Danish Ministry of the Environment
Environmental Protection Agency

# Survey of MTBE

Part of the LOUS-review

Version of Public Hearing

October 2013

**Title:**
**Survey of MTBE**

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**Published by:**

The Danish Environmental Protection Agency
Strandgade 29
1401 Copenhagen K
Denmark
www.mst.dk/english

**Year:**

2013

**ISBN no.**

[xxxxxx]

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# Preface

**Background and objectives**
The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011) includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding ongoing activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns the substance methyl-*tert*-butyl ether; MTBE. This substance was included in the first revision of the LOUS list in 2000 and has remained on the list since that time. The entry in LOUS for the substance is the common abbreviation of methyl-*tert*-butyl ether; MTBE (CAS No. 1634-04-4 and EINECS No. 216-653-1).

The main reason for the inclusion in LOUS is that MTBE appears on the EU list of substances with suspected endocrine disrupting properties in Category 1: Substances for which there is "evidence of endocrine disrupting activity in at least one species using intact animals".

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

**The process**
The survey has been undertaken by COWI A/S (Denmark) from March to October 2013. The work has been followed by an advisory group consisting of:

- Christina Ihlemann, Danish EPA (Chairman)
- Katrine Smith, Danish EPA
- Sidsel Dyekjær, Danish EPA
- Anne-Louise Jørgensen Rønlev, Danish EPA
- Anne Christine Duer, Danish Nature Agency
- Ulla Hansen Telcs, Confederation of Danish Industry
  (from 01.09.2013 substituted by Nikolai Stubkjær Nilsen)
- Michael Mücke Jensen, Danish Oil Industry Association
- Jesper Kjølholt, COWI (Project Manager).

Please note that the report does not necessarily reflect the views of all the members of the Advisory Group.

**Data collection**
The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower).
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Date on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA) and the INIRIS database.
- Waste statistics from the Danish EPA;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature.
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were sent to Danish and European trade organisations.

# Conclusion and summary

This review report concerns the substance methyl-*tert*-butyl ether, normally referred to by its abbreviation MTBE, which is one of 40 chemical substances on the Danish Environmental Protection Agency's (DEPA) so-called "List of Undesirable Substances" (LOUS). All of these substances are undergoing similar reviews over the period 2012-2015.

MTBE is a liquid at ambient temperature but has a boiling point of only 55 degrees Celcius. The substance is known to have a low threshold for odour and taste in water. The dominant use of MTBE is as an additive to petrol where its function is to increase the octane rating ("octane booster"). Minor uses include as a raw material in the production of high-purity isobutylene and as a specialty solvent in certain processes in the pharmaceutical industry.

**Regulatory aspects**

EU and Danish legislation as well as other regulatory instruments (e.g. international conventions) pertaining to MTBE have been examined as part of the review. It has been concluded that legislation in the EU as well as nationally in Denmark regulating the use of MTBE is limited regarding both the exposure of humans to MTBE and the emissions of MTBE to the environment. MTBE is not listed by ECHA as a substance of very high concern (SVHC).

At the EU level, a limit for MTBE content in petrol for vehicles exists, which is implemented into Danish legislation. Further, due to concern about the risk for contamination of groundwater resources, a voluntary agreement was made in Denmark in 2000 between industry and the Ministry of Environment. According to this agreement, MTBE would only be added to 98 octane petrol, which, additionally, would only be sold at a limited number of service stations. Though this agreement does not formally exist anymore, the situation is in reality unchanged with regard to the sale and use of 98 octane petrol in Denmark. No other initiatives to reduce the use of MTBE appear to exist at present in the EU, including Denmark. However, a substance evaluation of MTBE under REACH is scheduled for 2014 with France as Rapporteur MS.

At the EU level, only an indicative Occupational Exposure Limit exists, whereas in Denmark, environmental standards in air in the working environment (slightly lower than the EU indicative OEL) and limit values in fresh and marine surface waters, as well as in groundwater/drinking water, have been established.

**Manufacture and uses**

MTBE was introduced in Europe in 1973 as an octane booster for petrol and has been applied extensively for this use since then. However, in recent years the consumption has decreased as MTBE is gradually being replaced by (bio-) ETBE. This replacement has occurred mainly because of the introduction of EU requirements as to contents in fuel of components produced from renewable sources, such as bio-ethanol, a precursor of ETBE and more easily available than bio-methanol (precursor of MTBE). Thus, the production capacity of MTBE in the EU has decreased from about 3,300 ktonnes in 2002 to about 1,800 ktonnes in 2010 with an actual production volume in 2010 of about 1,600 ktonnes. Some of the produced MTBE is exported outside the EU but there is also an import to the EU, primarily from the USA.

Other uses of MTBE, such as as an intermediate in the production of high purity isobutylene or as a process solvent in the pharmaceutical industry, are quantitatively only of minor importance compared to its main use as petrol additive.

Due to the voluntary agreement between industry and the Danish government, mentioned above the annual consumption of MTBE for use in petrol is at a level of only a few hundred tonnes (registered use in 2012: less than 400 tonnes). The consumption of MTBE in Denmark for other purposes totalled about 14 tonnes in 2012. Updated information on import/export of MTBE in the EU has not been possible to obtain as separate figures for MTBE are not reported by Eurostat (only for a group of acyclic ethers, which includes MTBE).

**Waste aspects**
MTBE is not manufactured in Denmark and the extent of industrial uses (e.g. as a process solvent) is limited. MTBE-waste from such uses should be handled as hazardous waste and destroyed by incineration. The use of MTBE in mixtures and articles (in reality only 98 octane petrol) only results in a small volume of waste at service stations, which is subject to controlled collection and subsequent destruction, similar to industrial MTBE-waste.

**Environmental effects, fate and exposure**
The environmental hazards of MTBE were reviewed in the 2002 EU Risk Assessment Report (RAR), a document which is still considered valid. MTBE is not very toxic to aquatic organisms; the lowest acute EC50 is 136 mg/l (*Mysidopsis bahia*, marine crustacean) and the lowest chronic NOEC is 26 mg/l for the same species. The RAR does not mention possible endrocrine disrupting effects of MTBE in the environment and no valid information on this issue has been identified.

Due to the known strong odour and taste of low concentrations of MTBE in water, a tainting ("off-taste") study and an avoidance test, both with fish, have been conducted. The tainting study showed no off-taste at an exposure level of 15 µg/l but at 31 µg/l the taste of MTBE could be distinguished. The avoidance test with eel showed some attraction to the MTBE-treated zone at 30 µg MTBE/l.

No data on the toxicity of MTBE to terrestrial organisms were identified.

With regard to the environmental fate of MTBE, the substance was found to be not readily biodegradable in aquatic screening tests (OECD tests) in which only very limited biodegradation was observed. Based on the physico-chemical properties of MTBE and constants for sorption to particulates and organic matter, the substance is considered to be highly mobile in soil. The bioconcentration potential of MTBE is insignificant.

The high vapour pressure of MTBE will lead to partitioning to the atmosphere when MTBE is released to surface waters or soil surfaces. If introduced into subsurface soils or to groundwater, e.g. in connection with leakage from underground tanks or separation wells, MTBE may be fairly persistent since volatilization to the atmosphere is reduced significantly. Due to its relatively high water solubility combined with little tendency to sorb to soil particles, MTBE can be expected to migrate to local groundwater supplies. Degradation of MTBE in groundwater aquifers is slow to non-existent under both aerobic and anaerobic conditions. If degraded, the primary degradation product in soil and groundwater is TBA (Tertiary Butyl Alcohol).

At contaminated sites (petrol stations), MTBE has been found in concentrations above 5 µg/l (the limit value for drinking water) in slightly fewer than 50% of the cases. In wells not associated with contaminated sites, the average concentration for all samples where MTBE was detected peaked at 14 µg/l in 2001 and then gradually fell, until it was below 1 µg/l in 2009.

Monitoring of MTBE in the effluents from municipal wastewater treatment plants performed as part of the national Danish environmental surveillance programme (NOVANA) shows low levels of MTBE, i.e. average values of 0.03-0.04 µg/l. No Danish monitoring data on MTBE in the natural environment (soil, surface water, biota, ambient air) have been identified.

**Human health effects and exposure**

MTBE is of low acute toxicity via oral and dermal end inhalation routes in both humans and test animals. Effects observed in patients exposed to MTBE during treatment for gallstones include central nervous system effects and local burning sensations. The kidney is the main target organ after repeated dosing, in particular in male rats. MTBE is classified as a skin irritant but is not considered an eye or respiratory irritant. MTBE has not been shown to cause sensitisation in two guinea pig studies, considered sufficient in terms of, but not formally following, OECD guidelines. There are no observations available on sensitisation in humans.

MTBE is not considered a mutagen based on results from a number of bacterial tests and is considered to be of a non-genotoxic nature. No firm conclusions regarding the carcinogenic potential of MTBE and the relevance for humans can be drawn based on the different carcinogenicity studies. In conclusion, the rapporteur of the RAR considers MTBE as a borderline case between non-classification and Carc.Cat.3 (limited evidence of carcinogenic effect).

In the EU, MTBE is prioritised for further evaluation of endocrine disrupting effects. The Danish Centre on Endocrine Disrupters has evaluated MTBE and concluded that MTBE should be categorised as an endocrine disrupter Category 1.

Exposure to MTBE would occur primarily from its use as an additive in petrol. Because of the voluntary agreement in Denmark between industry and government to phase out MTBE in petrol, exposure in Denmark has been reduced considerably since 2000. Only 31 service stations in Denmark offer 98 octane petrol containing MTBE and all are equipped with vapour recovery to reduce the exposure. No Danish exposure values are available. The RAR estimates that the normal concentration of MTBE during refuelling is 1,000-10,000 µg/m$^3$. The duration is short, e.g. between 1 and 5 minutes, and the frequency is 2-3 times per week at the most. The reasonable worst-case (RWC) concentration is 300-29,000 µg/m$^3$ where the low end would correspond to the MTBE-level in petrol in Denmark.

Occupational exposure to MTBE in Denmark is also primarily related to exposure to MTBE-containing petrol. Results from worst case measurements and EASE estimations of the identified occupational exposures (RWC, 8 hour) taking into account the low concentration of MTBE in Danish petrol do not give rise to particular concern when comparing with the occupational exposure limit. Use in the pharmaceutical industry is not expected to result in any significant exposure.

Indirect exposure can occur through air, drinking water and food. No measurements have been identified for Denmark, but urban background levels are expected to be lower than the average for the EU. MTBE has been identified in groundwater at contaminated sites in concentrations above the water quality criteria. Estimated MTBE levels in food do not indicate that MTBE is of concern.

Based on the available data, the RAR concludes that at present there is no need for further information and/or testing and no need for risk reduction measures beyond those which are currently being applied. This is also true in relation to combined exposure.

**Alternatives to MTBE**

The alternatives described are all considered to be technically relevant alternatives to MTBE. ETBE and ethanol can be produced from biomass, where the evaluation of appropriateness is specific to the source of biomass used. The EU sets requirements for this in Directive 2009/28/EC on the promotion and use of energy from renewable sources.

The classification of the possible alternatives does not give any indication of serious health effects or environmental impacts. It should be noted, though, that the classification criteria do not include endocrine disrupting effects and e.g. possible risk of groundwater contamination or negative organoleptic properties of the substances and, hence, such aspects cannot be assessed through the classification. However, none of the mentioned alternatives to MTBE are included on EU's list of substances with endocrine disrupting properties in Category 1. On the other hand, ETBE, chemically closely related to MTBE, could be suspected of having similar properties e.g. with regard to mobility in soil.

**Conclusions**
MTBE is considered undesirable mainly due to its suspected endocrine effects and very low taste and odour thresholds. The current risk reduction measures ensuring minimum contamination of the environment, including groundwater and exposure of workers, are therefore important to uphold in the future. It is noted that no valid data on possible endocrine effects of MTBE in the environment has been identified.

MTBE has previously been registered as a major potential groundwater contaminant, primarily at service stations where petrol containing MTBE has been stored. These sites have all been cleaned up under the programme carried out by the Environmental Fund of the Danish Oil Industry Association, EOF; hence, the risk of further contamination from these sites is considered limited.

The implementation of the Statuary Order on minimisation of risk of soil and groundwater contamination at petrol stations (Statuary order nr 555 af 09/06/2001) has tightened the requirements for technical installations at petrol stations (e.g. storage tanks and pipelines) and the monitoring thereof. This tightening will reduce the risk of future groundwater contamination with MTBE substantially, alongside the reduction of the use of MTBE in petrol and the number of sites where such petrol is sold. This reduction is assumed to continue despite the fact that the previous voluntary agreement ensuring this reduction is no longer in force.

The classification of the possible alternatives to MTBE does not give any indication of serious health effects or environmental impacts. However, the classification criteria do not include endocrine disrupting effects and e.g. possible risk of groundwater contamination or odour/off-taste properties of the substances and, hence, such aspects cannot be assessed through the classification. None of the MTBE alternatives are included on the EU's list of substances with endocrine disrupting properties (Category 1) but ETBE, chemically closely related to MTBE, could be suspected of having similar properties e.g. with regard to mobility in soil.

# Sammenfatning og konklusion

Denne rapport omhandler stoffet methyl-*tert*-butyl-ether, normalt omtalt som MTBE, der er en af de i alt 40 stoffer på Miljøstyrelsens Liste over uønskede stoffer (LOUS). For alle disse stoffer udarbejdes tilsvarende rapporter i perioden 2012-2015.

MTBE er en væske ved stuetemperatur, men når sit kogepunkt allerede ved 55 grader Celcius. Stoffet er meget mobilt i jord og er kendt for at give afsmag og lugt selv i meget lave koncentrationer i vand. Hovedanvendelsen af MTBE er som tilsætningsstof (additiv) til motorbenzin, hvor dets primære funktion er at øge oktantallet. MTBE har derudover en række mindre anvendelser f.eks. som råmateriale til fremstilling af isobutylen og som opløsningsmiddel til visse synteser inden for farmaceutisk industri.

**Lovgivning og anden regulering**
Lovgivning i Danmark og EU samt andre former for aftaler (f.eks. internationale konventioner), der relaterer sig til MTBE er blevet gennemgået som del af projektet. Det konkluderes overordnet, at der kun i begrænset omfang er lovgivning i EU eller Danmark, der specifikt regulerer anvendelsen af MTBE og eksponeringen af mennesker eller miljø for stoffet.

I EU-lovgivningen angives et maksimalt indhold for MTBE i motorbenzin (22 %), der også er implementeret i dansk lovgivning. Som følge af bekymring for mulig forurening af den danske grundvandsressource blev der i Danmark i 2000 indgået en frivillig aftale mellem branchen og Miljøministeriet, der indebar, at MTBE fremover kun måtte tilsættes 98-oktan benzin og kun blive forhandlet på et begrænset antal tankstationer. Aftalen eksisterer formelt ikke længere, men i realiteten er situationen med hensyn til anvendelse og salg af MTBE-holdig benzin i Danmark uændret. Der er ikke identificeret andre eksisterende eller planlagte initiativer i EU eller Danmark til begrænsning af anvendelsen af MTBE. Dog er der for 2014 planlagt en stofevaluering af MTBE under REACH, som Frankrig vil være ansvarlig for.

På EU-niveau er der kun en vejledende grænseværdi for eksponering i arbejdsmiljøet, mens der i Danmark findes en egentlig grænseværdi, der er lidt lavere end EU-værdien. Desuden er der i Danmark fastsat kvalitetskrav for MTBE i såvel vandmiljøet som i grundvand/drikkevand.

**Fremstilling og anvendelser**
MTBE blev introduceret i Europa i 1973 som et middel til at hæve oktantallet i motorbenzin, og har været anvendt udbredt til dette formål lige siden. Dog er forbruget gået ned i de senere år, hvor MTBE i stigende grad er blevet erstattet af (bio)-ETBE (ethyl-analogen til MTBE) som følge af krav fra EU om, at et vist minimum af indholdskomponenterne i brændstoffer skal være produceret ud fra fornybare ressourcer. Her er råmaterialet bio-ethanol (til ETBE) lettere tilgængeligt og billigere end bio-methanol (til MTBE). Således er produktionskapaciteten for MTBE i EU-landene gået ned fra 3,3 mill. tons i 2002 til 1,8 mill. tons i 2010. Den reelle produktion var i 2010 ca. 1,6 mill. tons.

Der vides at der eksporteres en del MTBE ud af EU, men der er omvendt også en import til Europa, primært fra USA. Det har dog ikke været muligt at få opdaterede tal for denne import/eksport specifikt for MTBE da Eurostat kun opgør tallet for en samlet gruppe af acykliske ethere (heriblandt MTBE).

Som følge af den føromtalte frivillige danske aftale om begrænsning af brugen af MTBE til 98-oktan benzin er forbruget af stoffet i Danmark meget lavt, det samlede registrerede forbrug var således mindre end 400 tons i 2012, hvoraf omkring 14 tons var til andre formål end som benzinadditiv. Forbruget af 98-oktan benzin og dermed også forbruget af MBTE i benzin solgt i Danmark ventes at falde yderligere i de kommende år.

De andre anvendelser af MTBE, som intermediær ved syntese af isobutylen af høj renhed samt som opløsningsmiddel i farmaceutisk industri mv., er således kvantitativt af begrænset betydning ift. anvendelsen som additiv til benzin, både internationalt og i Danmark.

**Affald**

MTBE produceres ikke i Danmark og omfanget af industrielle anvendelser (f.eks. i farmaceutisk industri) er meget begrænset. MTBE-affald fra sådanne anvendelser skal bortskaffes og behandles som farligt affald, almindeligvis ved destruktion ved forbrænding på et specialanlæg. Anvendelsen af MTBE i produkter/artikler er i realiteten begrænset til anvendelsen i benzin (98 oktan) og denne resulterer kun i meget små mængder affald på tankstationer (bundslam i tanke), der indsamles og bortskaffes kontrolleret ved forbrænding lige som industrielt MTBE-affald.

**Miljømæssige effekter og opførsel samt eksponering**

De miljømæssige egenskaber ved MTBE er gennemgået grundigt i EU's risikovurderingsrapport fra 2002, der fortsat anses for at være gyldig og dækkende. MTBE udviser ret lav giftighed over for vandorganismer med en laveste akut EC50 på 136 mg/l for krebsdyret *Mysidopsis bahia* og en laveste kronisk NOEC på 26 mg/l for den samme art. EU's rapport omtaler ikke mulige hormonforstyrrende effekter af MTBE i miljøet og der er heller ikke fundet andre pålidelige oplysninger om dette emne i litteraturen.

På grund af den velkendte kraftige lugt og smag af stoffet i vand er der udført en test for undvigeadfærd (”avoidance”) hos fisk (ål) tillige med en undersøgelse af afsmag (”tainting”), ligeledes med fisk (regnbueørred) som undersøgelsesobjekt. Afsmagsundersøgelsen viste, at MTBE kunne smages ved et eksponeringsniveau på 31 µg/l, men ikke ved 15 µg/l, men testen for undvigeadfærd med ål pegede på en vis tiltrækning mod den MTBE-behandlede zone ved en koncentration på 30 µg/l.

Der er ikke fundet oplysninger om giftigheden af MTBE over for terrestriske organismer.

Hvad angår opførsel og skæbne af MTBE i miljøet er stoffet fundet ikke at være let bionedbrydeligt i akvatiske screeningstest efter OECD's guideline, hvor kun meget begrænset omdannelse kunne observeres. Ud fra stoffets fysisk-kemiske egenskaber og begrænsede bindingsevne til partikler og organisk stof vurderes MTBE at være meget mobilt i jord. Stoffets potentiale for bioakkumulering vurderes som meget lavt.

På grund af sit høje damptryk vil MTBE primært være at finde i atmosfæren når det afgives til overfladevand eller jordoverflader. Hvis stoffet slipper ud under jordoverfladen, f.eks. fra utætte benzinlagertanke, vil det være ret persistent da muligheden for afgivelse til luft vil være begrænset. På grund af MTBEs ret høje vandopløselighed og dets lave binding til jordpartikler kan stoffet forventes at kunne forårsage forurening af grundvand. Det har vist sig, at MTBE ikke nedbrydes, eller i hvert fald kun meget langsomt, i grundvandsmiljøer. Hvis der sker en nedbrydning er det primære nedbrydningsprodukt stoffet TBA (tertiær butylalkohol).

