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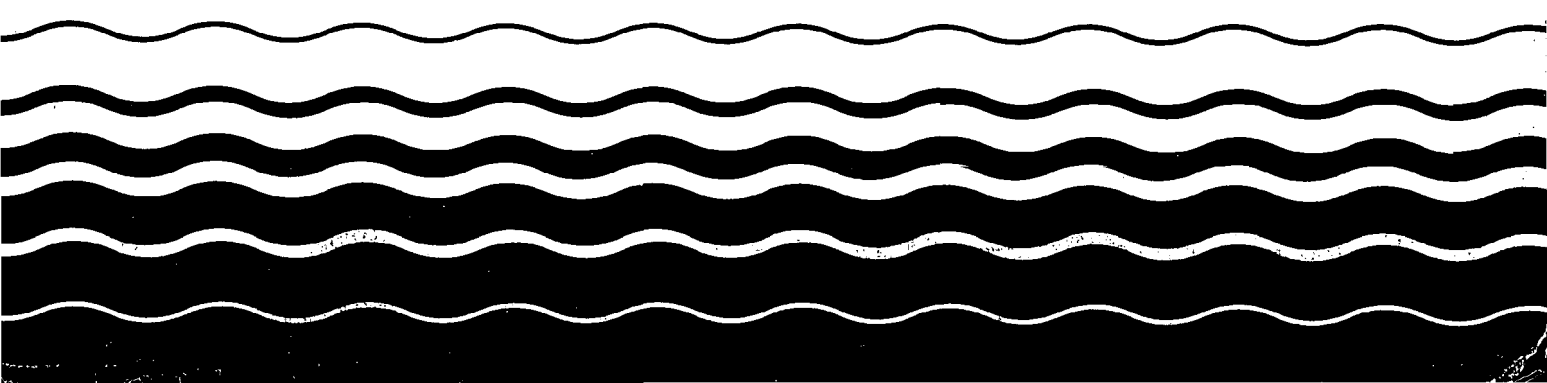
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Water

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# **An Exposure and Risk Assessment for Toluene**



#### **DISCLAIMER**

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AN EXPOSURE AND RISK ASSESSMENT  
FOR TOLUENE

by

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## FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

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## 1.0 TECHNICAL SUMMARY

The Monitoring and Data Support Division, Office of Water Regulations and Standards of the U.S. Environmental Protection Agency is conducting risk assessments for pollutants that may enter and traverse the environment thereby leading to exposure to humans and other biota. The program is in response to Paragraph 12 of the NRDC Consent Decree. This report is a risk assessment for toluene using available data and quantitative models where possible to evaluate overall risk.

### 1.1 MATERIALS BALANCE

Toluene is a highly volatile, colorless, aromatic liquid extracted primarily from petroleum and its products, and, to a lesser extent, from coal and coal products. Only 11% of the total production in 1978 (31,816,000 kkg) was isolated as pure toluene. The remaining 89% (27,400,000 kkg) is contained in gasoline, coal-derived light oils and tar, and catalytic reformat. Production of toluene results in estimated environmental releases of 4800 kkg, mostly to air.

Uses of toluene totaled 31,000,000 kkg; of this amount 92% was used in gasoline and 1% of the total supply was used as a solvent (7% in chemical synthesis). Toluene is used to synthesize benzene, toluene diisocyanate, and benzoic acid, among other organic chemicals. As a solvent, it is used in paints, inks, adhesives, cleaning agents, etc.

Estimated environmental releases are primarily (99.7% of total releases) to the air (1,100,000 kkg); 63% of which results from the distribution, vending and use of gasoline. Solvent use accounts for about one-third (370,000 kkg) of air emissions; manufacturing uses are responsible for about 0.1%. Estimated water discharges totaling 1200 kkg (0.11% of total toluene releases) are mostly (89%) due to spills of gasoline, oil, and toluene to surface waters. The remaining water discharges (118 kkg) originate from solvent uses, coal coking, POTW effluents, and wood preserving. Estimated releases to land totaling 1300 kkg constitute 0.12% of total environmental releases and are mainly (74%) a result of production (petroleum refining and coking operations).

Inadvertent sources, such as spills during transport of toluene, stationary fuel and coal refuse pile combustion, forest fires, etc. contributed about 33,000 kkg to the environment; 96% of which was released to the atmosphere.

### 1.2 ENVIRONMENTAL FATE

The dominant fate processes for toluene involve intermedia transfers to the atmosphere, where it undergoes oxidative destruction by hydroxyl radicals, a process with a half-life of less than two days. Discharges of toluene to land or water bodies will usually be followed by rapid depletions in toluene levels, predominantly because of rapid volatilization (half-life of 5 hours from water) and, to a much lesser degree,

microbial degradation under certain favorable conditions. Within soils, toluene may also be immobilized as a result of sorption onto organic matter; the rate of volatilization from soil has not been reported. Toluene moves rapidly through some soils, however, and has the potential to reach groundwater and consequently enter drinking water supplies.

Toluene has been found in water, air, sediments, and foods. In surveys made within the last five years, it has been detected in both surface and groundwater drinking supplies. It has been detected in 11% of the 236 surface supplies tested with a mean value of 0.15  $\mu\text{g}/\text{l}$ . The highest observed level was 19  $\mu\text{g}/\text{l}$ . Groundwater data are less well documented; however, in the U.S. EPA's Community Water Supply Study, toluene was detected in only 2 of 305 supplies. The maximum observed groundwater concentration was 100  $\mu\text{g}/\text{l}$  in a well reported in STORET; however, most observations were less than the detection limit (0.5 - 5  $\mu\text{g}/\text{l}$ ).

In ambient surface waters, 48% of the positive values were less than 10  $\mu\text{g}/\text{l}$  of toluene, with 14% of the samples above 100  $\mu\text{g}/\text{l}$ . Toluene was observed in samples from 14 of the 15 water basins in the continental United States. Samples of industrial or other effluent discharges taken in 11 of these basins (17 states) showed a similar distribution, with a maximum of 4600  $\mu\text{g}/\text{l}$  reported.

Samples of toluene in foods are quite limited. It has been measured in fish, nuts, potatoes and grape essence; however, the data are insufficient to indicate typical levels. It has been documented in cigarettes, however, with a net yield of about 0.1 mg/cigarette.

Atmospheric levels of toluene measured in urban areas averaged about 19  $\mu\text{g}/\text{m}^3$  and ranged from trace to 283  $\mu\text{g}/\text{m}^3$ . Rural and remote areas, on the other hand, averaged about 1  $\mu\text{g}/\text{m}^3$  and ranged from "trace" to 57  $\mu\text{g}/\text{m}^3$ . It appears that the mobile sources of toluene are the dominant cause of the observed air levels. However, some studies suggest that volatilization from gasoline is a significant source in addition to vehicle exhausts.

### 1.3 HUMAN HEALTH EFFECTS AND EXPOSURE

Toluene is a general, central nervous system (CNS) depressant, with a low toxicity. Its acute CNS effects that occur at high levels of exposure (often as a result of solvent abuse), include euphoria, ataxia, loss of consciousness, vomiting, tachycardia, and lead to respiratory paralysis and death if the exposure continues.

Other toxic effects include cardiotoxicity (presumably arrhythmia development), and possible permanent CNS damage and reproductive toxicity. With the exception of cardiotoxicity, these latter effects are difficult to ascribe to toluene exposure alone, because other organic solvents are usually present during human exposure episodes. Animal studies and some preliminary human studies suggest weak evidence of reproductive toxicity. However, further research is required before the



nature of the toxicity, toxic levels, and possible threshold levels can be identified.

The data base on the potential carcinogenicity of toluene is limited and inadequate for quantitative estimations of human risks. Presently available data indicate no toluene-induced carcinogenic or mutagenic effects in experimental animals. The U.S. EPA (1980b) has also stated that available oncogenic data are insufficient to evaluate the carcinogenic potential of toluene.

Human exposure to toluene may occur through ingestion, inhalation, and through the skin. Typical exposures (reported as per capita values) encountered in drinking water are about 0.5-3  $\mu\text{g}/\text{day}$ . Insufficient data exist to assess toluene ingestion in foods. However, fish consumption may result in the ingestion of 6.5  $\mu\text{g}/\text{day}$  toluene. The estimated maximum daily ingested amount is 38  $\mu\text{g}$  for water and 224  $\mu\text{g}$  for fish.

Inhalation levels are somewhat higher. An amount typical of urban areas (150 million people potentially exposed, as of 1970) is 210  $\mu\text{g}/\text{day}$ , while rural areas (54 million people potentially exposed, as of 1970) are usually an order of magnitude less -- 11  $\mu\text{g}/\text{day}$ . Nonoccupational exposure at gasoline stations can contribute 10  $\mu\text{g}$  to the daily intake of toluene. Cigarette smoking (54 million smokers, as of 1978) appears to have the highest exposure potential with an average smoker (30 cigarettes/day) receiving a 1560  $\mu\text{g}/\text{day}$  dose. Extreme inhaled doses are as high as 3170  $\mu\text{g}/\text{day}$  for urban residents. Occupational exposure at the OSHA standard may be as high as 3,600,000  $\mu\text{g}/\text{day}$ .

Percutaneous exposure is possible as a result of the use of consumer products. A 5-30 minute exposure for both hands in a 5% liquid toluene solution could result in an estimated intake of 200-1000  $\mu\text{g}/\text{per use}$ . Assuming a use rate of once per week, the estimated average daily exposure would be 23-140  $\mu\text{g}$ . Occupationally-exposed individuals, similarly exposed to pure liquid toluene might receive 3200  $\mu\text{g}$  per use over the same time period.

#### 1.4 AQUATIC EFFECTS AND EXPOSURE

Aquatic organisms exposed to toluene may experience changes in gill permeability and internal  $\text{CO}_2$  poisoning. The majority of acute toxic effects to fish and invertebrates occurs in the 10.0-100.0  $\text{mg}/\text{l}$  range. The most sensitive species tested is the striped bass ( $\text{LC}_{50} = 6.3 \text{ mg}/\text{l}$ ) and the most resistant, the mosquito fish ( $\text{LC}_{50} > 1000 \text{ mg}/\text{l}$ ). Data on environmental factors affecting the toxicity of toluene are not extensive; however, neither temperature nor water hardness has been found to have a significant effect. Based upon the limited toxicity data, no water quality criteria for aquatic life has been set for toluene.

Of the total amount of toluene discharged to the environment annually in the United States, less than 1% is directly discharged to water. Monitoring data indicate that the mean concentration of toluene in ambient and effluent water in 16 major river basins is less than 10 µg/l; 48% of the positive values in ambient waters were below this value. About 14% of the positive values exceeded 1.0 mg/l, which indicates that some potential for risk to aquatic systems exists.

### 1.5 RISK CONSIDERATIONS

The data base on the potential carcinogenicity of toluene is limited and inadequate for quantitative estimates of human risks. Presently, available data indicate no toluene-induced carcinogenic or mutagenic effects in experimental animals.

Toluene is widely dispersed in the human environment. However, the fate processes affecting the toluene released to the environment favor atmospheric destruction. In order to estimate the margins of safety for human populations at possible exposure levels, the latter were compared with the threshold limit value (TLV) of 100 ppm (377 mg/m<sup>3</sup>). The TLV was calculated to permit an absorption of 1.8 gr/day. Because this intake level was lower than the several no-observed-effect levels determined from animal experiments, it was used as a conservative basis for estimating margins of safety.

