Journal of Hazardous Materials 332 (2017) 10–18

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Vapor intrusion risk of fuel ether oxygenates methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME) and ethyl *tert*-butyl ether (ETBE): A modeling study

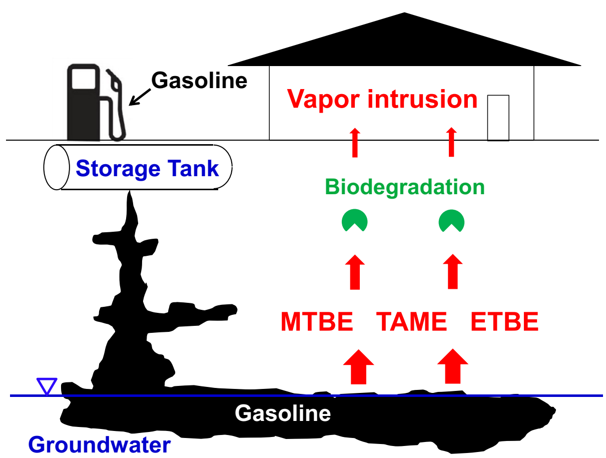
Jie Ma[a,b,*], Desen Xiong[a], Haiyan Li[a], Yi Ding[a], Xiangcheng Xia[a], Yongqi Yang[a]

[a] State Key Laboratory of Heavy Oil Processing, Beijing Key Lab of Oil & Gas Pollution Control, China University of Petroleum-Beijing, Beijing 102249, China
[b] State Key Laboratory of Petroleum Pollution Control, China University of Petroleum-Beijing, Beijing 102249, China

HIGHLIGHTS

- MTBE, TAME and ETBE can cause vapor intrusion problem.
- Ether oxygenate vapor intrusion may cause aesthetic problem (odour).
- EPA screening criteria for hydrocarbon is not applicable for ether oxygenates.
- A set of site-specific attenuation factors of MTBE, TAME, and ETBE are provided.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 November 2016
Received in revised form 13 February 2017
Accepted 26 February 2017
Available online 28 February 2017

Keywords:
Vapor intrusion
Mathematical model
Simulation
Odour
Fuel oxygenates

ABSTRACT

Vapor intrusion of synthetic fuel additives represents a critical yet still neglected problem at sites contaminated by petroleum fuel releases. This study used an advanced numerical model to investigate the vapor intrusion potential of fuel ether oxygenates methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and ethyl *tert*-butyl ether (ETBE). Simulated indoor air concentration of these compounds can exceed USEPA indoor air screening level for MTBE (110 $\mu g/m^3$). Our results also reveal that MTBE has much higher chance to cause vapor intrusion problems than TAME and ETBE. This study supports the statements made by USEPA in the Petroleum Vapor Intrusion (PVI) Guidance that the vertical screening criteria for petroleum hydrocarbons may not provide sufficient protectiveness for fuel additives, and ether oxygenates in particular. In addition to adverse impacts on human health, ether oxygenate vapor intrusion may also cause aesthetic problems (*i.e.*, odour and flavour). Overall, this study points

Abbreviations: PHCs, petroleum hydrocarbons; MTBE, methyl *tert*-butyl ether; TAME, tert-amyl methyl ether; ETBE, ethyl *tert*-butyl ether; PVI, petroleum vapor intrusion; UST, underground storage tank; VI, vapor intrusion; USEPA, United States Environmental Protection Agency; 3-D, three-dimensional; EDB, ethylene dibromide; DCA, 1,2-dichloroethane; RfD/RfC, Reference Dose/Concentration; ADI, Acceptable Daily Intake; MRL, Minimal Risk Level; VOC, volatile organic compounds; LNAPL, light non-aqueous phase liquid.

* Corresponding author at: State Key Laboratory of Heavy Oil Processing, Beijing Key Lab of Oil & Gas Pollution Control, China University of Petroleum-Beijing, Beijing 102249, China.
E-mail address: rubpmj@sina.com (J. Ma).

http://dx.doi.org/10.1016/j.jhazmat.2017.02.057

out that ether oxygenates can cause vapor intrusion problems. We recommend that USEPA consider including the field measurement data of synthetic fuel additives in the existing PVI database and possibly revising the PVI Guidance as necessary.

1. Introduction

Vapor intrusion risk at contaminated sites has received significant increased attention in recent years. Petroleum hydrocarbons (PHCs), such as benzene, toluene, ethylbenzene, and xylene (BTEX), are primary compounds of concern at petroleum vapor intrusion (PVI) sites [1–12]. However, PHCs are not the only compounds that may pose vapor intrusion threats to human health at PVI site. Fuel contains both PHCs and various non-PHC fuel additives. Current understanding of vapor intrusion risk of non-PHC fuel additives is still very limited. Ma et al. and Sihota et al. assessed the vapor intrusion risk of fuel ethanol [13–15]. Ma et al. investigated the vapor intrusion process of lead scavengers ethylene dibromide (EDB) and 1,2-dichloroethane (DCA) [16]. To our best knowledge, the vapor intrusion potential of fuel ether oxygenates received little attention by previous studies.

