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# Research and Development

## DRINKING WATER HEALTH ADVISORY FOR 1,2,4-TRIMETHYLBENZENE

## Prepared for

OFFICE OF DRINKING WATER

## Prepared by

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DRAFT: DO NOT CITE OR QUOTE

NOTICE

DISCLAIMER

This report is an external draft for review purposes only and does not constitute Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

# PREFACE

This Drinking Water Health Advisory was prepared for the Office of Drinking Water by the Office of Health and Environmental Assessment, Environmental Criteria and Assessment Office, Cincinnati, OH. These non-regulatory Health Advisories derive 1-day, 10-day, longer-term and lifetime health advisory levels for noncarcinogens, and carcinogenic potency values for known carcinogens.

In the development of this Health Advisory, the scientific literature has been inventoried and key studies have been evaluated. Both the published literature and information obtained from Agency program offices have been evaluated. The literature search is current through 1985. More recent information may have been added during the review process.

The first draft of this document was prepared by Syracuse Research Corporation under EPA Contract No. 68-03-3228. This document was subsequently revised after reviews by staff within the Office of Health and Environmental Assessment and the Office of Drinking Water, and outside experts.

This Health Advisory will become part of the EPA drinking water docket.

## I. INTRODUCTION

The Office of Drinking Water's nonregulatory Health Advisory Program provides information on health effects, analytical methodology and treatment technology that would be useful in dealing with contamination of drinking water. Health Advisories also describe concentrations of contaminants in drinking water at which adverse effects would not be anticipated to occur. A margin of safety is included to protect sensitive members of the population.

Health Advisories are not legally enforceable Federal standards. They are subject to change as new and better information becomes available. The Advisories are offered as technical guidance to assist Federal, State and local officials responsible for protection of the public health when emergency spills or contamination situations occur.

The Health Advisory numbers are developed from data that describe noncarcinogenic endpoints of toxicity. They do not incorporate quantitatively any potential carcinogenic risk from such exposure. For those chemicals that are known or probable human carcinogens according to the proposed Agency classification scheme, nonzero, 1-day, 10-day and longer-term Health Advisories may be derived, with attendant caveats. Health Advisories for lifetime exposures may not be recommended. For substances with a carcinogenic potential, chemical concentration values are correlated with carcinogenic risk estimates by employing a cancer potency (unit risk) value together with assumptions for lifelong exposure and the ingestion of water. The cancer unit risk is usually derived from a linearized multistage model with 95% upper confidence limits providing a low-dose estimate of cancer risk. The cancer risk is characterized as being an upper limit estimate, that is, the true risk to humans, while not identifiable, is not likely to exceed the upper limit estimate and in fact may be lower. While alternative risk modeling approaches may be presented, for example One-hit, Weibull, Logit or Probit, the range of risks described by using any of these models has little biological significance unless data can be used to support the selection of one model over another. In the interest of consistency of approach and in providing an upper-bound on the potential carcinogenic risk, the Agency recommends using the linearized multistage model.

## II. GENERAL INFORMATION AND PROPERTIES

### Synonyms

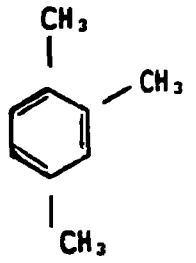
- Asymmetrical trimethylbenzene; uns-trimethylbenzene; psi-cumene; pseudocumene; pseudocumol; as-trimethylbenzene

### Uses

- 1,2,4-Trimethylbenzene is used in the manufacture of trimellitic anhydride, dyes, pharmaceuticals, perfumes, resins and pseudocumidine (Windholz, 1983). It is a component of gasoline (Verschueren, 1983).

### Properties

Chemical Structure




| | | |
|---|---|---|
| CAS # | 95-63-60 | |
| Chemical formula | $C_9H_{12}$ | |
| Molecular weight | 120.19 | |
| Physical state (at 25°C) | liquid | Windholz, 1983 |
| Melting point | -43.78°C | Windholz, 1983 |
| Boiling point | 170°C | Windholz, 1983 |
| Vapor pressure (25°C) | 2.03 mm Hg | Mackay and Shiu, 1981 |
| Specific gravity (20/4°C) | 0.8761 | Windholz, 1983 |
| Water solubility (25°C) | 57 mg/L | Mackay and Shiu, 1981 |
| Octanol/water partition coefficient (log $K_{ow}$) | 3.78 | Hansch and Leo, 1985 |
| Conversion factor (25°C, 760 mm Hg) | 1 mg/m³ = 4.91 ppm | |

| | | |
|---|---|---|
| Taste threshold (water) | - | |
| Odor threshold (water) | - | |
| Odor threshold (air) | 0.2 mg/m³ | Verschueren, 1983 |

