



**National Groundwater and
Contaminated Land Centre**

**The fuel
additive MTBE -
a groundwater
protection
issue?**



**ENVIRONMENT
AGENCY**

Introduction



Common additives to petrol world wide are Methyl Tertiary Butyl Ether, better known as MTBE and its sister compounds TAME (Tertiary Amyl Methyl Ether) and ETBE (Ethyl Tertiary Butyl Ether). Oxylate ethers such as MTBE were originally added to replace lead in petrol as "anti-knock" agents. Ethers are now seen by some to have a much broader role in reducing polluting emissions from cars. Industry and regulatory bodies, particularly in the USA, see ethers as the best way to reduce environmental impacts of petrol use. By providing extra oxygen for the combustion process, ethers reduce the amounts of unburnt hydrocarbons in exhaust emissions. In addition, they substitute for benzene and other aromatics in petrol and so help reduce public exposure to these potential carcinogens.

World wide production of MTBE is increasing, and greater use of this chemical can have both positive and negative impacts on the environment. In 1996, the Environment Agency commissioned a research project to better understand the issues and

environmental pressures (particularly on groundwater) associated with the use of MTBE. The findings of this study were published in an Agency R&D Technical Report (P11) entitled 'Threat to Potable Groundwater Supplies from the Fuel Additive MTBE'. Since the publication of this report, the debate over the environmental risks and benefits of greater use of MTBE has increased, particularly in the USA. Although use of MTBE is relatively low in the UK, this may change and it is necessary to understand how MTBE will impact on the UK environment and to learn from experiences in the USA.

Evidence suggests that the average British consumer buys petrol on price. Suppliers therefore formulate petrol to have the requisite octane rating, using the most cost effective additives. UK refiners currently add between 0% and 10% MTBE, by volume, but are legally entitled to use up to 15% in leaded or unleaded petrol. As MTBE is relatively expensive, it is only added in significant quantities to create Super Unleaded grades of petrol, where the



high octane rating can only be met using ether or alcohol additives. The octane levels required in leaded and un-leaded petrol are met by mixing the basic blend petrol with high-octane petrol.

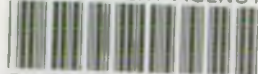
In the USA, there are strict legislative controls restricting lubricants added to petrol. High aromatic blending stocks have been reduced in favour of ether and alcohol additives. These increases the oxygen content of the petroleum and reduces volatility and emissions on combustion. In addition to legislation, fiscal incentives in the USA have also promoted the use of MTBE and methanol to reduce the aromatic content of petroleum. In the EU, however, there are no tax subsidies at present for using oxygenates in place of the high aromatic blend stocks.

In recent years, a number of pollution incidents have been identified in the USA and the UK where petrol (or gasoline) containing MTBE has contaminated groundwater. These pollution incidents may represent only a small fraction of the total groundwater polluted with MTBE.

One of the reasons for this is the comparatively recent appearance of MTBE in both the UK and the USA markets. It is likely therefore that many discharges into groundwater have not yet been detected as they have not yet reached receptors such as water supply boreholes, at which routine groundwater quality monitoring is undertaken. To date most site investigations and risk assessments carried out at sites contaminated with petrol have concentrated on the detection and quantification of BTEX compounds (Benzene, Toluene, Ethyl-benzene and Xylene) and Total Petroleum Hydrocarbons (TPH). Few investigations target MTBE and many laboratories are not equipped for routine analysis of MTBE.

In March 1999 California announced plans to phase out MTBE use by 2003. This followed a number of high profile incidents involving the loss of groundwater supplies due to MTBE pollution.

ENVIRONMENT AGENCY

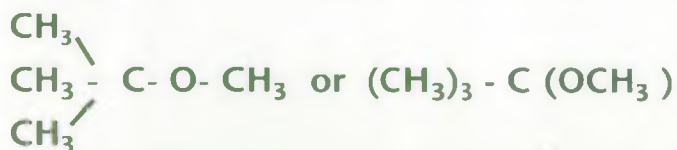
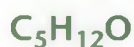


017617

Properties of MTBE

PROPERTY	VALUE	UNITS
Molecular Mass at 25°C	88.17	g mole ⁻¹
Specific Density at 25°C	0.7404	
Physical appearance	Colourless liquid	
Boiling Point	+ 55.2	°C
Melting Point	- 109	°C
Flash Point	- 28	°C
Ignition Temperature	+ 224	°C
Vapour Pressure at 20°C	200*	mm Hg
(Log K _{ow} at 20°C)		
Partition Co-efficient	1.1	
Henry's Law constant	4.5 x 10 ⁻⁴	atm m ³ mole ⁻¹
Water Solubility at 25°C	43	g l ⁻¹
*source API 1991a		

