EFOA

The European Fuel Oxygenates Association

MTBE

Resource Guide

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ABOUT THIS GUIDE

The adverse effects of automobile exhaust emissions on human health and the environment are a growing cause for concern. In recent years, governments around the world have initiated a number of legislative programs designed to bring about improvements in air quality. Some of these programs, for instance in Europe and the United States, have led to changes in the formulation of fuels.

An important element in the formulation of gasoline is the addition of oxygenates, replacing other fuel components, which were required to be substituted by different laws. The most commonly used oxygenate is methyl tertiary butyl ether (MTBE), a chemical compound derived primarily from natural gas. The widespread use of gasoline containing MTBE has resulted in significant air quality improvements.

However, an issue has arisen concerning the presence of MTBE in groundwater supplies, as a component of gasoline that has entered the environment through incorrect storage or handling. The groundwater controversy has generated a vast quantity of reports, scientific studies and media coverage, especially in the USA. Some of this information is based on sound science, while some is ill informed and misleading.

With the aim of helping both specialists and non-specialists alike to find their way through the mass of information on the subject, EFOA, the European Fuel Oxygenates Association, has produced the **MTBE Resource Guide**, today in its third edition, which brings together the latest factual and practical information on MTBE, including its use and handling, and the prevention and remediation of leaks and spills.

The **MTBE Resource Guide** is arranged in three sections:

Section 1, the **MTBE Database**, describes the **properties**, **applications** and **benefits** of MTBE, as well as the **health** and environmental issues associated with its use.

Section 2, the **Good Practice Guide**, explains how to **prevent contamination** by gasoline containing MTBE, and describes

emergency response and **remediation techniques** in the event of an accidental release.

Section 3, the **Website Directory**, lists and describes selected websites containing useful information on MTBE, gasoline and related subjects.

EFOA, the European Fuel Oxygenates Association, represents the major European producers of oxygenated fuels. Its current members are: Ecofuel, Innovene/BP, Neste Oil, Lyondell, Methanex, Oxeno, Polski Koncern Naftowy, SABIC Europe, Shell Chemicals and Total. Together, EFOA members companies represent 80% of the EU MTBE production capacity.

The core mission of EFOA is to act as a reliable, long-term source of information regarding the issues surrounding fuel oxygenates in gasoline. An important element of our work is the publication of the MTBE Resource Guide.

This Guide is intended to be a living document that is subject to regular updating. This third edition has been extensively revised compared to the original December 2000 edition and to the 2nd, October 2002 edition, to include the latest developments in technical and scientific understanding. We welcome comments and contributions from users of the guide. Please send them to:

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American Petroleum Institute

Association of Petroleum and Explosives Administration, United Kingdom

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CONCAWE

Finnish Environmental Institute

Ground-Water Remediation Technologies Analysis Center, United States

The Institute of Petroleum, United Kingdom

Mr. Bruce Hamilton, New Zealand

National Product Control Agency for Welfare and Health, Chemicals Department, Finland

Soils, Inc, United States

The United States Environmental Protection Agency

1. MTBE DATABASE

1.1 WHAT IS MTBE?

1.1.1 Product description

Methyl tertiary butyl ether (MTBE) is a chemical compound obtained from a reaction between methanol and isobutylene. Methanol is primarily derived from natural gas while isobutylene is derived either from natural gas or from by-products of fluid and steam crackers. MTBE is a clear, colourless, low-viscosity, flammable liquid with a distinctive, ether-like odour. Its principal use is as an additive to automotive fuels. When blended into gasoline, MTBE enhances octane ratings and improves fuel combustion, thus reducing harmful exhaust emissions.

1.1.2 Physical and chemical properties

1.1.2.1 Key blending properties

MTBE is an excellent fuel component, having the following key blending properties:

Blending RON	116 - 120
Blending MON	100 - 104
Reid Vapour Pressure at 38°C	8 psi/55 kPa (at 37.8°C/100°F)
Oxygen content	18,2 wt %
Density (15°C)	0,745 g/cm3
Boiling point	55,3° C

1.1.2.2 Detailed chemical properties

A detailed information package on MTBE's chemical properties is available in appendix no. 1.pdf
Source: ECETOC/EFOA Risk Assessment Report for Existing Substances.

1.2 MTBE IN GASOLINE

1.2.1 The nature of gasoline
1.2.1.1 Background
Gasoline is a complex mixture of natural hydrocarbons and other organic chemicals derived from crude oil. Modern gasoline is a heavily processed product, which also contains synthetic components such as various types of oxygenates, primarily ethers and alcohols.

This long-time automotive fuel has changed more than users may realise, to meet evolving engine and combustion technology. Gasoline was considered a worthless petroleum by-product before its commercial development in about 1863. It is difficult to establish who discovered it, but Joshua Merrill may have isolated gasoline in Boston while trying to refine kerosene. Gasoline was first used in air-gas machines to produce fuel that could be piped and burned in gaslights to illuminate mills and factories. It was the fuel used in 1876 in the first four-stroke cycle engine built by Nikolaus Otto in Germany.

From a simple straight run distillate, gasoline has come a long way to its current status as an automotive fuel that meets the complex demands of modern engine technology, environmental requirements, availability and price.

1.2.1.2 Gasoline Q & As
Further information on gasoline is available in the following documents:
http://www.cs.uu.nl/wais/html/na-dir/autos/gasoline-faq/.html
Source: Bruce Hamilton, New Zealand.

1.2.2 What are fuel oxygenates?
1.2.2.1 Uses of oxygenates
Historically, oxygenates were developed in the 1970s as octane enhancers to replace toxic additives like lead which were – and in some areas still are - being phased out of gasoline.

Replacement of lead was also necessary for modern engines with three-way catalytic converters. Many brands of gasoline sold today in Europe, and around the world, have some level of oxygenates to enhance octane rating. However, oxygenates are being used in gasoline for far more than just the replacement of toxic compounds (e.g. lead). Responding to requirements for cleaner, more breathable

air, oxygenated fuels are used to reduce ozone-forming smog, hazardous carbon monoxide pollution, and other toxic air pollutants.
Oxygenates are oxygen-rich compounds which, when they are added to motor vehicle fuels, make them burn more cleanly, thereby significantly reducing toxic tailpipe pollution. Although great strides have been made in reducing automotive emissions, air quality continues to be a serious concern in many areas, especially in large cities. Among industrialised nations, pollution from motor vehicles is responsible for nearly half of the human-caused nitrous oxides, two-thirds of the carbon monoxide (CO) and about half of the hydrocarbon emissions. Cleaner burning oxygenated fuels are one of the leading tools in fighting automotive air pollution.
Oxygenates are produced from a variety of feedstocks. Methanol, derived primarily from natural gas, is one feedstock used in the production of the most commonly used oxygenate, methyl tertiary butyl ether (MTBE).
Another oxygenate, ethanol, is derived primarily by fermenting corn and other agricultural products and is used directly as an additive or as a feedstock for the production of ethyl tertiary butyl ether (ETBE).

Isobutylene, which is the other feedstock used in both MTBE and ETBE production, is also derived from natural gas or as a by-product of petroleum refining.

1.2.2.2 Characteristics of oxygenates

Oxygenates contain oxygen atoms in addition to carbon and hydrogen atoms, whereas gasoline itself lacks oxygen atoms. The presence of oxygenates in gasoline promotes cleaner fuel combustion within the engine, boosts fuel octane values, and reduces vehicle air emissions. Two types of oxygenates are commonly added to gasoline: **alcohols** and **ethers**.

In **alcohols**, each oxygen atom is linked to a carbon atom and a hydrogen atom, forming a carbon-oxygen-hydrogen sequence. Ethanol is by far the most commonly used alcohol oxygenate. Other alcohols that are used (or that could potentially be used) as fuel oxygenates include methanol and tertiary-butyl alcohol (TBA). TBA is also of interest as a product of MTBE degradation and a potential impurity from MTBE manufacture.

In **ethers**, each oxygen atom is linked to two carbon atoms, forming a carbon-oxygen-carbon sequence. MTBE is by far the most commonly used ether oxygenate, due to its high octane properties, its fungibility, cost effectiveness and supply flexibility.

However, there is an increasing interest in ethyl tertiary-butyl ether (ETBE) due to its potential as a biofuel component.
Other ethers that are used (or that could potentially be used) as fuel oxygenates include tertiary-amyl methyl ether (TAME), tertiary-amyl ethyl ether (TAEE) and diisopropyl ether (DIPE).

1.2.3 Oxygenates in gasoline

1.2.3.1 Composition

In Europe, the typical content of MTBE in gasoline is 2-4% by volume, although higher concentrations are used in some areas, for example Finland, and for some fuel specifications. The oxygen content of current EU gasolines can be found in the "EU Fuel Quality Monitoring - 2003 Summary Report" (web link http://europa.eu.int/comm/environment/air/pdf/fqm_Summary_2003.pdf). In the majority of cases this will represent the volume of ethers used.

1.2.4 Benefits of MTBE in gasoline

1.2.4.1 Technical benefits

MTBE is the most widely used fuel oxygenate, due to its combination of technical advantages and supply availability. MTBE delivers high-octane value at relatively low cost. In addition, MTBE offers low water solubility (compared to e.g. alcohols), low reactivity and relatively low volatility. These characteristics allow refiners to overcome handling problems in the fuel distribution system posed by alcohol oxygenates. Another important reason for the widespread use of MTBE is feedstock flexibility. MTBE can either be made inside the refinery, using petroleum-derived raw materials, or it can be produced externally, using natural gas feedstocks, thereby ensuring ready availability and reducing dependence on crude oil for the production of automotive fuels.

Furthermore some quite recent studies have shown that the octane appetite of modern cars seems to differ from that of previous populations. It appears that the conventional measures of anti-knock quality (RON and MON) are no longer appropriate for modern engines. The modern Japanese and European cars equipped with knock sensors prefer fuels of high sensitivity and high RON. Adding MTBE in the gasoline is a way to improve these properties in the fuel.

1.2.4.2 Air quality benefits

MTBE provides considerable air quality benefits, which can be divided into two main categories. There are the direct effects, largely due to more complete fuel combustion, and the indirect effects, arising from the dilution of other, less desirable, gasoline pool components.

Direct effects include the reduction of specific pollutants limited by law, such as carbon monoxide (CO) and unburned hydrocarbons (HCs), as well as other serious pollutants such as particulate matter (PM) and ground-level ozone (O_3).

Indirect effects include the reduction of sulphur, olefins, aromatics and benzene levels, regardless of whether the fuel is used in current or older technology vehicles.

The extent of MTBE's air quality benefits depends on various parameters, such as the percentage of blended MTBE, the presence of catalyst devices, the type and age of engine and the driving cycle. Nevertheless, there is general agreement in the industrial and scientific communities on broad values.

Carbon monoxide: CO emission is reduced on average by at least the same percentage as MTBE content in gasoline.
Unburned hydrocarbons: For each 1 or 2% of MTBE, there is a 1% reduction in total HC emissions.
Particulate matter: It is estimated that each 1% of MTBE results in a 2 to 3% PM emission reduction.
Ozone: MTBE generates about half the ozone compared with iso/alkylates and one-tenth that of aromatics.
Benzene: It is estimated that, for each 1% of MTBE, there is an equivalent percentage reduction in benzene emissions, both evaporative and exhaust.
Olefins: MTBE displays low vapour pressure and low volatility compared to olefins. Converting olefins to MTBE in the refinery removes some of the most reactive and volatile components from the gasoline pool.
Lead: MTBE is an effective substitute for lead, a toxic compound that has been phased out in most parts of the world.