Margins of safety were calculated by dividing the daily absorbed dose at the TLV by the daily absorbed dose at the various nonoccupational exposure levels. As described in Section 5.1, human effects are assumed to depend on absorbed dose rate (e.g., mg/day) and not on exposure route. The lowest margin of safety for typical nonoccupational exposure to toluene is 1200 for cigarette smoking. Ingestion of toluene in drinking water was associated with margins of safety of at least 600,000, and more typically, 1,000,000. Inhalation of average levels of toluene in urban areas has a safety margin of 9000 for average concentrations. Therefore, the risks of adverse health effects resulting from exposure to toluene in water and air at commonly found levels, and from extreme levels less frequently observed are small.

Risks to aquatic biota are considered low because less than ten occurrences of toluene in ambient and effluent waters have been reported at concentrations in the range of known acute or chronic effects for aquatic organisms (1-10 mg/l). It is presumed that these levels result from localized discharges; thus no long-term effects to individual species, communities, or aquatic ecosystems are expected. Short-term effects on certain species may occur; however, these have not been documented in the natural environment.

## 2.0 INTRODUCTION

The Office of Water Planning and Standards, Monitoring and Data Support Division of the Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated included potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and estimate exposure of receptors to these substances. The results are intended to serve as a basis for developing suitable regulatory strategy for reducing the risk, if such action is indicated.

This document is an assessment of the exposures and risks associated with toluene in the environment. It includes summaries of comprehensive reviews of the production, use, distribution, fate, effects and exposure to toluene and the integration of this material into an analysis of risk.

Toluene is an aromatic, volatile, colorless liquid extracted primarily from petroleum and to a less extent from coal. Use as well as derivation of petroleum and petroleum products (i.e., gasoline and solvents) result in environmental releases of toluene as it may be a contaminant. The materials balance for toluene is described in Chapter 3.0.

The physical and chemical behavior of toluene is described in Chapter 4.0. Its properties are documented in the first section, followed by a compilation of monitoring data for all environmental media. The results of media-specific fate and intermedia transfer model used to predict concentration levels of toluene in the air and water within close proximity to significant toluene sources and equilibrium concentrations resulting from free exchange of toluene between air, soil, water, and sediments are presented next. A discussion of biodegradation of toluene and a summary of critical fate pathways conclude the chapter.

The most current research of effects upon human and nonhuman receptors, a description of the duration of exposure and the populations exposed to documented or predicted levels of toluene and a statement of risk comprise the later chapters of this report.

Presently, there are two sets of federal criteria for toluene: occupational air standards and water quality criteria. In water, a 424 mg/l has been set to protect humans from the toxic properties of toluene if only contaminated aquatic organisms are consumed. If both contaminated water and aquatic organisms are in the diet, the human health water quality criteria is 14.3 mg/l (U.S. EPA 1980).

The Occupational Safety and Health Administration has established standards for the regulation of toluene in the workplace. The time-weighted average concentration for 8 hours should not exceed  $754 \text{ mg/m}^3$  (200 ppm) (OSHA 1978).

Toluene concentrations in air were converted from ppm to  $\text{mg/m}^3$  by using the following relationship:  $1 \text{ mg/m}^3 = 3.77 \text{ ppm}$ . This factor was derived assuming 1 atm and  $25^\circ\text{C}$ , conditions, which were not absolute for all atmospheric measurements. However, monitoring data are seldom reported with the concurrent temperature and pressure; therefore, in the absence of these data, the conversion factor was used unilaterally for all values of toluene in air.

### REFERENCES

Occupational Safety and Health Administration (OSHA). OSHA Safety and Health Standard 29 CFR 1910. U.S. Department of Labor, Washington, D.C.; 1978.

U.S. Environmental Protection Agency (U.S. EPA). Ambient water quality criteria for toluene. Washington, D.C.: Office of Water Regulations and Standards; 1980.

### 3.0 MATERIALS BALANCE

#### 3.1 INTRODUCTION

This chapter presents data on the production and use of toluene, as well as data on the releases of toluene to the environment. A summary flow diagram of the toluene materials balance is presented in Figure 3-1. These data provide a framework for constructing gross estimates of the toluene distribution to and in the environment.

Direct production of toluene occurs by two routes, isolated and non-isolated. Approximately 11%, or  $3.4 \times 10^6$  kkg, of the total toluene produced in 1978 was isolated from petroleum sources (catalytic reformat, pyrolysis and gas and styrene manufacture) and coke ovens. In addition to 190,000 kkg contributed by imports, the remainder of the toluene input to this 1978 materials balance (over  $27 \times 10^6$  kkg) is accounted for by non-isolated sources: catalytic reformat, pyrolysis gasoline, and coal derived. The gasoline pool consumed approximately 92% of the toluene supply, mostly from nonisolated sources, plus back blending from isolated sources. The remaining 8% of the toluene supply was consumed in chemical synthesis and solvent uses.

The major mode of toluene release is atmospheric emissions, which reflect the low water solubility and high volatility of the compound (see Figure 3-1). Air emissions from gasoline use comprised about 63% ( $680 \times 10^6$  kkg) of all air emissions and released toluene, which had, for the most part, never been isolated as such. The next largest source of emissions, solvent use, accounted for 34% ( $370 \times 10^3$  kkg) and the use of toluene for chemical manufacturing accounted for only 0.07% (840 kkg).

Identified water discharges were primarily (89%) from toluene, oil and gasoline spills to surface waters, considered in the report as an inadvertent source. The remainder of the water discharges resulted from solvent use, coal coking operations, POTW effluent discharge, and wood preserving.

Transportation spills also contribute a significant percentage (19%) of the estimated toluene releases to land. However, the major source of land release of toluene (74% or 970 kkg) appears to be from production (petroleum refining and coking operations). An additional 8% comes from POTW sludge.

#### 3.2 PRODUCTION OF TOLUENE

Toluene is produced from petroleum and coal, although it may not necessarily be isolated from the resultant product. This section will discuss toluene production from both these sources, the associated environmental releases, and releases from inadvertent sources. Toluene production from isolated and unisolated sources is presented in Table 3-1.

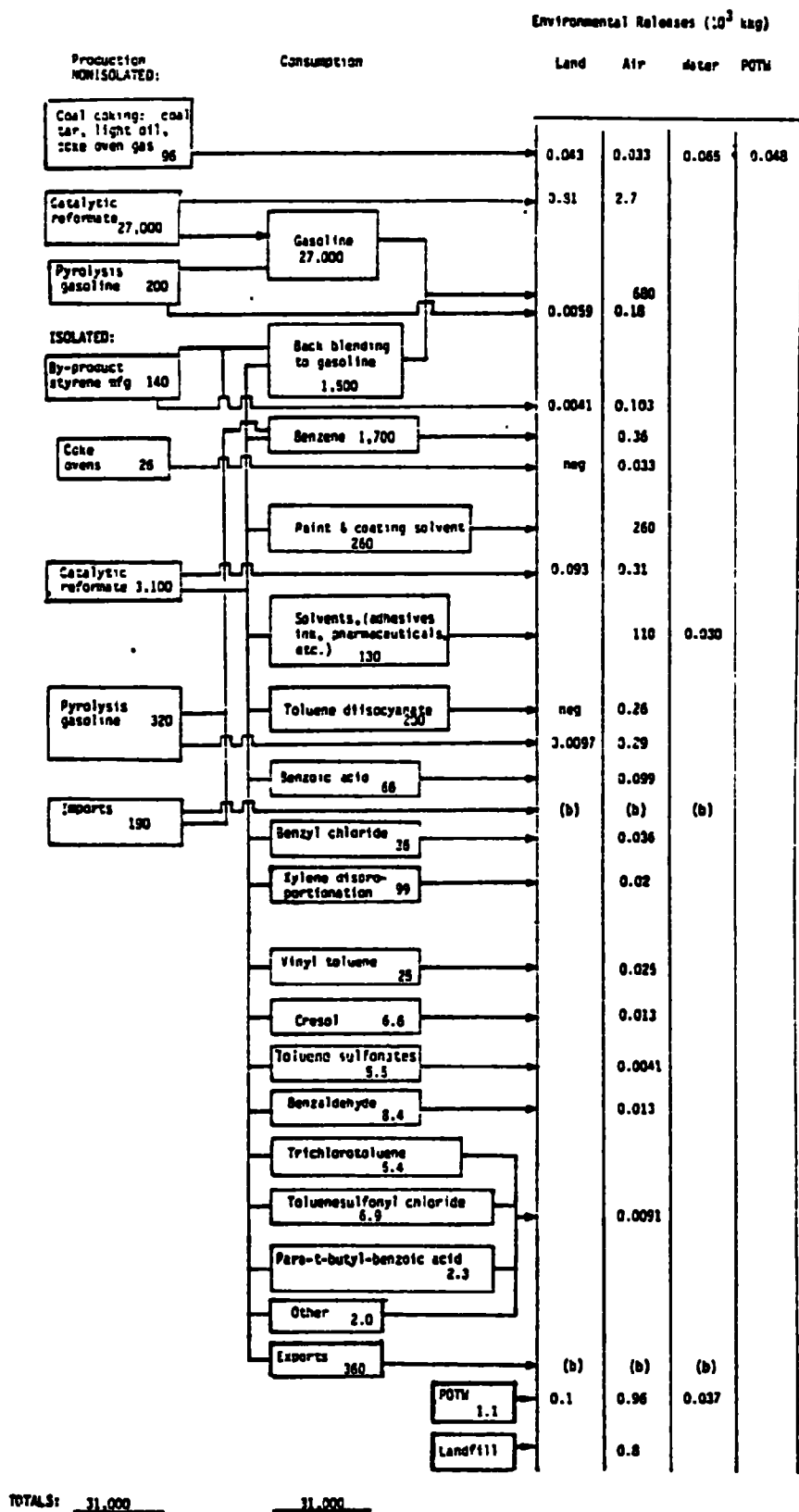


Figure 3-1. Toluene Materials Balance ( $10^3$  kg)<sup>a</sup>

<sup>a</sup>All values rounded to two significant figures; blanks indicate data not available.  
<sup>b</sup>See Table 3-2.

Environmental Releases ( $10^3$  kg)<sup>c</sup>

Inadvertent Sources	Land	Air	Water
Transportation Spills			
Oil	0.0056	-	0.4
Gasoline	0.23	-	0.68
Toluene	0.011	-	0.0022
Production			
Propylene Oxide	-	0.036	-
Polychloroprene	-	0.46	-
Ethylene - Propylene Rubber	-	0.09	-
Ethylene - Propylene Terpolymer	-	4.2	-
Insulation Board	-	-	neg
Hardboard	-	-	neg
Acrylonitrile	-	0.059	-
Combustion			
Coal Refuse	-	4.4	-
Stationary Fires	-	13.0	-
Forest Fires	-	7.0	-
Agricultural Burning	-	1.0	-
Structural Fires	-	<1	-
Miscellaneous			
Cigarette Smoke	-	0.053	-
Wood Preserving	-	-	0.0063
Other	-	0.008	-
Totals	1.3	1100	1.2

<sup>c</sup> No POTW releases from inadvertent sources were identified.

