with oxygenates in gasoline. The Panel would also provide independent advice and recommendations on ways to maintain air quality while protecting water quality. The panel members consisted of leading experts from the public health and scientific communities, automotive fuels industry, water utilities, and local and State governments. The Panel was charged to:

- Examine the role of oxygenates in meeting the nation's goal of clean air;

- Evaluate each product's efficiency in providing clean air benefits and the existence of alternatives;
- Assess the behavior of oxygenates in the environment;
- Review any known health effects; and
- Compare the cost of production and use and each product's availability-both at present and in the future.

The Panel also studied the causes of groundwater and drinking water contamination from motor vehicle fuels, and explored prevention and cleanup technologies for water and soil. The Panel was established under EPA's Federal Advisory Committee Act's Clean Air Act Advisory Committee, a policy committee established to advise the EPA on issues related to implementing the CAAA of 1990. It met six times from January-June, 1999; heard presentations in Washington, DC, the Northeast, and California about the benefits and concerns related to RFG and the oxygenates; gathered the best available information on the program and its effects; identified key data gaps; and evaluated a series of recommended alternatives based on their effects on air quality, water quality and stability of fuel supply and cost.

In September 1999, the Panel released its final report entitled, "Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline." [1]

Findings of the Blue Ribbon Panel

Based on its review of the issues, the Panel made the following overall findings:

- The distribution, use, and combustion of gasoline pose risks to our environment and public health.
- RFG provides considerable air quality improvements and benefits for millions of U.S. citizens.
- The use of MTBE has raised the issue of the effects of both MTBE alone and MTBE in gasoline. This Panel was not constituted to perform an independent comprehensive health assessment and chose to rely on recent reports by a number of state, national, and international health agencies. What seems clear, however, is that MTBE, due to its persistence and mobility in water, is more likely to contaminate ground and surface water than the other components of gasoline.
- MTBE has been found in a number of water supplies nationwide, primarily causing odor and taste concerns that have led water suppliers to reduce use of those supplies. Incidents of MTBE in drinking water supplies at levels well above EPA and state guidelines and standards have occurred, but are rare. The Panel believes that the occurrence of MTBE in drinking water supplies can and should be substantially reduced.

- MTBE is currently an integral component of the U.S. gasoline supply both in terms of volume and octane. As such, changes in its use, with the attendant capital construction and infrastructure modifications, must be implemented with sufficient time, certainty, and flexibility to maintain the stability of both the complex U.S. fuel supply system and gasoline prices.

Recommendations to Enhance Water Protection

Based on its review of the existing federal, state, and local programs to protect, treat, and remediate water supplies, the Panel made several recommendations to enhance public drinking water monitoring and remediation programs, enhance enforcement of underground storage tank replacement and upgrade programs, and enhance public education and clean-up programs for gasoline. The Panel's recommendations were intended to be implemented as a single package of actions designed to simultaneously maintain air quality benefits while enhancing water quality protections and assuring a stable fuel supply at reasonable cost.

Recommendations for Blending Fuel for Clean Air and Water

The Panel agreed broadly, although not unanimously, that even enhanced protection programs, like those in their recommendations, would not give adequate assurance that water supplies would be protected. The Panel also agreed that changes needed to be made to the RFG program to reduce the amount of MTBE being used while ensuring that the air quality benefits of RFG, fuel supply, and price stability are maintained.

Given the complexity of the nation's fuel system, the advantages and disadvantages of each of the fuel blending options the Panel considered, and the need to maintain the air quality benefits of the current program, the Panel recommended an integrated package of actions that should be taken by both Congress and EPA. The key elements of that package are:

- Action agreed to broadly by the Panel to substantially reduce the use of MTBE (with some members supporting its complete phase-out), and action by Congress to clarify federal and state authority to regulate and/or eliminate the use of gasoline additives that threaten drinking water supplies;
- Action by Congress to remove the current 2 percent oxygen requirement to ensure that adequate fuel supplies can be blended in a cost-effective manner while quickly reducing usage of MTBE; and
- Action by EPA to ensure that there is no loss of current air quality benefits.

The Panel's report served to provide a factual assessment of the issues, problems and recommendations associated with MTBE. The focus of the report was presenting an accurate picture of the MTBE situation nationwide.

Maryland's MTBE Task Force

In an effort to build upon the work done by EPA, the Maryland General Assembly determined that a more in-depth, Maryland-specific assessment of MTBE was needed. In May 2000, House Bill 823 created a Task Force on the Environmental Effects of MTBE. The Maryland Task Force consisted of 16 members from various government agencies, the petroleum and ethanol industries, and health professionals. The Task Force's responsibilities were to:

- Determine and assess the environmental and health risks associated with ground and surface water contamination from MTBE;
- Examine national and regional efforts concerning ground and surface water contamination from MTBE;
- Recommend a plan to minimize and counteract the environmental and health risks associated with ground and surface water contamination from MTBE; and
- Explore alternatives to MTBE, including ethanol and oxygenated fuel, which can be used for the purpose of reformulation of gasoline to reduce air toxic emissions and pollutants that form ground level ozone.

The Task Force held 16 meetings including an evening public meeting. Presentations from various experts on air and water quality, and energy and health impacts were made to the Task Force at these meetings, along with current reports and technical articles regarding MTBE from around the nation.

The Task Force's final report was completed in December 2001[2] and offered the following six recommendations:

- (1) MDE should continue the testing and assessment of wells and water supply systems for MTBE and other oxygenates used by the petroleum industry. Positive test results should result in the MDE conducting a follow-up source investigation as appropriate.
- (2) MDE should enhance the level of inspection and enforcement of underground storage tank (UST) systems and spill prevention programs and control the escape of MTBE and other gasoline constituents through improving technology and operation of UST systems, including the piping and distribution system.
- (3) Maryland should give careful consideration to eventually reducing or phasing out the use of MTBE in gasoline sold in Maryland. Since this is best addressed as a regional multi-state or national issue, specific steps should include working with Maryland elected officials to urge the U.S. Congress to develop a national solution to MTBE which should include repealing the federal Clean Air Act's 2 percent oxygen-by-weight mandate and establishing a renewable fuel program.

- (4) Additional health and energy studies on MTBE, ethanol, other oxygenates, and alternative gasoline formulations are being conducted by the U.S. Department of Energy, the U.S. EPA, other agencies and industry. The MDE should review those studies when completed and use their conclusions and recommendations to modify MDE policy, if appropriate.
- (5) MDE should implement, through public-private partnerships, expanded public outreach programs on the proper handling and disposal of gasoline. These outreach efforts should also include a broad-based program targeting owners and users of private wells on measures to prevent, detect, and treat contaminated water.
- (6) Maryland should provide adequate support to address the impact of MTBE and other oxygenates in gasoline on Maryland's water resources.

The recommendations of the Maryland Task Force were similar to those of EPA's Blue Ribbon Panel. Both recognized the need to enhance groundwater protections through increased inspection, testing, and assessments of wells and water supplies with the primary focus being early detection and remediation. They both also acknowledged the important air quality benefits of RFG and recommended that Congress act to remove the 2 percent oxygenate requirement while ensuring there is no loss of air quality benefits.

RECENT ACTIVITIES RELATED TO MTBE

In 2004, MDE found MTBE in groundwater at levels necessitating further action. To address this issue, MDE developed emergency regulations to reduce the risks of MTBE contamination where it is most serious; that is, in areas where groundwater is the source of water supply. The regulations require enhanced inspection for early detection and better containment of MTBE within gasoline storage systems in high-risk groundwater use areas. The regulations address many of the recommendations made earlier by both EPA's Blue Ribbon Panel and Maryland's MTBE Task Force.

The U.S. Congress continued discussions related to energy policy as well as MTBE use and liability through a variety of mechanisms, including federal energy legislation. In August 2005, Congress passed the Energy Policy Act of 2005 that contains important provisions relating to MTBE.

Maryland Law and MDE Regulations

In order to address Maryland's groundwater contamination issues, MDE, in the fall of 2004, developed emergency regulations to prevent MTBE and other petroleum products from reaching groundwater supplies in high-risk areas of Maryland. The emergency regulations, unanimously approved by the Joint Committee on Administrative, Executive and Legislative Review, require more frequent testing for vapors as well as liquid leaks and rigorous safeguards against leaks. The emergency regulations became effective January 26, 2005. The expiration date for the emergency status of these regulations was extended from July 26, 2005 to January 23, 2006. MDE is in the process of adopting them under the normal regulatory process that includes a

public hearing and comment period.

The primary focus of the regulations is in areas where wells are the primary source of household drinking water and local geology makes it impractical for homeowners to find an alternative water source. MDE has identified these areas around the state and has notified affected tank owners or operators.

Statewide the regulations require installation of double-walled pipes on all new regulated underground storage systems and built-in sensors to warn of leaks. Within the high risk groundwater use areas of the state, the regulations require increased groundwater sampling, mandate regular testing of tanks and fittings, and define steps that gas station owners and others must take when underground storage systems are suspected of contaminating groundwater.

Service stations and other underground storage facilities in areas covered by the regulations have to begin sampling of water in on-site domestic wells. They are also required to conduct annual tightness tests for fittings in catchment basins and containment sumps. Additionally, they are required to install and sample three groundwater monitoring wells. Sampling results must be reported to MDE.

If more than 20 parts per billion (ppb) of MTBE, more than 5 ppb of benzene, or more than 100 ppb of total BTEX (benzene, toluene, ethyl benzene and xylenes) are found in the monitoring wells, the operator is required to develop a corrective action plan as well as perform an advanced helium leak detection test, which is used to identify vapor leaks. In addition to repairing all leaks immediately, the operator is required to install a soil vapor extraction system in the tank area to remove vapors from the earth or other advanced technology to keep vapors within the tank system.

As a result of the implementation of the emergency regulations, MDE has observed an increase in the discovery of MTBE at active service stations. The early discovery of the presence of MTBE has allowed MDE and the underground storage tank (UST) owners to repair the UST system and take actions to ensure the MTBE does not spread further into the environment. Several monitoring well installations that resulted from the emergency regulations led to the discovery of direct impacts to private water supply wells. These discoveries allowed the immediate placement of protections on the supply wells, therefore addressing direct human consumption of MTBE.

In addition to these regulations, two bills passed in the 2005 Maryland General Assembly Session will also help prevent exposure to MTBE contamination. The first, House Bill 355- "Nontransient Noncommunity Water Systems- Methyl Tertiary Butyl Ether – Testing," requires the testing of water systems for the presence of MTBE. Nontransient noncommunity water systems are those that serve areas such as schools, nursing homes and daycare facilities. Previously these systems were not required to conduct testing. This bill fills an important gap by requiring these systems to test for MTBE contamination. In doing so, it limits exposure to MTBE by a significant at risk population. The second, House Bill 370- "Oil Spills-Methyl Tertiary Butyl Ether Oil Discharge-Groundwater Contamination," requires MDE to notify local health departments upon learning of groundwater contaminations, which in turn are required to

notify local property owners within a certain distance of a site found to be contaminated. By requiring notification, this bill helps remove potential MTBE exposure to at risk populations.

Federal Energy Policy Act of 2005

On August 8, 2005, President George W. Bush signed the federal Energy Policy Act of 2005 (EPACT2005). Several provisions of this law are of particular significance to RFG. The first provision removes the 2 percent oxygenate requirement in RFG, while the second provision mandates the increased use of renewable fuels, primarily ethanol and biodiesel.

Oxygenate Requirements

The EPACT2005 eliminates the 2 percent oxygenate requirement for RFG. The elimination of this requirement was effective immediately in California. For the rest of the country, including Maryland, the provision takes effect 270 days from the date of enactment (August 8, 2005). While this federal legislation removes the oxygenate requirement, it does not provide for a ban on MTBE.

Once the oxygenate requirement in RFG is removed in the spring of 2006, refiners will have more flexibility in determining how to produce compliant RFG. The Maryland gasoline marketplace may be supplied with any one of a number of gasoline blends including RFG with reduced amounts of MTBE, RFG with 10 percent ethanol, non-oxygenated RFG or a market mix of these fuels. Several refiners have hinted that they will discontinue the use of MTBE due to the lack of a federal oxygenate requirement and increased liability associated with its use. Refiners have also indicated that they will allow the market to determine which type of fuel they will provide to various regions. Ultimately, this decision will be based on feasibility and economics.

As a result of this new legislation, refiners and others associated with the petroleum industry have either begun phasing out the usage of MTBE or started setting timetables for its removal. An example is the Colonial pipeline, a major provider of fuel to the northeast. The Colonial pipeline provides approximately 90 percent of all of Maryland's gasoline and diesel fuel. On August 11, 2005, Colonial issued bulletin #1350 detailing their proposed strategy for limiting MTBE content in conventional gasoline that is shipped on the pipeline. The bulletin indicates that as of March 1, 2006, all conventional gasoline will be low MTBE, i.e. less than 0.50 percent by volume. Colonial is currently assessing its timeline for phasing MTBE out of RFG, which it believes will be sometime next year. Refiners are also making similar statements to minimize or eliminate the use of MTBE. With actions like this already in place it appears that the industry is already removing MTBE and making adjustments to the product.

Renewable Fuels Standard (RFS)

The EPACT2005 establishes the first-ever Renewable Fuels Standard (RFS) in federal law by requiring that at least 4 billion gallons of ethanol and biodiesel be used in 2006, increasing to at least 7.5 billion gallons per year (bgy) in 2012 – with an annual increase of approximately 700 million gallons per year. The RFS also creates a flexible credit trading mechanism for refiners to

optimize their use of ethanol. The Energy Information Administration (EIA) estimates the 7.5 bgy RFS will reduce nationwide oil consumption by 80,000 barrels of oil a day by 2012. EPA will be responsible for implementing and enforcing the RFS program. EPA must promulgate regulations requiring refineries, blenders, distributors, and importers to introduce or sell volumes of ethanol and biodiesel into commerce in accordance with the annual renewable fuels schedule below:

Yearly Ethanol Demand	
2006.....	4.0 bgy
2007.....	4.7 bgy
2008.....	5.4 bgy
2009.....	6.1 bgy
2010.....	6.8 bgy
2011.....	7.4 bgy
2012.....	7.5 bgy

The RFS is to be implemented no later than one year after enactment (August 8, 2005). If EPA fails to issue regulations to implement the RFS, the law contains a failsafe that requires ethanol and biodiesel to comprise 2.78% of the U.S. fuel supply in 2006 – approximately 4 billion gallons. Not later than October 31 of each year, EIA shall provide to EPA the volumes of gasoline projected to be sold into commerce in the U.S. By November 30 of each year, the EPA will publish, in the Federal Register, the renewable fuels obligations (expressed in terms of a volume percentage of gasoline sold) for each regulated entity to ensure that the RFS for the following year is met.

For 2013 and each year thereafter, the EPA shall establish a new RFS, based on the amount of ethanol expected to be sold into commerce each of those years. The use of ethanol and biodiesel in 2013 shall not be less than the percentage of 7.5 billion gallons to the total volume of the U.S. gasoline supply in 2012. The RFS must include a separate element calling for at least 250 million gallons of cellulosic ethanol starting in 2013.

Additional Requirements

The EPACT2005 also commissions four studies to gain better information for understanding the effects of the various new fuel provisions of this law. An ethanol permeation effects study and a report to Congress on boutique fuels are due within one year. Within two years, a report on the public health and environmental impacts of fuel additives is required. Finally, a fuel system requirements and harmonization study is required in June 2008.

The EPACT2005 also requires additional oversight of underground storage tanks, and increased monitoring and inspection. The states are required to report inspection findings to EPA as well as develop tank operator training and produce delivery bans regarding substandard tanks.

ALTERNATIVE OXYGENATES

In general, oxygenates fall into two chemical categories: ethers and alcohols. MTBE has been the leading ether-based oxygenate; others include ethyl tertiary-butyl ether (ETBE) and tertiary-amyl methyl ether (TAME). The primary alcohol oxygenates are ethanol, methanol, and tertiary-butyl alcohol (TBA).