Physical & Chemical Properties





Fate and transport

The movement of MTBE and other petroleum components in soil and groundwater will be controlled by numerous site-specific environmental conditions. These may include the quantity and duration of the petroleum release, soil type, depth to the water table, redox potential, pH, oxygen concentration, nutrient concentrations available to facilitate biodegradation, ambient temperature and rainfall. A large volume of petroleum leaking into the soil is likely to result in pollutants migrating downward to the water table. During this migration through the unsaturated zone, the various components in the petroleum may be subject to biodegradation, soil sorption, volatilisation, dispersion and dissolution.

MTBE being less dense than water, with a specific gravity of 0.74, will float on groundwater. However, MTBE can enter deep groundwater in response to natural or induced hydraulic gradients and diffuse recharge or by molecular diffusion and dispersion. The most likely causes of MTBE in deep groundwater is steep


vertical gradients caused by extraction wells or where vertical hydraulic gradients occur naturally.

Solubility and sorption

MTBE is highly soluble in water, having a solubility of an order of magnitude greater than other components of petroleum. Unlike many other organic chemicals, MTBE is poorly sorbed to carbon based substrates such as soil. These two physical properties have important consequences for the movement of MTBE in groundwater and the types of remediation technology that are likely to be effective in removing it from contaminated groundwater.

(Bio)degradation

The degradation of an organic compound refers to its transformation to simpler chemical components by biotic and abiotic reactions. Biological transformations or biodegradation often provides the predominant decay pathways for the breakdown of a wide range of organic compounds in water and soil. There are relatively few published studies on the



biodegradability of MTBE. Most early studies indicated that MTBE does not biodegrade rapidly in the environment and it was often reported as being recalcitrant. This is in part due to MTBE being a relatively new contaminant in the environment and as a result there has been limited evolutionary pressure for aquifer microorganisms to develop degradative capabilities for this compound. Nevertheless, bacteria have been isolated which are capable of degrading MTBE and recently published experimental findings of aerobic MTBE biodegradation at the Borden aquifer in Canada indicate that naturally occurring biological process may be important in degrading MTBE (Schirmer, M & Barker, J. 1998).

Human toxicity

Human toxicological data derived from both inhalation and oral routes of exposure suggest that MTBE is of low acute and subacute toxicity. It does not appear to be either a reproductive toxicant or to be mutagenic. There is ambiguous data relating to the carcinogenicity of MTBE. Despite the

current scientific debate, it appears that the threshold taste and odour concentration of MTBE (around $15\mu\text{g l}^{-1}$) is likely to be lower than any future human health-based guideline value.

Legislation

Legislation currently exists in both Europe and the USA controlling the use of MTBE. There is a fundamental difference in approach, however, which resulted in the USA broadly adopting legislation to encourage the use of MTBE, while in Europe legislation is in place to limit its use. Both regions also have a number of laws that indirectly influence the use and environmental impact of MTBE, such as air quality standards and controls on oil storage.



Legislation in the UK and Europe

Legislative Controls on the use of MTBE in the EU

After consultation with the motor and oil industries, the European Commission approved a Directive on the use of fuel oxygenates in December 1985. The Directive came into force in January 1988 (EU Directive on fuel oxygenates. 1/1/1988).

The following restrictions apply to the use of ether oxyates in both leaded and unleaded petrol:

- no more than 10% by volume in petrol freely transported over borders;
- no more than 15% by volume in petrol in any member state without supplementary labelling: above this volume labelling is mandatory.

Air quality legislation in the EU

Although MTBE demand in Europe is growing, the octane problem is not as great as in the USA. This is because

restrictions on blending components are not as severe but this is set to change with a new EU directive on fuel quality and vehicle emissions. The draft directive stems from the Auto/Oil programme, a tri-partite initiative between the European Commission and the oil and car industries designed to secure cost-effective compliance with air quality standards by 2010. The European Parliament has tightened up the original proposals and requires binding vehicle emission and fuel quality standards by 2005. The European Parliament also voted for tighter fuel quality standards by 2000. Negotiations are still continuing, but once the directive has been finalised it will be for member states to determine how to achieve these new standards.

