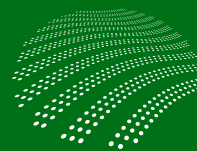


Cooperative Research Centre for **Contamination  
Assessment and Remediation of the Environment**

[www.crccare.com](http://www.crccare.com)



**CRCCARE**

*A safer, cleaner  
environmental future*



## TECHNICAL REPORT NO. 36

# Guidance for the assessment, remediation and management of MTBE

**Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report series, no. 36**  
December 2016

Copyright © CRC CARE Pty Ltd, 2016

This book is copyright. Except as permitted under the Australian Copyright Act 1968 (Commonwealth) and subsequent amendments, no part of this publication may be reproduced, stored or transmitted in any form or by any means, electronic or otherwise, without the specific written permission of the copyright owner.

ISBN: 978-1-921431-50-0

**Enquiries and additional copies:**

CRC CARE, C/- Newcastle University LPO, PO Box 18, Callaghan NSW, Australia 2308  
Tel: +61 (0) 2 4985 4941  
Fax: +61 (0) 8 8302 3124  
admin@crccare.com  
www.crccare.com

**This report should be cited as:**

CRC CARE 2016, *Guidance for the assessment, remediation and management of MTBE*, CRC CARE Technical Report no. 36, CRC for Contamination Assessment and Remediation of the Environment, Newcastle, Australia.

**Disclaimer:**

This publication is provided for the purpose of disseminating information relating to scientific and technical matters. Participating organisations of CRC CARE do not accept liability for any loss and/or damage, including financial loss, resulting from the reliance upon any information, advice or recommendations contained in this publication. The contents of this publication should not necessarily be taken to represent the views of the participating organisations.

CRC for Contamination Assessment and Remediation of the Environment

Technical Report no. 36

## **Guidance for the assessment, remediation and management of MTBE**

December 2016



## Executive summary

---

Methyl *tertiary*-butyl ether (MTBE) is not manufactured or used as an additive to petrol in Australia, although it may be present at levels up to 1% in imported fuels. There are sites that are known to be contaminated with MTBE, where that contamination occurred prior to the introduction of the *Fuel Quality Standards Act* in 2000 and the *Fuel Quality Standards Regulations* in 2001. In the Australian context, contamination of groundwater at legacy sites is thus an important consideration.

This document provides guidance in relation to the assessment, remediation and management of MTBE contaminated groundwater. MTBE will migrate rapidly from a source, through the soil profile, to groundwater and/or surface water. MTBE is degraded rapidly in surface waters, but it is relatively stable in groundwater. Once MTBE reaches groundwater it can migrate at almost the same speed as groundwater flow, given its solubility in water, and therefore can travel rapidly in the sub-surface.

MTBE when released to the environment through soils will preferentially enter groundwater or surface waters due to its high water solubility and low affinity for binding to soils. If MTBE is present in surface waters it will readily volatilise to air. MTBE has a low odour threshold which makes water unpalatable for drinking at MTBE concentrations well below those that would impact on human health. The screening level based on aesthetics can therefore be used to assess groundwater which is used, or may be used, for potable and non-potable purposes. Therefore, regulation of MTBE in groundwater in many jurisdictions is based on aesthetics, rather than toxicity to humans. For aquatic species, MTBE has relatively low acute and chronic toxicity, with marine species generally showing a greater sensitivity. International guidance for MTBE in soil and soil vapour is limited, as MTBE preferentially enters groundwater or surface waters.

The guideline provides MTBE-specific information for the assessment of potentially contaminated sites, and is intended to be consistent with the *National Environment Protection (Assessment of Site Contamination) Measure 1999* as amended in 2013 (ASC NEPM). The approaches to assessment, remediation and management of MTBE contaminated groundwater have been drawn from international guidance, as there are few Australian guidelines for MTBE. Odour and ecological screening criteria have been developed for Australian conditions to be used in the assessment and remediation of contaminated sites where MTBE is considered to be a contaminant of concern. This guidance on assessment and managing and/or remediating groundwater contamination comprises:

- an odour-based screening level in water
- ecological screening levels that have been derived using a methodology based on ANZECC & ARMCANZ (2000) and ASC NEPM (NEPC 2013), and
- contaminant-specific considerations to consider in site investigations, including the development of the conceptual site model (CSM).

The screening levels presented in this guidance are contaminant concentrations above which further investigation and evaluation may need to be undertaken. They are expected to assist decision-making in relation to the need for site-specific risk assessments. Schedules B4, B5a and B6 of the ASC NEPM provide general guidance

for conducting risk-based assessments. Guidance for the assessment of aesthetic issues, such as odour, is provided in schedule B1 of the ASC NEPM.

Individual jurisdictions have legislation that establishes remediation and management requirements for contaminated sites. The approaches being used for site assessment, remediation and management in each jurisdiction were reviewed during the development of this guideline to identify areas of consistency and points of difference. Where no Australian information was available, international sources were reviewed. Readers are advised to consult with their state or territory regulatory agency before commencing any remediation project to ensure that they are able to comply with specific jurisdictional requirements.

# Acknowledgements

---

Project Advisory Group members:

NAME		ORGANISATION
Dennis	Monahan	Chair
Andrew	King	BP Australia
Andrew	Pruszinski	Environment Protection Authority SA
Andrew	Miller	Department of Environment Regulation WA
Anne	Northway	EPA Victoria
Brian	Priestly	Monash University
Colin	Roberts	Caltex
Craig	Barnes	Airservices Australia
Damien	Davidson	Caltex
Damien	Home	VIVA Energy
Daniel	Walters	Environment Protection Authority ACT
Dave	Thomas	Chevron
David	Hartog	Department of Defence
Erwin	Benker	Environment Protection Authority NSW
Holly	Ainslie	Department of Infrastructure and Regional Development
Jack	Ng	University of Queensland
James	Higinbotham	Exxon Mobil
Janet	Macmillan	Department of Environment Regulation WA
John	Howell	WA Health
John	Mikac	Exxon Mobil
Paul	Barrett	Australian Institute of Petroleum
Peter	Gniel	Australian Institute of Petroleum
Rebecca	Hughes	Environment Protection Authority SA
Rod	Lukatelich	BP Australia
Sarah	Brown	Department of Defence
Stacey	Hannon	Department of Defence
Stuart	Rhodes	Rio Tinto
Tanya	Astbury	VIVA Energy
Terry	Soutberg	Air Services Australia
Tony	Bradshaw	EHP Queensland

CRC CARE also acknowledges the contribution made by:

- Lyn Denison of Pacific Environment – Toxikos for the compilation of this report
- Joytishna Jit of the Future Industries Institute, University of South Australia, for the management, coordination and compilation of this work, and
- Graeme Batley of CSIRO Land and Water Flagship for his peer review of this document.

## Abbreviations

---

ACR	Acute to chronic ratio
ANZECC	Australian and New Zealand Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
ASC NEPM	National Environment Protection (Assessment of Site Contamination) Measure 1999 as amended in 2013
AWQG	Australian Water Quality Guidelines
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CSM	Conceptual site model
DSI	Detailed site assessment
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ESL	Ecological screening level
GAC	Granular activated carbon
GIL	Groundwater investigation level
GV	Guideline value
LOEC	Lowest observed effect concentration
LTTD	Low-temperature thermal desorption
MATC	Maximum allowable toxicant concentration
MNA	Monitored natural attenuation
MPE	Multi-phase extraction
NEC	No effect concentration
MTBE	Methyl <i>tertiary</i> -butyl ether
NOEC	No observed effect concentrations
PSI	Preliminary site assessment
RAP	Remediation action plan
SAQP	Sampling analysis quality plan
SSD	Species sensitivity distribution
SVE	Soil vapour extraction
TAME	<i>Tertiary</i> -amyl methyl ether
TBA	<i>Tertiary</i> -butyl alcohol

UPSS	Underground petrol storage systems
US EPA	United States Environmental Protection Agency
WHO	World Health Organization



# Table of contents

---

<b>Executive summary</b>	<b>i</b>
<b>1. Introduction</b>	<b>1</b>
1.1 Purpose and scope of the Guideline	2
1.1.1 Underground petrol storage systems (UPSS) regulation in Australia	3
<b>2. Assessment of MTBE contaminated sites</b>	<b>5</b>
2.1 Preliminary site investigation (PSI)	6
2.2 Conceptual site model (CSM)	8
2.3 Detailed site investigation (DSI)	10
2.3.1 Groundwater modelling	11
2.3.2 Sampling analysis quality plan	12
2.3.3 Groundwater well installation	14
2.3.4 Environmental sampling	14
2.3.5 Analytical methods	15
2.3.6 Screening levels	15
<b>3. Considerations for the management of MTBE contaminated sites</b>	<b>16</b>
<b>4. Remediation</b>	<b>19</b>
4.1 Remediation options for MTBE contaminated groundwater	22
4.2 Remediation action plan (RAP)	25
<b>5. Monitoring and management</b>	<b>26</b>
5.1 Monitoring requirements	26
5.2 Site management measures	27
5.3 Case study – MTBE contaminated site in Western Australia	27
5.3.1 Background	27
5.3.2 Investigations	28
5.3.3 Remedial works:	28
5.3.4 MTBE outcome	29
<b>6. Conclusion</b>	<b>31</b>
<b>7. References</b>	<b>32</b>

## **Appendices**

---

Appendix A.	Derivation of odour screening level for MTBE	38
Appendix B.	Derivation of ecological screening criteria for MTBE	43

## **Table**

---

Table 1.	MTBE groundwater screening levels	5
----------	-----------------------------------	---

## **Figures**

---

Figure 1.	Difference in migration of MTBE compared with BTEX	3
Figure 2.	Schematic showing an example of MTBE contamination	9
Figure 3.	Map showing groundwater plumes containing hydrocarbons and MTBE at a legacy site, in 2014	30

# 1. Introduction

---

Methyl *tertiary*-butyl ether (MTBE) is the principal oxygenate and octane enhancer added to petrol by refineries worldwide due to its compatible blending properties and lower cost. It is described as an oxygenate – an oxygen-bearing additive used to reduce engine knocking and assist petrol burn more cleanly. World production capacity of MTBE is 21 Mt per annum, with a further 7 Mt per annum of capacity in construction or in planning. It is widely used in Europe and Asia.

The chemical properties and fate and transport of MTBE differ from other petroleum hydrocarbons. MTBE has higher water solubility and vapour pressure, and lower Henry's Law constant than other fuel hydrocarbons and therefore a higher affinity for soil moisture and groundwater (API 2000). Dissolved phase MTBE has a low tendency to adsorb to soil or volatilise to soil vapour, and has a lower potential for biodegradation compared with other petroleum hydrocarbons (API 2000). Site investigations need to consider the nature and extent of MTBE contamination separately from other petroleum hydrocarbons to ensure that potentially complete source-pathway-receptors linkages are identified and assessed.

MTBE will migrate rapidly from a source, through the soil profile, to groundwater and/or surface water. MTBE volatilises and degrades rapidly in surface waters (Heald 2005), however it is relatively stable in groundwater. Once MTBE reaches groundwater it can migrate at a similar speed to the groundwater flow and therefore can travel rapidly in the sub-surface (Environment Agency 2000).

MTBE is not manufactured in Australia and is not used as a fuel additive. The *Fuel Quality Standards Regulations 2001*, established under the *Fuel Quality Standards Act 2000*, allow MTBE to be present in imported fuels up to 1%. MTBE has been prohibited in petrol supplied in Western Australia and Queensland due to potential groundwater contamination concerns. MTBE is not added to fuels which are imported into Australia, however as MTBE is used in countries from which fuel is exported to Australia there is a risk of cross-contamination and the allowance of up to 1% MTBE is an acknowledgement of this situation.

Under the *Fuel Quality Standards Regulations 2001* racing fuels can be imported and used in Australia that contain MTBE if approval is received from the Minister for the Environment under the provisions of the regulations. According to the Department of Environment there are 70 approved organisations that provide fuel containing between 14–55% MTBE for car racing (as at April 2016). The location of fuel storage and use has the potential for contamination of soil and groundwater.

Australia has a strong reliance on imported fuels, which is likely to increase with local refineries closing down. In 2010–11, according to the Office of the Chief Economist (Office of Chief Economist 2016), 16,643 ML of petrol was produced in refineries in Australia (January 2016). This decreased to 14,478 ML in 2013–14 (a decrease of 7.2%) and 12,753 ML in 2014–15 (a decrease of 11.9%).

Over that period, imports of petrol increased from 2,653 ML in 2010–11 to 3,598 ML in 2013–14 and 5,434 ML in 2014–15, the majority being imported from Singapore and South Korea. In 2013–14, 2,210 ML was imported from Singapore and 1,092 ML from South Korea. The growth in imports is expected to increase. As MTBE is added to

petrol produced in Asia there is potential for cross-contamination of petrol supplied to Australia from these countries.

As MTBE is not manufactured or used in petrol refining in Australia, the main source of contamination is from leakage of fuel that contains less than 1% MTBE (in compliance with the *Fuel Quality Standards Regulations 2001*). It should be noted that the MTBE content in fuels is limited to 0.1% in WA. However, prior to the introduction of the *Fuel Quality Standards Act* in 2000 and the *Fuel Quality Standards Regulations* in 2001, MTBE was present in imported petrol at concentrations up to 15% in Australia. This has led to some legacy sites where MTBE contamination of groundwater has been confirmed.

MTBE when released to the environment through soils will preferentially enter groundwater or surface waters due to its high water solubility and low affinity for binding to soils (US EPA 2008). If MTBE is present in surface waters it will readily volatilise to air (Heald 2005). MTBE has a low odour threshold which makes any water unpalatable for drinking at levels well below those that would impact on human health (US EPA 2008). Therefore, regulation of MTBE in groundwater is usually based on aesthetics rather than toxicity to humans. For aquatic species MTBE has relatively low acute and chronic toxicity, with marine species generally showing a greater sensitivity.

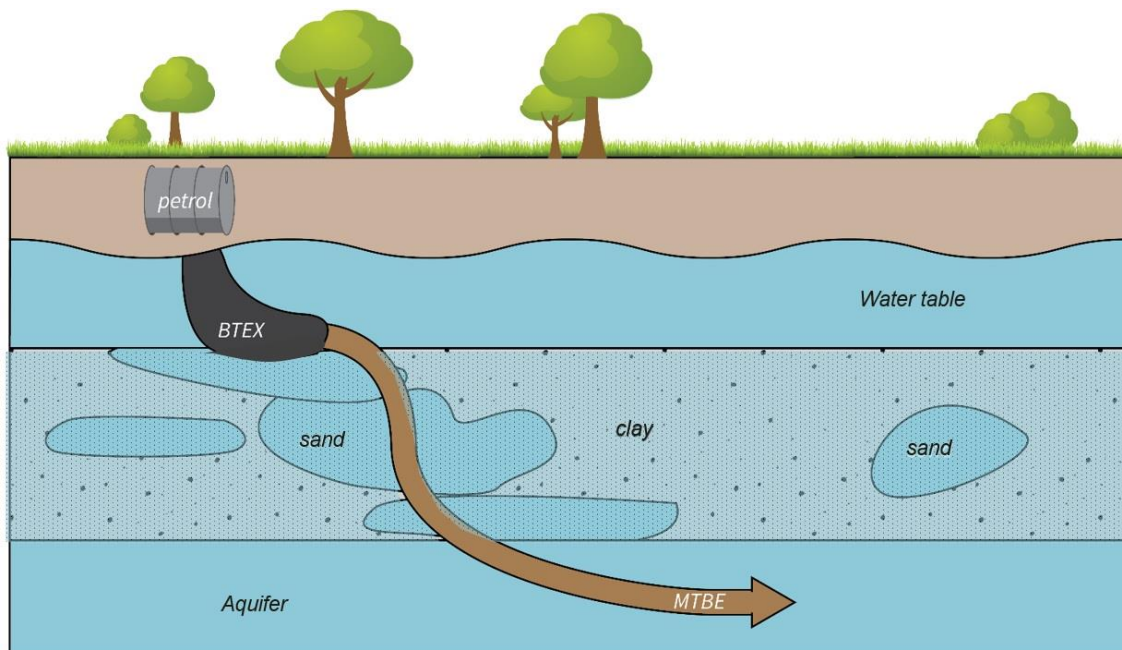
## 1.1 Purpose and scope of the Guideline

This guideline provides a framework for the assessment, remediation and management (including ongoing monitoring) of MTBE contaminated sites in Australia with a focus on groundwater, and is based on a review of national and international approaches to dealing with MTBE contaminated sites. The guideline incorporates an odour based screening level and an ecological screening level (ESL) for groundwater. The screening levels, if exceeded, may act as triggers for further investigation consistent with the role of investigation and screening levels in the *National Environment Protection (Assessment of Site Contamination) Measure 1999* as amended 2013 (ASC NEPM). The focus on groundwater is due to the fact that MTBE has a low affinity for binding to soils and is highly water soluble.

The methodology for assessment is consistent with the ASC NEPM framework with specific reference to the assessment of MTBE contaminated groundwater. The ASC NEPM presents a risk based framework for staged site assessment whereby a preliminary site investigation (PSI) may be conducted to determine the potential for contamination to be present and identify sources of contamination. A PSI may or may not include initial environmental sampling. Where the PSI identifies the presence or potential presence of contamination, a detailed site investigation (DSI) may be required. The following sections provide guidance on the PSI and DSI processes with a specific focus on issues specific to MTBE contamination.

One key component of the assessment for contaminated sites is the development of the conceptual site model (CSM). The development of the CSM is an iterative process based on information gathered through the PSI and DSI. If the site history indicates that there was fuel stored at a site prior to 2003 and is suspected or known to have contained MTBE, such as old service stations, then further assessment may need to be undertaken, depending on site-specific factors as well as regulator requirements. The CSM must take into account the different behaviour of MTBE in soils and groundwater

compared with petroleum hydrocarbon plumes (CRC CARE 2006), which is shown diagrammatically in figure 1. The development of the CSM is discussed in section 2 of this guideline.



**Figure 1: Difference in migration of MTBE compared with BTEX (aquifer shown) (adapted from Dr Stupp Consulting)**

The remediation technologies considered in this guideline are currently available in Australia and are used in the remediation of contaminated groundwater more broadly. It is important that practitioners remain flexible and adaptive in their approach(es) to the remediation of MTBE contamination, based on the evolution and availability of remediation technologies.

The main source of MTBE contamination in Australia is from leakage of fuel from underground petroleum storage systems (UPSS) or spills from petrol tankers. Most jurisdictions have regulations that govern the way UPSS are installed, monitored and decommissioned. As a result of the implementation of these regulations, there is a lower potential for contamination to be present from current and future UPSS and the potential for undetected releases of fuel containing MTBE is low. As such, the majority of site assessment and remedial activities are likely to occur at legacy sites, where there was a higher likelihood of releases involving MTBE. An overview of UPSS regulations is provided in section 1.1.1.

### **1.1.1 Underground petrol storage systems (UPSS) regulation in Australia**

All states and territories have regulations or guidance on the installation, operation and decommissioning of UPSS. Formal UPSS regulations are in place in NSW (NSW EPA 2014), Victoria (EPA Victoria 2014) and Tasmania (Tasmanian EPA 2010). The Department of Defence has issued a Directive for *Fuel Farms, Underground Petroleum Storage Systems (UPPS) and Underground Storage Tank (UST) Environmental Management* (2011). This directive outlines mandatory requirements for all Defence owned and operated sites where fuel storage systems are present (Department of Defence 2011). Failure to comply with UPSS regulations can result in penalties for both the owners and operators of a UPSS site.

Queensland, South Australia, the Northern Territory, ACT and Western Australia have published UPSS guidance and, in some cases regulate UPSS through other legislative instruments (e.g. *WA Dangerous Goods and Safety Act*). All jurisdictions refer to the Australian Standard AS 4897/2008: *The Design, Installation and Operation of Underground Petroleum Storage Systems* which provides guidance on requirements for installation, and monitoring UPSS, while AS 4976/2008: *The removal and disposal of underground petroleum storage tanks* provides guidance with regard to decommissioning of UPSS.