The extent to which any of these oxygenates are used to replace MTBE depends on availability, performance characteristics, and cost relative to other alternatives. For example, the long-term use of other ether-based oxygenates, such as ETBE or TAME, could be limited by the same water quality concerns associated with MTBE. As a class, ethers are soluble in water and resistant to biodegradation; consequently, ether contamination of soils and surface/groundwater environments is difficult to remediate. Although there is minimal scientific information or field data on the behavior of ETBE or TAME when leaked or spilled, these compounds are expected to behave much like MTBE because of their similar chemical compositions. Of the alcohol alternatives, use of methanol is likely to be limited by its toxicity and other undesirable characteristics when blended directly with gasoline. Meanwhile, supplies of TBA (an MTBE metabolite) are limited, as is production capacity. In addition, there is evidence that TBA may be carcinogenic.

The creation of the Renewable Fuels Standard ensures that ethanol will be the primary replacement for MTBE. It can be produced in quantities capable of supplanting a substantial portion of the MTBE market in the near term, is considered relatively low in toxicity compared to many other gasoline constituents, biodegrades readily, and does not adsorb to sediments or soils. Also, like MTBE, ethanol functions as an octane enhancer and can therefore displace other, more toxic octane enhancers.

Today there are 91 plants across the country with the capacity to produce more than 4 billion gallons of ethanol annually. Twenty-one plants are under construction and three major expansions will add another one billion gallons of capacity. With the likely decrease in the use of MTBE and the mandated RFS, ethanol will have an increasingly larger role in helping to meet the nation's fuel needs.

ENVIRONMENTAL IMPACTS OF USING ETHANOL

Air Quality

Maryland is required to use federal RFG to reduce VOC and NO_x emissions from vehicles. These emissions contribute to the formation of ground-level ozone. The oxygenate in RFG also helps to reduce CO emissions. The RFG program is a performance-based program meaning that RFG is refined to meet a specified EPA performance standard expressed in terms of percent reduction. Currently, RFG exceeds this performance standard by reducing VOCs by about 29%, NO_x by about 7% and air toxics by about 32%. The law also required RFG to contain an oxygenate like MTBE or ethanol that adds at least 2 percent oxygen by weight (which equates to 11 percent by volume). Passage of EPACT2005 eliminates the oxygenate requirement; however,

the percent of VOC and NO_x reductions obtained from RFG still apply whether the RFG contains oxygenates or not.

All oxygenates used in gasoline do not have the same overall emissions impact. Except for air toxics, the EPA emissions models for both on-road and off-road vehicles do not differentiate between using ethanol or MTBE in RFG. The models were developed with an oxygenate-neutral policy where all oxygen in the fuel is assumed to have the same effectiveness in reducing exhaust emissions, and emissions are assumed to change proportionally with oxygen concentration. Recent data and analysis from testing programs, however, show that there are higher emissions differences associated with the use of ethanol. Ethanol, at high levels, can increase NO_x emissions from on-road vehicles and ethanol increases “permeation” emissions from fuel system components (plastics and elastomers) in on-road vehicles, off-road vehicles, and portable gasoline containers.

Gasoline-related emissions inventories are made up of a combination of exhaust emissions and evaporative emissions. While exhaust emissions consist of unburned hydrocarbons (VOCs), NO_x, CO, and air toxics, evaporative emissions consist of VOCs only, since they are composed of the gasoline vapors that escape from all parts of the vehicle other than the tailpipe. Permeation VOC emissions are the portion of evaporative VOC emissions that seep through the plastic and elastomer materials of the vehicle’s fuel system and fuel containers. Gasoline related emissions are grouped into two general sources: on-road vehicles and the off-road engines, which are generally the smaller engines such as lawnmowers, chainsaws, power generators, etc. Even though these off-road sources consume a small portion of the gasoline pool, they represent a significant share of the gasoline related VOC inventory due to a lesser degree of emissions control than motor vehicles.

The impacts of RFG on Maryland’s emissions inventories have to be estimated using several emissions prediction models developed by EPA and California Air Resources Board (CARB). The on-road vehicle fleet emissions can be estimated using EPA’s MOBILE6.2 emissions model; however, this model does not differentiate between RFG with MTBE and RFG with 10 percent ethanol nor does it reflect the non-linear increase in NO_x emissions associated with the higher oxygen levels in 10 percent ethanol blends. The CARB Predictive Model is used to adjust the exhaust emissions for the effects of different fuels. The EPA’s NONROAD 2004 model is used to predict emissions from off-road equipment and vehicles. Since neither the EPA MOBILE nor NONROAD models include the effects of ethanol permeation, these effects had to be developed outside these models. All of these models are needed because none of them individually are capable of evaluating all the different impacts.

The EPA and CARB models have been in existence for many years and users are familiar with their results and limitations. However, the ethanol permeation effects are relatively new and are not addressed in these accepted models. Research is being conducted to quantify these impacts. To date, five studies have been conducted to evaluate ethanol’s impact on permeation VOC emissions. Summaries of the studies are provided below:

Coordinating Research Council (CRC) Study

When California implemented its Phase 3 RFG requirements, calling for the phase-out of

MTBE and replacement with ethanol, one of the issues raised during the Board Hearing was whether ethanol increased permeation emissions of VOC components through plastic and rubber parts in the fuel system of vehicles. CARB subsequently directed its staff to study this issue. The CARB and the CRC initiated a 2-year, 10-vehicle testing program to evaluate this issue. On September 20, 2004, CRC issued a detailed report summarizing the results of the testing. [3]

The testing program revealed that ethanol increases permeation emissions from on-road passenger cars and light duty trucks an average of an additional 1.4 grams per day per vehicle as compared to an MTBE blended fuel, under the test conditions of a diurnal temperature of 65° F to 105° F. The testing also found that this increase in permeation VOC emissions is sensitive to ambient temperature. At lower ambient temperatures, the emissions increase due to ethanol is lower, indicating a need to correct for differences in the ambient and test temperatures when estimating the increase in emissions.

AIR Permeation Study for API

Recognizing that the CRC data and report would be released, and desiring to determine the inventory impacts of expanding ethanol use, the American Petroleum Institute (API) contracted with Air Improvement Resources, (AIR) Inc. to determine, based on the CRC on-road data and other available data, the impact of ethanol on permeation emissions for on-road vehicles, off-road equipment, and portable containers. The study was conducted for several different areas of the country, including California, Atlanta, Houston, and the New York / New Jersey / Connecticut area. [4]

The study used the available data, developed temperature correction factors, and estimated the permeation VOC increases in the above geographical areas. For example, in California, the study estimated that ethanol increases permeation emissions from on-road vehicles, off-road sources, and portable containers by 25 tons per day (tpd) in 2003. The study further estimated that ethanol would increase VOC permeation by 24 tpd in the New York / New Jersey / Connecticut area.

AIR Study for the Southeast Michigan Council of Governments (SEMCOG)

AIR, Inc. also studied various gasoline and diesel fuel options for the Southeast Michigan Council of Governments.[5] SEMCOG evaluated a number of fuel options, including RFG with ethanol and RFG without ethanol. The methods used to estimate permeation emissions were consistent with the API report, and the NOx effects of ethanol were estimated with the California Predictive Model. The study found that RFG without ethanol, due to lower permeation VOC emissions, would have larger VOC benefits than RFG with ethanol. The study also found that RFG with ethanol would increase NOx emissions over the Michigan baseline fuel.

CARB Draft Study on Ethanol

The CARB recently released a draft study of the effects of ethanol in California. [6] Similar to the AIR study for SEMCOG, CARB estimated the permeation effects for on-road vehicles, off-road equipment, and portable containers. CARB also estimated NOx impacts for on-road vehicles. The draft study concluded that ethanol increases VOC

emissions by 45-75 tpd, and that NOx emissions increase by 21 tpd as compared to MTBE.

CARB Test Programs on Portable Containers

There is no specific CARB report on permeation of portable plastic fuel containers with and without ethanol; however, CARB has performed a number of tests with its certification fuel, which contains MTBE, and fuel containing 6 percent ethanol. A number of different portable containers were tested, and the average size was about 3.3 gallons. The average emission rate of MTBE fuel was 4.7 grams/day. For a 6 percent ethanol fuel, the average emission rate increased to 6.6 grams/day, representing about a 39% increase in VOC emissions.

Each of these studies concluded that the use of ethanol in RFG increased emissions.

RFG reduces CO, VOC, NOx, and air toxics emissions and is a critical component of Maryland's Ozone State Implementation Plan (SIP). Maryland's Ozone SIP is a compilation of laws, regulations, technical documents, and programs that, when implemented, are designed to allow the State to attain the federal air quality standard for ozone. The air quality benefits derived from the use of RFG have been included in the SIP. Any air quality benefits that would be lost due to no longer using MTBE would have to be replaced through additional control measures. Accordingly, if emissions increase from the use of ethanol as these studies predict, the resulting increase would have to be offset in the SIP. If Maryland does not attain the federal ozone air quality standard in the timeframe allotted (2010 under the 8-hour ozone standard), EPA is authorized to impose more ozone planning requirements, including additional local controls, a federal implementation plan (FIP), or immediate sanctions that could hinder economic growth (by increasing new source offset requirements) or affect federal highway funding.

Given the potential impact on air quality and Maryland's SIP, MDE subsequently requested AIR, Inc. to evaluate the overall air emissions impact of switching from RFG with 11 percent MTBE to either RFG with 10 percent ethanol, or non-oxygenated RFG in Maryland. AIR, Inc. published the results of their study in the document entitled "*Potential Maryland Air Emission Impacts of a Ban on MTBE in the Reformulated Gasoline Program*" on October 18, 2005. [7] The results of this study are summarized below. The full report is provided in Appendix A.

Maryland Analysis

This study used recent testing data on ethanol permeation effects conducted by the Coordinating Research Council. It also used test data and analyses of the effects of ethanol on NOx emissions developed by CARB. Three fuel cases were evaluated:

1. Baseline RFG with 11 percent MTBE
2. RFG with 10 percent ethanol
3. RFG without oxygenate

Meeting the RFG requirement of 2 percent oxygen by weight requires blending 11 percent MTBE by volume, but only 5.7 percent ethanol by volume. At 2 percent oxygen by weight,

simply replacing MTBE with ethanol leads to a loss in both gasoline volume and in gasoline octane. Federal regulations permit ethanol blending at 10 percent by volume, which mitigates these consequences. This analysis assumed ethanol blending at 10 percent by volume.

The analysis evaluated VOC, NOx, CO, and particulate matter (PM) emissions from three source categories: on-road gasoline vehicles, off-road gasoline equipment and vehicles, and portable gasoline containers. The evaluation year is 2007 and assumes that Maryland switches from the baseline gasoline to either of the alternatives in this timeframe.

The analysis used the EPA MOBILE6.2 model for MTBE emissions for on-road sources, and the CARB Predictive Model to adjust the exhaust emissions from gasoline vehicles for either 10 percent ethanol effects, or for no-oxygenate effects. Non-ethanol permeation evaporative emissions from on-road vehicles were estimated with MOBILE. For off-road equipment and off-road vehicles, the analysis used the EPA NONROAD2004 model for all three fuels. Unlike the MOBILE model, the NONROAD2004 model can be used for all cases, because the exhaust emissions of off-road equipment and vehicles are generally not equipped with catalytic converters, oxygen sensors and other equipment that is sensitive to differences in oxygenates. The exhaust emissions of these sources generally only respond to changes in oxygen concentration, not the type of oxygenate.

Since neither the MOBILE nor NONROAD models include the effects of ethanol permeation, these effects had to be developed outside the models. These emissions impacts were developed in a manner consistent with AIR's analysis for both API and SEMCOG.

Combining Results

The study examined the impact the fuel options had on all three of the identified source categories; on-road vehicles, off-road vehicles and equipment, and portable containers. The emissions effects were estimated separately and then combined using the following general equation:

$$\text{Total effect} = (\text{On-road effect}) + (\text{Off-road effect}) + (\text{Portable container effect})$$

Where:

On-road effect = (exhaust) + (evaporative) + (permeation)

Off-road effect = same as on-road but for off-road sources

Portable container effect = permeation effect

And where:

On-road exhaust effect = (MOBILE6.2 exhaust baseline) + (% change from Predictive Model)

On-road evaporative effect = change in MOBILE 6.2 evaporative emissions

On-road permeation effect = method used by AIR in API permeation study

Off-road exhaust effect = estimated by EPA NONROAD model

Off-road evaporative effect = estimated by EPA NONROAD model
 Off-road permeation effect = method used by AIR in API permeation study

Portable container permeation effect = method used by AIR in API permeation study

Results

This analysis concluded that using 10 percent ethanol would increase total ozone precursors (VOC+NOx) from between 11 to 16 tons/day on an average summertime day. This is equivalent to a 4 percent increase in VOC and NOx emissions from the baseline gasoline inventory. The analysis also concluded that using a non-oxygenated RFG would increase total VOC+NOx emissions by 7 tons/day on an average summertime day, which is equivalent to a 2 percent increase in VOC and NOx emissions from the baseline gasoline inventory. A summary of emission impacts resulting from a change to RFG with ethanol or non-oxygenated RFG is provided in Table 1.

**Table 1
 Overall Impacts of Ethanol RFG and Non-Oxygenated RFG in 2007**

Pollutant	Baseline Inventory-Gasoline (tons per day)	Net Ethanol Impact (tons per day)	Net Non-Oxygenated RFG Impact	% Change, Ethanol RFG	% Change, Non-Oxygenated RFG
VOC	233.5	2.9 - 7.6	10.0	1.2% - 3.1%	4.3%
NOx	134.1	8.5	-3.0	6.3%	-2.2%
CO	2997.2	-169.0	325.5	-5.6%	10.9%
PM	7.33	-0.22	0.34	-3.0%	4.6%

This analysis required the development of a baseline gasoline inventory with which to compare the emissions changes. This baseline inventory was created for VOC, NOx, CO and PM emissions from on-road vehicles and off-road equipment and vehicles. This baseline inventory does not include evaporative emissions from portable containers because they will not change with a change in oxygenate. This analysis is only estimating the increase in permeation VOC emissions resulting from the use of ethanol. The gasoline inventory values in the chart above are specific to this analysis and should not be compared to inventories in the SIP.

The data show that if Maryland’s RFG with MTBE is replaced by RFG with ethanol, VOCs could increase by 1 to 3 percent (depending on the extent of the permeation effect), NOx would increase by more than 6 percent, CO would decrease by close to 6 percent, and PM would be reduced by 3 percent. If the RFG with MTBE is replaced by a non-oxygenated gasoline, VOCs would increase by about 4 percent, NOx would be reduced by more than 2 percent, CO would increase by almost 11 percent, and PM would increase by almost 5 percent.

Studies indicate that the CO increases resulting from a non-oxygenated gasoline could be significant because CO is a weak ozone precursor. An EPA analysis of the tradeoff between CO and VOC in the Chicago area estimated that 45 tons of CO was worth 1 ton of VOC on a

reactivity and mass basis. Assuming this is also an appropriate ratio for Maryland, under the non-oxygenated RFG scenario, the CO increase of 325 tons/day could be equivalent to approximately 7.2 tons/day of additional VOC emissions. Although CO attainment is not a problem, the impact of these additional ozone precursor emissions will impact attainment of the ozone standard. Using the same ratio, the VOC equivalents derived from the CO benefit of converting to ethanol could produce additional benefits of 3.8 tons/day of VOC.

Review of the results from the on-road analysis indicates that a while a change from RFG with MTBE to either RFG with ethanol or non-oxygenated RFG increases emissions slightly, that overall the impact is least in these vehicles. The change to an ethanol-blended fuel had the largest impact on NOx emissions accounting for 6.6 tons/per day of the 8.5 tons/day increase.

Larger impacts were seen in the off-road analysis. Converting to ethanol RFG reduces off-road VOC emissions because these emissions are a function of the weight percent of oxygen instead of volume percent of oxygenate and the weight percent of oxygen is higher for ethanol than for MTBE. A change to non-oxygenated RFG increases VOCs by almost 8 tons/day of the 10 tons/day net increase for this fuel.

The permeation impact on VOCs from using ethanol account for the majority of the VOC increases. This analysis presented two approaches to estimating the permeation impact. The first approach assumed that the permeation impacts resulting from the use of a 10 percent ethanol blend are the same as with a 6 percent ethanol blend (level used in CARB analysis). The other approach assumed that the permeation impact is proportional to ethanol concentration. The difference in these approaches accounts for the range of impacts in the above table. The low end VOC impact in Table 1 (2.9 tons/day) is calculated using the 6 percent blend while the high end value was calculated using the 10 percent.