Air quality legislation in the UK

The UK legislation on air quality stems from air quality management provisions in the Environment Act 1995. Regulations following on from the Act have now been made which set out air quality objectives for seven pollutants. Local authorities will be



required to review air quality in their areas and assess whether those targets are likely to be achieved by 2005. Where they are unlikely to be met, the Authority must designate an Air Quality Management Area (AQMA) and prepare an action plan setting out measures to ensure compliance. The UK's strategy for managing air quality is set out in the 'National Air Quality Strategy' document. Part of the strategy to improve air quality, particularly in urban areas, is to encourage the improvement in vehicle and fuel technology. The strategy makes specific reference to encouraging the use of less polluting fuels, but does not specify what form these fuels might take.

Petroleum (Consolidation) Act 1928

The keeping of petrol is covered by the Petroleum (Consolidation) Act 1928. This Act requires that the keeping of petrol must be authorised by a licence. The Health and Safety Executive (HSE) has policy responsibilities, but the enforcement and licence issue role, and setting of

any conditions attached to it, are the responsibility of the Petroleum Licensing Authorities (PLAs).

The PLAs, which are normally within the Fire and Civil Defence Authorities, Local Authorities or, under certain circumstances, the HSE are responsible for regulating:

- the issue of licences and licence conditions under the Petroleum (Consolidation) Act 1928, and;
- the loading of petrol from road tankers at licensed premises.

Water Resources Act 1991

Under the Water Resources Act 1991 it is an offence to '...cause or knowingly permit any poisonous, noxious or polluting matter...to enter any controlled waters.' It is not necessary for an off-site impact to be caused for an offence to have been committed since groundwater, including that directly beneath a site, is classed as controlled water under the Act.

Groundwater Regulations 1998

The UK Environment Agencies have new powers under the Groundwater

Regulations 1998, which are necessary to fully transpose the EU Groundwater Directive (80/68/EEC) into UK law. This may have a significant impact on the storage of petrol in the UK because it requires that all List I substances (which include hydrocarbons and mineral oils) are prevented from entering groundwater. Some estimates suggest that up to one third of all retail service stations may have pollution problems, so there is likely to be a need to reassess how petrol is stored in many situations.

(Proposed) Oil Storage Regulations


The Department of the Environment, Transport and the Regions (DETR) is considering introducing regulations to set minimum standards for industrial and commercial oil storage facilities. The regulations would apply to all existing installations and those constructed or substantially reconstructed or extended after the regulations come into effect. The main provisions would concern design standards for oil storage tanks and containment systems. At existing

locations, powers would be given to the Environment Agency to serve notice requiring action to improve any installation that it considers poses a significant risk of causing water pollution.

Legislation in the USA

MTBE used to improve air quality

In 1996, 80% of the world's production of MTBE was used in the USA. The demand for oxygen additives in the USA is largely driven by regulations. Emission standards imposed by the 1990 Clean Air Act Amendments (CAA) are expected to require oxygenates in over 70% of the USA petroleum pool by 2000. The first phase of the CAA involves 44 areas of the country that failed the US Environmental Protection Agency (US EPA) emission standards for carbon monoxide. From November 1992 retailers in these areas were committed to selling petroleum containing at least 2.7% oxygen (by weight) in the winter months; this part



of the CAA is referred to as the Oxygenated Petroleum Programme. In March 1999 California announced a plan to end MTBE use in the state by 2003 and asked the federal EPA to waive the oxygenate requirements of CAA.

Oil storage legislation in the USA

The US EPA proposed extensive regulations in April 1987 requiring that all new Underground Storage Tanks (USTs) meet an updated specification. Within 3-5 years of the regulation coming into force all tanks were required to have leak and overflow detection devices. All existing USTs were to be upgraded or replaced within ten years. In addition, the US EPA has developed a series of standard test procedures for leak detection. These were developed to provide a consistent and rigorous evaluation procedure for determining the performance of leak detection methods.

Liability insurance is also required in the USA for all owners of petroleum USTs at production, refining marketing facilities or sites that handle over 10,000

gallons per month. This insurance covers accidental spillage and can be used to pay for remediation of pollution.

Drinking Water Standards and Regulation in USA

The USA has a variety of standards for MTBE in drinking water, but only in Florida are they legally binding.