As an example of the potential air quality benefits of MTBE, the following significant reductions of pollutants have been achieved through the use of reformulated gasoline containing 10-15% MTBE, compared to conventional gasoline:
20-25 % less carbon monoxide

10-15% less unburned hydrocarbons
About 30% less particulate matter
20-30% less benzene
5% less nitrogen oxides
15% less evaporative emissions
Reduction of ground-level ozone

In Finland, the widespread use of oxygenated fuel containing 9-13% MTBE has reduced CO emissions by 10-20% and hydrocarbons by 5-10%.

1.2.5 Extent of oxygenates use

1.2.5.1 World market

The ether oxygenates world market today can be reasonably approximated by using MTBE figures, as the volume of TAME and ETBE combined is far less than MTBE.

The MTBE market grew strongly in the 1990's. Since then the market has been broadly flat with growth in Asia compensating for reduced demand in the US. For instance, the 1999 world consumption of 20,700 kt/a was about double that of 1992. The driving force for the growth was the US Clean Air Act.

In 2003 world demand was 19,000 kt/a..

1.2.5.2 European market

The annual production volume of MTBE in the year 2003 in the EU was 2 612 000 tonnes. About 609 000 tonnes was imported and about 539 000 tonnes was exported outside the EU in the year 2003 (CMAI). The annual consumption of MTBE within the EU was hence 2 577 000 tonnes in the year 2003 (see table below)
For the future no substantial increase in MTBE usage is expected.

Production, import, export and consumption in EU in 2003 (tonnes/year) (1)

Production	Import into EU	Export outside EU	Consumption
2 612 000	609 000	539 000	2 577 000

(1) (CMAI)

More information on the use of MTBE in Europe, also obtained from the EU MTBE Risk Assessment Report, is available in appendix no. 3.pdf**.**

1.3. MTBE AND HUMAN HEALTH

1.3.1 Research on MTBE

1.3.1.1 Extensive studies

MTBE has been extensively studied and the consensus of opinion is that, when properly handled, MTBE blended gasoline is a safe product.

- The number and extent of scientific tests places MTBE within the top 2 percent of all tested substances.
- The first tests screening health risks were conducted in 1969 and 1972.
- As part of the US Environmental Protection Agency's approval for blending MTBE in unleaded gasoline in 1979, additional tests were conducted. They were followed by voluntary industry groups, who sponsored more extensive health studies on metabolism, reproductive function and subchronic inhalation exposure.
- In 1986, the industry established an extensive research programme under the US EPA's oversight and guidelines. This programme was completed in 1992. All the results and reports were submitted to the US EPA.
- The industry has continued voluntary testing to supplement available environmental and toxicological information on MTBE.

1.3.1.2 Health risk reviews

The weight of scientific evidence shows that MTBE has a low order of acute and sub-acute toxicity. It is not mutagenic, neurotoxic, nor is it a reproductive toxicant.

The following is a summary of the health hazard and risk evaluations and reviews published by well-recognised research entities, scientific and regulatory bodies.

1) CONCAWE appendix no. 2.pdf is the European Oil Companies' organisation (CONCAWE) publication no: 97/54, entitled "The health hazards and exposures associated with gasoline containing MTBE". It contains a section (Chapter 5) on "Comparison of the Health Hazards of Gasoline and Gasoline/MTBE Blends" which compares health aspects of traditional and oxygenated gasolines. No significant difference could be found.

2) WHO (World Health Organisation) The WHO International Programme on Chemical Safety (IPCS) says that "based on collective evidence, it appears unlikely that MTBE alone induces adverse acute health effects in the general population under common exposure conditions." More information can be found on the IPCS website in the Environmental Health Criteria Document No. 206. http://www.inchem.org/documents/ehc/ehc/ehc206.htm

3) ECETOC Furthermore, a scientific task force in Europe, the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) in Brussels examined the health risks associated with the use of MTBE and concluded that the risk characterisation for MTBE does not indicate concern for human health with regard to current occupations and consumer exposures.
The ECETOC Risk Assessment content List and Chapter 4.1.3, Risk Characterisation (on human health) can be found in appendix no. 3.pdf The full report, ECETOC Special report No.17 was published in December 2003.

4) EU-Risk Assessment MTBE has recently undergone a full health and environmental risk assessment according to EU-guidelines. The risk assessment was prepared on behalf of the EU-Commission by the Finnish Competent Authorities under review of Competent Authorities from European member States. Besides environmental effects all known health effects were evaluated, together with the potential for exposure, in order to assess the overall health risk that MTBE may present.

The EU Risk Assessment on MTBE was finalised in November 2001 and the conclusions were published in the Official Journal of the European Communities on 4th December 2001, see
http://europa.eu.int/eur-lex/pri/en/oj/dat/2001/l_319/l_31920011204en00300044.pdf.
The full Risk Assessment Report was published on September 20th, 2002 and is available on the ECB´s web page http://ecb.jrc.it/existing-chemicals/, click on ESIS, search for CAS# 1634-04-4, scroll down and view Final RAR, published in “European Risk Assessment Report Volume 19”.

5) RIVM In 2004 the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM) ordered the national Research Institute RIVM to derive solid risk limits for soil, sediment, groundwater, surface water, drinking water and for drinking water preparation. When deriving this risk limits co-ordination with the Risk Assessment Report from the EU RA (2002) took place. The report (76 p. in Dutch, with a short English abstract) can be downloaded in PDF format (320 kB) from Www.rivm.nl/bibliotheek/rapporten/711701039.html

A literature summary of the human health effects of MTBE can be found at:
http://sd.water.usgs.gov/nawqa/vocns/mtbe_hh_summary.html
While a bit out of date and superseded by various other concluding studies (e.g. the European Risk Assessment, see par. 1.3.3), this literature review by the *Oregon Health & Science University* is still useful.

1.3.2 Research conclusions

1.3.2.1 Carcinogenicity

The possible carcinogenicity of MTBE was intensively discussed in the past. However several independent bodies in Europe and the United States concluded recently that MTBE is **not** a **human** carcinogen.

1) In 1998 the **International Association of Research on Cancer (IARC)** - a World Health Organisation agency composed of leading cancer researchers, scientists and health professionals - classified MTBE in Category 3 ("not classifiable as to its carcinogenicity to humans"). This means that despite the large number and high quality of research studies, there is no evidence to establish a possible cancer risk to man from exposure to MTBE. **For reference, Category 3 also includes several large-volume everyday foodstuffs**. The IARC scale runs from 1 to 4. Substances in Group 1 are known to cause cancer in humans, those in Group 2A are probably carcinogenic, in Group 2B possibly carcinogenic and those in Group 4 are probably not carcinogenic. In this latter group, only one chemical (caprolactam) is classified. Gasoline is classified in Group 2B -- possible human carcinogen -- while benzene and alcoholic beverages are both classified in Group 1 -- known human carcinogens.

IARC data A Summary of Data Reported and Evaluation of IARC's report is available via the following Internet link: http://www-cie.iarc.fr/htdocs/monographs/vol73/73-13.html For definition of Groups, see Preamble Evaluation on the same page.

2) In the U.S., the **National Toxicology Program Executive Committee** (NTP) (a multi-agency review panel comprising: Agency

for Toxic Substances & Disease Registry, U.S. Consumer Product Safety Commission, U.S. EPA, Food & Drug Administration, National Center for Environmental Health, National Cancer Institute, National Institute of Environmental Health Sciences, National Institutes of Health, National Institute for Occupational Safety & Health, and the Occupational Safety & Health Administration) concluded that MTBE did **not** deserve to be listed as a "known" or "reasonably anticipated" human carcinogen. MTBE is not listed in the current NTP carcinogenicity report about chemicals which are known to cause human cancer. (See following website http://ntp-server.niehs.nih.gov/index.cfm?objectid=72016262-BDB7-CEBA-FA60E922B18C2540, 10th report on carcinogens).

3) **The State of California** also concluded that MTBE is not a human carcinogen and does not cause birth defects or infertility. MTBE is not on the current list of chemicals meeting California's Proposition 65 criteria for listing as "known to the state to cause cancer or reproductive toxicity". Further information can be found on: www.oehha.ca.gov/prop65.html (go to "current list of chemicals").

4) Furthermore, a scientific task force in Europe, examining the health risks associated with the use of MTBE concluded that, "MTBE is not carcinogenic according to the criteria set forth in the European Union's Directive on Dangerous Substances." The European Centre for Eco-toxicology and Toxicology of Chemicals (ECETOC) also concluded, "the risk characterisation for MTBE does not indicate concern for human health with regard to current occupations and consumer exposures."
The ECETOC Risk Assessment's (see chapter 1.3.1.2, item 3)

5) The rapporteur for the EU MTBE Risk Assessment, i.e. the National Product Control Agency for Welfare and Health, Chemicals Department, Finland and the Finnish Environmental Institute has announced in a press release (December 8th, 2000) that based on the assessment work performed in various scientific working groups, it will not suggest a carcinogenicity classification for MTBE. The EU-Commission has recently published official classification and labelling for MTBE in the Directive 2004/73/EEC from April 2004. MTBE is classified as an irritant and highly flammable substance only. More information under http://europa.eu.int/eur-lex/pri/en/oj/dat/2004/l_152/l_15220040430en00010311.pdf see Index No. 603-181-00-X

1.3.3 EU Risk Assessment

1.3.3.1 Introduction

MTBE has undergone an EU full health and environmental risk assessment. In 1997, MTBE was included in the third Priority List of substances selected for risk assessment under Council Regulation (EEC) 793/93 on the evaluation and control of the risk of existing substances. Finland was chosen as the Member State "Rapporteur" responsible for progressing the risk assessment on MTBE on behalf of the European Commission.

In the assessment process, all known health and environmental effects are evaluated, together with the potential for exposure, in order to assess the overall risk that a substance may present. The process includes a review of the appropriate classification and labelling of the substance.

The EU Risk Assessment on MTBE was finalised in November 2001 and the conclusions including risk reduction strategy were published in the Official Journal of the European Communities on 4th December 2001. The Risk Assessment Report was published on September 20th, 2002 as a hard copy and at ECB´s web page http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/mtbereport313.pdf

1.3.3.2. Summary of findings

After considering all the available information, the EU Rapporteur concluded that:

Exposure to MTBE was not expected to have any harmful impact on human health, the atmosphere or the environment. However risk reduction measures are necessary to protect ground water quality by introducing European minimum standards for technical equipment for MTBE use, especially for storing equipment. In many EU member states according regulations are already in force.

In the risk assessment report in 2002 it was mentioned that additional information is needed to characterise possible risk to the aquatic ecosystem regarding to the emission to surface water. Tests regarding tainting of fish by MTBE and avoidance of fish against water with MTBE impurities have since been conducted and an addendum to the risk assessment report was published in 2004. It concluded that neither fish tainting nor fish avoidance behaviour is occurring at a concentration of 15 µg/l which is far above typical MTBE concentration in surface water. The addendum is also available on the same website as the full report, see above.

1.3.4 Other health effects

Acute health effects from exposure to MTBE have also been considered and addressed in a number of studies.

In 1995, the World Health Organisation concluded that it is "unlikely that MTBE alone induces adverse acute health effects in the general population under common exposure conditions."

The strong taste and odour of MTBE mean that, even at very low concentrations, its presence makes drinking water unpalatable. The US EPA has recommended an MTBE concentration in drinking water of 20 to 40 ppb or below. These levels preserve the palatability of drinking water and are 20,000 to 100,000 times lower than the lowest concentration that has caused observable health effects in animals.