I grundvandet under forurenede grunde, hvor der har ligget benzintanke, er MTBE påvist i koncentrationer over kvalitetskravet for drikkevand (5 µg/l) i op imod 50 % af tilfældene. I boringer, der ikke var relateret til forurenede grunde, var gennemsnitskoncentrationen af MTBE i alle de prøver, hvor stoffet blev påvist, 14 µg/l i 2001, hvor niveauet var højest, men aftog herefter gradvist til under 1 µg/l i 2009.

I prøver af renset spildevand fra renseanlæg udtaget i forbindelse med det nationale miljøovervågningsprogram, NOVANA, er MTBE kun påvist i lave koncentrationer, dvs. 0.03-0.04 µg/l. Der er ikke fundet data for MTBE i miljøprøver af jord, overfladevand, biologisk materiale eller luft.

**Sundhedseffekter og eksponering af mennesker**
Den akutte giftighed af MTBE er lav i såvel forsøgsdyr som mennesker, både ved indånding, indtagelse gennem munden og optagelse gennem huden. Der er observeret effekter på centralnervesystemet samt lokalt en brændende fornemmelse hos mennesker, der er blevet udsat direkte for MTBE i forbindelse med behandling med stoffet mod galdesten. Nyrerne er fundet at være det primære målorgan ved gentagne udsættelser for stoffet, primært hos rotter af hankøn. MTBE er klassificeret som hudirriterende, men anses ikke for at virke irriterende på øjet eller på åndedrættet. Der er ikke fundet tegn på sensibilisering i studier med marsvin og der er ikke fundet studier om sensibilisering af mennesker.

MTBE anses ud fra resultater af et antal bakterietest ikke for at være et mutagent stof og det anses for at være af ikke-genotoksisk natur. Der har ikke kunnet drages definitive konklusioner mht. eventuelle MTBEs kræftfremkaldende egenskaber ud fra de foreliggende undersøgelser. I EU's risikovurderingsrapport for MTBE konkluderes det, at MTBE er et grænsetilfælde mellem ikke at kræve klassificering og at kræve klassificering som Carc.Cat.3 (mulighed for kræftfremkaldende effekt) efter de gamle klassificeringsregler i Stofdirektivet (Dir. 67/548/EEC).

I EU er MTBE prioriteret med hensyn til evaluering af mulige hormonforstyrrende effekter. Det danske Center for Hormonforstyrrende Stoffer har evalueret MTBE og konkluderet, at stoffet bør kategoriseres som hormonforstyrrende i Kategori 1 (virkning påvist i mindst én levende organisme).

Human eksponering for MTBE hidrører overvejende fra dets anvendelse som additiv til motorbenzin. På grund af den tidligere eksisterende frivillige aftale mellem den danske regering og branchen om at udfase MTBE fra benzin i Danmark, med undtagelse af 98 oktan benzin, er eksponeringen faldet betydeligt siden 2000. Kun 31 tankstationer i Danmark sælger 98 oktan benzin med MTBE. Samtlige disse stationer er forsynet med systemer til genvinding af dampe for at reducere eksponeringen. Der findes ingen danske data for eksponeringen.

I EU's risikovurderingsrapport vurderes det, at den typiske koncentration af MTBE i luften i forbindelse med påfyldning er omkring 1,000-10,000 µg/m$^3$. Varigheden af eksponeringen af kort, dvs. mellem 1 og 5 minutter, og frekvensen er maksimalt 2-3 gange om ugen. Koncentrationen i den såkaldte "reasonable worst-case" (RWC) er 300-29,000 µg/m$^3$, hvor den lave ende svarer til indholdsniveauet for MTBE i dansk benzin (98 oktan). Resultater af estimeringer foretaget med EASE-modellen (RWC, 8 timer) under hensyntagen til den lave koncentration af MTBE i dansk benzin giver ikke anledning til særlig bekymring når der sammenlignes med den tilladte grænseværdi i arbejdsmiljøet. Anvendelsen af MTBE i farmaceutisk industri vurderes ikke at give anledning til nogen betydende eksponering for stoffet.

Indirekte eksponering kan ske gennem luft, drikkevand og madvarer. Der er ikke identificeret nogen danske måleresultater, men baggrundsniveauet i danske bymiljøer forventes at være lavere end gennemsnittet for EU. MTBE er påvist i grundvand under forurenede grunde i koncentrationer over drikkevandskravet. Skønnede niveauer af MTBE i madvarer antyder ikke, at stoffet skulle give anledning til bekymring.

På baggrund af de eksisterende data konkluderes det i EU's risikovurderingsrapport, at der for øjeblikket ikke er behov for yderligere information eller testning eller for risikoreducerende tiltag ud over dem, som allerede findes – også i forhold til kombineret eksponering.

**Alternativer til MTBE**

De beskrevne alternativer til MTBE vurderes alle at være teknisk relevante. ETBE og ethanol kan produceres fra biomasse, hvor evalueringen af egnetheden vil være specifik ift. oprindelsen af den anvendte biomasse jf. kravene i EU's direktiv om biobrændstoffers bæredygtighed mv. (Dir. 2009/28/EF).

Klassificeringen af alternativerne antyder ikke, at der skulle være alvorlige sundheds- eller miljømæssige effekter forbundet med nogen af dem. Det skal dog bemærkes, at klassificerings-kriterierne ikke omfatter hormonforstyrrende effekter eller egenskaber knyttet til risiko for grundvandsforurening eller afsmag i vand eller fødevarer, hvorfor sådanne aspekter ikke kan bedømmes ud fra stoffernes klassificering.

**Konklusion**

MTBE betragtes som "uønsket" hovedsageligt på grund af stoffets mistænkte hormonforstyrrende egenskaber og meget lave tærskelværdier for lugt og smag i vand og fødevarer. De eksisterende risikobegrænsende foranstaltninger, der skal sikre minimal eksponering af miljøet, herunder af grundvandet, og i arbejdsmiljøet, er derfor vigtige at opretholde fremover. Det bemærkes, at der ikke er fundet pålidelige data om eventuelle hormonforstyrrende effekter af MTBE i miljøet.

MTBE er tidligere blevet identificeret som et potentielt hovedproblem i forhold til forurening af grundvand, primært omkring tankstationer, hvor der har været opbevaret MTBE-holdig benzin. De forurenede tankstationsgrunde er alle blevet oprenset under det undersøgelses- og oprensningsprogram, der er gennemført under Oliebranchens Miljøpulje, og derfor vurderes risikoen for yderligere forurening fra disse at være meget begrænset.

Implementeringen af bekendtgørelse nr. 555 (2001) om forebyggelse af jord- og grundvandsforurening fra benzin- og dieselsalgsanlæg har bevirket en stramning af kravene til de tekniske installationer på tankstationer, herunder lagertanke og rørledninger, og til monitering heraf. Disse stramninger vil, sammen med den stadig mindre anvendelse af MTBE-holdig benzin, yderligere reducere risikoen for fremtidige grundvandsforureninger med MTBE. Det forventes, at udviklingen i retning af et mindre salg af MTBE-bezin vil fortsætte selv om den tidligere frivillige aftale mellem branchen og regeringen formelt ikke eksisterer længere.

Klassificeringen af de mulige alternativer til MTBE antyder ikke, at der skulle være alvorlige sundheds- eller miljømæssige effekter forbundet med nogen af dem. Det skal dog bemærkes, at klassificeringskriterierne ikke omfatter hormonforstyrrende effekter eller egenskaber knyttet til risiko for grundvandsforurening eller afsmag i vand eller fødevarer, hvorfor sådanne aspekter ikke kan bedømmes ud fra stoffernes miljø- og sundhedsklassificeringer. Ingen af alternativerne er registreret af EU som værende potentielt hormonforstyrrende i Kategori 1, men ETBE, som er kemisk nært beslægtet med MTBE, kan forventes også at have miljø- og sundhedsmæssige egenskaber af samme karakter som MTBE (f.eks. med hensyn til mobilitet i jord).

# 1. Introduction to the substance

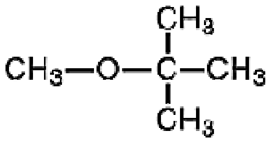
## 1.1 Definition of the substance

Methyl-*tert*-butyl ether is commonly abbreviated to MTBE (to be used in the report hereafter) and has CAS No. 1634-04-4 and EINECS No. 216-653-1. The IUPAC name is 2-methoxy-2-methylpropane. It is a man-made chemical with no known natural sources.

**TABLE 1**
NAME AND OTHER IDENTIFIERS OF MTBE

| | Substance name |
|---|---|
| EC number | 216-653-1 |
| CAS number | 1634-04-4 |
| Synonyms | Methyl-*tert*-butyl ether (MTBE)<br>2-methoxy-2-methyl propane |
| Molecular formula | $C_5H_{12}O$ |
| Molecular weight range | 88.15 |

The molecular structure of MTBE is as follows:



MTBE is considered chemically stable (European Commission, 2002). It does not polymerize or decompose under normal temperature conditions and, unlike many other ethers, does not tend to form peroxides during storage.

MTBE is known to have a rather strong, terpene-like odour and taste in water. The following odour and taste thresholds in water were used for the EU risk assessment of the substance (European Commission, 2002):

Odour threshold: 15 µg/l (reported range 2.5 - 190 µg/l)

Taste threshold: 40 µg/l (reported range 2.5 - 680 µg/l).

## 1.2 Physical and chemical properties

Some central physical and chemical properties of MTBE are presented in Table 3 below.

**TABLE 2**
PHYSICAL AND CHEMICAL PROPERTIES OF MTBE

| Property | | Reference |
|---|---|---|
| Physical state | Liquid | ECHA 2013a* |
| Melting point /Freezing point | - 108.6 °C | Do. |
| Boiling point | 55.3 °C | Do. |
| Relative density | 0.74 g/cm$^3$ (20 °C) | Do. |
| Vapour pressure | 33,000 Pa (25 °C) | Do. |
| Surface tension | 19.3 mN/m (25 °C) | Do. |
| Water solubility | 41,850 mg/L (20 °C; pH 7) | Do. |
| Log P (octanol/water) | 1.06 (20 °C; pH 7) | Do. |

* http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances.

## 1.3 Function of MTBE for main application areas

The dominant use of MTBE is as an additive to petrol, where its function is to increase the octane rating ("octane booster"). MTBE belongs to a group of chemicals with this function known as fuel oxygenates and was, until recently, the most widely used of such oxygenates in the EU. It has now been surpassed by the related ether ETBE.

Minor uses of MTBE include production of high-purity isobutylene and use as a speciality solvent e.g. as process reaction solvent in the pharmaceutical industry (European Commission 2002).

The European Commission (2002) states that 98.5% of the consumption in the EU (2.3 million tonnes in 1998) is as a fuel additive, while 1.2% is used for the production of isobutylene and only 0.3% as a solvent. During the last decade the consumption of MTBE is, however, believed to have decreased, mainly due to substitution by (bio-)ETBE (CONCAWE, 2012). This belief is due to the fact that fuel must currently have a certain minimum of components originating from biological material and that bio-ethanol is more easily available than bio-methanol (precursors of ETBE and MTBE, respectively).

# 2. Regulatory framework

This chapter gives an overview of how MTBE is addressed in existing and upcoming EU and Danish legislation, international agreements and by eco-label criteria.

Appendix 1 gives a brief, general overview of legal instruments in the EU and DK and how they are related. The appendix also gives a brief introduction to the chemicals legislation, explains the lists referred to in section 2.1.3, and provides a brief introduction to international agreements and selected eco-labelling schemes.

## 2.1 Legislation

This section first lists existing legislation addressing MTBE and then provides an overview of on-going or planned activities in relation to various REACH provisions.

### 2.1.1 Existing legislation

Table 3 provides an overview of existing legislation addressing MTBE. For each area of legislation, the table first lists the EU legislation (if applicable) and then possible transposition of this into Danish law and/or other national rules. The latter will only be elaborated upon in case of Danish rules differing from EU rules.

The EU legislation regulating the marketing and use of MTBE specifically is sparse and consists primarily of Directive 2009/30/EC on the specifications for petrol, diesel and gas oil, which is an update of Directive 98/70/EC. The directive establishes, among other aspects, the maximum content of MTBE ("ethers containing 5 or more carbon atoms per molecule") in market fuel at 22 % v/v (15 % in the former directive)[1]. However, other provisions in the directive, e.g. the permissible contents of oxygen and ethanol, have an indirect impact on the actual level of MTBE that can be added to fuels.

Directive 2009/28/EC on the promotion of energy from renewable energy sources establishes a target value for Bio-MTBE in Annex III, according to which 22 % of the energy content in MTBE produced on the basis of bio-methanol (35 MJ/kg) can be considered to originate from renewable resources (the target is that 10 % of the total energy used for transportation purposes is to be produced from renewable resources in 2020).

In Denmark, Directive 2009/30/EC is implemented in the national legislation by Statutory Order No. 366 of 15 April 2011, while Directive 2009/28/EC is implemented by Statutory Order No. 1402 of 15 December 2009. As for the EU directives, the provisions on maximum contents of oxygen and ethanol have a bearing amongst other factors (such as Xx, xx) on how much MTBE will be possible to add to fuels for vehicles in practice .

Waste is currently not considered a major issue in relation to MTBE, as most of the MTBE used in vehicles is combusted and thereby transformed (ultimately) to carbon dioxide and water. However, Statutory Order No. 555/2001 does contain provisions for collection and management of waste

[1] This is a consequence of a decision to increase the permitted level of ethanol in gasoline to 10 % (to enable a higher content of bio-fuel components in gasoline as required in EC directive 209/28/EC on energy from renewable sources), which corresponds to 3.7 % oxygen. This level of oxygen corresponds approximately to 22 % of "ethers containing 5 or more carbon atoms per molecule".

(sludges and other residues) at petrol and diesel service stations, which would include 98 octane petrol containing MTBE.

**TABLE 3**
EU AND DANISH LEGISLATION ADDRESSING MTBE

| Legal instrument *1 | EU/national | Substances | Requirements |
|---|---|---|---|
| **Legislation addressing quality and use of MTBE** | | | |
| Directive 98/70/EC on the quality of petrol and diesel fuels | EU | Petrol and diesel fuels including MTBE and other additives | Specification of max. contents of MTBE and other oxygenates in market fuels for vehicles (Annex I). Max. content 15% v/v. |
| Directive 2009/30/EC on the specifications for petrol, diesel and gas-oil | EU | Petrol and diesel fuels including additives | Updated version of 98/70/EC e.g. with regard to specification of max. contents of MTBE and other oxygenates in market fuels for vehicles (Annex I). Max. content increased to 22 % v/v. |
| Statutory Order no. 366 of 15.04.2011 (implements Dir. 98/70/EC and 2009/30/EC in Danish legislation) | DK | Petrol and diesel fuels including MTBE and other additives | Specification of max. contents of MTBE and other oxygenates in market fuels for vehicles (Annex I). Max. content 22 % v/v. |
| Directive 2009/28/EC on the promotion of the use of energy from renewable sources | EU | Renewable energy sources (bio-fuels) | Energy content of bio-MTBE (Annex III). Min. requirements to content of renewable energy components in fuels for transport. A minimum of 22 % should come from bio-methanol. |
| Statutory Order no. 1403 of 15.12.2009 on the sustainability of bio-fuels (implements Dir. 2009/28/EC in Danish legislation) | DK | Renewable energy sources (bio-fuels) | The Danish statutory order does not implement requirements to MTBE and related ethers as mentioned in Annex III of the EU Directive. |
| Statutory Order no. 1432 of 20.12.2012 on installations and activities where organic solvents are used | DK | VOC | Requirements to installations and activities where organic solvents are used, including pharmaceutical industry. |
| **Legislation addressing waste** | | | |
| Statutory Order No. 555 of 09.06.2001 on prevention of groundwater pollution from service stations | DK | Petrol and diesel for automobiles, which (may) contain MTBE | Among others, requirements regarding collection and management of storage tank sludge and residues in oil separators at service stations. |
| Statutory Order No. 650 of 29.06.2001 on landfill facilities | DK | MTBE (among many other substances) | Groundwater criteria that must be complied with at landfills (equal to drinking water criteria, see Statutory Order No. 1024 below) |
| **Legislation addressing emissions, and environmental and health quality criteria** | | | |
| Statutory Order No. 1022 of 25.08.2010 on requirements to the environmental quality of surface waters and to discharge of pollutants to rivers, lakes or the sea. | DK | MTBE (among many other substances) | Environmental Quality Standards for the aquatic environment:<br>AA-EQS for MTBE is 10 µg/L while MAC-EQS is 90 µg/L |

| Legal instrument *1 | EU/national | Substances | Requirements |
|---|---|---|---|
| Statutory Order No. 1024 of 31.10.2011 on water quality and control of water works and water distribution facilities | DK | MTBE (among many other substances) | Requirements to the maximum content of MTBE in drinking water when leaving the water works, at the entrance to the consumer's property, and at the consumer's tap.<br>The maximum permissible content is 5 µg/l. |
| Statutory Order No. 900 of 17.08.2011 on requirements to quality of environmental analyses | DK | MTBE (among many other substances) | Precision and sensitivity of MTBE analyses in water compartments and sediments. |
| **Legislation addressing work with substances and materials** | | | |
| Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work | EU | | MTBE is not specifically mentioned but is covered because it is classified as a dangerous chemical and it is and on the list of occupational limit values.<br>The Directive sets out rules for assessment and prevention of risks associated with hazardous chemical agents. |
| Danish Working Environment Authority Statutory Order No. 292 of 26/4/2001 on Work with Substances and materials (implements Directive 98/24/EC) | DK | | MTBE is not specifically mentioned but is covered because it is classified as a dangerous chemical and it is and on the list of occupational limit values.<br>The Order sets out rules for assessment and prevention of risks associated with hazardous chemical agents. |
| Directive 2009/161/EU on indicative occupational exposure limit values. | EU | MTBE (among many other substances) | Indicative occupational exposure limit for MTBE: 50 ppm (183.5 mg/m$^3$) |
| Danish Working Environment Authority (AT) Statutory Order No. 507 of 17 May 2011 on occupational limit values for substances and materials | DK | MTBE (among many other substances) | Occupational limit value (8 hours) for MTBE: 40 ppm (144 mg/m$^3$) |
| **Legislation addressing major accident hazards** | | | |
| Directive 96/82/EC of 9 December 1996 on the control of major accident hazards involving dangerous substances | EU | Highly flammable substances substances with a flash point lower than 21 $^o$ C (note 3(b)(2) | The Directive applies at qualifying quantities (tonnes) of MTBE of: 5000 tonnes (column 2) and 50000 (column 3) and sets out rules for prevention of accidents. |
| Statutory Order No. 1666 of 14/12/2006 on "control of major-accident hazards involving dangerous substances". (implements Dir. 96/82/EC in Danish legislation.) | DK | Highly flammable substances substances with a flash point lower than 21 $^o$ C (note 3(b)(2) | The order applies at qualifying quantities (tonnes) of MTBE of: 5000 tonnes (column 2) and 50000 (column 3) and sets out rules for prevention of accidents. |

| Legal instrument *1 | EU/national | Substances | Requirements |
|---|---|---|---|
| Danish Working Environment Authority Statutory Order No. 20 of 12/01/2006 on ”control with the work environment in relation to major-accident hazards involving dangerous substances | DK | Highly flammable substances substances with a flash point lower than 21 $^{o}$ C (note 3(b)(2) | The order applies at qualifying quantities (tonnes) of MTBE of: 5000 tonnes (column 2) and 50000 (column 3) and sets out rules for prevention of accidents. |

*1 Unofficial translation of name of Danish legal instruments.