The regulations and guidance aim to reduce the potential for leaks from UPSS, and provide operators with the tools to monitor and detect fuel releases before environmental harm occurs. Although the regulatory mechanisms may differ, all guidance and regulations contain the same key requirements. These include:

- Leak prevention approaches
  - UPSS design
  - UPSS equipment selection
  - correct installation methods and
  - repair, reuse or upgrade UPSS for which a failure has been identified (whether or not a leak has occurred).
- Leak detection systems
  - installation of leak detection systems
  - keeping records of the detection system design, operation, procedures, responsibilities, system checks, inspection etc, and
  - leak and spill response reporting, procedures, and mitigation.
- Environmental Management Plans
  - assessment of potential contamination, and
  - installation of groundwater monitoring wells.
- Removal and decommissioning of UPSS
  - systems not in use must be removed and decommissioned.

As indicated above, the requirements of the UPSS regulations and guidance are aimed at the prevention and early detection of any leakage and associated contamination arising from fuel leakage. There are also requirements for assessment of the site to determine any existing contamination prior to installation of any new tanks and to prevent any contamination or early detection of contamination of nearby groundwater. These requirements reduce the potential for leakage of fuels containing MTBE together with other petroleum hydrocarbons and therefore any subsequent contamination.

## 2. Assessment of MTBE contaminated sites

The framework for the assessment of contaminated sites in Australia is set out in the ASC NEPM. The framework provides a risk-based approach to the assessment of contaminated sites and includes:

- preliminary site assessment (PSI)
- development of conceptual site model
- detailed site assessment (DSI), and
- human health and/or ecological risk assessment.

If the preliminary site assessment and conceptual site model show that there is no risk to human health or the environment posed by contamination at the site, then a detailed site assessment and risk assessment may not be required.

The screening levels for MTBE shown in table 1 can be used to determine if further assessment is required. The aesthetic (odour based) screening level can be used to assess groundwater quality potentially impacted by specific site contamination where the groundwater is used, or may potentially be used, for potable and non-potable purposes. For other contaminants, the investigation and screening levels contained in the ASC NEPM should be used. It is emphasised that exceedance of the ecological screening levels (ESLs) does not necessarily imply that the contamination poses an unacceptable risk, and the ESLs should not be used as remediation targets, as this could result in unnecessary remediation. If the results of groundwater sampling show exceedances of the screening levels, then further assessment may need to be undertaken. If the DSI (see section 2.3) shows a potential risk to human health or the environment, then a site-specific risk assessment may be required.

**Table 1: MTBE groundwater screening levels**

	Screening level	Comment
Odour	15 µg/L	Consistent with WHO guidance for drinking water. Based on aesthetics not toxicity.
Ecological screening level – freshwater	32 mg/L	Provides 95% protection (see Appendix B, table 1) – these values are applicable to slightly-moderately disturbed ecosystems <sup>1</sup>
Ecological screening level – marine waters	13 mg/L	

The detailed derivation of the screening levels in table 1 is presented in Appendix A and Appendix B. Appendix B, table 4 also provides a comparison with some international values.<sup>2</sup>

Recreational water bodies should be aesthetically acceptable to recreational users (NHMRC 2008). Recreational water users can be deterred by objectionable smells associated with contaminated water. The odour based screening level for MTBE that has been adopted in this guideline for use in the assessment of potable groundwater

<sup>1</sup> For receiving environments considered to be of high ecological value (e.g. world heritage areas), a higher level of protection (i.e. 99%) may be appropriate. See Appendix B, table 3.

<sup>2</sup> Some jurisdictions consider short-term exposures for which aquatic toxicity values are higher than the values for long term exposures. For example, see US EPA findings for short-term exposures in Appendix B (details available at <https://www.epa.gov/wqc/aquatic-life-criteria-methyl-tertiary-butyl-ether-mtbe>).

should also be applied for the assessment of other sources of potable and non-potable water supplies including recreational waters.

If MTBE is found in groundwater, testing should be considered for *tertiary*-butyl alcohol (TBA) and formaldehyde (which are breakdown products of MTBE), depending on the site history and the extent of contamination. This is more likely to be important for legacy sites rather than recent contamination. Assessment of formaldehyde in groundwater should be done against the groundwater investigation level (GIL) in the ASC NEPM of 0.5 mg/L (note the threshold for formaldehyde is relatively high compared to the MTBE threshold concentration in water for odour of 15 µg/L). For TBA, for which a GIL is not included in the ASC NEPM, international guidelines can be used. When using such guidelines, an assessment of their derivation should be undertaken to ensure consistency with the risk levels adopted in the ASC NEPM, and justification of the choice of guideline should be provided in the DSI.

Groundwater sampling and analysis should follow guidance in AS/NZS 5667.11/1998, the ASC NEPM, and relevant state guidelines (see also section 2.3.5 on US EPA analytical methods). Where the outcomes of the PSI and DSI indicate there are potential risks to receptors at and surrounding a site, these risks may need to be quantitatively assessed using a site-specific risk assessment process. The health and ecological risk assessments should be undertaken as per guidance presented in enHealth (2012) and ASC NEPM respectively.

## 2.1 Preliminary site investigation (PSI)

The purpose of a preliminary site investigation (PSI) is to identify the potential sources of contamination and contaminants of concern, the receptors that may be exposed to contamination and the relevant exposure pathways. The process for conducting a PSI is established in the ASC NEPM. The scope of work should be sufficient to provide an initial indication of a site's contamination status, the nature and location of likely sources and receptors, and to determine whether a detailed site investigation (DSI) is warranted.

A review of the site history, physical setting including local geology and hydrogeology, and site conditions must be undertaken. The information collected should be used to develop an initial CSM for the site.

A site inspection should be undertaken to complement the findings of the desktop study and site history and to identify any additional relevant site information. It is recommended that interviews be conducted with current site owners and occupiers and, where practicable, previous site owners and occupiers.

It is essential that the location of the site, its history and any significant features be accurately and clearly identified. The PSI report should clearly identify any significant data gaps and include an assessment of the accuracy of the information collected. If the site history indicates that the site has been used for fuel storage, including old service stations, then the possibility of MTBE contamination should be considered, if the site was in operation before the *Fuel Quality Standards Regulations 2001* came into force. The results of the PSI, and the CSM, will determine whether a DSI is required.



The following information should be sought when investigating potential MTBE contamination during the PSI:

- Has fuel, especially petrol, ever been stored at the site?
  - If so during what period?
- In the case of petrol storage and distribution sites, where were the fuels been sourced from?
  - This information will assist in determining the likely proportion of MTBE in fuels currently and historically.
- Is there a history of leaks or large spills of MTBE containing fuels at the site?
- When did fuel releases occur at the site?
  - Identifying the year in which the fuel release occurred at the site assists in assessing the potential mass of MTBE likely to have been released (e.g. did fuel contain 15% MTBE or <1%?) and assessing how far it may have migrated if it reached groundwater.
- Was fuel released from above ground or sub-surface infrastructure?
  - MTBE contained in surface releases is likely to take longer to reach groundwater than sub-surface releases, depending upon the geology and hydrogeology of the site.
- What volume of fuel was released at the site? For what duration did fuel releases occur?
  - This information will assist in estimating the likely volume of MTBE which may have reached groundwater.
- Was any remediation or containment undertaken at the time of fuel release(s)?
  - Where releases occurred from infrastructure, immediate removal of impacted soils may reduce the potential for MTBE to migrate to groundwater aquifers.

Where it is identified that MTBE may have been present at the site and may have been released, more detailed investigation can be considered in order to verify the nature and extent of MTBE contamination - this will be guided by the CSM.

The ASC NEPM states that:

‘If the preliminary investigation shows a history of non-contaminating activities and there is no evidence or suspicion of contamination, further investigation is not required.’

Where there is sufficient site history information available to rule out the potential for MTBE to have been present at the site, no further consideration of MTBE contamination is required. However, if some uncertainty remains, further investigation may need to be conducted.

MTBE will migrate rapidly from a source, through the soil profile, to groundwater and/or surface water (Environment Agency 2000). MTBE volatises and degrades rapidly in surface waters (Heald 2005), however it is relatively stable in groundwater. Once MTBE reaches groundwater it can migrate at a similar speed as groundwater flow and

therefore can travel rapidly in the sub-surface (Environment Agency 2000). It is recommended that where a release is identified to have occurred, where possible interim source removal activities be conducted (e.g. excavation of impacted soils) in order to prevent MTBE from migrating to groundwater; or to reduce the mass of MTBE which may migrate to groundwater over time.

## 2.2 Conceptual site model (CSM)

A critical element of any site assessment is the development of a conceptual site model (CSM). The CSM describes the environmental setting, identifies contaminant sources (potential areas of concern and associated contaminants), modes of contaminant movement (migration pathways), the potential receptors (i.e. human and ecosystem components, including stygofauna) affected by the contamination, the environmental values needing protection, and how exposure may occur (exposure routes).

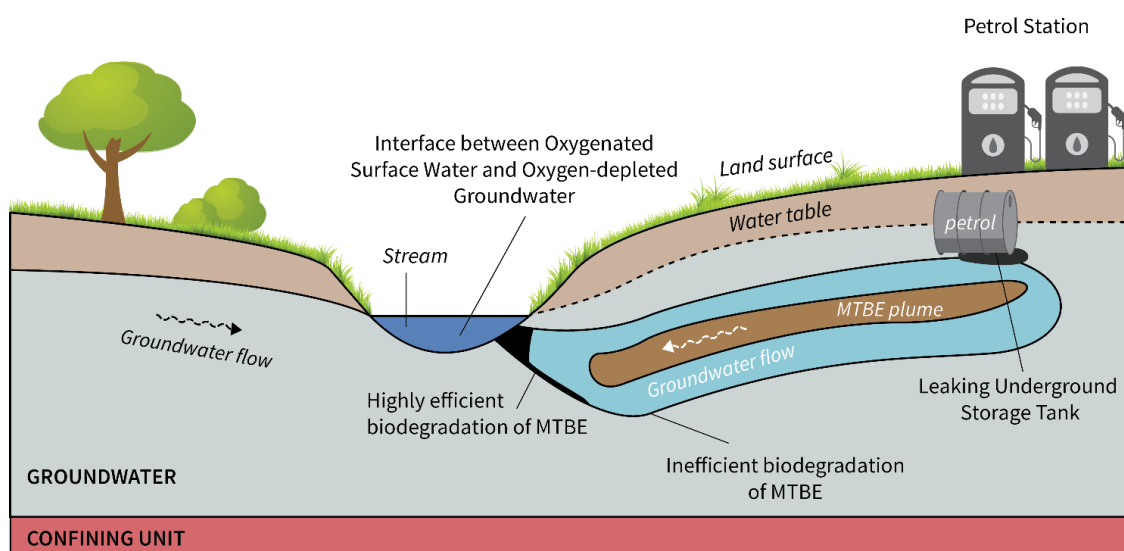
The development of a CSM is a dynamic process and it is important that all the information and data from each stage of an assessment are reviewed in an integrated manner (using a multiple-lines-of-evidence approach where appropriate) to refine the CSM and used to inform subsequent decisions on whether further investigation or management is necessary. Refer to the ASC NEPM schedule B2 for further general guidance on developing the CSM.

The initial CSM is constructed from the results of the PSI and is used to identify data gaps and inform a decision on whether detailed investigation is required. The CSM should be continually challenged and updated throughout the assessment process.

For sites that are potentially contaminated with MTBE the CSM should consider the following (see also figure 1):

- Contamination sources (including information identified through the PSI)
- Site geology and hydrogeology
- The depth to groundwater beneath the contamination source as this will influence the potential for MTBE to reach the aquifer
- The geological profile between the contamination source and groundwater, as this will also influence the potential for MTBE to reach the groundwater aquifer. MTBE will migrate more readily to the aquifer compared with other petroleum hydrocarbons, especially where soil moisture is present, and thus has the potential to be present in groundwater where other petroleum hydrocarbons are not detected.
- MTBE travels in groundwater at greater speed both vertically and horizontally than benzene, toluene, ethylbenzene, and xylenes (BTEX). It is therefore important to characterise both the horizontal and vertical profile of the groundwater plume for MTBE, not just BTEX. This involves sampling of groundwater from varying depths in the groundwater profile as well as horizontally delineating the dissolved MTBE groundwater plume.
- MTBE responds to localised groundwater gradients and aquifer recharge, which can result in a diving MTBE plume. This needs to be taken into consideration when preparing the CSM, and when determining placement of groundwater monitoring wells during site investigations.

Some of the above mentioned factors are shown diagrammatically in figure 2.



**Figure 2: Schematic showing an example of MTBE contamination. Adapted from South Carolina Water Science Centre.**

- Dissolved MTBE is subject to minimal retardation (which is the partitioning of a compound between soil and groundwater) in the groundwater aquifer, and thus MTBE can migrate at almost the same velocity as groundwater, especially in a sand or gravel aquifer. This should be taken into consideration when characterising a groundwater plume.
- Human and ecological receptors at the site and in surrounding areas.
- Who is likely to be exposed to MTBE present in groundwater at the site and in surrounding areas? For example are people extracting groundwater? Or is MTBE impacted groundwater discharging to surface water bodies?
- Exposure pathways via which identified receptors may be exposed.
- For humans the most significant exposure pathway for MTBE is ingestion via drinking water. The potential for extraction of groundwater for potable uses needs to be considered and assessed.
- MTBE has a high vapour pressure, but a low Henry's Law constant, so is most likely to partition into soil moisture rather than soil vapour. However, where soil moisture is low there is potential for MTBE vapour to migrate through the soil profile. Consideration of potential MTBE vapour intrusion should be included in the CSM in situations where soil moisture is low.
- For ecological receptors the main exposure pathway is via impacted surface water. Surface water may be impacted where there is potential for MTBE to discharge from groundwater to surface water. There may be a need to carry out groundwater modelling to account for local conditions where MTBE contaminated groundwater enters a surface water body. Consideration of the concentration of MTBE likely to discharge to surface water, and the potential time required for MTBE to volatilise should be included in the CSM – it should be noted that MTBE is likely to volatilise relatively quickly in surface waters.

Data gaps may be identified during the PSI and the development of the CSM. Where data gaps are considered to create uncertainty in the CSM, a detailed site investigation (DSI) should be conducted and should include investigations which aim to fill those data gaps. The resulting data can be used to update and refine the CSM.

With implementation of monitoring for UPSS, as required by states and territories, any leakage of petrol from underground tanks is expected to be detected at an early stage. This means that the migration of MTBE in soil and groundwater from leakage of fuel, already at <1% MTBE, should be minimal. The CSM should however consider the potential for MTBE migration beyond the BTEX plume. Sampling via the PSI or DSI should be conducted to determine the presence of MTBE.

For leakages involving racing fuels where MTBE concentrations were permitted at up to 55% v/v, assessment of MTBE contamination should be undertaken.

For legacy sites where leakage of fuels containing up to 15% MTBE may have occurred prior to the introduction of the *Fuel Quality Standards Regulations 2001*, the CSM should consider the presence of MTBE even if the BTEX plume has been contained or remediated. The CSM needs to take into account the greater mobility of MTBE in groundwater compared to BTEX, and thus sampling of the groundwater should be undertaken beyond the plume considered for BTEX. As indicated above, the CSM should also consider the interaction of the groundwater with any surface waters, to assess the potential risk of MTBE contamination. The local hydrogeology, aquifer flow and presence of surface waters need to be taken into account when assessing the potential for contamination by MTBE. The period and volume of the leakage (if available) need to be considered as well as the time since the leakage occurred. Consideration should also be given to monitoring and assessment of MTBE breakdown products, such as TBA and formaldehyde (see earlier section).

## 2.3 Detailed site investigation (DSI)

For a site where the PSI indicates that there is potential for MTBE contamination to be present, and there is the potential for sensitive receptors to be adversely impacted, a more detailed site investigation should be undertaken. If MTBE is present, the DSI should determine the nature and extent of MTBE independently of other petroleum hydrocarbons and relative to receptors and exposure pathways identified in the CSM. The chemical properties of MTBE are such that it will migrate readily to groundwater following a release, therefore most detailed site investigations will need to focus primarily on groundwater impacts and assessment of the nature and extent of the groundwater plume. The DSI process should be conducted in accordance with the requirements of the ASC NEPM, including the evaluation and determination of data quality objectives, and the subsequent preparation of a sampling analysis quality plan (SAQP) (see schedule B2). In particular, this process should ensure that:

- the necessary data are obtained to understand the extent of contamination both on and off-site and the potential risk posed by that contamination
- that the data are representative of site conditions
- the data represent the behaviour of the MTBE plume in surface and groundwater, and
- the data are of suitable quality to enable further site-specific risk assessment to be conducted where required.

The following sections outline the information that should be obtained during the DSI process for assessment of MTBE contamination including consideration of environmental media other than groundwater.

The information obtained through the DSI should be used to update the CSM. The updated CSM can be used to inform the need for remediation (and remediation options if required), and short and long term management actions for the site. The information from the DSI and updated CSM can be used to identify the potential risks posed by MTBE, and enable decisions to be made as to whether remediation (and if so, remediation options) or containment and management actions (short term or long term) is required at the site. It can also provide data to inform a site-specific risk assessment for the site, if relevant.

### **2.3.1 Groundwater modelling**

Groundwater modelling can be a useful tool in a MTBE site assessment. A groundwater model can:

- assist in understanding the extent of the MTBE plume
- assist in assessing the potential for MTBE to reach sensitive receptors (e.g. groundwater extraction bores) through identification of the furthest down-gradient point for MTBE migration, and
- inform decisions with regard to groundwater well locations to assist in MTBE plume delineation.

Information obtained from groundwater modelling can be used to develop the CSM, and inform the planning of detailed site investigation works (including development of the SAQP).

The following modelling methods should be considered for MTBE investigations:

- **Groundwater flow modelling** can be used for assessing the movement of MTBE because of its high solubility and the potential for it to move at a similar velocity and flow path to groundwater. Groundwater flow modelling paired with particle tracking can assist in determining the groundwater (and hence MTBE) flow direction, and the potential for groundwater (and thus MTBE) to migrate vertically between aquifer layers. This information can inform the design of the groundwater monitoring well network such that MTBE contamination can be delineated. This modelling method however does not account for MTBE specific properties and assumes that MTBE moves like groundwater with no consideration of degradation.
- **Fate and transport modelling** is a useful technique for estimating the size of an MTBE plume, and assessing the potential for MTBE to reach sensitive receptors. Fate and transport models enable the modeller to input MTBE specific chemical properties (e.g. limited retardation within the aquifer) and account for degradation (which is considered to be generally low for MTBE in anaerobic aquifers) within the aquifer. Therefore fate and transport modelling provides a more quantitative approach to understanding the MTBE plume and the potential risk posed by the MTBE contamination including the ability of MTBE to reach sensitive receptors.

Where field data are available they should be used to inform and validate the assumptions used in the groundwater model. When more detailed site investigation data become available, these should be used to validate the outcomes of the modelling to improve the accuracy of the model and therefore provide a more robust assessment of the fate and transport of MTBE in the aquifer.