Note, the taste and odour of MTBE are not a health problem but an issue of water quality.

1.4. MTBE AND THE ENVIRONMENT

1.4.1 Air

1.4.1.1 Behaviour of MTBE in air

MTBE is volatile and may be emitted to the atmosphere through evaporation during the distribution and use of gasoline containing MTBE.

When improperly handled this may lead temporarily and locally to very low concentrations in the air. Due to the solubility of MTBE in water, some of this atmospheric MTBE will tend to be washed out by rain and enter surface water and shallow groundwaters. As a result, it is sometimes possible to detect MTBE in shallow groundwaters at very low levels (below 1 µg/l).

Liquid MTBE and MTBE vapours are highly flammable, so all the appropriate safety precautions should be strictly observed during handling. An MTBE spill releases vapours below normal ambient temperatures. These vapours may travel long distances along the ground and are explosive in air at concentrations of between 1.3 and 8% by volume.

Any MTBE in the atmosphere is destroyed within days by photo-oxidation reactions.

1.4.1.2 Impact of MTBE in air

The highest exposure to air-borne MTBE experienced by the public is during vehicle refuelling. However, exposures are generally less than 35 mg/m^3 and are only at such levels for very short periods. Very small quantities may also be discharged unburned from vehicle exhausts: levels of approximately 0.05g/km have been reported.

Higher exposures for longer periods may be experienced by workers during the production, storage and distribution of MTBE itself, and also of gasoline containing MTBE. Typical occupational exposures are 4 to 45 mg/m^3 during MTBE handling, and 0.3 to 20 mg/m^3 during gasoline handling. These can be compared with the occupational exposure limit for MTBE of 92 mg/m^3 in the UK (8 hour TWA). In most other European countries the limit is higher: up to 180 mg/m3.

Although MTBE's distinctive smell makes the vapours easy to detect, there is no indication that they persist long enough in the air at a level which would, according to latest scientific information, cause harm to the environment or to human health.

1.4.1.3 Background levels of MTBE in air / water

(Germany, Switzerland & The Netherlands)

Most amounts of MTBE released into the environment will be distributed in the atmosphere. Due to photochemical degradation the half life time in the atmosphere is 3-6 days. However MTBE background concentrations can be measured there. The EU-Risk Assessment report mentioned background levels in the US between 0.7 and 2.7 µg/m3. The Swiss Department for Environment, Transport, Energy and Communication (BUWAL) have reported levels between 0.04 and 2.5 µg/m3 for Germany and Switzerland. (Report "Abschätzung der Altlastenrelevanz von Methyl-tert-butylether (MTBE)", including an English summary, to be downloaded from :http://www.umwelt-schweiz.ch/buwal/de/fachgebiete/fg_altlasten/service/mtbe/index.html

In the same report BUWAL stated the level in lakes and rivers for Germany and Switzerland was 0.05 µg/l. See appendix no. 4.pdf. There seems to be already an equilibrium between atmosphere and groundwater concentrations in many areas. However near filling stations the levels may be up to 50 times higher than the general background level.
A survey about the levels in drinking water wells in some parts of Germany is given by Klinger et al. In 91% of the measurements in rural area the MTBE concentration was lower than the detection limit of 0.05µg/l and also in 51% of urban areas. The medium concentration in urban area groundwater was calculated to be 0.17µg/l. The German Federal Environment Agency (UBA) has published in 2000 a report about " Possible Impacts on the Environment Caused by the Use of MTBE as a Fuel Additive in Germany and Western Europe", which mentioned only a very few cases of groundwater concentrations up to some hundred µg/l. See appendix no. 5.pdf. They have evaluated the situation with the conclusion that the contamination of aquifers in Germany is so small that no harmful effects are anticipated. The figures mentioned show that the concentrations in surface water and groundwater are lower than the reported values in the US.

Lake Zürich (Switzerland)

From 2002 – 2004 Lake Zürich in Switzerland was monitored for the presence of fuel components. This study (“Occurrence and Fate of

Methyl tert-Butyl ether (MTBE) and Aromatic Hydrocarbons in a Holomictic Lake used as a drinking water supply (Lake Zurich)") by Schmidt, T.C. et al., was published in Water Research 38, 1520-1529.

From this study table 1:

Compound	Max./mean concentration in Epilimnion (boating season) [ug/l]	Max./mean concentration in Epilimnion (off-season) [ug/l]	Max./mean concentration in Hypolimnion [ug/l]
MTBE	1.4 / 0.20	0.10 / 0.058	0.048 / 0.037
Benzene	0.16 / 0.046	0.10 / <0.02	<0.02
Toluene	0.40 / <0.1	<0.1 / <0.1	<0.1
o-Xylene	0.18 / 0.054	0.035 / <0.03	<0.03
m-/p-Xylene	0.46 / 0.11	0.067 / <0.03	<0.03

The study concludes that MTBE and BTEX are nearly completely volatilised before vertical lake mixing occurred in winter. "Due to the density stratification of holomictic lakes there is hardly any water exchange in summer and thus transport of dissolved contaminants between epi- and hypolimnion. If contaminants are almost completely eliminated during the stratification period, their concentration in the hypolimnion will remain very low even over longer periods. Drinking water is typically extracted well below the thermocline, therefore no risk is expected for the drinking water supply in the lakes."
The study concludes: 'In order to further reduce emissions of unburned fuel into surface water, limitations in the use of high-emitting 2-stroke engine types in motorboats should be considered."

The Netherlands Case

In 2001 the National Institute for Public Health and the Environment (RIVM) in the Netherlands conducted a drinking water measurement programme in co-operation with the Netherlands Waterworks Association (VEWIN) for MTBE in drinking water and the corresponding sources.
From the abstract of this report:
"*This study, consisting of two sampling periods, shows a generally low concentration of MTBE in drinking water at the selected drinking water plants. The selection of sampling locations was based on the vulnerability of the water catchment area. Measurements in the June/July period showed a concentration of <0.01 µg/l in 22 samples of raw water; the average concentration was 0.07 µg/l and the highest 0.42 µg/l. The average concentration in drinking water in*

September/October was 0.09 ug/l and the maximum 2.9 µg/l. This maximum concentration was unusual, considering that the second highest value was 0.14 µg/l MTBE. The raw water (both groundwater and surface water) samples registered a concentration of <0.5 µg/l; the highest concentration in surface water was 3.2 µg/l. However, at one location a relatively high concentration (11.9 µg/l) was found in an individual groundwater well. This contamination could be attributed to a local source.
The main conclusion is that MTBE occurs in drinking water, although the concentrations are generally very low (<0.14 µg/l), with a maximum value of 2.9 µg/l. No effects on health are expected. It is, however, recommended to screen for MTBE in groundwater at locations with a history or experience of soil contamination. Taking precautions for future spills at petrol stations remains priority number one."

The RIVM report is available at :
http://www.rivm.nl/bibliotheek/rapporten/703719001.html

In 2004 the Dutch Ministry of the Environment VROM prepared a project in which a number of sites will be examined for occurrence of MTBE in groundwater close to petrol stations. This project, which is planned to take place in 2005, consists of three phases:

1) Approx. 100 – 150 sites will be prepared, distributed evenly between urban and rural areas, different soil types and inside / outside water extraction areas.

2) Research of available dossiers of these sites, to optimise a boring and sampling strategy.

3) Fieldwork and reporting.

The project is expected to be finalised by mid-2005.

USA / California
MTBE was first found in drinking water sources in the early and mid 1990s in the counties of San Francisco and Los Angeles, respectively. In February 1997 the Department of Health Services (DHS) adopted a regulation that included MTBE as an unregulated chemical for which monitoring was required by certain public water systems. Subsequently, required monitoring has been associated with compliance with MTBE's Maximum Contaminant Levels (MCLs).

As of March 1, 2005, the DHS database includes MTBE analytical results reported for ~13,200 sources, where "sources" may include both raw and treated drinking water wells and surface water sources, distribution systems, blending reservoirs, and other sampled entities. Nearly all of the results are non-detects.
The DHS database contains 116 sources that have two or more reported MTBE detections at any concentration. These occurred in 31 counties. Counties with the greatest number of sources reporting MTBE detections are Los Angeles (28 sources), El Dorado (12), San Diego (11), Kern (7), Monterey (6), Lake (5), Alameda (4), San Francisco (4), Orange (3), Merced (3), and San Mateo (3). Ten counties had two sources with MTBE detections, and ten had single sources.
Of the 116 sources, 87 reported a peak detection > 3-µg/L (the DLR), distributed as follows:

- 31 sources in 13 counties reported a peak detection > 13 µg/L. These were in the counties of Los Angeles (6 sources), Kern (5), San Diego (5), Monterey (3), Riverside (2), Sacramento (2), and San Francisco (2). Six counties each had one source.
  13 ugl/l is the primary maximum contaminant level for MTBE which is the enforceable regulatory standard under the State's Safe Drinking Water Act.
- 28 sources in 15 counties reported a peak detection > 5 µg/L but ≤ 13 µg/L. These were in the counties of Los Angeles (11) and San Diego (3), and Monterey (2). Twelve counties each had one source.>
  5 ugl/l is the secondary maximum contaminant level for MTBE designed to address taste and odour concerns.
- 28 sources in 19 counties reported a peak detection ≥ 3 µg/L but ≤ 5 µg/L. These were in the counties of Los Angeles (5), El Dorado (4), Orange (2), and San Diego (2). Fifteen counties each had one source.
  3 ug/l is the detection limit for reporting purposes. This is the level at which the DHS is confident about the quantification of the level of MTBE.

According to the source the numbers presented above should be considered draft, since they may change with subsequent updates.
Source: www.dhs.ca.gov/ps/ddwem/chemicals/MTBE/mtbeindex.htm

A 2002 study by US-based law firm White Environmental Associates using data from the California's SWRCB (State Water Resources Control Board) and Department of Health Services (DHS) revealed that out of 16,000 wells in California 4,227 are ADI (abandoned, destroyed or inactive), of which 2,028 were ADI due to exceedance of the MCL (Maximum Contaminant Limits) for

-	Natural Constituents	1,162 wells
-	Solvents	329 wells
-	Nitrates	313 wells
-	Pesticides	196 wells
-	Benzene	14 wells
-	MTBE	14 wells +
Total		2,028 wells

Source: Sheet 39 in

http://www.calgasoline.com/MEA_000E.PDF

1.4.2 Soil and groundwater

1.4.2.1 Behaviour of MTBE in soil and groundwater

In practice, when a gasoline release occurs on the ground or subsurface, then, depending of the release rate and magnitude and site characteristics, it stays in the form of a Non-Aqueous Phase Liquid (NAPL) for a shorter or longer time.
If the release was subsurface, it immediately begins to migrate sideways and downwards into the soil pores and also begins to dissolve into soil water gradually forming a subsurface plume, which may contain a NAPL phase and a contaminated water phase. It also begins to volatilise into soil gas.

In the case where the release was on the ground, then the events are slower as the released gasoline has to penetrate through the soil surface and maybe also a tarmac or another type of pavement. In this case, the volatilisation into air may considerably reduce the volume that finally enters the subsurface. A few litres' release may disappear completely into air.

If the release was large, then a situation similar to the subsurface release case will develop.

The behaviour of any fuel component in soil, soil pores and ground water depends on a few physicochemical characteristics of the component, i.e.:

- **Water solubility.** MTBE's and other ether oxygenates' solubility in water is very much higher than that of the hydrocarbon components of gasoline, i.e the potential to dissolve into ground water is higher than that of the hydrocarbon components, such as Benzene, Toluene, Ethylbenzene and Xylene.