State Drinking Water Standards

Florida	50 $\mu\text{g l}^{-1}$
---------	-------------------------

State Drinking Water Guidelines (US EPA 1993)

Connecticut	100 $\mu\text{g l}^{-1}$
-------------	--------------------------

Massachusetts	50 $\mu\text{g l}^{-1}$
---------------	-------------------------

Maine	50 $\mu\text{g l}^{-1}$
-------	-------------------------

Michigan	40 $\mu\text{g l}^{-1}$
----------	-------------------------

New Hampshire	100 $\mu\text{g l}^{-1}$
---------------	--------------------------

New Jersey	700 $\mu\text{g l}^{-1}$
------------	--------------------------

US EPA standards released in 1997 : advisory limits of 20- 40 $\mu\text{g l}^{-1}$

There are no directly equivalent standards for MTBE in drinking water in the UK.



Monitoring groundwater for MTBE.

There is insufficient data at present to make any accurate assessment of the current risk posed by MTBE to UK groundwater resources. So far, there are few reported case studies of groundwater contamination by MTBE in Europe and the UK. Very little routine monitoring data of MTBE in either drinking water sources or groundwater resources are available and the data that is available has largely come from specific pollution incident studies. The lack of data makes it impossible to assess the widespread occurrence of MTBE in UK groundwater and likewise the threat it poses to general resource quality. Based on the limited data available, MTBE has been detected in rural, urban and industrial areas and in a range of aquifers, albeit at concentrations less than the taste and odour threshold. The Agency intends to increase the monitoring of MTBE in order to improve its understanding of

the nature of this chemical in UK groundwater and the possible interaction with surface waters.

A survey carried out in 1996 showed that 5 out of 8 Environment Agency Regions had recorded instances of MTBE in groundwater. However, no special attention is paid to water supplies located close to petroleum outlets (where the risk of spillage and leaking tanks is high). At the time of the survey only one water services company routinely monitored for MTBE, although 40% paid particular attention to water supplies located near to retail service stations and of these 30% detected MTBE. A monitoring strategy is being developed.

During 1993/4, as part of the US Geological Survey's National Water Quality Assessment (NAWQA) programme, a sixteen state survey of pollutants in groundwater was undertaken. A total of sixty volatile organic compounds (VOCs) were measured at each location, including MTBE. The programme was designed to determine baseline groundwater quality, against which future trends in



water quality within sixty of the largest and most important river basins were to be established. Sampling wells were selected on a 'grid based random sampling' approach. MTBE was detected in groundwater across the study area, but was found most often at urban sites (27%) compared to those in rural locations (1.3%). Of the sixty VOCs analysed, MTBE was the second most frequently detected in samples of shallow groundwater from urban areas. It was concluded that a combination of spills, fugitive emissions, leaking underground storage tanks and un-burnt petroleum from poorly operating vehicles could account for the wide distribution of MTBE in the study locations.

The US EPA gives advice on how to monitor and sample sites already contaminated with MTBE. It notes that because MTBE behaves differently from other petroleum hydrocarbons when released into the environment, a site investigation may need to be modified to properly characterise the area of MTBE contamination. It has been observed that the relatively high

solubility of MTBE, when combined with heterogeneous groundwater flow behaviour, may result in the MTBE dissolving into the groundwater in pulses. This results in large and rapid changes in contaminant concentrations. Pulses, which may be caused by groundwater flow through anisotropic aquifer systems, groundwater head fluctuations or infiltration of rainwater, may necessitate frequent groundwater sampling to determine actual MTBE concentrations and levels of risk to down-gradient receptors. The frequency of sampling should take account of the local hydrogeology and the number of monitoring wells. Accurate sampling data is essential to determining the impact of MTBE at a particular site.

Case studies

UK case study: East Anglia

In 1988, a site in the Agency's Anglian region was contaminated by the release of unleaded fuel from an underground tank. Groundwater in the chalk aquifer and at a public supply borehole was affected by the release. 'Pump and Treat' and 'air-sparing' technologies were used to mitigate the effects of the release. Monitoring and testing at the site was undertaken which produced the following conclusions.

- MTBE is persistent in groundwater by comparison with BTEX (Benzene, Toluene, Ethyl-Benzene and Xylenes) components.
- The MTBE plume exhibits little retardation in comparison to other BTEX components. The MTBE plume is larger than the BTEX plumes and contaminates greater volumes of groundwater. This is consistent with experiences in the USA.