While the scope of this analysis did not include an evaluation of the impact on greenhouse gases (GHG), the use of ethanol-blended fuels does provide GHG benefits. According to Argonne National Laboratory, 10 percent ethanol blends reduce greenhouse gases (GHG) emissions by 12-19 percent. Ethanol produced from cellulose could reduce GHG emissions even further. The use of ethanol-blended fuels reduced CO₂-equivalent greenhouse gas emissions by approximately 7 million tons in 2004, equal to removing the annual greenhouse gas emissions of 1.04 million cars from the road.

Groundwater Quality

Ethanol is believed to be one of the least toxic of gasoline components, but little is known regarding ethanol's behavior in petroleum underground storage tank (UST) releases. Contamination of drinking water by ethanol-blended gasoline is not expected to pose public health risks from a drinking water resource concern. Surface spills of ethanol on water can result in consumption of dissolved oxygen, however, causing fish kills.

Ethanol is 100 percent soluble in water and at high concentrations, ethanol may cause other gasoline constituents to become more soluble in water. However, it is believed that ethanol blends of 10 percent or less will have minor effects on the dissolution of benzene, toluene, ethyl

benzene, xylene (BTEX), and other gasoline compounds into the groundwater. Current ethanol blends of 10 percent or less do not appear to increase the extent of BTEX plumes. In higher ethanol concentrations, ethanol extends plumes of benzene and toluene up to 25 percent. Ethanol's rapid biodegradation depletes oxygen, nutrients, and anaerobic electron acceptors in the soil and water, so other compounds in gasoline will biodegrade more slowly in water. If anaerobic conditions are created due to the biodegradation of ethanol, the concentration of other naturally occurring minerals, such as iron and manganese, may be increased in the groundwater, creating a further nuisance. These factors may increase the length of time of spill investigations and complicate cleanup actions at the sites, thus increasing costs.

Ethanol biodegrades more rapidly than MTBE, as MTBE is resistant to biodegradation. MTBE spreads farther and faster than other constituents of gasoline. It is not likely ethanol will persist in groundwater for a significant time relative to BTEX and MTBE. The remediation of ethanol-contaminated gasoline in soils is estimated to have a minimal impact on the current cleanup technologies; however, this has yet to be field-tested. The remediation of ethanol-contaminated gasoline in water would likely require scaled-up bioremediation technology. Because the ethanol may extend the contamination plumes, more water wells may be affected by a UST release. Carbon filters currently used to treat contaminated drinking water and remove MTBE at release sites will not be effective with gasoline containing ethanol.

Other Concerns

There may be a concern regarding epoxy or polyester tank linings installed prior to 1980. It is possible that ethanol may make polymer/plastic/elastomer compounds brittle and prone to more rapid replacement for tank system lining materials, secondary containment materials, adhesives, glues, sealants, gaskets, dispensing equipment parts, gauges, submersible pump equipment, hoses, and nozzles. When using an ethanol blended gasoline, tank operators will need to drain water from the tank bottoms more frequently, due to ethanol's affinity for water. Before accepting any ethanol fuels, the USTs will need to be inspected and certified as acceptable for containing ethanol.

ECONOMICS OF USING ALTERNATIVE OXYGENATES

With the elimination of the oxygenate requirement in RFG in May 2006, it is likely that the industry will provide any one, or a combination of, compliant RFG fuels. This section looks at the economic impact of changing from the baseline fuel, RFG with MTBE, to either an RFG with 10 percent ethanol or a non-oxygenated RFG fuel. The results are summarized in Table 2.

Base Case-RFG with MTBE

MDE is adopting regulations requiring owners of new and existing underground storage tank systems in high-risk groundwater areas of the State to implement groundwater monitoring and additional leak testing in efforts to prevent smaller releases of petroleum products into groundwater sources used for drinking water. MDE's enhanced leak monitoring program will not only detect previously unidentified leaks from underground storage systems but it will also allow earlier detection and response. This scenario was selected as the base case since the

regulations apply to all gasoline and are designed to protect groundwater from any petroleum contamination, not just MTBE.

MDE estimates there are approximately 541 facilities that have an underground storage tank in the high-risk groundwater use area. Approximately 75 percent of these facilities were able to successfully demonstrate that the construction, operation and location of the UST system were not a threat to the groundwater within a half-mile radius, and therefore were exempt from the new regulations. This leaves 135 existing UST facilities within the high-risk use areas that will be impacted by these regulations and will be required to install wells and conduct monitoring and sampling. Of these 135 facilities, approximately 30 of them already have monitoring wells on-site. The remaining 105 facilities will have to install new monitoring wells.

The first year costs of the regulations for the facilities with existing wells will be different from the first year cost for the facilities that have to install new wells. The facilities with existing wells will only need to comply with the monitoring and sampling requirements of the regulations. The cost of complying with this portion of the regulations is estimated at \$5,700 per facility. The first year costs for the facilities without a monitoring well will be higher since they will be required to both install the well and perform monitoring and sampling. The first year costs for these facilities are estimated to be \$14,740 per facility. The total, year one cost for implementing the MDE regulations is estimated to be \$1.7 million dollars.

During the second and subsequent years, all 135 facilities will be required to perform annual monitoring and sampling at an estimated cost of \$5,700 per facility. The total recurring, annual cost of these regulations is approximately \$770,000. The detailed cost estimates for implementing the regulation is provided in Appendix B.

RFG with 10 Percent Ethanol

Gasoline with 10 percent ethanol contains 2-3 percent less energy per gallon due to the lower energy content of ethanol, resulting in a loss in fuel economy. Later model year vehicles equipped with oxygen-sensors (built since the mid-1980's), generally show about a 2 percent fuel economy loss when operating on a 10 percent ethanol blended fuel. In older vehicles, the improvement in combustion due to the leaning-out effect of ethanol may partially compensate for the loss in energy content of the fuel and fuel economy may be only slightly degraded. Theoretically, motorists will have to purchase additional fuel to offset the small loss in fuel economy.

While MTBE and ethanol have high octane (which is desirable in all gasoline) as well as high oxygen content and essentially no sulfur, benzene, aromatics, or olefins, they also differ in significant ways. MTBE blending has minimal effect on gasoline RVP (Reid vapor pressure or volatility) but blending ethanol increases RVP by approximately 1.0 pounds per square inch (psi). Simply replacing MTBE with ethanol in RFG would raise its RVP such that it would not comply with either the RFG VOC emission standard (as determined by the Complex model) nor the applicable RVP standard. Gasoline RVP and volatility are more of a concern during the summertime when ozone formation is greatest. In order to produce a complying summertime ethanol blended RFG, refiners will have to use a different base gasoline for blending. Other

high-RVP blendstocks (such as butanes (which have high octane), pentanes, and light straight run naphtha) must be removed from the baseline gasoline to maintain the RVP of the resultant ethanol blend at a complying level. Theoretically, the different blendstock gasoline will cost more to produce.

Maryland's gasoline is transported into the Mid-Atlantic region via the Colonial and Plantation pipelines. As is the case for all alcohols, ethanol blended fuel cannot be transported by pipeline due to its affinity for water. Water is not desirable in fuel and Maryland's fuel quality regulations prohibit the sale of gasoline containing undissolved water. Therefore, ethanol will have to be transported to Maryland by other means, most likely by railcar. Since ethanol will not be blended in the fuel at the refinery, it will have to be blended (into compatible blendstock gasoline from the pipelines) at the Maryland terminals, requiring the installation of additional equipment. Several states that are currently using ethanol have the advantage of having a local ethanol production facility. Maryland currently does not have a local ethanol production facility that it can use for its supply. Until a local production facility is available the state will always be vulnerable to supply issues, which could adversely affect both the price and quality of the fuel. There are several businesses that have expressed interest in developing and building an ethanol production facility in the State of Maryland. MDE is working cooperatively with these business interests to ensure that if such a facility is built in meets all of Maryland's performance standards for production, emissions, and economics. MDE will continue to work with these groups and if successful these facilities could remove any supply issues reduce the cost of ethanol in the state.

The net annual cost to the State of using RFG with 10 percent ethanol can be determined by adding the increased cost due to loss of fuel economy, the increased cost of producing a summertime blendstock gasoline, and the cost of offsetting emissions increases. In determining the cost of reduced fuel economy, the price of gasoline was assumed to be \$2.25 (the national average at the time of this report). The cost of producing a summertime blendstock was assumed to be 5 cents per gallon. According the Maryland Office of the Comptroller, in fiscal year 2004 (July 2003-June 2004), approximately 2.7 billion gallons of gasoline were sold in the state. For this analysis, 85 percent of the total gasoline, or 2.3 billion gallons, was assumed to be RFG. Finally, the cost of offsetting the emissions increases was assumed to be \$5,000/ton. The net cost to the State economy of using RFG with 10 percent ethanol would be approximately \$181 million annually.

Non-oxygenated RFG

Both MTBE and ethanol have higher octane than the gasoline that they are typically blended with, so when these oxygenates are removed, other gasoline properties (aromatics, benzene, and olefins) must be adjusted to accommodate this octane loss. While many different fuel properties for non-oxygenated gasoline are possible, all involve increasing high-octane components to some degree to replace lost octane while simultaneously meeting the minimum RFG performance standard.

Eliminating MTBE use also reduces a refinery's gasoline production capability because not only MTBE's volume but also its octane and other blending properties are lost. For example, MTBE's octane allows a refinery to increase total gasoline production by blending gasoline with

some low-cost (but low octane) natural gasoline. Without MTBE, the refinery loses the volume provided by natural gasoline (or other low-octane blendstocks). The refinery makes up some of the lost gasoline by diverting some distillate material to gasoline which reduces the refinery's distillate production. Using 10 percent ethanol in RFG to replace MTBE will reduce the volume shortfall, but only in part. Making up the full production shortfall caused by eliminating MTBE use would require the refiner to process additional crude oil, import more gasoline or invest in expanded refinery capacity. [8]

These effects have an impact on the production of fuel year round. Assuming a year round price differential of 7 cents per gallon, the net cost to the state economy for a non-oxygenated gasoline is \$174 million annually.

Table 2

Cost Variable	Annual Cost to State		
	Current Base Case	10% Ethanol Case	No Oxygenate Case
Maintaining MTBE	\$770,000	---	---
Higher Gasoline Consumption with loss in Energy 2,300 million gals/year x 2% x \$2.25 per gallon	---	\$103 million	---
Higher Summer Gasoline Prices from \$0.5 per gallon 2,300 million gals/year x \$0.05 per gallon x 0.5 year	---	\$58 million	---
Higher Year Around Gasoline Prices 2,300 million gals/year x \$0.07 per gallon	---	---	\$161 million
Increase in Ozone Precursors (VOC and NOx) 11 tons per day x \$5,000 per ton x 365 days	---	\$20 million	---
Increase in Ozone Precursors (VOC and NOx) 7 tons per day x \$5,000 per ton x 365 days	---	---	\$13 million
Net Annual Cost to State Economy	\$770,000	\$181 million	\$174 million

BIOREMEDIATION

Introduction

Once petroleum products including MTBE are discovered in the groundwater system, it is important to begin the remediation process as quickly as possible. Bioremediation has been shown to be an effective way to remove petroleum from the groundwater. Bioremediation is used throughout Maryland and natural bioremediation is always the final polishing mechanism used on sites that have utilized other groundwater treatment methods.

Bioremediation is the process by which microscopic organisms, through metabolic processes, break down contaminants to non-toxic substances. Essentially, it is the exploitation of a naturally occurring biological process to achieve contaminant destruction. All petroleum constituents are biodegradable by naturally occurring microbes present in the environment. In order to function properly, bacteria require oxygen, nutrients (carbon, nitrogen, phosphorus), a pH level within an acceptable range, and a relatively warm temperature. In engineered approaches, systems are created which supply the proper nutrients and oxygen to the microorganisms and ensure that there is contact between the contaminated material and the microorganisms.

Bioremediation Within Soil [9]

In petroleum remediation, the hydraulic conductivity of the soil must be considered. For example, in a complex layer system, the coarse sand layers will clean up faster than the tighter clay layers. The complexity of some of the geologic formations found in Maryland limits the degree of cleanup that can be attained. In a simple coarse sand formation, cleanup can be thorough enough to remove the contaminants to a very low level. However, in complex or fractured formations, cleanup times may be lengthy. Bioremediation results in complex formations are more variable, and higher levels of contaminants usually remain after the suite of applicable remediation methods are tried.

Since biodegradation occurs more quickly at the surface than it does in the subsurface, excavated contaminated soil removes the source of contamination more quickly and thoroughly than *in-situ* soil treatment. Excavated soil can be biodegraded through land farming or composting. In land farming, petroleum contaminated soil is spread out in a controlled area with a liner and berm, and soil is tilled with fertilizer and microbial additives to speed up biodegradation. In composting, the soil is spread more vertically, rather than horizontally, and aerated using a pipe system. Adding sawdust or woodchips to make the clay more porous in order to assist with the biodegradation activity further treats tight clay soil. All land farming methods require a large amount of space.

In the subsurface, biodegradation of petroleum constituents by soil microbes is slower, due to several limiting factors. These include: reduced availability of oxygen and nutrients, soil temperature and any large volumes of liquid phase hydrocarbons (LPH) floating on the water

table. Soil microbes are unable to break down significant volumes of free product; however, they are quite effective at removing residual and dissolved petroleum constituents.

Bioremediation of Groundwater

To further aid subsurface biodegradation of petroleum products in groundwater, additional oxygen, nutrients, or microbes can be added. Most technologies for the subsurface bioremediation of petroleum focus primarily on delivering additional oxygen to the subsurface microbes. These technologies include: oxygen-releasing compounds; oxygen diffusers using special membranes and electrodes; and chemical oxidation using injections of high oxygen chemical mixtures such as air, peroxide, and ozone. Additionally, nutrients, special surfactants, iron-chelating compounds, propane and/or butane can be injected into the subsurface to improve microbe performance. All of these technologies are limited by the tightness and complexity of the subsurface.

Use of Chemical Oxidation

It is claimed that chemical oxidation shows promise in destroying petroleum products. This remediation occurs by stimulating the in-situ biological process. The advantages MDE has noted with chemical oxidation are:

1. Relatively inexpensive and an unobtrusive way to clean up small pockets of high dissolved and low LPH in a few wells.
2. Reaction runs to completion and does not appear to generate adverse/harmful byproducts.
3. Can speed up time to closure after more conventional methods, such as pump and treat and soil vapor extraction (SVE), have reached the point of diminishing returns.
4. Can be useful in selected locations where wells persistently show low LPH and/or high dissolved levels and have not responded to EFRs, surfactant treatments, wicking and hand bailing.
5. Relatively inexpensive pilot testing can be conducted to test remediation effectiveness.

The MDE notes the following limitations associated with chemical oxidation:

1. Potential impacts from aggressive chemical reaction. Use may be inappropriate close to an underground storage tank field, utility corridor, or buildings.
2. May cause ground/pavement heaving or subsidence. This can adversely impact parking lots, roadways, and utility corridors.
3. May push vapors ahead of the reaction and cause their movement into buildings through preferential flow paths such as drains, gravel beds, sewer lines, etc.

4. Inappropriate for sites with more than approximately 1/2 inch of LPH/floating product.
5. Incomplete penetration in layered geology with clay lenses.
6. Requires separate injection points around wells of interest and adequate monitoring points to judge the remediation's effectiveness.
7. One time application of oxygen to stimulate microbial growth does not appear to be a long-term solution.
8. Hydrogen peroxide should be mixed with a chelated iron specific to site conditions to limit violence of the reaction and ensure penetration in the aquifer. Pilot testing is absolutely necessary.

MDE has concluded that chemical oxidation is a viable remediation technology for many sites in the State. Some sites have physical limitations, so applicability may be restricted. Chemical oxidation is not a solution for all groundwater problems. This is especially true at sites with large amounts of LPH. The MDE requires that all requests for oxidation use be reviewed with careful attention to the monitoring well network and site-specific conditions. Requests must include a strong detailed proposal and pilot testing. The MDE considers requests on a case-by-case basis and carefully takes into account the delivery method proposed.