Occurrence

- In methodology reports (i.e., no mention was made of efforts to ensure representative samples), 1,2,4-trimethylbenzene was reported in single samples of drinking water in Cincinnati, OH at a concentration of 0.127 µg/L (Coleman et al., 1984) and in drinking water from Kitakyushu, Japan at a concentration of 3.3 µg/L (Shinohara et al., 1981). Concentrations ranging from 0.002-0.540 µg/L have been detected in seawater from the Narragansett Bay (Wakeham et al., 1983).

- The mean atmospheric concentration of 1,2,4-trimethylbenzene in various urban/suburban areas in the United States is reportedly 1.2 ppb (5.9 µg/m³), and the mean concentration is reportedly 0.580 ppb (2.8 µg/m³) in rural/remote areas (Brodzinsky and Singh, 1982). 1,2,4-Trimethylbenzene is emitted in the exhaust from highway vehicles (Hampton et al., 1982).

Environmental Fate

- Based on experimental equilibrium data (Hine and Mookerjee, 1975), the Henry's Law constant for 1,2,4-trimethylbenzene at 25°C is 0.00563 atm-m³/mole. Given this value and using the method of Lyman et al. (1982), the volatilization half-life of 1,2,4-trimethylbenzene from a river 1 m deep flowing 1 m/sec with a wind velocity of 3 m/sec is estimated to be 3.4 hours. Thus, 1,2,4-trimethylbenzene is expected to be highly volatile from water.

- The rate of biodegradation of 1,2,4-trimethylbenzene in natural water cannot be predicted from the available data. In combination with the other water soluble compounds of petroleum oil, 1,2,4-trimethylbenzene was biodegraded using a seawater inoculum (van der Linden, 1978) and a groundwater inoculum (Kappeler and Wuhrmann, 1978). Perry (1979) reported the co-oxidation of 1,2,4-trimethylbenzene by Nocardia corallina V-49. Various strains of Pseudomonas are capable of biodegrading 1,2,4-trimethylbenzene (Kunz and Chapman, 1981; Omori and Yamada, 1969).

## III. PHARMACOKINETICS

### Absorption

- Alkylbenzenes in general are absorbed into the blood from various portals of entry (Gerarde, 1959), with inhalation and percutaneous absorption being the most important routes of industrial exposures. Mikulski and Wiglusz (1975) as well as Cerf et al. (1980) demonstrated the uptake of 1,2,4-trimethylbenzene after oral administration in rats and rabbits. Sandmeyer (1981) listed the systemic toxicity of 1,2,4-trimethylbenzene via inhalation in mice, indicating that absorption of this chemical does occur.

### Distribution

- Gerarde (1959) reported that due to their high lipophilicity, ~85% of alkylbenzenes in blood are bound to red blood cells. Alkylbenzenes generally accumulate in tissues with high lipid content.

### Metabolism

- In general, alkylbenzenes are metabolized by side chain oxidation to form alcohols or carboxylic acids. These compounds are then conjugated with glucuronic acid or glycine for urinary excretion. These reactions probably occur primarily in liver microsomes (Gerarde, 1959).

- Mikulski and Wiglusz (1975) reported that after a single oral dose of 1200 mg/kg of 1,2,4-trimethylbenzene to male Wistar rats, a total of 62.5% of the dose was excreted in the urine as glycine, sulfuric acid and glucuronic acid conjugates. The elimination half-lives for these conjugates were 9.5 hours for glycine conjugates, 22.9 hours for glucurmide and 37.6 hours for organic sulfates.

- Cerf et al. (1980) administered 0.5 mL/kg/day (438 mg/kg/day) 1,2,4-trimethylbenzene by gavage to male albino rabbits for 5 days. The two principal metabolites found in urine were 2,4-dimethylbenzoic acid and 3,4-dimethylhippuric acid.

- Bakke and Scheline (1970) reported that the only phenolic metabolite detected in the urine of two rats within 48 hours after an oral dose of 1,2,4-trimethylbenzene was 2,4,5-trimethylphenol. This metabolite amounted to only a fraction (0.05%) of the original dose of 1,2,4-trimethylbenzene.