Statutory Order No. 1022 of 25 August 2010 on environmental quality standards and requirements for discharges of polluting substances to rivers, lakes and the sea establishes environmental quality standards (EQS) for MTBE (among many other substances) in freshwater environments and marine waters. The annual average EQS (AA-EQS) for MTBE in both fresh and saltwater is 10 µg/L while the short term EQS (MAC-EQS) is 90 µg/L.

Statutory Order No. 1024 of 31 October 2011 on water quality and control of waterworks and water distribution facilities also comprises a threshold value for MTBE in groundwater/drinking water of 5 µg/L. This threshold value for MTBE in groundwater is also listed in the annex to Statutory Order No. 650 of 29 June 2001 on requirements for landfill facilities. It should be mentioned that this is a national Danish requirement regarding the quality of groundwater/drinking water, which is not included in the corresponding EC directives (98/83/EC for drinking water and 99/31/EC for the landfill of waste).

The Danish EPA (2010) has published a list of environmental quality criteria for several chemical substances in soils and drinking water. There is at present no criterion for MTBE in soil, while the criterion for groundwater/drinking water is the same as stated in Statutory Order No. 1024/2011, i.e. 5 µg/L. However, it is stated that a level of max. 2 µg/L should be aimed for.

With regard to limitation of air pollution from installations, the Danish EPA (2002, revised in 2008) has issued a Guideline for Air Emission Regulation. Closely related to this guideline are the C-value Guidelines, including the contribution values (in Danish: B-værdier). The C-value for MTBE is 0.3 mg/m$^3$.

In the working environment, the Danish limit value for 8 hour exposure to MTBE is 40 ppm (144 mg/m$^3$) (Statutory Order No. 507 of 17 May 2011), while the corresponding indicative EU limit value according to Directive 2009/161/EU is 50 ppm (183.5 mg/m$^3$).

### 2.1.2 Classification and labelling

The harmonised classification and labelling of MTBE is shown in Table 4. It shows that the substance is a flammable liquid (cat. 2) and a skin irritant (Cat. 2). MTBE is not classified with regard to environmental properties.

**TABLE 4**
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

| Index No | International Chemical Identification | CAS No | Classification | |
|---|---|---|---|---|
| | | | Hazard Class and Category Code(s) | Hazard statement Code(s) |
| 603-181-00-X | tert-butyl methyl ether; MTBE; 2-methoxy-2-methylpropane | 1634-04-4 | Flam. Liq. 2<br>Skin Irrit. 2 | H225<br>H315 |

The Classification of MTBE according to the Dangerous Substance Directive (67/548/EEC) is: F; R11 and Xi; R38.

The majority of industrial classifications submitted to ECHA are in agreement with the harmonised classification. An additional classification as Eye Irrit. 2 is suggested by 28 out of 1435 notifiers. Otherwise, deviations are only with regard to the labelling (choice of pictograms) and, therefore, most likely due to typing mistakes.

Furthermore, MTBE is included on the EU list of substances with suspected endocrine disrupting properties in Category 1: Substances for which there is *"evidence of endocrine disrupting activity in at least one species using intact animals"*.[2]

### 2.1.3 REACH

**Substance evaluation**
Table 5 shows that MTBE is scheduled for REACH substance evaluation under the Community Rolling Action Plan by 2014 with France as Rapporteur Member State. The suspected endocrine disrupting properties combined with the high tonnage/exposure potential are the grounds for concern.

**TABLE 5**
SUBSTANCES IN THE DRAFT COMMUNITY ROLLING ACTION PLAN, 2013-2015 UPDATE (ECHA, 2012)

| CAS No | EC No | Substance Name | Year | Member State | Initial grounds for concern |
|---|---|---|---|---|---|
| 1634-04-4 | 216-653-1 | Methyl-*tert*-butyl ether | 2014 | France | Suspected Endocrine Disruptor; Exposure/high tonnage and exposure for workers and consumers |

**Registry of Intentions**
The Registry of Intentions by ECHA and Member States' authorities list the existing proposals for restriction, for harmonised classifications and labelling and for identifying a chemical as a Substance of Very High Concern (SVHC). It also shows the possible intentions for introducing further restrictions on the import, use and marketing of a substance.

As of March 2013, MTBE is not included in the Registry of Intentions.

**Candidate list**
As of September 2013, MTBE is not included in the candidate list of SVHCs.

**Authorisation List / REACH Annex XIV**
Annex XIV is a list of substances requiring authorisation for continued use in the EU.
These substances are selected from the candidate list. As long as MTBE is not on the candidate list, it cannot be included in Annex XIV.

### 2.1.4 Other initiatives/agreements

[2] European Commission, DG ENV: http://ec.europa.eu/environment/endocrine/strategy/substances_en.htm

Whereas the official Danish legislation pertaining to the use of MTBE in petrol is in accordance with the EU legislation, the actual situation in Denmark is significantly different from that in the other EU Member States. This situation is due to an agreement made in November 2000 (and renewed in 2004) between the Danish Oil Industry Association (OFS, 2000) and the Danish Ministry of Environment, which came into effect in the summer of 2001. According to the agreement, MTBE and related ethers are only allowed for use in 98 octane petrol. The background for the agreement was a concern in the Ministry of Environment that the use of MTBE could pose a significant risk of severe groundwater contamination as demonstrated in several cases, e.g. in California, USA. This concern led to the formulation in 1998 by the Danish EPA (Miljøstyrelsen) of a national action plan for MTBE (Miljøstyrelsen, 1998).

The agreement also significantly reduced the number of service stations where 98 octane petrol could be purchased by establishing strict requirements on the technical standards of the stations with regard to prevention, detection and collection of possible spills or leakages (Statutory Order No. 555/2001).

However, due to judicial issues related to possible constraints to competition, around 2005 the Danish Competition and Consumer Authority expressed some reluctance concerning the agreement, which was therefore discontinued. However, in practice the situation has so far continued unchanged on an individual, non-formalised basis.

To the knowledge of the Danish Oil Industry Association (EOF, 2013, pers. comm.) there are no other existing or ongoing initiatives in other EU Member States regarding restrictions on the use or sale of MTBE.

## 2.2 International agreements

Table 6 gives an overview of various international agreements addressing the use, trade, transboundary movement and/or emissions of hazardous chemical substances. As appears from the table, MTBE is not addressed as a specific substance by the listed conventions.

**TABLE 6**
INTERNATIONAL AGREEMENTS ADDRESSING MTBE

| Agreement | Substances | How MTBE is addressed |
|---|---|---|
| **OSPAR Convention** | MTBE | Not addressed |
| **HELCOM (Helsinki Convention)** | MTBE | Not addressed |
| **Rotterdam Convention (PIC Convention)** | MTBE | Not addressed |
| **Stockholm Convention** | MTBE | Not addressed |
| **Basel Convention** | MTBE | Not addressed |
| **Convention on Long-range Transboundary Air Pollution (CLRTAP)** | MTBE | Not addressed |

## 2.3 Eco-labels

MTBE is not addressed, either as a substance or a component of certain types of petrol, by the EU or Nordic labelling schemes (the EU "flower" and the Nordic "Swan"). In general, petrol is not a product category being eco-labelled.

## 2.4 Summary and conclusions

EU and Danish legislation is targeted towards the use of MTBE in petrol and related human exposure and environmental emissions during this use and waste handling. At the EU level, a limit for the contents in petrol for vehicles exists, which is implemented into the Danish legislation. In addition to this, a voluntary agreement was made in Denmark in 2000 between industry and the Ministry of Environment according to which MTBE was only to be added to 98 octane petrol, which, additionally, would only be sold at a limited number of service stations. Though this agreement does not formally exist anymore, the situation is in reality unchanged with regard to the sale and use of 98 octane petrol in Denmark. Due to the suspected endocrine disrupting properties and the widespread use of MTBE in Europe, a REACH substance evaluation is planned for 2014. No other current risk management activities on MTBE have been identified.

In the EU, only an indicative Occupational Exposure Limit exists, whereas for the Danish situation, a limit value for MTBE in air in the working environment has been introduced (slightly lower than the EU indicative OEL). Furthermore, official standards for MTBE concentrations in fresh and marine surface waters and in groundwater/drinking water have been established and are implemented through national statutory orders. This comes as a result of concern about MTBE in Denmark's environment, leading to the formulation of a National Action Plan in 1998 and the identification of the substance as "undesirable" (LOUS list).

# 3. Manufacture and uses

## 3.1 Manufacture and use of MTBE

### 3.1.1 Manufacturing processes

According to the Risk Assessment Report (RAR) for MTBE published by the European Chemicals Bureau (European Commission, 2002), commercial production of MTBE started in Europe in 1973 and in the USA in 1979. MTBE manufacturing typically takes place in petroleum refineries but also in other organic industrial chemical plants.

The principal way of synthesizing MTBE is by reaction of isobutene (isobutylene) with methanol over an acidic ion-exchange resin catalyst under pressure and at a relatively low temperature; 38-93 °C (the reaction is reversible and can also be used to produce high-purity isobutene from MTBE). It can also be synthesized from methanol, *tert*-butyl alcohol (TBA) and diazomethane.

There are four different sources of isobutene for the MTBE synthesis:

- "Field butanes" i.e. mixed butanes isomerised and dehydrogenated to yield isobutene;
- propylene oxide;
- steam cracker C4s (where isobutene is simply extracted as a by-product from the cracking), and
- fluid catalytic cracker C4s (very similar to steam cracking).

The plants producing the two former feedstocks are often big, having capacities at or exceeding 500,000 tonnes/year (European Commission, 2002). The types of MTBE plants are:

- Refinery-based plants using Fluidized Catalytic Cracking Units (FCCU).
- Refinery-based plants using FCCU and raffinate feed.
- Merchant plants using raffinate feed.
- Merchant plants using TBA from propylene oxide production.

### 3.1.2 Manufacturing sites

In 1997, there were 25 companies in Europe producing MTBE at 35 facilities in 11 different EU countries. About 30 % of the total tonnage of about 3.0 million tonnes was produced in 1997 in The Netherlands, while 18 % was produced in France, 13 % in Germany and 10 % in Spain (European Commission, 2002). There has never been any production of MTBE in Denmark.

The leading European oil producers' environmental branch organisation, CONCAWE, reports that in 2010 there were about 55 facilities with fuel oxygenate production capacity in the EU, with 50 % of the production capacity was located in Germany, France and the Netherlands (CONCAWE, 2012). The two largest production facilities are located in The Netherlands and France, each with a capacity of close to 600,000 tonnes/year.

An overview of location and capacity of plants within the European Union producing MTBE, ETBE and TAME in 2010 is given in Figure 1 below. As seen, the production of MTBE is distributed throughout many European countries (15) with most of the production units being located in Italy, Romania and the UK.

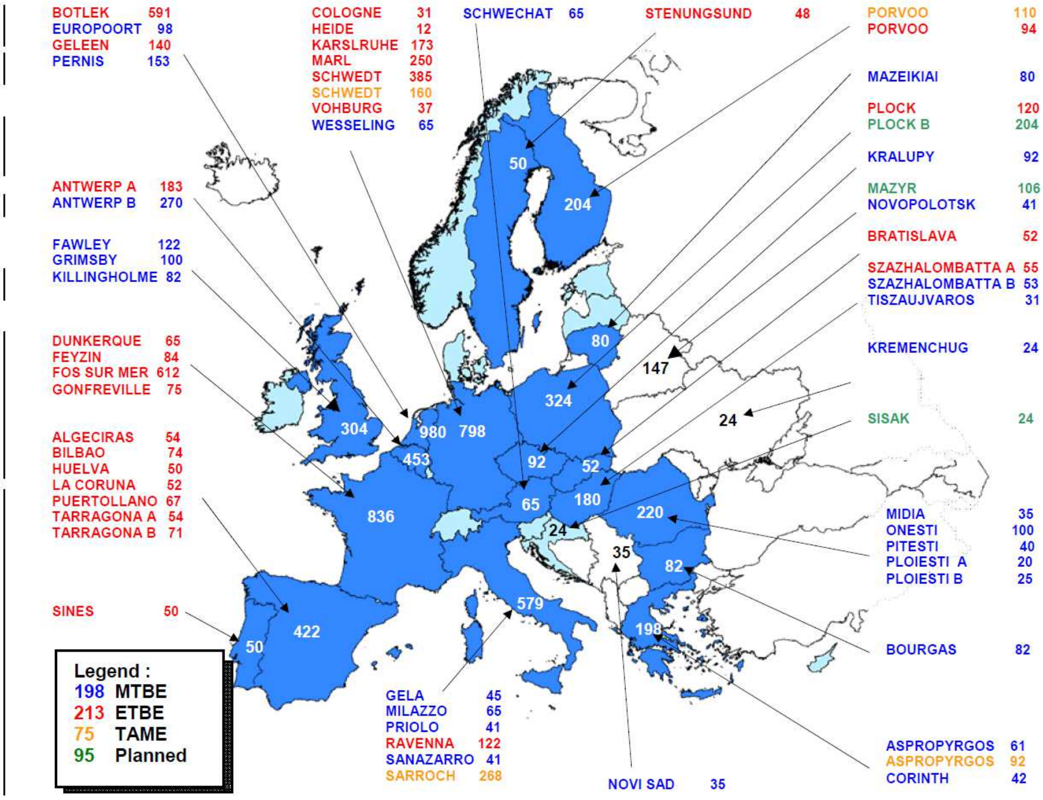



**FIGURE 1**
**OVERVIEW OF PRODUCTION FACILITIES FOR MTBE, ETBE AND TAME IN EUROPE IN 2010. PRODUCTION CAPACITIES IN KTONNES/YEAR. ACTUAL PRODUCTION VOLUMES MAY BE DIFFERENT. COUNTRIES IN WHITE WERE NOT PART OF THE STUDY (REPRODUCED FROM CONCAWE, 2012).**

Figure 2 shows the recent trends in the EU production capacities of MTBE, ETBE and TAME. As seen, MTBE production capacity has been reduced by almost 50% since 2002 and replaced by (bio-) ETBE. See section 3.1.3 for actual production volumes.

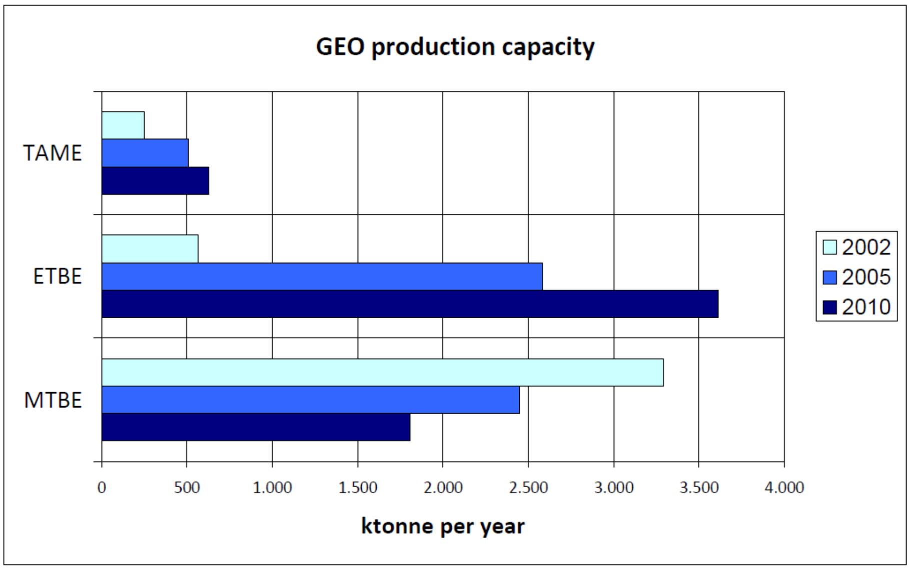



**FIGURE 2**
**TRENDS IN THE PRODUCTION CAPACITIES OF MTBE, ETBE AND TAME IN THE EU, 2002 – 2010 (REPRODUCED FROM CONCAWE, 2012).**

### 3.1.3 Manufacturing volumes

MTBE is not, and never was, manufactured commercially in Denmark. The Danish production volume is zero.

In the EU, the actual MTBE production volume in 1997 was 3,030,200 tonnes, of which 2,126,400 tonnes were consumed in the EU and 903,800 tonnes were exported (European Commission, 2002).

The Fuel Ether REACH Consortium (FERC) formed for registration of MTBE in the EU has about 60 members with an accumulated volume of 1,000,000 – 10,000,000 tonnes/year. REACH volumes cover import to, as well as manufacturing in, the EU. All individual submissions are above the highest REACH tonnage trigger of 1000 tonnes/year. None of the consortium members are located in Denmark.

**TABLE 7**
IDENTIFIED MTBE PREREGISTRATION WITH INDICATION OF REGISTERED TONNAGE AS OF JUNE 2013.

| CAS No | EC No | Substance name *1 | Abbr. | Registered, tonnage band, t/y *2 |
|---|---|---|---|---|
| 1634-04-4 | 216-653-1 | Methyl-*tert*-butyl ether | MTBE | Individual Submission:<br>10,000-100,000<br>Joint submission:<br>1,000,000-10,000,000 |

*1 Chemical name according to pre-registration/registration.
*2 As indicated in the lists of pre-registered and registered substances at ECHA's website.
For each separate registration (which may cover more than one manufacturer) the registered tonnage is indicated.

In 2010, the total production capacity for petrol oxygenates (MTBE, ETBE and TAME) in the EU was 6.05 million tonnes in total. More than 3.5 million tonnes of this capacity was for production of ETBE, while that for MTBE was approximately 1.8 million tonnes. The production of ETBE has increased dramatically since 2002, while MTBE production has declined to about 60 % of the 2002 capacity (CONCAWE, 2012).

According to the EU RAR for MTBE (European Commission, 2002), the worldwide production capacity in 1994 was 20.6 million tonnes/year. The actual worldwide production was about 15 million tonnes in 1995 and about 21 million tonnes in 1999. Updated figures on worldwide production have not been identified.

An overview of the European production capacities for petrol ether oxygenates (GEO) in different EU countries is shown in Figure 3 below (CONCAWE, 2012).

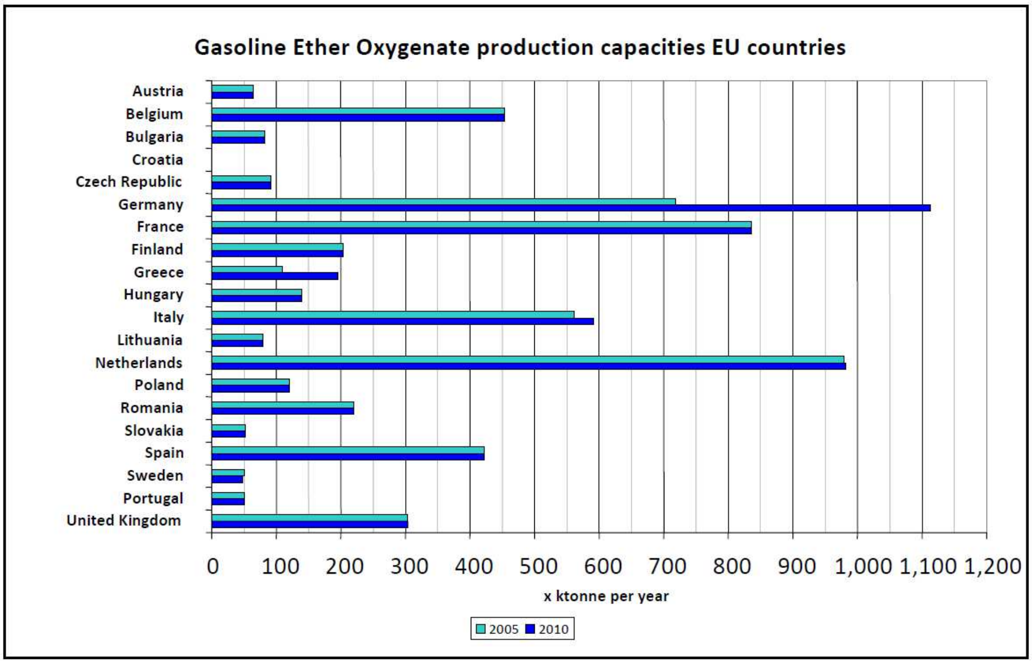



**FIGURE 3**
**OVERVIEW OF PRODUCTION CAPACITIES FOR MTBE, ETBE AND TAME IN DIFFERENT EUROPEAN COUNTRIES IN 2005 AND 2010 (REPRODUCED FROM CONCAWE, 2012).**

According to the European Fuel Oxygenates Association, EFOA (pers. comm., 2013), the actual production volume of MTBE in the EU was approx. 1.4 million tonnes in 2009, 1.6 million tonnes in 2010 and 2.0 million tonnes in 2011. EFOA did not have any information about the worldwide production volume for MTBE.