### 2.3.2 Sampling analysis quality plan

This guidance focuses on groundwater, but air, soil and soil vapour may also need to be considered depending on the site. The SAQP, as outlined in schedule B2 of the ASC NEPM, should include:

- **The type of environmental media** which requires sampling based on information obtained in the PSI. If MTBE is being assessed, sampling can include:
  - **Groundwater** both in the source area and between the source and identified groundwater receptors. Given the solubility of MTBE in water, MTBE will move at a rate similar to groundwater and will be found at greater distances from the source than other petroleum hydrocarbons. Sampling for MTBE needs to extend beyond sampling for petroleum hydrocarbon plumes. The extent of the sampling, both laterally and (possibly) vertically, should be guided by the results of any groundwater modelling.
  - **Soil** MTBE moves rapidly through the soil profile as it adsorbs weakly to soil and will preferentially partition to soil moisture and migrate to groundwater. Where applicable, sampling should be conducted in the source area and between the source and identified groundwater receptors. While there is limited international guidance for MTBE in soil, Western Australia has adopted an aesthetics based soil criterion of 0.5 mg/kg (WA DEC 2010, WA Department of Environment Regulation 2014).
  - **Soil vapour** where vapour intrusion is likely to be an exposure pathway. Given the low concentrations of MTBE in fuels currently used in Australia and the introduction of regulations for UPSS including requirements for monitoring and leak detection in some states, the risk of vapour intrusion from recent releases is considered to be low. For legacy sites prior to the introduction of the *Fuel Quality Standards Regulations* (2001), where fuel containing higher concentrations of MTBE (up to 15%) were used, there is the potential for vapour intrusion. This potential should also be considered in situations where leakage of racing fuels is known to impact a groundwater aquifer.
  - A review of international regulations incorporating MTBE vapour intrusion screening levels showed that few such levels are available. The New Jersey Department of Environmental Protection (2013) has reviewed state and federal screening levels in the United States and derived generic Vapour Intrusion Screening Levels for a number of chemicals including MTBE, and also updated the guidance for their application.<sup>3</sup> The New Jersey screening levels are the most recently developed for groundwater and soil vapour (and indoor air) and are conservative compared with those in other US jurisdictions. For example, New Jersey vapour intrusion screening levels for MTBE for groundwater are provided for different soil types (e.g. 580 µg/L for sandy soil, 1,100 µg/L for loamy sand, 1,800 µg/L for sandy loam and 2,600 µg/L for loam soil). Table 2 also lists additional generic screening levels for soil used in New Jersey, as a reference only.

---

<sup>3</sup> For more information, see NJ Department of Environmental Protection website: <http://www.nj.gov/dep/srp/guidance/vaporintrusion/>

- Overseas screening levels/guidelines may be used in site assessments, however their use must be justified taking into account Australian conditions (e.g. soil types) and exposure parameters, as well as site-specific factors. In addition, their derivation should be consistent with that for Australian guidance – e.g. 1 in 100,000 for cancer risk and a hazard quotient of one for non-cancer endpoints. The New Jersey screening levels are based on non-cancer health outcomes and a hazard quotient of one, and the New Jersey generic MTBE vapour intrusion screening levels are, for residential 470 µg/m<sup>3</sup> and for non-residential 2400 µg/m<sup>3</sup>.
- **The number of samples of each environmental media**, including:
  - **Groundwater** – The number, location, depth and screening interval of groundwater wells should have regard to the identified source of MTBE at the site, and the location of identified sensitive receptors (e.g. where groundwater is identified to be extracted for potable uses) identified in the CSM. MTBE should be delineated on-site and between the source and sensitive receptors such that MTBE contamination in extracted groundwater can be assessed.
  - It is important to consider the soil type within the aquifer under investigation when determining the screen depth and interval to make sure that representative groundwater samples are collected, and that the groundwater plume is adequately characterised.
  - **Soil** – The number and depth of soil samples should be determined in accordance with guidance provided in the ASC NEPM and AS 4482.7/2005. Soils sampled outside the source zone or away from highly impacted groundwater may not provide useful information with regard to MTBE contamination, due the low affinity for binding to soil.
  - **Soil vapour** – The number, location and depth of soil vapour wells should be strategically selected to include areas where groundwater and soil contamination have been found. MTBE is most likely to be present in soil vapour close to a soil source where soil moisture is low, and above a dissolved phase groundwater plume.
- **Frequency and pattern of groundwater sampling.** The low affinity of MTBE to soil means that MTBE concentrations in groundwater may increase after rainfall events where water infiltration can cause increased mobilisation of MTBE to the groundwater aquifer. It is important to design a groundwater sampling plan that enables both temporal and spatial assessment of the MTBE plume such that MTBE flux, between the source and groundwater, can be determined.
  - **Details of analytes and parameters to be monitored in environmental media.** Where MTBE is suspected to be present at a site, analysis for MTBE breakdown products should be considered. These include TBA and formaldehyde. Given that MTBE breaks down slowly in anaerobic conditions, for sites suspected of recent contamination sampling of breakdown products may not be required.
  - For legacy sites (where contamination occurred prior to the introduction of limits on MTBE in imported petrol (pre-2001)) sampling may be required for TBA and formaldehyde.

- It is also recommended that initial investigations of legacy sites include analysis of other common oxygenates such as tertiary-amyl methyl ether (TAME) and ethyl tertiary-butyl ether (ETBE) (for further information, refer to White *et al* 2002; US EPA 2003).
- Analytical methods – see section 2.3.5.

### 2.3.3 Groundwater well installation

As the behaviour of MTBE in groundwater differs from petroleum hydrocarbons (including BTEX) it is important to have a detailed understanding of the aquifer(s) present at the site and the potential preferential pathways for groundwater flow which may alter the spread of MTBE contamination.

MTBE tends to follow groundwater gradients and flows, and will move more rapidly in areas of high hydraulic conductivity. This can result in movement of MTBE in the aquifer on both vertical and horizontal planes. When designing a sampling program for groundwater it is important to consider the characteristics of the aquifer and to place groundwater wells in appropriate locations to enable full characterisation of the MTBE plume as well as assessment of exposure pathways for sensitive receptors.

Multi-level wells with short screens enable sampling across discrete portions of the aquifer to determine whether there is potential for vertical migration of the MTBE plume and thereby increase the accuracy of the characterisation of the MTBE plume. If individual wells with longer screens are used there is potential for the discrete changes in MTBE groundwater concentrations across the aquifer to be missed, and therefore the MTBE plume may be ineffectively characterised. Well design should be informed by the CSM.

### 2.3.4 Environmental sampling

Environmental sampling should be targeted to enable assessment of the nature and extent of MTBE contamination relative to identified sensitive receptors. Sampling should be undertaken in accordance with the ASC NEPM and include appropriate quality assurance/quality control. The text below provides guidance for sampling of environmental media specific to MTBE:

- **Sampling of soils and sediments** for MTBE within the source zone will enable chemical characterisation of the release. Away from the source zone, MTBE is most likely to be present in soil moisture or groundwater and therefore soil sampling is not recommended. For legacy sites only screening samples of soil may be required close to the aquifer. The main issue at a legacy site, where the release has been contained or removed, is groundwater contamination. When sampling soils within the source zone it is important to consider the potential for cross contamination from shallower depths, and so sampling methods which are designed to prevent cross-contamination should be considered. These methods include:
  - open barrel samplers (or non-sealed samplers) – these should only be used when they are advanced through hollow-stem augers or a drive casing that prevents cross contamination.
  - piston samplers, which are sealed with a watertight piston until they reached the desired sample depth. This sampling technique allows the tool to be pushed



through heavily contaminated soil or water without cross-contaminating the sample.

- **Groundwater** contamination should be the primary focus of environmental sampling at MTBE contaminated sites. Because of the tendency for MTBE to partition to water it is not readily expected that volatilisation will be a significant concern during groundwater sampling. However, it is important to take due care to reduce volatilisation during sampling to ensure that samples are representative of groundwater conditions. Groundwater should be sampled using techniques which reduce the potential for volatilisation of MTBE and MTBE breakdown products (e.g. low-flow sampling) as per other volatile contaminants of concern (e.g. benzene).
- **Soil vapour** sampling may be required at sites where a source of petroleum hydrocarbons and MTBE is present beneath a building or in the area where a building will (or may) be constructed (see section 2.3.2 for further guidance as to when soil vapour sampling may be required). MTBE is often detected at low concentrations or not detected in soil vapour sampled above a groundwater source because of MTBE's tendency to partition to water over soil vapour. Where sampling of MTBE in soil vapour is required it can be undertaken as per petroleum hydrocarbons (refer to CRC CARE Technical Report No. 23 (2013)).
- **Surface water** sampling should be undertaken where there is potential for MTBE impacted groundwater to discharge to waterways. There are no specific sampling methods for MTBE in surface water, however care should be taken to ensure that samples are collected from locations and depths which provide data to enable assessment of exposure pathways for humans and ecological receptors (e.g. close to the point of groundwater discharge). Note that MTBE will readily volatilise when in contact with air.

### **2.3.5 Analytical methods**

There are four analytical methods commonly used for the analysis of MTBE in different environmental samples: US EPA Methods 8020, 8021, 8260 and 8261 and (a modified) ASTM Method D4815. The US EPA recommend that US EPA Method 8260 be used because the presence of other petroleum hydrocarbons in the sample does not create interference when this method is applied (US EPA 2003). US EPA Methods 8020 and 8021 are cheaper, but high concentrations of petroleum hydrocarbons in the sample can result in false positives or in overestimation of MTBE concentrations. Where US EPA Method 8020 or Method 8021 is used, the US EPA recommend that at least one confirmatory analysis with US EPA Method 8260 be undertaken per site (US EPA 2003).

### **2.3.6 Screening levels**

The results of groundwater sampling should be compared with the screening levels in table 1 to determine if further investigation and/or management is required. Schedules B4, B5a and B6 of the ASC NEPM in particular provide guidance for risk assessments. Guidance on the assessment of aesthetic issues, such as odour, is provided in Schedule B1 of the ASC NEPM.

### 3. Considerations for the management of MTBE contaminated sites

---

Remediation of contaminated soil and groundwater from leaking UPSS will be driven by the toxicity of BTEX, not MTBE, although the presence of MTBE may increase the cost of clean-up due to the more rapid transport of MTBE in groundwater (Day 2000; US EPA 2005; Wilson *et al* 2005). For older spills at legacy sites where contamination is limited to shallow ground water and is not threatening a drinking water supply, a containment approach or monitoring-only scenario may be appropriate.

The decision-making framework for management and remediation centres on the development and continual modification of the CSM. The CSM is the progressive assemblage of information regarding the distribution of contaminants at a site and its hydrogeological setting. The CSM describes the release scenario, surrounding land use, geology, aquifer locations, and the likely distribution of contaminants, including MTBE, at the site, existing and projected water use patterns, and other factors considered when making decisions about a site. It functions as the framework for the investigation, remediation, and ultimately the closure of the site and serves as the basis for communication between responsible parties, regulators, and other interested parties.

Response time is critical for MTBE. A quick response to a release greatly increases the ability to check the spread of the MTBE and to clean up the mass of the release. This will eliminate the risk to groundwater. Because time is critical, priority should be given to sites that pose the greatest risk to groundwater. This will be determined through the CSM for the site. There may be more need for vertical definition of MTBE plumes and more reliance on active clean-up technologies, such as soil vapour extraction, in situ groundwater remediation, and groundwater pump and treat systems, than for fuels not containing MTBE. Compared to benzene, MTBE is highly soluble and mobile in water. MTBE is fairly persistent in groundwater and sediments since it is resistant to most biodegradation processes in anaerobic environments. MTBE is also readily volatile, with an odour that can be readily detected in water at low concentrations (see Appendix A).

After the source area and pathways to receptors have been adequately characterised, a decision on whether remediation is required can be made and an appropriate remedial option selected and implemented. Remediation priorities can be assigned on a broader scale, if required, after sufficient data have been collected to estimate the travel time for the contaminant plume to reach a receptor, as a part of the PSI and development of the CSM. At this point in the process, a decision as to whether the site requires remediation or not is made. If required, the priority for remediation should consider the estimated plume travel time to the nearest down-gradient receptor and timeframe for intended use of the aquifer. Other risks should be identified through the development of the CSM or may be required by the state or territory regulator. Redevelopment of the land or property transfers may influence the timeframe for any remediation and/or management actions beyond consideration of potential impacts on groundwater or surface waters.

If an initial spill clean-up has resulted in limited MTBE contamination such that groundwater reaching a downgradient well will be below the screening levels, no

further remediation should be required. Some sites, however, may require expedited interim remedial action prior to completion of the site investigation to contain the source and minimise the risk to sensitive receptors. Resources should be directed to those sites that pose the greatest and most immediate threat to nearby receptors. If MTBE contamination is found in an area that is located:

- within a 300 m radius of a groundwater aquifer or surface water body used as a source of drinking water
- above an aquifer that is a source of water supply for a community, or
- in an area having a high degree of hydrogeologic susceptibility to contamination (e.g. near-surface fractured bedrock that is close to a community water supply);

the area should be considered as vulnerable and site assessment and management should be assigned a high priority.

For sites where there is new or recent contamination, the risk from fuels containing less than 1% MTBE should be low unless in close proximity to a groundwater aquifer or surface waters used for potable water use. Implementation of the UPSS Regulations should assist in rapid identification of a leak and containment actions thereby minimising the risk. Any spillage from an accident during transportation of fuel should be contained as a priority. An assessment of potential contamination of waterways should be conducted as an initial response to any incident.

A significant leak of racing fuels containing up to 55% MTBE must be contained as a priority. This should be done prior to more detailed site assessments especially in areas where groundwater or surface water is in close proximity. The PSI and DSI (if required) will enable the risks posed by the release to be determined and ongoing management and/or remediation actions to be identified.

Legacy sites are more difficult to assess. The longer the timeframe between the release of fuel containing MTBE and the site assessment, the more widespread the potential contaminated plume, making assessment, management and remediation more difficult. Where the CSM has identified that there is no groundwater aquifer or surface water body that may be affected by the contamination and the source has been removed or contained, then remediation of MTBE contaminated soil may not be required. If a plume has entered an aquifer and the plume is widespread, remediation may not be practical. If the levels are below the screening levels in table 1 and the source has been removed or contained, then remediation is unlikely to be required. Periodic monitoring may be beneficial to ensure that the situation does not change over time. If the screening levels are exceeded but the plume is so widespread that it is not practical to remediate, then consideration should be given to the implementation of institutional controls to restrict the use of the groundwater, so that it cannot be used for purposes for which it is unsuitable. The CSM for the site should identify any ecological receptors that may be impacted by the plume. Where practical, management measures should be considered so that further risk to these receptors is minimised.

Periodic groundwater monitoring is used to supplement the initial assessment data, and to confirm assumptions about the CSM, where relevant. The objective of groundwater monitoring is to determine if the site conditions meet regulatory requirements, and may include evaluating seasonal changes in site conditions, documenting evidence of source depletion, evaluating plume stability or migration, or assessing the effectiveness of remediation actions. If there is reason to believe

downward migration of contaminants may be occurring, clustered monitoring wells or other methods of determining vertical gradients should be used to determine the extent to which vertical migration occurs. While assessment strategies may differ between BTEX and MTBE, periodic monitoring strategies are similar. The potentially more rapid rate of migration of oxygenates should be considered when determining an appropriate sampling frequency and monitoring well spacing. Data from periodic monitoring should be interpreted and used to update the CSM. Variations in concentration over time at individual wells can be used to understand source depletion and potential hydraulic influences on plume migration. Concentrations may be analysed over distance along a plume centreline to assess plume stability and thus potential threat to nearby receptors. Concentrations of MTBE and other contaminants of concern can be determined over time at appropriately located monitoring locations downgradient of the source and oriented along the direction of groundwater flow. The trend in concentrations at these points will confirm whether the plume is shrinking, stable, or expanding (e.g. if the plume is shrinking, concentrations will decrease over time or space; if the plume is stable, concentrations will remain relatively constant over time and space).

## 4. Remediation

---

Because MTBE behaves differently in soil and water to petroleum hydrocarbons, the choice of an effective remediation technology may differ when MTBE is present with other fuel contaminants at a site.

Remediation of MTBE from the environment should be undertaken when:

- a release that contains MTBE is identified to have occurred and is determined to impact adversely on groundwater or surface waters.
- MTBE is present in soils and the risk of exposure to humans or contamination of groundwater or surface waters is considered unacceptable.
- groundwater contamination (e.g. exceedances of the screening levels) impacts on the environmental values of the aquifer (e.g. drinking water).

Individual jurisdictions may have additional requirements as to when remediation is required. Understanding the relevant legislation in the relevant jurisdiction, and consulting with the regulator when developing the objectives of, and approaches to, remediation of the site, is critical in guiding the decision making for the remediation of a site.

The remediation objectives should provide a clear indication of what is to be achieved by the remediation process and be clearly stated in the remediation action plan (RAP). The following factors should be considered when determining the remediation objectives:

- the threat the contamination poses to human health or the environment – in particular, groundwater
- any environmental values related to the site and use of the groundwater
- associated factors such as:
  - social considerations including community acceptance and intergenerational equity
  - technical aspects (physical ability to remove, treat, contain or manage the chemical substances within a reasonable timeframe), and
  - financial aspects (cost of remediation including waste treatment).

Further guidance on establishing remediation objectives can be found in the National Remediation Framework.

Once the remediation objectives have been defined it is necessary to use site-specific information to determine which remedial options are feasible. Remediation options should be selected based on the effectiveness of removal of MTBE (as well as breakdown products and other contaminants) such that sensitive receptors are protected.

As spills of petrol typically move slowly through groundwater and are biodegraded over time, many are left in place to undergo bioremediation at no cost other than monitoring and temporarily replacing the water supply. MTBE, however, moves with groundwater and can render groundwater non-potable at low levels (see table 1 and Appendix A). Therefore, responses to spills involving MTBE need to be swift, and may require much

more aggressive management and remediation than those involving other petroleum hydrocarbons.

Removing high concentrations of MTBE at the subsurface is much more cost effective than extracting water or vapour with low concentrations. At many sites, aggressive interim remediation in the source area can help diminish the chances of creating a large diluted plume of MTBE. Large dilute plumes are more difficult to remediate and have impacts that are more widespread. In many cases, source area remediation may reduce subsurface impacts sufficiently to protect surrounding water quality. Sites with plumes that could impact drinking water wells may require implementation of plume containment measures, which may include groundwater extraction and treatment at on-site or off-site remedial extraction wells.

The physical and chemical properties of MTBE limit the selection of ex situ treatment methods. Due to its high solubility, most of the MTBE mass can dissolve quickly into groundwater, making pumping an efficient method for removing large quantities of the contaminant (US EPA 2004). Fewer aquifer volumes are required to remove all of the MTBE than are required to remove other slowly desorbing petroleum hydrocarbons, as MTBE does not adsorb significantly to soil, and pump and treat often can be an effective remediation technology for MTBE. As with petroleum hydrocarbons, however, diffusion is also a factor controlling the remediation timeframe. If micropores exist within the aquifer that are not readily influenced by groundwater flow, transfer of a contaminant from the micropores to the macropores will occur through the slow process of diffusion, which means that pump and treat may not always be an efficient remediation method for MTBE contamination (ITRC 2005; Rasa *et al* 2011).

A 1991 American Petroleum Institute study determined that air stripping alone was the most cost-effective technology for remediating water containing 20 ppm MTBE down to a level of 10 ppb, though MTBE's high solubility means that air strippers must use a higher volume of air than is required for other petroleum contaminants, such as benzene (API Publication No. 4497). MTBE remediation can require more extraction wells and associated equipment (e.g. pumps, lines) than for other fuel contaminants because MTBE may travel farther and faster than the rest of the plume, resulting in a larger plume size. UV-catalysed oxidation with hydrogen peroxide has been used to treat water and off-gases. Air sparging can also be used, though the method typically is appropriate only in homogeneous sands, and also could require greater volumes of air to volatilise the MTBE than do other petroleum-related contaminants. Air sparging also enriches the oxygen content of the groundwater, which can enhance MTBE as well as BTEX aerobic biodegradation. When used as a biodegradation aid, considerably less air is needed than when trying to volatilise the MTBE (ITRC 2005).