Figure 3-1. (Concluded)



Table 3-1. Toluene Production, 1978 (kkg/yr)

Source	Quantity <sup>a</sup>	Environmental Releases <sup>b</sup>			
		Air	Water	Land	POTW
<u>Isolated</u>					
Catalytic Reformat	3,110,000	310	neg	93	
Pyrolysis Gasoline	324,000	290	neg	9.7	
Styrene Manufacture	135,000	103		4.1	
Coke Ovens	26,000	33		neg	
Imports	192,000		(c)	(c)	
Exports	-364,000		(c)	(c)	
SUBTOTAL	3,400,000	740	neg	110	
<u>Nonisolated</u>					
Catalytic Reformat	27,100,000	2,700	neg	810	
Pyrolysis Gasoline	197,000	180	neg	5.9	
Coal Coking:					
Nonprocessed light oil	52,000	21	35	23	26
Nonrecovered light oil	22,000	2.9	15	9.8	11
Coal tar	22,000	8.9	15	9.8	11
SUBTOTAL	27,393,000	2,900	65	860	48
TOTAL	30,816,000 <sup>d</sup>	3,600	65	970	48

Sources: SRI, 1979 and USITC, 1979

<sup>a</sup> See Appendix A Notes and Tables A-1, A-2 and A-3 for references and calculations.

<sup>b</sup> Blanks indicate data not available.

<sup>c</sup> See Section 3.2.4, transportation spills.

<sup>d</sup> Values may not add due to rounding.

### 3.2.1 Production of Isolated Toluene

Only 11% of the toluene produced is isolated as such. Although crude oil contains low concentrations of toluene (1.3% by weight; Green and Morrell, 1953), it is isolated only from catalytic reformat, pyrolysis gas and as a by-product of styrene manufacture. Less than 1% of the total toluene produced is coal derived.

#### 3.2.1.1 Catalytic Reformat

Of all toluene produced (isolated and nonisolated) in 1978, about 10% or  $3.1 \times 10^6$  kkg was derived from catalytic reformat (SRI 1979, see Appendix A notes). Catalytic reformat is produced by catalytically dehydrogenating selected petroleum fractions to yield aromatic hydrocarbons. Although the concentration of toluene in catalytic reformat ranges from 14 to 27%, this report will use a toluene content of 20% (SRI 1979) for estimation purposes. The 1978 catalytic reforming capacity for toluene production was about  $4.6 \times 10^6$  kkg (SRI 1979). The locations, capacities, production, and emissions for plants that produce toluene directly from petroleum feedstocks are listed in Table A-4 (Appendix A).

#### 3.2.1.2 Pyrolysis Gasoline

About 1% ( $324 \times 10^3$  kkg) of total 1978 toluene production was derived from pyrolysis gasoline (SRI 1979, see Appendix A notes). Pyrolysis gasoline is a by-product from the cracking of hydrocarbon feeds to form olefins. The yield of toluene from pyrolysis gasoline is a function of the feedstock and the severity of cracking (see Table A-5, Appendix A). Toluene production may vary from 1 to 145 kg/kkg ethylene (SRI 1979). The estimated annual capacity for toluene production from pyrolysis gasoline is  $447 \times 10^3$  kkg (SRI 1979). The locations, capacities, production, and estimated environmental releases for the facilities are presented in Table A-4 (Appendix A). Pyrolysis gasoline is either processed for aromatics recovery or blended into gasoline, although some companies sell the pyrolysis gasoline.

#### 3.2.1.3 Styrene Manufacture

About 0.4% ( $135 \times 10^3$  kkg) of all toluene produced in 1978 was produced as a by-product of styrene manufacture (SRI 1979, USITC 1979, see Appendix A notes). When ethylbenzene is dehydrogenated to produce styrene, 0.04-0.07 liter of toluene per kg styrene is produced as a by-product. The locations, toluene production, styrene production capacities, and environmental releases for the plants are presented in Table A-6 (Appendix A).

#### 3.2.1.4 Coal Sources

Toluene production from coal amounted to 0.08% ( $26 \times 10^3$  kkg) of the total (USITC 1979). When coal is carbonized to produce coke, about 10.6 liters of light oil are produced per kkg coal carbonized. This light oil may be isolated and processed to recover the toluene it contains (12-20% by volume) (SRI 1979, U.S.' DOI 1976). If the light oil is not processed for aromatics recovery, it may be burned as fuel, used as a solvent for phenolics recovery, sold to tar distillers or petroleum refiners to be added to gasoline or used for aromatics recovery. Approximately 30% (by capacity) of the coke oven operators recover toluene from light oil, even though 90% practice light oil recovery (EPA 1979b). The coke plants that recover light oil are listed in Table A-7 (Appendix A).

#### 3.2.1.5 Exports and Imports

Exports and imports of toluene (in 1978, were  $384 \times 10^3$  kkg and  $192 \times 10^3$  kkg, respectively (USITC 1979). Environmental releases from this category are covered as spills under inadvertent sources (Section 3.2.4).

#### 3.2.2 Nonisolated Toluene

Approximately 89% ( $27 \times 10^6$  kkg) of the toluene produced in 1978 was not isolated as such. Nonisolated toluene is derived from catalytic reformat, pyrolysis gas, and coal coking operations.

##### 3.2.2.1. Catalytic Reformat and Pyrolysis Gasoline

Approximately  $27.1 \times 10^6$  kkg of toluene were contained in catalytic reformat in 1978 (SRI 1979, USITC 1979, see Appendix A notes for calculations). Most of this is blended into gasoline to improve the octane rating. Pyrolysis gasoline that is not processed for toluene recovery may also be used for this purpose. An estimated  $197 \times 10^3$  kkg of unrecovered toluene was contained in pyrolysis gasoline in 1978 (SRI 1979).

##### 3.2.2.2 Coke Ovens

Coke oven light oil is recovered by 90% of the coke oven operators. This amounted to  $612 \times 10^6$  liters, of which  $238 \times 10^6$  liters were processed to produce various chemicals. Assuming that the unprocessed oil has a toluene content of 16% by volume,  $52 \times 10^3$  kkg of toluene were contained in this source (U.S. DOE 1979, SRI 1979). From the remaining 10% of the coke oven plants that do not recover light oil, an estimated  $22 \times 10^3$  kkg of toluene were contained in the oil (see Appendix A notes).

Coke oven tar is another source of unisolated toluene. Although some toluene is produced by distillation of the tar, it is also burned as fuel or kept for other uses. The estimated total amount of toluene contained in coke oven tar was  $22 \times 10^3$  kkg (see Appendix A notes).

### 3.2.3 Environmental Releases

Toluene releases may arise from process losses, fugitive emissions, or storage losses from production; these data are presented in Table 3-1. The emission factors used are presented in Table A-1 (Appendix A, EPA 1980d). Releases shown from each source are from production of both isolated and nonisolated toluene (see Appendix A). Discharges to water from petroleum refineries are assumed to be negligible, because toluene was not detected in 10 of 11 samples and was present at levels below the quantification limits (1-10 µg/l) in only one sample (EPA 1979g). Releases calculated from coking operations are based upon the disposition of effluents from coking operations (Table A-3) as well as the emission factors presented in Table A-1 (EPA 1979h, EPA 1980d). Water recycled to quenching operations is arbitrarily assumed to release its toluene equally to land and air. Releases from imports and exports are covered in transportation spills (Section 3.2.4).

### 3.2.4 Inadvertent Sources

Because of the widespread and voluminous use of petroleum- and coal-derived oils, fuels and solvents that may contain toluene, it is difficult to quantify all the inadvertent sources of release to the environment. A list of the major contributing sources is presented in Table 3-2 and the derivations of the data are discussed in Appendix A. Note that the majority of toluene releases are to the atmosphere. Combustion, however, contributes over 80% of the atmospheric emissions of toluene. Furthermore, about 35% of this figure is comprised of uncontrolled sources, such as forest, agricultural, and structural fires.

The inadvertent release of toluene from manufacturing processes occurs primarily from three sources: feedstock contamination; by-product formation; presence in oils used in processing or in control of waste emissions. The latter source is exemplified by acrylonitrile manufacture, where oils are layered on waste ponds to control the release of other volatile organic pollutants. Ethylene-propylene rubber and terpolymer manufacture utilize extender oils, which can contain toluene, to improve the viscosity of the elastomer (see Appendix B, Table B-1).

The estimated 53-kkg of toluene released in sidestream smoke from cigarettes is small in comparison to the other inadvertent sources. However, this represents a widespread source, with a potential for high exposure among the population subgroup that either smokes or is often in contact with smokers.

### 3.3 USES OF TOLUENE

This section includes information on the consumption in the U.S. of toluene and environmental releases from these uses. Toluene uses are grouped into three main categories: gasoline, chemical synthesis, and solvent. The following is a brief discussion of each, while environmental releases from uses are summarized in Section 3.3.4. Table 3-3 is a summary materials balance for the various use categories.

Table 3-2. Inadvertent Sources of Toluene Releases to the Environment, 1978<sup>a</sup>

Source	Environmental Releases (kkg)		
	Air	Water	Land
<b>Transportation Spills</b>			
Oil		400	5.6
Gasoline		680	230
Toluene		2.2	11
Propylene Oxide - Chlorohydrin Process	36 <sup>b</sup>		
Polychloroprene	460 <sup>b</sup>		
Ethylene - Propylene Rubber Manufacture	90		
Ethylene - Propylene Terpolymer Production	4,200 <sup>b</sup>		
Wood Preserving		6.3	
Insulation Board Manufacture		neg	
Wet - Process Hardboard Manufacture		neg	
Acrylonitrile Manufacture	59		
Combustion of Coal Refuse Piles	4,400		
Stationary Fuel Combustion	13,000		
Forest Fires	7,000		
Agricultural Burning	1,000		
Structural Fires	<1,000		
Cigarette Smoke	53		
Other <sup>c</sup>	8 <sup>b</sup>		
<b>TOTAL</b>	<b>31,000</b>	<b>1100</b>	<b>250</b>

<sup>a</sup>See Appendix A for derivation of figures in this Table. All values are rounded to two significant figures.

<sup>b</sup>Source: EPA, 1978b.

<sup>c</sup>Includes releases from production of Malathion, Dimethoate and Ronnel.

### 3.3.1 Gasoline

As mentioned in Section 3.2, most of the toluene used in gasoline is never isolated, but rather is a component of various refinery streams, primarily catalytic reformat. Isolated toluene can also be back-blended into the gasoline pool for improvement and adjustment of its antiknock quality (octane number). A total of  $28.5 \times 10^6$  kkg (92% of the total U.S. toluene demand) was consumed for use in gasoline in 1978,  $26 \times 10^6$  kkg of which had not been recovered but instead blended directly as part of a benzene-toluene-xylene (BTX) stream.

### 3.3.2 Chemical Synthesis

Use of toluene as raw material for various chemical manufacturing processes utilized approximately 7% ( $2.2 \times 10^6$  kkg) of the total toluene produced in 1978. The flow charts in Appendix D describe the major synthetic pathways that utilize toluene as the basic building block.

#### 3.3.2.1 Benzene

1 Benzene production via hydrodealkylation uses  $1.7 \times 10^6$  kkg toluene or 5.5% of total toluene production, and is the major use of toluene in chemical synthesis. The producers, locations, capacities, toluene consumption, and environmental releases relating to benzene production from toluene are listed in Table 3-4.

Approximately 20-25% of the benzene supply is derived from dealkylation. The contribution of this source varies in response to benzene demand and toluene demand for other uses (e.g., gasoline). The average yield for benzene is about 94%, corresponding to 1.1 kkg toluene required per kkg benzene produced (SRI 1979).

#### 3.3.2.2 Manufacture of Toluene Diisocyanate

The manufacture of toluene diisocyanate (TDI) consumes  $2 \times 10^5$  kkg or 0.6% of the 1978 total toluene produced (SRI 1979). Toluene diisocyanate is used in urethane polymers, primarily for flexible foams in furniture cushions. The producers of toluene diisocyanate, their locations and plant capacities are presented in Table 3-5.