The volume of MTBE produced in the EU in recent years for uses other than as a fuel additive is not known but is much less than this. The EU RAR (European Commission, 2002) mentions that the volume of MTBE in 1997 used for other purposes was about 1.5 % of the total volume.

## 3.2 Import and export

### 3.2.1 Import and export of MBTE in the EU

According to the EU RAR (European Commission, 2002), the import of MTBE to the EU decreased from 317,000 tonnes in 1994 to 187,000 tonnes in 1997, and then increased again to 291,000 tonnes in 1999. During the same period, the export of MTBE from the EU increased markedly from 207,000 tonnes in 1994 to 935,000 tonnes in 1999. Eight-three percent of the exported volume was exported to the USA and Canada.

Specific, updated figures for the import/export of MTBE at the EU level have not been identified.

CONCAWE (2012) states that “detailed import and export numbers of GEO in the EU are currently not known” (GEO = Gasoline Ether Oxygenates). However, it is mentioned that in 2003, 539,000 tonnes were exported out of the EU while the corresponding import figure was 609,000 tonnes. A peak import from the USA was reached in 2006 (caused by the phasing-out of MTBE in petrol in the USA[3]) at almost 1,000,000 tonnes. In 2009, the import from the USA had decreased to 250,000 tonnes.

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[3] In the USA, Congress passed The Energy Policy Act in 2005 that removed the oxygenate requirement for reformulated gasoline (RFG). At the same time, Congress also instituted a renewable fuel standard. In response,

**European statistics on manufacture and import/export of MTBE on its own**
Eurostat (2012) has no figures on the import and export of MTBE as a separate chemical substance, only as part of a group of various acyclic ethers with the CN8 code:

2909 - Ethers, ether-alcohols, ether-phenols, ether-alcohol-phenols, alcohol peroxides, ether peroxides, ketone peroxides (whether or not chemically defined), and their halogenated, sulphonated, nitrated or nitrosated derivatives.

This group is considered too diverse to use for estimating import/exports of MTBE.

### 3.2.2 Import and export of MTBE in Denmark

The import of MTBE and other ethers as retrieved from Statistics Denmark (2013) is shown in the table below.

**TABLE 8**
DANISH IMPORT AND EXPORT OF ETBE AND OTHER ETHERS (INCLUDING MTBE) (STATISTICS DENMARK, 2013)

| CN8 code | Text | Import, t/y | | Export, t/y | | Production t/y | |
|---|---|---|---|---|---|---|---|
| | | Average 2007-2011 | 2012 | Average 2007-2011 | 2012 | Average 2007-2011 | 2012 |
| 29091910 | Tert-butyl ethyl ether (ethyl-tertio-butyl-ether, ETBE) | 502.8 | 57.4 | 0.57 | 0 | 0 | 0 |
| 29091990 | Acyclic ethers and halogen-, sulfo-, nitro- or nitroso derivatives of these (except diethyl ether and tert-butyl ethyl ether [ethyl-tertio-butyl-ether, ETBE]) | 13,000 | 4,220 | 130.4 | 23.1 | 0 | 0 |

According to information obtained from the Danish Oil Industry Association (EOF, formerly named OFS) (2013, pers. comm.), the import to and export from Denmark of MTBE used as a fuel additive has decreased considerably in recent years. Thus, the total import in 2007 was 30,077 tonnes while the same figure in 2012 was only 3,985 tonnes. Most of this tonnage was re-exported in the form of MTBE-oxygenated petrol formulated at Danish refineries. Complete figures for the period 2007-2012 are provided in Table 9 below.

According to information from the Danish Oil Industry Association (EOF, 2013, pers. comm.), formulated 98 octane petrol is not imported to Denmark anymore.

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the refiners made a wholesale switch removing MTBE and blending fuel with ethanol. According to EPA's RGF Survey Data, MTBE has not been used in significant quantities in RFG areas since 2005. A similar decrease in MTBE use has also been observed in conventional gasoline areas (US EPA, 2013).

**TABLE 9**
IMPORT/EXPORT FIGURES FOR MTBE USED AS FUEL ADDITIVE TO/FROM IN DENMARK, 2007-2012. SOURCE: DANISH OIL INDUSTRY ASSOCIATION (EOF, 2013, PERS. COMM.)

| Substance | Year | Import (tonnes) | Export (tonnes)* | Consumption in Denmark (tonnes)* |
|---|---|---|---|---|
| MTBE | 2007 | 30,077 | 28,977 | 1,100 |
| | 2008 | 26,988 | 26,238 | 750 |
| | 2009 | 13,435 | 13,035 | 400 |
| | 2010 | 23,004 | 22,754 | 250 |
| | 2011 | 11,698 | 11,498 | 200 |
| | 2012 | 3,985 | 3,410** | 575** |

* Approximate figures

** Exact figures, reported to the Danish Prodcut Registry in August 2013

## 3.3 Uses of MBTE

### 3.3.1 Uses of MTBE in the EU

The vast majority of the MTBE consumed in the EU is used as an additive (octane booster) in petrol. The EU Risk Assessment Report (RAR) for MTBE (European Commission, 2002) reports that 98.5 % of the total volume of MTBE produced in the EU in 1997 was allocated to this usage. The current EU legislation (Directive 2009/30/EC) allows as much as 22 % content of MTBE in petrol (previously only 15 %); however, normally the percentage used in petrol is significantly lower. In the RAR, average contents of MTBE in 1997 in different European countries are presented that range from 0.2 % (Denmark) to 8.5 % (Finland) with most levels between 1.5 and 4.0 %. The levels have tended to increase in later years due to the phasing out of lead, restrictions on content of aromatics in petrol etc. CONCAWE (2012) reports a median level of 4.25 % in the period 2000-2009.

Of the remaining 1.5 % of the consumption of MTBE in the EU in 1997 (corresponding to about 30,000 tonnes), 1.2 % was used for production of high-purity isobutene while the last 0.3 % were for different uses as a solvent, e.g. in the pharmaceutical industry (all these uses considered to be in closed systems). Minor application areas include use as chromatographic eluent and as a therapeutic agent for *in vivo* dissolution of cholesterol gallstones in humans (European Commission, 2002).

### 3.3.2 Uses of MTBE in Denmark

The uses of MTBE are, in principle, the same as in the EU in general. However, due to the voluntary agreement in Denmark in 2000 (renewed in 2004) between industry and the government to phase out the use of MTBE in petrol except in 98 octane petrol, the relative distribution of the total consumption of MTBE in the main use categories differs slightly from the EU figures mentioned above. Today, there is limited use of 98 octane petrol in Denmark, which is only for sale at 31 service stations nationwide (EOF, 2013).

Thus, the total amount of MTBE imported to Denmark in 2012, as registered by the Danish Product Register (2013)[4], was approx. 391 tonnes, of which 377 tonnes or 96 % was registered in the

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[4] The Danish Product Register includes substances and mixtures used occupationally and which contain at least one substance classified as dangerous in a concentration of at least 0.1% to 1% (depending on the classification of the substance). MTBE is only classified as a Class 2 Skin Irritant. For the other non-classified substances, the registration will only occur if they are constituents of mixtures which are classified and labelled as dangerous due to the presence of other constituents. The data consequently do not provide a complete picture of the presence of the substances in mixtures placed on the Danish market. On the other hand, for substances included

categories "fuel" and "fuel additives". The remaining 14 tonnes (4 %) were registered under a number of different categories, primarily different uses as a solvent or as "raw material". There is a current use of MTBE in Denmark as a process solvent in a few specific productions within the pharmaceutical industry (Danish EPA, 2013, pers. comm.).

It is noted that there is a significant discrepancy between the figure for consumption as a fuel additive in Denmark provided by the Danish Association of Oil Industries, EOF (Table 9), and the figures registered by the Danish Product Register (PR). The reason for this discrepancy appears to be an error in the reporting of data to the PR (Statoil, pers.comm. 2013). Updated figures have been reported to the PR after the data collection for this report was finalised (see, however, the corrected figures for 2012 in Table 9).

## 3.4 Historical trends in use

The production and use of MTBE as a fuel additive in the EU peaked in the late 1990s but now tends to be replaced by ETBE in several countries, which is reflected in the MTBE consumption being only slightly more than 50 % of the consumption 10-12 years ago.

In Denmark the use and consumption of MTBE as a fuel additive has decreased significantly following the voluntary phase-out agreement between the oil industry and the Danish government in 2000, and today the consumption is only a small fraction of what it was before 2000.

No information has been obtained on the historical trends in use for the various application areas for MTBE other than as fuel additive.

## 3.5 Summary and conclusions

MTBE was introduced as an octane booster for petrol in 1973 in Europe and has been applied extensively for this use since then; however, in recent years the consumption has decreased as MTBE is gradually being replaced by (bio-) ETBE. This decrease is mainly due to the introduction of EU requirements regarding contents in fuel of components produced from renewable sources such as bio-ethanol, which is a precursor of ETBE and is more easily available than bio-methanol (precursor of MTBE). Thus, the production capacity of MTBE in the EU has decreased from about 3,300 ktonnes in 2002 to about 1,800 ktonnes in 2010. Some of the produced MTBE is exported outside the EU but there is also an import to the EU, primarily from the USA.

Other uses of MTBE, e.g. as an intermediate in the production of high purity isobutylene or as a process solvent in the pharmaceutical industry, are quantitatively only of minor importance compared to the main use as a petrol additive (in the range of 1-2%).

Due to a voluntary agreement between industry and the Danish government, since 2000 the use of MTBE in petrol in Denmark has been restricted to 98 octane petrol, sold only at a very limited number of service stations. The agreement is now formally discontinued but the situation remains unchanged and therefore the annual consumption of MTBE for use in petrol is at a level of only a few hundred tonnes. The consumption of MTBE in Denmark for other purposes totalled about 14 tonnes in 2012.

Updated information on import/export of MTBE in the EU has not been possible to obtain.

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in mixtures used for formulation of other mixtures in Denmark (e.g. those included in raw materials used for production of paint), the quantities may be double-counted as both the raw material and the final mixture in the register. As stated above, the amounts registered are for professional use only, but for substances used for the manufacture of mixtures in Denmark, the data may still indicate the quantities of the substances in the finished products placed on the market both for professional and consumer applications.

# 4. Waste management

### 4.1 Waste from manufacture and industrial use of MTBE

There is no manufacture of MTBE in Denmark and therefore no waste generation from processes related to the synthesis and production of the substance in Denmark. Neither is the use of MTBE as a chemical intermediate to produce high-purity isobutylene relevant to Denmark.

The industrial applications of MTBE also include use as a process solvent in the pharmaceutical industry and as a solvent and chromatographic eluent in laboratories. MTBE-containing waste from these uses must, according to Danish legislation, be disposed of as hazardous waste.

### 4.2 Waste products from the use of MTBE in mixtures and articles

The vast majority of MTBE is used as an additive to 98 octane petrol. By this use, MTBE is combusted and thereby transformed to water and carbon dioxide; therefore, the use as a fuel additive does not in itself lead to generation of waste. However, at service stations selling 98 octane petrol, a limited amount of water and sludge may build up in storage tanks over time (perhaps 100-200 litres in one tank) and will be removed when needed; however, typically only once every 10th year in connection with the mandatory inspection of the tanks according to the current Danish legislation (EOF, 2013, pers. comm.)[5]. Such waste is classified as hazardous waste and, in Denmark, will typically be transported to Nord A/S (formerly named Kommunekemi) for destruction by incineration, thereby not generating amounts of waste for disposal of any practical significance.

The EU RAR (European Commission, 2002) mentions that MTBE is also used therapeutically to dissolve cholesterol gallstones in humans *in vivo*. This is considered to be a very minor use of MTBE, not leading to waste generation of any significance (waste would be disposed of as hazardous waste).

### 1. Release of MTBE from waste disposal

Based on the above, it is estimated that virtually no MTBE is disposed of as waste and, hence, release from waste disposal is not a relevant issue for this chemical substance.

### 4.3 Summary and conclusions

MTBE is not manufactured in Denmark and the extent of industrial uses (e.g. as process solvent) is limited. MTBE-waste from such uses should be handled as hazardous waste and destroyed by incineration. The use of MTBE in mixtures and articles, actually mainly including 98 octane petrol, only results in small volumes of waste at service stations, which is subject to controlled collection and subsequent destruction similar to industrial MTBE-waste. The vast majority of MTBE will be combusted during its use as a petrol additive.

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[5] Statuary order no. 555 of 09.06.2001 on prevention of soil and groundwater contamination from service stations contains requirements for measuring of liquid volumes in oil separators and related alarms which may trigger emptying at more frequent intervals.

# 5. Environmental effects and fate

## 5.1 Environmental hazard

### 5.1.1 Environmental classification

None.

### 5.1.2 Effects in the aquatic environment

The EU RAR for MTBE (European Commission, 2002) finds that there is a reasonable amount of data from studies of an acceptable quality available for assessment of effects of MTBE in the aquatic environment. An overview of the results of the main studies, all with endpoints based on measured concentrations, is presented in Table 10 below.

**TABLE 10**
OVERVIEW OF DATA ON TOXICITY OF MTBE TO AQUATIC ORGANISMS IN LABORATORY STUDIES (DATA FROM EUROPEAN COMMISSION, 2002).

| Group | Species | Study type | Endpoint | Value (mg/l) |
|---|---|---|---|---|
| Fish, freshwater | *Pimephales promelas* | 96, flow-through or static renewal | LC50 | 672-980* |
| | *Onchorhynchus mykiss* | 96 h, flow-through | LC50 | 887 |
| | *Lepomis macrochirus* | 96 h, flow-through | LC50 | 1054 |
| | *Pimephales promelas* | 7 days, static renewal | NOEC | 234 |
| | *Pimephales promelas* (eggs) | 31 days, flow-through | IC20 | 279 |
| Fish, marine | *Menidia beryllina* | 96 h, static renewal | LC50 | 574 |
| | *Gasterostus aculeatus* | 96 h, flow-through | LC50 | 929 |
| | *Cyprinodon variegatus* | 96 h, flow-through | LC50 | 1358 |
| Invertebrates, freshwater | *Daphnia magna* | 48 h, flow-through or static renewal | EC50 | 472-681** |
| | *Cerodaphnia dubia* | 48 h, static renewal | LC50 | 340 |
| | *Daphnia magna* | 21 days, flow-through | NOEC | 51 |
| Invertebrates, marine | *Mysidopsis bahia* | 96 h, flow-through | EC50 | 136 |
| | Five other marine species | 96 h, flow-through | EC50/LC50 | 150-306 |
| | *Mysidopsis bahia* | 28 days, flow-through | NOEC | 26 |
| Algae | *Selenastrum capricornutum* | 96 h, static | ErC50 | 184 |
| | *Selenastrum capricornutum* | 96 h, static | IC20 | 103 |

* Summary of four studies (3 of 4 were flow through)

** Summary of three studies (1 flow through)

It appears from the above data that, whereas the toxicity of MTBE to freshwater and marine species of fish seems to be approximately the same, the substance tends to be more toxic to marine species of invertebrates than to freshwater species. The toxicity level for algae corresponds to the toxicity for marine invertebrates. In any case, the ecotoxicity is so low that it does not qualify for environmental classification of MTBE with respect to aquatic toxicity.

Therefore, the critical endpoints are the acute EC50 of 136 mg/l for the marine invertebrate *Mysidopsis bahia* and the corresponding chronic NOEC of 26 mg/l for the same species.

Based on the data presented above, the EU Commission (2002) calculates a PNEC of 2.6 mg/l for the aquatic compartment.

In an addendum to the EU RAR (European Commission, 2003), results of a fish tainting study and a fish avoidance test with MTBE are presented:

The fish tainting test was carried out with rainbow trout (*Onchorhynchus mykiss*) and showed that it was possible to taste MTBE in fish exposed to a concentration (measured) of 31 µg/l at a significance level of 5 %, while no such effect could be distinguished at an exposure level of 15 µg/l.

Possible avoidance behaviour was studied in a flow-through test with juvenile stages of eel (*Anguilla anguilla*) exposed to a concentration of MTBE in water of 30 µg/l. The eels were allowed to move freely between the fully exposed zone ("impact zone") and a control zone with clean water (and a mixed zone in between). A significant difference in the distribution of the eels between the two zones was noted; the eels were significantly more present in the exposed zone than in the control zone.

Thus, the eel, a species known to have a very sensitive olfactoric system, apparently does not show avoidance behaviour at the concentration tested (rather the opposite). However, as eels are known to be attracted to organic molecules it cannot be excluded that other species with different feeding behaviour would try to avoid MTBE exposure.

The RAR (European Commission, 2002) does not contain any data or make mention of information on endocrine-disrupting effects of MTBE in the environment and no valid information on this issue has been identified in other data sources identified and reviewed in this project.

### 5.1.3 Effects in the terrestrial environment

The EU RAR (European Commission, 2002) does not identify any data on the toxicity of MTBE to terrestrial or soil dwelling organisms. Therefore, a PNEC for the soil compartment was calculated using aquatic data and the equilibrium partitioning method. Using this method, a $PNEC_{SOIL}$ of 0.730 mg/kg wwt was determined.

It is also concluded that due to the low bioconcentration factors (BCFs) of MTBE (calculated and measured), secondary poisoning is not likely.

### 5.1.4 Effects in the air compartment

MTBE is considered to be only a negligible contributor to depletion of ozone (European Commission, 2002). There is no information about MTBE as a greenhouse gas.

## 5.2 Environmental fate

### 5.2.1 Partitioning/distribution

Basic physico-chemical properties of MTBE (see section 1.2) of relevance for the assessment of the distribution in the environment are e.g. the vapour pressure, the water solubility and the octanol-water partitioning coefficient.

From the vapour pressure and water solubility, a Henry's Law Constant, H, of 56.7 Pa·m³/mol at 20 ºC is derived (there are measured values between 43.8 and 53.5 Pa·m³/mol) indicating that MTBE volatilises easily from water to air (European Commission, 2002).

Using a level 1 fugacity model, the theoretical distribution between the main environmental compartments was found to be 93.9 % in air, 6.05 % in water and 0.05 % in soil. At lower temperatures, the fraction in air will be lower and the fraction in water correspondingly higher (European Commission, 2002).

Physisorption is the dominant sorption mechanism for MTBE while chemisorption is not expected. Some sorption on minerals will take place but sorption to organic material is a more significant process. The organic carbon normalised partitioning coefficient between water and soil, $K_{OC}$, is estimated by QSAR to be in the range 9-12, which indicates a high potential for mobility in soil with a resulting high likelihood of groundwater contamination in case of spills or tank/pipeline leakages (European Commission, 2002).

### 5.2.2 Fate in the aquatic environment

The EU RAR (European Commission, 2002) concludes, based on results from the OECD 301D d tests (Closed Bottle test), that MTBE is not readily biodegradable in water. In one of the tests conducted, no degradation at all was observed after 28 days (the duration of the test) while in another test, 1.8 % degradation was observed after 28 days. No data on inherent biodegradability are available.

Some non-standard tests indicate that aerobic biodegradation can take place to some extent, and in a few cases even rapidly, under favourable conditions (high density of bacteria, rather high MTBE concentration) by special groups of microorganisms adapted to MTBE. A major degradation product was found to be *tert*-Butyl alcohol (TBA). Under anaerobic conditions in water/sediment systems, MTBE was found to degrade slowly in one study (152 days) and not at all in another study after 249 days.