Bioreactors have been found to be effective for treating MTBE (ITRC 2005; Hicks *et al* 2014). Bioreactors generally are used in either suspended growth or attached growth configurations. In *Suspended Growth Bioreactors* – including plug flow, completely mixed or continuously stirred tank reactor, batch and sequencing batch, activated sludge, and membrane bioreactors – cells are suspended within the reactor unit. Typically, contaminated water is circulated within an aeration basin or passed through an aerated column or pipe (ITRC 2005). In *Attached Growth Bioreactors* (fixed-film or immobilised cell reactors) – including fluidised-bed, fixed/packed bed, trickling filter bioreactors, and rotating biological contactors – cells are established on an inert substrate. Attached growth reactors may retain slow-growing bacteria that wash out from suspended growth reactors (ITRC 2005).

MTBE is biodegradable under both aerobic and anaerobic conditions through the use of biostimulation (introduction of oxygen or other additives) or bio-augmentation (Salanitro 2000; ITRC 2005; Bruce *et al* 2013). For example, bio barriers consisting of oxygen bubbled through the groundwater and a bio-augmented oxygen curtain bubbled through the groundwater in a zone perpendicular to groundwater flow were successful in reducing MTBE concentrations to acceptable levels. The unaugmented treatment zone had a significant lag time (>200 days), while significant decreases of MTBE were noted in the bio-augmented zone in 30 to 60 days (Johnson *et al* 2003). For more information on bio barriers, see Johnson *et al* (2004).

In situ chemical oxidation also can be an effective technique for some MTBE plumes; as with other chemical contaminants, the size of the plume to be remediated will determine the cost effectiveness of the treatment (ITRC 2005).

Phytoremediation has been used at sites having MTBE contamination. It relies on multiple processes to accomplish the removal of contaminants from shallow groundwater. Each of these processes is affected by chemical properties as well as site-specific conditions. The biodegradability of MTBE affects treatment processes in the rhizosphere, where the conditions support an abundance of metabolically active bacteria and fungi that may enhance contaminant degradation. The relatively high solubility and low organic partition coefficients of oxygenates generally limits significant removal through phytostabilisation but facilitates removal through root uptake. In addition, volatility and Henry's Law constants may affect the removal through phytovolatilisation (US EPA 2004; ITRC 2005).

Under certain circumstances, monitored natural attenuation (MNA) may be useful for addressing MTBE releases (ITRC 2005); however, MNA is appropriate only in conjunction with source control and remediation of high concentrations. Light non-aqueous phase liquid is removed prior to implementing MNA, and in many cases active remediation of high dissolved concentrations will be necessary prior to MNA. MNA limited in application to the fringes of the plume may be appropriate with other active remediation technologies in the source area (ITRC 2005). For further information on MNA of MTBE, see Davis and Erickson (2004), Wilson *et al* (2005), and Zeeb and Wiedemeier (2007).

In soil, the very high vapour pressure and low affinity for sorption to soil means that MTBE responds well to soil vapour extraction (SVE) and low-temperature thermal desorption (LTTD), typically without any costs beyond those needed for remediating other petroleum constituents. SVE or LTTD must be used soon after a release, however, because MTBE moves rapidly from the soil into the groundwater. High oxygen content facilitates the biodegradation of MTBE. Bioremediation methods for soil treatment (e.g. bioventing, biopiles) may be effective if the appropriate microbes are available (ITRC 2005).

As MTBE does not adsorb significantly to carbon (US EPA 2004), MTBE is not a good candidate for removal via granular activated carbon (GAC).

As indicated above, selection of the most appropriate remediation technology for a MTBE-impacted site, as for most sites, is dependent on a thorough understanding of the site characteristics, history of the spill, and the limitations of the technology. Further information on potential remediation options for MTBE in groundwater is presented in section 4.1.

## 4.1 Remediation options for MTBE contaminated groundwater

As MTBE is largely considered to be a groundwater issue, the following information focuses on remediation options for removal of MTBE from groundwater. Multiple remediation techniques may be required, depending upon the remediation objectives and the effectiveness of the adopted approach. The main technologies available for remediation of MTBE in groundwater in Australia are:

- **Pump-and-treat/Groundwater extraction**
  - In general, remediation using pump-and-treat systems is effective for removing highly soluble chemicals from contaminated soils (California EPA 2004). This remedial method is expected to be effective for removal of MTBE from groundwater aquifers because of MTBE's high water solubility and low retardation factor. Pump-and-treat is expected to be more effective at removing MTBE from the sub-surface compared to BTEX compounds. However, it is noted that the potential for extended migration of MTBE compared to BTEX should be taken into consideration when designing the pumping system, and the need to expand the system beyond what is necessary for BTEX remediation to provide greater opportunity to capture the MTBE plume. Extraction wells may also need to be placed downgradient of the leading edge of the contaminant plume to prevent further expansion of the MTBE plume.
  - Once groundwater is pumped to the surface it will need to be treated prior to disposal. Air stripping is an effective treatment to remove MTBE from extracted groundwater.
- **Soil vapour extraction (SVE)** (often used in tandem with air sparging)
  - SVE is an in-situ remediation technology which reduces concentrations of volatile contaminants in the unsaturated or vadose zone (California EPA 2004). Sub-surface air flow is induced through the use of blowers or vacuum pumps, and vapours from sub-surface contaminants are extracted using a well which is screened above the aquifer. Where geological conditions are considered suitable for SVE, the effectiveness of this treatment is dependent upon the properties of the contaminants being extracted (e.g. Henry's Law constant, vapour pressure and water solubility).
  - The effectiveness of MTBE removal using SVE is dependent primarily on the vapour pressure of MTBE and its volume percentage in the original source. MTBE has a higher vapour pressure than BTEX compounds and so it is expected that MTBE can be removed from the sub-surface more readily than other fuel compounds. SVE is most effective at removing MTBE when it is present in the unsaturated zone (i.e. hasn't migrated to the groundwater aquifer, or is still migrating downwards from the source). SVE is considered most effective when used soon after a spill or release has occurred. However, once MTBE reaches the groundwater aquifer other groundwater remediation technologies will need to be used in conjunction with SVE (California EPA 2004).



- **Multi-phase extraction (MPE)** – concurrent soil vapour and groundwater extraction and treatment.
  - MPE involves application of a vacuum to a well for the removal of both soil vapour and groundwater. This is usually done in conjunction with dewatering in the vicinity of the well which enables vacuum-induced air flow to access contaminated soils in the capillary fringe and below the previous level of groundwater (California EPA 2004).
  - MPE is considered to be highly effective for removal of both MTBE and BTEX from the subsurface. MPE works on the same basic principles as pump-and-treat and SVE. The mass removal of MTBE using MPE increases as soil moisture content decreases. MTBE removal is also increased with application of a higher vacuum to the sub-surface.
- **Air stripping**
  - Air stripping is the process of removing volatile organic compounds from water by increasing the surface area of the contaminated water exposed to air (California MTBE Research Partnership 2006). This process can be achieved using packed towers, diffused aeration, tray aeration, and spray aeration. The effectiveness of this remediation method is greater for compounds with a high Henry's Law constant. MTBE has a low Henry's Law constant compared to BTEX compounds, and so air stripping can be more difficult and costly for remediation of MTBE than for BTEX compounds (California MTBE Research Partnership 2006). For >90% removal of MTBE from groundwater, multiple air stripping devices, connected in series, are required. Also high water-to-air ratios are required to remove MTBE from water effectively, although this method can be effectively used to remove MTBE from groundwater.
- ***In-situ* air sparging**
  - *In-situ* air sparging involves the injection of air to the saturated zone to circulate air through the groundwater aquifer to increase volatilisation and degradation of organic contaminants (California MTBE Research Partnership 2000). During air sparging contaminants transfer from the aqueous phase into the sparged air channels and are advected away. MTBE has relatively low soil sorption and high solubility which results in high dissolved phase MTBE concentrations and low soil-phase MTBE concentrations. Though MTBE has a higher affinity for water than BTEX compounds, it is still amenable to volatilisation following application of air sparging methods. Therefore MTBE will volatilise from the dissolved phase and has a lower potential for partitioning to the soil phase (binding to soils) as the vapour migrates through the sub-surface compared to BTEX compounds which readily bind to soils (California MTBE Research Partnership 2000).
  - The higher the equilibrium vapour phase concentration of a contaminant (which is dependent upon the solubility of the compound and the percentage volume in the fuel source) the more effective *in-situ* air sparging is for that contaminant. MTBE has a higher equilibrium vapour phase concentration than BTEX compounds therefore *in-situ* air sparging is considered to be an effective treatment for MTBE in groundwater.

- ***In-situ* chemical oxidation**

- *In-situ* chemical oxidation involves the use of oxidising compounds to convert contaminants to benign free-radical products (California MTBE Research Partnership 2000). MTBE does not have any double bonds in its chemical structure, unlike BTEX compounds, and thus is not as easily oxidised as BTEX compounds. Hydrogen peroxide (with or without ferrous iron) can be used for the destruction of MTBE, however it is noted that there is potential for highly exothermic reactions to occur (which may result in explosions) where the incorrect amount of hydrogen peroxide is added. So careful research and thorough understanding of the risks associated with this method should be undertaken prior to considering this as a remedial option (California MTBE Research Partnership 2000; ITRC 2005). There is also potential for breakdown of MTBE to create intermediate products such as TBA, aldehydes, ketones, carboxylic acids and acetone, some of which can be more difficult to break down than MTBE. However some potential breakdown products, such as acetone are more biodegradable than MTBE. In order to assess the potential success of using this method for remediation, it is important to understand the chemicals required to degrade MTBE and the potential formation of intermediates.

- ***In-situ* bioremediation**

- This method involves the use of microorganisms to either destroy or immobilise contaminants (ITRC 2005). Most laboratory studies indicate that bioremediation strategies which involve direct metabolism, co-metabolism, bio-augmentation or some combination thereof can be successful in remediating MTBE impacted sites. However, conditions at the site need to be amenable to biological activity and oxygen/nutrient delivery (ITRC 2005).

- **Natural attenuation**

- Natural attenuation includes the natural processes which reduce, restrict and/or eliminate contaminant migration in subsurface environments. The major components of natural attenuation include: retardation, dilution, degradation, and volatilisation. Key considerations for natural attenuation include the stability of the plume (whether it is shrinking or expanding) and if natural attenuation can protect off-site receptors (ITRC 2005).
- MTBE is neither readily retarded by aquifer materials nor easily volatilised from groundwater. The microbes which degrade standard petroleum hydrocarbons (e.g. BTEX) differ from those that are able to degrade MTBE. MTBE microbes have been found to multiply at a much lower rate than other petroleum hydrocarbon microbes (US EPA 2005), and as such may be present at much lower levels than other microbes. In the absence of detectable microbial activity causing MTBE removal from groundwater, dispersion is likely to be the primary MTBE attenuation mechanism. Therefore the overall mass of MTBE is likely to be reduced at a slower rate than other petroleum hydrocarbons. Detailed predictive groundwater modelling and long-term monitoring are required to understand the potential for natural attenuation and to understand whether it is effective. Overall natural attenuation is considered to be less effective for MTBE remediation compared to other petroleum hydrocarbon products (ITRC 2005;

US EPA 2005). However, where no sensitive receptors are present this remedial option may be the most cost effective and provide a means of monitoring the nature and extent of the plume over time.

- **Granular activated carbon (GAC)**

- GAC is used to remove organic contaminants, and it not a remediation method in itself. The efficiency of removal of organic contaminants using GAC is dependent upon the characteristics of the GAC and the physical and chemical properties of the adsorbate (California MTBE Research Partnership 2000; 2001). GAC made from coconut shell is found to adsorb MTBE better than coal-based GAC. In general, GAC is not considered to be as effective for removal of MTBE from groundwater compared with other organic contaminants for which GAC is regularly used (e.g. BTEX) (California MTBE Research Partnership 2000; 2001; ITRC 2005). The poor adsorptive characteristics of MTBE on GAC cause breakthrough to occur at a higher rate than for other contaminants, and thus more regular GAC replacement is necessary. Background water quality, high concentrations of natural organic matter and co-contaminant concentration can also affect MTBE removal efficiencies and increase the amount of GAC required and thus the cost of groundwater treatment.

## **4.2 Remediation action plan (RAP)**

Once the most cost-effective remedial option(s) have been selected, a site-specific remediation action plan (RAP) should be prepared to outline the specific details of the remedial approach and the remediation outcome (e.g. MTBE groundwater concentrations suitable for drinking water).

The RAP should take into consideration the nature and extent of MTBE contamination and outline the process for determining when remediation objectives have been reached. Where relevant, the RAP should also include ongoing requirements for monitoring following completion of the remediation program. Where relevant, this may include the development of site management plans consistent with site-specific factors and regulatory requirements (see section 5.2).

## 5. Monitoring and management

---

### 5.1 Monitoring requirements

Where the site has an on-going operational UPSS, management, monitoring and mitigation measures are required to be implemented, under UPSS regulations, to reduce the potential for future environmental impacts. This includes installation of leak detection systems to enable the operator to quickly act following detection of a leak to reduce the potential for fuels (and MTBE) to spread away from the source.

Regardless of the remediation method selected the following ongoing monitoring is likely to be required where unacceptable MTBE impacts are present in groundwater:

- Monitoring of groundwater MTBE concentrations at the leading edge of the plume, between the groundwater plume and identified sensitive receptors (particularly where groundwater may be extracted).
- Monitoring of groundwater within the source area to assess potential rebound MTBE concentrations and determine whether remediation has successfully reduced the size of the plume.
- Where monitored natural attenuation is selected as an option for remediation, the groundwater quality and potential for groundwater impacts to be attenuating needs to be monitored. The time over which monitoring will be required will depend on the size of the MTBE plume and concentration of MTBE in groundwater.

A groundwater monitoring plan should be included as part of remedial planning, and should take into account site-specific factors including: distance to sensitive receptors, likelihood of the MTBE plume reaching the receptors, nature and extent of impacts.<sup>4</sup>

A groundwater monitoring program should include the following objectives:

- Determination of whether MTBE concentrations are decreasing based on expected outcomes of remediation.
- Detect changes in sub-surface conditions which may alter the efficiency of remediation techniques (e.g. hydrogeological, chemical, microbial or other changes).
- Detect breakdown products (e.g. TBA) which may be formed and mobilised as a result of remedial activities.
- Verify that contaminants are not reaching down-gradient receptors.
- Detection of any new releases to the environment which may reduce the effectiveness of the remedial approach.
- Detect changes in groundwater flow rates or directions which may alter MTBE migration and result in the MTBE plume moving in a different direction.
- Verification of remedial objectives being attained.

The frequency and scale of monitoring will be dependent on a number of site specific factors, including the potential for MTBE to reach sensitive receptors. The monitoring program developed for the site should specify the number and location of wells to be monitored, the frequency of monitoring and the groundwater parameters to be monitored to achieve the above objectives.

---

<sup>4</sup> Additional relevant management or monitoring plans may also be required by regulators.

Groundwater sampling and analysis should follow guidance from AS/NZS 5667.11/1998, the ASC NEPM, and relevant state guidelines. See also section 2.3.5.

## 5.2 Site management measures

The management measures required for MTBE contamination will vary depending upon the site, the identified sensitive receptors and the remedial method adopted (where required). Where there is potential for drinking water, or sensitive surface water bodies to be impacted, the groundwater MTBE plume should be managed to prevent (as much as possible) the potential for the environmental values of groundwater to be adversely affected.

Management measures may include:

- Notifying nearby groundwater users of the potential for groundwater contamination and what to look out for (i.e. the smell, taste of MTBE) and let them know what they should do if they suspect that MTBE contamination may be present in their groundwater well(s).
- Undertaking preventative steps to reduce the potential for MTBE in groundwater to impact on surface water environments.
- Prepare a site management plan which outlines management measures which are required at a site to reduce potential exposure to MTBE.
- Implement institutional controls, such as groundwater restricted use zones, if groundwater is contaminated with MTBE.

For operational petroleum storage and distribution facilities, ongoing management of storage infrastructure should be undertaken as per UPSS regulations or guidance in the relevant jurisdiction. This includes consideration of the potential for ongoing fuel supplies to contain MTBE and assessment of future spills and leaks for MTBE. Where recent spills and leaks are identified, intermediate remediation (e.g. removal of impacted soil) should be undertaken to prevent migration of MTBE to the groundwater aquifer.

## 5.3 Case study – MTBE contaminated site in Western Australia

This is a case study of an investigation of a groundwater plume containing hydrocarbons and MTBE. For simplicity the case study focuses on the legacy MTBE contamination.

### 5.3.1 Background

- Site location – corner of small commercial precinct in the Perth metropolitan area.
- Site located in predominantly residential area with many houses having a shallow domestic bore used for garden irrigation and other non-potable uses.

Site history:

- Operated as a service station from 1970–2001.
- Change in operator in 1990 – new operator upgraded majority of infrastructure, no information to suggest contamination present prior to this.

- Site became known to authorities when residents down hydraulic-gradient of the service station reported petrol odours in domestic bore water (2000).
- Groundwater present at 2–5 mbgl across the area of impact. Groundwater is present within an unconfined sand aquifer and flows in a southerly direction before discharging into a major river system, located approximately 600 m away.

### **5.3.2 Investigations**

Site investigation in 2001:

- 4 wells on-site, and 17 wells off-site
- Hydrocarbon plume ~ 250 m long by ~50 m wide
- 11 Private domestic bores identified down-gradient of the site
- Groundwater impacts on site and directly down gradient in 2001:
  - B 10–15 mg/L
  - T 20–40 mg/L
  - E 1–3 mg/L
  - X 10–15 mg/L
- Impacts identified in numerous domestic bores. The results from the most impacted private bore (centre of plume) are:
  - B 1 mg/L
  - T 3 mg/L
  - E 0.5 mg/L
  - X 3 mg/L
- Regular groundwater monitoring events from 2001 onwards to assess plume degradation.
- Groundwater and soil vapour investigations of the source site and downgradient properties not yet closed out.

### **5.3.3 Remedial works**

- Remediation works, including removal of tanks and infrastructure and enhanced aerobic bioremediation, were conducted in 2001–2003.