In TDI manufacture, toluene is nitrated to dinitrotoluene, which is catalytically reduced to toluene diamine (see Appendix D). Toluene diamine is then phosgenated to the final TDI product. Approximately 0.7 kkg toluene is consumed per kkg TDI produced (SRI 1979).

Table 3-3. Toluene Materials Balance: Uses, 1978 (kkg/yr)<sup>a</sup>

Use	Input <sup>b</sup>	Environmental Releases		
		Air <sup>c</sup>	Water	Land
<u>Gasoline</u>				
Non-Recovered	27,000,000 <sup>d</sup>	} 680,000 <sup>e</sup>	neg	neg
Back Blended	1,500,000 <sup>f</sup>			
<u>Solvent Uses</u>				
Paint and Coatings Solvent	260,000	260,000 <sup>g</sup>	neg <sup>g</sup>	neg <sup>g</sup>
Adhesives, Inks, Pharmaceu- ticals, Others	130,000 <sup>h</sup>	110,000 <sup>h</sup>	30 <sup>i</sup>	
<u>Chemical Synthesis</u>				
Benzene	1,700,000	360	} neg	
Toluene Diisocyanate	200,000	260		
Benzoic Acid	66,000	99		
Benzyl Chloride	36,000	36		
Xylene Disproportionation	99,000	20		
Vinyl Toluene	25,000	25		
p-Cresol	6,600	13		
Toluene Sulfonates	5,500	4.1		
Benzaldehyde	8,400	13		
Trichlorotoluene	5,400	} 9.1		
Toluenesulfonyl Chloride	6,900			
Para-t-Butyl-Benzoic Acid	2,300			
Other	2,000			
Total	31,000,000	1,050,000	30	neg

<sup>a</sup>All values rounded to two significant figures; blank spaces indicate data not available.

<sup>b</sup>Source: SRI, 1979.

<sup>c</sup>Source: EPA, 1980d.

<sup>d</sup>99% from catalytic reformat.

<sup>e</sup>Includes 19,000 kkg from marketing; 13,000 kkg evaporative loss during use; 640,000 kkg from auto exhaust. See Appendix A for derivations.

<sup>f</sup>Primarily from styrene manufacture and pyrolysis gasoline.

<sup>g</sup>All is assumed released to the atmosphere (EPA, 1980d).

<sup>h</sup>15% is assumed used as fuel, with the remainder emitted during use (EPA, 1980d). We assume that 6,100 kkg/yr emitted from solvent evaporated during degreasing (EPA, 1978b) is included in this emission total.

<sup>i</sup>See Table 3-7 for breakdown by industry.

Table 3-4. Toluene Consumption and Environmental Releases: Benzene Production, 1978 (kg/yr)<sup>a</sup>

Company	Location	Benzene Capacity <sup>b</sup>	Toluene Used	Environmental Releases		
				Air <sup>c</sup>	Water	Land
American Petrofina	Port Arthur, TX	77,000	59,000	12		
	Big Spring, TX	130,000	100,000	20		
Ashland Oil	Catlettsburg, KY	120,000	91,000	18		
Coastal States	Corpus Christi, TX	200,000	160,000	32		
Commonwealth	Penuelas, PR	380,000	300,000	60		
Crown	Pasadena, TX	77,000	59,000	12		
Dow	Freeport, TX	84,000	65,000	13		
Gulf	Alliance, LA	160,000	120,000	24		
	Philadelphia, PA	67,000	52,000	10		
Monsanto	Alvin, TX	130,000	100,000	20		
Phillips	Guayama, PR	270,000	210,000	42		
Quintana-Howell	Corpus Christi, TX	250,000	200,000	40		
Shell	Odessa, TX	23,000	18,000	3.6		
Sun	Corpus Christi, TX	67,000	52,000	10		
	Toledo, OH	210,000	160,000	32		
	Tulsa, OK	50,000	39,000	7.8		
Total		2,300,000	1,800,000	360		

<sup>a</sup>All values rounded to two significant figures; blank spaces indicate data not available.

<sup>b</sup>SRI, 1979. Toluene use based on 1.23 kkg toluene required per kkg benzene produced; data exclude toluene disproportionation. Plants are assumed to operate at 62-63% of capacity.

<sup>c</sup>Emission factor and breakdown: see Appendix A, Table A-1.



### 3.3.2.3 Other Chemical Intermediate Uses

The remaining major uses of isolated toluene in chemical synthesis (see Table 3-3) include the manufacture of xylenes by disproportionation (99,000 kkg), benzoic acid (66,000 kkg), benzyl chloride (36,000 kkg), vinyl toluene (25,000 kkg), benzaldehyde (8400 kkg) and p-Cresol (6600 kkg). Each of these uses accounts for less than 1% of the total toluene supply. Xylenes have well-known uses in the gasoline pool and as solvents. Benzoic acid is used as a chemical intermediate, chiefly in the manufacture of phenol. Most of the benzyl chloride produced is used to manufacture PVC flooring plasticizers or benzyl alcohol. Vinyl toluene is used in resin manufacture. Benzaldehyde is utilized in the manufacture of perfumes, dyes, flavorings, and pharmaceuticals; and p-Cresol is used primarily to manufacture 2,6-di-tert-butyl-p-cresol (BHT).

The producers, capacities, locations, toluene consumption, and estimated environmental releases for these chemical manufacturing uses are presented in Table 3-6. In addition, Appendix D details the various reaction pathways for each, as well as for some of the minor chemical end products, including: toluene sulfonyl chloride (raw material for saccharin); toluene sulfonates (used as a surface active agent in powder detergents, heavy-duty liquids); trichlorotoluene or benzotrichloride (organic synthesis, dye intermediate); para-t-butyl-benzoic acid (resin manufacture intermediate); dodecyltoluene (precursor in germicide manufacture); and nitrotoluenes (dye intermediates). The last military facility to produce trinitrotoluene (TNT) closed down in 1977.

### 3.3.3 Solvent Uses

Approximately 10% (390,000 kkg) of the isolated toluene supply was utilized as solvents in 1978 (SRI 1979; see Table 3-3). This total is divided between paint and coating carrier solvents (260,000 kkg) and formulation or cleaning solvents in the adhesives, ink, pharmaceutical and other industries (130,000 kkg). The wide scope of toluene applications as a formulation solvent can be seen in the list of commercial products containing toluene, presented in Appendix B (see Table B-2). The volatile nature of toluene facilitates its use as a fast-drying cleaning (e.g., cold cleaning degreasing) or carrier (e.g., paints, inks, leather finishing) solvent. The pharmaceutical industry uses toluene as a raw material in production processes, and as an anthelmintic agent against roundworms and hookworms, primarily in domestic dogs (Krinsky 1980).

Table 3-5. Toluene Releases from Toluene Diisocyanate Producers, 1978 (kkg/yr)<sup>a</sup>

Company	Location	TDI <sup>b</sup> Capacity	Toluene <sup>c</sup> Use	Environmental Releases		
				Air <sup>d</sup>	Water	Land <sup>e</sup>
Allied Chemical	Moundsville, WV	36,000	20,000	26		} neg
BASF Wyandotte	Geismar, LA	45,000	25,000	32		
Dow Chemical	Freeport, TX	45,000	25,000	32		
DuPont	Deepwater, NJ	32,000	17,000	22		
Mohay Chem. Corp.	Baytown, TX	59,000	32,000	41		
	New Martinsville, WV	45,000	25,000	32		
Olin Corp.	Ashtabula, OH	14,000	7,300	9.3		
	Lake Charles, LA	45,000	25,000	32		
Rubicon Chems. Inc.	Geismar, LA	18,000	10,000	13		
Union Carbide <sup>f</sup>	S. Charleston, WV	25,000	13,000	17		
Total		360,000	200,000	260		

<sup>a</sup>All values rounded to two significant figures; blank spaces indicate data not available.

<sup>b</sup>Source: SRI, 1979.

<sup>c</sup>Based on 0.7 unit of toluene consumed per unit of TDI produced, and TDI produced at 79% of capacity (SRI, 1979); usage distributed per capacity.

<sup>d</sup>Emission factor and breakdown: see Appendix A, Table A-5.

<sup>e</sup>Less than one kkg. Based on 558 kkg centrifuge residue per plant, probably no more than 100 ppm toluene, by analogy to dichlorobenzene (EPA, 1977c,d; Lewis, 1975).

<sup>f</sup>Union Carbide Corp. permanently shut down this plant in December, 1978. Thus, the production profile for TDI and toluene consumption shown do not reflect today's market.

Table 3-6. Toluene Consumption and Environmental Releases from other Toluene Chemical Intermediate Users, 1978 (kkg)<sup>a</sup>

Company	Location	Production Capacity	Toluene Used	Environmental Releases		
				Air <sup>C</sup>	Water	Land
<u>Benzyl Chloride Producers</u>						
Monsanto	Bridgeport, NY	36,000	16,000	16		
	Sauget, IL	36,000	16,000	16		
Stauffer	Edison, NJ	5,400	2,700	2.7		
UOP, Inc.	E. Rutherford, NJ	1,400	450	1.0		
Total		79,000	35,000	36		
<u>Benzoic Acid Producers</u>						
Kalama	Kalama, WA	63,000	33,000	50		
Monsanto	St. Louis, MO	4,500	2,300	3.5		
Velsicol	Beaumont, TX	23,000	12,000	18		
	Chattanooga, TN	27,000	14,000	21		
Pfizer	Terre Haute, IN	2,700	1,400	2.1		
Tenneco	Garfield, NJ	6,800	3,200	4.8		
Total		130,000	66,000	99		
<u>Xylene Disproportionation Producers</u>						
ARCO	Houston, TX	89,000	48,000	9.6		
Sun	Marcus Hook, PA	92,000	50,000	10		
Total		181,000	98,000	20		
<u>Vinyl Toluene Producer</u>						
Dow Chem. Corp.	Midland, MI	27,000	25,000	25		
<u>p-Cresol Producer</u>						
Sherwin Williams	Chicago, IL		6,600	13		
<u>Benzaldehyde Producers</u>						
Kalama	Kalama, WA		1,680	2.5		
	Eddystone, PA		1,680	2.5		
Stauffer	Edison, NJ		1,680	2.5		
Tenneco	Garfield, NJ		1,680	2.5		
UOP	E. Rutherford, NJ		1,680	2.5		
Total			8,400	13		

Source: EPA, 1980d.

<sup>a</sup> All values rounded; blank spaces indicate data not available.

<sup>b</sup> See Appendix A, Table 3-6 for derivation of consumption.

<sup>c</sup> See Appendix A, Table A-1 for emission factors and breakdown.

### 3.3.4 Environmental Releases

The environmental releases of toluene resulting from its use are summarized in Table 3-3. The toluene release factors and other information necessary to derive these totals are presented in the Appendix A notes (as cited in Table 3-3) and Tables 3-4, 3-5, and 3-6, which list environmental releases from specific chemical producers (i.e., benzene, TDI, and other chemicals, respectively). Table 3-7 summarizes flow data and toluene loading to water from various industries and Table 3-8 is a regional breakdown of toluene emissions during gasoline marketing. Appendix C contains two tables listing industrial wastewaters in which toluene has been detected, and the frequency of occurrence. Finally, Appendix D diagrammatically presents the location of environmental release points from the chemical synthesis uses of toluene.