Excretion

- Gerarde (1959) reported that alkylbenzenes in general are eliminated unchanged through the lungs or as biotransformation products in the urine. The urinary metabolites (glycine and glucuronide conjugates) are water soluble. A small amount of the parent compound may be excreted in urine, but this is limited by its low water solubility. The amount of the parent compound eliminated through the lungs in exhaled air depends on the concentration in the blood and the vapor pressure.

- Mikulski and Wiglusz (1975) reported the following elimination half-times for 1,2,4-trimethylbenzene metabolites in male Wistar rats: 9.5 hours for glycine conjugates; 22.9 hours for glucuronide and 37.6 hours for organic sulfates.

## IV. HEALTH EFFECTS

### Humans

#### Short-Term Exposure

- No data on short-term exposures to humans by 1,2,4-trimethylbenzene were located in the available literature.

#### Longer-Term Exposure

- The only published report of human exposures (Baettig et al., 1958) describes an occupational health investigation of 27 painters working in a plant using the solvent Fleet-X DV 99. Chemical analysis of this solvent showed that it consisted of 97.5% aromatic hydrocarbons and 2.5% of paraffinic and napthenic hydrocarbons. Spectography identified >50% of the solvent to be 1,2,4-trimethylbenzene and >30% to be 1,3,5-trimethylbenzene. Rough quantitation of the exposure levels to the solvent, using indicator tubes for benzene and its homologs, demonstrated air concentrations between 10 and 60 ppm. If these vapors were exclusively trimethylbenzenes, this would correspond to a concentration range of 2.0-12.2 mg/m$^3$. Compared with 10 unexposed unskilled workers as controls, clinical findings in the exposed included: subjective complaints of central nervous system characteristics (vertigo, headaches, drowsiness), chronic asthma-like bronchitis (classification criteria not specified), hyperchromic anemia (<4.5 million erythrocytes/mm$^2$) and disturbances in blood clotting.

## Animals

### Short-Term Exposure

- After absorption into the blood, alkylbenzenes in general have two principal toxic effects in tissues; irritation and injury of endothelial tissue and central nervous system depression (Gerarde, 1959).

- Gerarde (1959) reported that 2.5 mL of a mixture of trimethylbenzene isomers in olive oil (1:1 v/v) administered by gavage to rats weighing 250 g caused death in 7/10. No other details were reported. Given an average density of 0.87 for the trimethylbenzene mixture (Windholz, 1983), the average trimethylbenzene dose was ~4.4 g/kg.

- Cameron et al. (1938) conducted short-term inhalation exposures to rats and mice with a sample from coal tar fractional distillation containing ~70% crude aromatics of the 1,2,4-trimethylbenzene-1,3,5-trimethylbenzene type. No pathological changes were noted in the major organs of rats (n=8) and mice (n=10) exposed to 1800-2000 ppm of this sample (8852-9836 mg/m$^3$ assuming exclusive trimethylbenzene content; experiments were performed at 20°C and 760 mm Hg is assumed) for 48 and 12 continuous hours to rats and mice, respectively. No adverse effects were noted in six rats exposed to the same sample at 1800-2000 ppm for 14 exposures of 8 hours each.

### Dermal/Ocular Effects

- Gerarde (1959) reported that direct skin contact with liquid alkylbenzenes causes vasodilation, erythema and irritation.

### Longer-Term Exposure

- Bernshtein (1972) reported that inhalation of trimethylbenzene (mixture of 1,2,3-, 1,2,5- and 1,3,5-isomers) at 1000 mg/m$^3$, 4 hours/day for 6 months inhibited phagocytic activity of leukocytes in rats.