Specific Maryland Site Considerations

All petroleum remediation methods approved for implementation by the MDE try to set up conditions favorable for bioremediation. Free phase product is first removed from the groundwater by excavation, pumping, soil vapor extraction, and/or sparging. Soil vapor extraction and sparging will remove volatile constituents to low levels, with the added benefit of increasing the oxygen flow to soil microbes, thus increasing biodegradation rates. In a typical petroleum remediation project, these methods remove about 70 percent of the mass of petroleum constituents. Case closure, then, is based on monitoring data demonstrating that biodegradation is occurring and will remove the remaining dissolved contamination to low, safe levels.

Use In Maryland

Of the 2,300 open cleanup cases in Maryland, several are using enhanced bioremediation. The types being used are: microbe addition, oxygen release compounds (ORC), ISOC, chemical oxidation and propane injection. The MDE in conjunction with Maryland Environmental Service is sponsoring a test of butane sparging at a gasoline impacted site in Havre De Grace Maryland. The test is designed to evaluate the effectiveness of butane sparging as a remediation tool. This test project is in final design stages and will be field installed the spring of 2006. The remaining sites in Maryland will, or are, using natural bioremediation as a last step or polishing technology to achieve case closure.

Areas that MDE is reviewing for improved use of bioremediation in Maryland include: (1) inoculating the bottom of excavations before placing clean fill; (2) hybrid approaches of product

removal and SVE/Sparging such as dual phase extraction under a high vacuum; (3) hybrid polishing technologies – such as using surfactants to flush residual product – followed by chemical oxidation and SVE/sparging to deliver the most oxygen possible to soil microbes. These state of the art technologies are already being used by the Oil Control Program to upgrade old remediation systems that have reached the point of diminishing returns, as well as for new releases, to speed up the time to attain case closure.

Appendix C contains specific, technical information obtained from the Interstate Technology Regulatory Council (ITRC).[10] Excerpts from the ITRC document, “Overview of Groundwater Remediation Technologies for MTBE and TBA,” were extracted and edited by MDE for clarification and inclusion in this report.

Summary

MDE finds the use of bioremediation a legitimate remediation tool, both in the short and long term. As noted in this report some level of natural bioremediation occurs at every remediation site. The ability to augment the natural bioremediation can be limited based on site specific conditions but has been proven very successful at various sites throughout Maryland and the nation. The ability to use bioremediation will increase with time as the science related to this technology improves.

The MDE will continue to encourage the use of bioremediation and biostimulation at petroleum impacted sites. As with all remediation technologies the responsible party has the right and is required to evaluate feasibility and the options available to them and propose a corrective action that is protective of public health and the environment and is also cost effective and feasible to implement.

ETHANOL CLEAN-UP

The most logical replacement for MTBE as an oxygenate is ethanol. The MDE felt it was reasonable to provide information on ethanol cleanup when it is released to groundwater. The differences between ethanol and MTBE with regard to their expected impacts on the subsurface of the environment are based largely on their initial concentration in the aqueous plume, the very different rates that they degrade, and possibly their residence time in the non-aqueous phase. MTBE is relatively recalcitrant to biodegradation and therefore able to migrate a significant distance from the release. Thus it can have a negative impact on groundwater quality for extended periods. Ethanol is rapidly biodegraded, preferentially to the other components of gasoline, however, its behavior in the environment is not well documented. It is expected that a release of neat ethanol will potentially be degraded in periods from several days to one or two years. Both ethanol and MTBE have a relatively high solubility in water and high mobility in the subsurface. Ethanol, the more soluble, is completely miscible in water (100 percent soluble, compared with 4 to 5 percent for MTBE). Once released to the environment, alone or in a gasoline mixture, both ethanol and MTBE readily dissolve in rainwater, surface water, and groundwater. Three environmental transport properties associated with ethanol are of particular concern:

- Depletion of oxygen and other nutrients in groundwater due to rapid biodegradation of ethanol that may inhibit the degradation of more toxic components in gasoline (e.g., BTEX) and make the dissolved plume of these components longer.
- A surface tension effect that takes place when ethanol is in contact with a layer of gasoline on top of the water table. This effect can cause the gasoline to spread laterally.
- A potential cosolvency effect from a release of neat ethanol or ethanol-blend with high concentrations of ethanol that may make other gasoline constituents (e.g., BTEX) in soil or groundwater more soluble.

The biodegradation of ethanol in the soil and water environment would first deplete the oxygen and then the anaerobic electron acceptors, potentially preventing or reducing the rate of biodegradation of the benzene, toluene, ethylbenzene, and xylenes (BTEX) constituents in gasoline. This may result in longer BTEX plumes. MTBE does not interfere with the natural biodegradation of the other gasoline components, most importantly BTEX.

Lab studies and mathematical models have estimated the potential for ethanol-blended gasoline to cause the toxic BTEX compounds of gasoline to travel from 1.1 up to 2.5 times farther than a standard gasoline blend without ethanol. This may be a serious problem, however, the predicted lengths of the ethanol BTEX plumes will still be shorter than MTBE plumes resulting from reformulated gasoline. Although ethanol degrades rapidly when released to the environment under favorable conditions, if spilled as a neat product where a stabilized zone of petroleum-contaminated soil and groundwater plumes already exist (e.g., oil terminals), it can remobilize the gasoline components and cause lateral spreading of liquid petroleum and 10-fold increases in the concentration of benzene and other aromatic constituents of gasoline (i.e., BTEX). This may cause contamination of groundwater and nearby wells.

Small spills of ethanol, such as incidental spillage at gas stations and homeowner spills, are not expected to enhance the migration of benzene. In fact, because of the high biodegradability of ethanol, it is not expected that such small spills will have any significantly different impact on groundwater quality compared with non-oxygenated gasoline. This is in stark contrast to the widespread instances of drinking water contamination with MTBE from minor spills of MTBE gasoline. For one-time releases of larger quantities of ethanol blended gasoline (e.g., a tanker truck accident), the effects of co-solvency are not expected to significantly affect the extent of the resulting plume. In this case, the incident would be known, and as in the case of conventional gas formulation, appropriate and prompt responses, evaluation, and followup would be taken. Much of the technology developed to remediate gasoline and MTBE in soil can be expected to work on the remediation of neat ethanol and ethanol blended gasoline. However, these tools have not been tested on environmental releases, so until they are we will not know precisely which methods will work the best and how effective they will be.

Ethanol plumes should be no more difficult to control hydraulically than MTBE plumes. Treatment technologies that rely on the physical separation of ethanol from groundwater are not effective. While biodegradation of ethanol in the environment is rapid, removal of ethanol from drinking water once pumped out of a well or reservoir is problematic. Its high solubility makes it

virtually impossible to treat using absorptive filters that are effective on private wells for other gasoline contaminants. However, the rapid biodegradation of ethanol makes it unlikely that this oxygenate will affect as many wells as have been affected by MTBE unless the concentration of ethanol exceeds the attenuative capacity of the aquifer segment between the source area and the receptor.

Biological treatment technologies are effective for ethanol contamination, as ethanol is highly biodegradable. The expected high concentrations of ethanol in plumes and the resulting high levels of BOD will probably require that treatment systems utilizing in-situ bioremediation technologies have larger capacities over those currently in use. The effectiveness of natural attenuation cannot be predicted because there is not enough information regarding the effect of ethanol plumes on the concentrations of terminal electron acceptors or the ability of those plumes to overcome the assimilative capacity of aquifers through which they are traveling prior to impacting a receptor.

The physical properties of ethanol differ significantly from those of petroleum hydrocarbons and MTBE. These properties cause ethanol to behave quite differently when it is dissolved in an LNAPL than when it is dissolved in groundwater. Thus the remediation of soils (which may contain LNAPLs) must be addressed differently from that of groundwater.

Soil

Ethanol blended gasoline has three characteristics that differ from MTBE gasoline and that may have an affect on the remediation of ethanol-contaminated soils:

- Ethanol may flow more easily in the vadose zone,
- The potential for phase separation may increase the rate of interphase mass transfer of the ethanol from LNAPL to groundwater, and
- Ethanol can readily biotransform once it dissolves in water (Rice et. al., 1999).

Regardless of the oxygenate used, gasoline in soil will consist of approximately 90 percent petroleum hydrocarbon. This major fraction of the fuel is anticipated to control the technologies employed in soil remediation. As with MTBE-gasoline spills, the standard course of action for ethanol spills will be to perform an investigation after the initial response to characterize the nature and extent of contamination and then to design a remediation system using the technology most suited to the site conditions.

Because the additional extent (if measurable) of an ethanol LNAPL pool has not yet been quantified, it is premature to speculate on how ethanol will affect either capital or operation and maintenance costs. The enhanced interphase mass transfer and ready biotransformation of ethanol may serve to reduce the time required for soil remediation compared with MTBE gasoline spills, but once again, the significance of these phenomena as applied to cost and effort is speculation.

Water

The experience of regulatory agencies regarding the addition of MTBE to gasoline may provide some general insight into the potential switch over to ethanol as a fuel additive. Groundwater

that is contaminated with MTBE can be treated, but with more difficulty and at greater expense than contamination with BTEX compounds. MTBE-contaminated groundwater can be treated by air stripping and the use of granular activated carbon. MTBE is difficult to separate from water because of its physical properties. It does not volatilize from water into air as easily as BTEX compounds and does not adsorb strongly onto granular activated carbon (GAC). It has been estimated that the introduction of MTBE into the fuel supply has increased the cost of spill cleanups by approximately 30 percent. [11]

The problems associated with the treatment of ethanol in a drinking water supply could be the same type as those posed by MTBE, only at a level that is orders of magnitude more difficult. The commonly employed wellhead treatment technologies rely on physical processes to separate a contaminant from the water within which it has dissolved. These technologies take advantage of the compound's ability to effect a phase transfer of the dissolved contaminant between water and either a gas or a solid, without reducing the mass or toxicity of the contaminant itself. The best examples of such technologies are air strippers and GAC. Based on minimum air to water ratios, MTBE is 10 times more difficult to treat with an air stripper than benzene. In theory, ethanol will be 82 times more of a problem than MTBE. The adsorption capacity of GAC for MTBE is about a third of that for benzene. In the field, this causes rapid MTBE breakthrough and requires oversized carbon vessels that are closely monitored and changed often to ensure reliable treatment. The adsorptive capacity of GAC for ethanol is 1/1600th of that for MTBE. The difficulty with trying to forecast the effects of ethanol on the costs of groundwater remediation is rooted in several significant factors regarding the fate and transport of ethanol in the environment that are unknown at this time.

CONCLUSION

The use of ethanol as a gasoline additive will likely have minimal impact on the technology employed or the costs associated with groundwater or soil remediation. However, the overall impact on remediation activities is not yet well understood. Although, MDE does predict fewer water supply impacts and the reduction of leaks from underground tank operations should ethanol be used in place of MTBE.

APPENDIX A

Potential Maryland Air Emission Impacts of a Ban on MTBE in the Reformulated
Gasoline Program

**Potential Maryland Air Emission Impacts of a Ban on MTBE in the
Reformulated Gasoline Program**

October 18, 2005

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1.0 Summary

The State of Maryland has considered legislation that would ban the use of MTBE (methyl tertiary butyl ether) in the gasoline. This study examines the possible impacts on air emissions if MTBE use were to be discontinued. Since the recently passed Energy Policy Act of 2005 will remove the oxygen standard in the reformulated gasoline (RFG) program in the Spring of 2006, the Maryland gasoline marketplace might have a choice of using either an RFG with 10% ethanol or non-oxygenated RFG (or a market mix of both). Therefore, both replacement RFG options are considered in the air emission analysis in this study.

The results from this study show that using 10% ethanol will “increase” total ozone precursors (VOC + NO_x) by as much as 15.8 tons during an ozone exceedance day. This increase is equivalent to about a 7 percent increase in VOC and NO_x emissions from the on-road gasoline motor vehicle fleet. The results also show that switching to a non-oxygenated RFG will increase total VOC +NO_x emissions by 7.0 tons during an ozone exceedance day which is equivalent to about a 3.2 percent increase from the on-road gasoline motor fleet. The emissions total for non-oxygenated gasoline does not include the large increase in CO emissions (325 tons per day), which is also a weak ozone precursor, that might be equivalent to increasing VOCs by another 7.2 tons per day.

Since Maryland continues to experience ozone exceedances under the new tighter federal ozone standards, the increase in air emissions from switching to either an ethanol-blended or a non-oxygenated RFG will likely need to be offset with additional emissions controls and their related costs. There is also a risk that ozone levels might increase by more than the percentage increases in the tons of the ozone precursors since the atmospheric VOC reactivity of any replacement for MTBE in gasoline will be much higher. Although EPA’s RFG complex model projects that switching from MTBE to these other fuel formulations would also increase localized air toxics emissions from the vehicle fleet by 6 to 14 percent, the absolute total increase in air toxics for Maryland is not estimated in this study due to insufficient information for air toxic emissions from gasoline related off-road equipment sources.

This analytical comparison study uses the latest known science for estimating the fuel composition effects on gasoline related emissions from both mobile sources (on-road gasoline motor vehicle fleet) and off-road sources (small gasoline engines). These enhancements in estimating emissions are currently not reflected in the EPA emission models used by states for predicting VOC and NO_x emissions in Ozone SIPs (state implementation plans). The inclusion of off-road engine sources in this study is important since they represent a larger share of gasoline related emissions in the air basin emissions inventory than those from on-road vehicles. The most significant improvement in estimating emissions is the relatively recent knowledge that using ethanol in gasoline will significantly increase VOC permeation emissions through the vehicle plastics and elastomers in contact with the fuel by about 65 percent or more when compared to an MTBE fuel blend. This increase in permeation emissions affects evaporative emissions from on-road vehicles, off-road equipment and off-road vehicles, and portable gasoline containers. In addition, using 10% ethanol will increase the oxygen content by about 60 percent in the gasoline which then contributes to about a 4.5 percent increase in NO_x emission from on-road vehicles. Because of these recent improvements in estimating emissions, this

analysis shows that switching from MTBE to either a 10% ethanol blend RFG or a no oxygenate RFG will result in a significant increase in ozone precursors into Maryland's air basin during a potential ozone episode day.

2.0 Introduction

Maryland is required to use federal Reformulated Gasoline, or RFG, which is a cleaner burning gasoline formulation that reduces pollutants from vehicles which form ozone, or ozone “precursors” (volatile organic compounds, or VOC, exhaust oxides of nitrogen, or NO_x, and also exhaust carbon monoxide, or CO - a weak ozone precursor). Relative to a 1990 baseline, RFG reduces total vehicle VOCs by about 29%, NO_x by about 7% and air toxics by about 32%. Until the recent Energy Policy Act of 2005 was passed, the law required that this federal RFG must contain an oxygen containing compound like MTBE or ethanol that adds at least 2 weight percent oxygen up to 3.5 weight percent. However, after the passage of the recent Energy Policy Act, the law no longer requires that RFG contain oxygen beginning in May of 2006. However, the percent reductions in VOCs and NO_x of RFG at the local regional level still apply, whether the RFG contains oxygen or not. Since air toxic reductions targets in RFG are a national average requirement for individual refiners, local air toxics can increase without the use of MTBE.

Besides reducing emissions from on-road vehicles, the addition of oxygen in RFG is the only fuel property change that also reduces the exhaust VOC and CO emissions from the less sophisticated off-road gasoline engines. The inclusion of emission effects on off-road engine sources in this study is important since they now represent a larger share of the gasoline related emission inventory than emissions from on-road vehicles. The current RFG contains about 11 volume percent MTBE (2 % oxygen), which is a very clean burning, high octane, and easy-to-use oxygenate that has blended in gasoline since 1979. However, the state legislation requires the state to determine the impact of not using MTBE. The likely result would be a gasoline that either contains 10 volume % ethanol, or no oxygenate, or both. The choice of which gasoline to supply is a decision of the gasoline marketers based on feasibility and economics.