MTBE:

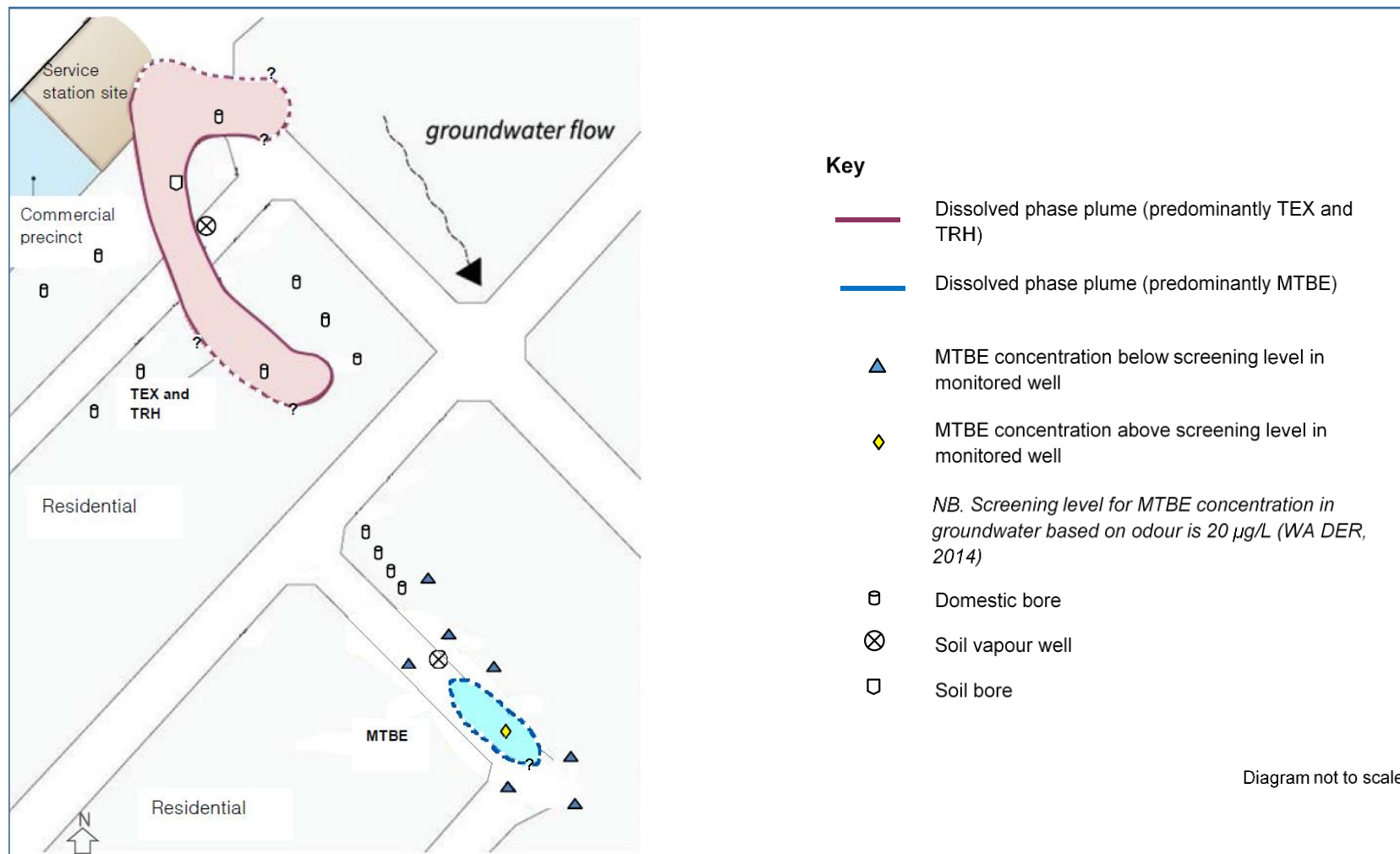
- Not originally identified as a contaminant of concern - first analysed in 2012.
- Not detected at/near the source site. Detected in five wells at the most down hydraulic gradient extent of the monitoring well network.
- Concentrations ranged from 5–50 µg/L, and increased with increasing distance from the source site (i.e. detached MTBE plume).
- Concentrations were below levels that may pose a human health or ecological risk, however, they exceeded the WA non-potable criterion (12 µg/L (aesthetic) (WA DoH 2006), revised to 20 µg/L in 2014 (WA DER 2014).
- Odour complaints made in 2000 may have been due in part to the presence of MTBE in bore water.

- Further groundwater monitoring was undertaken in 2014 – the results confirmed the previous reported concentrations – see figure 3.
- Further down-gradient monitoring was required to delineate the down-gradient extent of MTBE concentrations. One well was installed 100 m further down-gradient from detected MTBE in 2015 – no MTBE was detected.

#### **5.3.4 MTBE outcome**

Risk assessment demonstrated that the MTBE impacted groundwater is suitable for domestic non potable use however an odour may be present. Note BTEX concentrations are below levels of detection in the MTBE affected area. The relevant properties have been classified as 'decontaminated' under the *WA Contaminated Sites Act 2003*. The reasons for this classification refer to the potential for odour in groundwater. This classification includes the standard requirement in WA that users should sample and analyse groundwater before use to ensure it is suitable for its intended use.

**Figure 3 Map showing groundwater plumes containing hydrocarbons and MTBE at a legacy site, in 2014.**





## 6. Conclusion

---

This Technical Report provides guidance on the processes for the assessment, management and remediation of MTBE contaminated groundwater. The guidance for assessment is consistent with the requirements of the ASC NEPM. Odour and ecological screening levels for MTBE in groundwater have been developed to assess in the assessment of potential contamination and to guide risk-based management decisions.

The guidance in this report provides a practical basis for the assessment and management of MTBE contaminated sites and differentiates where appropriate between legacy sites compared with potentially new sites contaminated by MTBE contaminated fuels. The restriction on the amount of MTBE in fuels currently used in Australia (with the exception of racing fuels) and strict regulations for UPSS means that the potential risk of MTBE contaminated groundwater is much lower than prior to the introduction of the *Fuel Quality Standards Regulations 2001*. However, contamination from legacy sites and where racing fuels are used and stored may still be significant and needs to be assessed and managed in accordance with the risk posed.

## 7. References

---

API 2000, *Strategies for characterizing subsurface releases of gasoline containing MTBE*, publication Number 4669, American Petroleum Institute, Regulatory and Scientific Affairs, <[www.api.org/environment-health-and-safety/clean-water/groundwater/oxygenates/~media/A0EDE318DCD9450A8D7120ED845AA5B9.ashx](http://www.api.org/environment-health-and-safety/clean-water/groundwater/oxygenates/~media/A0EDE318DCD9450A8D7120ED845AA5B9.ashx)>

Bruce, CL, Salanitro, JP, Johnson, PC, & Spinnler, GE 2013, 'Bioaugmentation for MTBE Remediation', in *Bioaugmentation for Groundwater Remediation*, SERDP ESTCP Environmental Remediation Technology, pp. 289–312.

California EPA 2004, *Evaluation of MTBE Remediation Options*, California Environmental Protection Agency State Water Resources Control Board.

California MTBE Research Partnership 2000, *Treatment technologies for removal of MTBE from drinking water: Air stripping, advanced oxidation processes, granular activated carbon, synthetic resin sorbents*, National Water Research Institute, Fountain Valley, California, USA.

California MTBE Research Partnership 2001, *Treatment technologies for removal of MTBE from drinking water: Air stripping, using granular activated carbon*, National Water Research Institute, Fountain Valley, California, USA.

California MTBE Research Partnership 2006, *Removal of MTBE from drinking water: Case studies*, National Water Research Institute, Fountain Valley, California, USA.

CRC CARE 2006, *Natural attenuation: A scoping review*, CRC CARE Technical Report no. 3, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

CRC CARE 2013, *Petroleum hydrocarbon vapour intrusion assessment: Australian guidance*, CRC CARE Technical Report no. 23, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Davis LC & Erickson LE 2004, A review of bioremediation and natural attenuation of MTBE. *Environmental Progress*, 23(3):243–252.

Day, MJ 2000, 'Fate and transport of fuel components below slightly leaking underground tanks', *Soil Sediment and Groundwater*, MTBE Special Issue, pp. 21–24.

Department of Defence 2011, *Directive for fuel farms, underground petroleum storage systems (UPPS) and underground storage tank (UST) environmental management*, Australia.

Department of Environment 2001, *Fuel Quality Standards Regulations (updated 2003)*, Australia.

Department of Health Western Australia 2014, *Contaminated sites ground and surface water chemical screening guidelines*, Department of Health Western Australia, Western Australia, Australia.

Department of the Environment 2008, *Fuel Standard (Petrol) Determination 2001*, made under section 21 of the *Fuel Quality Standards Act 2000*, Fuel Standard (Petrol) Amendment Determination 2008 (No. 1), Department of the Environment, Commonwealth of Australia, Australia.

Dr Stupp Consulting, *MTBE-Grundwasserfahnen*,  
<[www.mtbe.de/grundwasserfahnen.html](http://www.mtbe.de/grundwasserfahnen.html)>.

enHealth 2012, *Environmental health risk assessment: Guidelines for assessing human health risks from environmental hazards*, Department of Health and Ageing and enHealth Council, Australia.

Environment Agency UK 2000, *Guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater*, R&D Publication 95, viewed June 2000, <[www.gov.uk/government/uploads/system/uploads/attachment\\_data/file/297675/srdpub95-e-e.pdf](http://www.gov.uk/government/uploads/system/uploads/attachment_data/file/297675/srdpub95-e-e.pdf)>.

EPA Victoria 2014, *Guidelines on the design, installation and management requirements for underground petroleum storage systems (UPSSs)*, EPA Victoria, Australia.

Heald, PC, Schladow, SG, Reuter, JE & Allen, BC 2005, 'Modeling MTBE and BTEX in lakes and reservoirs used for recreational boating', *Environmental Science & Technology*, vol. 39, iss. 4, pp. 1111–1118.

Hicks, KA, Schmidt, R, Nickelsen, MG, Boyle, SL, Baker, JM, Tornatore, PM, Hristova, KR & Scow, KM 2014, 'Successful treatment of an MTBE-impacted aquifer using a bioreactor self-colonized by native aquifer bacteria', *Biodegradation*, vol. 25, no. 1, pp. 41–53.

ITRC 2005, *Technical and regulatory guidance for in-situ chemical oxidation of contaminated soil and groundwater*, Interstate Technical and Regulatory Council, Washington DC, USA.

Johnson, PC, Bruce, CL & Miller, KD 2003, *In-situ bioremediation of MTBE in groundwater*, NFESC Technical Report TR-222-ENV, Naval Facilities Engineering Service Center, sponsored by the Environmental Security Technology Certification Program, Arlington, Virginia, USA.

Johnson, PC, Miller, KD & Bruce, CL 2004, *A practical approach to the design, monitoring, and optimization of in situ MTBE aerobic biobarriers*, NFESC Technical Report TR-2257-ENV, Naval Facilities Engineering Service Center, sponsored by the Environmental Security Technology Certification Program, Arlington, Virginia, USA.

NEPC 2013, *National Environmental Protection (Assessment of Site Contamination) Measure 1999, as amended 2013*, National Environment Protection Council, Australia.

New Jersey Department of Environmental Protection 2013, *Vapour intrusion screening levels*, <[www.nj.gov/dep/srp/guidance/vaporintrusion/vig\\_update\\_tables.pdf](http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig_update_tables.pdf)>.

NHMRC 2008, *National water quality management strategy, Guidelines for managing risk in recreational water*, National Health and Medical Research Council, Australia.

NSW EPA 2014, *Protection of the Environment Operations (Underground Petroleum Storage Systems) Regulation 2014*.

Office of Chief Economist 2016, *Australian Petroleum Statistics*, Issue 234, Department of Industry, Innovation and Science, Australian Government, Australia.

Rasa, E, Chapman, SW, Bekins, BA, Fogg, GE, Scow, K & Mackay, DM 2011, 'Role of back diffusion and biodegradation reactions in sustaining an MTBE/TBA plume in alluvial media', *Journal of Contaminant Hydrology*, vol. 126, iss. 3–4, pp. 235–247.

Salanitro, JP, Johnson, PC, Spinnler, GE, Maner, PM, Wisniewski, HL & Bruce, C 2000, 'Field-scale demonstration of enhanced MTBE bioremediation through aquifer bioaugmentation and oxygenation', *Environmental Science and Technology*, vol. 34, no. 19, pp. 4152– 62.

Tasmanian EPA 2010, *Environmental management and pollution control (underground petroleum storage systems) Regulations 2010*.

US EPA 2004, *Technologies for treating MTBE and other fuel oxygenates*, United States Environment Protection Agency, Washington DC, USA.

US EPA 2005, *Monitored natural attenuation of MTBE as a risk management option at leaking underground storage tank sites*, United States Environment Protection Agency, USA.

US EPA 2008, 'Chapter 13: MTBE', *Regulatory determinations support document for selected contaminants from the second drinking water contaminant candidate list (CCL 2)*, EPA Report 815-R-08-012, United States Environment Protection Agency, USA.

WA Department of Environment Regulation 2014, *Contaminated sites guideline: Assessment and management of contaminated sites*, <[www.der.wa.gov.au/yourenvironment/contaminated-sites/61-contaminated-sites-guidelines](http://www.der.wa.gov.au/yourenvironment/contaminated-sites/61-contaminated-sites-guidelines)>

White, H, Lesnik, B & Wilson, J 2002, 'Analytical methods for fuel oxygenates', *L.U.S.T.LINE: A Report on Federal and State Programs to Control Leaking Underground Storage Tanks*, United States Environmental Protection Agency, <[archive.epa.gov/oust/mtbe-a/web/pdf/ll42analytical.pdf](http://archive.epa.gov/oust/mtbe-a/web/pdf/ll42analytical.pdf)>.

Wilson, JT, Kaiser, PM & Adair, C 2005, *Monitored natural attenuation of MTBE as a risk management option at leaking underground storage tank sites*, National Risk Management Research Laboratory, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, OH, USA, p. 74.

Zeeb, P & Wiedemeier, TH 2007, *Technical Protocol for Evaluating the Natural Attenuation of MTBE*, Publication No. API 4761, American Petroleum Institute Publishing Services, Washington DC, USA.

## Further References

---

ACGIH 1996, 'Documentation of the threshold limit values and biological exposure indices', in *Supplements to the 6th edition*, American College of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio, USA.

AIHA 2013, *Odor thresholds for chemicals with established health standards*, 2nd Edition, American Industrial Hygiene Association (AIHA), Falls Church, Virginia, USA.

Arp, H P & Schmidt, TC 2004, 'Air–water transfer of MTBE, its degradation products, and alternative fuel oxygenates: The role of temperature', *Environmental Science and Toxicology*, vol. 20, iss. 5405–5412, pp. 38.

ATSDR 1996, *Public Health Statement – Methyl-Tert-Butyl Ether*, Centers for Disease Control, Springfield, Virginia, USA.

ATSDR 2014, *Medical management guidelines for formaldehyde*, Toxic substances portal, Agency for Toxic Substances and Disease Registry, viewed 4 March 2015, <[www.atsdr.cdc.gov/mmg/mmg.asp?id=216&tid=39](http://www.atsdr.cdc.gov/mmg/mmg.asp?id=216&tid=39)>.

Bengtsson, BE & Tarkpea, M 1983, 'The acute aquatic toxicity of some substances carried by ships', *Marine Pollution Bulletin*, vol. 14, pp. 213–214.

BenKinney, MT, Barbieri, JF, Gross, JS & Naro, PA 1994, *Acute toxicity of methyl tertiary-butyl ether to aquatic organisms*, presented at 15th Annual SETAC Meeting, Denver, CO, USA, 30 October–3 November.

California EPA 2000, *Guidelines for investigation and clean-up of MTBE and other ether-based oxygenates*, California Environmental Protection Agency State Water Resources Control Board, Sacramento, California, USA, <[www.waterboards.ca.gov/ust/cleanup/docs/mtbe\\_finaldraft.pdf](http://www.waterboards.ca.gov/ust/cleanup/docs/mtbe_finaldraft.pdf)>.

Chen, J, Ma, J, Cao, W, Wang, P, Tong, S & Sun, Y 2009, 'Sensitivity of green and blue-green algae to methyl tert-butyl ether', *Journal of Environmental Sciences*, vol. 21, pp. 514–519.

CRC CARE 2014, *Development of guidance for contaminants of emerging concern*, Technical Report no. 32, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

Deeb, RA, Scow, KM & Alvarez-Choen, L 2000, 'Aerobic MTBE biodegradation: an examination of past studies, current challenges and future research directions', *Biodegradation*, vol. 11, iss. 2–3, pp. 171–186.

Environment Agency UK 1999, *The fuel additive MTBE – a groundwater protection issue?*, National Groundwater and Contaminated Land Centre, Environment Agency, <[www.gov.uk/government/uploads/system/uploads/attachment\\_data/file/290463/scho0499bisf-e-e.pdf](http://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290463/scho0499bisf-e-e.pdf)>.

European Commission 2004, *Provisional SCOEL position for EOL: Recommendation from Scientific Committee on Occupational Exposure Limits for tert-butyl methyl ether*.

Fischer, A, Oehm, C & Werner, P 2005, 'Biotic and abiotic transformations of methyl tertiary-butyl ether (MTBE)', *Environmental Science and Pollution Research (international)*, vol. 12, no. 6, pp. 381–6.

Iowa Department of Public Health 2015, *IDPH toxicology manual – ethanol, methanol, tert-butyl alcohol*, viewed 4 March 2015.

Little, AD 2001, *MTBE and the requirements for underground storage tank construction and operation in member states*, A report to the European Commission.

Maine Department of Environmental Protection 2009, *Remediation guidelines for petroleum contaminated sites in Maine*, Maine Department of Environmental Protection, USA.

Martinez, PM 2002, *Biodegradation of methyl tert-butyl ether (MTBE) and its breakdown products by propane and iso-pentane grown Mycobacterium vaccae and Graphium sp.: cometabolism, inhibition, kinetics, and modeling*, PhD thesis, Oregon State University, Oregon, USA.

NHDOES 2009, *Environmental fact sheet – methyl t-butyl ether (MTBE): Health information summary*, New Hampshire Department of Environmental Services, Concord, NH, USA.

NHMRC 2008, *National water quality management strategy, Guidelines for managing risk in recreational water*, National Health and Medical Research Council, Australia.

NHMRC & NRMMC 2011, 'National water quality management strategy', *Australian drinking water guidelines*, National Health and Medical Research Council and National Resource Management Ministerial Council, Australia.

NWRI 2004, *Evaluation of MTBE remediation options*, Centre for Groundwater Restoration and Protection, National Water Research Institute (NWRI).

Oak Ridge National Laboratory 2009, *Acute exposure guideline levels (AEGLs) for methyl tertiary-butyl ether*, US Department of Energy, Oak Ridge, TN, USA.

Russom, CL, Bradbury, SP & Broderius, SJ 1997, 'Predicting modes of toxic action from chemical structure: acute toxicity in the fathead minnow (*Pimephales promelas*)', *Environmental Toxicology and Chemistry*, vol. 16, pp. 948–967.

Ruth, JH 1986, 'Odor thresholds and irritation levels of several chemical substances: A review', *American Industrial Hygiene Association Journal*, vol. 47, no. 3, pp. 142–151.

Schulman, AE 2011, *Statistical analysis of MTBE odor detection thresholds in drinking water*, US EPA, Washington DC, USA.

Smith, SL & Duffy, LK 1995, 'Odor and health complaints with Alaskan pipelines', *Chemical Health and Safety*, vol. 2, pp. 32–38.

Tarkpea, M & Svanberg, O 1982, 'The acute toxicity of motor fuels to brackish water organisms', *Marine Pollution Bulletin*, vol. 13, no. 4, pp. 125–127.

US EPA 1994, *Chemical summary for methyl-tert-butyl ether*, Office of Pollution Prevention and Toxics, United States Environment Protection Agency, USA.

US EPA 1998, *Remediation of MTBE contaminated soil and groundwater*, EPA 510-F-97-015, Office of Solid Waste and Emergency Response, USA.

US EPA 2004, *State actions banning MTBE (statewide)*, EPA420-B-04-009, viewed 6 May 2015, <[www.epa.gov/mtbe/420b04009.pdf](http://www.epa.gov/mtbe/420b04009.pdf)>.

US EPA 2013, *Methyl tertiary-butyl ether (MTBE) overview*, United States Environment Protection Agency, USA, viewed 13 May 2015, <[www.epa.gov/MTBE/faq.htm](http://www.epa.gov/MTBE/faq.htm)>.

US EPA 2014, *Methyl tertiary-butyl ether (MTBE) – drinking water*, viewed 4 March 2015, <[www.epa.gov/mtbe/water.htm](http://www.epa.gov/mtbe/water.htm)>.

Werner, I, Koger, CS, Deanovic, LA & Hinton, DE 2001, 'Toxicity of methyl-tert-butyl ether to freshwater organisms', *Environmental Pollution*, vol. 111, pp. 83–88.

WHO 1998, *Methyl tertiary-butyl ether*, Environmental Health Criteria 206, International Programme on Chemical Safety, World Health Organisation, Geneva, Switzerland.

## APPENDIX A.

### Derivation of odour screening level for MTBE

This Appendix presents information on reported aesthetic thresholds for MTBE in water and soil. A number of thresholds for odour associated with MTBE concentrations in water have been published. MTBE has a low odour threshold which makes water unpalatable for drinking at MTBE concentrations well below those that would impact on human health. A summary of available data is given in table 1.