Based on analogy with other ethers, the potential for bioconcentration appears to be minor. In a Japanese study using Japanese carp and a flow-through water system with exposure over a 4-week period, it was found that the highest measured BCF for whole tissue was 1.5 (Fujiwara et al. 1984). Following the end of exposure, tissue levels rapidly declined. A BCF of 3 was estimated from octanol/water partition coefficients for the fathead minnow (ASTER 1995; Veith and Kosian 1983). Based on these results, the bioconcentration potential for MTBE may be rated as insignificant.

### 5.2.3 Fate in soil and groundwater

The high vapour pressure of MTBE will lead to partitioning to the atmosphere for MTBE releases to surface waters or soil surfaces. In model systems, half-lives (first-order kinetics) in moving water have been estimated in the neighbourhood of 4.1 hours. If introduced into subsurface soils or to groundwater, e.g. in connection with leakage from underground tanks or separation wells, MTBE may be fairly persistent since volatilization to the atmosphere is reduced significantly. Where MTBE is introduced as part of a petrol mixture from the above mentioned sources, its relatively high water solubility combined with low tendency to sorb to soil particles can be expected to encourage migration to local groundwater supplies. This result is accordance with the findings described in Section 5.3.1.

Degradation of MTBE in groundwater aquifers is slow to non-existent (Dakhel et al. 2003). Biodegradation of MTBE has been observed under both aerobic and anaerobic conditions in laboratory tests, and the US EPA (2000) concludes anaerobic degradation of MTBE to be difficult. The European Commission (2002) also concludes that biodegradation of MTBE in soil under aerobic and especially anaerobic conditions is slow, and favorable conditions for degradation are difficult to attain. The primary degradation product in soil and groundwater is TBA (Tertiary Butyl Alcohol), but few investigations of contamination by MTBE include the degradation products (Smith et al, 2002). See chapter 7 (alternatives to MTBE) for properties of TBA.

### 5.2.4 Fate in the atmosphere

MTBE is degraded by photo-induced hydroxyl radicals in air with a half-life of 3-7 days while photolysis is not an important mechanism (CONCAWE, 2012). The main degradation product is *tert*-butyl formiate; minor amounts of methyl acetate, acetic aldehyde and formaldehyde are formed. These substances are all naturally occurring substances and can be considered general VOCs.

## 5.3 Environmental exposure

### 5.3.1 Sources of release

Releases from service stations to air are related to filling tanks with 98 octane petrol. Total evaporative losses to air during refuelling of cars is on the order of 0.15 kg/tonne petrol when vapour recovery systems are used, as is the case at modern service stations in Denmark. With an MTBE content of approx. 10 %, this corresponds to approx. 30 kg MTBE per year.

The emission of MTBE to air while filling up with petrol containing MTBE has been registered by Hartle (1993) as being 1 to 4 ppm in the breathing zone and 0.001 to 0.1 ppm inside the car (1 ppm = 3.57 mg/m$^3$). The Health Effects Institute in the US (2004) measured concentrations in the breathing zone of 0.2 to 1.5 ppm. The Finnish Occupational Health Institute measured average concentrations of MTBE in the air at service stations of around 0.001 ppm in 1996, when MTBE in petrol was common (Vainiotalo et al, 1996).

As the primary use of MTBE in Denmark has been as an oxygenate in petrol (since 1985), MTBE is closely related to the risk for soil and groundwater contamination in connection with service stations etc. where petrol is stored.

Since 2001, MTBE has only been in use in 98 octane petrol, which is used by a limited number of cars. The number of service stations providing 98 octane petrol has therefore been reduced substantially. In 2002, 128 service stations were registered, distributed across the country. The new regulation regarding the control of contamination at petrol stations is expected to reduce the present and future risk for petrol contamination at these stations. According to information from the sector, the number of service stations providing 98 octane is 31 at present (EOF, 2013).

Based on statistics from Energi- og Olieforum (EOF, 2013), the total consumption of automotive petrol fell from 1.99 mio. m$^3$ in 2011 to 1.85 mio. m$^3$ in 2012, while the consumption of 98 octane petrol decreased from 9000 m$^3$ in 2011 to 2000 m$^3$ in 2012.

According to information from the oil companies that refine oil in Denmark, one of them no longer uses MTBE in their products, while in 2012 the other reduced its use to less than 20 % of what it was in 2007. Based on recent information from EOF, 98 octane petrol is not imported to Denmark any longer, and has not been for a while.

Two surveys carried out in 2003 and 2006 (for Funen County and the Danish EPA, respectively, Funen County, 2001) showed that MTBE could be found in groundwater at more than 80 % of the closed down service stations and approx. 75 % of the service stations in use. The surveys also showed that at approx.75 % of the stations surveyed, the concentration of MTBE in the groundwater was above the water quality criteria of 5 µg/l. At almost all of the stations where MTBE was found, the contamination extended beyond the site borders.

The release of MTBE to surface waters from treatment plants for urban wastewater is limited, as reflected in the very low levels observed in the effluents from such plants (e.g. reported in “Point Sources 2011” by Naturstyrelsen, 2012), see section 5.3.4.

No data have been identified on the content in road runoff from separate outlets.

### 5.3.2 Environmental monitoring, air

MTBE is not included in the Danish environmental surveillance programme, NOVANA, for the air compartment. No air monitoring data have been identified.

### 5.3.3 Environmental monitoring, soil and groundwater

Due to the properties of MTBE[6], analysis for the substance is generally not carried out in soil.

In 2006, Oliebranchens Miljøpulje (the Environmental Fund of the Danish Oil Industry Association, EOF) reported to the Danish EPA about their findings of MTBE in relation to contaminated petrol station sites. The findings are summarised in Table 11. The costs are not only related to the clean-up of MTBE, but also other contaminants.

TABLE 11
SUMMARY OF MTBE FINDINGS IN DANISH GROUNDWATER AT CONTAMINATED SERVICE STATIONS AND TOTAL CLEAN-UP COSTS (NOT ONLY MTBE) (OM, 2006)

| MTBE, µg/l | Within groundwater extraction areas (number) | Outside groundwater extraction areas (number) | Average clean-up costs (DKK, excl. VAT) |
|---|---|---|---|
| < 5 | 38 | 82 | 464,000 |
| 5 – 30 | 9 | 16 | 622,000 |
| 30 – 100 | 6 | 19 | 699,000 |
| 100 – 1000 | 16 | 16 | 770,000 |
| 1000 – 10,000 | 6 | 9 | 1,392,000 |
| > 10,000 | 4 | 8 | 1,715,000 |
| Total | 79 | 150 | 625,000 |

As can be seen from the table, 48 % of the samples were above the quality criteria of 5 µg/l. This is a smaller percentage than the one registered by the authorities in 2002 and 2003 (see 5.3.1). The report does not provide information about the number of cases in which MTBE was detected in concentrations above the detection limit (≈ 1 µg/l) but below the quality criterion (5 µg/l).

In 2011, GEUS (Geological Survey for Denmark and Greenland) carried out a study for the Danish EPA with the aim of investigating the information in the JUPITER database with respect to the presence of a number of organic contaminants in Danish groundwater and their development over

[6] High solubility and low sorption

time (Brüsch &Villholt, 2011). One of the objectives was to evaluate the results of the effort to reduce impact from point sources. MTBE was one of the contaminants investigated.

GEUS has compiled data from the GRUMO database of projects. For the whole period investigated, 1997 to 2009, MTBE has been analysed approx. 7300 times and been identified in slightly more than 1000 occasions. The number of water samples analysed per year has varied substantially. In 2001, where the largest number of samples was analysed (1979), MTBE was found in app. 5 % of the samples and in concentrations above the water quality limit of 5 µg/l in 0.5 % of the samples. In the earlier years, this percentage was between 1 and 3 %, while during the last 3 years of the period it has been below 1 % on average.

In the whole period, MTBE has been found in 409 wells, corresponding to approx. 12 % of the wells analysed for MTBE. The wells encompass both water supply wells and monitoring wells.

The development in average concentrations for the samples analysed can be seen in Figure 4. In this figure, data from investigations related to contaminant cases are not included. It can be seen from the figure that the average concentration has decreased over time.

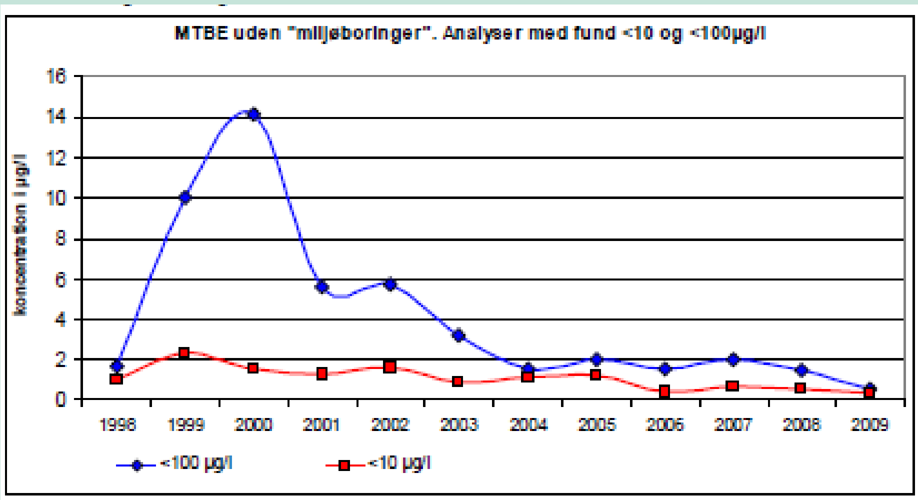


**FIGURE 4**
DEVELOPMENT IN AVERAGE CONCENTRATION OF MTBE IN DANISH GROUNDWATER PER YEAR FOR SAMPLES WHERE MTBE WAS FOUND FOR THE PERIOD 1998 TO 2009. SAMPLES FROM CONTAMINATED SITES EXCLUDED. DATA FROM THE JUPITER DATABASE. THE BLUE CURVE SHOWS THE AVERAGE CONCENTRATION OF ALL SAMPLES WHERE THE CONCENTRATION WAS BELOW 100 µG/L (841 SAMPLES), AND THE RED CURVE SHOWS THE DEVELOPMENT IN THE AVERAGE OF ALL SAMPLES WHERE THE CONCENTRATION WAS BELOW 10 µG/L (760 SAMPLES).

MTBE is measured as part of the general survey of groundwater quality in Denmark. The extent (number of wells, number of samples) varies from year to year. Only one water supply has registered MTBE at least 5 times in the period from 2006 to 2010 (GEUS, 2011).

Similar results have been registered in other EU countries where monitoring for MTBE has been carried out, e.g. Finland and the UK (European Commission, 2002).

### 5.3.4 Environmental monitoring, effluents and surface water

MTBE is included in the national Danish environment and nature surveillance programme, NOVANA, for the period 2011-2015 in the categories "point sources" (WWTP effluents) and "streams" (NOVANA, 2011).

In the preceding national surveillance programme for the aquatic environment, NOVA 2003, MTBE was included in the categories "groundwater", "streams", "lakes", "WWTPs" (effluent and sludge) and "stormwater" (Miljøstyrelsen, 2000).

The most recent monitoring data concerning municipal wastewater treatment plants (MWWTP) from the NOVANA programme are shown in the table below.

No data on contents of MTBE in separate rainwater outlets (road runoff etc.), industrial effluents or watercourses in Denmark have been identified.

TABLE 12
MOST RECENT MONITORING DATA FOR MTBE IN OUTLET FROM POINT SOURCES FROM THE NATIONAL DANISH MONITORING AND ASSESSMENT PROGRAMME

| Substance | Point source | Number of samples *1 | Average µg/L | Median µg/L | Year | Source |
|---|---|---|---|---|---|---|
| MTBE | WWTP | 40 (6) | 0.03 | 0.00 | 2011 | Naturstyrelsen, 2012 |
| MTBE | WWTP | 36 (8) | 0.04 | - | 2004 | Miljøstyrelsen, 2005 |

*1 Number of positive samples in brackets
<d.l. : Below detection level. n.i.: not indicated

It is outside the scope of this report to summarise MTBE monitoring data from outside Denmark.

## 5.4 Environmental impact

The EU risk assessment of MTBE (European Commission, 2002) concludes that only with regard to intermittent releases to surface water from terminal site storage tank bottom water is there a need for limiting the environmental risks. The RAR identifies a need for more information to adequately characterise the risks to the aquatic ecosystem regarding the emission of the substance to surface water, more specifically a need for investigation of avoidance behaviour in fish. This issue has, together with tainting of fish, been addressed in an addendum to the RAR. Eels were found to be somewhat attracted to MTBE at the tested concentration of 30 µg/l.

MTBE has previously been registered as a major potential groundwater contaminant, primarily at service stations where petrol containing MTBE has been stored. The impact is related to the odour and taste that the presence of MTBE gives rise to, rather than toxicity. Since MTBE is barely degradable in the groundwater aquifer, if at all, contaminant plumes can spread to large areas and be maintained for a long time.

## 5.5 Summary and conclusions

The environmental hazards of MTBE were reviewed in the 2002 EU Risk Assessment Report (RAR), which is still considered valid in terms of MTBE properties. MTBE is not very toxic to aquatic organisms, the lowest acute EC50 being 136 mg/l (*Mysidopsis bahia*, marine crustacean) and the lowest chronic NOEC being 26 mg/l for the same species.

In an addendum to the RAR, a tainting study and an avoidance test with fish have been conducted. The tainting study showed no off-taste at 15 µg/l, but at 31 µg/l, the taste of MTBE could be discerned. The avoidance test with eel showed some attraction to MTBE at 30 µg/l.

No data on the toxicity of MTBE to terrestrial or soil-dwelling organisms were identified in the RAR.

MTBE is not readily biodegradable in aquatic screening tests, in which limited biodegradation was observed. Based on the physico-chemical properties of MTBE and constants for sorption to particulates and organic matter, the substance is considered to be highly mobile in soil. The bioconcentration potential of MTBE is insignificant.

The high vapour pressure of MTBE will lead to partitioning to the atmosphere for MTBE being released to surface waters or soil surfaces. If introduced into subsurface soils or to groundwater, e.g. in connection with leakage from underground tanks or separation wells, MTBE may be fairly persistent since volatilization to the atmosphere is reduced significantly. Due to its relatively high water solubility combined with low tendency to sorb to soil particles, MTBE can be expected to encourage migration to local groundwater supplies.

Degradation of MTBE in groundwater aquifers is slow to non-existent. This is true for both aerobic and anaerobic conditions. If degraded, the primary degradation product in soil and groundwater is TBA (Tertiary Butyl Alcohol).

At contaminated sites (petrol stations), MTBE has been found in concentrations above 5 µg/l in a little less than 50 % of the cases. These sites have all been cleaned up under the programme carried out by the Environmental Fund of the Danish Oil Industry Association (EOF). This programme has included clean-up of all petrol related compounds, including MTBE, to levels set by the region in charge. In wells not associated with contaminated sites, the average concentration for all samples where MTBE was detected peaked at 14 µg/l in 2001 and then gradually fell to below 1 µg/l in 2009.

Monitoring of MTBE in effluents from wastewater treatment plants performed as part of the Danish environmental surveillance programme show low levels of MTBE i.e. average values of 0.03-0.04 µg/l. No Danish monitoring data from the natural environment (soil, surface water, biota, ambient air) have been identified.

# 6. Human health effects

## 6.1 Human health hazard

### 6.1.1 Classification

MTBE is subject to harmonised classification as a skin irritant (cat. 2) and as a highly flammable liquid (cat 2).

**TABLE 6.1**
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

| Index No | International chemical identification | CAS No | Classification | |
|---|---|---|---|---|
| | | | Hazard Class and Category Code(s) | Hazard statement Code(s) |
| 603-181-00-X | MTBE<br>2-methoxy-2-methylpropane<br>tert-butyl methyl ether | 1634-04-4 | Flam.Liq. 2<br>Skin Irrit. 2 | H225<br>H315 |

### 6.1.2 Toxicokinetics

Toxicokinetic data are available in the RAR for MTBE (European Commission, 2002) and summarised in the following. MTBE is rapidly absorbed by the oral and inhalatory route and available data suggest that MTBE, with its combination of polar and non-polar characteristics, is a moderate skin penetrant under occlusive (closed) conditions. In open contact the high volatility will limit skin absorption due to rapid evaporation. MTBE is widely distributed in the body tissues, reaching similar levels in soft tissues as in blood, indicating that distribution is determined by solubility. A 10-fold higher concentration may be reached in fat. *In vitro* studies show a specific binding of MTBE to male rat protein in the kidney.

Metabolism of MTBE seems to be qualitatively similar in rats and humans. MTBE is metabolised to formaldehyde and t-butanol (TBA). Formaldehyde has not been measured *in vivo* following MTBE exposures but is believed to be rapidly metabolised to formic acid and CO2, or become incorporated into the one-carbon pool[7].

Saturation of metabolism has been indicated in rat studies after intraperitoneal (i.p.) administration of MTBE or following inhalation exposure to 8000 ppm for 6 hours. In humans inhaling up to 75 ppm for four hours, there was no sign of saturation. Most MTBE is excreted as urinary metabolites, and less than half is exhaled unchanged (the opposite is the case with high uptake rate). The elimination half-time for MTBE in blood is about 0.5 hour in the rat and about 10 times longer in humans.

[7] Pool of metabolites with one carbon atom

TBA is more soluble in water and blood and is expected to be distributed rather evenly in body water and not to be stored in any particular tissue compartment. Clearance is suggested to take place through metabolism, since little unchanged TBA is excreted in exhaled air or urine. TBA is further metabolised to α-hydroxy-isobutyric acid, 2-methyl-1,2-propanediol, TBA conjugates and acetone. The metabolism appears to have limited capacity, as the elimination half-time for TBA in blood was 3 hours in the rat and on the order of 10 hours in humans, both after exposure to low levels of MTBE. This was also true among patients with high MTBE (and TBA) body burdens received during dissolution of gall bladder stones.

A number of clinical studies with human volunteers are reported in the literature. The specific background for carrying out the tests in humans and the guidelines providing the basis for conducting these studies are not specified in the reviewed literature. However as the substance can be used for treating patients with gallstones, they most likely originate from pharmaceutical testing. It should, however, be emphasised that according to ECHA guidance documents on the hazard assessment of chemicals under REACH, good quality data from human experimental toxicity studies should only be used as appropriate, in well-justified cases.

In a clinical study with 14 volunteers exposed to MTBE by the oral, dermal and inhalation routes, the metabolite TBA was found in higher concentrations in blood following oral administration than after inhalation or dermal administration. Levels were still elevated above pre-exposure baseline levels at 24 hours. It was suggested that this finding was due to the occurrence of first-pass metabolism[8], based on TBA's water solubility and its blood/air partition ratio, which would reduce its ability to be eliminated by exhalation. A dermal permeation coefficient was estimated to be 0.028 cm/h, similar to that of ethyl ether (Health Canada, 2006).

The RAR (European Commission, 2002) concludes that the generation of formaldehyde in MTBE metabolism is of particular toxicological interest because of the reactive and mutagenic properties. However, the limited database available suggests that formaldehyde produced intercellularly from MTBE at rates which are lower than those of its further metabolism have lacking or diminished reactivity.

### 6.1.3 Acute and chronic toxicity

The toxicology of MTBE has been intensively investigated and data are available from both humans and test animals. Information on effects in humans is available from investigations involving volunteers, from investigations of occupational exposures, representatives exposed to MTBE in petrol, and from medicinal use of MTBE introduced into the gall bladder to dissolve the gallstones.

Based on the available information, MTBE is concluded to be of low acute toxicity via oral, dermal and inhalation routes in both humans and test animals. The principal effects observed in patients exposed to MTBE during treatment are effects on the central nervous system with symptoms including drowsiness, nausea and vomiting. Local burning sensations were also frequent. In a study involving 27 gallstone patients treated with MTBE for typically 5 hours, a mean concentration of 0.5 mM (maximum about 1 mM) of both MTBE and its TBA metabolite were measured in blood. This is considered a high body burden, about 17 times higher than the levels obtained following inhalation exposure over four hours to 75 ppm MTBE. Assuming a direct correlation between developed blood concentrations and inhaled levels of MTBE, the measured body burden corresponds to the level which could be achieved from inhalation exposure to 1200 ppm. At blood MTBE levels of approximately 1 mmol/l, signs of intra-vascular haemolysis can be detected (European Commission, 2002).