Many policy makers are under the false impression that all oxygen-containing compounds used in gasoline have about the same overall emissions impact. Except for air toxics, even the EPA emission models for both on-road and off-road vehicles do not differentiate between using ethanol or MTBE in RFG since these models were developed with an oxygenate-neutral policy where all oxygen in the fuel is assumed to have the same effectiveness in reducing exhaust emissions, and that emissions are assumed to change only linearly (or proportional) with oxygen concentration. Recent data and analysis from testing programs, however, show that there are significantly higher emission differences associated with the use of ethanol. Ethanol can increase NO_x emissions from on-road vehicles at the higher oxygen levels, and ethanol also increases “permeation” VOC emissions from fuel system components (plastics and elastomers) in on-road vehicles, off-road vehicles, and portable gasoline containers. MTBE, however, does not increase NO_x or VOC permeation emissions relative to a non-oxygenated gasoline. The oxygen in both compounds reduces exhaust carbon monoxide (CO) emissions which is a weak ozone precursor.

This study evaluates the overall air emissions impact of a switching RFG from 11 % MTBE to either 10 % ethanol, or no oxygenate in Maryland. The study uses recent testing data on ethanol permeation effects conducted by the Coordinating Research Council, a research group

funded by the automobile and oil companies. It also uses test data and analyses of the effects of ethanol on NOx emissions developed by the California Air Resources Board.

This report is organized into the following sections:

- Background
- Methodology Used in the Study
- Maryland Gasoline Characteristics
- Permeation VOC Emissions
- Atmospheric Reactivity of VOCs
- Results
- Discussion

There are three additional sections:

- References
- Appendix 1: Analysis of Oxygen Effects of Two-Stroke Engines
- Appendix 2: Background on Air Improvement Resource, Inc.

3.0 Background

Gasoline related emission inventories are made up of a combination of exhaust emissions and evaporative emissions. While exhaust emissions are made up of unburned hydrocarbon emissions (VOCs), NO_x, CO, and air toxics, the evaporative emissions are made up only of VOCs since they represent those gasoline vapors that escape from all parts of the vehicles other than that from the exhaust pipe. Permeation VOC emissions are the portion of evaporative VOC emissions that permeate through the plastic and elastomer materials in the vehicles fuel system and fuel containers that are in contact with the fuel. Gasoline related emissions are also grouped into two general sources of gasoline users which are the on-road vehicles and the off-road engine sources that are generally the smaller engines such as lawnmowers, chainsaws, power generators, etc. Even though these off-road sources consume only about 5% of the gasoline, they represent a significant share of the gasoline related VOC inventory (50+%).

The impacts of RFG on state emissions inventories can be estimated using a number of emission prediction models developed by EPA and CARB (California Air Resource Board). The vehicle fleet emissions can be estimated with EPA's MOBILE6.2 emissions model, and all states except California that have implemented RFG programs use the MOBILE model to estimate the benefits of RFG.¹ The EPA's MOBILE model which estimates on-road vehicle emissions, however, does not differentiate between RFG using MTBE and RFG using 10% ethanol. One reason for showing no difference is because data on the permeation characteristics of ethanol have only recently become available, and neither the MOBILE model nor EPA's model for estimating emissions from off-road equipment and vehicles (NONROAD) have been updated for these ethanol permeation effects. Another reason is that EPA emission models do not reflect the non-linear increase in NO_x emissions associated with the higher oxygen levels in the 10% ethanol blends. Lastly, the EPA emission models do not include a model for small portable gasoline containers used for storing fuel for the off-road engines.

This section briefly reviews five studies which have presented the results of ethanol's impact on permeation VOC emissions. The five studies are:

- The Coordinating Research Council (CRC) Study
- The AIR, Inc. Permeation Study for the API
- The AIR, Inc. Fuels Study for Southeast Michigan Council of Governments
- California Air Resources Board Draft Study of Ethanol Effects
- California Air Resources Board Test Program for Permeation from Portable Containers

3.1 CRC Study

When California implemented its Phase 3 RFG requirements calling for the phase-out of MTBE and replacement with ethanol, one of the issues raised during the Board Hearing was whether ethanol increased permeation emissions of VOC components through plastic and rubber

¹ California uses its own emissions models. EMFAC is used for on-road vehicles, and OFFROAD is used for off-road equipment and vehicles, and portable gasoline containers.

parts in the fuel system of vehicles. The Air Resources Board directed their staff to study this issue. The CARB and the Coordinating Research Council (CRC) initiated a 2-year, 10-vehicle testing program to evaluate this issue. On September 20, 2004, CRC issued a detailed report summarizing the results of the testing. [1]

The testing program revealed that ethanol increases permeation emissions from on-road passenger cars and light duty trucks an average of 1.4 grams per day (g/day) per vehicle as compared to an MTBE fuel, under the test conditions of a diurnal temperature of 65° F to 105° F. The testing also found that this increase in permeation VOC emissions is sensitive to ambient temperature. At lower ambient temperatures, the increase in emissions due to ethanol is lower, so this indicated a need to correct for any differences in the ambient and test temperatures when estimating the increase in emissions.

3.2 AIR Permeation Study for API

Recognizing that the CRC data and report would be released, and desiring to determine the inventory impacts of expanding ethanol use, the American Petroleum Institute (API) contracted with AIR, Inc. to determine, based on the CRC on-road data, and other data that is available, the impact of ethanol on permeation emissions for on-road vehicles, off-road equipment, and portable containers. The study was conducted for several different areas of the country, including California, Atlanta, Houston, and the New York/New Jersey/Connecticut area. [2]

The study used the available data, developed temperature correction factors, and estimated the permeation VOC increases in the above geographical areas. For example, in California, the study estimated that ethanol increases permeation emissions from on-road vehicles, off-road sources, and portable containers by 25 tons per day (tpd) in 2003. The study further estimated that ethanol would increase VOC permeation by 24 tons per day in the New York/New Jersey/Connecticut area. These VOC increases are on the order of 5-6% of on-highway State Implementation Plan (SIP) VOC for New York and New Jersey areas.

3.3 AIR Study for SEMCOG

AIR also studied various gasoline and diesel fuel options for the Southeast Michigan Council of Governments. [3] SEMCOG evaluated a number of fuel options, including RFG with ethanol, RFG without ethanol, 100% ethanol in conventional gasoline, and other options. The methods used to estimate permeation emissions were consistent with the API report, and the NOx effects of ethanol were estimated with the California Predictive Model. This study found that RFG without ethanol would have larger VOC benefits than RFG with ethanol, due to lower permeation VOC emissions. The study also found that RFG with ethanol would increase NOx over Michigan baseline fuel, and that 100% ethanol fuel in Michigan gasoline would increase both NOx and VOC. The state of Michigan is currently considering lower RVP as a cost-effective means to further reduce VOC emissions.

3.4 California ARB Draft Study on Ethanol

The California Air Resources Board recently released a draft study of the effects of ethanol in California. [4] Similar to the AIR study for SEMCOG, ARB estimated the permeation effects for on-road vehicles, off-road equipment, and portable containers. ARB also estimated NOx impacts for on-road vehicles. This draft study concluded that ethanol increases VOC by 45-75 tpd, and that NOx increases by 21 tpd in California with ethanol as compared to MTBE.

3.5 California Air Resources Board Test Programs on Portable Containers

There is no specific ARB report on permeation of portable plastic fuel containers with and without ethanol, however, ARB has performed a number of tests with its certification fuel, which contains MTBE, and fuel containing 6 % ethanol. The data, which was obtained by AIR, Inc, is shown in Table 12 of the API study referenced earlier. [2] Basically, a number of different portable containers were tested, and the average size was about 3.3 gallons. The average emission rate on MTBE fuel was 4.7 g/day, and on fuel containing ethanol was 6.6 g/day, for an increase in VOC emissions of about 39%.

4.0 Methods

This section discusses the methods used to estimate emission impacts of converting to ethanol use in Maryland's RFG program.

4.1 Fuel Cases

Three fuel cases are being evaluated in this study, as follows:

#1: Baseline RFG with 11% MTBE

#2: RFG with 10% ethanol

#3: RFG without oxygenate

Detailed fuel properties for both of these fuel cases are developed in Section 5. In this study, the gasoline sales in the state of Maryland are assumed to be fully switched from MTBE to either ethanol or a non-oxygenate gasoline in calendar year 2007.

4.2 Pollutants and Evaluation Years

This study evaluates VOC, CO, and NO_x, and PM emissions from on-road gasoline vehicles, off-road gasoline equipment, and portable gasoline containers. The evaluation year is 2007.

4.3 Models Used

This analysis uses the EPA MOBILE6.2 model for MTBE emissions for on-road sources, and the California ARB Predictive Model to adjust the exhaust emissions from gasoline vehicles for either 10% ethanol effects, or for no-oxygenate effects. Non-ethanol permeation evaporative emissions from on-road sources are estimated with MOBILE, as are the other evaporative emissions (hot soak, running loss, and diurnal).

For off-road equipment and off-road vehicles, this analysis uses the EPA NONROAD2004 model for all three fuels. Unlike the MOBILE model, the NONROAD2004 model can be used for all cases, because the exhaust emissions of off-road equipment and vehicles are generally not equipped with catalytic converters, oxygen sensors and other equipment that is sensitive to differences in oxygenates. These exhaust emissions of these sources generally only respond to changes in oxygen concentration, not the type of oxygen.

One change was made to the default NONROAD2004 model emissions response. The NONROAD model shows very little effect of oxygen content on VOC and PM emissions from two-stroke off-road engines, and was based on emission tests of only one engine. This analysis located tests on five other engines, and developed an updated VOC and PM response curve. This is further discussed in Section 4.3.1 below.

Since neither the MOBILE nor NONROAD models include the effects of ethanol permeation, these effects had to be developed outside the models. These emission impacts were

developed in a manner consistent with AIR's analysis for both API and SEMCOG, discussed earlier. The ethanol permeation impacts are discussed in more detail in Section 6.

4.3.1 Oxygen Effect on VOC and PM Emissions from Off-road 2-stroke Engines

As on-road vehicle emissions have been reduced, the proportion of VOC and PM emissions from off-road equipment has increased, thus, the effects of different fuels on these engines are more significant.² EPA developed the impacts of oxygen on off-road engines on the basis of one Yamaha two-stroke Moped engine. [5,6] These test results showed that increasing oxygen by 1% (by weight) reduced VOC by 0.6%, increased NOx by 18.6% (NOx is very low on these engines compared to VOC, and so this percent increase on a mass basis is almost insignificant), and reduced CO by 0.4%.

An examination of the literature turned up two other sources with tests of two-stroke engines that were tested on both oxygen and non-oxygenated gasolines. One study evaluated effects of ethanol fuel on emissions from snowmobile engines. [7] A second study by The College of Engineering Center for Environmental Research and Technology (CE-CERT) evaluated two 4.5 hp Sachs engines. [8] In all, five 2-stroke engines have been tested in various programs. This study developed oxygen impacts on HC, CO, NOx, and PM emissions from the 5 engines, as described in Attachment 1. The emission effects are shown in Table 1, as compared to the NONROAD model.

Source	HC	CO	NOx	PM
NONROAD	-0.6%	-6.5%	+18.6%	-
5-engine database	-2.4%	-3.0%	+9.5%	-2.6%

Table 1 indicates that the 5-engine database compiled for this study shows greater HC, and PM reductions, and less NOx increase than the 1 engine utilized in the NONROAD2004 model. The CO reduction is a little lower with the 5-engine database. The NONROAD2004 model was therefore updated for these oxygen effects, prior to running the model for any of the three fuel scenarios.

4.4 Vehicle Miles Traveled for On-road Vehicles

Vehicle miles traveled for 2007 was obtained directly from the state of Maryland, and is shown in Table 2.

² Off-road engine emissions standards have been implemented by the EPA and ARB, but the overall reductions are not yet as great as for on-road vehicles.

Region	LDGV	LDGT12	LDGT34	HDGV
Baltimore Area	12415.1	8098.1	2792.2	466.8
Calvert County	363.4	237.0	81.7	15.3
Cecil County	604.7	394.4	136.0	37.6
Charles County	588.6	383.9	132.4	23.4
Frederick County	1353.6	882.9	304.4	72.0
Kent County	131.0	85.5	29.5	6.1
Montgomery County	3772.0	2460.4	848.3	134.3
Prince George's County	4318.6	2816.9	971.3	139.2
Queen Anne's County	462.2	301.5	104.0	19.9
Rural Areas	2880.8	1879.1	647.9	128.0
Washington County	948.8	618.9	213.4	54.3

4.5 On-road Vehicle, Off-road equipment, and Container Populations

On-road vehicle, off-road equipment, and container populations for Maryland for calendar year 2007 are needed to estimate permeation impacts from each of these sources.

On-road vehicle populations for estimating permeation impacts were provided by the state. Off-road equipment and vehicle populations were determined directly from EPA's NONROAD2004 model. The NONROAD2004 model does not include portable container populations, but ARB's OFFROAD model includes both offroad equipment and portable container populations, and the percent of portable containers to gasoline equipment for the state is 47.3%. For this analysis, portable container populations in Maryland were determined by estimating the off-road gasoline equipment populations from the NONROAD model, and applying the ratio of portable containers to off-road gasoline equipment in OFFROAD to the NONROAD populations.

All of the populations for 2007 are shown in Table 3 below.

Source	Estimated 2007 Population
On-road gasoline vehicles (LDGVs, LDGTs, HDGVs)	4,231,214
Off-road gasoline equipment*	2,606,853
Portable gasoline containers (plastic only)	1,234,026

*2 stroke and 4-stroke engines

4.6 Other Inputs

AIR used the temperatures and speeds provided by Maryland. These are outlined in Table 4 below.

Table 4. Minimum and Maximum Temperatures and Speeds			
Region	Min Temp (F)	Max Temp (F)	Speed (mph)
Baltimore Area	67.6	94	40.65
Calvert County	68.5	95	39.49
Cecil County	67.6	94	42.52
Charles County	68.5	95	35.31
Frederick County	68.5	95	41.45
Kent County	67.6	94	37.28
Montgomery County	68.6	95	33.81
Prince George's County	68.5	95	36.83
Queen Anne's County	67.6	94	40.83
Rural Areas	67.6	94	36.66
Washington County	67.6	94	40.21

4.7 Method of Combining Model Results

As noted above, the fuel options affect 3 major sources: on-road vehicles, off-road equipment and vehicles, and portable containers. This study examines the effects from all three sources. The general equation used to estimate these effects is the following:

$$\text{Total effect} = \text{On-road effect} + \text{off-road effect} + \text{portable container effect}$$

Where:

Onroad effect = Exhaust effect + Evaporative effect + permeation effect

Off-road effect = Same as on-road, but for off-road sources

Portable container effect = Permeation effect

And where:

Exhaust effect from onroad vehicles = MOBILE6.2 exhaust baseline * % Change from Predictive Model

Evaporative effect from onroad vehicles = change in evaporative emissions as estimated by MOBILE6.2 directly

Permeation effect from onroad vehicles = method used by AIR in API permeation study

Exhaust effect from off-road vehicles = estimated by EPA NONROAD model

Evaporative effect from off-road vehicles = estimated by EPA NONROAD model

Permeation effect from off-road vehicles = method used by AIR in API permeation study

Permeation effect from portable containers = method used by AIR in API permeation study

5.0 Maryland Fuel Characteristics - 2007

Detailed fuel property estimates for the three fuels are shown in Table 5. The information for the baseline MTBE was based on survey data published by the EPA. [9]

Ethanol RFG properties were derived from the MTBE fuel property data, with the exception of the T50 level (temperature at which 50% of fuel is distilled). Examination of data from Delaware and Connecticut has shown that the T50 value with ethanol would increase about 5° F from the level with MTBE. Most of the other properties are not expected to change from the levels found in current gasoline containing MTBE in Maryland (properties that are expected to change are shown in **bold** type).

Both ethanol and MTBE have higher octane than gasoline that they are typically blended with, so when these oxygenates are removed, other gasoline properties (aromatics, benzene, and olefins) must be adjusted to reflect the increase non-oxygenated octane and loss of a clean diluent, while attempting to still meet the RFG emission reductions. To replace octane lost by removing oxygen, the aromatics, benzene, and olefins were increased, and the RVP was slightly reduced, so that the RFG requirements for VOC, NO_x, and toxics were still met using EPA's Complex Model. The controlling pollutant is VOC; with this gasoline there is some NO_x and toxics over-performance of the RFG specifications. While many different fuel properties for non-oxygenated gasoline are possible, all would involve increasing higher-octane components to some degree to replace lost octane, while simultaneously meeting the minimum RFG performance requirements.

