Biodegradation of MTBE

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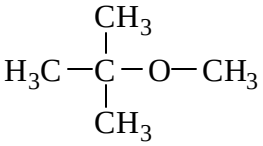
Methyl *tertyl*-butyl ether (MTBE) and similar compounds (such as ethyl ter-butyl ether, tert-amyl methyl ether) are used to reduce atmospheric emissions of carbon monoxide and volatile organics. More than 30% of all gasoline in the US contains these oxygenated compounds, the most common of which is MTBE, at up to 15% by volume [1,2].



MTBE

24 billion lb of MTBE produced in the US in 1993, the second largest chemical production.

Its widespread use and the continuing problem of leaking underground storage tanks, as resulted in MTBE becoming the second most common contaminant of urban groundwaters. [2,3]. Starting in 1992 with reports of illnesses associated with exposure to MTBE in Alaska and Connecticut, concerns of possible health effects of MTBE have increased. MTBE has a relatively high aqueous solubility and low adsorption to aquifer solids compared to gasoline hydrocarbons, especially BTEX. Thus, MTBE moves faster than BTEX in groundwaters, often presenting a threat to receptors. For example, [4]:

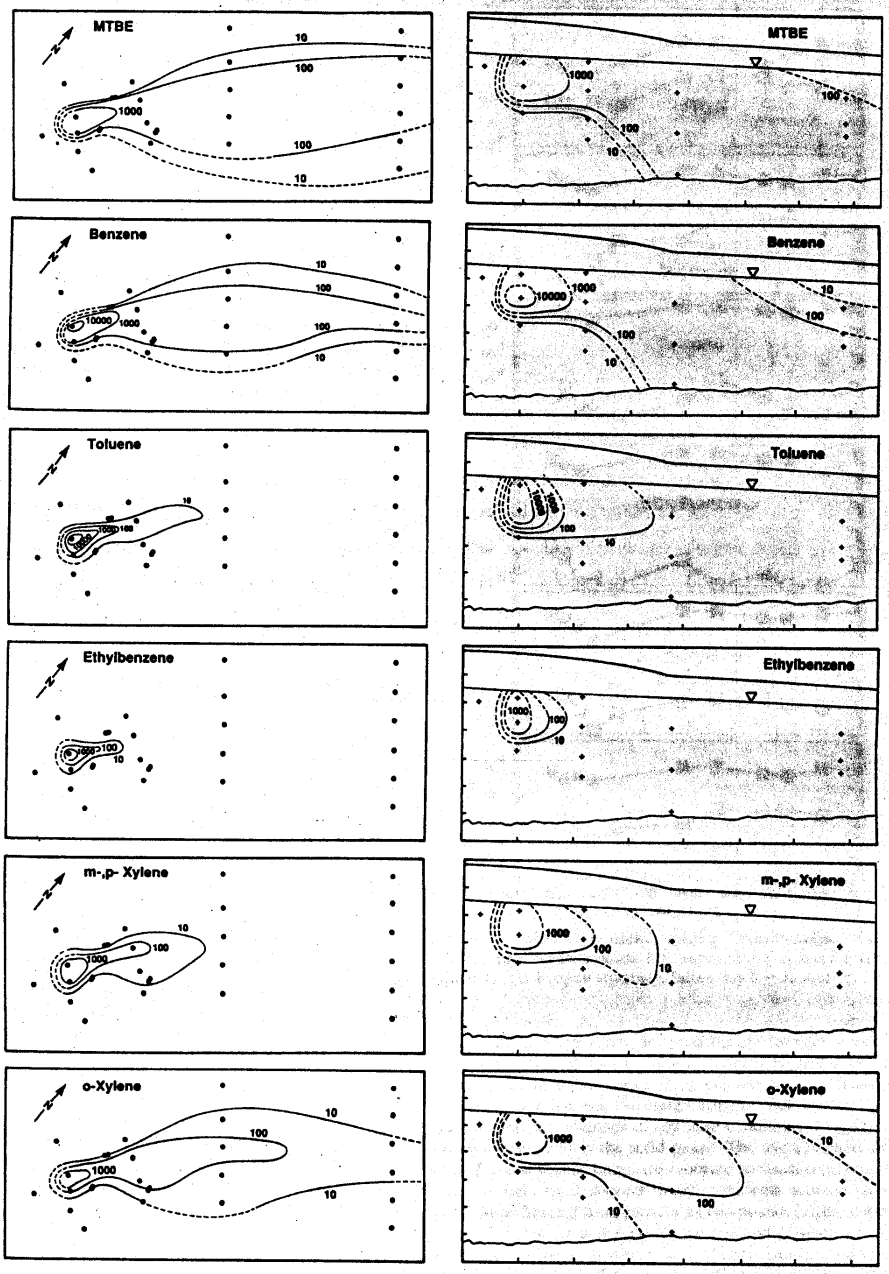
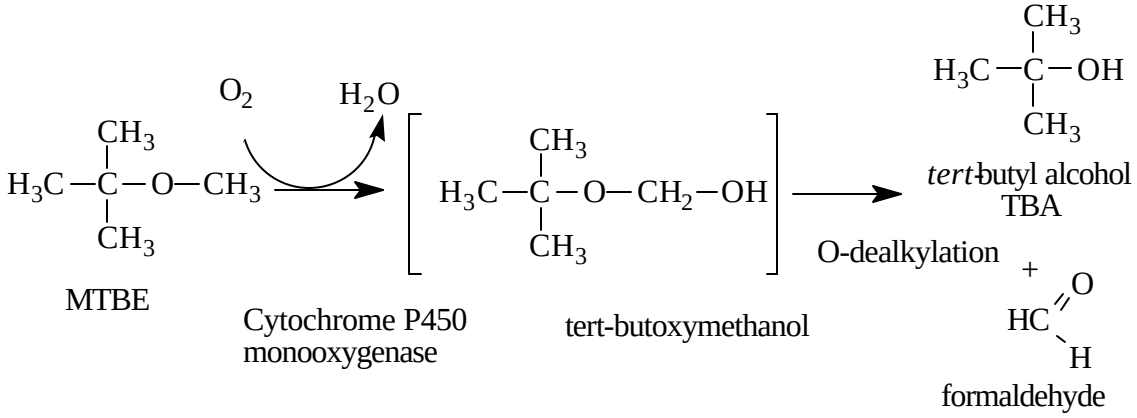