- Baettig et al. (1958) exposed male rats (n=8) by inhalation 8 hours/day, 5 days/week to an approximate concentration of 1700 ppm of the solvent Fleet-X DV 99 (see chemical analysis description under human longer-term exposure section) for 4

months. Rats (sex and number not specified) were also exposed to 500 ppm of the solvent for 70 days. Assuming the solvent content to be exclusively trimethylbenzenes, these exposures correspond to 8360 and 2459 mg/m$^3$, respectively. Differences between exposed rats and controls were determined for the following: mortality, behavior, weight, drinking water and food intakes, urine dilution and concentration tests, urinary phenol excretion and red and white differential blood cell counts. Four of the 8 rats exposed to 8360 mg/m$^3$ died within the first 2 weeks whereas none died in the 2459 mg/m$^3$ exposure group. Body weight was decreased in both exposure groups but the effect was confounded by a decrease in food intake. Severe excitation with subsequent narcosis and ataxia toward the end of the daily exposure period was exhibited in the high exposure group but only indicated in the 2459 mg/m$^3$ group. These phenomena receded within a few hours postexposure. Increases in water intake, urinary diuresis and excretion of free, total and bound phenols were noted in the exposed rats. Blood analysis also revealed a relative lymphopenia and neutrophilia in the exposed rats. Histologic examination of the kidney, liver, spleen and lungs was performed only on five animals (those that initially died were replaced) of the high exposure group. Pathologic changes included cloudy swelling and fatty infiltration in the kidney, peripheral fatty infiltration in the liver, an increase in secondary nodules in the spleen, and marked congestion of the pulmonary capillaries with alveolar wall thickening.

**Reproductive Toxicity**

- Data regarding the reproductive toxicity of 1,2,4-trimethylbenzene could not be located in the available literature.

**Developmental Toxicity**

- Data regarding the developmental toxicity of 1,2,4-trimethylbenzene could not be located in the available literature.

**Mutagenicity**

- Data regarding the mutagenicity of 1,2,4-trimethylbenzene could not be located in the available literature.

### Carcinogenicity

- Data regarding the carcinogenicity of 1,2,4-trimethylbenzene could not be located in the available literature. The chemical has not been selected for carcinogenicity testing (NTP, 1987).

## V. QUANTIFICATION OF TOXICOLOGICAL EFFECTS

Health Advisories are based upon the identification of adverse health effects associated with the most sensitive and meaningful noncarcinogenic endpoint of toxicity. The induction of this effect is related to a particular exposure dose over a specified period of time, most often determined from the results of an experimental animal study. Traditional risk characterization methodology for threshold toxicants is applied in HA development. The general formula is as follows:

$$\frac{\text{(NOAEL OR LOAEL) (BW)}}{\text{[UF(s)] (\_\_\_\_ L/day)}} = \text{\_\_\_\_mg/L (\_\_\_\_µg/L)}$$

where:

NOAEL = No-Observed-Adverse-Effect Level (the exposure dose in mg/kg bw/day)

or

LOAEL = Lowest-Observed-Adverse-Effect Level (the exposure dose in mg/kg bw/day)

BW = Assumed body weight of protected individual (10 kg for child or 70 kg for adult)

UF(s) = Uncertainty factors, based upon quality and nature of data (10, 100, 1000 or 10,000 in accordance with NAS/ODW or Agency guidelines)

___ L/day = Assumed water consumption (1 L/day for child or 2 L/day for adult)

### 1-Day Health Advisory

Data were not sufficient for derivation of a 1-day HA for 1,2,4-trimethylbenzene.

### 10-Day Health Advisory

Data were not sufficient for derivation of a 10-day HA for 1,2,4-trimethylbenzene.

## Longer-Term Health Advisory

Data were not sufficient for derivation of a longer-term health advisory. Although significant results were indicated in both the Bernshtein (1972) and the Baettig et al. (1958) studies, the exposures were to mixtures of trimethylbenzenes, which makes quantitation of single components equivocal. Additional deficits include the lack of more than one exposure level and detail (e.g., number of animals not specified, degree of inhibition not quantitated) in the Bernshtein (1972) study. The Baettig et al. (1958) animal investigations lacked proper reporting of results (i.e., statistical analyses either not done or not specified) and techniques, was not comprehensive in scope (i.e., histologic examination performed on a limited number of animals in the high exposure group only) and used small numbers of animals. The human study also lacked quantification of symptoms/effects, was performed on a small number and lacked appropriate follow-up.

