Position Paper on Petroleum Ether Oxygenate Use, Behaviour, And Risk Management In South Africa

By the NICOLA Petroleum Ether Oxygenate Working Group

Champion: Kirby Gimson

Working Group Members: Dipitseng Manamela, Ian Luden and Charles Mills

Reviewed by: Hayley Thomas, Takalani Telekisa and Mpho Mavhega

July 2024

INTRODUCTION

Petroleum ether oxygenates (EOs) are hydrocarbon compounds that contain one or more oxygen atoms and are commonly used as gasoline additives to improve combustion and decrease exhaust emissions. During a petroleum spill or release, EOs may enter the subsurface and contaminate soil and/or groundwater. EOs have become an important group of groundwater pollutants due to their physio-chemical properties (i.e. chemical structure, high water solubility, log Kow, Koc, low biodegradability, low taste and odour threshold). This has significance in South Africa due to the prevalent and growing use of groundwater resources.

The scope of this paper is focused on NICOLA's position for the assessment and management of impacts related to ether oxygenates from soil or groundwater sources. The objectives for this paper include:

- Provide an overview of existing knowledge about EOs, including the origins of EO components for petroleum blending, the distribution of EOs in fuels throughout South Africa (and by association, Africa since many other African countries generally follow standards and guidelines from South Africa), and the identification of EOs of key interest.
- Provide a brief overview of best practice for assessing EO contamination in the subsurface; and
- Provide a brief overview of assessing and managing potential risks from EOs.

SOURCES OF ETHER OXYGENATES

Oxygenates have been used to increase the volume and octane of petroleum. In the late 1970s and early 1980s, as lead was removed from petroleum, petroleum producers used oxygenates to offset the loss in octane from the removal of lead. Oxygenates have been used as an emission control strategy to reduce carbon monoxide (CO) and, to a lesser extent, hydrocarbon emissions from motor vehicles. Apart from ethanol, the most common oxygenate compounds used globally include: methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), tertiary butyl alcohol (TBA), ethyl tertiary butyl ether (ETBE), di-isopropyl ether (DIPE), and tertiary amyl ethyl ether (TAEE) (Loana G. Petrisor, 2006).

In South Africa, no mineral oil refinery has manufactured any EOs used for petroleum blending in the past, nor are any planning (at time of writing) to manufacture these in the future. This is predominantly due to the lack of ethanol supply in South Africa which is required in the manufacturing process. Secunda Synfuels Operations, a coal-based synthetic fuels manufacturing facility located in Secunda Mpumalanga, however commissioned a TAME plant (understood to be pre-2002), to make the component for petroleum blending. This product has been included in petroleum sold in the inland areas in South Africa (Baart, 2022).

SANS 1598 is the petrol standard that regulates the quality of fuel in South Africa. This standard limits the additions of ethers to 22% (v/v) for C5+ ethers for Clean Fuels and is also the limit that importers will use for imports if they allow for the use of ethers.

Currently around 70% of petrol is imported into South Africa, with most through the port of Durban. As a rule of thumb, petroleum companies have historically limited imports petrol containing MTBE due to the potential for it to enter groundwater due to spillages or leaks in the supply chain and its affects thereon. The logistics of petroleum distribution in South Africa are shared between various petroleum companies with the principle of interchangeability. Petroleum supplies in South Africa are therefore readily exchangeable across the supply system, subject to meeting the requirements of SANS 1598. The implication is that petroleum cannot be guaranteed as ether oxygenate free (Baart, 2022).

Historically the two EOs commonly understood to have been present (if at all), and therefore have the greatest relevance for soil and groundwater investigations/risk assessments, are MTBE and TAME. It is currently unknown whether other EOs such as DIPE and ETBE are present in imported fuels, or if they are added to fuels in South Africa. However, as a conservative approach, these compounds should be considered as potentially present and tested for when conducting a contaminated land assessment.

BEST PRACTICE FOR ASSESSING ETHER OXYGENATE CONTAMINATION

The best practice for assessing EO contaminations is a phased approach. The first phase is the physical characterization of the site – considering the topography of both the surface and the bedrock structure of the soil and the aquifer. The second phase is the characterization of the distribution of the contaminations using data from collected soil and groundwater samples. This phase must incorporate information gathered during the initial phase, such as groundwater flow direction and bedrock structures (e.g. fractures) that may influence the fate and transport, mobility, and spatial distribution of the EO contaminant plume. The final phase is the interpretation of all the information collected to define an integrated strategy for remediation of the site.

FATE & TRANSPORT OF ETHER OXYGENATES

The fate and transport of EOs is important to understand when assessing EO contamination. Each contaminant has certain physio-chemical properties and behaviours that must be understood to assess EO contamination, and to manage any identified potential risks to receptors from EO contamination. For example, EOs tend to be highly soluble and mobile in groundwater, highly volatile in the unsaturated zone (i.e. from a NAPL source), and moderately volatile in groundwater (i.e. from a dissolved phase source). These physio-chemical properties have been documented to typically result in dissolved phase EO plumes within groundwater. Additional information on each substance may be found through various sources (USEPA guidance, Technical Position Papers, EU risk assessment, etc).