Table 5. Fuel Properties for Baseline and Ethanol Gasoline in Maryland			
Property	MTBE RFG	Ethanol RFG	Non-oxygenate RFG
Oxygen (wt %)	2.07	3.4	0.0
Nominal Volume %	11	10	0
Benzene (vol %)	0.59	0.59	0.66
RVP (psi)	6.81	6.81	6.71
Aromatics (vol %)	19.1	19.1	25.5
Sulfur (ppm)	30	30	30
Olefins (vol %)	11.43	11.43	12.8
T50 (°F)	201	206	210
T90 (°F)	331	331	331
MTBE (vol %)	10.3	0.0	0.0
Ethanol (vol %)	0.0	10.2	0.0
TAME (vol %)	1.1	0.0	0.0

The EPA Complex Model used to develop some of the properties in Table 5 is based on pre-Tier 1 vehicles (pre-1994 model year), and may not be the best indicator of the percent changes in emissions of the fleet. The ARB Predictive Model, used by refiners in California, is more current in terms of having more vehicles of a more recent vintage, and updated statistical techniques. It is designed to represent the California fleet in calendar year 2005. A review of the

documentation of both the Complex and Predictive Models compels the author to conclude that the Predictive Model is a better indicator of the percent changes in exhaust emissions of the Maryland fleet than the EPA Complex Model. The above fuel property data in Table 5 was therefore inputted into the ARB Predictive Model. As indicated in the SEMCOG report, the Predictive Model estimates the change in emissions of any gasoline versus a reference gasoline, so procedures developed in the SEMCOG analysis were used to compare the two fuels in Table 5 to each other. The changes in exhaust VOC and NOx emissions are shown in Table 6.

Table 6. Predictive Model Results		
(% change from MTBE to either Ethanol or non-Oxygenate RFG)		
Fuel Change	Pollutant	% Change
MTBE to Ethanol	Exhaust VOC	+2.8%
	Exhaust NOx	+5.6%
MTBE to Non-Oxygenate	Exhaust VOC	+6.1%
	Exhaust NOx	0.0%

As noted in Table 6, the switch from MTBE to ethanol is expected to increase VOC by 2.8% and NOx by 5.6% in on-road gasoline vehicles. The increase in exhaust VOC is primarily due to the change in T50 levels, and the increase in NOx is due to ethanol. Since the fuel RVPs of the MTBE and ethanol RFG are expected to remain the same, there is no change in non-ethanol related permeation emissions and the other evaporative emissions (hot soak, diurnal, and running loss). There is an increase in ethanol-related permeation emissions, however, which is discussed in Section 6.

For a non-oxygenated gasoline, VOC is expected to increase by 6.1% and NOx is not expected to change. The increase in exhaust VOC is due to the addition of aromatics, benzene, and olefins which raise octane.

This study did not examine the changes in overall toxics, because the study includes non-road engines as well as on-road vehicles, and it is currently not possible to evaluate changes in fuel impacts on toxics for nonroad engines. Nonetheless, the ARB Predictive Model and EPA's RFG Complex Model for on-road vehicles provide an indicator of the difference in air toxics for onroad vehicles. The change in air toxics for the different fuels used in this study is shown in Table 7.

Table 7. Percent Change in Total Onroad Toxics from MTBE Fuel to Either Ethanol RFG or non-Oxy RFG		
	EPA RFG Complex Model	Calif Predictive Model
Fuel Change	Mass Basis	Risk Weighted Basis
MTBE to Ethanol RFG	+ 6 %	No change
MTBE to non-Oxy RFG	+ 14 %	+24%

Table 7 indicates that with ethanol, there is no change in total risk weighted air toxics. With the non-oxy RFG, there is a 24% increase in total on-road risk weighted air toxics and a 14% increase the mass of air toxics. Off-road toxics would also increase for this fuel, although it is not known by how much.

6.0 Permeation VOC Emissions

A recent extensive testing program conducted by the Coordinating Research Council shows that ethanol blends increase permeation VOC emissions from on-road vehicles by about 65% as compared to a MTBE blended fuel. Also, data from the California Air Resources Board shows that permeation VOC emissions also increase for off-road equipment, and portable containers used to store gasoline for off-road equipment and off-road vehicles. Based on the studies to date, the increase in permeation VOC's is a phenomena that is unique to ethanol blends and not other oxygenates such as ethers or MTBE. In fact, of the three fuels tested in the CRC study, MTBE blends had the lowest permeation emissions and were about 15% lower than the straight hydrocarbon blend, but this difference between MTBE blends and straight hydrocarbon is not conclusive since it fell within the statistical accuracy of the study data. Based on these results, using ethanol in the gasoline apparently increases the gasoline's solvency action on the non-metallic materials in contact with the fuel, which then contributes to higher permeation of the gasoline components through these materials as VOC emissions into the atmosphere.

The permeation effects of ethanol in this report are based on the results from the CRC study, and utilize the estimation methods developed in the study by AIR for the American Petroleum Institute (API). [2] Generally, the ethanol permeation impacts are a function of the population of the various sources (on-road vehicles, off-road equipment and vehicles, and portable containers), the ethanol permeation increase for each type of source, and the temperature correction factors for this permeation increase. The AIR study developed all these inputs for California, Atlanta, Houston, and the New York/New Jersey/Connecticut areas, but the same techniques have been applied in Maryland.

Permeation increases due to ethanol for various sources are shown as grams per day per unit of source (g/day/unit) in Table 8. These emission increases are for a 65-105° F test procedure with an average temperature of 85° F, and are corrected to the average temperature of the counties in shown in Table 4.

Table 8. Permeation VOC Increases for Various Sources due to Ethanol		
Source	Model Year Group	VOC Permeation Increase (g/day/unit)
On-road gasoline vehicles	Pre-1991	2.03
	1991-1995	0.86
	Enhanced evap (phase-in schedule varies by vehicle class)	0.80
	Tier II evap (phase-in schedule varies by vehicle class)	0.43
Off-road gasoline equipment	All	0.40
Recreational vehicles and recreational marine	Pre-2008	0.40
	2008+	0.123
Plastic portable fuel containers	All	1.86

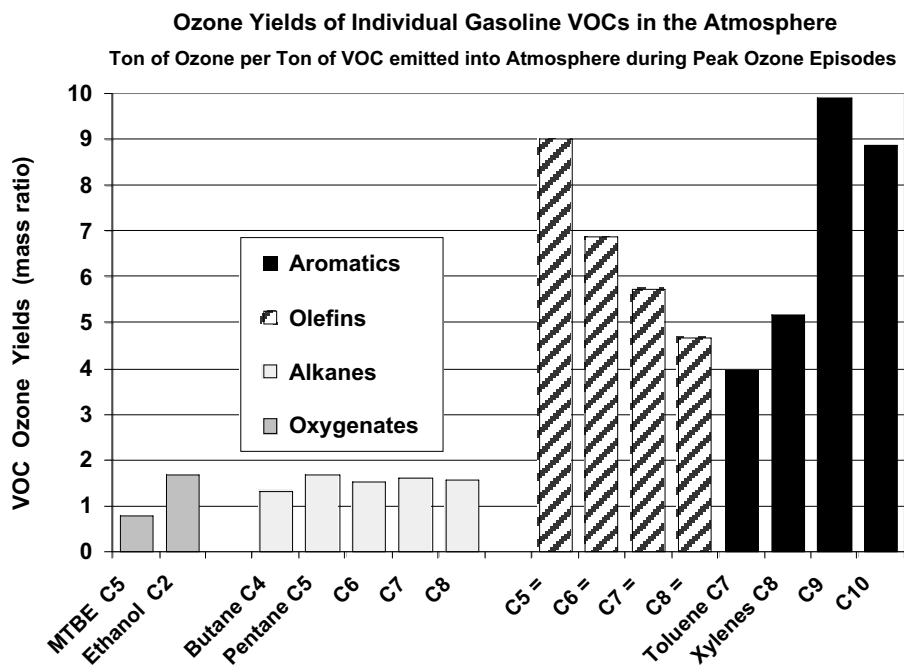
The values in Table 8 were developed on CRC tests that used E6 (6 volume % ethanol blend), instead of E10 (10 volume % ethanol blend), which will be used in Maryland. Assuming that permeation is a function of the ethanol content in the fuel, it is possible that this assumption could understate the ethanol permeation impact. While further testing of E10 is planned by the Coordinating Research Council, this analysis also estimated the emission impact as if the permeation impact is proportional to ethanol concentration in the gasoline. For the sensitivity case, permeation emissions were assumed to be 66% higher (10%/6%) because of the use of E10, instead of E6 in Maryland.

7.0 Atmospheric Reactivity of VOCs

Most state ozone control programs and inventory analysis will focus on controlling the total mass of ozone precursors emitted into the atmosphere such as NO_x and VOCs under an implied assumption that all mobile source VOCs are equally potent in generating ozone on ozone episode days. However, vehicle VOC emissions are actually a large mixture of many different VOC components which produce different yields of ozone in the atmosphere depending on each VOC's individual chemical configuration or make-up which then effects it rate of reactivity in producing ozone. The VOCs found in gasoline are generally classified into four chemical groups which also determine their atmospheric reactivity. These four groupings are alkanes (paraffins), olefins, aromatics and oxygenates which then can be further differentiated by the number of carbon (C) atoms found in each individual VOC structure. Each of these VOCs that make up the VOC's in gasoline will have different levels of ozone producing reactivity associated with them as shown in Figure 1. These ozone yields reflect the ozone produced by each type of VOC under maximum incremental reaction (MIR) ozone producing conditions found in the atmosphere. These reactivity yields have been developed by Dr. Carter for use by the CARB (California Air Resource Board) in their ozone control programs. [10]

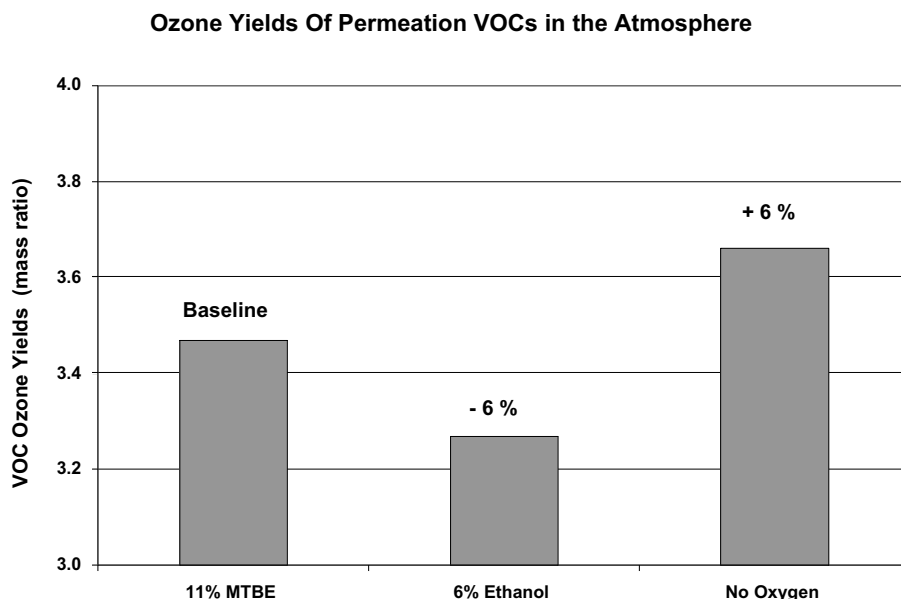
What is apparent from this data is that olefins and aromatics are very reactive in generating higher amounts of ozone in the atmosphere while alkanes (paraffins) and oxygenates are much slower or less reactive in generating ozone. Of all compounds blended in gasoline, MTBE is the least reactive (lowest ozone forming) which then suggests that any gasoline component used to replace MTBE will increase the overall reactivity of the VOC mixtures associated with gasoline's evaporative emissions.

Figure 1



This effect on VOC ozone yield can be observed in the recent CRC permeation study discussed earlier. [1] Figure 2 shows the calculated changes in ozone yield for the permeation VOC mixture for each of the three fuels in the study. Although ethanol has a higher reactivity than MTBE, the average reactivity of the ethanol VOC mixture is lowest because ethanol represents such a large percentage of the increased VOCs with the ethanol blend.

Figure 2



The daily permeation VOC masses per vehicle associated with each of the three fuels are shown in Figure 3. When the effects of the reactivity are applied against the VOC masses associated with the daily VOC permeations, the ozone production per vehicle for each of the three fuels can be calculated and is shown in Figure 4.

Therefore, when taking the reactivity of the VOC mixtures into consideration, the results from this CRC permeation study would suggest that the permeation VOCs from the ethanol blend would increase the ozone contribution by 55% compared to the MTBE blend, and the non-oxygenated blend would increase the ozone contribution by about 20%.

In this study, the change in reactivity of the VOC emission mixtures are not taken into consideration, but are shown here to illustrate that MTBE as a VOC is relatively inert in the atmosphere when it comes to generating ozone. Therefore, switching from MTBE to the other more reactive gasoline components might result in higher ozone production than would be estimated by just using percent changes in the VOC mass emission related to the use of the various fuels.

Figure 3

Average Permeation VOCs per Day from Vehicles

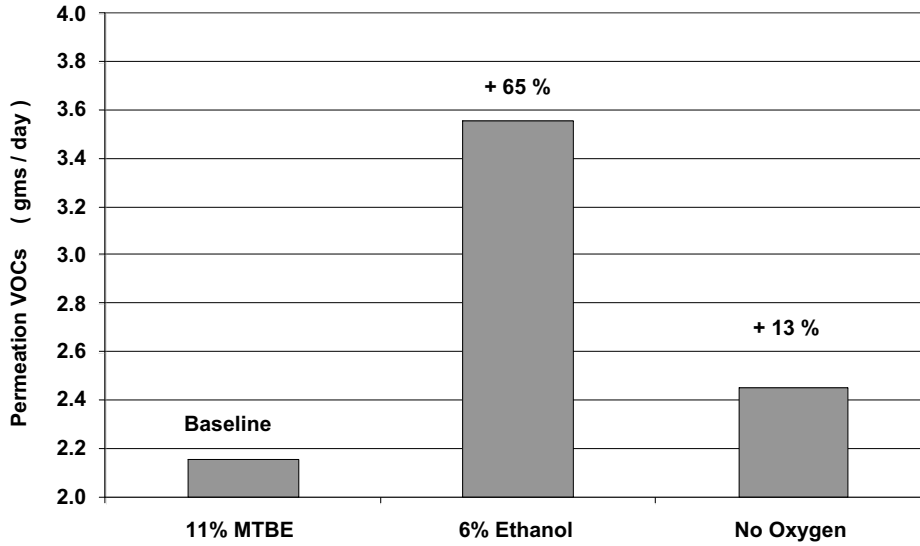
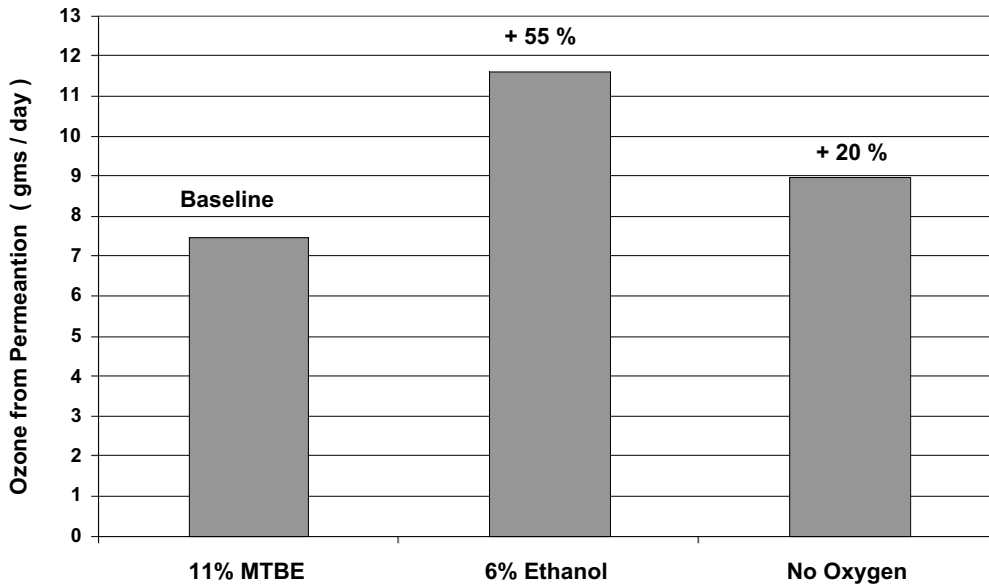


Figure 4

Calculated Ozone Production From Permeation VOCs per Vehicle



8.0 Results

8.1 Baseline Inventories

Baseline on-road and off-road VOC, CO, and NO_x emission inventories for Maryland are shown in Table 9. This inventory summary does not include the portable container VOC inventory in the baseline, because this analysis is only estimating the increase in VOC emissions by adding the increase in permeation emissions for containers and vehicle fuel systems due to ethanol being added to the fuel.