- **Solids - water partition coefficient (Koc).** Koc is a measure of a dissolved component's tendency to adsorb into soil particles from water. High adsorption slows the travelling of the component in the ground water flow.
- **Vapour pressure**, is a measure of the components' ability to vaporise from its liquid form into the gas phase.
- **Henry's law constant (KH)** , is a measure of a component's characteristic to partition between the dissolved phase and gas phase. High KH values facilitate a component's volatilisation from ground water into soil gas. Consequently, MTBE has a relatively low tendency to volatilise out of water.
- **Retardation factor** describes a component's relative retardation in soil and ground water due to its physicochemical properties and various soil and ground water related characteristics. In favourable conditions, retardation slows the migration of the contamination in the subsurface soil and ground water.
- **Biodegradability** describes the capability of the soil and ground water microbes to break down a component. In general, gasoline hydrocarbons and alcohols are relatively easily biodegraded, whereas ether oxygenates' biodegradation rates in natural conditions tend to be lower.

The following table is an excerpt from an API publication n° API 4699, "Strategies for Characterising Subsurface releases of Gasoline Containing MTBE.

Table A-1. Comparison of Physical Properties of BTEX and Oxygenates

Chemical	Pure Phase Solubility	log K_{oc}	Vapor Pressure	Henry's Law Constant	Retardation Factor	
	mg/L	log l/kg	mm Hg	Dimensionless	Soil Condition A[1]	Soil Condition B[2]
Benzene	1,780	1.5 - 2.2	76 - 95.2	0.22	1.59	3.38
Toluene	535	1.6 - 2.3	28.4	0.24	1.75	3.99
Ethylbenzene	161	2.0 - 3.0	9.5	0.35	3.66	11.6
m-Xylene	146	2.0 - 3.2	8.3	0.31	4.34	14.4
Ethanol	Miscible	0.20 - 1.21	49 - 56.5	0.00021 - 0.00026	1.04	1.17
Methanol	Miscible	0.44 - 0.92	121.6	0.00011	1.04	1.16
TBA	Miscible	1.57	40 - 42	0.00048 - 0.00059	1.31	2.25
MTBE	43,000 - 54,300	1.0 - 1.1	245 - 256	0.023 - 0.12	1.09	1.38
ETBE	26,000	1.0 - 2.2	152	0.11	1.33	2.34
TAME	20,000	1.3 - 2.2	68.3	0.052	1.47	2.89
DIPE	2,039 - 9,000	1.46 - 1.82	149 - 151	0.195 - 0.41	1.37	2.47

Notes:
See text for abbreviations
Data from Zogorski *et al.* (1997). Values at 20 or 25 °C
1 = Soil Condition A: f_{oc}=0.001 mg/mg, bulk density=1.75 kg/L, porosity=0.25
2 = Soil Condition B: f_{oc}=0.004 mg/mg, bulk density=1.75 kg/L, porosity=0.25

While the current understanding of the transport and fate of MTBE in groundwater is generally based on laboratory and field studies undertaken in North America, the University of Sheffield was the first to report on the transport and fate of MTBE in a European dual-porosity aquifer:

http://www.solinst.com/Res/cmt/UKChalk/UKChalk.html. The case described is an urban retail petroleum filling station in southern England overlying the Chalk aquifer, the most important aquifer system in the UK.

1.4.2.2 Impact of MTBE in soil and groundwater

MTBE's subsurface behaviour has been extensively studied and documentation on empirical experiences and theoretical approaches is extensive. Therefore, it is recommended to open the API Publication No: 4699, February 2000 via the following Internet link: http://api-ep.api.org/filelibrary/4699c.pdf.

This very comprehensive document, "Strategies for Characterising Subsurface Releases of Gasoline Containing MTBE" is free for downloading. It covers all essential areas of the topic and is a respected reference. *Note: This document is 1.7 MB and contains 120 pages - it is advisable to study the Table of Contents first in* appendix no. 6.pdf

The API website is a major source of useful MTBE-related information, documents and reports covering the most important issues related to soil and groundwater contamination by MTBE and gasoline blended with MTBE and other ether oxygenates, and measures needed to mitigate and remediate the situation.

Another useful source of information is the MTBE Remediation Handbook. Published in the United States (2003), this book documents the technology to clean up MTBE in a rational and economic manner. Published in the United States but useful around the world, and based on extensive experience in managing and cleaning up spills of gasoline, this new book documents the technology to clean up MTBE in a rational and economic manner.

The MTBE Remediation Handbook will ensure a comprehensive understanding of the cleanup approach, including a careful and adequate site characterisation, the selection of an appropriate technology or sequence of technologies, and sound engineering design. You will find EFOA's contribution in Section III - Remediation Case Studies, "Remediation Experiences in Finland".
The book is edited by Ellen E. Moyer and Paul T. Kostecki, and published by Amherst Scientific Publishers.

Both the Table of Contents and the Book Order Form are available at http://www.aehs.com/publications/catalog/remediation.htm

Other books, reports, articles, summaries and conference proceedings are available in abundance, largely also via the Internet. See also the Website Directory section included in this guide.

2. GOOD PRACTICE GUIDE

2.1 Preventing contamination

With very few exceptions, all of the advice given here for preventing contamination of soil and ground water by MTBE, are the same as have been applicable for traditional gasoline for tens of years.

2.1.1 Importance of prevention

Gasoline - with or without MTBE - should not be allowed to contaminate soil or groundwater. In most countries, strict regulations exist to prevent gasoline leaks and spills, unfortunately these are not always properly enforced. Oil companies, their distributors and retail site operators have comprehensive procedures in place for the safe storage and handling of gasoline.

No component of gasoline, including MTBE, is capable of seeping through properly designed, constructed, tested and maintained systems. A responsible attitude and good operating practices will prevent leaks and spills, and the resulting contamination of soil and groundwater. Nevertheless, human error or equipment failure may lead to an accidental release. In such cases, immediate steps must be taken to deal with the situation. Delays or attempts to cover up the incident can lead to more serious pollution, greatly increased clean-up costs and significant legal penalties.

2.1.2 Storage and handling of gasoline

2.1.2.1 Key checkpoints

Environmental protection at retail sites should focus on a simple common sense principle: **prevent leaks and spills - but if an incident does happen, clean up the mess immediately.**

To put the principle effectively into practice, procedures, systems and technical installations need to be focused on:

- leak/spill prevention, detection and containment
- emergency response
- site investigations and risk assessments

- remediation as needed

Tools in this work are:
- proper design and installation of equipment, facilities and structures
- regular inspection of facilities and equipment
- adequate maintenance and control
- site personnel guidance, training and supervision

Some key technical/operational considerations are:
- pavement and its material
- oil separators, yard drainage, sewer systems
- overfill prevention systems
- spill catch basins for filling connections
- drip pans under pumps
- liners and soil venting tubing under forecourt, tank pits and filling areas
- piezometers and monitoring programmes
- electronic leak detection devices (electronic level control, VOC-detectors in the tank pit and under the filling areas)
- proper operating procedures, including maintenance
- operating personnel guidance, training and supervision

These technologies need not be generally applied, but must be considered case by case, depending on site hydrogeology and other relevant aspects.

As in any other case, the effectiveness of technological and operational procedures will depend on the level of actual compliance. Therefore, some sort of inspection or (internal) auditing procedure will increase the effect of such procedures.

The positive effects of improving both the level of enforcement (leading to increased compliance) and the level of technical integrity (leading to a reduction in leaks) are clearly described in a presentation and accompanying paper "MTBE / UST's: A True Perspective". This paper was presented at an environmental law conference in California (November 2002). The presentation can be downloaded from http://www.calgasoline.com/MEA_000E.PDF and the accompanying text from http://www.calgasoline.com/MEA_000F.PDF

One outcome of the EU Risk Assessment on MTBE refers to tank bottom waters: the water phase incidentally accumulated at the bottom of MTBE storage tanks. Proper treatment of this water phase is an essential component in reducing water pollution.

A different issue in the USA concerns MTBE found in water in small concentrations, especially in certain recreational lakes, some of which also serve as water reservoirs. In those cases, the problem is not caused by leaking storage tanks, but by recreational boats' 2-stroke gasoline-driven outboard motors, which blow exhaust gases directly into the water. Combustion in such motors is less than complete, therefore a relatively large proportion of unburned fuel - including MTBE - ends up in the water

2.1.2.2 Detailed best practice guidelines

In most countries, oil industry associations, together with the relevant authorities, have produced comprehensive instructions and recommendations on proper technical installations and operational procedures.

The Institute of Petroleum documents listed below were prepared by the industry, including representatives from the multinational oil companies and the authorities, and were produced for the UK. However, the technical and operating principles and practices described are generally applicable.

A brief summary and Chapter 2 (Risk Assessment) of: "Guidance for the Design, Construction, Modification and Maintenance of Petrol Filling Stations", November 1999, a document published by The Association for Petroleum and Explosives Administration (APEA) and The Institute of Petroleum (IP), United Kingdom can be found in appendix no. 7.pdf

The following (appendix no. 8.pdf) is an American approach to the same topic. It is The California MTBE Research Partnership's report "Survey of Current UST Management and Operation Practices" and contains a lot of valuable information on the topic.

Another IP document, "**Environmental Guidelines for Petroleum Distribution Installations**", May 1996, describes the proper installations specifically from the environmental protection point of view. The contents list and summary is available in appendix no. 9.pdf.

In 2001, Arthur D. Little prepared a report for the European Commission assessing whether groundwater within the European Union (EU) faces a similar potential for widespread contamination by MTBE as has already occurred in the USA, and whether this risk is mitigated by controls or obligations present in Member States that may or may not exist in the USA. The report, which can be downloaded from http://www.environmental-expert.com/articles/article1001/article1001.htm, concludes: "*Widespread MTBE contamination on the same scale as in the USA (especially California) is unlikely. The risk of groundwater contamination is unlikely to increase, given important differences between the USA and the EU, although robust enforcement of the existing Member State regulatory framework is required to ensure this risk remains low in the future*."

2.1.3 Storage and handling of neat MTBE

2.1.3.1 Basic guidelines

The water solubility of neat MTBE, its effect on some elastomeric polymers, and fire fighting foam requirements are different from those for gasoline. Except for these differences, design and operation standards applicable to gasoline storage and handling facilities also apply to MTBE.

Generally, all technical requirements and operational practices which apply for gasoline are applicable for neat ether oxygenates and also gasolines containing ether oxygenates, with the following exceptions:

- gasket materials compatibility to be checked
- vapour recovery design, capacity to be checked
- storage tanks should have floating roofs and domes
- tank bottom water phases to be directed to waste water treatment
- special emphasis on leak prevention/detection and soil/groundwater protection
- emergency response: oxygenates-compatible extinction foams, adsorbents
- minimised response time for soil/groundwater remediation in case of a leakage or splash
- medical emergency response

With respect to spills or leaks, owners and operators of installations that handle gasoline should be well aware of local, regional and national regulations and legislation. As a minimum, EFOA recommends to alert local water authorities in any major gasoline spill or leakage whether there is MTBE or other ether oxygenates involved or not. The same applies even for small spills and leakages in sensitive areas.

Neat MTBE is a chemically stable, highly flammable, and highly volatile liquid. Although it is relatively non-toxic to humans, it behaves as an anaesthetic when very high vapour concentrations are inhaled. It does not polymerise, nor will it decompose under normal conditions of temperature and pressure. Unlike most ethers, MTBE does not tend to form peroxides (auto-oxidise) during storage.