Figure 3. Plan views and cross sections of the MTBE, benzene, toluene, ethylbenzene, m-, p-xylene, and o-xylene plumes (April 1995). Concentrations are in micrograms per liter.

Furthermore, like many compounds with C-O-C bonds, MTBE appears to be somewhat recalcitrant in most groundwater environments, degrading slower than the BTEX compounds. For example, only 15-65% of added MTBE was mineralized under aerobic conditions in 50 days by diverse sediments.[5]

Early reports found little or no anaerobic degradation of MTBE [6,7], but recent studies suggest a slow mineralization under denitrifying conditions (about 20% in 80 days).[8] MTBE may be rapidly degraded when anaerobic groundwater becomes oxygenated.[9,10]. There are frequent reports of inhibition of MTBE degradation by presence of other organics. Degradation of MTBE is often incomplete, possibly due to metabolic use of only part of the molecule [11]. Aerobic consortia are able to completely degrade MTBE [12,13].

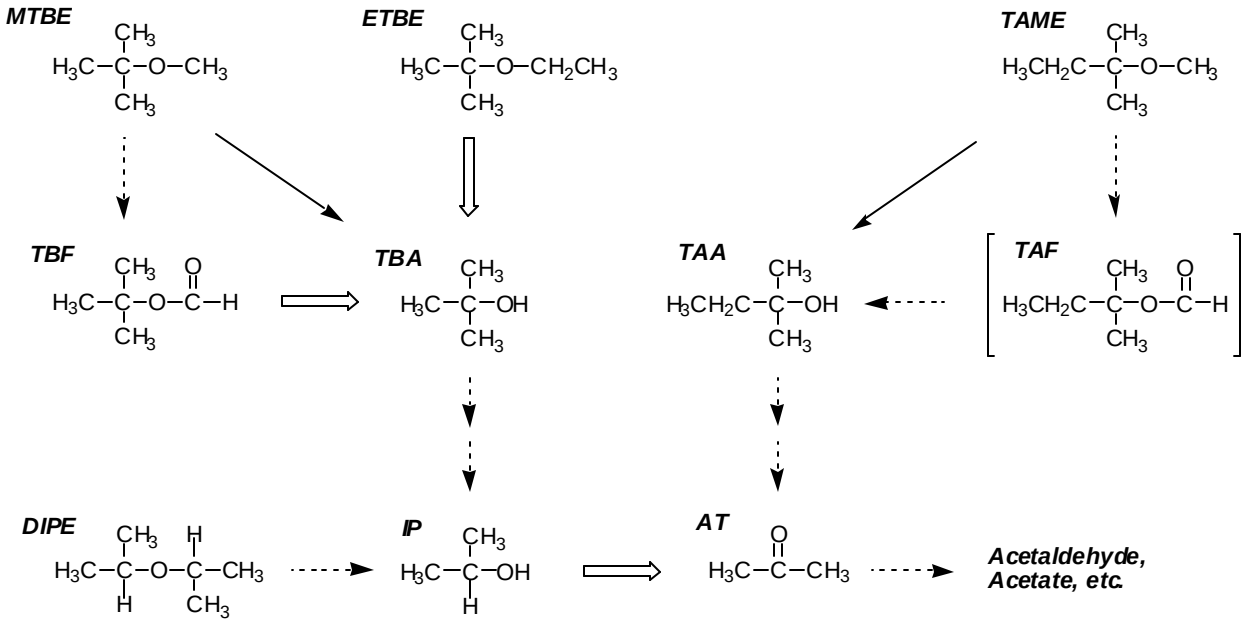
All known MTBE degradation involves oxidation by monooxygenase enzymes, for example, cytochrome P450s:



TBA is often observed in the environment [12], and is a sign of the degradation of MTBE since TBA accumulates transiently. TBA is also a common metabolite of mammalian metabolism of MTBE (by cytochrome P450). TBA's further degradation may also involve cytochrome P450 [2]. Bacterial and fungal degradation of MTBE appears to be most commonly cometabolic,

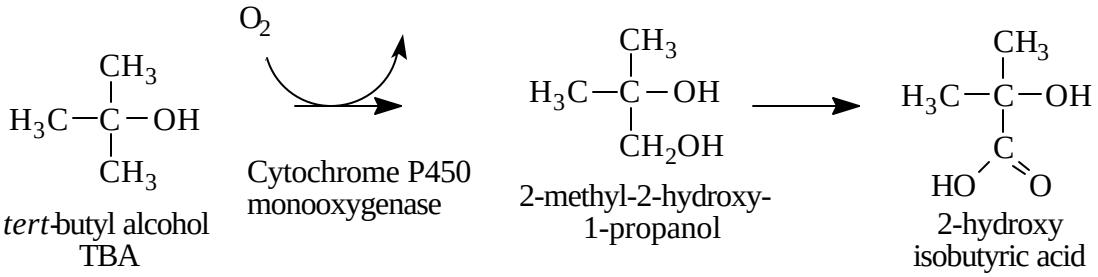