Ether oxygenates such as methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and ethyl *tert*-butyl ether (ETBE) are blended with gasoline to increase octane rating and decrease exhaust emissions. The USA produced 8.8 million tons of MTBE alone in1998, although production declined after 2000 [17]. MTBE is currently the most widely used oxygenate in many Asian countries such as China. Since 1997 MTBE has been used as a substitute for tetraethyl lead in unleaded gasoline in China. In 2015, China consumed 7.3 million tons of MTBE in gasoline for on road use and the average MTBE blending ration in Chinese gasoline was 6.08%. In Europe, MTBE is progressively being replaced by ETBE and TAME as a result of European Biofuels Directive 2003/30/EC and 2009/28/EC. In 2011, Europe consumed 3 million tons of ETBE [18]. TAME is primarily used in Finland and Italy and also in other European countries and in the USA [19,20].

Contamination of the soil and groundwater environments by ether oxygenates is a worldwide environmental problem. MTBE leakage has resulted in more than 250,000 contaminated sites in the United States alone [21]. The US Geological Survey reported that MTBE was one of the most frequently detected volatile organic compounds in groundwater [22]. Since 1990s, ether oxygenates were also detected in groundwater and surface water in many European countries [23] and more recently have been found in groundwater of China [24]. Although MTBE has been banned in the USA and may be phased out in other countries, it is found to persist in many subsurface environments for a long time due to its recalcitrance to biodegradation. As volatile compounds, ether oxygenates may cause vapor intrusion problems.

In 2015, the U.S. Environmental Protection Agency (USEPA) released a technical guidance for addressing petroleum vapor intrusion (PVI) at leaking underground storage tank (UST) sites [1]. In this guidance, USEPA established screening distance criteria for petroleum hydrocarbon (PHC) based on compiling field-measured data in the USEPA PVI database [1]. However, non-PHC ether oxygenates are neither included in the USEPA PVI database nor part of the EPA recommended screening criteria, despite the possibility of the coexistence of high level of ether oxygenates at UST sites [21]. Non-PHC ether oxygenates are not included in the USEPA PVI database since individual states do not routinely monitor these chemicals. Therefore, as it is acknowledged in USEPA PVI Guidance (Section 10), the separation distance criteria can not be used for non-PHC constituents [1]. More peer reviewed studies are required to improve our understanding on the use of screening distances for ether oxygenates.

In addition to adverse impacts on human health, ether oxygenates exhibit an unpleasant odor for which the human olfactory system is highly sensitive [25]. Odour and flavour thresholds of MTBE, TAME and ETBE are usually lower than other volatile groundwater contaminants [25]. Impacts of MTBE contamination on drinking water aesthetic quality (odour) are well recognized [25,26]. However, to our best knowledge, the aesthetic impact from ether oxygenates vapor intrusion process has not been assessed.

This study used an advanced three-dimensional (3-D) numerical model to simulate the process of subsurface migration and vapor intrusion into indoor air of MTBE, TAME, and ETBE under different site conditions. The aesthetic impact associated with ether oxygenates vapor intrusion and the applicability of current USEPA screening distance methods for ether oxygenates were assessed.

2. Methodology

2.1. Physico-chemical properties of ether oxygenates

Table S1 in the Supplementary Data shows the physico-chemical properties of MTBE, TAME and ETBE. For comparison, the properties of representative groundwater contaminants including benzene, trichloroethylene (TCE), 1,2-dibromoethane (EDB) and 1,2-dichloroethane (DCA) are also provided in Table S1. Among the chemicals listed in Table S1, MTBE has the highest water solubility and the lowest octanol-water (K_{ow}) and soil organic carbon-water partition coefficients (K_{oc}), thus MTBE would be very mobile in groundwater with low adsorption by soil organic matter and low retardation by the soil matrix. Compared to MTBE, both TAME and ETBE have lower water solubility and higher K_{ow} and K_{oc}. Compared to benzene, MTBE has a higher vapor pressure and thus will volatilize more easily from the non-aqueous phase liquid (NAPL) source [27]. Compared to benzene, MTBE has lower Henry's law constant and thus will be less volatile from groundwater source. The Henry's law constants of TAME and ETBE are five and four times higher than that for MTBE respectively, indicating TAME and ETBE are more volatile from contaminated groundwater than MTBE.

2.2. Toxicity of ether oxygenates

The acute and chronic toxicity of MTBE has been extensively investigated. Exposure to high level of MTBE-containing fuel can cause headache, nausea, cough, dizziness, eye irritation, and dyspnea [24]. However, the potential carcinogenic effect of MTBE on humans remains a matter of debate [28]. MTBE has been found to be mutagenic to animals [29]. Nevertheless, the International Agency for Research on Cancer (IARC) has categorized MTBE in Group3 ("not classifiable as to its carcinogenicity to humans") [30]. USEPA established a drinking water advisory for MTBE based on taste and odour criteria at the level of 20–40 μg/L which is much higher than that of benzene/TCE/1,2-DCA (5 μg/L) and EDB (0.05 μg/L). The WHO has not established a health-based guideline value for MTBE in drinking water because any guideline value based on adverse