- The 'Pump and Treat' system was only partially effective in containing aqueous phase contaminants.
- The 'Pump and Treat' system was unsuccessful at removing the floating (free-phase) petroleum contaminant.
- The effectiveness of 'Pump and Treat' systems for MTBE may be limited by the ability of the system to recover the contaminant adsorbed to organic or clay particles in the aquifer, or held within pore spaces as a result of high pore-throat breakthrough (capillary) pressures.
- Vapour extraction techniques proved the most effective technique at removing the pollutants from the aquifer.

USA case study: California

In 1990, the US Clean Air Act obliged areas with poor air quality to add oxygenates to their petrol to increase the oxygen content and improve combustion, thereby reducing noxious



emissions. California is a good example where action has been taken to overcome air pollution but has resulted in major problems in the water environment. MTBE has now widely contaminated groundwater and surface water in California, primarily as a result of leaking underground storage tanks and pipelines and the use of motorized vessels on lakes and reservoirs.

In late 1995, authorities in the city of Santa Monica, California detected MTBE in a well that supplied the city with drinking water. In June the following year the problem had escalated and the city authorities were forced to shut down some of the potable supply groundwater wells. As a result of the MTBE contamination, the city lost 71% of its local water supply. About half of its total water consumption must now be bought from outside sources at a cost of \$3.5 million a year.

Until recently oil companies in the USA unanimously supported the use of MTBE, but in October 97, Tosco, the largest independent oil refiner in the

USA wrote to the California Air Resources Board asking them to 'take decisive action immediately to begin to move away from MTBE'. Tosco warned that extensive contamination would result in huge costs to restore the state's drinking water.

Sources of MTBE pollution

Defining the source of MTBE pollution in groundwater is essential to prevent further contamination and to protect vulnerable aquifers. MTBE can enter the environment by either point or diffuse sources.

Point sources

MTBE is usually discharged into the environment as a component of petroleum. Pollution incident data suggests the most important point sources are spills and leaks from both underground and above ground storage tanks, pipelines and transportation accidents and by disposal of contaminated soil at landfills, following the excavation and removal of soils from contaminated sites.



Diffuse sources

Diffuse sources are also a possible cause of groundwater contamination; examples include atmospheric deposition and storm water run-off from highways (Squillace *et al* 1995). MTBE is released into the atmosphere from a variety of sources including industrial discharges, mobile sources such as emissions from motor vehicles and also during refuelling of vehicles. It is sobering to reflect that each time a car petrol tank is refilled with around 50 litres of petrol then 50 litres of vapour are forced out. Few studies have measured MTBE concentrations in the atmosphere, but recent evidence indicates evaporative emissions from vehicles are higher than was originally thought, suggesting this may be an important route for MTBE to enter the environment (Stump 1990, Calvert 1993).

Petroleum distribution system

The majority of petroleum (55-60%) is transported from the refinery to the marketing terminal through pipelines (Environment Agency R&D Technical

Report 11). Around 5-10% is transported by road tanker, with the remainder shipped from the refinery by barge and tanker. Petroleum is not currently moved in any significant amounts by rail, although rail often plays a major role in moving oxygenates to their blending locations.

Refineries may blend petroleum components continuously and then deliver directly to a pipeline, or they may batch blend the petroleum into shipping tanks. Long pipelines often have intermediate breakout tanks that are necessary for efficient operation of the pipeline. Most pipelines have multiple delivery points along the line. All these locations represent potential points of failure or long-term leakage. Since MTBE blended petroleum is usually compatible with standard storage and distribution systems, the blending process usually occurs at the refinery, but MTBE can also be added at marketing terminals. Release of MTBE into the environment through spillage generally occurs as a consequence of petroleum spills.



These could include leakage associated with:

- refinery tanks and receiving facilities;
- corrosion or damage to fuel storage and distribution systems;
- failure of valves and pump seals associated with pipeline distribution systems;
- spillages during dispensing;
- spillages from tankers during delivery or transportation.

In order to ensure spillage is kept to a minimum, accurate monitoring of leakage is needed at all points in the distribution system. A range of leak detection and safety systems could help to minimise the effects of failure and leakage. These may include:

- storage tanks and underground lines with secondary containment and interstitial monitoring systems;
- tank overfill protection, and under-pump check valves;
- fill-pipe spill containment (i.e. appropriate bunds or watertight man-chambers);

- spillage containment around dispensers (i.e. impermeable forecourts with appropriate drainage);
- the use of appropriate petroleum resistant materials;
- accurate wet-stock management systems.