Source	Exhaust VOC	Evaporative VOC	CO	NO _x	PM ₁₀
On-road gasoline vehicles	46.4	55.3	1230.4	117.9	0.9
Off-road gasoline equipment and off-road gasoline vehicles	113.3	18.5	1766.8	16.2	6.4
Total mobile, gasoline	159.7	73.8	2997.2	134.1	7.3

The baseline inventory is 160 tons per day (tpd) of VOC (exhaust + evaporative), 2997 tpd of CO, 134 tpd of NO_x, and 7.3 tpd of PM. These inventories may be somewhat different than the SIP inventories estimated by the state, because the state follows a much more detailed EPA approved procedure for estimating local inventories. However, the estimates developed in this study are sufficiently accurate since the focus of this analysis is on the “relative difference” in inventories due to a switch from MTBE to ethanol in the gasoline.

8.1.1 Effect of Changes in the NONROAD Model on Emissions

Table 10 shows the changes in VOC, CO, NO_x, and PM emissions from the default NONROAD model to the model used in this study, which was revised for the effects of fuel oxygen content on the emissions of 2-stroke engines.

Fuel	Pollutant	NONROAD Default	Updated NONROAD	Ratio (Updated/Default)
MTBE RFG	Exhaust THC	82.0	78.7	0.96
	CO	233.6	236.3	1.01
	NO _x	3.8	3.3	0.86
	PM ₁₀	6.3	6.0	0.95
Ethanol RFG	Exhaust THC	81.3	76.0	0.93
	CO	210.2	214.8	1.02
	NO _x	4.5	3.6	0.81
	PM ₁₀	6.3	5.8	0.91

The results in Table 10 show reductions in 2-stroke HC, NO_x, and PM, and a slight increase in CO. The 4-stroke results were checked and they showed no change, and the 2-stroke results were also checked when the oxygen level in weight percent was set to 0.0, and these also showed no change, as anticipated. The updated model is used in the remainder of this analysis.

8.2 Emission Changes Due to Ethanol

8.2.1 On-Road Vehicles

On-road VOC, CO, and NO_x gasoline vehicle inventories in 2007 with MTBE, ethanol, and non-oxy RFG are shown in Table 11.

Pollutant	Baseline – MTBE	Ethanol	No-Oxygenate	Change to Ethanol	Change to non-Oxygenate
Exhaust VOC	46.4	47.7	49.3	1.3	2.8
Evap VOC	55.3	55.3	55.0	0.0	-0.3
CO	1230.4	1230.4	1292.8	0.0	62.4
NO _x	117.9	124.5	117.9	6.6	0.0
PM ₁₀	0.9	0.9	0.9	0.0	0.0

The exhaust VOC and NO_x inventory increases are estimated by applying the percent increases in Table 4 by the MTBE inventories above. The CO inventory does not change, because the MOBILE model does not differentiate between RFG with MTBE and RFG with ethanol. The non-permeation related evaporative emissions change slightly because of the change in RVP (see RVP in Table 5).

8.2.2 Off-Road Vehicles

Off-road vehicle and equipment inventories in 2007 in Maryland on MTBE, ethanol, and non-oxy RFG fuels are shown in Table 12. Converting to ethanol RFG reduces off-road exhaust VOC because the emissions are a function of weight percent of oxygen instead of volume percent of oxygenate, and the weight percent of oxygen is higher for ethanol than for MTBE. The change to a no-oxy RFG will increase exhaust VOC by almost 8 tpd. For evaporative VOC, there is no change to an ethanol RFG, but there is a slight reduction in evaporative VOC (0.4 tpd) for no-oxy RFG because the fuel is estimated to have a 0.1 lower RVP. CO emissions display the same directional trends as VOC. NOx emissions increase for the ethanol fuel, but are reduced for the non-oxy RFG. Finally, ethanol will reduce PM by minus 0.2 tpd, but the non-oxy fuel will increase PM from two-stroke engines by 0.3 tpd.

Pollutant	MTBE	Ethanol	Non-Oxy RFG	Change to Ethanol	Change to non-Oxy
Exh VOC	113.3	108.2	121.1	-5.0	7.8
Evap VOC	18.5	18.5	18.1	0.0	-0.4
CO	1766.8	1597.8	2029.8	-169.0	263.0
NOx	16.2	18.1	13.2	1.9	-3.0
PM	6.4	6.2	6.7	-0.2	0.3

8.2.3 Permeation VOC Impacts

The permeation VOC impacts from using ethanol are shown in Table 13. The first estimate assumes that the permeation impacts in Maryland with 10% ethanol are the same as with 6% ethanol. The other assumption is that the permeation impact is proportional to ethanol concentration. Overall, VOC emissions in Maryland will increase by 6.6 -11.0 tpd due to the permeation effects of ethanol for the ethanol RFG. There is no change in permeation emissions for the non-oxy RFG.

Source	Based on 6% testing	Proportional to concentration
On-road gasoline vehicles	3.3	5.5
Off-road gasoline vehicles and off-road gasoline equipment	1.0	1.7
Portable gasoline containers	2.3	3.8
Total	6.6	11.0

8.2.4 Summary of Impacts

The summary of emission impacts for a change to either ethanol RFG or no-oxy RFG is shown in Table 14. In this table, we have assumed that the permeation effects are proportional to ethanol concentration (see Table 13).

Pollutant	Baseline Inventory – Gasoline (tons per day)	Net Ethanol Impact (tons per day)	Net Non-Oxy RFG Impact	% Change, Ethanol RFG	% Change, non-Oxy RFG
VOC	235.5	2.9 to 7.3	10.0	1.2% to 3.1%	4.3%
NO _x	134.1	8.5	-3.0	6.3%	-2.2%
CO	2997.2	-169.0	325.5	-5.6%	10.9
PM	7.33	-0.22	0.34	-3.0%	4.6%

Table 14 shows that if Maryland bans MTBE and is replaced by ethanol RFG, VOC would increase by 1-3%, depending on the extent of the permeation effect, NO_x would increase by 6%, CO would be 6% lower, and PM would be reduced by 3%. If the MTBE RFG is replaced by a non-oxygenated gasoline, VOC would increase by 4%, NO_x would be reduced by 2%, CO would increase by almost 9%, and PM would increase by 5%. If the MTBE gasoline is replaced by a 50/50 mix of the two fuels, VOC would increase by 3-4%, NO_x would increase by 2-3%, CO would increase by 3%, and PM would increase by 2%. This analysis assumes no “commingling” of the two fuels (commingling is discussed further in the next section).

The CO increases that would result with a non-oxygenated gasoline are not insignificant. CO is a weak ozone precursor, but the size of the changes is significant. EPA’s analysis of the tradeoff between CO and VO in the Chicago area estimated that that 45 tons of CO was worth 1 ton of VOC on a reactivity and mass basis. [11] Thus, if this is an appropriate ratio also for Maryland, the VOC equivalents derived from the CO benefit of converting to ethanol from MTBE would be worth about 169/45 tpd, or 3.8 tpd of VOC. This may mitigate part of the 7.1 tpd VOC permeation increase. However, under the no-oxy RFG scenario, CO increases by 325 tpd, which may be equivalent to about 7.2 tpd VOC. This would add to the already 10.4 tpd of VOC that would be experienced with non-oxy RFG.

9.0 Discussion

This study shows that switching from RFG with MTBE to RFG with ethanol or non-oxy RFG, or some combination thereof would have a variety of emission impacts in the state. If the ethanol/non-oxy mix were 50/50, all four pollutants, VOC, CO, NO_x, and PM, would increase. Since the state has been experiencing ozone exceedences with the new more stringent 8-hour ozone standard, these increases in emissions will likely need to be offset by emission reductions from other sources for the state to attain and then maintain the 8-hour ozone standards.

In addition to the uncertainties in which type a fuel will replace RFG with MTBE – an ethanol RFG or non-oxy RFG or some combination – there are uncertainties in the effects for each replacement fuel. Table 14 showed a range of benefits if either a ethanol RFG or non-oxy RFG were used. If both fuels were supplied by gasoline marketers, the range of impacts would lie somewhere in that range, with some qualifications as indicated in the sections below.

The following discussion expands on some of the uncertainties in this analysis for the ethanol and non-oxy RFG.

9.1 Ethanol RFG

9.1.1 VOC

The range in VOC impacts of 1% to 3% increases comes from the uncertainty in the impact of 10% ethanol blends on permeation emission increases. The 1% figure assumes that the permeation increases are the same at 10 vol % ethanol as at 6 vol % ethanol which is the ethanol concentration used in the CRC permeation study. The 3% increase assumes the permeation increase is proportional to ethanol concentration in the gasoline. The Coordinating Research Council is conducting further testing of 10% vol ethanol blends, and the results of this study should be available later this year.

This analysis also assumes that “all” vehicles traveling in Maryland are filled with RFG blends using either all ethanol, or all non-oxy RFG, which essentially would be assuming that only one of the two fuel formulations would be sold in Maryland. However, with the oxygen standard being removed from RFG, it is entirely possible that both fuels might be sold in the Maryland marketplace which then introduces the possibility for increased evaporative VOC emissions via a situation known as commingling. When both types of fuels are offered in the marketplace, then some vehicles will sometimes fill up with ethanol containing gasoline, and at other times with non-ethanol containing fuel in their tanks. These vehicles that switch back and forth will suffer increased VOC emissions due to increased RVP from the commingling of the two fuels in the tank. Commingling of ethanol and non-ethanol fuels with the same RVP results in a fuel mixture that has a higher RVP, which thereby increases evaporative VOC emissions. Commingling has been assumed to be zero in this analysis. However, if both fuels are offered in the marketplace, it may increase evaporative VOCs by about 0.5 ton per day over the simple averaging of the two fuel cases considered here.

The permeation VOC emission increases from off-road equipment in this analysis are based on lawnmowers. Lawnmowers have relatively small fuel tanks compared to other off-road equipment and vehicles. It is likely that the permeation impacts for off-road equipment are actually higher than estimated in this analysis; in fact, California ARB estimates a higher permeation VOC impact for off-road equipment.

9.1.2 NO_x

The on-road NO_x impacts of ethanol are based on the current ARB Predictive Model. The Coordinating Research Council has completed additional testing of the effects of ethanol on NO_x emissions, and ARB plans to update its Predictive Model based on this testing later this year. The off-road NO_x impacts are based on EPA's NONROAD model; no updates to this model for the NO_x impacts are expected.

9.1.3 CO

The fact that oxygenates reduce CO from the on-road and off-road fleet is well known and quantified in both the MOBILE6.2 and NONROAD models. The major debate concerns the relative reactivity of CO as an ozone precursor.

9.1.4 PM

In this analysis, we did update the effects of oxygen on PM for 2-stroke off-road engines. It is likely that oxygen in the fuel also reduces PM from on-road vehicles and particularly "smoking" vehicles, although this effect has not been estimated or included in the MOBILE6.2 model. Also note that these PM estimates are only for primary PM which is emitted directly in the exhaust of these engines. These PM estimates do not include the amount or effect on secondary PM that are secondary aerosols which are formed by the atmospheric reaction of some of the exhaust gases. A significant source of carbonaceous PM in the atmosphere is the secondary aerosols formed by partially oxidizing the unburned gasoline aromatics found in the exhaust gases of gasoline engines. Therefore, reducing the amount of aromatics in the exhaust or the amount of exhaust and evaporative VOC from gasoline vehicles and equipment should also reduce the amount of carbonaceous secondary PM formed in the atmosphere.

9.2 Non-Oxy RFG

9.2.1 VOC

For on-road vehicles, the non-permeation related evaporative emissions are simply tied to the RVP; if the RVP is a little lower than current, the evaporative emissions will be lower, and if the RVP is a little higher than current, then evaporative emissions will be a little higher. In this case there is no ethanol, so there is no increase in permeation emissions under this scenario. We have used the ARB Model to assess the impact on exhaust VOC. The model is the best we have for this application, although a new Predictive Model may be available soon that utilizes more test data from CRC. The major uncertainty in this respect is how much the aromatics, benzene, and olefins will increase to make up lost octane.

The evaporative emissions for nonroad vehicles behave similarly to RVP as onroad vehicles. The exhaust emissions are primarily a function of the oxygen content. One issue with respect to offroad equipment is that the current NONROAD model does not include running loss, hot soak, or diurnal emissions. If these emissions were included there would be larger swings in the RVP effect on evaporative emissions.

9.2.2 NO_x

For both on-road and off-road vehicles, the reduction in NO_x due to this scenario is a direct results of the reduction in ethanol. The amount of the decrease in NO_x is probably more uncertain for on-road vehicles. The CRC will be shortly releasing test data from its E-67 program, which tested a variety of ethanol and non-ethanol fuels. Preliminary indications are that there is still an ethanol effect on NO_x for new technology vehicles (I.e., LEVII and Tier II vehicles).

9.2.3 CO

The loss in CO benefits for both on-road and off-road vehicles if oxygen is removed from RFG is well known. There is much less impact of the other fuel parameters on CO.

9.2.4 PM

PM emissions in on-road gasoline and off-road gasoline engines come from combusting fuel lubricating oil, and metals, and sulfur. As far as the fuel is concerned the three most important properties of the fuel that affect PM are sulfur, aromatics, and oxygen content. Sulfur is being drastically reduced through the Tier 2/sulfur controls. But aromatics are expected to increase with this fuel, along with the loss of oxygen, which reduces PM. The increase in aromatics in gasoline may also have an effect on the carbonaceous secondary PM formed in the atmosphere from the engine exhaust gases that has been discussed in the previous PM section.

10.0 References

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Attachment 1
Analysis of Oxygen Effects on Two-Stroke Engine Emissions

The NONROAD model oxygen effects for two-stroke engines are based on tests on one moped engine tested on both MTBE and ethanol blends at two different oxygen levels. The results are shown in Table 1-1 below. Note that EPA did not estimate a PM effect. The “average” effects were used in NONROAD.

Fuel Used	HC (%/% oxygen)	NOx (%/% oxygen)	CO (%/% oxygen)
2.7% oxygen	-0.4	18.4	-0.4
3.4% oxygen	-0.8	18.8	-12.5
Average effect	-0.6	18.6	-6.5

Additional 2-stroke engine tests were identified in this study, from a 1997 SAE paper which discussed tests on two snowmobiles, and from a study by CE-CERT, which examined ethanol effects on two 4.5 SACHS engines. The characteristics of these engines are shown in Table 1-2 (engines 2-5; engine 1 is the moped engine referenced by the EPA), and the emission test results of these engine tests, along with the data referenced by EPA, are summarized in Table 1-3.