Two aspects of toluene environmental releases during use are most striking: the large contribution to air emissions from gasoline and solvent use and the low levels of release to water and land, although data are limited. The 680,000 kkg of toluene released from gasoline use is the sum of 19,000 kkg from marketing losses (see Table 3-8), 18,000 kkg evaporative emissions during use and 640,000 kkg from automobile exhaust. These emissions are based on information presented in Appendix A (Section 3, Table 3-3). The total amount of toluene used in paints and coatings is assumed completely volatilized during application. Approximately 15% of the toluene marketed for use in adhesives, inks, pharmaceuticals, and others is estimated to be used as fuel, with the remainder emitted (EPA 1980d). For purposes of this materials balance, it is assumed that the 6100 kkg toluene emitted from degreasing operations (EPA 1978b) are included in this 110,000 kkg total.

The dearth of quantitative water and land release data is at least partially a function of the fact that toluene is a volatile compound. The available information, however, indicates that toluene is present in a number of industrial wastewater streams (see Appendix C, Tables C-1 and C-2), although the total annual loading is probably low (see Table 3-7; Appendix C, Tables C-1 and C-2). Similarly, the only information on land releases of toluene, from TDI manufacture, shows a negligible amount of toluene disposed to land in centrifuge residue (see Table 3-5, footnote "e").

### 3.4 MUNICIPAL DISPOSAL OF TOLUENE

This section deals with the ultimate disposition of toluene discharged to municipal waste facilities. The latter include publicly owned treatment works (POTWs) and urban refuse landfills or incinerators.

Table 3-7. Wastewater Loading of Toluene: Various Industries

Industry	Wastewater Concentration (µg/l)	Wastewater Flow (10 <sup>6</sup> l/day)	Percent Occurrence	Mass Loading <sup>a</sup> (kg/yr)
Ink Formulating <sup>b</sup>	1,600 <sup>c</sup>	0.092	87	0.038
Textile Products <sup>d</sup>	14 <sup>e</sup>	2,000	46	3.8
Gum and Wood Chemicals <sup>f</sup>	2,000 <sup>e</sup>	0.11 <sup>g</sup>	78	0.052
Paint Formulating <sup>h</sup>	990 <sup>e</sup>	2.8	87	0.72
Leather Tanning <sup>i</sup>	78 <sup>c</sup>	200	25	1.2
Pharmaceutical <sup>j</sup>	515	250	62	24
TOTAL				30 <sup>k</sup>

<sup>a</sup>Based on a 300 day operating year.

<sup>b</sup>All data from EPA, 1979a.

<sup>c</sup>Untreated wastewater.

<sup>d</sup>All data from EPA, 1979b, except percent occurrence (EPA, 1980a).

<sup>e</sup>Treated Effluent.

<sup>f</sup>All data from EPA, 1979c, except percent occurrence (EPA, 1980a).

<sup>g</sup>See Appendix A for derivation, based on production and flows in various industry subcategories.

<sup>h</sup>All data from EPA, 1979d.

<sup>i</sup>All data from EPA, 1979e, except percent occurrence (EPA, 1980a).

<sup>j</sup>All data from EPA, 1980b.

<sup>k</sup>Values do not add due to rounding.

Table 3-8. Toluene Emissions from Gasoline Marketing

Region	Number of Sites <sup>a</sup>	Toluene Emissions (kg/yr) <sup>b</sup>
New England	11,105	920
Middle Atlantic	28,383	2,300
East North Central	42,270	3,500
West North Central	23,304	1,900
South Atlantic	37,286	3,100
East South Central	16,313	1,400
West South Central	28,336	2,300
Mountain	12,815	1,100
Pacific	<u>26,647</u>	<u>2,200</u>
Total	226,459	19,000 <sup>c</sup>

Source: EPA, 1980d.

<sup>a</sup>Total number of service stations.

<sup>b</sup>Based on 0.004735 kg hydrocarbon lost from gasoline marketing (bulk and service stations)/kg gasoline consumed; it is assumed toluene is 1.26 wt% of the hydrocarbon emission (CARB, 1975; EPA, 1975a).

<sup>c</sup>Values do not add due to rounding.

#### 3.4.1 POTWS

Input of toluene to POTWs largely depends on variations in industrial discharges feeding the POTWs and the types of industry in a particular municipality. A recent EPA (1980e) study of selected urban POTW facilities with secondary treatment and varying feed conditions produced a materials balance of toluene shown in Table 3-9.

An overall materials balance, presented in Table 3-10, can be constructed using a total POTW flow of approximately  $10^{11}$  l/day (EPA 1978c) and median values of 30.5  $\mu\text{g/l}$  (influent) and 1  $\mu\text{g/l}$  (effluent) for toluene (see Table 3-9). It is assumed, for purposes of these calculations, that influent and effluent flow rates are equal, i.e., that water loss from sludge removal and evaporation are small compared to influent flows. Using these assumptions, 37 kkg toluene were discharged to water from POTWs in 1978, while there was an input of 1100 kkg (see Table 3-10).

Toluene discharged in sludge can be estimated from the toluene concentration in sludge and quantity of dry sludge produced annually,  $6.0 \times 10^6$  kkg (EPA 1979i). Assuming the median toluene concentration of POTW wet sludge to be 833  $\mu\text{g/l}$ , (see Table 3-9), and that wet sludge is 95% water by weight, approximately 100 kkg of toluene are discharged in sludge. As ocean dumping of sludge is mandated to cease by 1981 and assuming that more stringent air quality standards curb incinerator use (EPA 1979i), the 100 kkg of toluene contained in sludge are assumed discharged to land.

The toluene released to the atmosphere may be estimated from POTW data on influent versus effluent and sludge loadings, given the following assumptions: (1) toluene recycled within the activated sludge process will eventually be "wasted"; (2) the toluene biologically degraded is negligible; and (3) toluene is lost to the atmosphere by mechanical stripping, or aeration (note: volatilization is the primary environmental transport mode for toluene). Thus, an estimated 960 kkg of toluene is released to the atmosphere from POTWs.

#### 3.4.2 Urban Refuse

The three options for handling urban refuse are energy recovery (primarily by incineration), material recovery, and disposal through incineration or landfills. Urban refuse can be divided into two major components: a combustible fraction (paper, cardboard, plastics, fabrics, etc.) and a noncombustible fraction (ferrous and nonferrous metals, glass, ceramics, etc.). There are no data, however, concerning toluene emissions from municipal incineration, but toluene is probably destroyed with over 99.9% efficiency (MacDonald *et al.* 1977). In formulated products using toluene as a solvent, it is probably sometimes disposed of directly as municipal waste. Although no data were available on the total loading of toluene to landfills, it has been detected in

Table 3-9. Toluene Distribution in POTWs and Sludge, Selected Urban Sites<sup>a</sup>

Plant	Average Flow (10 <sup>6</sup> l/day)	Concentrations (µg/l)		
		Influent	Effluent	Sludge
1	340	28	4	NAd
2	30	5	3	336
3	42	15	1	54
4	320	36	0	984
5	83	37	0	199
6	27	191	20	423
7	190	15	1	4615
8	87	229	288	7635
9	200	8	0	1100
10	87	12	<1	3000
11	160	50	2	503
12	150	23	7	14652
13	64	10	<1	9500
14	53	73	1	26800
15	27	4	1	927
16	550	33	1	418
17	57	72	2	833
18	240	34	<1	31
19	260	60	3	32
20	450	22	<1	53
Median Values		30.5	1	833

Source: EPA, 1980e.

<sup>a</sup>Percentage of flow contributed by industrial sources ranges from <1 to 35%.

<sup>b</sup>Composite grab samples, taken once every four hours, for 24 hours.

<sup>c</sup>Included primary and secondary sludge; grab sample.

<sup>d</sup>Not available



Table 3-10. Toluene Materials Balance: Municipal POTWs and Refuse (kkg/yr)

Source	Input	Air	Land	Water
POTW <sup>a</sup>	1100 <sup>b</sup>	960 <sup>c</sup>	100 <sup>d</sup>	37 <sup>b</sup>
Urban Incineration Landfill	unknown unknown	unknown 800 <sup>e</sup>	unknown unknown	unknown

<sup>a</sup>Publicly Owned Treatment Works.

<sup>b</sup>Figures calculated from EPA data (see Table 3-9): based on 10<sup>11</sup> l/day total POTW flow and median values for influent (30.5 µg/l) and effluent (1 µg/l) toluene concentrations.

<sup>c</sup>Mathematical difference between Input and Land and Water values.

<sup>d</sup>Based on a median value for wet sludge loading of toluene, 833 µg/l; wet sludge is 95% water by weight; 6.0 x 10<sup>6</sup> kkg dry sludge produced annually (EPA, 1979i; see Table 3-9).

<sup>e</sup>Based on 0.8 x 10<sup>6</sup> kkg/yr total hydrocarbons released from solid waste (EPA, 1979b); 0.1% toluene (SCQAMD, 1979).

air samples at a few sites (EPA 1980a). It is possible to estimate the amount of toluene released to the atmosphere, based on  $0.8 \times 10^6$  kkg/yr total hydrocarbons released from solid waste (EPA 1977b). Assuming that toluene comprises 0.1% of total hydrocarbons (SCQAMD 1979), a total release of 800 kkg toluene/yr is estimated (see Table 3-10).

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## 4.0 FATE AND DISTRIBUTION OF TOLUENE IN THE ENVIRONMENT

### 4.1 INTRODUCTION

The following section describes the pathways of toluene into the environment. The toluene releases from all known sources to the three physical media (air, soil and water) are traced through the environment to the human and biotic receptors. First, data on the physical, chemical, and biological characteristics of toluene are reviewed. The pathways and processes that result in transfer of toluene from one medium to another are analyzed. One method of doing this is a simple "partitioning" model, supplemented by consideration of the relative rates of the transfer processes. The next step is to evaluate major fate processes, such as chemical transformation, that may occur in the media of interest in which toluene is most likely to reside. The processes considered include chemical transformation and biodegradation within the media of interest.

The loading rates, intermedia transfer processes, and intramedia transformation/degradation processes are then used to estimate probable ranges of concentration of toluene in the environmental media. This is done by calculations involving "single compartment" models and by the U.S. EPA's EXAMS (Exposure Analysis Modeling System) model. The final step is to summarize the critical pathways, ranges of concentrations of the pollutant in environmental media, and compare these with the available monitoring data.

For toluene, the results of the materials balance analysis indicate the estimated environmental releases are predominantly to the air (99% or 1,100,000 kkg), the remaining 0.2% is discharged to water or disposed of on land.

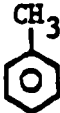
The fate of toluene released to all three environmental media--air, soil, water--is considered in the fate analysis in this section.

### 4.2 PHYSICAL, CHEMICAL, AND BIOLOGICAL CHARACTERISTICS OF TOLUENE

Toluene is an organic chemical whose physical and chemical characteristics have been relatively well documented. Table 4-1 summarizes the physico-chemical data that are directly relevant to the partitioning and movement of toluene in the environment, and additional basic information on properties of the bulk chemical that may be useful in evaluating fate in particular situations (e.g., spills).

Toluene is moderately volatile as evidenced by the equilibrium vapor pressure of 29 Torr at 25°C. However, the water solubility (535 mg/l) indicates that aqueous media are also important. The low values of the partition coefficients and bioconcentration factor in Table 4-1 suggest that toluene is less likely to accumulate in soil, sediment, or biotic environmental compartments than in air or water.