Petroleum storage in the UK and Europe

Currently there is no single approach to underground storage tank management in Europe because of differences in environmental setting and political approach in the various member states. The threat posed to groundwater resources by Leaking Underground Storage Tanks (LUSTs), has been recognised in Europe for over twenty years, however, there is presently little use of external leak detection technology. Where monitoring technology has been developed it has generally focused on assessing accurate stock records, rather than specifically addressing environmental protection issues. Sophisticated monitoring equipment is now available to measure

tank contents and the presence of fuel in soil and groundwater outside the storage system. These facilities can help to detect leaks.

Releases at filling stations can be attributed to five main factors:

- customer spills during dispensing on forecourts, which some estimate at around 1,000 litres a year per site;
- poorly maintained or specified drainage and oil/water separators;
- leaks from fuel delivery pipework - experience indicates that leaks from pipework are the most common problem at retail sites;
- tank leaks of both liquid and vapour;
- overfilling during tanker deliveries.

The prescriptive regulatory requirements for environmental protection on the UK oil industry are currently less stringent than in parts of Western Europe and North America. Consequently standards of underground storage installation construction and protection, and associated environmental monitoring adopted at many sites is insufficient to prevent releases of fuel and pollution

of water resources. Regulation of fuel storage in the UK has concentrated solely on health and safety issues, associated with the explosive and fire risks of petrol, and has often neglected environmental considerations associated with petrol or other less flammable fuels such as diesel.

Petroleum storage in the USA

The US EPA is concerned about potential groundwater contamination from LUSTs. The US EPA expects 75% of all tanks to fail within the next decade. It has also estimated that about 22% of the 1,230,000 petroleum storage tanks at more than 500,000 sites in the USA have leaked as of July 1994.

In 1984, the US EPA compiled a report detailing over 12,000 petroleum releases from Underground Storage Tanks (USTs). Analysis of the data revealed some interesting statistics about petrol spillage:

- reported releases of petroleum into the environment showed a marked increase since 1974 (over 2,500 reported in 1984 compared to about 200 in 1974);

- most releases were in areas with relatively corrosive soils (high moisture, low pH);
- 80% of leaks were due to corrosion or structural failure;
- 84% of leaking tanks were bare steel;
- 11% of leaking tanks were glass reinforced plastic (GRP);
- 90% of the releases were at retail or other commercial establishments;
- greater than 40% of the leaks involved an excess of 500 gallons;
- most leaks (70%) were detected by sight or smell;
- groundwater was contaminated in 45% of releases;
- more than 700 private wells and 40 municipal wells were reported as being contaminated.

Risk assessment for groundwater pollution

The UK Government is committed to promoting the redevelopment of contaminated land and remediation of groundwater within a risk-based context, taking account of land-use and environmental setting. Where groundwater is, or is likely to be contaminated, risk-based remedial goals should be developed that are protective of human health, the environment and other relevant receptors.

The Environment Agency and DETR are currently developing guidance on risk assessment procedures and methodologies for the assessment of risks to groundwater resources from land and groundwater contamination, and for the derivation of site-specific remedial goals in the event that the risks are deemed unacceptable.

The following guidance is due to be released by late 1999 (see references for further details):



- Model Procedures for the Management of Contaminated Land, CLR11: Procedure for Risk Assessment.
- ConSim
- Methodology for the Derivation of Remedial Targets for Soil and Groundwater to Protect Water Resources.

Comparable approaches have been adopted in the USA, such as the American Society for Testing of Materials' protocol for Risk Based Corrective Action (RBCA). It should be noted that RBCA may not be directly applicable to the UK without modifications to the assumptions made within the protocol, due to legislative requirements particular to the UK.

Remediation of MTBE contaminated soils and groundwater

MTBE can be removed from groundwater, along with other petroleum components, by

conventional remediation methods, although it may increase the cost and duration of remedial works. A range of techniques exists for MTBE removal from groundwater (see below), some have proved more effective though than others. As with all remediation technologies site-specific conditions will play a fundamental role in the option selection process.

Soil Vapour Extraction

Soil Vapour Extraction (SVE) has been shown to be an effective technology for the remediation of soil contaminated with volatile and semi-volatile organic compounds, such as BTEX and MTBE.

SVE is an in situ soil treatment technology that removes volatile contaminants from soil in the unsaturated zone (above the water-table) by extracting the contaminant vapours with a vacuum that is applied to the subsurface. The contaminated vapours are then treated to remove the organic compounds (by air-water stripping or granular activated carbon - GAC) before being vented to atmosphere.