Engine	Source	Use	HP	Brand	Age
1	SAE911222	Moped	6	Yamaha	?
2	SAE972108	Snowmobile	64	1997 Polaris	New
3	SAE972108	Snowmobile	56	1995 Arctco	2 years
4	CE CERT	Unknown	4.5	SACHS	New
5	CE CERT	Unknown	4.5	SACHS	Old

Engine	Oxygen	HC-Only Fuel (g/kW-hr)				Fuel Containing Oxygenates (g/kW-hr)			
		HC	CO	NOx	PM	HC	CO	NOx	PM
1	3.18	183	183	2.45	7.83	177	143	3.76	7.34
2	3.43	201	548	0.68	2.41	155	476	0.59	1.82
3	3.43	209	487	0.66	4.63	220	459	0.70	4.51
4	2.05	269	621	0.57	2.27	244	579	0.51	2.19
5	2.05	210	486	0.47	1.44	202	470	0.42	1.36
Avg	2.83	214	465	0.94	3.72	199	425	1.20	3.45

Table 1-4 shows the absolute difference in average emissions with test results in Table 1-3, and also the percent change in emissions per weight percent of oxygen.

Table 1-5. Emission Reductions Due to Oxygen				
Parameter	HC	CO	NO _x	PM
Difference in emissions, g/kW-hr	15	40	-0.26	0.27
Percent difference per weight percent of oxygen	2.4%	3.0%	-9.5%	2.6%

Table 1-5 shows that while the percent increase for NO_x appears large, its affect on a mass basis is very small. The reductions for the other pollutants, while smaller in percent terms, are much more significant on a mass basis because of their much higher baseline levels.

Attachment 2

Background on Air Improvement Resource, Inc.

Air Improvement Resource was founded in 1994, and conducts emissions, ambient air quality, and meteorological related research for a variety of industrial and governmental concerns. AIR has four employees, and is located near Detroit, Michigan. AIR is most widely known for its work on many projects with the two Federal and two California on-road and off-road emissions models. Recent projects include:

- Analyzing carbon monoxide emissions data on certification vehicles to determine impacts of cold temperatures (Coordinating Research Council)
- Estimating the emission changes associated with different fuels in the Southeast Michigan Area (SEMCOG, Alliance of Automobile Manufacturers, and American Petroleum Institute)
- Analysis of the emission inventory impacts of ethanol permeation (American Petroleum Institute)
- Analysis of the impact of MMT in gasoline in emissions in the U.S. and Canada (Alliance of Automobile Manufacturers and Canadian Vehicle Manufacturers Association)
- Revisions to the ARB OFFROAD Emissions Model (California Air Resources Board)
- Revisions to the EPA NONROAD Emissions Model (Environmental Protection Agency)
- Evaluation of options for meeting California's Phase 3 Exhaust and Evaporative Emission Standards for Small Gasoline Off-road Engines (Briggs and Stratton Corporation, and Engine Manufacturers Association)
- Ongoing evaluation of the EPA MOVES Model (Alliance Of Automobile Manufacturers)
- Evaluation of New ARB On-road EMFAC Model (Alliance of Automobile Manufacturers, and Engine Manufacturers Association)

The three technical employees of AIR are Tom Darlington, Dennis Kahlbaum, and Jon Heuss. Tom Darlington is an engineer with 25 years developing emission models, with experience at the EPA, Detroit Diesel Corporation, General Motors, and as a consultant. Dennis Kahlbaum is a meteorologist/ computer programmer with 25 years experience programming emission models, analyzing meteorological and emission data, and forecasting weather trends, with experience at Computer Sciences Corporation (for EPA), Consumers Energy Corporation, and AIR. Jon Heuss is a Principal Scientist with 40 years experience at General Motors who has played a major role in the review of the national and state ambient air quality standards. More information on the company can be found at "airimprovement.com."

APPENDIX B

Estimated Cost of MDE Regulation

Estimated Cost for MDE Regulation Implementation

Parameter		Maryland High-Risk Groundwater Use Areas*	Data Source
Number of Existing UST Locations	A	541	MDE estimate of existing gasoline UST facilities within High Risk Use Areas
Number of Sites Exempt	B	406	MDE estimate of sites with available public water or demonstrated containment
Number of Sites Requiring Groundwater Monitoring	C	135	=A-B
Number of Sites with Existing Monitoring Wells	D	30	=C-E
Number of Sites Requiring New Monitoring Well Installation	E	105	MDE estimate
Year 1 Cost Per Site	F	\$14,740	MDE estimate
Annual Cost Per site	G	\$5,700	MDE estimate
Total Year 1 Cost	H	\$1,718,700	=(GxD+FxE)
Total Annual Cost	I	\$769,500	=CxG

*Baltimore, Carroll, Cecil, Frederick, and Harford Counties

APPENDIX C

Overview of Groundwater Remediation Technologies for MTBE and TBA

ITRC

February 2005

MTBE-Specific Remediation

When biodegradation is the primary process used to achieve remediation of Methyl Tertiary-Butyl Ether (MTBE), tert-butyl alcohol (TBA), or other contamination within the subsurface environment, the remedial process is termed in-situ bioremediation (ISB). At sites where bioremediation of contaminants occurs without human intervention, the remediation process is referred to as “intrinsic bioremediation,” “bioattenuation,” or “monitored natural attenuation.” When the conditions at a site require the implementation of a system to accelerate the rate of microbial mediated degradation reactions or to stimulate the activity of microorganisms by optimizing environmental conditions, the process is often referred to as “enhanced in situ bioremediation.” Enhanced in situ bioremediation (which consists of adding chemicals to stimulate biological activity [biostimulation] or adding microbes [bioaugmentation], or a combination of the two) typically involves the use of a system to supply oxygen or additional electron acceptors. In some cases, nutrients, such as phosphorus and nitrogen and/or other growth-stimulating materials are also added (NRC 1993). If dissolved MTBE and or TBA cannot be used by indigenous microbial communities, as the sole source of carbon and energy, the addition of a primary substrate may be needed. Finally, if the indigenous microbial community is not capable of contaminant degradation at an appreciable rate, the addition of a laboratory-enriched microbial community at the site may be necessary. This type of enhanced in situ bioremediation is referred to as bioaugmentation.

It is generally accepted that MTBE and TBA can be degraded aerobically by both naturally occurring and/or cultured microorganisms. However, the details of the biological processes and the factors controlling the rate of MTBE and TBA degradation remain the subject of research and debate. Despite this uncertainty, the use of ISB, typically engineered ISB, for MTBE and TBA has been reported to achieve a measure of success in both field tests and commercial-scale cleanups.

The results from most laboratory and limited field studies suggest that bioremediation strategies involving direct metabolism, cometabolism, bioaugmentation, or some combination thereof can be used successfully at MTBE-affected sites if conditions at the site are amenable to biological activity and oxygen/nutrient delivery.

ISB approaches for the destruction of MTBE in groundwater aquifers involve the use of either aerobic or anaerobic systems. A discussion of both is detailed below. MTBE has been shown to be biologically metabolized or cometabolized under aerobic conditions. However, the metabolism of MTBE and TBA may not continue if anaerobic conditions develop. Therefore, the most important parameters to be measured prior to and during an aerobic ISB application are dissolved oxygen (DO) concentrations; concentrations of MTBE, TBA, Benzene, Toluene, Ethelbenzene, and Xylene (BTEX), and other gasoline constituents; and in some cases, MTBE and TBA degradation products such as acetone.

Field data have been presented which suggest that MTBE degrades naturally in groundwater aquifers. Degradation rate and lags between contaminant bioavailability and bioutilization are variable and site-specific, but the rate/lag is generally [far] slower than for BTEX.

Despite the laboratory and field data presented in published literature that suggest that the natural aerobic biodegradation of MTBE and TBA is a functional process, there are no known reports of the process being relied upon for the protection of a sensitive receptor. This situation is largely due to the fact that most plumes are anaerobic because the natural aerobic biodegradation has been overwhelmed by the flux of contaminants and the available oxygen has been consumed. However, there are a few case studies where significant natural aerobic biodegradation of MTBE in groundwater has been observed at locations of MTBE-contaminated groundwater discharge to surface-water receptors (Landmeyer et al. 2001).

Engineered In-Situ Bioremediation Approaches for Aerobic Biodegradation of MTBE

The addition of amendments can greatly increase the rate and extent of biological processes. Several configurations are effective for engineering ISB at MTBE-impacted sites, including direct injection of amendments, groundwater recirculation, the use of permeable reactive barriers (PRBs) or panels, soil vapor extraction and biosparging. As mentioned in the introduction, an engineered aerobic ISB approach can involve the addition of a number of amendments to stimulate biological activity in the subsurface. This option includes the addition of electron acceptors (e.g., oxygen), nutrients (e.g., nitrogen and phosphorus), cosubstrates (e.g., propane and butane), or exogenous microorganisms. Oxygen sources include air, oxygen, hydrogen peroxide, and oxygen-release compounds.

Case studies involving the direct injection of materials to enhance ISB at MTBE-affected sites are presented below. Of course, the major challenge of an engineered aerobic ISB approach involving the injection of amendments to the subsurface is the ability to contact the amendment with MTBE and the appropriate microbial populations.

Bioaugmentation Combined with Oxygen Injection

The most comprehensive studies of bioaugmentation combined with oxygen injection have been conducted at the Port Hueneme, California Naval Exchange Service Station, where an MTBE plume extends over 4,000 feet in length, 400 feet in width, and 10 feet in thickness. BTEX and TBA are also present. Studies at this site have involved the injection of both mixed and pure cultures of microorganisms into various zones of the aquifer, in addition to the addition of air and pure oxygen.

In a study at the same site, a mixed bacterial culture designated BC-4, which was enriched by researchers at Shell Global Solutions, was also used to evaluate the feasibility of bioaugmentation (Salanitro et al. 2000). Three plots were evaluated in this study: a control plot where no treatment was performed, a plot supplemented with oxygen only, and a plot supplemented with oxygen and augmented with BC-4. The results of this study again provided evidence of successful biostimulation with oxygen injection alone; however, oxygen injection was shown to be less effective than the combined effect of oxygen and BC-4 injection. Furthermore, a longer lag time was observed when oxygen was used exclusively.

In summary, studies have shown that the addition of microbial mixes in combination with oxygen is more successful at remediation than simply adding oxygen, a microbe mix, or pure

microbes alone. It is worth noting that almost all of the studies and literature available indicates that TBA breaks down much more readily than MTBE.

Results from this project show that use of ISB at Port Hueneme is expected to lead to cost savings exceeding \$30M relative to a pump-and-treat approach (Miller 2002). A recent report describing the design, monitoring, and optimization of this type of aerobic MTBE-treating biobarrier was recently published (Johnson, Miller, and Bruce 2004). This report emphasizes the following main issues: (a) the need to fully delineate the source zone(s) to ensure all MTBE sources are treated by the barrier, (b) the suggested use of pulsed oxygen (rather than air) injections to maximize the zone of oxygenation and to provide continuing rather than temporary oxygenation, and (c) the ability of this system to treat not only MTBE and TBA but also other gasoline co-contaminants (e.g., BTEX).

The report also outlines several important considerations affecting the use of bioaugmentation with commercially available or cultivated indigenous microbial cultures versus the alternative of stimulating indigenous microbial communities by the addition of oxygen alone (biostimulation). The principal issues addressed here are (a) the significant uncertainties associated with microcosm studies designed to assess whether indigenous organisms can be stimulated to effective levels in a particular environment and (b) the extended time (>1 year) that may be required to establish effective indigenous microbial communities capable of treating the existing contaminants. Although the collective experiences with in-situ oxygenation approaches at Port Hueneme all observed MTBE treatment through biostimulation, the use of bioaugmentation should be viewed as a means to reduce the time needed establish a stable and effective MTBE- and TBA-degrading microbial community in the treatment zone.

Factors Affecting the Success of Aerobic Biodegradation of MTBE

The reported field pilots of aerobic biodegradation of MTBE and TBA suggest common site characterization parameters should be considered when evaluating aerobic ISB as a pilot- or field-scale remedy. The physical parameters that are of primary relevance to ISB are hydraulic conductivity, hydraulic gradient, and organic content of the aquifer.

The following chemical parameters also affect MTBE and TBA degradation:

- contaminant concentrations,
- oxygen concentration,
- pH,
- organic and inorganic electron donor concentrations,
- electron acceptor concentrations,
- nutrient concentrations, and
- nontarget inorganics that can consume oxygen (such as ferrous iron).

These parameters can help determine which amendments would be helpful and how well they can be delivered to the contamination. Other site conditions such as access, available utilities, and depth to groundwater are also important to consider. In general, the best sites have highly permeable, homogeneous hydrogeology and sufficient natural nutrients. On the other hand,

fractured-rock, low-permeability ($K < 10^{-4}$ cm/sec), highly stratified deposits do not make good areas for successful aerobic ISB.

Performance

To date, performance information regarding the use of aerobic ISB is not widely available. Performance is highly site specific and largely a function of the skill of the remediation practitioner in discerning what amendments are needed and bringing microorganisms, contaminants, and amendments into contact with one another. The availability of complete case studies of remedial-scale applications is expected to increase as ISB becomes a more frequently attempted and/or accepted remedy at MTBE-affected sites.

Cost

To date, cost information regarding the use of aerobic ISB applications is limited. Based on the costs involved in establishing a 500-foot biobarrier at Port Hueneme, it is estimated that future installation costs are between \$800 and \$1,050 per linear foot for aquifers less than 30 feet bgs (ESTCP 2003a). Approximately 70% of these costs are associated with the bioaugmentation of the aquifer. The annual Operation and Maintenance (O&M) costs for a 500-foot biobarrier are estimated at approximately \$75,000. Approximately 60% of these costs are associated with sampling and analysis, the remainder is split evenly between utility costs and maintenance of the oxygen generating and distribution system. As with the availability of MTBE case studies, the availability of cost information is expected to increase as ISB becomes a more frequently attempted and/or accepted remedy at MTBE-impacted sites.

Anaerobic MTBE Bioremediation

Anaerobic biological processes take place in the absence of oxygen. Alternative electron acceptors include nitrate, ferric iron, manganese (IV), sulfate, and carbon dioxide.

Evidence for MTBE Anaerobic Biodegradation

A study conducted in 1994 investigated the biodegradation of MTBE under denitrifying, sulfate reducing, and methanogenic conditions in microcosms using soil and groundwater from three different sites (Yeh and Novak 1994). The authors found no evidence of MTBE biodegradation under anaerobic conditions when nutrients and a hydrogen source were not added, or under denitrifying conditions or sulfate-reducing conditions when nutrients and a hydrogen source were added. The removal of MTBE was only shown to take place under methanogenic conditions and in the absence of more easily degraded organic compounds.

A study conducted in 2000 evaluated the biodegradation of MTBE under methanogenic conditions in soil samples collected from a former fuel farm in North Carolina (Wilson et al. 2000). MTBE was degraded in the microcosms after more than 300 days and in some microcosms only after all other degradable compounds (e.g., alkylbenzenes) were depleted. More recently, Finneran and Lovley (2001) reported the anaerobic biodegradation of MTBE and TBA in aquifer materials from a contaminated site. MTBE and TBA were shown to degrade under iron-reducing conditions in the presence of humic substances. The authors speculated that

the humic matter served as an electron shuttle, thereby facilitating the oxidation of MTBE and TBA. Finally, researchers have demonstrated that MTBE can be degraded under a range of electron acceptor conditions including nitrate-, iron- and sulfate-reducing conditions (Bradley et al. 2001a, 2001b; Bradley, Chapelle, and Landmeyer 2002; Landmeyer et al. 2001; Somsamak, Cowan, Haggblom 2001).

U.S. Geological Survey (USGS) work indicated that TBA degraded under aerobic, nitrate-reducing, manganese (IV)-reducing, and sulfate-reducing conditions; however, it did not under iron-reducing and methanogenic conditions after 198 days of incubation. TBA persistence under strongly reducing conditions has also been observed by others (Somsamak, Cowan, Haggblom 2001; Kolhatkar et al. 2002).

Limitations of Anaerobic In-situ Bioremediation Applications

While these studies have reported the anaerobic biodegradation of MTBE in soil and groundwater samples from MTBE-impacted sites, there are no studies documenting the successful application of an engineered anaerobic ISB approach in the field. Knowledge regarding ways to enhance anaerobic processes in the field is currently limited, and no known engineered anaerobic ISB applications have been attempted. However, given that the majority of gasoline-impacted plumes are anaerobic (Kolhatkar, Wilson, and Dunlap 2000; McLoughlin et al. 2001), it is important to continue evaluation of the fate of MTBE and TBA and by-products of incomplete degradation such as acetone under anaerobic conditions.

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