TABLE 4-1. PHYSICAL-CHEMICAL PROPERTIES OF TOLUENE  
RELATED TO ENVIRONMENTAL DISTRIBUTION

<u>Property</u>	<u>Value</u>	<u>Reference</u>
Molecular Formula	C <sub>7</sub> H <sub>8</sub>	
Molecular Structure		
Molecular Weight	92.13 g	Weast (1975)
Melting Point, °C	-95	Weast (1975)
Boiling Point, °C	110.6	Weast (1975)
Density, g/ml	0.8669 at 20°C	Weast (1975)
Water Solubility, mg/l	470 at 16°C	Verschueren (1977)
	515 at 20°C	Verschueren (1977)
	535 at 25°C	Callahan <u>et al.</u> (1979)
Vapor Pressure, Torr	22 at 20°	Verschueren (1977)
	29 at 25°C	Callahan <u>et al.</u> (1979)
	37 at 30°C	Sax (1979)
	40 at 31.8°C	Verschueren (1977)
Saturation Vapor	110 at 20°C	Verschueren (1977)
Concentration, g/m <sup>3</sup>	184 at 30°C	Verschueren (1977)
Octanol: Water		
Partition Coefficient	490	Callahan <u>et al.</u> (1979)
Organic Carbon		
Partition Coefficient (K <sub>oc</sub> )	339 at 25°C	SRI (1980)
Bioconcentration Factor (K <sub>p</sub> )	102 at 25°C	SRI (1980)



The toluene ring can be attacked by highly reactive species, such as hydroxyl radical or ozone, which may be present in the environment. Reaction with hydroxyl radical is an important environmental fate process.

Biological degradation of toluene can be accomplished by both individual species and mixed microbial populations isolated from various environmental media. Biodegradation is indicated as a possibly important intramedia fate process for both soil and water systems. Proper conditions to support these processes must hold, however.

#### 4.3 LEVELS MONITORED IN THE ENVIRONMENT

Monitoring data for concentrations of toluene in the environment have been collected and analyzed for air and water; data relating to concentrations in soil and biota are not as readily available. Literature reviews and the STORET Water Quality Information System were the main sources of monitoring data for toluene. This section describes specific monitoring data for toluene concentrations in various media.

##### 4.3.1 Water Concentrations

This section presents monitoring data of toluene concentrations in drinking and well waters, and ambient and effluent waters.

##### 4.3.1.1 Drinking and Well Waters

In several U.S. EPA surveys of the nation's drinking water, toluene has been detected in both raw and finished drinking supplies. Table 4-2 lists mean values and ranges of toluene concentrations in surface supplies.

Data collected in ten U.S. cities showed that toluene was detected in six of the ten supplies. Only two of the six cities where toluene was detected had levels above the detection limit; these concentrations were 0.1  $\mu\text{g/l}$  (Cincinnati, OH); 0.7  $\mu\text{g/l}$  (Philadelphia, PA). The remaining four, Tucson, AZ; Lawrence, MA; Grandforks, ND; and Terrebonne Parish, LA showed a wide distribution of toluene across the country (U.S. EPA 1975) (Table 4-2).

The National Organic Monitoring Survey (NOMS) was conducted in three phases. During Phase I, however, toluene was not measured. Data collected in Phases II and III do show concentrations of toluene in 1 of 111 and in 3 of 11 finished-water supplies, respectively. No quantitative value of toluene was given for Phase II, and of the 3 finished water samples in Phase III, only two actual concentrations were given: 0.5 and 19  $\mu\text{g/l}$  (U.S. EPA 1978).

TABLE 4-2. TOLUENE CONCENTRATIONS IN SURFACE SUPPLIES  
OF DRINKING WATER

<u>Location or Study</u>	<u>Mean (ug/l)</u>	<u>Range or Observation (ug/l)</u>	<u>Reference</u>
Cincinnati, OH		0.1	U.S. EPA (1975)
Philadelphia, PA		0.7	U.S. EPA (1975)
Tucson, AZ		D	U.S. EPA (1975)
Lawrence, MA		D	U.S. EPA (1975)
Grand Forks, ND		D	U.S. EPA (1975)
Terrebonne Parish, LA		D	U.S. EPA (1975)
Waterford, NY	5.2	ND-19	Kim and Stone (1979)
Niagara Falls, NY	0.22	0.005-0.6	Kim and Stone (1979)
New Orleans, LA			
finished water		1.51	Dowty <u>et al.</u> (1975)
deionized, filtered		3.00	
<u>NOMS Data</u>			
Phase II	Detected in 1/111 supplies		U.S. EPA (1978)
Phase III			
City A		D	
City B		0.5	
City C		19	
Cities D-K		ND	
<u>CWSS Data</u>			
3 surface supplies	2.5	<0.5-6.1	Brass (1981)
97 surface supplies		ND	Brass (1981)
Tuscaloosa, AL		D	Bertsch <u>et al.</u> (1975)
Washington, DC		1.0	Scheiman <u>et al.</u> (1974)
Miami, FL		D	Coleman <u>et al.</u> (1976)
Ottumwa, IA		D	Coleman <u>et al.</u> (1976)
Evansville, IN		D	Kleopfer (1976)
Kansas City, KS		ND	Kleopfer (1976)
Johnson County, KS		ND	Kleopfer (1976)
New Orleans, LA		ND-0.1	Keith <u>et al.</u> (1976)

TABLE 4-2. TOLUENE CONCENTRATIONS IN SURFACE SUPPLIES  
OF DRINKING WATER (Continued)

<u>Location or Study</u>	<u>Mean (<math>\mu\text{g/l}</math>)</u>	<u>Range or Observation (<math>\mu\text{g/l}</math>)</u>	<u>Reference</u>
Kirkwood, MO		ND	Kleopfer (1976)
Jefferson City, MO		D	Kleopfer (1976)
Cincinnati, OH		0.1	Coleman <u>et al.</u> (1976)
Cincinnati, OH		D	Kopfler <u>et al.</u> (1975)
Philadelphia, PA		D	Suffett and Radziul (1975)
Philadelphia, PA		0.7	Coleman <u>et al.</u> (1976)
Houston, TX		D	Bertsch <u>et al.</u> (1975)
Seattle, WA		D	Coleman <u>et al.</u> (1976)

- 
- Mean value for surface supplies for data  $> D = 1.3 \mu\text{g/l}$  ( $n=27$ ),  
assumes  $D = 0.1 \mu\text{g/l}$ , and using mean where given.
  - Mean value of all data = 0.15 ( $n=236$ )  
assumes  $D = 0.1 \mu\text{g/l}$  and  $ND = 0$ .
  - Mean value of all data = 0.24 ( $n=236$ )  
assumes  $D = 0.1 \mu\text{g/l}$  and  $ND = 0.1 \mu\text{g/l}$
- 

Notes:

D = Detected but not quantified.  
ND = Not detected.

The Community Water Supply Survey (CWSS) conducted by the U.S. EPA tested 452 water utilities, representing 106 surface and 330 ground-water supplies. There is concern over the possibility of false negatives and underestimated concentrations due to a 1-2 year delay in analysis. This is especially possible in the case of toluene, a volatile, low molecular weight aromatic. Toluene was detected in 3 out of 100 surface water supplies with a median concentration of 0.85 and a mean of 2.5  $\mu\text{g/l}$  for positive values. It was detected in 2 out of 307 groundwater supplies with measured concentrations of  $< 0.5$  and 0.62  $\mu\text{g/l}$ .

Dowty and coworkers (1975) examined the drinking water sources in the New Orleans area for the occurrence and origin of aromatic and halogenated aliphatic hydrocarbons. Three drinking water sources were examined: (1) a New Orleans municipal water treatment facility before, during, and after processing; (2) a commercial source of bottled artesian water; and (3) a commercial source of deionized charcoal-filtered finished water (Table 4-2). Relative concentrations at the treatment facility were computed from gas chromatographic data. They show toluene levels at 0.67  $\mu\text{g/l}$  in the Mississippi River water at the facility influent, 0.57  $\mu\text{g/l}$  in the clarifier effluent stage of treatment, and 1.51  $\mu\text{g/l}$  in the finished water. The higher relative percent of toluene in finished water appeared after the chlorination procedure. Concentrations of 6.11  $\mu\text{g/l}$  were found in the commercially bottled artesian water and 3.00  $\mu\text{g/l}$  in the commercial deionized charcoal-filtered water.

In 1978, the New York State Department of Health and the United States Geological Survey examined 39 wells for 112 organic chemical contaminants in groundwater supplies (Table 4-3). Toluene was one of the 10 most commonly found organic chemicals detected in 33 (or 85%) of the wells tested. The maximum level of toluene detected was 10  $\mu\text{g/l}$  (Kim and Stone 1979). No other data were provided.

The Kim and Stone (1979) study also included data from an organic contamination reconnaissance of 30 aquifers and found toluene in samples from 25. Concentration values for the individual contaminants were not given; however, the sum of the concentrations of organic contaminants was never  $>222 \mu\text{g/l}$  in 8 samples, and a mean of 0.22  $\mu\text{g/l}$ .

Eighty-seven percent of the observations recorded in STORET (U.S. EPA 1980) for toluene in well water, which may be used for human consumption, are less than the commonly-used detection limit of 5  $\mu\text{g/l}$ . Only 3 of the 143 observations recorded exceeded a concentration of 25  $\mu\text{g/l}$ ; these ranged from 42 to 100  $\mu\text{g/l}$ .

TABLE 4-3. TOLUENE CONCENTRATIONS IN GROUNDWATER  
SUPPLIES OF DRINKING WATER

<u>Location</u>	<u>Range or Observation</u> ( $\mu\text{g/l}$ )	<u>Reference</u>
New Orleans bottled artesian	6.11	Dowty <u>et al.</u> (1975)
New York State 33 wells	Maximum = 10	Kim and Stone (1979)
6 wells	ND	Kim and Stone (1979)
25 aquifers	Toluene Data not Separated	Kim and Stone (1979)
5 aquifers	ND	Kim and Stone (1979)
STORET Wells	<div style="border: 1px solid black; border-radius: 50%; width: 40px; height: 40px; display: flex; align-items: center; justify-content: center; margin: 0 auto;"> 87% &lt; 5 </div> Maximum = 100	STORET (1980) STORET (1980)
CWSS Supply A	< 0.5	Brass (1981)
Supply B	0.62	Brass (1981)
305 Supplies	ND	Brass (1981)

Notes:

ND = Not Detected

Obviously, the type of treatment affects the concentration of toluene in finished drinking water. Using closed-loop stripping analysis (CLSA), Coleman et al. (1976) evaluated the effect of granular activated carbon (GAC) on the removal of organic contaminants from drinking water. The documented results for twenty-five components of the CLSA for GAC influents and effluents on the initial startup, toluene was detected at 29 ng/l in the influent and at 18 ng/l in the effluent, when approximately one million gallons of water passed through the filter. After one month, with the same filter in place, sampling indicated the presence of toluene in the influent at 10 ng/l and in the effluent at 5 ng/l.

#### 4.3.1.2 Ambient and Effluent Waters

The STORET system appears to be the primary data base for information regarding toluene in ambient and effluent waters. Table 4-4 exhibits a percentage distribution of all ambient and effluent concentrations of toluene for the major river basins and the United States.