Table 1: Reported Odour Thresholds for MTBE in Water

Threshold concentration in water (µg/L)	Context	Source
15	Taste and odour threshold	WHO 2005, WHO 2008
15	Aesthetic objective (odour threshold)	Health Canada 2006
15–180	Odour detection thresholds	Davis & Farland 2001
20	Odour threshold	US EPA 2011
<5	Limited number of individual odour thresholds	Shen <i>et al</i> 1997
20–40	Acceptability of drinking water maintained if below this	US EPA 1997
13 5	Primary standard Secondary standard	California EPA 1999
12	Drinking water standard for aesthetic values Domestic non-potable groundwater use	WA DEC 2010 (since superseded) [citing ADWG 2004; DOH 2006 (both now withdrawn)]
12	Potable water and domestic non-potable use	WA DEC 2010 (since superseded)
20	Interim screening level	WA DER 2014, WA DOH 2014

Some studies suggest that odour tends to have a lower threshold of detection than taste, whereas others show the opposite relationship (WHO 2005). The taste and odour responses reported in four studies were in the range of 24–135 µg/L and 15–180 µg/L, respectively. The four studies all used small panels and gave a wide range of results, indicative of the variability in individual responses (US EPA 1997) and also indicating a relative lack of standardised methods. They included studies by:

- Young (1996), in which the geometric means for taste and odour were 48 and 34 µg/L, respectively
- the American Petroleum Institute (API 1993), in which calculated threshold values were 39 µg/L for taste, 45 µg/L for odour detection and 55 µg/L for odour recognition
- Prah *et al* (1994), in which the median threshold odour concentration of MTBE in distilled water was 180 µg/L, and



- Dale *et al* (1997), in which the range for 60% probability of detecting the odour of MTBE in odour-free water was 43–71 µg/L, whereas the corresponding range for taste was 24–37 µg/L.

WHO (2005) refers to a study specifically designed to set an odour threshold for MTBE in drinking water, which used a panel of 57 people and a protocol based on the American Society for Testing and Materials (ASTM) Method E679-91 (Stocking *et al* 2001). Eight concentrations of MTBE in water ranging between 2 and 100 µg/L were used with a 1.75 step factor. The geometric mean detection threshold for the 57 subjects and the recommended odour threshold was 15 µg/L. The ASTM Method E679-91 has since been replaced by E679-04 (2011), which aligns it essentially with the European and Australian standards. However, given the large panel size of 57 individuals, it is highly likely that the median result is consistent with the result that would be achieved using the standard 4–8 person panel with the newer standard.

Whilst the data above provide a relatively large range of values, the lower end of the range (~12–15 µg/L) is reasonably consistent and may be used in setting a standard at which odour issues may not occur for the general population. Very low and very high reported values call into question methodology, such as sensitivity and repeatability of the method itself and the effects of individual variability which may not have been addressed in a standardised way.

Small differences of concentration in the range 12–15 µg/L are considered to be insignificant in relation to odour and taste thresholds: the sensory response to chemical concentrations is non-linear: a given percentage increase in measurable concentration will yield a significantly lower perceived increase in strength (Schulz, Balch, & Bowly 2002).

Sitting at a significantly lower value, the California secondary standard of 5 µg/L is based on the general criteria of consumer acceptance, using parameters such as odour, taste, and appearance as measures of acceptability, and specifically takes into account the results of evaluations that include more sensitive individuals among the general population, not simply the median or typical response. Given the low potential for MTBE in Australian conditions to impact on large populations where very sensitive individuals are more likely to be encountered in significant numbers, such a stringent approach is not considered necessary.

It is recommended that a MTBE value for water of 15 µg/L, consistent with the WHO Guideline for drinking water quality be adopted for Australia. The WHO Guidelines are one of the most important sources of advice on the safety and acceptability of drinking water around the world. They are used as the basis for standards in a substantial part of the world and are respected for their independence and transparency. WHO bases its evaluations on international peer-reviewed assessments.

The toxicology of MTBE indicates that while it induces tumours in rodents, there is inconclusive evidence as to the significance to humans and the mechanism appears to be a high-dose, non-genotoxic phenomenon. MTBE can be detected in water by taste and odour at low concentrations. WHO considered that it was unnecessary to set a health-based guideline value, since any such value would be substantially above the concentration at which MTBE could be detected by taste and odour (WHO 2005)

Apart from the direct impact of taste and odour, potential tainting of fish taken from contaminated waters is also a consideration. Petersen and Moller (2001) reported on

testing of taste and odour detection in fish kept in controlled environments with known MTBE concentrations in water. Triangular forced choice testing was employed using 8 panellists each testing fish raised in a given concentration of MTBE 6 times, yielding 48 tests per concentration sample. The results showed that the taint threshold was approximately 30 µg/L, which is significantly higher than the recommended threshold for drinking water. Hence, no separate recommendation for fish taint is required.

MTBE is relatively volatile (vapour pressure 245 mm Hg, Henry's Law constant  $5.5 \times 10^{-4}$  atm-m<sup>3</sup>/mol), and will volatilise readily from soil surfaces or water (US EPA 1994a and 1994b). It does not adsorb readily to soil particles and is mobile (Health Canada 2006). Hence, in the absence of groundwater, MTBE in soil is not considered to be a significant risk although there is very little literature on this aspect.

In Western Australia, the screening level in soil for MTBE is 0.5 mg/kg based on odour grounds (WA DER 2014). This value should be considered if an investigation of MTBE soil contamination is required. In Morgenroth & Arvin (2003), the threshold for odour is 0.3 mg/kg. An extensive search found no further references with regard to soil concentration and odour.

## Recommendation

For groundwater, the following MTBE threshold relating to odour is recommended:

**Table 2: Recommended threshold concentration for odour**

Environmental media	Recommended threshold concentration	Comment
Water	15 µg/L	Consistent with the WHO Guideline (2005) for MTBE in drinking water

If MTBE is found in groundwater, testing should also be done for formaldehyde and TBA, especially at legacy sites. Assessment of formaldehyde in groundwater should be done against the GIL in the ASC NEPM of 0.5 mg/L (NEPC 2013).

## References

- American Petroleum Institute 1993, *Odor threshold studies performed with gasoline and gasoline combined with MtBE, EtBE and TAME*, Washington, DC, American Petroleum Institute (API No. 4592) [cited in US EPA, 1997].
- Australian Drinking Water Guidelines 2004, *National Water Quality Management Strategy*, National Health and Medical Research Council and Natural Resource Management Ministerial Council, Canberra
- California Environmental Protection Agency (EPA) 1999, *Public health goal for MTBE in drinking water*, Office of Environmental Health Hazard Assessment, Scaramento, USA.
- Dale, MS, Moylan, MS, Koch, B & Davis, MK 1997, *MTBE: Taste and odor threshold determinations using the flavor profile method*. Presented at the Water Quality Technology Conference, 9–13 November 1997, Denver, CO [cited in US EPA, 1997]

- Davis, JM & Farland, WH 2001, 'Forum: The paradoxes of MTBE', *Toxicological Sciences*, vol. 61, pp. 211–217.
- Health Canada 2006, *Guidelines for Canadian drinking water quality : Guideline Technical Document – MTBE*, Health Canada, Ottawa, Ontario, Canada.
- Morgenroth, E & Arvin, E 2003, 'The European perspective of MTBE as an oxygenate in fuels', in *Managing for health ecosystems*, Lewis Publisher, Boca Raton Florida.
- Petersen, GI & Møller 2001, *Evaluation of threshold values for tainting of fish (Oncorhynchus mykiss) by methyl tertiary butyl ether (MTBE)*. Report, June 2001. Danish Environmental Protection Agency [cited in Addendum to the Environmental Risk Assessment for tert-Butyl methyl ether (MTBE)]
- Prah, JD, Goldstein, GM, Devlin, R, Otto, D, Ashley, D, House, D, Cohen KL & Gerrity, T 1994, 'Sensory, symptomatic, inflammatory, and ocular responses to and the metabolism of methyl tertiary-butyl ether in a controlled human exposure experiment', *Inhalation Toxicology*, vol. 6, pp. 521–38. [cited in US EPA 1997]
- Shen, YF, Yoo, LJ, Fitzsimmons, SR & Yamamoto, MK 1997, *Threshold odor concentrations of MTBE and other fuel oxygenates*, San Francisco, Preprints of Papers Presented at the 214th American Chemical Society National Meeting, pp. 407–409.
- Schulz, T, Balch, A & Bowly, S 2002, 'Odour intensity measurement: An overview of its potential for use in odour impact assessment and control', *Clean Air and Environmental Quality*, vol. 36, no. 3, pp. 38–42.
- Stocking, AJ, Suffet, IH, McGuire, MJ & Kavanaugh, MC 2001, 'Implications of an MTBE odor study for setting drinking water standards', *Journal of the American Water Works Association*, vol. 93, pp. 95–105. [cited in WHO 2005]
- US EPA 1994a, *Chemical summary for Methyl-Tert-Butyl Ether*, Office of Pollution Prevention and Toxics, Environmental Protection Agency, United States.
- US EPA 1994b, *Chemicals in the environment: Methyl-tert butyl ether (CAS NO. 1634-04-4)*, Chemical fact sheet, viewed 13 May, 2015, <[www.epa.gov/chemfact/f\\_mtbe.txt](http://www.epa.gov/chemfact/f_mtbe.txt)>.
- US EPA 1997, *Drinking water advisory: Consumer acceptability advice and health effects analysis on methyl tertiary-butyl ether (MTBE)*, Report EPA-822-F-97-008, Office of Water, Environmental Protection Agency, United States.
- US EPA 2011, *2011 Edition of the Drinking Water Standards and Health Advisories*. Report EPA-820-R-11-002, Office of Water, Environmental Protection Agency, United States.
- Western Australia Department of Health (WA DOH) 2006 *Contaminated Sites Reporting Guideline for Chemicals in Groundwater*.
- Western Australia Department of Health (WA DOH) 2014 *Contaminated Sites Ground and Surface Water Chemical Screening Guidelines*.
- Western Australia Department of Environment and Conservation (WA DEC) 2010, *Assessment levels for soil, sediment and water*, Department of Environment and Conservation Perth, WA, Australia.

Western Australia Department of Environment Regulation (WA DER) 2014, *Assessment and management of contaminated sites*, Department of Environment Regulation, Perth, WA, Australia.

World Health Organization (WHO) 2005 *Methyl tertiary-Butyl Ether (MTBE) in Drinking-water*. Background document for development of WHO Guidelines for Drinking-water Quality. Geneva, Switzerland

World Health Organization (WHO) 2008 *Guidelines for Drinking-water Quality*. Fourth Edition, Geneva, Switzerland

Young WF, Horth, H, Crane, R, Ogden, T & Arnott, M 1996, 'Taste and odor threshold concentrations of potable water contaminants', *Water Research*, vol. 30, pp. 331–340 [cited in US EPA, 1997]

## APPENDIX B.

---

### Derivation of ecological screening criteria for MTBE

---

An extensive literature search was conducted to identify aquatic toxicity data for MTBE for both freshwater and marine aquatic organisms. Databases and other information sources searched were US EPA ECOTOX (US EPA 2015), the relevant Australasian ecotoxicology database (Warne & Westbury 1999), and the ECETOC database (ECETOC 2003a). Other information sources searched included the scientific literature databases Science Direct, TOXLINE and PubMed. A general online search was also conducted using the search engines Google and Google Scholar. Keywords used for the search were “methyl tertiary-butyl ether”, “MTBE” and the CAS registry number “1634-04-4”.

The Australian Water Quality Guidelines (AWQG) specify that the preferred data for deriving trigger values come from multi-species toxicity tests, i.e. field or model ecosystems (mesocosm, microcosm, artificial stream) tests that represent the complex interactions of species in the field (ANZECC & ARMCANZ 2000). However, few such studies exist and none were identified for MTBE. Hazard (toxicity) is most frequently predicted using concentration-effect data from single species toxicity tests which measure effects on individuals. However, the protection goals are generally wider i.e. populations, communities and ecosystems. As there is no universal single ‘sensitive’ test species, predictions should be based on the likely effects of a toxicant to a range of test species (OECD 2006). Single species aquatic toxicity data for MTBE were thus identified for both freshwater and marine organisms for a range of trophic levels.

#### Screening and selection of toxicity data

The end-point of a test is the biological effect that is measured in that test. Several different end-points may be measured in the one test. The most common acute test end-point is mortality, measured by  $LC_{50}$ , the lethal concentration that kills 50% of test organisms in a given time, usually after 4 days for fish or 2 days for some invertebrates. The  $EC_{50}$ , the effect concentration that causes a specified effect in 50% of test organisms in a given time, is usually reported when it is difficult to accurately determine mortality and some surrogate end-point such as immobility is measured which, if the test was extended, would lead to mortality. Other effects, such as behaviours, etc. can also be measured in an acute test. As the  $LC_{50}$  is measuring a clearly defined effect and calculations are from the middle of the dose-response curve,  $LC_{50}$  data are more robust than chronic data.

A wide variety of biological endpoints are measured in chronic toxicity tests. These can be subdivided into groups: functions of life; behavioural; and biochemical endpoints. Functions of life include mortality, reproductive impairment, hatchability, immobilisation and inhibition of growth. Behavioural end-points include: mobility, motility, burial rate, ventilation rates, swimming rate, phototactic responses and feeding rate. Biochemical end-points include: inhibition of bioluminescence, induction and activity of a range of enzymes, changes in DNA and of the ratio of DNA and RNA, histopathological lesions, and immune system dysfunction. In the current version of the AWQG only ‘ecologically relevant’ endpoints that measure detrimental effects on populations, communities and ecosystems (e.g. death, immobilisation, growth (individual or population) and

reproductive impairment) are used to derive trigger values. No toxicity data that measure effects below the individual level of organisation (e.g. subcellular, biochemical) can be used. However, in light of the rapid expansion of this field of ecotoxicology, such data could in the future be used, provided their ecological relevance can be demonstrated. This would have to be done on a case by case basis (Warne *et al* 2014a). The existing AWQG approach was therefore adopted in this study for the derivation of a guideline trigger value for MTBE.

There are some basic screening requirements for validity of toxicity tests outlined in section 8.3 of the AWQG (ANZECC & ARMCANZ 2000) and also published by Warne (Warne 2001). The principal quality criteria for acceptance of data were that the test procedure was well described with reference to an official guideline (e.g. OECD, ASTM, US EPA) if possible, and test concentrations were measured with an adequate analytical method. This latter requirement is particularly pertinent for MTBE due to its high volatility; hence data from tests with no analytical monitoring were not accepted. Once the unsuitable toxicity data was removed, the next step was to assess the quality of the remaining data.

#### *Toxicity data quality assessment scheme*

A quality assessment method based on the protocol used within the US EPA ECOTOX database (US EPA 1994) was used for the AWQG (ANZECC & ARMCANZ 2000). This method assessed whether appropriate experimental designs, chemical analyses and statistical techniques were employed to derive the toxicity data. This method was subsequently reviewed and further improved (Hobbs *et al* 2005). The Hobbs *et al* aquatic scheme assessment procedure has also recently been modified for screening terrestrial ecotoxicity data used to derive ecological investigation levels in contaminated soils (Schedule B5b, ASC NEPM). This quality assessment procedure was therefore applied to the toxicity data used in this study (Hobbs *et al* 2005). Using this scheme, the toxicity data quality was assessed by means of awarding scores based on a series of twenty questions designed to ascertain the scientific rigour of the testing reported in each paper. In this scheme, the scores awarded for each question are summed to obtain the total score expressed as a percentage of the total possible score for that type of data (e.g. freshwater/non-metals/non-plants = 91). The data are classed as being of unacceptable, acceptable, or high quality, depending on whether the quality score is  $\leq 50\%$ , 51–79% or  $\geq 80\%$  respectively. Table 1 presents the data quality scheme applied in this study (Hobbs *et al* 2005).

#### *Data type requirements*

In the current AWQG, the recommended minimum data requirement to derive a site specific trigger value is toxicity data for at least five species that belong to at least four taxonomic groups and there are no requirements for specific phyla or specific organisms to be part of the minimum data requirements (ANZECC & ARMCANZ 2000). Whilst the AWQG are less demanding and not as prescriptive as other International guideline requirements (US EPA 1999; European Commission 2002; CCME 2007) minimum data requirements are not expected to change in the proposed guideline revision (Warne *et al* 2014a). To overcome some of the limitations of small datasets, a more rigorous method for indicating the reliability of the resulting guidelines values and rules governing the types of statistical distributions that can be applied to the toxicity data are proposed (Warne *et al* 2014a; 2014b).

The most frequently used toxicity measures used to derive trigger values are hypothesis-based values such as the no observed effect concentrations (NOECs) and the lowest observed effect concentrations (LOECs). Both of these types of data have come under persistent criticism as recently summarised (Fox *et al* 2012).

Toxicity endpoints obtained through regression-based statistical data evaluation (i.e. NEC (no effect concentration) or EC<sub>x</sub> values identifying low-effects thresholds) will therefore be the preferred toxicity endpoints (over NOEC and LOEC) in the revised guidelines with the understanding that the replacement of the use of NOECs with a combination of NEC, EC<sub>x</sub> and NOEC will, for some time be unavoidable (Warne *et al* 2014a). The current guidelines recognised the limitations of NOEC data and recommended their use for guideline trigger value derivation be phased out as EC<sub>10</sub> data became available (ANZECC & ARMCANZ 2000). To encourage the generation of EC<sub>10</sub> data, LC<sub>10</sub> and NOEC data will initially be deemed to be equivalent, and combinations of such data can be used to derive trigger values (Warne *et al* 2014a). Hence in this study where a chronic NOEC was reported it was considered to be quantitatively equivalent to a chronic EC<sub>10</sub>.

Chronic rather than acute toxicity data are preferred to derive guideline trigger values for toxicants, as they are more appropriate to achieve the overall aim of the AWQG to provide life-long protection for aquatic organisms and hence, it is assumed, for aquatic ecosystems (Warne *et al*, 2014a). The datasets for acute toxicity tests are however much greater than that for chronic tests. In the proposed revisions to the guidelines it is anticipated that there will be increased flexibility to expand datasets. Where there are insufficient chronic data to derive a screening level (or guideline value), acute toxicity data converted to chronic equivalent data, can be included and acute EC/IC/LC<sub>50</sub> data should be used for this purpose. Conversion of an acute LC<sub>50</sub> to a chronic EC<sub>10</sub> requires division by a chemical specific acute to chronic ratio (ACR). The ACRs are determined as the ratio of acute EC<sub>50</sub> to chronic NOEC. In the absence of a chemical specific ACR, a default assessment factor (AF) of 10 is applied. Chronic EC/IC/LC<sub>50</sub>, LOEC and maximum allowable toxicant concentration (MATC) can be converted to chronic EC<sub>10</sub> values by dividing by 5, 2.5 and 2 respectively. These factors are those that were used previously to convert acute EC/LC<sub>50</sub> data to chronic NOECs (ANZECC & ARMCANZ 2000; Warne 2001).

Increasing the types of toxicity measures that can be used has the benefit of increasing sample sizes used for species sensitivity distributions (SSDs) which, consequently, increases the confidence in the derived trigger values. In SSD methods, each species is given equal weighting and a single value is used to represent the sensitivity of each species. The method of deriving toxicant screening level by SSDs requires data for at least five species that belong to at least four taxonomic groups. Where there is more than one data point for the same exposure period and species, a single value is used to represent each species. In determining a single sensitivity value for each species, equal importance (weighting) is given to each species in calculating the SSD and the resulting screening level (Warne 2001). BurrliOZ is the SSD method used to derive toxicant trigger values in the AWQG and was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (Campbell *et al* 2000) based on the earlier work by Shao (2000).