MTBE is non-reactive. It does not react with air, water, or common materials of construction. The reactivity of MTBE with oxidising materials is probably low, however, without definitive information, it should be assumed that MTBE reacts with strong oxidisers, including peroxides.

MTBE may hydrolyse in the presence of some acids. MTBE is very stable in the presence of reducing agents and reactive monomers.

Bulk quantities of neat MTBE should be received, stored, processed, and disposed of only in facilities designed for those purposes. Storage systems should be inspected for elastomer compatibility before introducing MTBE for the first time. After initial inspection, storage systems should be operated as outlined in the product safety bulletin. Appropriate emergency notification and response systems for fire and spill management should be in place at each facility where MTBE is received, stored, or used. MTBE should be handled only by workers trained in safe handling methods and response to emergencies such as spills or fires.

For more information regarding safe handling and storage, please see the MTBE Product Safety Bulletin

2.1.3.2 MTBE Product Safety Bulletin

An MTBE Product Safety Bulletin is provided under appendix no. 10.pdf.

2.2. EMERGENCY RESPONSE

2.2.1 Single EU emergency call number

112 is the single emergency call number for the European Union. It was established by Council Decision on 29 July 1991. This decision ensures that European citizens in distress situations can call **112** and get assistance through the emergency services in all Member States. Thus, anyone travelling within the Union will have to remember only one number and this guarantees quicker and more efficient intervention.

In some areas, the traditional fire brigade, police and ambulance numbers are still valid. However, the **112** number can also do the same job.
In most countries, the organisation behind Emergency Call Number **112** is capable of arranging all kinds of emergency services, including response to environmental incidents of any magnitude.

The National Emergency Call Centres (**112**) also have access to industry and transportation emergency response networks, i.e. they are well connected and effective.

Due to the practical experience of Emergency Response personnel, they are also an excellent source of information and contacts with the appropriate authorities and even consultants.

2.2.2 Links to MSDS, Product Safety Bulletin

The following links open the MSDSs (Material Safety Data Sheets) for

MTBE (Guidance document) (appendix no.11.pdf)
MTBE (Lyondell) (appendix no. 12.pdf)

MTBE Product Safety Bulletin

MTBE is a volatile, highly flammable, slightly water soluble, liquid petrochemical with some harmful characteristics. It must therefore be handled as any other such petrochemical - with respect. In many characteristics, it is very similar to gasoline.
Appendix 10 is the content list of a safety handbook on MTBE, its technical and physico-chemical data, installations required for proper storing, loading and general handling of MTBE, emergency response instructions, etc. The instructions are also applicable to MTBE blended gasoline.

2.2.3 Steps in emergency response

Note : The above described MTBE Product Safety Bulletin, Appendix 10, contains detailed information on MTBE's hazardous properties and basics in Emergency Procedures.

In the event of an accidental and serious release of gasoline with or without MTBE, several actions will be required.
Firstly, the authorities will have to be notified as soon as possible. In the meantime, the standard operating procedures of the afflicted organisation or company will come into force. Most countries require

both companies and towns to have a local emergency response plan. Should an organisation not have such plans and procedures in place, the following basic safety precautions apply to any major spill or transportation incident involving chemicals.

Note: If there is a potential soil or groundwater contamination risk, contact a competent consultant immediately.

Approach cautiously from upwind

Resist the urge to rush in until the situation has been fully assessed. Do not walk into or touch spilled material. Avoid inhalation of fumes, smoke and vapours.

Secure the scene

Isolate the area; ensure the safety of people and the environment; keep people away from the scene and outside the safety perimeter; allow room to move and remove equipment.

Identify the hazards

Use placards, container labels, shipping documents, MSDSs, TREM cards and/or knowledgeable persons at the scene. Evaluate all available information and consult the recommended guides to reduce immediate risks.

Assess the situation

Consider the following:

- Is there a fire, a spill or a leak?
- What are the weather conditions?
- What is the terrain like?
- Who/what is at risk: people, property or the environment?
- What actions should be taken, e.g. evacuation, dyking?
- What resources (human, equipment) are required, and are they readily available?
- What can be done immediately?

Obtain help

Advise your headquarters to notify responsible agencies and call for assistance from qualified personnel. Ensure that local fire and police departments have been notified. Before calling, have the following information to hand:

- Contact names and telephone numbers
- Location and nature of problem
- Name and identification number of material(s) involved
- Shipper/consignee/point of origin

- Carrier name/truck number
- Container type and size
- Quantity of material transported/released
- Local conditions (weather, terrain, proximity to houses, waterways, etc)
- Injuries and exposures

Decide on site entry
Enter the area only when wearing appropriate protective gear: efforts to rescue people, protect property or the environment will fail if you become part of the problem.

Respond appropriately
Establish a command post and lines of communication. Rescue casualties if possible and evacuate if necessary. Maintain control of the site. Continually reassess the situation and modify the response accordingly.

2.2.4 First Aid

The website below leads to the "GESTIS data base on hazardous substances" of the German Berufsgenossenschaften (German insitutions for statutory accident insurance and prevention). This site contains easy-to-find First Aid information of paramedic personnel and doctors on a wide variety of products, including MTBE http://biade.itrust.de/biaen/lpext.dll?f=templates&fn=main-h.html

This is the English search page. If you enter the CAS-No. 1634-04-4 you get access to a screen where you can choose information for MTBE. Click there you arrive at the General information page about MTBE "Identification". At the bottom of this page you can click on several subchapters, e.g. occupational health and First Aid information.

See also the individual MSDSs in the chapter above.

2.3. Remediation

2.3.1 Site investigations

2.3.1.1 Need for investigations

A site investigation is crucial when assessing the risk a soil and/or groundwater contamination incident may pose towards the environment and human health. Therefore, considerable effort should be made to conduct a proper site investigation, especially if there is reason to believe the contamination might be serious and/or at a critical location such as an active aquifer or in the middle of an urban community.

This is the wrong place to cut costs. On average, the site investigation cost is small compared to the actual remediation. It may prove costly if new boreholes and sampling are needed over and over again. Doing it once properly is generally the least expensive way, as a well designed and performed investigation saves time by facilitating the permitting authority's decision-making, and may eliminate the need for further actions. A superficial and inadequate investigation report does not instil confidence and may lead to continuing requests from the authority to complete the investigation more thoroughly.

However, in an emergency situation such as a large gasoline spill or leak, there is not always time for a full-scale investigation. If the incident has happened in an area where there is no need to worry about underground utility conduits or sewers etc, then a quick soil venting operation may be the best solution, provided the environmental authority and fire brigade agree.

2.3.1.2 Role of the authorities

In most European countries, soil and groundwater remediation work is regulated. Commencing such work may require a report to the authority and often even a permit.

It is generally advisable to make contact with the authority before starting an intended remediation project, particularly in major contamination cases, where the authority may be able to offer help and advice in planning the site investigation and risk assessment, thus increasing the project's effectiveness and keeping the cost within limits. This, however, depends very much on the legislation and administrative practices in the area and, of course, the magnitude and severity of the matter.

2.3.1.3 Detailed site investigation guidelines

The Institute of Petroleum (UK) has published a document named "Guidelines for Investigation and Remediation of Petroleum Retail Sites," which covers all the essential points on this topic. The contents list can be found in appendix no. 13.pdf.

2.3.2 Practical advice

2.3.2.1 Need for consultant

If there is a soil and/or groundwater contamination problem (e.g. at a retail site), suspected or actual, it must be taken seriously, especially in those cases where the site sits on an aquifer, or is close to a community or private water supply. Also, the risk of migration to an adjacent lot should not be underestimated. Even if there has apparently been only a small leakage or spill, it must be dealt with promptly. Several small leaks left untreated may accumulate over years and could eventually pose a major problem.

Site investigation, risk assessment and potential remediation are not jobs for the layman - they require the services of a specialist. Comprehensive knowledge and understanding of the geological/hydrogeological, chemical, technical and safety aspects of the situation, as well as practical experience, are needed to perform those tasks properly.

Another very important factor is cost versus performance. Put simply, there is a lot of money at stake, as there can be a big difference in cost between various approaches to achieving the same mitigation or remediation result. These days most authorities accept the Risk Based Corrective Action principle, which means taking just those steps that are really needed to eliminate the actual risk. Further actions may not only be very expensive, but also unnecessary.

In most countries in Europe, soil and especially groundwater contamination must be reported to the authorities and necessary mitigation actions started. Understanding the legal requirements, practice and all the necessary procedures is not easy and therefore **hiring an environmental consultant would be a wise move**.

In most oil company-related retail chains, environmental and legal advice and guidance on these issues are available in-house. However, independent retail operators may have to find their own way. To help them, we have added a section to describe consultants' necessary qualifications and some other important elements, as well as how to find consultants.

2.3.2.2 Consultant's role

In the event of a large leak, overfill or other accidental release, either recent or in the past, which has caused considerable volumes of gasoline to get into the ground, a site investigation is needed to assess the risk to human health and the environment, and to initiate necessary actions.

The need for a site investigation may also arise when selling, buying, leasing, dismantling, shutting down or otherwise quitting or transferring the ownership or operational responsibility - and often also environmental liabilities at the same time - to another party.

The necessary qualifications for an environmental consultant include:

- theoretical background in geology and hydrogeology
- lots of experience in soil/groundwater investigation/remediation
- risk-based problem solving approach
- good reputation for getting things done, recent written references
- consultant or consulting company in good financial shape
- proven practical experience and knowledge of local regulations and authority: inexperience in this may be costly
- good negotiating skills
- willingness to take a strong stand if the problem owner is underestimating or even hiding the real problem
- good office practices (standards, reporting, archives etc.)

It is in the problem owner's interest to define clearly and keep careful control of the consultant's work, especially in relation to costs, expected performance and contact with the authorities. A second opinion by another person experienced in such cases is advisable. Anything larger than a minor job should be awarded on a written contract only. The contract drafts are mostly written by consultants or their associations and therefore the problem owner should consult his own legal adviser.

2.3.2.3 How to find a consultant

The quickest and simplest methods are often the most effective: asking colleagues in the industry for their recommendations, or checking the local phone book's Yellow Pages.

If all the options above fail, one can turn to the local authorities or fire brigade for assistance and recommendations, as they have experience in working with consultants in such cases.
Also, the 112 number (Emergency Call Centre) may be able to help.

There are various other potentially useful sources:

European Options :

1)FIDIC
Clicking the link below opens the FIDIC website's front page. FIDIC is primarily a European Consulting Engineers' Association, but it does, however, cover several continents. The website contains a list of National Consultant Associations with contact details, including website links and e-mail addresses. There is also a search program to find environmental consultants with specific experience, for instance, in soil remediation in a specific country. Advice on how to select a consultant is also given, as well as suggestions for basic contracts.

Finding a suitable consultant directly from this website may be tedious. Therefore, it is advisable to contact the National Association, the communication information path is as follows:
Click www.fidic.org, / National Associations / Country.

2)EFCA
A similar service is available at www.efcanet.org, which opens the web site of the European Federation of Engineering Consultancy Associations (EFCA)
Click the www.efcanet.org, / Members / Members Directory / Country, and a country's associations website opens, indicating communication data. EFCA's Member National Associations' list can be downloaded by the PDF icon on EFCA's Home Page.

3) NICOLE
NICOLE, the **Network of Industrially Contaminated Land in Europe**, is a network for all aspects of industrially contaminated land. Its members come from industrial companies (problem holders), service providers/technology developers, universities and independent research organisations (problem solvers) and governmental organisations (policy makers).
Click **http://www.nicole.org**

US options :

1) The Environmental Yellow Pages
www.enviroyellowpages.com

2)DACON
This website is operated by World Bank and Inter-American Development Bank. It contains tender notices, information on on-going projects and a consultant list.