##### Ambient Waters

The STORET (U.S. EPA 1980) monitoring data on ambient waters reflect sampling activities in 32 states, with results that show extremely low concentrations. Of the 453 ambient concentrations recorded, 86 or 19% are unremarked values; of these, 48% is no higher than 10 µg/l (78% is no higher than 50 µg/l, and 86% no higher than 100 µg/l). Remarked values (detection limits) range from 0 to 1000 µg/l and unremarked values ranged from 0 to 3900 µg/l. A detection limit of 0 is remarked as material analyzed for but not detected. The most frequently used detection limits are 5 and 10 µg/l. Table 4-5 exhibits unremarked (above the detection limit) monitoring data on toluene concentrations in 17 states.

Shelton and Hites (1978) identified nearly 100 compounds from Delaware River water samples taken in 1976 and 1977. The particular segment of river sampled is located amidst a heavily-industrialized area (chemical manufacturing plants) and is a direct source of drinking water for several cities in the Philadelphia metropolitan area. Toluene was detected in the vapor stripping analysis of the October water samples; quantification was not possible, however. Toluene was not detected in water samples collected during the winter and summer seasons.

##### Effluent Waters

STORET monitoring data for toluene in effluent waters reflect sampling activities in 24 states. Of 510 recorded concentrations, the majority of effluent concentrations recorded are remarked, 60%; the most frequently used detection limits are 0.01, 1 and 5 µg/l.

TABLE 4-4. PERCENTAGE DISTRIBUTION OF AMBIENT AND EFFLUENT TOLUENE CONCENTRATIONS FOR MAJOR RIVER BASINS AND THE UNITED STATES<sup>a</sup>

Major River Basin	Concentration (µg/l)									
	Number of Observations	Ambient <sup>b</sup>				Number of Observations	Effluent <sup>c</sup>			
		Percentage of Observations					Percentage of Observations			
		≤10	10.1-100	100.1-1000	>1000		≤10	10.1-100	100.1-1000	>1000
Northeast	1		100			103	84	9	4	3
North Atlantic	14	100				48	88	6	6	
Southeast	110	93	4	4		100	87	10	3	
Tennessee River	16	81	6	6	6	28	96	4		
Ohio River	54	98		2		70	84	11	3	1
Lake Erie	2		100							
Upper Mississippi	18	67	22	11		64	69	30	2	
Lake Michigan	30	20	77	3		6	100			
Missouri River	34	44	53	3		16	100			
Lower Mississippi	8	88		13						
Colorado River	3	100				1	100			
Western Gulf	15	100				1	100			
Pacific Northwest	80	99	1			45	91	7	2	
California	5	100								
Great Basin	1	100								
Puerto Rico	1	100								
Unlabelled	1	100								
UNITED STATES	393	83	14	3		482	85	11	3	1

Source: STORET data (U.S. EPA 1980).

<sup>a</sup>This compilation includes both remarked and unremarked values. Remarked values are generally below the detection limit. The detection limit is included in the distribution. Some observations are omitted during aggregation if station labeling information is incomplete (e.g., no entry of latitude/longitude for monitoring station).

<sup>b</sup>407 ambient stations reporting.

<sup>c</sup>229 effluent stations reporting.

TABLE 4-5. RANGES OF UNREMARKED VALUES OF AMBIENT TOLUENE CONCENTRATIONS FROM MONITORING DATA IN SEVENTEEN STATES

<u>State</u>	<u>Number of Observations</u>	<u>Range of Unremarked Values (<math>\mu\text{g/l}</math>)</u>
Alabama	3	42 - 3900
California	12	0.1 - 1
Florida	1	13
Illinois	7	1 - 5
Indiana	1	2
Iowa	5	14 - 390
Kansas	3	28 - 46
Kentucky	1	285
Minnesota	2	1
Missouri	21	3 - 150
Nebraska	6	14 - 120
New Jersey	2	2 - 15
North Carolina	10	1 - 374
Pennsylvania	1	2
South Carolina	4	8 - 490
Tennessee	1	2
Washington	6	0.0 - 24
Overall	86	0.0 - 3900

Source: STORET data (U.S. EPA 1980).



Jungclaus and coworkers (1978) analyzed wastewater, receiving water, and sediments from a specialty chemicals manufacturing plant for organic compounds. Wastewater and receiving water samples were gathered from November 1975 to September 1976; sediment samples were gathered from January 1976 to September 1976. Toluene was identified in receiving waters through vapor stripping experiments only and could not be quantified. In the industrial wastewaters, toluene concentrations ranged from 13 to 20  $\mu\text{g/l}$ , based on direct aqueous injection. Toluene was not detected in sediment samples.

In 1979, Feiler conducted a pilot study of two publicly owned treatment works (POTWs) to characterize the impact of toxic pollutants on POTW operations. Plant A handled more industrial wastewater than Plant B, which reflected a lower incidence of organic pollutants than the former. Toluene was detected in each of the 41 influent samples analyzed at Plant A, and was detected in 95% of the 40 final effluent samples analyzed. At Plant B, toluene was detected in 32, or 76%, of the 42 influent samples and in 71% of the 41 final effluent samples. Samples from the influent point of Plant A showed a maximum toluene concentration of 440  $\mu\text{g/l}$  and median of 13  $\mu\text{g/l}$ . At the influent point of Plant B, the maximum toluene concentration was 37  $\mu\text{g/l}$  and the median was 10  $\mu\text{g/l}$ .

A survey of two municipal wastewater treatment plants for toxic substances was conducted in the state of Ohio at Muddy Creek and at Dayton (U.S. EPA 1977). The plant at Muddy Creek treated primarily domestic wastewater; and the plant at Dayton combined industrial-domestic influent. At the Muddy Creek plant, toluene concentrations were measurable in 3 of the 15 influent samples taken. Levels ranged from 1 to 5  $\mu\text{g/l}$ . Toluene concentrations, measurable in 21% of the 14 final effluent samples, were 1  $\mu\text{g/l}$ . At the more industrial treatment plant of Dayton, toluene concentrations, measurable in 13 of the 15 influent samples, showed a range of 8-150  $\mu\text{g/l}$ . In the final effluent, toluene concentrations, measurable in 36% of the final effluent samples, ranged from 1 to 10  $\mu\text{g/l}$ .

As with ambient sampling data, 17 states show unremarked data from monitoring of toluene (Table 4-6). The range of unremarked value was observed to be ND to 4600  $\mu\text{g/l}$ . Table 4-4 exhibits a percentage distribution of all effluent concentrations of toluene by major river basin in the United States.

In 1977, Versar, Inc. calculated the gross annual discharges of toluene to the nation's waters for 1976. The monitoring data obtained from the U.S. EPA's Effluent Guidelines Division are presented in Table 4-7. The concentrations of toluene in these effluents ranged from 11 to 100,000  $\mu\text{g/l}$ , although 9 of the 12 (75%) effluents reported were <40  $\mu\text{g/l}$ .

TABLE 4-6. RANGES OF UNREMARKED VALUES OF EFFLUENT TOLUENE CONCENTRATIONS FROM MONITORING DATA IN SEVENTEEN STATES

<u>State</u>	<u>Number of Observations</u>	<u>Range of Unremarked Values (<math>\mu\text{g/l}</math>)</u>
Alabama	1	18
Connecticut	14	0.8 - 3300
Florida	1	580
Georgia	26	1 - 140
Idaho	1	242
Illinois	7	0 - 2
Kansas	5	2 - 1050
Kentucky	3	1 - 4600
Maine	2	1 - 39
Missouri	62	1 - 200
New Jersey	16	0.1 - 200
New York	25	0.2 - 1040
North Carolina	1	8
Ohio	26	1 - 101
Oregon	4	3 - 15
Virginia	3	3.5 - 46
Washington	8	0 - 20
Overall	205	0 - 4600

Source: STORET data (U.S. EPA 1980).

TABLE 4-7. CONCENTRATIONS OF TOLUENE IN INDUSTRIAL EFFLUENTS

<u>Industry</u>	<u>Mean Concentration<sup>a</sup></u> ( $\mu$ g/l)	<u>Number of Plants in 1976</u>
Wood Preserving	1620	30
Wood Furniture Finishing	100,000	4000
Steam Electric Generating Station		405
Cooling Cycle Effluents	58	
Ash Pond Effluents	35.5	
Treatment Plant Effluents	<u>22</u>	
TOTAL	115.5	
Petroleum Refining	35	<sup>b</sup>
Coal Mining	11	5673
Organic Chemical Mfg.	<sup>c</sup>	<sup>b</sup>
Textiles		
Woven Fabric Dye Finish	13	187
Wool Dye Finish	12.5	28
Knit Fabric Dye Finish	19.2	69
Nonferrous Metals		
Primary Aluminum	32	31
Secondary Copper	34.6	12

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<sup>a</sup>Versar Inc. (1977).

<sup>b</sup>Calculated on the amount of product handled.

<sup>c</sup>Data given as total waste amount per industry sector, not as effluent concentrations.

Analysis of toluene during wastewater treatment was performed by Feiler (1980), while Levins et al. (1980) considered, in detail, toluene levels in wastewaters from various source-types for 4 cities. The Feiler study included data for 20 cities on toluene concentrations in influents, primary and secondary process effluents and sludges, and in digested and combined sludges. These data are summarized in Table 4-8.

The data of Levins et al. (1980) indicate that wastewater toluene levels may be equally high from both commercial and industrial sources and these levels are 1-2 orders of magnitude above those found in residential wastewaters. The combined influent levels from both studies cover the same range. Effluent levels tended to be below 1  $\mu\text{g/l}$  while sludge concentrations were in the 10-27,000  $\mu\text{g/l}$  range.

#### 4.3.1.3 Rainwater and Other Precipitation

None of the available literature reported the level of toluene in rainwater, snow, or sleet.

#### 4.3.2 Concentrations in Sediment

STORET data (U.S. EPA 1980) record less than 100 observations of toluene concentrations in sediment. Of these observations, 91% had toluene concentrations  $\leq 10 \mu\text{g/kg}$  dry weight; 7% of the observations were  $>500 \mu\text{g/kg}$ . The recorded concentrations reflect conditions for nine states in the South and West: Texas, Louisiana, California, Oregon, Washington, Idaho, New Mexico, Nevada, and Alabama. The higher concentrations were observed in the vicinity of an industrial area of San Francisco.

#### 4.3.3 Concentrations in Foods

##### 4.3.3.1 Fish Tissue

Sampling data for toluene in fish tissue are quite limited. At present, only six states have fish tissue data maintained in the STORET system. These states are: Oregon, Texas, Louisiana, Idaho, Washington, Alaska, and California. Of the 59 observations, the maximum concentration of toluene in fish tissue is 35  $\text{mg/kg}$  wet weight and the average concentration is 1  $\text{mg/kg}$ . Ninety-five percent of the samples are  $<1 \text{ mg/kg}$ .

##### 4.3.3.2 Other Foods

Toluene has been identified but not quantified in several nuts: roasted filberts (Kinlin et al. 1972), and peanuts and macadamia nuts (Crain and Tang 1975, Walradt et al. 1971). Stevens et al. (1967) found toluene in grape essence and Nursten and Sheen (1974) detected toluene in cooked potatoes.