## Lifetime Health Advisory

The lifetime HA represents that portion of an individual's total exposure that is attributed to drinking water and is considered protective of noncarcinogenic adverse health effects over a lifetime exposure. The lifetime HA is derived in a three step process. Step 1 determines the Reference Dose (RfD), formerly called the Acceptable Daily Intake (ADI). The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious health effects during a lifetime, and is derived from the NOAEL (or LOAEL), identified from a chronic (or subchronic) study, divided by an uncertainty factor(s) times an additional uncertainty factor. From the RfD, a Drinking Water Equivalent Level (DWEL) can be determined (Step 2). A DWEL is a medium-specific (i.e., drinking water) lifetime exposure level, assuming 100% exposure from that medium, at which adverse, noncarcinogenic health effects would not be expected to occur. The DWEL is derived from the multiplication of the RfD by the assumed body weight of an adult and divided by the assumed daily water consumption of an adult. The lifetime HA in drinking water alone is determined in Step 3 by factoring in other sources of exposure, the relative source contribution (RSC). The RSC from drinking water is based on actual exposure data or, if data are not available, a value of 20% is assumed for synthetic organic chemicals and a value of 10% is assumed for inorganic chemicals.

If the contaminant is classified as a known, possible or probable carcinogen, according to the Agency's classification scheme of carcinogenic potential (U.S. EPA, 1986), then caution must be exercised in making a decision on how to deal with possible lifetime exposure to this substance. The risk manager must balance this assessment of carcinogenic potential and the quality of the data against the likelihood of occurrence and significance of health effects related to noncarcinogenic endpoints of toxicity. In order to assist the risk manager in this process, drinking water concentrations associated with estimated excess lifetime cancer risks

over the range of 1 in 10,000 to 1 in 1,000,000 for the 70 kg adult drinking 2 L of water/day are provided in the Evaluation of Carcinogenic Potential Section.

Data were not sufficient for derivation of a lifetime health advisory for the same reasons specified for the longer-term health advisory.

Evaluation of Carcinogenic Potential

Pertinent data regarding the carcinogenicity of 1,2,4-trimethylbenzene could not be located in the available literature. This chemical has not been scheduled for carcinogenicity testing (NTP, 1987). IARC has not evaluated the carcinogenic potential of 1,2,4-trimethylbenzene.

Applying the criteria described in the U.S. EPA's Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986a), 1,2,4-trimethylbenzene may be classified in Group D: Not classified. This category signifies that the evidence is insufficient to assess the agent's carcinogenic potential.

## VI. OTHER CRITERIA, GUIDANCE AND STANDARDS

ACGIH (1980, 1985) recommended a TLV of 25 ppm (~5 mg/m$^3$) and a STEL of 35 ppm (~7 mg/m$^3$) for mixed trimethylbenzenes. These numbers are based largely on human experience with trimethylbenzenes.

## VII. ANALYTICAL METHODS

Analysis of 1,2,4-trimethylbenzene is by a purge-and-trap gas chromatographic procedure used for the determination of volatile aromatic and unsaturated organic compounds in water (U.S. EPA, 1985a). This method calls for the bubbling of an inert gas through the sample and trapping volatile compounds on an adsorbent material. The adsorbent material is heated to drive off compounds onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the method analytes, which are then detected by the photoinonization detector. This method is applicable to the measurement of 1,2,4-trimethylbenzene over a concentration range of 0.06-1500 µg/L. Confirmatory analysis is by mass spectrometry (U.S. EPA, 1985b). The detection limit for confirmation by mass spectrometry has not been determined.

## VIII. TREATMENT TECHNOLOGIES

Very little information is available on treatment technologies capable of removing 1,2,4-trimethylbenzene from water.

Muller et al. (1981) presented mass transfer coefficients for non-polar volatile organic compounds, including 1,2,4-trimethylbenzene. They concluded that in bubble aeration systems mass transfer rates for volatile compounds depend on mass transfer rate coefficients as well as the degree of saturation of the exit gas.

U.S. EPA (1986b) estimated the feasibility of removing 1,2,4-trimethylbenzene from water by air stripping, employing the engineering design procedure and cost model presented at the 1983 National ASCE Conference on Environmental Engineering. Based on chemical and physical properties and assumed operating conditions, 90% removal efficiency of 1,2,4-trimethylbenzene was reported by a column with a diameter of 5.8 ft and packed with 15 ft of 1 inch plastic saddles. The air-to-water ratio required to achieve this degree of removal effectiveness is 25. Actual system performance data, however, are necessary to realistically determine the feasibility of using air stripping for the removal of 1,2,4-trimethylbenzene from contaminated drinking water.

In summary, the amenability of 1,2,4-trimethylbenzene to air stripping has been clearly established. Selection of air stripping to attempt 1,2,4-trimethylbenzene removal from contaminated drinking water must be based on a case-by-case technical evaluation and an assessment of the economics involved.

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