Low Temperature Thermal Desorption

Low Temperature Thermal Desorption (LTTD) is also an in situ soil treatment technology, but in this instance the soil and soil gas are heated to enhance volatilisation of contaminants from the soil matrix. Off-gases must be treated in the same manner as those produced by a SVE operation, and it is important to control the temperature to ensure that ignition of combustible vapours does not occur.

Air sparging

Air sparging is not particularly effective at removing MTBE from water. This in situ technique involves injecting air beneath the water-table to volatilise the contaminants. Because MTBE has a relatively high solubility in water, larger volumes of air are needed to volatilize MTBE compared to other petroleum based pollutants such as the BTEX compounds. Initial field experiments suggest two to five times more air is needed to treat a given volume of water with MTBE compared to a similar volume of water with other

VOC compounds, assuming the MTBE concentration is less than $5,000\mu\text{g l}^{-1}$.

'Pump and Treat'

In contrast to many other organic pollutants, pumping contaminated groundwater and treating it above ground ('Pump and Treat') may be a cost-effective remediation technology for MTBE. This is because MTBE does not adsorb strongly to soil so removal by pumping groundwater is likely to be relatively rapid. In addition, because it is highly soluble, most of the MTBE mass may quickly dissolve into groundwater making pumping an efficient method of removing large quantities of contaminant.

Following removal of contaminated groundwater, it will need to be treated at the surface (for example by air stripping or GAC) before being returned to the ground or being discharged to watercourse or sewer. It should be noted, however, that granular activated carbon is not particularly effective at separating MTBE from water. This treatment uses the sorption capacity of the activated



carbon to adsorb the pollutant. As MTBE has a very low absorption capacity GAC is only about 1/3 to 1/8 as effective in removing MTBE as it is in removing benzene.

Monitored Natural Attenuation

Recent studies of MTBE plumes in North America, and in particular the Borden aquifer of Ontario, Canada have shown that, under preferential hydrogeochemical conditions, natural biodegradation of MTBE can occur within groundwater systems, (Schirmer & Barker, 1998). Degradation kinetics were significantly slower than those for the BTEX compounds. If hydrogeological conditions allow, however, and risk-assessment demonstrates environmental impacts are acceptable throughout the predicted duration of the contamination, it may be appropriate to manage the risks associated with an MTBE pollution by adopting a monitored natural attenuation strategy.

Information on other technologies can be found in the draft Contaminated

Land Research Report CLR11: Model Procedure for the Evaluation and Selection of Remedial Measures.

At a glance

MTBE:

- is used as an additive in petrol;
- increases the oxygen content of petroleum and results in lower aromatic hydrocarbon emissions from vehicles, but it may increase emissions of NO_x and aldehydes;
- is relatively non-toxic to humans, but can be detected by taste and odour at low concentrations (5-15µg l⁻¹);
- is more soluble than other components of petrol and, if spilt, will consequently travel further and contaminate greater volumes of groundwater than the other components of petrol;
- and other oxygenates have only been used in recent years and so the full extent of groundwater pollution may not be evident yet.

Since MTBE is relatively slow to biodegrade, any pollution incidents now could impact on the quality of the environment for years to come. Consequently whatever decision is taken on the future use of MTBE must be based on sound scientific information and take an integrated environmental approach that incorporates the principles of sustainability;

- is relatively recalcitrant (in comparison to BTEX compounds) and will remain in the environment for extended periods;
- can often be detected beyond the outer fringes of a BTEX plume.

Certain States in the USA, particularly California, have a major problem with contamination of drinking waters sources with MTBE. We must learn from the American experience.

Further monitoring is needed to get a better understanding of the extent of the MTBE pollution in the UK. The Environment Agency intends to extend investigations into the presence of MTBE in the environment and to

assess its impact on integrated groundwater and surface water systems.

References and further guidance

ConSim Environment Agency 1994. Produced by: Golders Associates UK limited, Landmere Lane, Edwalton, Nottingham NG 4DG

Calvert W.S 1993 Achieving acceptable air quality: some reflections on controlling vehicle emissions: Science V. 261

DETR & Environment Agency, 1999. Handbook of Model Procedures for the Management of Contaminated Land. Contaminated Land Research Report CLR11: Procedure for Risk Assessment. (Draft).

DETR & Environment Agency, 1998. Handbook of Model Procedures for the Management of Contaminated Land. Contaminated Land Research Report CLR11: Procedure for the Evaluation and Selection of Remedial Measures. (Draft).