### *Freshwater toxicity data*

The toxicological dataset for the freshwater aquatic toxicity studies identified for MTBE is summarised in table 1. Within this table each study was classified as high, acceptable or unacceptable quality based on its quality assessment score (Hobbs *et al* 2005). Only toxicity data classified as 'high' and 'acceptable' were used to derive the freshwater screening level as per Hobbs *et al* (2005). It should be noted that studies classified as 'unacceptable' may in fact represent acceptable studies; however in some cases it was not possible to access the complete article to confirm that validity criteria were met. For ease of interpretation of table 1, each of the studies are categorised into four groups – bacteria, algae, invertebrates and vertebrates. A total of 22 individual study endpoints were deemed to be of high or acceptable quality and could therefore be employed for derivation of the screening level for MTBE. Of this number, seven endpoints were classified as chronic studies, these were with the cyanobacterium *Synechococcus leopoliensis* and two algae *Selenastrum capricornutum* (2 studies) and the diatom *Navicula pelliculosa*, and a 5- and 21- day reproduction study in the *Cladocera ceriodaphnia dubia* and *Daphnia magna* respectively, and a 7 day early life stage study in the fish *Pimephales promelas*. The remainder of the studies were identified as acute toxicity tests.

#### *Toxicity to bacteria*

A single study with the cyanobacteria *Synechococcus leopoliensis* reported a chronic (5 day) NOEC of 1976 mg/L (Rousch & Sommerfield 1998). As stated earlier, where chronic NOECs are reported they can be considered equivalent to chronic EC<sub>10</sub> values and hence the NOEC value did not require manipulation. A recent study reported on the microbial toxicity of MTBE using fluorescent and bioluminescent reporter strains (Roslev *et al* 2015), however due to the biochemical nature of these endpoints, these studies were not considered appropriate for deriving screening levels (ANZECC & ARMCANZ 2000). A genotoxicity study was also identified with MTBE with *Salmonella* tester strains but as the ecological relevance of this bacterial species is questionable this study was also not considered appropriate (Kado *et al* 1998).

#### *Toxicity to algae*

Two publications were identified for use in the derivation of the screening level. The first reported a 4 day EC<sub>50</sub> of 491 mg/L MTBE for the unicellular green algae *Selenastrum capricornutum* (Wong *et al* 2001). A 4 day value for microalga is considered as a chronic endpoint and therefore this value was converted to a chronic EC<sub>10</sub> by dividing the EC<sub>50</sub> value by 5. The second paper reported chronic NOEC values for the green algae *Selenastrum capricornutum*, and the diatom *Navicula pelliculosa* (Rousch & Sommerfield 1998). The chronic NOECs were therefore considered equivalent to chronic EC<sub>10</sub> values and did not require manipulation.

#### *Toxicity to invertebrates*

Eight relevant studies were identified in five literature sources which reported on the toxicity of MTBE to freshwater invertebrates. These comprised separate studies on two insects (*Chironomus tentans*, *Hexagenia limbata*) (Wong *et al* 2001), one test on the amphipod *Hyalella Azteca* (Wong *et al* 2001), four separate tests on two cladocerans (3 x *Daphnia magna*, 1 x *Ceriodaphnia dubia*) (Hockett 1997; Wong *et al* 2001; both cited in ECETOC 2003b) and a study on the snail *Physa gyrina* (Wong *et al* 2001). Of these eight studies, six were identified as acute endpoints (2–4 days) and two



reproduction tests on each of the cladocerans were identified as chronic. Of the acute tests all of the endpoints reported EC<sub>50</sub> values. As only acute studies were reported no chemical specific ACR values were available for *C. tentans*, *H. limbata*, *H. azteca*, *P. gyrina* and these values were therefore converted to an EC<sub>10</sub> using the default assessment factor of 10. It should be noted that for the *D. magna* and *C. dubia* studies reported by (Wong *et al* 2001), ACR values of 9.2 and 1.7 respectively could be derived based on the ratio of acute EC<sub>50</sub> to chronic NOEC. As with the other invertebrate studies however the default AF of 10 was also applied to these studies so that a more conservative value (greater toxicity) was considered.

#### *Toxicity to vertebrates*

Eight relevant studies on the toxicity of MTBE to freshwater fish were identified. These comprised a study on the bluegill (*Lepomis macrochirus*) (Wong *et al* 2001), four separate studies on the fathead minnow (*Pimephalus promelas*) (Veith *et al* 1983; Gieger *et al* 1988; Hockett 1997, API 1999), two separate studies on the rainbow trout (*Oncorhynchus mykiss*) (Hockett 1997; Nadaffi *et al* 2008) and a study on the zebrafish (*Danio rerio*) (Moreels *et al* 2006). Of these eight studies, seven were identified as acute endpoints (4 days) and one early life stage test on the fathead minnow identified as chronic (table 1). As with the invertebrate tests, a default AF was applied to convert the reported acute LC<sub>50</sub> values to chronic EC<sub>10</sub> values to use in the screening level derivation process.

For the purpose of deriving a freshwater screening level for MTBE, data from seven taxonomic groups comprising thirteen different species passed the data quality assurance process and hence the minimum data requirements of the AWQG (i.e. four taxonomic and five species) were met. These data are presented in table 1 below. The data were sorted by species, then endpoint and finally by duration of exposure. For each combination of species and endpoint the longest exposure duration is usually selected, unless as is the case here with *D. magna* that the toxicity estimate from a shorter duration is lower, in such cases the lower value is selected. If there are multiple values for the longest duration then the geometric mean is calculated. The lowest resulting value for each combination of species and endpoint is then selected as the sensitivity value for that species. The sensitivity values were then entered in the SSD software program BurrliOZ.

**Table 1 Application of data selection rules to generate the freshwater toxicity data used in BurriOZ**

Taxonomic group	Species	Endpoint	Duration (days)	EC <sub>10</sub> (mg/L)	Value for each combination of species, endpoint and duration	Lowest value for each combination of species and endpoint	Lowest value for species	Acute or Chronic
Cyanobacteria	<i>S. leopoliensis</i> (Rousch & Sommerfield 1998, Wong et al 2001)	Growth	5	1976	1976	1976	1976	Chronic
Green Algae	<i>S. capricornutum</i> (Wong et al 2001)	Growth	4	98.2	98.2	98.2	98.2	Chronic EC <sub>50</sub> converted to chronic EC <sub>10</sub>
	<i>S. capricornutum</i> (Rousch & Sommerfield 1998, Wong et al 2001)	Growth	5	2462	2462			Chronic
Diatom	<i>N. pelliculosa</i> (Rousch & Sommerfield. 1998)	Growth	3	2252	2252	2252	2252	Chronic
Insect	<i>C. tentans</i> (Wong et al 2001)	Immobility	2	174.2	174.2	174.2	174.2	Acute converted to chronic with AF of 10
	<i>H. limbata</i> (Wong et al 2001)	Immobility	4	58.1	58.1	58.1	58.1	Acute converted to chronic with AF of 10
Crustacean	<i>H. Azteca</i> (Wong et al 2001)	Immobility	4	47.3	47.3	47.3	47.3	Acute converted to chronic with AF of 10
	<i>D. magna</i> (Wong et al 2001)	Immobility	2	47.2	50.6	50.6	50.6	Acute converted to chronic with AF of 10
		Immobility	2	54.2				Acute converted to chronic with AF of 10
		Immobility	4	72	72			Acute converted to chronic with AF of 10

		Reproduction	21	51	51	51		Chronic
	<i>C. dubia</i> (Wong <i>et al</i> 2001)	Immobility	2	34	34	34	34	Acute converted to chronic with AF of 10
		Reproduction	5	202	202	202		Chronic
Mollusc	<i>P. gyrina</i> (Wong <i>et al</i> 2001)	Immobility	4	55.9	55.9	55.9	55.9	Acute converted to chronic with AF of 10
Fish	<i>L. macrochirus</i> (Wong <i>et al</i> 2001)	Lethality	4	105.4	105.4	105.4	105.4	Acute converted to chronic with AF of 10
	<i>P. promelas</i> (Gieger <i>et al</i> 1988)	Lethality	4	67.2	77.5	77.5	77.5	Acute converted to chronic with AF of 10
	<i>P. promelas</i> (Veith <i>et al</i> 1983)	Lethality	4	70.6				Acute converted to chronic with AF of 10
	<i>P. promelas</i> (Hockett 1997, Wong <i>et al</i> 2001)	Lethality	4	98				Acute converted to chronic with AF of 10
	<i>P. promelas promelas</i> (early-life stage) (API 1999)	Growth	31	279	279	279		Chronic
	<i>O. mykiss</i> (Nadaffi <i>et al</i> 2008)	Lethality	4	77.3	82.8	82.8	82.8	Acute converted to chronic with AF of 10
	<i>O. mykiss</i> (Hockett 1997, Wong <i>et al</i> 2001)	Lethality	4	88.7				Acute converted to chronic with AF of 10
	<i>D. rerio</i> (Moreels <i>et al</i> 2006)	Lethality	2	67.7	67.7	67.7	67.7	Acute converted to chronic with AF of 10

## Marine toxicity data

The toxicological dataset for the marine aquatic toxicity studies identified for MTBE are summarised in table 2. Within this table each study was classified as high, acceptable or unacceptable quality based on its quality assessment score (Hobbs *et al* 2005). Only toxicity data classified as high were used to derive the marine water screening level. It should be noted that studies classified as unacceptable may in fact represent acceptable studies; however in some cases it was not possible to access the complete article to confirm that validity criteria were met. For ease of interpretation of table 2 each of the studies are categorised into three groups i.e. algae, invertebrates and vertebrates. Of the relevant literature reviewed, two papers addressing 13 individual study endpoints were deemed to be of high quality and could therefore be employed for derivation of the screening level for MTBE. Of this number only two endpoints were classified as chronic studies, these were a 3-day growth inhibition with the diatom *Skeletonema costatum* and a 28-day reproduction study with the mysid shrimp *Americamysis bahia*. The remainder of the studies were identified as acute toxicity tests.

### Toxicity to bacteria

No relevant studies were identified for MTBE toxicity and ecologically relevant marine bacteria. It should be noted that several studies were identified that reported on the toxicity of MTBE to the marine bioluminescent bacteria *Vibrio fischeri* (Gupta & Lin 1995; Hernando *et al* 2003; Roslev *et al* 2015), however due to the biochemical nature of this endpoint, these studies were not considered appropriate for deriving screening levels (ANZECC & ARMICANZ 2000).

### Toxicity to algae

Two publications reporting on two separate algal studies were identified for use in the derivation of the marine water screening level. The first reported a 2 day  $IC_{50}$  of 2236 mg/L MTBE for the giant kelp (brown algae) *Macrocystis pyrifera* (Bay & Brown 2000). Based on test duration this test was considered an acute (short-term) test, this value was therefore converted to a chronic  $EC_{10}$  using the default assessment factor of 10. The second study investigated MTBE toxicity with the marine diatom *Skeletonema costatum* (Rausina *et al* 2002). The 3 day value for growth inhibition is considered a chronic endpoint and therefore this value was converted to a chronic  $EC_{10}$  by dividing the  $EC_{50}$  value by 5.

### Toxicity to invertebrates

Nine relevant studies on the toxicity of MTBE to marine invertebrates were identified in two literature sources. These comprised of eight studies on crustaceans (*Americamysis bahia*, *Palaemonetes pugio*, *Callinectes sapidus*, *Rhepoxynius abronius*, *Holmesimysis costata*, *Grandidierella japonica*), and a study on a mollusc (*Mytillus galloprovincialis*) (Rausina *et al* 2002) and an echinoderm (*Strongylocentrotus purpuratus*) (Bay & Brown 2000). Of these eight studies, seven were identified as acute endpoints (2–7 days) and one reproduction test on the mysid shrimp *A. bahia* was identified as chronic. Of the acute tests all of the endpoints reported  $IC/EC/LC_{50}$  values. As only acute studies were reported no chemical specific ACR values were available for *P. pugio*, *C. sapides*, *R. abronius*, *H. costata*, *G. japonica*, *M. galloprovincialis* and *S. purpuratus* and these values were therefore converted to an  $EC_{10}$  using the default assessment factor of 10. It should be noted that both an acute (4-day) and chronic (28-

day) endpoint was reported for *A. bahia* (Rausina *et al* 2002), so that an ACR value of 7.2 could be derived based on the ratio of acute EC<sub>50</sub> to chronic NOEC. As with the other invertebrate studies however the default AF of 10 was also applied to these studies.

#### *Toxicity to vertebrates*

One relevant publication was identified which reported on the toxicity of MTBE to two marine fish, the three-spined stickleback (*Gasterosteus aculeatus*) (Rausina *et al* 2002), and a study on the sheepshead minnow (*Cyprinodon variegatus*) (Rausina *et al* 2002). Both these studies reported acute endpoints (4-day) and a default AF of 10 was applied to convert the reported acute LC<sub>50</sub> values to chronic EC<sub>10</sub> values to use in the screening level derivation process.

For the purpose of deriving a marine screening level for MTBE, data from six taxonomic groups comprising of twelve different species passed the data quality assurance process and hence the minimum data requirements of the AWQG (i.e. four taxonomic and five species) were met. These data are presented in table 2 below. The data was sorted by species, then endpoint and finally by duration of exposure. For each combination of species and endpoint the longest exposure duration is usually selected, unless as is the case here with *A. bahia* that the toxicity estimate from a shorter duration is lower, in such cases the lower value is selected. If there are multiple values for the longest duration then the geometric mean is calculated. The lowest resulting value for each combination of species and endpoint was then selected as the sensitivity value for that species. The sensitivity values were then entered in the SSD software program BurrliOZ.

**Table 2 Application of data selection rules to generate the marine toxicity data used in BurrliOZ**

Taxonomic group	Species	Endpoint	Duration (days)	EC <sub>10</sub> (mg/L)	Value for each combination of species, endpoint and duration	Lowest value for each combination of species and endpoint	Lowest value for species	Acute or Chronic
Green algae	<i>M. pyrifera</i> (Bay & Brown 2000)	Growth	2	223.6	223.6	223.6	223.6	Acute converted to chronic with AF of 10
Diatom	<i>S. costatum</i> (Rausina <i>et al</i> 2002)	Growth	3	55.8	55.8	55.8	55.8	Chronic EC <sub>50</sub> converted to chronic EC <sub>10</sub>
Crustacean	<i>A. bahia</i> (Rausina <i>et al</i> 2002)	Lethality	4	20	20	20	20	Acute converted to chronic with AF of 10
		Reproduction	28	26	26	26		Chronic
	<i>P. pugio</i> (Rausina <i>et al</i> 2002)	Lethality	4	16.6	16.6	16.6	16.6	Acute converted to chronic with AF of 10
	<i>C. sapidus</i> (Rausina <i>et al</i> 2002)	Lethality	4	30.6	30.6	30.6	30.6	Acute converted to chronic with AF of 10
	<i>R. abronius</i> (Rausina <i>et al</i> 2002)	Immobility	4	29.4	29.4	29.4	29.4	Acute converted to chronic with AF of 10
	<i>H. costata</i> (Rausina <i>et al</i> 2002)	Lethality	7	14.1	14.1	14.1	14.1	Acute converted to chronic with AF of 10
	<i>G. japonica</i> (Rausina <i>et al</i> 2002)	Lethality	4	15.5	15.5	15.5	15.5	Acute converted to chronic with AF of 10
Mollusc	<i>M. galloprovincialis</i> (Rausina <i>et al</i> 2002)	Normal Survival	2	112.2	112.2	112.2	112.2	Acute converted to chronic with AF of 10
Echinoderm	<i>S. purpuratus</i> (Bay & Brown 2000)	Normal Survival	3	134.1	134.1	134.1	134.1	Acute converted to chronic with AF of 10
Fish	<i>G. aculeatus</i> (Rausina <i>et al</i> 2002)	Lethality	4	92.9	92.9	92.9	92.9	Acute converted to chronic with AF of 10
	<i>C. variegatus</i> (Rausina <i>et al</i> 2002)	Lethality	4	135.8	135.8	135.8	135.8	Acute converted to chronic with AF of 10

## BurrliOZ software

A species sensitivity distribution (SSD) is a probabilistic model of the distribution of the toxicity of particular contaminant to a defined range of species representing a specified number of taxonomic groups. Based on a collection of estimated no/low effect (i.e. EC<sub>10</sub>) toxicity data collected for a range of species, the BurrliOZ software provides the ability to fit several standard distributions and estimate the concentrations of chemicals such that a given percentage of species will not be unacceptably affected with a known probability. This threshold concentration is often known as the protecting concentration or, for the Australian and New Zealand Water Quality Guidelines is termed a trigger value (TV). The BurrliOZ software was the SSD method used to derive all of the toxicant trigger values in the AWQG.

The user typically requires the concentration corresponding to the statement that:

q% of the species should be protected if the concentration of the chemical is less than the estimated protecting concentration,

where q is typically a large percentage (such as 90% or 95%).

The current version BurrliOZ 2.0 (release v1.1) was used in this report and is available free to download at <https://research.csiro.au/software/burrlioz/>. The distributions considered in the current version are the log-logistic, and Burr Type III. Improvements from the original version used in the AWQG include the provision of confidence intervals (CI) associated with the trigger values. The 95% CI are a measure of the uncertainty associated with predicting the trigger value using the statistical distribution that best fits the available toxicity data. The calculated sensitivity values for the freshwater species (table 1) and marine species (table 2) were then entered into BurrliOZ to derive the respective SSD.

As there was sensitivity values for >8 species for both freshwater and marine datasets the adequacy of sample size was considered as good (Warne *et al* 2014b). The choice of model for fitting the data is automatically selected by BurrliOZ depending on the number of observations, consistent with the AWQG derivation method ( $n < 8$  – log logistic;  $n \geq 8$  – Burr Type III), hence a Burr Type III distribution was used to fit both sets of data. The result SSD graphs for the freshwater and marine species are presented in figure 1. Visual of assessment of fit for both graphs were deemed good, as adequate data points (13 and 12 for freshwater and marine data respectively) allowed a good spread of data along the fit model.