requiring the presence or induction by growth substrates, such as propanol or diethyl ether. Alkanes, especially pentane, have also been reported to support the cometabolism of MTBE.[14]

A bacterium capable of aerobic growth on MTBE as sole source of carbon and energy has been isolated [15], probably a new member of the Leptothrix group.[16] Its pathway for MTBE degradation is shown here:



Pathways for complete biodegradation of MTBE and three other gasoline oxygenates (ETBE, TAME, and DIPE) by an isolate designated PM1 [17]

Propanotrophic bacteria are reported to degrade MTBE cometabolically, by action of a cytochrome P450 [2]. Up to 60% of MTBE was mineralized in 25 hr by one strain. Either propane or 2-propanol could be used as a growth substrate. Degradation proceeded through TBA to 2-methyl-2-hydroxy-1-propanol to 2-hydroxy isobutyric acid.



tert-butyl alcohol
TBA

Further degradation of the isobutyric acid was slow.

A diethyl ether degrading fungus, *Graphium* sp strain ATCC 58400, one of the few eukaryotes known to degrade gaseous alkanes, can cometabolize MTBE. The initial attack is by cytochrome P450 activity, with formation of *tert*-butyl formate prior to the appearance of TBA.

Ethanol is likely to replace MTBE as an oxygenate in gasolines. Although ethanol degrades readily under aerobic and anaerobic conditions, two caveats suggest problems may arise from spills of fuels containing ethanol: ethanol increases the solubility of BTEX and ethanol degradation is likely to deplete oxygen rapidly before significant BTEX degradation occurs.[18]

References

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