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FACT SHEET

Update on Emerging Contaminants: **Fuel and Fuel Additives**

Environmental Contaminant Treatment

The fuels that propel modern society have been found in water supplies all over the world. Examples of fuel-related contaminants include the fuel oxygenates methyl tertiary-butyl ether (MTBE) and ethyl tertiary-butyl ether (ETBE), gasoline components including benzene, toluene, ethylbenzene, and xylene (BTEX) and the propellant hydrazine. Some or all of these fuel constituents can be found at a majority of the United States Environmental Protection Agency's (USEPA) National Priority List Sites.

FUEL OXYGENATES

Fuel oxygenates help gasoline burn more completely, reducing emissions of carbon monoxide and ozone from automobiles. Oxygenates were first used in 1979 when MTBE began to replace lead in gasoline as an octane enhancer. Their use increased in 1990 with the passage of the Clean Air Act (CAA), which mandated the use of oxygenates in fuels in areas where automotive emissions significantly impacted air quality. Oxygenated fuels containing up to 15% MTBE were introduced. Of the several oxygenates available, MTBE was the most widely used due to its low price and wide availability. State mandates requiring the use of oxygenates resulted in widespread distribution of MTBE throughout the United States.
It has also been used in Europe. Production of MTBE rose to as high as fourth in the list of manufactured organic compounds in the U.S., with 220,000 barrels per day being produced in 1999. According to the USEPA, several states including California, Colorado and New York have implemented a complete ban on the use of MTBE in gasoline.

CHEMICAL PROPERTIES OF MTBE

CHEMICAL NAME:	Methyl tertiary-Butyl Ether (MTBE)
CHEMICAL FORMULA:	$C_5H_{12}O$
MOLECULAR WEIGHT:	88.15
VAPOR PRESSURE:	245 mm Hg at 25 °C
HENRY'S LAW CONSTANT:	0.587 L-atm/mol at 25 °C
SOLUBILITY IN WATER:	43,000-50,000 mg/L

MTBE is a semi-volatile, chemically unreactive molecule that has a distinct, unpleasant odor. It is highly soluble in water, sorbs poorly to soil grains, and has a low volatility. This combination of properties makes MTBE very persistent and mobile in groundwater, allowing it to travel farther and faster than other gasoline components. MTBE enters the environment through several routes, including leakage from underground storage tanks, accidental spills of fuels, and releases from recreational vehicles in reservoirs.

TOXICITY AND REGULATION OF MTBE

In laboratory tests on animals, MTBE has produced cancer at high levels of exposure. Routes of human exposure include breathing of gasoline fumes, touching of skin by gasoline, or drinking or showering in water contaminated with MTBE. It has been designated a possible human carcinogen by the USEPA. The USEPA has set non-enforceable drinking water advisory levels for MTBE of 20 parts per billion (ppb) based on odor and 40 ppb based on taste. MTBE is listed on the USEPA's Contaminant Candidate List (CCL3) and in the Unregulated Contaminant Monitoring Rule (UCMR). California has set a primary maximum concentration level (MCL) of 13 ppb and a secondary (customer acceptance level) MCL of 5 ppb. Many other states have set drinking water regulations for MTBE (see table below).

MTBE REGULATIONS IN SELECTED U.S. STATES

STATE	LIMIT (ppb)
California	13 µg/L
Colorado	15 µg/L
Florida	20 µg/L
Maine	35 µg/L
Maryland	20 µg/L
New Hampshire	13 µg/L
New Jersey	70 µg/L
New York	10 µg/L
Oregon	13 µg/L
Pennsylvania	20 µg/L
Rhode Island	40 µg/L
Vermont	40 µg/L

BTEX COMPOUNDS – CHEMICAL PROPERTIES, USES, AND REGULATIONS

Benzene, toluene, ethylbenzene, and xylenes, commonly known as BTEX, are found naturally in petroleum, and are extracted for commercial use. Benzene (C6H5) is the parent compound for a group of organic chemicals known as aromatic hydrocarbons. Many commonly used products: plastic, nylon, resins, pesticides, rubber, and many detergents, contain an aromatic chemical structure.

TROJAN UV

FACT SHEET

From various toxicological studies, the USEPA has determined that benzene is a human carcinogen. Included also in this group of aromatics are toluene, C6H5(CH3), and xylenes C6H4(CH3)2. Toluene is found in varnishes, paint products and adhesives, while xylenes are used as solvents, in printing processes, and as paint thinners. Lastly, ethylbenzene (C8H10) is used in the production of other chemicals (mainly styrene), and can be found in products such as insecticides, inks, and paints. Large amounts of each of these four compounds are produced every year around the world. USEPA regulatory standards in drinking water for BTEX compounds are listed in the table, top right. One or more BTEX compounds have been detected in roughly half of the 1430 National Priority List contamination sites in the U.S. Because of their presence in gasoline, frequently groundwater contaminated with MTBE is also contaminated with BTEX.