Click http://tenders.dgmarket.com/dacon, which selection opens a large consulting companies' list, arranged by country. There is also a search function.

3) Soil and especially groundwater problems are a hot topic in the United States, and there are large numbers of environmental consultants, some of whom have been developing and testing innovative remediation technologies - often with federal or state funding. Many of the American consultants have had offices in Europe for several years. European environmental consultants are usually well aware of technology developments in the USA.

There are several websites for American consultants, often sub-sites in very large websites, often titled Vendor Information. Those can be found especially on the EPA and API websites. For example, the Appendix C.24 Vendor Information System for Innovative Treatment Technologies (VISITT) can be opened by clicking http://www.frtr.gov/matrix2/appd_c/appd_c24.html

VISITT contains data on vendors of innovative remediation technologies to treat ground water in situ, soils, sludges, and sediments, including soil washing, thermal desorption, solvent extraction, bioremediation, and in situ vitrification. VISITT does not include established technologies such as incineration and ex situ ground water treatment. Technologies may be at the bench-, pilot- or full-scale. Each vendor profile includes company information, technology description, and applicable media, waste, and contaminants. Other information may include unit cost, performance, waste limitation, hardware and capacity, project names and contacts, treatability study capabilities, and references.
VISITT version 5.0 contains information on 350 technologies offered by 204 developers and vendors. About 73% of the technologies in VISITT are available commercially at full scale. About 70% of vendors provide performance data.

EPA's Technology Innovation Office has also developed a companion database to VISITT, called VendorFACTS, which contains data for site characterisation technologies.
Try these. The databases are large, especially the VISITT as it is linked with several other interesting US EPA and other websites. It also contains a formidable collection of information on various remediation technologies.

The websites are so large that getting lost is easy. It is advisable to take time and also have a notepad and pen handy to make notes of the browsing path and maybe also a printer to print the front pages of various websites to facilitate navigation next time.

2.3.3 Environmental risk assessment of the site

2.3.3.1 Introduction

Most competent authorities have accepted a Risk Based Corrective Action philosophy (RBCA), i.e. remediation is not usually required beyond what is necessary to eliminate the risk to human health from contaminants. This is an important philosophy with major implications for the cost of mitigation or remediation. The difference between doing everything possible and doing what is really needed can translate into a significant amount of money. Performing a site remediation to the point where the last gram of fuel components has been removed or destroyed on site may mean that the last gram is prohibitively expensive.

Here are some reference documents :

Plume Formation Transport and Modeling.pdf
Presentation is a useful introduction to Conceptual Modelling Principles
Conceptualisation of hydrocarbon releases
- factors affecting plume length and concentration (physics, chemistry, biology, sampling)
- modelling considerations
- uncertainty in model calculations
- case studies

OnSite-Calculator.pdf
The US EPA developed on-site calculators accessible in internet are discussed. Very useful source of information.

Site Characterization.pdf
A useful introduction to leakage site assessment and characterization principles.
Several related website addresses are given for reference

Ex-Situ Bio for MTBE and TBA.pdf
Case studies give a good overview on soild/groundwater remediation in large leakage cases contaminating public drinking water sources. Includes site assessment and project management description.

Biodegradation and In Situ Bioremediation.pdf

The presentation gives an excellent overview on biotechnical in-situ processes capability and applicability in remediation of soil and groundwater contaminated by fuel oxygenates. Remediation cost elements are also discussed.

Ex-Situ Bio for MTBE and TBA.pdf
The presentation gives an excellent overview on several biotechnical ex-situ processes capability and applicability in remediation of groundwater contaminated by fuel oxygenates. Reactors and other equipment are described.

A Comparison of 3 Ex-situ Treatment Systems.pdf
An extensive remediation case study of a very large and difficult fuel contamination plume. Site assessment and remediation methods and results have been described as well as general project management.

Monitored Natural Attenuation for MTBE & TBA.pdf
The presentation covers several issues in using MNA in MTBE and other fuel oxygenates in remediation of soil and groundwater. Conditions, where MNA is an acceptable method are described and similarly also situations where MNA should not be accepted as a sole process.
Useful information can be extracted from extensive case studies in this presentation.

Air Sparging.pdf
This presentation provides key information on the applicability, requirements and equipment of this remediation process as well as an extensive list of relevant information sources

2.3.3.2 Site Assessment Studies

Numerous studies have been performed and reports published on Site Assessment. Two are provided here:

1) The American Petroleum Institute (API) approach *Strategies for Characterising Subsurface Releases of Gasoline Containing MTBE, API Pub. No: 4699.*
The document uses the principles of risk-informed decision making to guide the assessment of sites affected by MTBE and other oxygenates. Risk-informed decision making considers risk factors related to sources, exposure pathways and receptors. The centrepiece of this approach is the development of a conceptual site model (CSM). A new decision framework developed by API helps the environmental site

assessor to determine an appropriate starting point or an initial level of assessment from which the CSM can be confirmed.

Important risk factors are discussed in the report along with descriptions of characterisation tasks suggested for various levels of assessment. The report describes how current expedited site assessment techniques can be applied to the collection and field analysis of soil, soil gas and groundwater samples. A comprehensive guide to direct push assessment and monitoring tools, with emphasis on their proper use at MTBE-affected sites is also provided.

In addition to presenting state-of-the-art strategies for MTBE site assessment, the report is an excellent reference on the chemical and physical properties of oxygenates, their use in gasoline and behaviour in the subsurface environment. Analytical methods appropriate for MTBE detection are also discussed.

This report (pdf format) is available for downloading now at: http://api-epapi.org/filelibrary/4699c.pdf and it is free of charge.

2) Concawe, the European oil companies' association, has published a similar document, Report No: 2/97, which is more European. The Foreword, Contents list and Summary of the Concawe document are available in appendix no. 14.pdf

The complete Concawe report 2/97 is available in appendix no. 15.pdf below. It is also downloadable.

2.3.4. Remediation Technologies

2.3.4.1 Introduction

The current discussion and concern about groundwater contamination in the USA and Europe is due to recently detected evidence of fuel spills and leaks that have actually been happening for several decades. Some have taken place at storage sites and terminals but the majority have occurred at retail fuel stations, which is why this guide is focusing on retail sites.
Generally, the situation is getting better due to improvements in technical installations and operating practices at retail stations. In the meantime, there is a lot of risk assessment and remediation work to do at past release sites, to understand and eliminate the contamination.

MTBE has attracted attention to groundwater contamination because with its introduction in 1973. It brought several specific properties that distinguish it from other components:

- it has a very low taste and odour threshold, which means it is noticeable at low concentrations;
- it is more soluble in water, so in certain conditions it tends to spread faster and further through the soil, creating a "halo" effect around the spill;
- it biodegrades more slowly and therefore may persist in the environment for longer periods.

A different issue in the USA concerns MTBE found in water in small concentrations, especially in certain recreational lakes, some of which also serve as water reservoirs. In those cases, the problem is not caused by leaking storage tanks, but by recreational boats' 2-stroke gasoline-driven outboard motors, which blow exhaust gases directly into the water. Combustion in such motors is less than complete, therefore a relatively large proportion of unburned fuel - including MTBE - ends up in the water.

Splashing gasoline while filling up from containers, e,g, jerrycans, may also contribute to the problem, although probably on a minor scale. This picture may have been repeated to some degree in Europe.

Early intervention

The problem of MTBE in groundwater is not inherent to the product itself, but has mainly arisen from careless handling. It is an avoidable issue, which can be successfully resolved through co-operation between the oil industry, oxygenate producers, water companies and regulators. Early, preferably immediate, intervention following an accidental release of gasoline and its components is the key to minimising the extent and cost of remedial action and is essential to protect public health and the environment.

Although the sense of urgency may seem less, dealing with past releases is equally important. In the case of a major past incident, the contamination plume continues moving along its natural path and given time, may develop into a serious problem.

The common misconception, that remediating MTBE contamination is extremely expensive, is based on the experience of past releases in the United States, which were left for years to cover vast areas and go deep. Removal of traditional gasoline contamination of similar size would be just as costly. The reason for these long delays is unique to the USA, where the legal practice of punitive damages discouraged oil companies from taking action, since such an initiative could mean acceptance of liability.

Remedial action

There is a large array of well-proven remediation technologies for treating soil and groundwater contaminated by conventional gasoline. In general, these methods are applicable to gasoline containing MTBE. The most common methods are excavation of the contaminated soil (dig and dump), soil venting, air stripping, activated carbon or other adsorbent treatment and biological degradation. Traditional pump-and-treat technologies available for water treatment plants have been proven effective in remediation of gasoline-contaminated water, even if it contains MTBE.

The hydrocarbons and oxygenates do degrade naturally in the subsurface soil and groundwater due to microbial activity. However, especially for ether oxygenates such as MTBE, the reaction rates are slow because electron acceptors, such as oxygen, are quickly depleted in contaminated soil and groundwater and are recharged only slowly. As a result, contaminated groundwater may have significant contaminant concentrations but depleted electron acceptors, whereas the overlying unsaturated zone may contain oxygen but low contaminant concentrations.

Key principles

The following information on remediation technologies is intended to provide a general understanding of the available options.

When carrying out remediation work, a few key principles should not be forgotten:

- in acute gasoline spills/leaks, time is of the essence
- early contact with the appropriate authority is recommended
- importance of consultant/contractor selection
- an investigation very seldom reveals everything - there is always an element of uncertainty left
- a risk-based approach should be applied
- **importance of contamination source (such as leaking equipment or contaminated soil) removal or control**
- the effectiveness of a technology is largely dictated by the geological/hydrogeological conditions
- there are no two identical cases
- often various technologies are needed, in sequence or in combination

- contracting the remediation work to a consultant and/or specialist firm is best done on a written contract basis, clearly defining the respective liabilities
- due to uncertainties involved, cost estimates also tend to be uncertain. A lump-sum contract may or may not work
- especially when dealing with contaminated groundwater, the problem owner should not always expect quick and inexpensive remediation.

An abundance of information on soil and groundwater remediation is available from bookstores, libraries, conference proceedings, international publications and of course, the Internet. This guide includes a **Website Directory**, which lists several useful Internet sites. The total volume of information available via those sites and their reference links is enormous. Most of the websites contain both soil and groundwater remediation technologies.

Note: The websites are large, comprehensive and mostly well organised. However, it is advisable to take plenty of time, have a notepad and pen handy and systematically browse through the material. Keeping notes of the search path facilitates further visits to useful websites. Printing the websites' and subsites' front pages helps navigation later on.

2.3.4.2 Soil remediation

This section outlines the major clean-up technologies that have become well established in commercial soil remediation. Generally, the technologies available today are:

- safe
- not prohibitively costly, provided that prompt action is taken

There are many companies offering clean-up services with these methods and a reasonable case history has been built up. There are numerous remediation research topics and innovative techniques which are being investigated, for instance phytoremediation and electricity-enhanced techniques such as electro-osmosis, electrical heating and microwave heating, which are all emerging technologies holding substantial promise and which have been applied successfully on a small scale.

Under natural conditions, biodegradation of MTBE in soil and groundwater may be slow. The main reasons are lack of oxygen and lack or too small population of specific micro-organisms. This can be enhanced in two ways: adding oxygen and selecting and adding appropriate micro-organisms and in some cases nutrients. The first can be done by a technique commonly known as air sparging. Addition of oxygen can further enhance the process.

