Environmental problems of gasoline oxygenated additives (ETBE, MTBE)

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Gasoline oxygenated additives such as ethyl tert-butyl ether (ETBE), methyl tert-butyl ether (MTBE), teramil methyl ether (TAME) and diisopropyl ether (DIPE) are oxygen-rich chemicals synthesized from raw materials. raw materials such as methanol, bioethanol and isobutylene.

These additives are added to unleaded gasoline to increase the fuel octane grade, improve combustion efficiency and reduce emissions of carbon monoxide, ozone, nitrogen oxides in combustion vehicles. Historically (before 2000) MTBE was the most widely used ether oxygenate in North America and much of Europe. However, currently the most common ether oxygenate in different European countries is ETBE ($(CH_3)3C O–CH_2CH_3$). The market share of ETBE in European production of oxygenated ethers has grown from 15% in 2002 to 60% in 2010. ETBE production in 2020 exceeds 3 million tonnes and is expected to grow by 4% annually (Merchant Research and Consulting Ltd, 2020).

The widespread use of ether oxygenate has led to their increased presence as contaminants in soil, surface water bodies, and groundwater. In the case of MTBE, due to the high concentrations originally used in reformulated fuels in North America, it has generated large plumes of this contaminant in some aquifers. This is not the case with ETBE plumes, which tend to be much smaller, mainly due to the lower solubility of ETBE in water and the proportion used in gasoline.

Contamination of groundwater with oxygenated ether renders the water unsuitable for drinking due to its low taste and odor thresholds, which range between 2 µg L^{-1} and 1 µg L^{-1}. The final fate of ETBE in contaminated soils and groundwater is determined by the microbial degradation capacity present in the subsoil. ETBE is now more likely to be released into groundwater as the sole ether oxygenate in fuel formulations, as opposed to historically when mixed ether oxygenate, for example MTBE and TAME, were used. Compared to MTBE, the scientific literature on the biodegradation of ETBE in soils and groundwater is relatively limited and is mainly based on laboratory tests with few field studies. However, it appears that the behavior of ETBE in groundwater is very similar to that of MTBE, despite the differences in its physical and chemical properties. To date, a relatively restricted range of microorganisms have been identified with the ability to degrade ETBE aerobically as a source of carbon and energy, or through cometabolism using alkanes as growth substrates.

These microorganisms can degrade ETBE aerobically through a common pathway with MTBE and TAME, using similar genes and enzymatic systems, but giving rise to different intermediate compounds, depending on their specific structure.

It is unknown the reason why ETBE presents low rates of microbial growth and cellular yield when it is used as a carbon source. The microorganisms and pathways that facilitate anaerobic biodegradation of ETBE have not yet been elucidated, although very limited studies suggest that anaerobic biodegradation may occur under mixed redox conditions. **Based on our experience, bioaugmentation** (addition of exogenous ETBE-degrading microorganisms), **is considered the most suitable alternative for the treatment of ETBE.** Studies related to the limitation in the treatment of ETBE through the application of different oxidizing agents, such as sodium persulfate or sodium percarbonate in in-situ chemical oxidation projects, and also the low biodegradation rates of ETBE by indigenous microorganisms in processes of biostimulation also supports our opinion.

Following this line of work, **Envirotecnics is developing an ETBE and TBA degrading inoculum to be used in bioaugmentation projects in sites contaminated with gasoline and in particular with ETBE.** The project includes the following milestones:

1. Sequential microbial enrichment process that degrades ETBE and TBA.
2. Isolation and cultivation of pure strains that degrade ETBE and TBA.
3. Study of the degrading capacity of the strains and the consortium.
4. Taxonomic identification through complete 16s RNA sequencing of the 4 selected strains.

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Information adapted from “Biodegradation and fate of ethyl tert-butyl ether (ETBE) in soil and groundwater: a review”. S.F. Thornton, H.C.G. Nicholls, S.A. Rolfe, H.E.H. Mallinson, M.J. Spencer. J. Hazard. Mater., 391 (2020).

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TECHNICAL TEAM

Envirotecnics has technical team specialized in bioremediation, soil washing and in situ chemical oxidation (ISCO) projects that ensure the correct application of reagents in industrial sites and petrol stations as well as the environmental monitoring of remediation and/or decontamination.

Our projects

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