[8] First-pass metabolism refers to the situation where after oral dosing and absorption, the substances pass through the portal vein into the liver and undergo a degree of metabolism by the liver enzymes, which can result in a reduced amount reaching the systemic circulation.

$LD_{50}/LC_{50}$ values obtained from animal studies have not triggered classification. Typical symptoms observed in animal studies include decreased ability for muscle coordination and hypoactivity.

MTBE is classified as a skin irritant but not considered an eye or respiratory irritant. Signs of pulmonary irritation were observed in mice when exposed to 30,000 mg/m$^3$ for one hour by inhalation but this finding was not supported by lung lavage measurements or observations in humans.

MTBE has not been shown to cause sensitisation in two guinea pig studies, considered sufficient with respect to but not formally following OECD guidelines. There are no observations available on sensitisation in humans (European Commission, 2002).

The kidney is the main target organ after repeated dosing, particularly in male rats. Mild liver effects were also observed in a 13-week study with rats exposed by inhalation, supported by a 2-year carcinogenicity study in rats. A NOAEC of 800 ppm for inhalation was selected in the RAR based on the 13-week study. A NOAEL of 300 mg/kg was chosen for oral administration based on findings in the rat liver (weight increase of liver, increased AST and cholesterol levels) in a 90-day study (European Commission, 2002).

MTBE is not considered a mutagen based on results from a number of bacterial tests. One positive result was obtained in an Ames test with S9 metabolic activation, suggesting formaldehyde involvement. As formaldehyde was generated outside the cell, it was not considered to reflect MTBE metabolism in a realistic manner. Based on these studies and results from a range of other mutagenicity / genotoxicity studies *in vitro* and *in vivo* showing the non-genotoxic nature of MTBE, the RAR (European Commission, 2002) concludes that MTBE cannot be considered a mutagen.

Several studies investigating the carcinogenic potential of MTBE are available and discussions are ongoing regarding the evaluation and human significance of the findings from these studies, in the light of the conclusions regarding the non-genotoxic nature of MTBE as well.

Summary tables from the RAR (European Commission, 2002) providing overviews of the neoplastic and proliferative lesions seen in studies with mice and rats are shown in Table 13, Table 14 and Table 15.

**TABLE 13**
**NEOPLASTIC LESIONS IN MALE FISHER-344 RAT EXPOSED TO MTBE (EUROPEAN COMMISSION, 2002)**

| Proliferation lesion | Lesion incidence in percentages per dose of animals examined | | | |
|---|---|---|---|---|
| | 0 ppm | 400 ppm | 3,000 ppm | 8,000 ppm |
| Parathyroid adenomas[9] | 0% | 0% | 8% | 2% |
| Renal tubular cell tumours[10] (adenomas / carcinomas) | 2% / 0% | 0% / 0% | 10% / 6% | 26% / 0% |
| Testicular interstitial cell tumours (adenomas) | 64% | 70% | 82% | 84%*) |

*) Statistically significantly different from control ($p<0.01$)

9 Usually benign tumour of the parathyroid
10 Kidney tumours in the small tubes of the kidney

TABLE 14
PROLIFERATIVE LESIONS IN CD-1 MICE (EUROPEAN COMMISSION, 2002)

| Proliferative lesion | Lesion frequency in percentages per dose group of animals examined | | | |
|---|---|---|---|---|
| | 0 ppm | 400 ppm | 3,000 ppm | 8,000 ppm |
| Hepatocellular hypertrophy (♀) | 10% (49) | 12% | 20% | 30% (49)* |
| Hepatocellular hypertrophy (♂) | 8% | 4% | 6% | 18% |
| Hepatocellular adenomas / carcinomas /combined (♂) | 22% / 4% / 25% | 22% / 8% / 24% | 18% / 6% / 24% | 24% / 16% / 33% |
| Hepatocellular adenomas / carcinomas /combined (♀) | 4% / 0% / 4% | 2% / 2% / 4% | 4% / 0% / 4% | 20%** / 2% / 22% |
| Cystic hyperplasia of uterine endometrium (♀) | 52% | 35% (48) | 30%* | 12%** |

Numbers in parenthesis represent the total number of animals examined, otherwise 50 examined in all dose groups
* = Statistically significantly different from control ($p<0.05$)

** = Statistically significantly different from control ($p<0.01$)

TABLE 15
SUMMARY OF PROLIFERATIVE LESIONS SEEN IN SPRAGUE-DAWLEY RAT (EUROPEAN COMMISSION, 2002)

| Proliferative lesion | Lesion frequency in percentages per dose group of animals examined | | |
|---|---|---|---|
| | 0 mg/kg | 250 mg/kg | 1,000 mg/kg |
| Lymphoimmunoblastic dysplasia,♀ (§) | 5% | 26.7% | 20% |
| Lymphoma & Leukaemia,♀ | 3.3% | 11.7% | 20% |
| Proportion of lymphoma | 100% | 85% | 91.7% |
| Testis interstitial Cell Hyperplasia (focal + diffuse/ focal) | 6.7% /25% | 13.3% / 37.5% | 15.0% / 2.2% |
| Testis interstitial Cell adenomas | 3.3% | 3.3% | 18.3%* |

Sixty animals examined in all cases
* = Statistically significantly different from control ($p<0.05$)
§ = Dysplasias observed in animals bearing lymphoma or leukaemia are not included

Discussions regarding the observed lesions have led to the following conclusions in the RAR (European Commission, 2002):

Development of kidney tumours in Fisher-344 rats is expected to be related to proliferation caused by MTBE interaction with α2u-globulin, which only occurs in male rats. In addition, induction of tumours requires extremely high concentrations (3000 ppm); the relevance for humans is therefore likely to be insignificant.

With regard to the liver tumours in CD-1 mice, the difference between the occurrence of carcinoma in the high dose group and the controls was not statistically significant, and when all malignant liver tumours were summed, there was also no difference from the controls. MTBE causes changes in oestrogen-sensitive tissues without affecting the serum oestrogen level. The RAR concludes that there may be a connection between these changes and the increased amount of liver adenomas in the high dose female group, but there is no evidence of such a theory. Proliferation increased by MTBE may have contributed to the generation of tumours at high doses needed to produce liver adenomas, but the relevance for man is questionable. MTBE did also not express promoter activity when tested with N-nitrosodiethylamine (European Commission, 2002).

Several mechanisms are discussed in relation to the aetiology[11] of Leydig Cell Tumours (LCT) in Fisher-344 and Sprague-Dawley rats. The RAR concludes that there is evidence that MTBE causes an increase of LCT in rats, but limited data are available upon which to draw conclusions regarding the mode of action behind the induction. It is also unclear how differences in physiology and anatomy between rat and human testes contribute to the susceptibility to LCT. High doses are also required for the development of LCT. The overall conclusion is therefore that no definitive conclusion can be drawn about the relevance of these tumours due to lack of knowledge. Relevance to humans is not expected to be very significant (European Commission, 2002).

With regard to haematopoietic neoplasms[12] in Sprague-Dawley rats and parathyroid hyperplasia[13] and neoplasia[14] in Fisher-344 rats, no firm conclusions can be drawn regarding carcinogenicity. This is due to limitations in study reporting in the study with Sprague-Dawley rats, and in the case of proliferative changes seen in the parathyroid, the possibility that these changes are a result of chronic renal failure (European Commission, 2002).

The primary metabolite of MTBE, formaldehyde, has been classified as "probably carcinogenic to humans" by IARC. Based on available studies it appears that the formaldehyde, which is endogenously formed from MTBE in mouse liver cells, does not lead to a significant increase of DNA-crosslinks. In addition, formaldehyde is rapidly metabolised to formic acid catalysed by formaldehyde dehydrogenase, available in a wide range of tissues. The RAR does not consider formaldehyde to be a relevant factor in the tumour formation seen with MTBE.

In carcinogenicity studies with TBA in Fisher-34 rats, an increase in adenoma incidence was observed. The incidence was not statistically significant but exceeded the historical controls. Overall MTBE has been shown to produce tumours in both mice and rats, and development of testicular interstitial adenomas observed in two separate rat strains suggests that MTBE is a rodent carcinogen. However, no firm conclusions regarding the relevance for humans can be drawn based on the different carcinogenicity studies. In conclusion, the rapporteur of the RAR considers MTBE to be a borderline case between non-classification and Carc.Cat.3 (limited evidence of carcinogenic effect) (European Commission, 2002). This conclusion, reached in 2002, has not triggered harmonised classification of MTBE for carcinogenicity.

The International Agency for Research on Cancer (IARC) has concluded that there is inadequate human evidence, and limited animal evidence, for the carcinogenicity of MTBE, leading to an overall evaluation of MTBE as "not classifiable as to its carcinogenicity to humans."

[11] The study/science of the causes or origin of disease.
[12] Neoplasms (benign or malignant tumours) located in the blood and blood-forming tissue (the bone marrow and lymphatic tissue).
[13] Parathyroid hyperplasia is the enlargement of all four parathyroid glands. The parathyroid glands are glands in the neck that produce parathyroid hormone (PTH).
[14] Abnormal growth of cells, which may lead to neoplasm.

Effects on fertility were studied in 1-generation and 2-generation studies in rats exposed via inhalation. No significant treatment-related effects were observed. Based on results from developmental toxicity studies in mice and rats, it was also concluded that MTBE is not considered toxic to foetal development. Although sternebrae malformations were observed at high doses in mice, they were considered to be a result of marked maternal toxicity and not to be treatment-related (European Commission, 2002).

### 6.1.4 Endocrine disruption properties

The RAR (European Commission, 2002) concludes that MTBE exerts different effects on the endocrine system at high doses. Increased metabolism of oestrogen is observed in mouse liver, which does not affect the level of free hormone and MTBE appears to have a slight antioestrogen-like activity at very high doses.
Observed effects include:

- Weight loss and morphological changes in uterine;
- Altered oestrous cycle length;
- Increased interstitial testosterone level;
- Decreased serum testosterone and LH (no indication of mode of action);
- Elevated corticosterone and aldosterone levels (continued exposure to high levels), and
- Clear decrease in serum corticosterone level (later phase of chronic study).

The significance of e.g. the altered morphology of the adrenal gland is not clear and no NOAEL is assigned in the RAR because data are insufficient.

The Danish Centre on Endocrine Disrupters (DCED)[15] has evaluated MTBE as part of 22 SIN List 2.0 substances according to the Danish proposal on criteria for endocrine disrupters (DCED, 2012). Proposed criteria are as follows:

***Category 1 - Endocrine disrupter***

Substances are placed in category 1 when they are known to have produced ED adverse effects in humans or animal species living in the environment or when there is evidence from animal studies, possibly supplemented with other information, to provide a strong presumption that the substance has the capacity to cause ED effects in humans or animals living in the environment.
The animal studies shall provide clear evidence of ED effect in the absence of other toxic effects, or if occurring together with other toxic effects, the ED effects should be considered not to be a secondary non-specific consequence of other toxic effects. However, when there is e.g. mechanistic information that raises doubt about the relevance of the adverse effect for humans or the environment, category 2a may be more appropriate.
Substances can be allocated to this category based on:

- Adverse in vivo effects where an ED mode of action is highly plausible
- ED mode of action in vivo that is clearly linked to adverse in vivo effects (by e.g. readacross).

***Category 2a - Suspected ED***

Substances are placed in category 2a when there is some evidence from humans or experimental animals, and where the evidence is not sufficiently convincing to place the substance in category 1. If for example limitations in the study (or studies) make the quality of evidence less convincing, category 2a could be more appropriate. Such effects should be observed in the absence of other toxic effects, or if occurring together with other toxic effects, the ED effect should be considered not to be a secondary non-specific consequence of other toxic effects.
Substances can be allocated to this category based on:

- Adverse effects in vivo where an ED mode of action is suspected
- ED mode of action in vivo that is suspected to be linked to adverse effects in vivo

[15] Center for Hormonforstyrrende Stoffer (CEHOS) (in Danish)

- ED mode of action in vitro combined with toxicokinetic in vivo data (and relevant non test information such as read across, chemical categorisation and QSAR predictions)

***Category 2b – Substances with indications of ED properties (indicated ED)***
Substances are placed in category 2b when there is in vitro/in silico evidence indicating potential for endocrine disruption in intact organisms. Evidence could also be observed effects in vivo that could be ED-mediated.

Brief study summaries are available in the DCED evaluation. The evaluation of available *in vitro* and *in vivo* data are cited below (DCED, 2012):

***In vitro***
Li *et al.* (2006) investigated the toxicity of methyl tert-butyl ether (MTBE) on mouse spermatogenic cells in vitro. The results suggest that a high dose MTBE could exert a direct toxic effect on Sertoli cells that would impair their function and subsequently impair spermatogenesis or even cause cell death. The Sertoli cell is a terminally differentiated testicular cell in the adult that is required to maintain the process of spermatogenesis. Sertoli cells have multiple functions such as providing the cytoarchitectural support and microenvironment for developing spermatogenic cells.

***In vivo***
The effects observed in animal studies of adult rats include: decreased relative ovary and pituitary weights and increased oestrous cycle length (Moser *et al.* 1998), decreased serum testosterone, DHT, LH, prolactin and T3 levels (Williams *et al.* 2009), increased abnormal sperm percent and irregular histopathology of testes and altered levels of testosterone, LH, FSH (Li *et al.* 2008). Thus the effects observed in adult rats include both adverse effects (increased abnormal sperm percent, irregular histopathology of testes) and relevant mode of action data (altered levels of testosterone, LH and FSH).

DCED concludes that MTBE should be categorised as an endocrine disrupter Category 1, based on direct toxic effect *in vitro* on Sertoli cells resulting in impaired spermatogenesis and MTBE resulting in decreased testosterone in rat Leydig cells at high doses. From studies with adult rats, the significant effects included decreased relative ovary and pituitary weights and increased oestrus cycle length, decreased prolactin and T3 levels, increased abnormal sperm percent and irregular histopathology of testes and altered levels of testosterone, LH (luteinising hormone) and FSH (follicle stimulating hormone).

MTBE has been prioritised for REACH substance evaluation in 2014, triggered by suspected endocrine disrupting effects and its widespread use.

### 6.1.5 No-effect levels

**Occupational exposure limit values**
Occupational exposure limit values for MTBE for selected European countries are presented in Table 16.

TABLE 16
OCCUPATIONAL EXPOSURE LIMIT VALUES FOR MTBE FOR SELECTED COUNTRIES

| | Limit value 8-hours | | Limit value short term | |
|---|---|---|---|---|
| | ppm | mg/m³ | ppm | mg/m³ |
| Belgium | 40 | 146 | 100 | 367 |
| Denmark | 40 | 144 | 80 | 288 |

| | Limit value 8-hours | | Limit value short term | |
|---|---|---|---|---|
| | ppm | $mg/m^3$ | ppm | $mg/m^3$ |
| European Union[1] | 50 | 183.5 | 100 | 367 |
| France | 50 | 183.5 | 100 | 367 |
| Germany | 50 | 180 | 75 | 270 |
| Sweden | 30 | 110 | 60 | 220 |
| The Netherlands | | 180 | | 360 |
| United Kingdom | 25 | 92 | 75 | 275 |

[1] Indicative OEL (see Chapter 2)

It can be seen that the Danish OELs fall between less stringent (e.g. France and EU) and more stringent (e.g. UK and Sweden) levels.

**Derived no-effect levels and limit values**

Derived no-effect levels for MTBE registered under REACH are shown in Table 17. The DNELs are based on information from a joint submissionand are established by the registrant for the different exposed populations and for the different exposure types. ECHAs dissemination website does not include the full justification behind the values. DNELs are used for risk assessment of specific exposure situations.

TABLE 17
DERIVED NO-EFFECT LEVELS (DNELS) FOR MTBE (ECHA, 2013A)

| Population / - route | Exposure | Value | Sensitive endpoint |
|---|---|---|---|
| Workers<br>- inhalation | Long term exposure<br>- systemic | 178.5 $mg/m^3$ | Repeated dose toxicity |
| | Acute/short term<br>- systemic | No threshold available | - |
| | Long term exposure<br>- local effects | No threshold available | - |
| | Acute/short term<br>- local effects | 357 $mg/m^3$ | Irritation (respiratory tract) |
| Workers<br>- dermal | Long term exposure<br>- systemic | 5100 mg/kg bw/day | Repeated dose toxicity |
| | Acute/short term<br>- systemic | No threshold available | - |
| | Long term exposure<br>- local effects | No threshold available | - |
| | Acute/short term<br>- local effects | No threshold available | Skin irritation/corrosion |

| Population / - route | Exposure | Value | Sensitive endpoint |
|---|---|---|---|
| General population - inhalation | Long term exposure - systemic | 53.6 mg/m$^3$ (AF: 1.7) | Repeated dose toxicity |
| | Acute/short term - systemic | No threshold available | - |
| | Long term exposure - local effects | No threshold available | - |
| | Acute/short term - local effects | 214 mg/m$^3$ (AF: 1.7) | Irritation (respiratory tract) |
| General population - dermal | Long term exposure - systemic | 3570 mg/kg bw/day | Repeated dose toxicity |
| | Acute/short term - systemic | No threshold available | - |
| | Long term exposure - local effects | No threshold available | - |
| | Acute/short term - local effects | No threshold available | Skin irritation/corrosion |
| General population - oral | Long term exposure - systemic | 7.1 mg/kg bw/day | Repeated dose toxicity |
| | Acute/short term - systemic | No threshold available | - |

## 6.2 Human exposure

### 6.2.1 Direct exposure

**Consumers**

Petrol refuelling is the only known consumer use scenario where inhalation exposure is the principal route of exposure. Exposure of the consumer will depend on the presence of a vapour recovery unit. In the RAR (European Commission, 2002), it is estimated based on a source from 1998 that the proportion of stations with vapour recovery during refuelling is 38-90% in the six most advanced countries. The percentage of stations with vapour recovery in Finland in 1998 was 5%. In Denmark, all 31 stations (both "stage I" and "stage II")[16] offering petrol with MTBE are equipped with vapour recovery (EOF 2013, pers. comm).

Due to the voluntary agreement in Denmark between industry and government to phase out the use of MTBE in petrol except in 98 octane petrol, the MTBE consumption and exposure have been reduced considerably since 2000 when the agreement was made. Currently, the consumers

[16] **Stage I** petrol vapour recovery system aims to recover petrol vapour emitted from the storage and distribution of petrol between oil terminals and service stations. **Stage II** petrol vapour recovery system means equipment aimed at recovering the petrol vapour displaced from the fuel tank of a motor vehicle during refuelling at a service station and which transfers that petrol vapour to a storage tank at the service station or back to the petrol dispenser for resale; (DIRECTIVE 2009/126/EC of 21 October 2009 on Stage II petrol vapour recovery during refuelling of motor vehicles at service stations).

potentially exposed to MTBE are primarily those who are driving and repairing classical cars that use 98 octane petrol.

MTBE concentrations measured in the breathing zone of 40 randomly selected customers in Finland during refuelling showed average concentrations of 15.3 mg/m$^3$ without recovery and 3.4 mg/m$^3$ with recovery. The temperature varied between 10-17°C and the duration between 6-49 seconds (23 seconds on average). The wind speed was 2-4 m/s.

Measurements from Italy of attendant personnel (similar exposure as consumers in individual measurements) showed geometric means between 0.1 and 0.44 mg/m$^3$ with a range of 0-2.46 mg/m$^3$. A lower MTBE-content is likely the reason behind these figures, which are lower as compared to the Finnish results. More measurements are available and as such, it would be expected the highest concentrations are measured for individuals using pumps without "stage II" controls.

Based on the mean values available, the RAR estimates that the normal concentration of MTBE during refuelling is 1-10 mg/m$^3$. The duration is short, e.g. between 1 and 5 minutes, and the frequency is 2-3 times per week at the most. The reasonable worst-case (RWC) concentration is 0.3-29 mg/m$^3$. The lower value represents an MTBE content of 2.8 vol. % of MTBE and the upper value represents the situation in Finland, where the petrol contained 11 vol. % at the time.