In general, remediation technologies can be grouped into categories using physical, chemical or biological methods. The various techniques usually work well when applied to a specific type of contamination, however, a universal technique solving all contamination problems does not exist. Due to the potentially complex geological and contaminant nature of many contaminated soils, it is frequently necessary to apply several techniques, often in sequence, to reduce the concentrations of contaminants to acceptable levels.

Remediation techniques can also be categorised by the means with which they effect remediation. Some methods will eliminate wastes through reactions which produce benign (or at least less harmful) products. Thermal and biological methods (employing bacteria) are typical examples. Other methods, e.g. soil washing, incineration and vapour extraction, will concentrate wastes, resulting in a mass that may be easier - ie less costly - to manage. Another approach is to fix the contaminants in place, (a method called soil stabilizing), thus eliminating or greatly reducing the risk of exposure to the public.

Traditionally, the simplest way to remediate contaminated soil has been just to excavate the contaminated soil mass and locate it somewhere else, a method called "Dig and Dump". In such cases, oil and gasoline components typically decompose by microbial action, which can be considerably speeded up with proper stack composting arrangements.

Today this is not always possible, or acceptable. Ever-tightening requirements and regulations for establishing and operating a dumpsite have resulted in fewer dumpsites being available, as well as greatly increased waste disposal costs. The transportation of contaminated soil has also become strictly regulated. For instance, in some areas, transporting and also dumping heavily gasoline-contaminated soil is totally forbidden. However, in minor incidents, excavation is still the most effective way to solve the problem.

The websites listed below are all very large and comprehensive with various subsites and Internet links. As everybody knows how to use an excavator, these websites typically present more advanced technologies. Some of them also contain technologies that apply to groundwater remediation.

Special note

Non-Aqueous Phase Liquid (NAPL), i.e Free Phase Hydrocarbon Liquids Recovery
Removing the contamination source from the soil, (in this case, a free phase of gasoline from the soil pores or from the top of the soil or groundwater) is of paramount importance to a successful remediation effort. If source removal is not properly performed, the remaining contamination is capable of feeding unacceptably high concentrations of gasoline components into the groundwater, or seeping through basement walls to contaminate the air in the basement, or maybe in the whole house, for a long time.

Also, gasoline is capable of seeping through some polymer pipe materials to the extent that it may create problems with household water supplies. Gasoline smell and taste in tap water is not uncommon at sites where the soil is severely contaminated with gasoline or diesel, and the water supply pipes are made from polymer materials.

Free-product removal can be a tricky and costly exercise, even when performed by experts. The following Internet link gives access to a presentation page of API publication No: 4729, August 2003, http://groundwater.api.org/lnapl/

appendix no. 16.pdf describes the design of free product removal installations and procedures.

The reader should note that the document is very technical. It is included mainly for use by scientists and consultants. Information on free product removal methods can also be found at several websites included in this Guide.

Hazardous Waste Clean-Up Information Website is an American (EPA) website that provides information about innovative treatment technologies to the hazardous waste remediation community. It describes programmes, organisations, publications and other tools for federal and state personnel, consulting engineers, technology developers and vendors, remediation contractors, researchers, community groups, and individual citizens. The site is managed by EPA's Technology Innovation Office and is intended as a forum for all waste remediation stakeholders.

Note: The website below is very large and contains a number of sub-sites. It is advisable to take time and have a notepad and pen handy and systematically browse through the material. Keeping notes of the search path facilitates further visits to useful material. Printing the front pages of the various sites and subsites helps navigation later on.

www.clu-in.org
A short presentation of the contents and intent of this very useful and comprehensive EPA website covering the whole range of soil and ground water contamination related problems:

EPA Remediation and Characterisation InnovativeTechnologies (EPA REACH IT)

Do you need reliable information about remediation and characterization technologies? Would you like to know about sites at which those technologies are being implemented? EPA REACH IT* can help.

EPA REACH IT, sponsored by EPA's Technology Innovation Office, is a new system that lets environmental professionals use the power of the Internet to search, view, download and print information about innovative remediation and characterisation technologies. EPA REACH IT will give you information about more than 750 service providers that offer almost 1,300 remediation technologies and more than 150 characterisation technologies.

EPA REACH IT combines information from three established EPA databases, the Vendor Information System for Innovative Treatment Technologies (VISITT), the Vendor Field Analytical and Characterisation Technologies System (Vendor FACTS), and the Innovative Treatment Technologies (ITT), to give users access to comprehensive information about treatment and characterization technologies and their applications. It combines information submitted by technology service providers about remediation and characterization technologies with information from EPA, the U.S. Department of Defense (DOD), the U.S. Department of Energy (DOE), and state project managers about sites at which innovative technologies are being deployed. Those sources together provide you with up-to-date information, not only about technologies you can use to characterize or remediate a site, but also about sites at which those technologies are being used and the service providers that offer them.

* EPA REACH IT is best viewed using Netscape Navigator or Microsoft Internet Explorer, version 4.0 or higher.

A very useful sub-site of the above is
http://clu-in.org/products/citguide, which opens a website with descriptions of various technologies, especially written for non-experts.

The Technology Innovation Office produced this series of **Citizen's Guides to Understanding Innovative Treatment Technologies**, which are four-page fact sheets that explain, in basic terms, the operation and application of innovative treatment technologies for remediating sites.

2.3.4.3 Groundwater remediation

Groundwater contamination, with the consequent potential to contaminate drinking water, is the key concern of the general public and the authorities.

The remediation of MTBE-contaminated groundwater was initially considered to be impossible, or at least extremely difficult. This belief had its origins in the low biodegradability, low affinity for organic carbon and relatively high water solubility of MTBE, as well as the fact that it does not evaporate from water as easily as other gasoline components (lower Henry's Law Constant). However, now that more thorough research has been carried out, various effective remediation techniques have been found.

There are in fact several existing and commercially available methods, such as air stripping, steam stripping, diffused aeration, and adsorption, which are able to remove MTBE from groundwater, especially so when the ground water is pumped and treated in on-the-ground facilities, i.e. pump - and - treat.

However, if the source of the contamination, (i.e. contaminated soil or even free phase product) is not removed swiftly, the remediation can take a long time and thus be very costly. In cases where a private well, serving one or two houses, has been contaminated, the immediate implementation of remediation methods such as Granulated Activated Carbon Adsorption (GAC) in the form of an in-line filter before the well water is used as drinking water, has proven to be adequate and quite cost effective.

Early studies on MTBE contamination of groundwater stated that the compound was either non-biodegradable or very resistant to biodegradation. However, recent research has shown that MTBE can be degraded both aerobically and anaerobically, although the anaerobic intrinsic degradation is slow. The research has found that there are naturally occurring microbes capable of using MTBE as a sole carbon and energy source. Such micro-organisms seem to be widespread, but initially in low numbers that take time to reach a sufficiently dense population to sustain MTBE degradation. Laboratory experiments have clearly shown that biodegradation of MTBE is feasible. Recent field experience from various case studies confirmed this conclusion.

Methods such as the trickling biofilter, membrane bioreactor, and in situ biological treatment, which specifically use the biodegradability of MTBE, are emerging and have demonstrated great potential.

Selection of the remediation strategy and technique to be used in each situation should be done only after a careful evaluation of site-specific properties, since soil characteristics and hydrogeological conditions on site, as well as the possible presence of other contaminants, generally play an important role in selecting a strategy.

When contaminated soil or groundwater is detected, the response should consist of a few key steps. This applies to all contaminants, including MTBE:

- Immediate control and cessation of the release, including repair or removal of the release source
- Removal of free product in both saturated and unsaturated (vadose) zone
- Removal of remaining product (this generally takes most time.)

Efforts in the last steps of remediation are of little value if the preceding steps have not been taken. In fact, initiating remediation under such conditions can worsen the situation, as contaminants may be forced to migrate further.

A rapid response to the detection of a contamination incident is essential to limit the spreading of the contamination. This holds true specifically for MTBE, as its properties enable quicker migration in both unsaturated and saturated soil than other gasoline components.

Abundant and up-to-date information on various technologies is available via the Internet, for instance at:

Ground Water Remediation Technologies Analysis Center's Website

www.gwrtac.org - a large website on various innovative remediation technologies, vendor information, etc. This is one of several US EPA websites, most of which are interlinked.

An excerpt from the front page and a sub page of GWRTAC's website is given below.

Note: This website is very large and it contains a number of sub-sites. It is advisable to take time and have a notepad and pen handy and systematically browse through the material. Keeping notes of the search path facilitates further visits to useful material. Printing the front pages helps navigation later on.

The Groundwater Remediation Technologies Analysis Center (GWRTAC) compiles, analyzes, and disseminates information on innovative groundwater remediation technologies. GWRTAC prepares reports by technical teams selectively chosen from:

Concurrent Technologies Corporation (CTC), the University of Pittsburgh, and other supporting institutions.

The GWRTAC documentation provides - among other material - 3 categories of reports and compilations on groundwater remediation technologies:

- **Remediation Technologies**
- **Technical Documents - Technology Overview Reports**
- **Technical Documents - Technology Evaluation Reports**

Each category presents a slightly different view of the subject, describing different technologies and various levels of detail. A sample is given below.

Remediation Technologies:

GWRTAC focuses on innovative in situ groundwater and soil remediation technologies as compared to the standard "pump and treat" approach for groundwater, or soil excavation and treatment. Many of the remedial activities summarised within GWRTAC are in situ technologies requiring no groundwater extraction; however, means of enhancing pump and treat are also addressed. GWRTAC includes those remediation technologies which, through design and/or application, improve groundwater quality and are integral to groundwater clean up.

The link below opens brief descriptions of technologies that are currently included in GWRTAC's list of Technical Documents on-line: http://www.gwrtac.org/html/techs.html
Reference to GWRTAC's Glossary of Hydrogeology Terms may be useful during reading of the technology descriptions.

www.ngwa.org is a useful source of additional information on soil and especially groundwater contamination, although it does not provide direct technology descriptions or evaluations.

http://www.mst.dk/project/NyViden/1999/03070000.htm is a Danish study by the Institute of Microtechnology, Technical University of Denmark and the Institute for the Water Environment: "Remediation of MTBE-contaminated groundwater" (Prof. Erik Arvin, 1999). It summarizes the principles of various remediation techniques and assesses the usefulness of the techniques, providing a useful overview.

http://www.enzymetech.com/applications/mtbe/mtbe_degrades.htm gives access to a company that uses biological systems and dissolved oxygen in in situ treatment

http://www.estcp.org/projects/cleanup/CU-0015.cfm refers to information from Environmental Security Technology Certification Program (ESTCP) called "In Situ Remediation of MTBE-Contaminated Aquifers Using Propane Biosparging".

http://www.aptwater.com/assets/tech_papers/Paper-TBAMTBE.pdf is a paper by Applied Process Technology, Inc (2004), presenting results from several pilot studies and fullscale remediation sites in which an Advanced Oxidation Process (ozone / hydrogen peroxide) was used to remove TBA and MTBE from contaminated groundwater.

http://www.shellglobalsolutions.com/bioremedy/documentation/index.htm leads to the site of consultant Shell Global Solutions, summing up a dozen of projects and papers on (bio)remediation of MTBE contaminated sites. It also contains information on Biobarriers and BioGAC (microbes seeded on granular activated carbon).