U.S. MCL'S FOR BTEX

CHEMICAL	USEPA MCL (ppb)
Benzene	5
Toluene	1,000
Ethylbenzene	700
Xylene	10,000

HYDRAZINES

The term "hydrazines" encompasses a group of versatile and widely-used compounds that contain two nitrogen atoms joined by a single covalent bond. Included in this group are hydrazine, 1,1-dimethylhydrazine (also known as unsymmetrical dimethylhydrazine or UDMH), monomethylhydrazine (MMH), and 1,2-dimethylhydrazine (also known as symmetrical dimethylhydrazine). Hydrazine was first isolated in 1887 but was not developed for use until World War II. Hydrazines are clear, colorless liquids that are highly reactive and highly flammable. Hydrazine, UDMH and MMH are among the highest performing storable liquid rocket fuels. Apart from their use as rocket propellants, the applications of hydrazine include (Powell, 1968):

- Medicinal (pharmaceuticals, antibacterial compounds and antihistamines)
- Agricultural (herbicides and growth regulators)
- Metals manufacturing (metal plating of glass and plastics, anti-tarnishing agent)
- Chemical processing (Chlorine scavenger, polymeric inhibitor)
- Soaps and Detergents
- Energy (fuel cells, boiler feed water treatment)

1,1-dimethylhydrazine has also been implicated in the formation of another potential carcinogen and environmental contaminant, N-nitrosodimethylamine (NDMA), a compound formed from precursor chemicals and chlorine/chloramine in water treatment facilities. Based on research studies on animals, hydrazine compounds have been classified by the USEPA as probable human carcinogens. Another government branch, the U.S. Department of Health and Human Services, has determined that hydrazine and 1,1-dimethylhydrazine are known human carcinogens.

CHEMICAL PROPERTIES OF HYDRAZINES

CHEMICAL NAME:	Hydrazine
CHEMICAL FORMULA:	NH_2NH_2
MOLECULAR WEIGHT:	32.05
VAPOR PRESSURE:	14.38 mm Hg at 25 ºC
HENRY'S LAW CONSTANT:	6.1x10-4 L-atm/mole
SOLUBILITY IN WATER:	miscible

TREATMENT ALTERNATIVES – ULTRAVIOLET (UV) LIGHT

MTBE is readily oxidized (Kommineni et al, 2002) and can be cost-effectively treated by Trojan Technologies' UV- oxidation Systems. Other treatment technologies are less effective. Due to its mild affinity for carbon, adsorption methods require long contact times and large amounts of carbon, making it infeasible for many treatment scenarios. In addition, MTBE's relatively low Henry's Law coefficient makes air stripping difficult. Large air-to-water ratios are required and off-gas treatment may also be required, depending on the site location. Similar problems arise in the treatment of ETBE. However, UV-oxidation using UV and hydrogen peroxide to generate hydroxyl radicals is effective at breaking down these fuel additives.

BTEX compounds and hydrazine are also easily treated with Trojan's UV-oxidation systems. These compounds can be treated cost-effectively with UV in a variety of applications, including groundwater remediation, drinking water treatment, and industrial water treatment. When BTEX compounds are present in combination with other more difficult-to-treat contaminants (such as 1,4-dioxane or NDMA), a Trojan UV-oxidation system will treat both simultaneously.

TROJANUV – TREATING MULTIPLE CONTAMINANTS WITH ONE UV SYSTEM

As a further benefit of Trojan UV-based processes for fuel and fuel additives treatment, due to reactions initiated by the hydroxyl radical, the water is also treated for many other dissolved organic contaminants potentially present in the water, including endocrine disruptor chemicals, NDMA, 1,4-dioxane, and pesticides.

Trojan offers the industry standard in Environmental Contaminant Treatment (ECT). Trojan's UV-photolysis and UV-oxidation systems are capable of cost-effectively breaking down environmental contaminants such as MTBE, pesticides, NDMA, endocrine disruptors, 1,4-dioxane, and taste and odor-causing compounds from a variety of water streams. With its optimized technology, Trojan is the leader in ECT, offering the most cost-effective, highest quality UV solutions available. For more information on treating multiple contaminants with Trojan's UV solutions, including fuel and fuel additives treatment, please contact Trojan Technologies.

References:

Powell, R. 1968. Hydrazine Manufacturing Processes. Noyes, Park Ridge; Kommineni, S. N., Z. Chowdhury, J. Croue, and N. Corin. 2002. MTBE; Removal Using UV/Peroxide Oxidation – Pilot Study Results. Design Considerations, and Treatment Costs, in Proceedings of the AWWA Annual Conference, New Orleans. June 16-20, 2002.

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