BEST PRACTICE FOR ASSESSING POTENTIAL RISKS FROM ETHER OXYGENATE CONTAMINATION

It is important to determine whether the identified EO contamination could pose a significant risk to human health or the environment. Once this is determined, then specific information relevant to the potential risk must guide decisions on how best to manage risks posed by EO contamination. Potential risks can be identified by the source-pathway-receptor (S-P-R) concept, which assesses whether a particular receptor could be exposed to a source of contamination through a specified exposure or migration pathway.

RELEVANT PATHWAYS & ACCEPTABLE EXPOSURE CONCENTRATIONS

The key exposure pathways for ether oxygenates include human health (direct exposure from drinking water and vapour inhalation from impacted groundwater or soil), aesthetic (taste and odour in drinking water and odour from vapour intrusion from groundwater or soil) and ecological (impact to fresh water or marine environments).

Relevant acceptable exposure concentrations are available in the South African Framework for the Management of Contaminated Land (FMCL) which includes soil screening values (SSVs) for MTBE in soil. Additionally, the FMCL references guidelines that were used in the derivation of SSV1 (protection of water resource), including the World Health Organisation (WHO) guideline for MTBE, which represents the minimum value at which MTBE could be detected via odour in drinking water (15 µg/L). There are currently no promulgated ecological or human health risk screening criteria for contaminants in groundwater in South Africa, but where these have been calculated, they tend to be several orders of magnitude higher than those calculated for taste and odour pathways.

Acceptable exposure concentrations for TAME (*taste: 128 µg/L; odour: 194 µg/L*) are available in the European Union Risk Assessment Report (ECHA, 2006). Those for ETBE (*taste: 47 µg/L; odour: 49 µg/L*) are available in the Interagency Assessment of Oxygenated Fuels (NSTC, 1997), and those for DIPE (*taste: 15 µg/L; odour: 0.8 µg/L*) have been referenced in the Journal of Applied Toxicology (Amoore & Hautala, 1983).

Due to the low concentrations at which EOs can be detected via taste or odour in drinking water, the presence of EOs at concentrations which exceed these aesthetic exposure pathways are most likely to drive corrective action.

RISK MANAGEMENT

If potential risks to human health or the environment are posed by the ether oxygenate contamination, then action may be required to manage the identified risks.

Risk management actions may include remediation (treating the contamination at the source, e.g. within soil or groundwater) or risk mitigation (reducing the risk that the contamination poses to receptors by intercepting the pathway between a source and a receptor). For example, installing a granular activated carbon (GAC) filter on a groundwater abstraction borehole would treat the abstracted groundwater prior to its point of use, but would not necessarily treat the contamination at the source (within the subsurface). A non-remedial risk mitigation method may be adopted when remediation is impractical or not feasible, or as an interim measure where urgent action is required to manage a risk. A Remediation Alternatives Analysis (RAA) should be completed to select the most appropriate risk mitigation and/or remediation technology based on the known information (geology, hydrogeology, contaminant mass and distribution, and potential risks that need to be mitigated).

CONCLUSION

In summary, NICOLA's position is that ether oxygenate contamination and the associated risks should be considered when conducting site assessments associated with petroleum fuel releases. The information contained herein is intended to provide contaminated land specialists in Africa with an overview of some of the key factors to consider when assessing ether oxygenate contamination. This paper is not a technical guidance document, and technical considerations must be taken into account during an assessment by consulting with technical experts and other technical guidance documents associated with ether oxygenates. It is necessary that the investigations of both the potential health effects and the environmental occurrence of ether oxygenates, and some oxygenates continues.

AUTHORS AND CONTRIBUTORS

Kirby Gimson (ERM)

Dipitseng Manamela (Dihlashana Consulting)

Ian Luden (SRK)

Charles Mills (Mills and Otten)

Hayley Thomas (Shell) (Review)

Takalani Telekisa (DFFE) (Review)

Mpho Mavhega (DFFE) (Review)

REFERENCES

Amoore, J.E. and Hautala, E. (1983). *Odor as an Ald to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution*. Journal of Applied Toxicology, 3, 272-290.

ASTM International Inc. (2013). ASTM E2876-13. *Standard guide for integrating sustainable objectives into cleanup. West Conshohocken*, PA: ASTM International.

Baart, K. (2022). *South African Petroleum Industry Association (SAPIA)*, email correspondence: NICOLA Ether Oxygenate Position Paper.

Department of Environmental Affairs, Republic of South Africa, (2010). Framework for the Management of Contaminated Land.

European Chemicals Agency (ECHA). (2006). European Union Risk Assessment Report: 2-methoxy-2-methylbutane (TAME).

Gomez, J., Brasil, T. and Chan, N. (1998). *An Overview of the Use of Oxygenates in Gasoline, California Environmental Protection Agency*, California Air Resource Board Stationary Source Division.

Kool, T. (2020). *The Complete Guide to Oxygenates*, https://oilprice.com/Energy/Energy-General/The-Complete-Guide-To-Oxygenates.html.

Loana G. Petrisor. (2006). *Use of Oxygenates to Date a Gasoline Release, Environmental Forensics*. 7:2, 103-104, DOI: 10.1080/15275920600667088.

National Science and Technology Council (NSTC). (1997). Interagency Assessment of Oxygenated Fuels.

World Health Organisation. (2022). Guidelines for drinking-water quality, fourth edition incorporating the first and second addenda (ISBN 978-92-4-004506-4).