2.3.4.4 Drinking water remediation

Remediation of large supply wells

The California MTBE Research Partnership has conducted comprehensive research on drinking water remediation technologies. The Introduction from the Executive Summary of the research report is presented below, with a link to the actual Executive Summary (MS Word format - total of 20 pages, at the end of this chapter, ie. appendix no. 17.pdf)

The results of the research indicate that, should MTBE removal from drinking water become necessary due to exceedance of the organoleptic or other limits, the cost of such service is not intolerably high. The table on page 12 of the Executive Summary gives information on the clean up costs in different cases.

Treatment Technologies for Removal of MTBE from Drinking Water

- Air Stripping
- Advanced Oxidation Processes
- Granular Activated Carbon
- Synthetic Resin Sorbents

Second edition - Executive Summary

Introduction

This Executive Summary is being published as a stand-alone summary of the key findings from the report, "Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water: Air Stripping, Advanced Oxidation Processes, Granular Activated Carbon, and Synthetic Resin Sorbents, Second Edition (MTBE Treatability, 2000)".

The complete report is available from the National Water Research Institute (NWRI) in hardcopy or as a CD-ROM. The report presents the results of an extensive feasibility study of methyl tertiary butyl ether (MTBE) removal from drinking water. The study was conducted to evaluate the most promising and/or widely accepted technologies used to remove volatile organic compounds from drinking water: namely, air stripping, advanced oxidation processes (AOPs), granular activated carbon (GAC), and synthetic resin sorbents. These technologies were evaluated as they apply specifically for removal of MTBE.

The first edition of this document was published in December 1998. The second edition (MTBE Treatability, 2000) is a significant improvement on the first edition. The most notable changes are the addition of a new chapter on synthetic resin sorbents, refinement and update of costs for all technologies, significant revisions to the AOP section, a new introductory chapter, and a new chapter with overall conclusions and recommendations (appendix no. 17.pdf)

Treatment of water supply from private water wells
Soil, Sediment & Ground Water, MTBE Special Issue 2000. The article, Impact of Small Engine Spills and Treatment of Private Drinking Wells, in the above issue gives a good view on the topic. (appendix no. 18.pdf)

Soil, Sediment & Ground Water, MTBE Special Issues 2001. The Spring 2001 issue also contains other very easy-to-read and informative articles on various topics around soil and groundwater contamination.

The complete issue is available at :

www.aehsmag.com/issues/2001/spring/index.htm

The March/April 2003 issue of the Soil, Sediment & Water magazine contained an article "Bioremediation in Bedrock: Using Bioremediation to Treat Dissolved BTEX and MTBE in Fractured Bedrock". It is available at http://www.aehsmag.com

3. WEBSITE DIRECTORY

The following four websites are large, comprehensive and useful sources of information and are referred to in various chapters in this document.

www.api.org
www.epa.gov
www.gwrtac.org
www.ngwa.org

The following websites provide information on technologies, companies and events in the soil decontamination field. All are non-commercial sites and lead to other useful information sources.

The most comprehensive network of websites for soil decontamination is that in the United States. Of the many sites produced the most important are described below:

http://www.frtr.gov
This is the parent site for the US government agencies active in remediation technologies. The central organisation is Federal Remediation Technologies Roundtable (FRTR), which also is linked to the home pages of seven agencies: Department of Defense (DoD), Environmental Protection Agency (EPA), Department of' Energy (DoE), Department of the Interior (DoI), Department of Commerce (DoC), Department of Agriculture (DoA) and the National Aeronautics and Space Administration (NASA).

http://clu-in.org
The Hazardous Waste Clean-up Information website provides information about innovative treatment technologies to the hazardous waste remediation community. It describes programmes, organisations, publications and other tools for federal and state

personnel, consulting engineers, technology developers and vendors, remediation contractors, researchers, community groups, and individual citizens. The site is managed by EPA's Technology Innovation Office and is intended as a forum for all waste remediation stakeholders.

http://www.epareachit.org
EPA REACH IT, sponsored by EPA's Technology Innovation Office, is a new system designed to permit users to search, view, download, and print information about innovative remediation and characterisation technologies:

EPA REACH IT gives information about over 750 service providers in the US that offer almost 1,300 remediation technologies and more than 150 characterisation technologies. EPA REACH IT combines information from three established EPA databases, the Vendor Information System for Innovative Treatment Technologies (VISITT), the Vendor Field Analytical and Characterisation Technologies System (Vendor FACTS), and the Innovative Treatment Technologies (ITT), to give users access to comprehensive information about treatment and characterisation technologies and their applications. It combines information submitted by technology service providers about remediation and characterisation technologies with information from EPA, the Department of Defense, the Department of Energy, and by state project managers about sites at which innovative technologies are being employed. Those sources together provide up-to-date information about technologies to characterise or remediate a site, and about sites where those technologies are being used and the service providers that offer them.

http://www.calgasoline.com/studies.htm - A file rather than a website, giving an overview of a larger number of studies and presentations, covering not just remediation aspects, but also the political side (California Executive Orders), Underground Storage Tanks, Economics, International Community Assessments and drinking water & health effects.

Other useful United States Environmental Protection Agency websites:

http://www.epa.gov/tio
The Technology Innovation Office (TIO) of the United States Environmental Protection Agency (EPA) was created in 1990 to act as

an advocate for new technologies. TIO's mission is to increase the applications of innovative treatment technologies to contaminated waste sites, soils, and groundwater. TIO has encouraged and relied on co-operative ventures with other partners to accomplish most of its early goals. This effort to leverage resources has lead to numerous joint efforts that have enhanced the state of remediation. Since its creation, TIO has worked with many partners inside EPA, in other federal agencies, and in the private sector to improve the understanding of remediation treatment technologies and reduce impediments to their widespread use.

http://www.epa.gov/ORD
The Office of Research and Development (ORD) is the scientific and technological arm of the EPA. Comprised of three headquarters offices, three national research laboratories and two national centres, ORD is organised around a basic strategy of risk assessment and risk management to remediate environmental and human health problems.

ORD focuses on the advancement of basic peer-reviewed scientific research and the implementation of cost-effective, common sense technology. Fundamental to ORD's mission is a partnership with the academic scientific community, through extramural research grants and fellowships to help develop the sound environmental research necessary to ensure effective policy and regulatory decisions.

http://www.epa.gov/ORD/SITE
The Superfund Innovative Technology Evaluation (SITE) Programme was established by the EPA's Office of Solid Waste and Emergency Response and the Office of Research and Development (ORD). The SITE Programme is administered by ORD National Risk Management Research Laboratory in the Land Remediation and Pollution Control Division (LRPCD), headquartered in Cincinnati, Ohio. The SITE Demonstration Programme encourages the development and implementation of innovative treatment technologies for hazardous waste site remediation.

http://www.rtdf.org
The Remediation Technologies Development Forum (RTDF) was established in 1992 by the EPA to identify what government and industry can do together to develop and improve the environmental technologies needed to address their mutual clean-up problems in the safest, most cost-effective manner. The RTDF fosters public and private sector partnerships to undertake research, development, demonstration and evaluation efforts focused on finding innovative

solutions to high priority problems. The RTDF has grown to include partners from industry, several federal and state government agencies and academia who voluntarily share knowledge, experience, equipment, facilities, and even proprietary technology to achieve common clean-up goals.

http://www.epa.gov/superfund
Public concern over the extent of uncontrolled dumping of hazardous chemical waste and abandoned warehouses and industrial sites led the US Congress to establish the Superfund programme in 1980 to locate, investigate, and clean up the worst sites nationwide. The EPA administers the Superfund programme in co-operation with individual states and tribal governments. This website provides an overview of the Superfund programme, highlights key steps in the Superfund cleanup process, guides users to enforcement information, lists EPA's Superfund offices and partnership organisations, and provides answers to frequently asked questions.

European websites covering Soil and Ground Water remediation issues

These websites typically cover large scope environmental contamination issues in Europe and provide potentially useful authority, technology developer and service provider contacts.

http://www.caracas.at
CARACAS is a Concerted Action initiative within the Environment and Climate Programme of the European Commission, DG Environment (former DG XII). About 16 European countries participated in the CARACAS project with scientists from **national environmental authorities and research organisations., i.e,** CARACAS is primarily an authority network and is involved with current research initiatives on contaminated land risk assessment in Europe and identifies priority research tasks for future R&D programmes

http://www.clarinet.at
The **Contaminated Land Rehabilitation Network For Environmental Technologies in Europe,** CLARINET's primary objective is to develop technical recommendations for sound decision making on the remediation of contaminated sites in Europe.

http://www.nicole.org
NICOLE, the **Network of Industrially Contaminated Land in**

Europe, is a network for all aspects of industrially contaminated land. Its members come from industrial companies (problem holders), service providers/technology developers, universities and independent research organisations (problem solvers) and governmental organisations (policy makers).

http://www.cordis.lu
Provides information on a vast range of research, development and innovation activities undertaken on a European level. **This website is one of the main EU information sites.**

www.shef.ac.uk/gprg/publications/pdf/gprgpaper_2004_chisala_tait_lerner.pdf
In this report of the **University of Shefield**, UK (2004) the risk of MTBE to urban groundwater is evaluated. It does so by predicting the MTBE propable pollution status of groundwater at all locations in the city of Nottingham using a risk-based tool called Borehole Optimisation System (BOS).

Other websites of various organisations working on the soil/ groundwater issues and, especially, including Central, East and South-East European countries:

http://www.mtbe.de
This site is set up by the German company Grundwasser-Consulting und Risiko-Services Dr Stupp Consulting GmbH, located in Bergisch-Gladbach. It contains useful information about remediation. The site contains links to other useful German remediation sites, e.g.

- http://www.sanierungsverfahren.de/
- http://www.sicherungsverfahren.de/
- http://www.grundwassersanierung.de/
- http://www.hydroservices.de/

http://www.eea.eu.int
The European Environment Agency is a central node of an extended network, the **European Environment Information and Observation Network (EIONET).** This website provides very easy access to various European Environmental Agencies and well structured information on environmental issues in several languages. Also, several data bases are accessible via this website.

http://www.gnet.org/about/

The Global Network of Environment and Technology (GNET) is a general site for environmental issues, providing large scope world wide information on the environmental issues. Sponsored partly by the US Dept. of Energy, GNET also assists government scientists and researchers to commercialise innovative environmental technologies.

http://www.rec.org

The **Regional Environmental Center for Central and Eastern Europe (REC)** is specializing on environmental issues in those areas and is headquartered in Szentendre, Hungary.

4. APPENDICES

appendix no. 1.pdf General substance information

appendix no. 2.pdf The health hazards and exposures associated with gasoline containing MTBE

appendix no. 3.pdf Risk assessment report for existing substances

appendix no. 4.pdf Klinger et al Wasserkonzentrationen

appendix no. 5.pdf UBA publication

appendix no. 6.pdf Strategies for characterizing subsurface releases of gasoline containing MTBE

appendix no. 7.pdf Guidance for the design, construction, modification and maintenance of petrol filing stations

appendix no. 8.pdf Survey of UST management and operation practices

appendix no. 9.pdf Environmental guidelines for petroleum distribution installation

appendix no. 10.pdf MTBE Product Safety Bulletin

appendix no.11.pdf MSDS guidance document

appendix no. 12.pdf MTBE Material Safety Data Sheet

appendix no. 13.pdf Guidelines for investigation and remediation of petroleum retail sites appendix no. 14.pdf European oil industry guidelines for risk-based assessment of contaminated sites

appendix no. 15.pdf Complete Concawe report

appendix no. 16.pdf Free-product recovery systems of petroleum hydrocarbon liquids

appendix no. 17.pdf MTBE Treatability 2000

appendix no. 18.pdf Impact of small engine spills and treatment of water supplies from private drinking wells