Environment Agency, 1996.
Groundwater Pollution: Evaluation of
the Extent and Character of
Groundwater Pollution from Point
Sources in England and Wales.

Environment Agency, 1996. R&D
Technical Report P11; Threat to
Potable Groundwater Supplies from
the Fuel Additive MTBE.

Environment Agency, 1998. Policy
and Practice for the Protection
of Groundwater.

Environment Agency, 1999.
Methodology for the Derivation of
Remedial Targets for Soil and
Groundwater to Protect Water
Resources. (Draft).
R&D Technical Report P186

United States Environmental
Protection Agency, 1998. MTBE Fact
Sheet #2: Remediation of MTBE
Contaminated Soil and Groundwater.

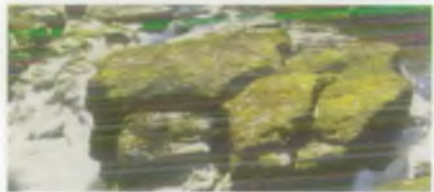
United States Geological Survey.
Environmental behaviour and fate of
Methyl tert-Butyl Ether (MTBE).
Fact Sheet FS-203-96.

Schirmer, M & Barker, J, 1998.
A Study of Long-Term MTBE
Attenuation in the Borden Aquifer,
Ontario, Canada. Groundwater
Monitoring & Remediation,
Spring 1998.

Squillace P.J & Zogorski J.S. A
Preliminary Assessment of the
Occurrence of Possible Sources of
MTBE in Groundwater of the
United States, 1993-94, United S
tates Geological Survey, 1995.

Stump FD, Knapp KT 1990. Seasonal
impact of oxygenated organics with
petroleum on motor vehicle tail pipe
and evaporative emissions. Journal of
Air & Waste Management Association
V40, no 6.

R&D Technical Reports can be
obtained from the R&D section of
Environment Agency Regional Offices.



MANAGEMENT AND CONTACTS:

The Environment Agency delivers a service to its customers, with the emphasis on authority and accountability at the most local level possible. It aims to be cost-effective and efficient and to offer the best service and value for money.

Head Office is responsible for overall policy and relationships with national bodies including Government.

Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol BS32 4UD

Tel: 01454 624 400 Fax: 01454 624 409

Internet World Wide Web www.environment-agency.gov.uk
www.environment-agency.wales.gov.uk

ENVIRONMENT AGENCY REGIONAL OFFICES

ANGLIAN

Kingfisher House
Goldhay Way
Orton Goldhay
Peterborough PE2 5ZR
Tel: 01733 371 811
Fax: 01733 231 840

MIDLANDS

Sapphire East
550 Streetsbrook Road
Solihull B91 1QT
Tel: 0121 711 2324
Fax: 0121 711 5824

NORTH EAST

Rivers House
21 Park Square South
Leeds LS1 2QG
Tel: 0113 244 0191
Fax: 0113 246 1889

NORTH WEST

Richard Fairclough House
Knutsford Road
Warrington WA4 1HG
Tel: 01925 653 999
Fax: 01925 415 961

SOUTHERN

Guildbourne House
Chatsworth Road
Worthing
West Sussex BN11 1LD
Tel: 01903 832 000
Fax: 01903 821 832

SOUTH WEST

Manley House
Kestrel Way
Exeter EX2 7LQ
Tel: 01392 444 000
Fax: 01392 444 238

THAMES

Kings Meadow House
Kings Meadow Road
Reading RG1 8DQ
Tel: 0118 953 5000
Fax: 0118 950 0388

WALES

Rivers House/Plas-yr-Afon
St Mellons Business Park
St Mellons
Cardiff CF3 0LT
Tel: 01222 770 088
Fax: 01222 798 555



For general enquiries please call your local Environment Agency office. If you are unsure who to contact, or which is your local office, please call our general enquiry line.

ENVIRONMENT AGENCY GENERAL ENQUIRY LINE

0645 333 111

The 24-hour emergency hotline number for reporting all environmental incidents relating to air, land and water.

ENVIRONMENT AGENCY EMERGENCY HOTLINE

0800 80 70 60



Printed on Clovercoat, the Environment Agency's own recycled, totally chlorine free paper. Clovercoat is made from 100% post consumer waste - including the Agency's own waste paper - supplied to the mill through a paper recycling merchant. The making of this paper meets all of the Agency's stringent environmental standards.



**ENVIRONMENT
AGENCY**