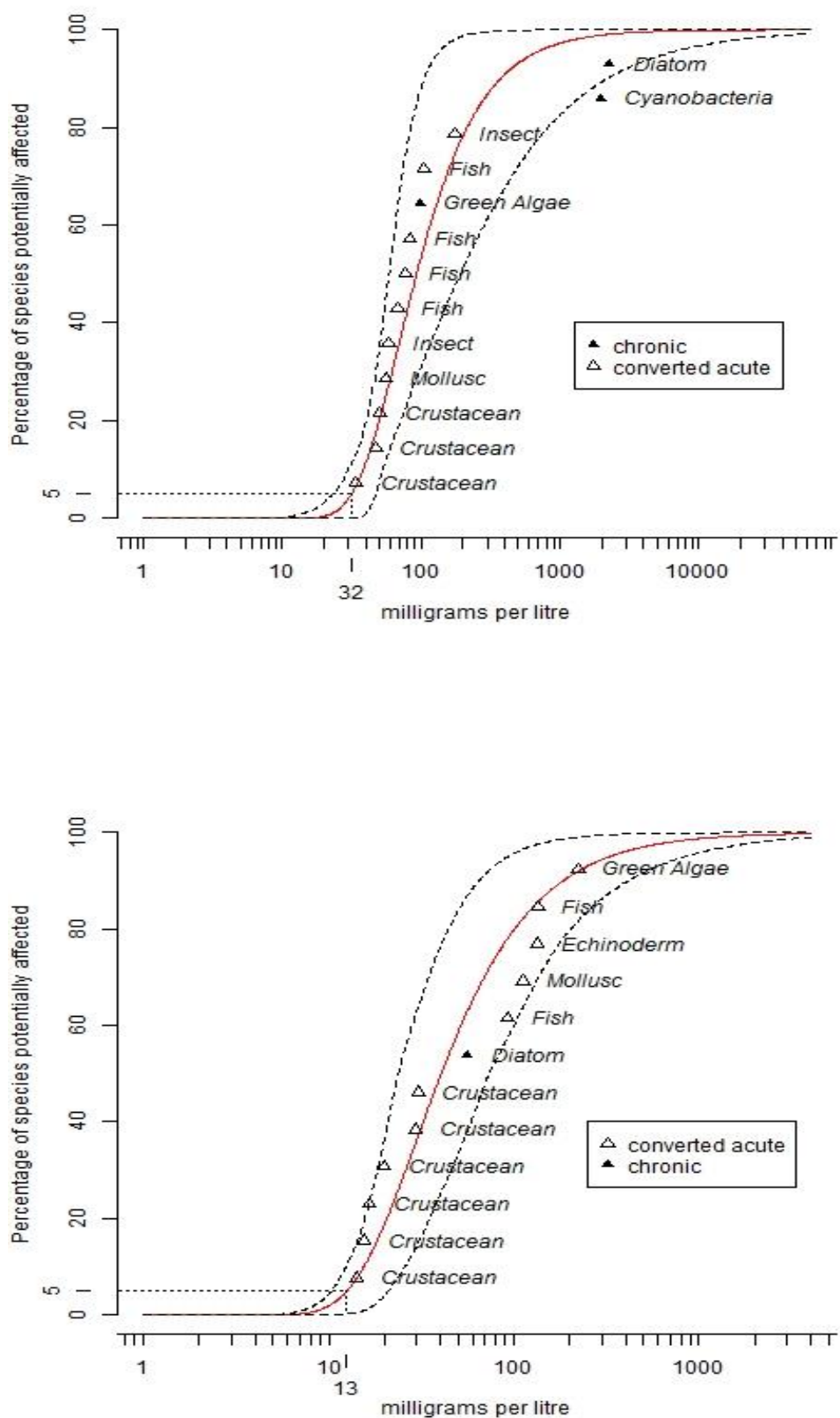


Figure 1 Species Sensitivity Distribution graphs for freshwater (top) and marine (bottom)



## Calculate screening levels for different levels of protection

The level of protection chosen for deriving the guidance values reported in the AWQG were selected for slightly-moderately disturbed ecosystems and was the median of the distribution of PC95 estimates. A 95% level of protection and 50% certainty was selected as a 95% level of protection should be sufficient to protect the ecosystem provided keystone species are considered, and a 50% level of certainty provides a robust and defensible guideline figure (ANZECC & ARMCANZ 2000).

The screening levels derived from the respective SSD for both aquatic ecosystems are reported in table 3 for various protection levels. The 95% species protection level with associated CIs is highlighted for both and these are also shown graphically in figure 2. Screening levels (mg/L) at the 95% protection level were determined as 32 and 13 for freshwater and marine aquatic ecosystems respectively.

**Table 3 MTBE Screening levels for freshwater and marine ecosystems at various protection levels**

Aquatic Ecosystem	Protection level (%)	Screening level (mg/L)	Lower 95% CI	Upper 95% CI
Freshwater	99	23	14	40
	<b>95</b>	<b>32</b>	<b>23</b>	<b>47</b>
	90	38	30	52
	80	50	40	68
Marine	99	8.9	7.2	17
	<b>95</b>	<b>13</b>	<b>10</b>	<b>22</b>
	90	15	12	27
	80	21	15	35

## Incorporating bioaccumulation into the screening levels

Secondary poisoning can occur if contaminants accumulate from the ambient environment in the tissues of organisms (bioaccumulation) that are then consumed by other organisms and the concentration in tissue thereby increases up the food chain. In such a situation, the species at most risk are the species higher in the food web (the predators). Typically chemicals with log  $K_{ow}$  (octanol-water partition coefficient) or log BCF (bio concentration factor) values greater than 4 are considered to have the potential to accumulate. In the AWQG, if an SSD approach was used to derive a trigger value for contaminants that could potentially biomagnify, such values were derived at the higher (precautionary) 99% protection level (ANZECC & ARMCANZ 2000). The low octanol-water partitioning coefficient of MTBE ( $K_{ow} = 1.24$ ) indicates that it will not accumulate in human or animal fatty tissue and it is therefore not considered a biomagnifying compound. As biomagnification and secondary poisoning should only be addressed for contaminants that show biomagnification potential MTBE screening levels reported at normal protection levels (i.e. 95%) are deemed appropriate.

## Reliability of derived screening levels

In determining the reliability classifications to be applied to the freshwater and marine screening levels derived for MTBE using the SSD method, the following three parameters are assessed:

1. adequacy of sample size
2. data type i.e. order of preference is chronic, chronic and converted acute, acute only, and
3. adequacy of fit to data.

For derivation of both screening levels an adequate number of data points was used (>8) and the data type was a combination of chronic and converted acute values. In addition the adequacy of the fit of both SSD models was classified as good based on the well distributed representation of the data points along the fit model.

The recommendations to improving the assessment of the reliability of trigger values in the updated guidelines propose five reliability levels based on the three parameters above, namely very high, high, moderate, low and very low (Warne *et al* 2014a) (Warne *et al* 2014b). Based on the sample size, data type employed and the adequacy of fit for the respective SSD, both screening levels derived are considered as **moderate reliability** screening levels.

### Evaluating the appropriateness of the derived screening levels

In this study, moderate reliability screening levels (95% protection level) for freshwater and marine aquatic life have been determined at 32 and 13 mg/L respectively. The toxicity data collated in this study for both aquatic ecosystems demonstrated that MTBE has relatively low acute and chronic toxicity, with marine species generally showing a greater sensitivity. Toxicity values were determined to be several orders of magnitude higher than typical groundwater and surface water concentrations reported (Wong, et al., 2001), (Rausina *et al* 2002). The lowest acute and chronic value for freshwater species was 340 mg/L (2 day EC<sub>50</sub>, *C. dubia*) and 51 mg/L (21 day NOEC, *D. magna*) respectively. The lowest acute and chronic value for marine species was 141 mg/L (7 day LC<sub>50</sub>, *H. costata*) and 26 mg/L (28 day NOEC, *A. bahia*) respectively. In the AWQG, to determine if the 95% protection level failed to protect key species the following rules were applied:

1. The trigger value (TV) should not normally be within a 3-fold margin of an established acute LC<sub>50</sub> or EC<sub>50</sub>. This was regardless of whether the trigger value was a moderate (from acute data) or high reliability (from chronic data).
2. For a moderate reliability TV the value should not normally be above experimental chronic NOECs

In this study the screening levels for freshwater and marine were both >10-fold larger than their respective lowest acute values. Furthermore, both screening levels were below their respective lowest experimental NOECs. On this basis there is satisfactory confidence in the adequacy of the derived screening levels to be protective of their respective aquatic ecosystems.

Analytical detection methods are capable of detecting low parts per billion (ppb) levels of MTBE in fuel contaminated groundwater (US EPA 2003). MTBE concentrations over several orders of magnitude (from ppb to ppm concentrations) have been detected in US groundwater (USGS 1995). Whilst no verified reports could be located to confirm

actual values detected in Australia, concentrations of 6–7830 µg/L (ppb) sourced from a LinkedIn survey by the Australian Remediation Industry Cluster are stated in a recent CRC technical report (CRC CARE 2014a). The fact that the screening levels derived in this study are above the reported MTBE analytical detection levels and the highest (worst case) reported concentration of MTBE in Australian groundwater provides further assurance that these levels will provide adequate protection for key species.

As no Australian aquatic studies were identified in this research it was not possible to incorporate local studies or species into the screening level derivation. As typically there is a paucity of such studies, the AQWG (ANZECC & ARMCANZ 2000) and proposed revisions (Warne *et al* 2014a) do not therefore place any preference on the use of toxicity data from relevant Australia or New Zealand species.

For deriving some screening levels, toxicity is known to be dependent on other physical and chemical factors (e.g. metals and pH). Whilst it is possible that such properties or combination thereof may influence the toxicity of MTBE, no reports of any toxicity modifying factor for MTBE toxicity was reported in the literature.

As a final test of appropriateness, the derived screening levels were compared to other international water quality guidelines for MTBE (table 4). It should be noted that the US and European guidelines also report guidelines for acute exposure however as the AWQG (ANZECC & ARMCANZ 2000) and those derived in this study are reflective of chronic exposures, only the chronic values are used for comparative purposes. Overall it can be seen that the derived values of 32 and 13 mg/L are similar to those derived for other international jurisdictions.

**Table 4 Comparison of derived screening levels with International guidance values.**

	Australian Screening Level <sup>5</sup>	US Guidelines <sup>6</sup> (Mancini <i>et al</i> 2002)	Canada <sup>7</sup> (CCME 2007)	European Union (ECETOC 2003b)
Freshwater mg/L	<b>32</b>	51 (short term exposure) 151 (long term exposure)	10	2.6 <sup>8</sup>
Marine mg/L	<b>13</b>	18 (short term exposure) 53 (long term exposure)	5	

The derived screening levels fall between the Canadian values and those derived by the US EPA. The European PNEC was derived for aquatic life hence there was no differentiation between freshwater and marine ecosystems as with the other three values. The PNEC was derived by dividing the lowest chronic NOEC by an assessment factor of 10. The screening levels derived as part of the current study were the only ones derived using the SSD approach.

The National Water Quality Management Strategy and many of the underlying water quality guidelines (e.g. AWQG) are examples of international collaboration and harmonisation. Whilst different scientific methodologies and approaches were used to

<sup>5</sup> Levels derived in this study using SSD approach

<sup>6</sup> Calculated as a criterion continuous concentration (CCC) for chronic exposure

<sup>7</sup> This value was calculated by multiplying the most sensitive chronic endpoint by a safety factor of 0.1

<sup>8</sup> This is a predicted no effect concentration (PNEC) for continuous release (chronic) situations.

derive the values listed in table 4 above there are ongoing activities to increase international collaboration and harmonisation in application of the SSD approach including its application in European regulatory frameworks such as the Water Framework Directive and REACH (ECETOC 2014).

## References

Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC & ARMCANZ) 2000, *National water quality management strategy, Australian and New Zealand guidelines for fresh and marine water quality*. Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand.

American Petroleum Institute (API) 1999, *Early-life stage toxicity of methyl tertiary-butyl ether (MTBE) to the fathead minnow (Pimephales promelas) under flow-through test conditions*, ENSR Environmental Toxicology Laboratory for American Petroleum Institute.

Bay, SM & Brown, JS 2000, *Assessment of MTBE discharge impacts on California marine water quality*. Final report prepared for State Water Resources Control Board California. Agreement number 8-168-250-0, Southern California Coastal Water Research Project, Westminster, California, USA.

Campbell, E, Palmer, MJ, Shao, Q & Wilson, D 2000, 'BurliOZ: a computer program for the estimation of the trigger values for the ANZECC and ARMCANZ water quality guidelines', in *ANZECC & ARMCANZ National Water Quality Management Strategy*, Australian and New Zealand Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

Canadian Council of Ministers of the Environment (CCME) 2007, *A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life 2007*, Canadian Council of Ministers of the Environment (CCME), Winnipeg, Canada.

CRCCARE, 2014. *Environmental impact of priority contaminants: A literature review*. Technical report no. 29, Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

ECETOC 2003a, *Aquatic hazard assessment II*, ECETOC Technical Report 91, European Centre for Toxicology of Chemicals, Brussels, Belgium.

ECETOC 2003b, *Risk assessment report for existing substances methyl tertiary-butyl ether*, Special Report no. 17, European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, Belgium.

ECETOC 2014, *Estimating toxicity thresholds for aquatic ecological communities from sensitivity distributions*, ECETOC workshop report no. 28, European Centre for Ecotoxicology and Toxicology of Chemicals, Amsterdam, Brussels, Belgium, 11–13 February 2014.

European Commission 2002, *European Union risk assessment report tert-butyl methyl ether*, European Chemicals Bureau, Luxembourg.

Fox, DR, Billoir, E, Charles, S, Delignette-Muller, ML & Lopes, C 2012, 'What to do with NOECs/NOELS – prohibition or innovation?', *Integrated Environmental Assessment and Management*, vol. 8, iss. 4, pp. 764–766.

Gieger, DL, Call, DJ & Brooke, LT 1988, *Acute toxicities of organic chemicals to Fathead Minnows (Pimephales promelas)*, Center for Lake Superior Environmental Studies, University of Wisconsin, Superior, WI, USA.

Gupta, G & Lin, YJ 1995, 'Toxicity of methyl tertiary-butyl ether to *Daphnia magna* and *Photobacterium phosphoreum*', *Bulletin of Environmental Contamination and Toxicology*, vol. 55, pp. 618–620.

Hernando, MD, Ejerhoon, M, Fernandez-Alba, AR & Chisti, Y 2003, 'Combined toxicity effects of MTBE and pesticides measured with *Vibrio fischeri* and *Daphnia magna* bioassays', *Water Research*, vol. 37, pp. 4091–4098.

Hobbs, DA, Warne, MS & Markich, SJ 2005, 'Evaluation of criteria used to assess the quality of aquatic toxicity data', *Integrated Environmental Assessment and Management*, vol. 1, iss. 3, pp. 174–180.

Hockett, JR 1997, ENSR, Fort Collins, Colorado, USA [cited in Wong et al 2001 and ECETOC 2003b]:

*Acute toxicity of MTBE (methyl tertiary-butyl ether) to Daphnia magna under static-renewal test conditions*, Study 0480-378-003-001, NTIS Accession Number OTS0573643

*Acute Toxicity of MTBE (methyl tertiary-butyl ether) to Ceriodaphnia dubia under static-renewal test conditions*, Study 0480-378-007-001, NTIS Accession Number: OTS0573646

*Short-term sub-chronic toxicity of MTBE (methyl tertiary-butyl ether) to Ceriodaphnia dubia under static-renewal test conditions*, Study 0480-378-004-001, NTIS Accession Number OTS0573647

*Acute Toxicity of MTBE (methyl tertiary-butyl ether) to the fathead minnow (Pimphales promelas) under flow through test conditions*, Study 0480-378-001-001, NTIS Accession Number OTS0573648

*Acute Toxicity of MTBE (methyl tertiary-butyl ether) to the rainbow trout (Oncorhynchus mykiss) under flow through conditions*, Study 0480-378-002-001, NTIS Accession Number OTS0573644

Kado, NY, Kuzmicky, PA, Loarca-Pina, G & Mumtaz, MM 1998, 'Genotoxicity testing of MTBE in the Salmonella microsuspension assay and mouse bone marrow micronucleus test', *Mutation Research*, vol. 412, pp. 131–138.

Mancini, ER, Steen, A, Rausina, GA, Wong, DCL, Arnold, WR, Gostomski, FE, Davies, T, Hockett, JR, Stubblefield, WA, Drott, KR, Springer, TA & Errico, P 2002, 'MTBE ambient water quality criteria development: A public/private partnership', *Environmental Science and Technology*, vol. 36, pp. 125–132.

Moreels, D, Van Cauwenberghe, K, Debaere, B, Rurangwa, E, Vromant, N, Bastien, L, Diels, L, Springael, D, Merckx, R & Ollevier, F 2006, 'Long term exposure to environmentally relevant doses of methyl-tert-butyl ether causes significant reproductive dysfunction in the zebrafish (*Danio rerio*)', *Environmentally Toxicology and Chemistry*, vol. 25, pp. 2388–2393.

- Nadaffi, K, Nabizadeh, R & Baiggi, A 2008, 'Bioassay of methyl tertiary-butyl ether (MTBE) toxicity on rainbow trout fish', *Journal of Hazardous Materials*, vol. 154, pp. 403–406.
- NHMRC 2008, *National water quality management strategy, Guidelines for managing risk in recreational water*, National Health and Medical Research Council, Australia.
- OECD 2006, *OECD Guidelines for the Testing of Chemicals, Section 2. Summary of Considerations in the Report from the OECD Expert Group on Ecotoxicology, OECD Guidelines for the Testing of Chemicals, Section 2*, Organisation for Economic Cooperation and Development (OECD) Publishing, Paris, France.
- Rausina, GA, Wong, DC, Arnold, WR, Mancini, ER & Steen, AE 2002, 'Toxicity of methy tert-butyl ether to marine organisms: ambient water quality criteria calculation', *Chemosphere*, vol. 47, pp. 525–534.
- Roslev, P, Lentz, T & Hesselsoe, M 2015, 'Microbial toxicity of methyl tert-butyl ether (MTBE) determined with fluorescent and luminescent bioassays', *Chemosphere*, vol. 120, pp. 284–291.
- Rousch, JM & Sommerfeld, MR 1998, 'Liquid-gas partitioning of the gasoline oxygenate methyl tert-butyl ether (MTBE) under laboratory conditions and its effect on growth of selected algae', *Archives of Environmental Contamination and Toxicology*, vol. 34, pp. 6–11.
- Shao, Q 2000, 'Estimation for hazardous concentrations based on NOEC data: an alterntative aproach', *Environmetrics*, vol. 11, iss. 5, pp. 583–595.
- US EPA 1994, *AQUIRE (Aquatic toxicity information retrieval)*, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continental Ecology Division, Duluth, Minnesota, USA.
- US EPA 1999, *Water quality guidance for the Great Lakes system. Federal Register, 40 CFR Part 142, July 1.*, United States Environmental Protection Agency, Washington, DC, USA.
- US EPA 2003, *Underground storage tanks factsheet. Analytical methodologies for fuel oxygenates*, United States Environmental Protection Agency, Washington, DC, USA.
- US EPA 2015, *ECOTOX User guide: ECOTOXicology Database System*, version 4.0, accessed 30 April, 2015, <[www.epa.gov/ecotox/](http://www.epa.gov/ecotox/)>.
- USGS 1995, *A preliminary assessment of the occurence and possible sources of MTBE in groundwater of the United States, 1993-94*, U.S. Geological Survey Open-File Report 95-456, accessed 06 May, 2015, <[sd.water.usgs.gov/nawqa/pubs/ofr/ofr95.456/ofr.html](http://sd.water.usgs.gov/nawqa/pubs/ofr/ofr95.456/ofr.html)>.
- Veith, GD, Call, DJ & Brooke, LT 1983, 'Structure-toxicity relationships for the fathead minnow; *Pimephales promelas*: Narcotic industrial chemicals', *Canadian Journal of Fisheries and Aquatic Sciences*, vol. 40, pp. 743–748.
- Warne, MSJ & Westbury, AM 1999, 'A compilation of toxicity data for chemicals to Australasian species, part II: organic chemicals', *Australasian Journal of Ecotoxicology*, vol. 5, pp. 21–85.

Warne, MSJ 2001, 'Derivation of the ANZEEC and ARMCANZ water quality guidelines for toxicants', *Australasian Journal of Ecotoxicology*, vol. 7, pp. 123–136.

Warne, MSJ, Batley, GE, Braga, O, Chapman, JC, Fox, DR, Hickey, CW, Stauber, JL & Van Dam, R 2014a, 'Revisions to the derivation of the Australian and New Zealand guidelines for toxicants in fresh and marine waters', *Environmental Science and Pollution Research*, vol. 21, pp. 51–60.

Warne, MSJ, Batley, GE, Braga, O, Chapman, JC, Fox, DR, Hickey, CW, Stauber, JL & Van Dam, R 2014b, *The new method for calculating water quality guidelines for Australia and New Zealand*, poster presentation at SETAC Asia/Pacific 2014 Conference, SETAC Asia-Pacific.

Wong, DC, Arnold, WR, Rausina, GA, Mancini & Steen, AE 2001, 'Development of a freshwater aquatic toxicity database for ambient water quality for methyl tertiary-butyl ether MTBE', *Environmental Toxicology and Chemistry*, vol. 20, pp. 1125–1132.



**CRC CARE**

ATC Building  
University of Newcastle  
Callaghan NSW 2308  
Australia

**Postal**

C/- Newcastle University LPO  
PO Box 18  
Callaghan NSW 2308  
Australia

**Contact us**

**P:** +61 2 4985 4941  
**E:** admin@crccare.com

**[www.crccare.com](http://www.crccare.com)**



Australian Government  
Department of Industry,  
Innovation and Science

**Business**  
Cooperative Research  
Centres Programme