No measurements of dermal exposure caused by refuelling of a car or motor boat are available. Dermal deposition/exposure estimated using EUSES resulted in a potential dermal deposition of 11.4 µg/kg without considering evaporation. Input data were:

- Duration of contact per event: 0.5 hour
- Surface area of exposed skin (palm of a hand): 200 cm$^2$
- Average concentration of substance in product: 0.08 g/cm$^2$
- Volume of diluted products contacting the skin: 0.01 cm$^3$
- thickness of layer of product on skin: 0.1 mm.

Skin contact is, however, not expected to happen regularly, and the RAR considers the potential dermal exposure to be insignificant.

**Occupational exposure**

MTBE is primarily used as a petrol additive and, consequently, the occupational exposure is mainly related to production, formulation, transporting, distribution, service stations, maintenance operations, automotive repair and related sources, and to drivers and professionals using vehicles or in contact with vehicles using MTBE-containing petrol. Exposure from the use of MTBE as a solvent may also occur in the pharmaceutical industry and various laboratories (European Commission, 2002).

In Denmark there is no production of MTBE and therefore no related exposure from this activity. Exposure from transportation, distribution, work at the 31 service stations with 98 octane, maintenance operations, automotive repair and related sources may result in occupational exposure, but no newer monitoring data are available for Danish conditions. The number of drivers and professionals using vehicles with 98 octane petrol is most likely low, since mainly classic cars use 98 octane.

Use of MTBE as a solvent in the pharmaceutical industry is expected to take place under strictly controlled conditions. In laboratories, the amounts are expected to be small and the substance would be expected to be handled under fumehoods, using laboratory equipment and protective gloves.

Results from EASE-estimations of reasonable worst-case exposures for relevant identified scenarios from the RAR are presented in Table 18.

**TABLE 18**
**SUMMARY OF OCUPATIONAL EXPOSURE ESTI MATES FOR MTBE (EUROPEAN COMMISSION, 2002)**

| Industrial category | Duration of exposure | | Reasonable worst case, TWA(8h) | EASE-model exposure estimation (8h) | | Source of data |
|---|---|---|---|---|---|---|
| Job | Actual period h/d | Frequency d/a | mg/m3, by measured concentrations | Inhalation, mg/m3 | Dermal exposure, mg/cm2/d | |
| Production | 2 | 200 | 50 (undiluted)<br>25 (sampling and laboratory work) | 1,800-3,600 (0-0.36 closed process) | (undiluted)<br>0.1-1 (sampling and laboratory work) | Industry |
| Formulation | 2 | 200 | 50 (undiluted and fuel)<br>25 (sampling and laboratory work) | 1,800-3,600 (undiluted),<br>360-504 (11vol%),<br>72-180 (2.8 vol%) | 0-0.1 (undiluted);<br>0.1-1 (undiluted, sampling and laboratory work) | Industry |
| Transporting | 4 | 200 | 100 (undiluted: ship, rail car loading,)<br>30 (fuel: ship, truck loading)<br>25 (sampling and laboratory work) | 1,800-3,600 (undiluted),<br>360-504 (11 vol%),<br>72-180 (2.8 vol %) | 0.1-1 (undiluted);<br>0.01-0.1 (11 vol%);<br>0.003-0.03 (2.8 vol%) | Industry |
| Distributing | 4 | 200 | 40 (11 vol% fuel)<br>30 (2.8 vol% fuel) | 360-504 (11 vol%),<br>72-180 (2.8 vol%) | 0.01-0.1 (11 vol%);<br>0.003-0.03 (2.8 vol%) | Industry;<br>Hakkola et al. (1996b);<br>Saarinen et al. (1998);<br>Vainiotalo et al.1999b) |
| Service stations | 3 | 200 | 20 (11 vol%)<br>3 (2.8 vol% ) | 360-504 (11 vol%)<br>72-180 (2.8 vol%) | 0.01-0.1 (11vol%);<br>0.003-0.03 (2.8 vol%) | Industry;<br>Hakkola et al. (1999);<br>Vainiotalo et al. (1999a) |
| Maintenance | 4 | 150 | 60 (production, formulation and transportation)<br>40 (distributing and service stations, 11 vol%)<br>30 (distributing and service stations, 2.8 vol%) | 1,800-3,600 (undiluted)<br>720-1080 (11 vol%) 504-720 (2.8 vol%) | 1-5 (undiluted);<br>0.1-0.6 (11 vol%);<br>0.03-0.14 (2.8 vol%) | Industry |
| Automotive repair | 2 | 200 | 10 ( 11 vol%)<br>3 ( 2.8 vol% ) | 360-504 (11 vol%)<br>72-180 (2.8 vol%) | 0.01-0.1 (11vol%);<br>0.003-0.03 (2.8 vol%) | Buchta (1993) |
| Drivers and other professionals | 10 min/d | 200 | 0.2 | 360-504 (11 vol%)<br>72-180 (2.8 vol%) | Very low | Buchta (1993) |
| Solvent use of MTBE | 2 | 60 | 25 (undiluted 97.5%); (expert judgment) | 360-720 (undiluted) | 0.1-1 (undiluted) | Industry |

As can be seen from the table, the EASE modelling gave much higher results than the measured concentration. In the RAR, the differences are explained as a result of the fact that the EASE modelling does not consider fluctuating exposures and variable exposure times. It does also not consider amounts (volumes) of exposed products. Furthermore, the exposure predictions given directly by EASE are only exposures for 8-hour work and the frequency and duration of the peaks are unknown. The EASE model was judged as being the only reasonable way to evaluate the dermal exposure (European Commission, 2002).

From the table it can be seen that the estimated 8-hour exposure (inhalation) to MTBE from petrol containing 2.8 vol. % MTBE is between 72 and 180 mg/m$^3$ in all but one scenario. Considering the low concentration of MTBE in petrol in Denmark (0.2%), it must be expected that the estimated value will be below the Danish occupational exposure level of 144 mg/m$^3$. Only in the case of exposure related to maintenance (distributing and service stations) would the EASE-estimated exposure be considerably higher, i.e. 504-720 mg/m$^3$. However, the reasonable worst case exposure by measured concentrations is shown as 30 mg/m$^3$, well below the exposure limit.

### 6.2.2 Indirect exposure

**Air**

A summary of exposure estimates via ambient air from the RAR (European Commission, 2002) is presented in Table 19.

**TABLE 19**
**EXPOSURE TO MTBE VIA INHALATION SCENARIOS**

| Relevant area/scenario | Source of MTBE | Estimated duration of exposure | Typical concentration μ g/m3 | Percentage of population |
|---|---|---|---|---|
| Urban background | Car exhausts, rain | 12/24 hours/day | 0.5-3 | About 98% |
| Areas polluted by refineries<br><br>or contaminated area | Industry, petrol stations | 12 hours/day | 5-100 | < 1% |
| Perimeter of petrol stations | Petrol stations, car exhausts | 12-24 hours/day | 4-14[1] | < 1% |
| Commuting in car or bus | Car exhausts, refuelling | 1-2 hours/day | 15-70 | ? |
| Pump area of service station | Refuelling, spills, cars | 1-5 min./day,<br>1-3 visits/week | 100-500 | 15% |

Note: The representative concentration ranges are based on published data presented in Table 4.23 and 4.24 and Appendix Table A.7.
[1] 4 -14 ug/m3 are the mean ambient concentrations in the perimeters (50 m) of four stations studied by Vainiotalo et al. (1998c). It is assumed that the indoor concentration is the same, since the release of MTBE from the station is continuous and diffusion to the indoor air does not remarkably decrease the concentration.
[2] Adjacent roads with high traffic density (about 15,000 cars/day) contribute to the MTBE levels observed (Vainiotalo, pers.comm.).

No measurements have been identified for Danish ambient air conditions. However, due to the agreement to phase out MTBE, the urban background must be expected to be lower than the average for EU.

## Soil

Exposure via soil is not considered relevant as MTBE will evaporate or leach into the groundwater.

## Drinking water

A table with MTBE concentrations in potable water sources from different geographical areas in the EU is presented in the RAR. Data for the Danish situation are presented in Table 20.

TABLE 20
MTBE IN POTABLE WATER SOURCES IN DENMARK (EUROPEAN COMMISSION, 2002)

| Location | Year(s) | n | Results (µg/L) | Remarks / sampling site | Source |
|---|---|---|---|---|---|
| Denmark | ? | 6 sites | 42-547,000* | Extractable / potable water aquifiers, mixed loading | Miljøstyrelsen (1998)** (unpublished) |
| Copenhagen, Denmark | 1997 | 25/8 | 0.1-0.15 | Potable groundwater | Miljøstyrelsen (1998)** (Unpublished) |

*) Expected to be measurements from contaminated sites.
**) Danish Environmental Protection Agency (DEPA)

The concentration of MTBE in drinking water and groundwater in monitoring wells not directly related to contaminated sites is estimated at 0.1-1 µg/L based on the available data. For the Reasonable Worst Case scenario, a concentration of 15 µg/L is regarded as the maximum concentration for drinking water. At this concentration, the organoleptic odour threshold is exceeded and the public/municipal potable water source would not likely be used any longer. The Danish water quality criterion is 5 µg/L.

More recent Danish Measurements reported in 2006 presented in section 5.3.3 show that 48% of the samples taken in relation to contaminated sites were above the quality criteria. The measured concentrations ranged from < 5 µg/l to > 10,000 µg/l.

MTBE in tap water would result in the following exposures, as stated in the RAR:

- Through ingestion of drinking water and food, an assumption is made that the daily ingestion is 2.0 L, thus triggering an intake of 0.2 µg/day,
- Inhalation of MTBE volatilising from tap water during showering and bathing. According to Stern *et al.* (1997), the dose is estimated to be $2.7 * 10^{-3}$ g/kg/day,
- Dermal absorption of MTBE during showering and bathing (geometric mean of daily dose is assessed to be $2.6 * 10^{-5}$ µg/kg/day), and
- Other water contact activities.

## Food

An overview of estimated human intake from indirect exposure in local and regional scenarios calculated using EUSES is shown in Table 21. In the different local assessment scenarios, all food products come from the vicinity of a point source of concern. In the regional assessment, all food products are taken from the regional model environment.

TABLE 21
ESTIMATED HUMAN INTAKE OF MTBE IN MG/KG BW/DAY, LOCAL AND REGIONAL (EUROPEAN COMMISSION, 2002)

| Scenario | Drinking water | Fish | Leaf crops | Root crops | Meat | Milk | Air | Total intake mg/kg/d |
|---|---|---|---|---|---|---|---|---|
| Production | 0.24 | 0.022 | 0.0003 | 0.001 | 0.000002 | 0.00003 | 0.059 | 0.324 |
| Formulation | 0.010 | 0.0009 | 0.00001 | 0.00005 | $7*10^{-6}$ | 0.000001 | 0.003 | 0.014 |
| Processing 1 | 0.007 | 0.0006 | 0.00002 | 0.00004 | $5.41*10^{-8}$ | 0.000001 | 0.004 | 0.012 |
| Processing 2 | 0.005 | 0.00005 | 0.001 | 0.001 | $5*10^{-7}$ | 0.000009 | 0.237 | 0.244 |
| Processing 3 | 0.005 | 0.0005 | 0.00005 | 0.0001 | $5*10^{-8}$ | $1*10^{-6}$ | 0.01 | 0.016 |
| Regional | 0.00004 | 0.000004 | $8*10^{-7}$ | $3*10^{-7}$ | $6*10^{-10}$ | $1*10^{-8}$ | 0.0002 | 0.0002 |

A Tolerable Daily Intake (TDI) of 0.1 mg/kg bw/day has been derived using an overall safety factor of 1000 and a NOAEL established on a 90-day study (Larsen, 1998).

According to ASTDR (1996), there is no indication that MTBE is a concern in any raw or processed food items.

## 6.3 Bio-monitoring data

No biomonitoring data for Denmark have been identified.

## 6.4 Human health impact

**Consumers**

The RAR (European Commission, 2002) concludes that petrol refuelling is the only known consumer use scenario where inhalation exposure is the principal route of exposure. The NOAELs obtained from inhalation experiments were compared with the highest measured air concentration met in a European petrol station and it was concluded that at present there is no need for further information and/or testing, and no need for risk reduction measures beyond those which are being applied. This conclusion is drawn for all toxicological end-points.

**Workers**

For workers, the general conclusion in the RAR regarding the identified uses of MTBE as a fuel additive and laboratory solvent is that at present there is no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already. Only for long-term local endpoints in relation to maintenance operations and automotive repair the conclusion is that there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

**Humans exposed via the environment**

With all the indirect exposure sources combined, EU Commission (2002) concluded that at present there is no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already. This conclusion was drawn for all toxicological end-points.

**Combined exposure**

Using the worst-case uptake from consumer use and indirect exposure via the environment combined, and the worst-case occupational exposure, the RAR also concludes that at present there is no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied – in relation to combined exposure.

## 6.5 Summary and conclusions

The EU risk assessment (European Commission, 2002) is identified as the most recent comprehensive evaluation of MTBE; it therefore provides the main background for the present evaluation.

MTBE is of low acute toxicity via oral and dermal end inhalation routes in both humans and test animals. Effects observed in patients exposed to MTBE during treatment include central nervous system effects and local burning sensations. The kidney is the main target organ after repeated dosing, particularly in male rats. MTBE is classified as a skin irritant but not considered an eye or respiratory irritant. MTBE has not been shown to cause sensitisation in two guinea pig studies considered sufficient with regard to, but not formally following OECD guidelines, and there are no observations available on sensitisation in humans.

MTBE is not considered a mutagen based on results from a number of bacterial tests and is considered to be of non-genotoxic nature. No firm conclusions regarding the carcinogenic potential of MTBE and the relevance for humans can be drawn based on the different carcinogenicity studies. In conclusion, the rapporteur of the 2002 RAR considers MTBE to be a borderline case between non-classification and Carc.Cat.3 (limited evidence of carcinogenic effect). However, MTBE is not currently subject to harmonised classification for carcinogenicity. This lack of classification is in line with the IARC evaluation "not classifiable as to its carcinogenicity to humans."

In the EU, MTBE has been prioritised for REACH substance evaluation in 2014, triggered by suspected endocrine disrupting effects and its widespread use. The Danish Centre on Endocrine Disrupters has evaluated MTBE and concluded that MTBE should be categorised as an endocrine disrupter Category 1.

Exposure to MTBE occurs primarily from its use as an additive in petrol. Because of the voluntary agreement in Denmark between industry and government to phase out MTBE in petrol, exposure in Denmark has been reduced considerably since 2000. Only 31 service stations in Denmark offer 98 octane petrol containing MTBE; all are equipped with vapour recovery to reduce the exposure. No Danish exposure values are available. The RAR estimates that the normal concentration of MTBE during refuelling is 1,000-10,000 µg/m$^3$ (1-10 mg/m$^3$). The duration is short, e.g. between 1 and 5 minutes, and the frequency is 2-3 times per week at most. The reasonable worst-case (RWC) concentration is 300-29,000 µg/m$^3$ (0.3-29 mg/m$^3$) where the low end would correspond to the MTBE-level in petrol in Denmark.

Occupational exposure to MTBE in Denmark is also primarily related to exposure to MTBE-containing petrol. Results from EASE exposure estimations (RWC, 8 hour) taking into account the low concentration of MTBE in Danish petrol do not give rise to particular concern when comparing with the occupational exposure limit. Use in the pharmaceutical industry is not expected to result in any significant exposure.

Indirect exposure can occur through air, drinking water and food. No measurements have been identified for Denmark, but urban background levels are expected to be lower than the average for the EU. MTBE has been identified in groundwater at contaminated sites in concentrations above the water quality criteria. Estimated MTBE-levels in food do not indicate that MTBE is a concern.

Based on the available data, the RAR concludes that that at present there is no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied for human health protection – also in relation to combined exposure. However, as noted, further risk reduction may be put in place as a result of the upcoming REACH substance evaluation.

# 7. Information on alternatives

## 7.1 Identification of alternatives

### 7.1.1 Alternatives to MTBE as a fuel additive

MTBE is used in petrol as a means to raise the octane number. In principle, there are two ways to avoid the use of MTBE: changing the composition of the petrol in a way that in itself raises the octane number, or using another oxygenate. The first method was used in Denmark around 2000 to avoid the use of MTBE in petrol of 92 or 95 octane. This, in connection with changes in the construction of automobile motors, reduced the need for oxygenates substantially (section 3.3.2).

In connection with the implementation of the fuel directive, the Danish oil industry stated that it would be possible to produce petrol without MTBE from one of the Danish refineries from the second half of 2002, and from the other from the beginning of 2003 if sufficient high octane alkylate could be imported. Otherwise, the change would occur from 2004 if the production facilities had to be altered (OFS, 2003). Information was not given as to which changes in production were necessary, and it is not known whether such changes have been implemented.

Alongside MTBE, a number of other oxygenates have been used in other countries and they are still the primary alternatives to MTBE in high octane petrol. The choice of which oxygenate is used in which country is made primarily according to the specific development in production and import of oxygenates in the specific country. Earlier, MTBE was overall the most common oxygenate in Europe but tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE) were also used in relatively large quantities, the latter primarily in Russia, France and Italy (Smidt *et al.*, 2000). However, as shown in section 3.1.2, in recent years ETBE has taken over the position as the leading fuel oxygenate in Europe. The main reason for this being that ETBE can be produced from bioethanol, which is cheaper and more easily available than biomethanol, and is easier to mix with petrol than with ethanol. This is a contribution to the use of biofuels in the transport sector as required by EU.

In the EU, according to Directive 98/70/EC amended by Directive 2009/30/EC, there are limits set on the maximum concentration of the different oxygenates that may be used in order to avoid adverse impacts on start and driving (cold start, acceleration), corrosion of plastic parts or unacceptable fuel economy. These limits are given in Table 22.

EU also sets requirements for the amount of biobased fuel that is placed on the Member States' markets (5,75 %, calculated on the basis of energy content) of all petrol and diesel for transport purposes by 31 December 2010 (EU Directive 2003/30/EC).

Both ethanol and ETBE can be produced from a number of different types of biomass, including biomass waste products, which would make them the preferred additives in this context.

TABLE 22
MAXIMUM CONCENTRATIONS OF DIFFERENT OXYGENATES ALLOWED IN PETROL IN EU

| Substance | Abbreviation | Maximum allowable concentration, % |
|---|---|---|
| Methyl-*tertiary*- butyl ether | MTBE | 22 |
| Ethyl *tertiary*-butyl ether | ETBE | 22 |
| Tertiary amyl methyl ether | TAME | 22 |
| Ethanol | | 10 |
| Methanol | | 3 |
| Tertiary butyl alcohol | TBA | 7 |

### 7.1.2 Technical aspects

Table 23 gives an overview of some relevant technical properties of a number of possible alternatives to MTBE, while other relevant physico-chemical properties are given in Table 24.

Methanol is generally not used as an oxygenate in petrol, because the resulting vapour pressure of the petrol is too high, leading to high air emissions directly from the engine. Methanol is therefore not included in the below overview.

TABLE 23
TECHNICAL PROPERTIES OF POSSIBLE ALTERNATIVES TO MTBE

| Substance | Abbre-viation | Density, $g/cm^3$ | Vapour pressure (RVP), kPa | Heating value, GJ/tonne | Oxygen content, % | Octane number |
|---|---|---|---|---|---|---|
| Ethanol | | 0.79 | 124 | 26.7 | 34.8 | 110 |
| Tertiary butyl alcohol | TBA | 0.79 | 48 | 35,2 | 21.6 | 100 |
| Tert-amyl alcohol | | 0.81 | 41 | 37.5 | 18.2 | 97 |
| Methyl tertiary butyl ether | MTBE | 0.75 | 55 | 35 | 18.2 | 110 |
| Ethyl tertiary butyl ether | ETBE | 0.75 | 28 | 36 | 15.7 | 112 |
| Methyl tertiary amyl ether | TAME | 0.75 | 10 | 37.7 | 15.7 | 105 |
| Diiso propyl ether | DIPE | 0.73 | 20 | 37.4 | 15.7 | 105 |

Ethanol raises RVP (Reid Vapour Pressure) when blended with petrol in concentrations up to 5-10 %. During the summer period, blending ethanol in petrol raises the RVP from approx. 60 kPa to 70 kPa, thus leading to greater evaporation of VOCs from the canister.

California's EPA has carried out calculations based on a combination of their model for calculation of emissions from cars and a model for the calculation of ozone generation. Their calculations show that even though the volatilization of VOCs increases due to the higher RVP caused by addition of ethanol, this process may not generate more ozone, since the emitted VOCs contain more oxygen and are less reactive (Whitten, 1999). They have also demonstrated that exchanging MTBE for ethanol will reduce the emission of CO and formaldehyde by 3 – 6 % and increase the acetaldehyde emission by 4 %, while the other emissions will remain unaltered (Ca EPA, 1999).

Potter & Argyropoulos (2001) conclude that emissions of VOCs, $NO_X$ and CO will be reduced twice as much through the use of ETBE instead of ethanol. This finding is based on theoretical evaluations and not on tests in test motors.

The water solubility of ethanol can possess a risk for phase separation if water gets into a petrol ethanol blend.

The automobile industry (in the form of the Alliance of Automobile Manufacturers) mentions that ethanol does not cause problems in the motor, and that ethanol enhances the combustion efficiency (AAM, 2004).

Risk of groundwater contamination from the other oxygenates has not been investigated to the same degree as MTBE, but Franklin *et al.* (2000) suggests that it would be the same, if they were used in similar amounts.

**TABLE 24 PHYSICAL-CHEMICAL PROPERTIES OF DIFFERENT OXYGENATES**

| Substance | Boiling point, ºC | Solubility in water, g/l | Solubility from petrol, g/l | Log $K_{OW}$ (25 ºC) | Log $K_{OC}$ (25 ºC) | Henry's constant |
|---|---|---|---|---|---|---|
| Ethanol | 78.3 | miscible | 57 | -0.32 – 0.16 | -0.14 – 1.77 | 0.0002 |
| Tertiary butyl alcohol | 82.2 | miscible | 25 | 0.35 | 0.37 – 1.57 | 0.0005 |
| Tert-amyl alcohol | 91.2 | miscible | no data | | | |
| Methyl tertiary butyl ether | 55.3 | 42 - 54 | 5.5 | 0.94 – 1.3 | 0.55 – 1.91 | 0.02 – 0.12 |
| Ethyl tertiary butyl ether | 72.8 | 7.7 - 26 | 3.3 | 1.74 | 0.75 – 2.2 | 0.11 |
| Methyl tertiary amyl ether | 86.3 | 11.5 - 20 | 2.4 | 1.55 | 1.27 – 2.2 | 0.05 - 0.08 |
| Diiso propyl ether | 65.4 | 2 - 12 | no data | 1.52 – 2.03 | 1.13 – 1.82 | 0.2 – 0.4 |

### 7.1.3 Environmental and health aspects

The harmonised classifications of the possible alternatives are presented in Table 25. For one possible alternative (ethyl tertiary butyl ether (ETBE)), no harmonised classification is available; the industry self-classification suggested by most notifiers is presented in Table 26.

**TABLE 25**
**HARMONISED CLASSIFICATION OF POSSIBLE ALTERNATIVES TO MTBE ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)**

| Index No | International Chemical Identification | CAS No | Classification | |
|---|---|---|---|---|
| | | | Hazard Class and Category Code(s) | Hazard statement Code(s) |
| 200-578-6 | Ethanol | 64-17-5 | Flam. Liq. 2 | H225 |
| 200-889-7 | Tert-butyl alcohol (TBA) | 75-65-0 | Flam. Liq. 2<br>Eye Irrit. 2<br>Acute Tox. 4<br>STOT SE 3 | H225<br>H319<br>H332<br>H335 |

| Index No | International Chemical Identification | CAS No | Classification | |
|---|---|---|---|---|
| | | | Hazard Class and Category Code(s) | Hazard statement Code(s) |
| 200-908-9 | Tert-amyl alcohol (TAA) | 75-85-4 | Flam. Liq. 2<br>Skin Irrit. 2<br>Acute Tox. 4<br>STOT SE 3 | H225<br>H315<br>H332<br>H335 |
| 213-611-4 | Methyl tertiary amyl ether (TAME) | 994-05-8 | Flam. Liq. 2<br>Acute Tox. 4<br>STOT SE 3 | H225<br>H322<br>H336 |
| 203-560-6 | Diiso propyl ether (DIPE) | 108-20-3 | Flam. Liq. 2<br>STOT SE 3 | H225<br>H336 |

**TABLE 26**
**INDUSTRY SELF-CLASSIFICATION OF THE ALTERNATIVE ETBE ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)**

| Index No | International Chemical Identification | CAS No | Classification*) | |
|---|---|---|---|---|
| | | | Hazard Class and Category Code(s) | Hazard statement Code(s) |
| 211-309-7 | Ethyl tertiary butyl ether (ETBE) | 637-92-3 | Flam. Liq. 2<br>STOT SE 3 | H225<br>H336 |

*) Classification suggested by most notifiers.

The classification of the possible alternatives does not give any indication of serious health effects or environmental impacts. It should be noted, though, that the classification criteria do not include endocrine disrupting effects or provide information on e.g. risk for groundwater contamination or negative organoleptic properties of the substances. However, none of the mentioned alternatives to MTBE are included on the EU's list of substances with endocrine-disrupting properties in Category 1.

### 7.1.4 Alternatives to MTBE in the production of isobutylene

MTBE decomposes under suitable conditions directly to isobutylene and is therefore used specifically for production of high-purity isobutylene. This is a very specialized type of process which does not take place in Denmark; therefore, possible alternatives have not been investigated further in this study.

### 7.1.5 Alternatives to MTBE for use as a solvent

MTBE is known to be used as a process solvent in the pharmaceutical industry (including in Denmark) for a few specialized processes. No details on these processes are available for confidentiality reasons and it is therefore not possible to discuss possible alternatives. However, as indicated in Chapter 3, the volume for this application is limited.

## 7.2 Historical and future trends

The main use of MTBE has been as an oxygenate in petrol in passenger cars (more than 98 % of the total quantity produced in the EU (European Commission, 2002)). This use started in the second half of the 1970s, with low levels of MTBE (2 – 5 %) used at the time to boost the octane rating of unleaded petrol. Later, higher levels (typically 11 – 15 %) were added to promote more efficient combustion.

Starting when MTBE was discovered to be a major threat to groundwater due to its high solubility, low sorption and low degradability, the use in petrol has been reduced in several countries (including Denmark) to only encompass high octane petrol. Because of the development over time in motor engines, these types of petrol are only used in a limited number of cars.

MTBE has been detected as a groundwater contaminant in a number of cases related to petrol stations. These stations have been cleaned up as part of the remediation program carried out by the oil companies in Denmark. MTBE has also been detected at other water borings, but the content has been reduced substantially over the years (below 1 µg/l in the measured borings in 2009).

## 7.3 Summary and conclusions

*Alternatives to MTBE as a fuel additive*
The alternatives described are all considered to be technically relevant alternatives to MTBE in petrol. ETBE and ethanol can be produced from biomass, where the evaluation of their appropriateness is specific to the source of biomass used, for which the EU sets out requirements in Directive 2009/28/EC on the promotion and use of energy from renewable sources. At the European level, bio-ETBE has to a significant extent replaced MTBE during the last decade, as ETBE is easier and cheaper to produce from such sources than MTBE.

The classification of the possible alternatives does not give any indication of serious health effects or environmental impacts. It should be noted, though, that the classification criteria do not include endocrine-disrupting effects or give information on e.g. mobility in soil or negative organoleptic properties of the substances and, hence, such aspects cannot be assessed through the classification. However, none of the mentioned alternatives to MTBE are included on the EU's list of substances with endocrine-disrupting properties in Category 1. On the other hand, ETBE, being chemically closely related to MTBE, could be suspected of having properties similar to MTBE, e.g. with regard to mobility in soil.

*Alternatives to MTBE for use as a solvent*
No details on alterternatives were found. However, the consumption of MTBE for this purpose is very limited.

# 8. Abbreviations and acronyms

| | |
|---|---|
| ADI | Acceptable daily intake |
| BCF | Bioconcentration factor |
| CEFIC | European Chemical Industry Council |
| CLP | Classification, Labelling and Packaging Regulation |
| DCED | Danish Centre for Endocrine Disrupters (Center for Hormonforstyrrende Stoffer) |
| DT | Degradation time |
| $EC_n$ | Effect concentration where n % of the species tested show the effect |
| ECB | European Chemicals Bureau |
| ECHA | European Chemicals Agency |
| EFOA | European Fuel Oxygenates Association |
| EFSA | European Food Safety Authority |
| EPA | Environmental Protection Agency |
| EOF | The Danish Oil Industry Association |
| EQC | Equivalent level of concern |
| EQS | Environmental Quality Standard |
| EU | European Union |
| HELCOM | The Baltic Marine Environment Protection Commission (Helsinki Commission) |
| Kow | Octanol/water partitioning coefficient |
| Koc | Organic carbon/water partitioning coefficient |
| Kp | Partial pressure equilibrium constant |
| LC | Lethal effect concentration |
| LOUS | List of Undesirable Substances (of the Danish EPA) |
| MWWTP | Municipal waste water treatment plant |
| NMC | Nation Mean Concentration |
| NOAEL | No observable adverse effect level |
| NOEC | No observable effect concentration |
| NOVANA | Danish national monitoring and assessment programme |
| OECD | Organisation for Economic Co-operation and Development |
| OSPAR | Convention for the Protection of the Marine Environment of the North-East Atlantic |
| PEC | Predicted environmental concentration |
| PNEC | Predicted no effect concentration |
| PR | Produktregistret (The Danish Product Register) |
| QSAR | Quantitative Structure and Activity Relationship |
| RMS | Rapporteur Member State (in the EU) |
| RWC | Reasonable Worst-Case |
| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| SIDS | Screening Information Data Sets |
| STP | Sewage treatment plant |
| SVHC | Substance of Very High Concern |
| TGD | Technical guidance document |
| ThOD | Theoretical oxygen demand |
| TDI | Tolerable daily intake |

# References

Andersen, L. & Hansen, J.B. (2006): Vurdering af MTBE og alternative additiver. Erfaringer, miljøvurdering og forsyningssikkerhed. Miljøprojekt 1086. teknologiprogrammet for jord- og grundvandsforurening. Miljøstyrelsen.

Alliance of Automobile Manufacturers (2004): Cleaner fuels make cleaner cars, http://www.autoalliance.org

Alliance of Automobile Manufacturers (2004): What really affects fuel economy? The Facts on Consumers and Fuel Economy.

American Chemistry Council (2005): High Production Volume (HPV) Chemical Challenge Program Test Plan For: Diisopropyl Ether (DIPE) CAS NO. 108-20-3 Prepared by: ExxonMobil Chemical Company Shell Chemical LP

Brüsch, W. & Villholt, K. (2011): Punktkilders påvirkning af grundvandsressourcens kvalitet. Miljøprojekt nr. 1395. Miljøstyrelsen.

California EPA (1999): Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline. Final Report to the California Environmental Policy Council. Health and Environmental Assessment of the
Use of Ethanol as a Fuel Oxygenate. Volume 3. UCRL-AR-135949.

Clark, J.J.J. (2003): Tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards. In Oxygenates in Gasoline Environmental Aspects. Edited by Diaz A.F and Drogos D.L. ACS Symposium Series 799. American Chemical Society, Washington DC.

Dakhel, N; Pasteris, G; Werner, D & Höhener, P (2003): Small- Volume Releases of Gasoline in the Vadose Zone: Impact of the Additives MTBE and Ethanol on Groundwater Quality, *Environmental Science and Technology*, vol. 37, pp. 2127- 2133.

Danish EPA (2011). Listen over uønskede stoffer 2009 (List of undesirable substances 2009). Environmental Review 3/2011. Danish EPA, Copenhagen.

ECHA (2012). ECHA proposal to Member States. Draft Community Rolling Action Plan (CoRAP) update for years 2013-2025. European Chemicals Agency. 23 October 2012.

ECHA (2013a). Registered substances. Information on ECHA's website at: Available at: http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances.

ECHA (2013b). Candidate List of Substances of Very High Concern for Authorisation. Available at: http://echa.europa.eu/da/candidate-list-table

ECHA (2013c). Fourth Annex XIV recommendation - 17 January 2013. Available at: http://echa.europa.eu/documents/10162/13640/4th_a_xiv_recommendation_17jan2013_en.pdf

Energi- og olieforum (2013). Energinoter & Statistik 2012/13.

European Commission (2002). European Union Risk Assessment Report, *tert*-butyl methyl ether. Final Report, 2002. Prepared for Finland by Finnish Environment Institute. 279 pp.

European Commission (2003). Addendum to the European Union Risk Assessment Report, tert-butyl methyl ether on studies of tainting and avoidance behaviour in fish. Addendum document R313_0408_env_addendum.doc prepared by DHI.

Eurostat (2013). Eurostat 2012. External trade by CN8 database.

Franklin, P.M., Koshland, C.P., Lucas, D. & Sawyer, R.F. (2000): Clearing the Air: Using Scientific Information to Regulate Reformulated Fuels. Environmental Science & Technology, vol. 34, no. 18, pp. 3857-3863.

Funen County (2001): Hvor ofte findes MTBE og i hvilke koncentrationer? En opsamling af resultater fra Fyns Amt. ATV Winter Meeting. Later updated in 2003 as background for Danih EPA: Risikovurdering af MTBE i forhold til grundvandet. Miljøprojekt no. 785.

Hartle, R:W.; Kelly, J.E.; Burton, N.C. & Cook, C. (1993): Health Hazard Evaluation report for MTBE. NIOSH.

Happel, A.M.; Beckenbach, E.H. & Halden, R.U. (1998): An Evaluation of MTBE Impacts to California Groundwater Resources, Lawrence Livermore National Laboratory of California State Water Resources Control Board. UCRL-AR-130897.

Health Effects Institute (1996): The Potential health Effects of Oxygenates added to gasoline. A Review of the current Literature.

Larsen, P.B. (1998). Evaluation of health hazards by exposure to methyl tert-butyl ether (MTBE) and estimation of limit values in ambient air, soil and drinking water. The Institute of Food Safety and Toxicology. Danish Veterinary and Food Administration. Report. 30 pp.

Miljøstyrelsen (1998). Handlingsplan for MTBE (National Action Plan for MTBE). June 1998.

Miljøstyrelsen (2000). NOVA-2003. Programbeskrivelse for det nationale overvågningsprogram for overvågning af vandmiljøet i Danmark, 1998-2003 (Programme description for the national programme for surveillance of the aquatic environment in Denmark, 1998-2003) . Redegørelse nr. 1, 2000. Miljøstyrelsen. Bilag 2.

Miljøstyrelsen (2005). Punktkilder 2004 (Point sources 2004). www.mst.dk.

Naturstyrelsen (2012). Punktkilder 2011 (Point sources 2011). Rapport, 100 pp. www.nst.dk

NOVANA (2011). Det Nationale Overvågningsprogram for Vand og Natur. 2011-2015. Programbeskrivelse [The national monitoring programme for surveillance of water and nature. 2011-2015]. Nature Agency, National Environmental Research Institute (NERI) and Geological Survey of Denmark and Greenland (GEUS), Denmark.

OFS (2003): Redegørelse til Miljøstyrelsen for muligheder for at producere benzin fra 2005 med og uden MTBE (Statement to the Danish EPA on the possibilities of producing petrol from 2005 with and without MTBE).

OFS (2000). MTBE og 98 oktan benzin (MTBE and 98 octane gasoline). Letter from OFS (Oliebranchens Fællesrepræsentation (Danish Petroleum Industry Association)) to the Minister of Environment, Svend Auken. 3rd November 2000.

Oliebranchens Miljøpulje (2006): Opgørelse af MTBE fund på OM-II sager.

Schmidt, T.C., Schirmer, M, Wiess, H. & Haderlein, S.B. (2004): Microbial degradation of methyl tert-butyl ether and tert-butyl alcohol in the subsurface. Journal of Contaminant Hydrology

Schmidt, T.S., Morgenroth, E., Schirmer, M., Effenberger, M. & Haderlein, S.B. (2000): Use and Occurrence of Fuel Oxygenates in Europe.

Statistics Denmark (2013). Udenrigshandel, produktion og forsyning [Foreign trade, production and supply]. Available at: http://www.dst.dk/da/informationsservice/oss/UHprod.aspx

US EPA(2013): Mehtyl Tertiary Butyl Ether (MTBE). Overview, http://www.ea.gov/mtbe/faq.htm

US PA (2000): Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions, EPA/600/R -00/006.

Vainiotalo, S.; Peltonen, Y.; Ruonakangas, A. & Pfäffli, P. (1999): Customer Exposure to MTBE, TAME, C6 Alkyl Methyl Ethers, and Benzene during Gasoline Refueling, Environmental Health Perspectives, Vol. 107, no. 2,

# Appendix 1: Background information to Chapter 2 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with Chapter 2.

**EU and Danish legislation**
Chemicals are regulated via EU and national legislation, the latter often being a national transposition of EU directives.

**There are four main EU legal instruments:**
- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).

The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a "comitology" procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation to some extent regulates chemicals via various general or sector-specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

## Chemicals legislation

### REACH and CLP

The REACH Regulation[17] and the CLP Regulation[18] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below briefly summarises the REACH and CLP provisions and gives an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

### (Pre-)Registration

All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered deadlines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

### Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

### Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

### Restriction

If the authorities conclude that that there is a risk to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

### Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed upon at the EU level and can be found in CLP Annex VI. In addition to

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17 Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

18 Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC) - classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemical substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publishes the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

**Ongoing activities - pipeline**
In addition to listing substances already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA website also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These are briefly summarised below:

**Community Rolling Action Plan (CoRAP)**
The EU Member States have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) has been developed and published, indicating when and by whom a given substance is expected to be evaluated.

**Authorisation process; candidate list, Authorisation list, Annex XIV**
Before a substance is included in REACH Annex XIV, and thus subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[19]
2. It has to be prioritised and recommended for inclusion in Annex XIV (these can be found as Annex XIV recommendation lists on the ECHA web-site)
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA website).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA website.

**Registry of intentions**
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intentions in relation to Annex XV dossiers, divided into the three types of Annex XV dossiers:
- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and

[19] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

- withdrawn intentions and withdrawn submissions.

**International agreements**

**OSPAR Convention**
OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance;
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out;
- guidelines or guidance setting out the way that any programme or measure should be implemented, and
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

**HELCOM - Helsinki Convention**
The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

**Stockholm Convention on Persistent Organic Pollutants (POPs)**
The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

**Rotterdam Convention**
The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

**Basel Convention**
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention centre around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management, and
- a regulatory system applying to cases where transboundary movements are permissible.

**Convention on Long-Range Transboundary Air Pollution, CLRTAP**
Since 1979 the Convention on Long-range Transboundary Air Pollution (CLRTAP) has addressed some of the major environmental problems of the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation.

The aim of the Convention is that Parties shall endeavour to limit and, as far as possible, gradually reduce and prevent air pollution including long-range transboundary air pollution. Parties develop policies and strategies to combat the discharge of air pollutants through exchanges of information, consultation, research and monitoring.

The Convention has been extended by eight protocols that identify specific measures to be taken by Parties to cut their emissions of air pollutants. Three of the protocols specifically address the emission of hazardous substances, of which some are included in LOUS:

- The 1998 Protocol on Persistent Organic Pollutants (POPs); 33 Parties. Entered into force on 23 October 2003.
- The 1998 Protocol on Heavy Metals; 33 Parties. Entered into force on 29 December 2003.
- The 1991 Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes; 24 Parties. Entered into force 29 September 1997.

### Eco-labels

Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products:

**EU flower**

The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

**Nordic Swan**

The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval processes related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark’s website (according to Statutory Order no. 447 of 23/04/2010).

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