TABLE 4-8. CONCENTRATIONS OF TOLUENE IN WASTEWATERS  
AND SLUDGES FROM POTWs

<u>Study</u>	<u>Mean Values</u>	<u>Range of Means for Each City</u>	<u>Reference</u>
<u>Four-city Study</u>			
<u>Influents</u>			
Residential	2.6	ND-11.9	Levins <u>et al.</u> (1980)
Commerical	11.0	1.1-27.6	Levins <u>et al.</u> (1980)
Industrial	52.3	5.4-123.8	Levins <u>et al.</u> (1980)
Combined	25.6	1.9-60.2	Levins <u>et al.</u> (1980)
Tap Water	0.3	ND-1.0	Levins <u>et al.</u> (1980)
<u>Twenty-city Study</u>			
Combined Influent	44.4	4-229	Feiler (1980)
Effluents	3.05 <sup>a</sup>	ND-288	Feiler (1980)
Primary Sludges	1906	40-8810	Feiler (1980)
Secondary Sludges	2566	3-14,652	Feiler (1980)
Combined Sludges	3815	54-26,857	Feiler (1980)
Digested Sludges	1230	124-2524	Feiler (1980)
Percent Removal	90	40-100	Feiler (1980)

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<sup>a</sup>Mean calculated assuming ND=0 and excluding the one effluent value that exceeded the influent, also the only value in the hundreds of µg/l range.

#### 4.3.4 Concentrations in the Atmosphere

Atmospheric toluene can occur as the result of contributions from stationary sources (refineries, chemical plants, solvent users, and gasoline marketing and distribution facilities), mobile sources (vehicles), and localized sources (tobacco smoke). Vegetation has been known to emit hydrocarbons, especially terpenes, but it is a negligible source of toluene.

##### 4.3.4.1 Contributions from Stationary and Mobile Sources

Toluene concentrations in the atmosphere of urban areas (including areas with high chemical production), and rural and remote areas from various studies beginning as early as 1963 are summarized in Table 4-9. The urban areas with high chemical production had average toluene concentrations ranging from 0.19 to 59.52  $\mu\text{g}/\text{m}^3$ . Because of the concern about motor vehicle emissions, Los Angeles is the most studied urban area. Data on this city show toluene concentrations decreasing since the 1963-65 period when Leonard *et al.* (1976) recorded concentrations at 226  $\mu\text{g}/\text{m}^3$ . In 1979, Singh *et al.* recorded an average toluene concentration of 45  $\mu\text{g}/\text{m}^3$  in this city. This average concentration is comparable with that of other urban areas. Similar concentrations of toluene were recorded for both urban areas and areas with high chemical production--33  $\mu\text{g}/\text{m}^3$  in Phoenix, AZ, and 34  $\mu\text{g}/\text{m}^3$  in Denver, CO. Atmospheric toluene concentrations in rural and remote areas are generally <1  $\mu\text{g}/\text{m}^3$ .

Sexton and Westburg (1980) monitored ambient air near an automobile painting plant at Jamesville, WI, to investigate the effect of painting emissions on ambient ozone levels. From an individual hydrocarbon identification analysis during fumigation by painting emissions, the atmospheric toluene concentration within 1 mile of the plant was 601  $\mu\text{g}/\text{m}^3$ . At three sampling stations (800 feet above the ground) downwind of the automotive plant, toluene concentrations were measured at 75.5  $\mu\text{g}/\text{m}^3$  4 miles from the plant, 84.5  $\mu\text{g}/\text{m}^3$  at 7 miles, 64.5  $\mu\text{g}/\text{m}^3$  at 9 miles, and 55.5  $\mu\text{g}/\text{m}^3$  at 11 miles. These concentrations range from 10 to 15 times higher than the background toluene concentration of 5.5  $\mu\text{g}/\text{m}^3$  approximately 1 mile northeast of the automotive plant.

Toluene was the most abundant aromatic hydrocarbon, constituting 35-40% of the total concentration of aromatics, when Lonneman *et al.* (1968) conducted gas chromatographic analyses in Los Angeles in 1966 to relate aromatic hydrocarbon levels to atmospheric photochemical reactivity. A total of 136 samples was collected in downtown Los Angeles, Pasadena, Lennox, and West Los Angeles. The average concentration of toluene was 0.14  $\text{mg}/\text{m}^3$  and the maximum was 0.49  $\text{mg}/\text{m}^3$ . The average and maximum concentrations of the total aromatics were 0.41  $\text{mg}/\text{m}^3$  and 1.26  $\text{mg}/\text{m}^3$ , respectively.

TABLE 4-9. TOLUENE CONCENTRATIONS IN THE ATMOSPHERE OF  
URBAN, RURAL AND REMOTE AREAS

<u>Location</u>	<u>Concentrations (<math>\mu\text{g}/\text{m}^3</math>)</u>		<u>Reference</u>
	<u>Average</u>	<u>Range</u>	
URBAN AREAS			
<u>With High Chemical Production</u>			
South Charles, WV	0.19	0.15 - 0.27	Pellizzari (1979)
Birmingham, AL	7.51	0.80 - 17.96	Pellizzari (1979)
Baton Rouge, LA	0.61	0.11 - 0.88	Pellizzari (1979)
Houston, TX	5.86	0.80 - 11.22	Pellizzari (1979)
Magma, UT	1.30	0.88 - 1.65	Pellizzari (1979)
Upland, CA	27.69	2.99 - 56.53	Pellizzari (1979)
El Paso, TX	18.58	0.19 - 71.85	Pellizzari (1979)
El Dorado, AK	28.27	9.58 - 52.20	Pellizzari (1979)
Elizabeth, NJ	<u>59.52</u>	7.20 - 149.60	Pellizzari (1979)
Average	17		
<u>Other Urban Areas</u>			
Phoenix, AZ	33.05	2.07 - 148.34	Singh <u>et al.</u> (1979)
Oakland, CA	11.91	0.57 - 64.88	Singh <u>et al.</u> (1979)
Los Angeles, CA	44.89	4.37 - 204.45	Singh <u>et al.</u> (1979)
Denver, CO	23.52	1.09 - 92.74	Singh <u>et al.</u> (1980)
Houston, TX	38.94	3.92 - 247.5	Singh <u>et al.</u> (1980)
St. Louis, MO	5.73	0.39 - 24.32	Singh <u>et al.</u> (1980)
Riverside, CA	21.87	1.7 - 75.66	Singh <u>et al.</u> (1980)
Los Angeles, CA (1963-65)	225.97	a	Leonard <u>et al.</u> (1976)
Los Angeles, CA (1971)	191.50	a	Leonard <u>et al.</u> (1976)
Los Angeles, CA (1973)	84.26	a	Leonard <u>et al.</u> (1976)
Los Angeles, CA - Downtown (1967)	113	37 - 189	Altshuller <u>et al.</u> (1971)
Los Angeles, CA - Suburb (1967)	52.8	22 - 87	Altshuller <u>et al.</u> (1971)
Denver, CO	34.47	283.42 (max)	Russel (1977)
Lake Charles, LA	2.3	a	Harden <u>et al.</u>
Albany, NY	4.98	a	Altwicker <u>et al.</u> (1977)
Troy, NY	3.83	a	Altwicker <u>et al.</u> (1977)
Riverside, CA	<u>a</u>	34.47-68.94	Stephens (1973)
Mean for all Urban Areas (including data from 1977 on)	19		

TABLE 4-9. TOLUENE CONCENTRATIONS IN THE ATMOSPHERE OF  
URBAN, RURAL AND REMOTE AREAS (Continued)

<u>Location</u>	<u>Concentrations (<math>\mu\text{g}/\text{m}^3</math>)</u>		<u>Reference</u>
	<u>Average</u>	<u>Range</u>	
RURAL AND REMOTE AREAS			
Grand Canyon, AZ	Trace	Trace	Pellizzari (1979)
Camel's Hump, VT	3.71	a	Robinson <u>et al.</u> (1973)
Hell's Canyon, ID	1.13	a	Robinson <u>et al.</u> (1973)
Moscow Mt., ID	0.75	a	Robinson <u>et al.</u> (1973)
Point Reyes, CA	0.75	a	Robinson <u>et al.</u> (1973)
Brethway-Gunderson Hill, WA	0.38	a	Robinson <u>et al.</u> (1973)
Remote Air Masses <sup>b</sup>	a	0.2-57.45	Robinson <u>et al.</u> (1973)
Gabriel Mts., CA	ND		Stephens (1973)
Mean for Rural Areas <sup>c</sup>	1.0		

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<sup>a</sup>Information not supplied.

<sup>b</sup>Tropical, polar, and equatorial air masses, including pacific coast, and pacific and Atlantic inland masses.

<sup>c</sup>Assumed ND=0, Trace=0.1  $\mu\text{g}/\text{m}^3$  and excluded remote air masses.



Pilar and Graydon (1973) observed concentration variations related to automobile traffic by sampling simultaneously several locations in the urban Toronto area. The overall average concentration of toluene was calculated as  $115 \mu\text{g}/\text{m}^3$ , the maximum concentration was  $720 \mu\text{g}/\text{m}^3$  in Toronto, Canada. The times of maximum toluene concentration in downtown Toronto were similar to those found in Chicago and Los Angeles around 7:00 a.m., 3:00 p.m., and 9:00 p.m. In Toronto's Centre Island, where only official vehicles are allowed, concentrations of toluene were consistently lower. The air concentration ratio averaged to 2.6 for toluene when site data from the island and downtown Toronto were compared. One notable result of the Pilar and Graydon (1973) study was that the ratio of benzene to toluene was less in the atmosphere than in motor vehicle exhausts. The authors suggested that "the relatively high toluene:benzene ratio in gasoline vapor points to the possibility of direct evaporation of gasoline as a source."

In 1961, Altshuller and Bellar (1963), demonstrated that rapid repetitive analysis of small volume samples taken from polluted atmospheres are possible with gas chromatographs containing flame ionization detectors. Experiments in the downtown Los Angeles area showed that only a small fraction of the hydrocarbons present in the atmosphere are highly reactive in producing smog manifestations. Toluene concentrations ranged from  $0.10$  to  $0.23 \text{ mg}/\text{m}^3$ , with an average concentration of  $0.17 \text{ mg}/\text{m}^3$ .

In a later study, Altschuller et al. (1971) showed that atmospheric concentrations of toluene (along with other hydrocarbons) are largely associated with motor vehicle emissions. Variations in ratios throughout the day were considered consistent with the difference in rates of reactions of these individual hydrocarbons. This study compared a suburb of Los Angeles with the downtown area and determined extrapolated peaks of about  $77$  and  $180 \mu\text{g}/\text{m}^3$  in the diurnal curves, respectively. The nighttime levels in the suburb were between  $45$  and  $50 \mu\text{g}/\text{m}^3$ , while in the downtown area, they were about  $75$  to  $85 \mu\text{g}/\text{m}^3$ . The overall average values were  $113 \mu\text{g}/\text{m}^3$  for downtown and  $52.8 \mu\text{g}/\text{m}^3$  for the suburban area. The levels exceeded by 10% of the values were  $189$  and  $86.7 \mu\text{g}/\text{m}^3$  for the downtown area and the suburban area, respectively.

#### 4.3.4.2 Contributions by Vegetation

Volatile hydrocarbons are sometimes emitted by vegetation in significant amounts; the alkyl benzenes are often minor constituents of such emissions. Toluene, however, is emitted predominantly by a tropical tree, the tolu, from which it gets its name, and therefore significant amounts are not produced in the United States (NRC 1980).

#### 4.3.4.3 Contributions from Cigarettes

Measurements by several researchers cited in NRC (1980) indicated that the alkyl benzenes included in cigarette smoke occurred only in the smoke as combustion products, and were not found in the tobacco itself. The range of observations of the net yield of toluene from one cigarette was 46-164  $\mu\text{g}$  (Johnstone et al. 1962, Grob 1965). The NRC calculated that if 0.1 mg toluene is the net yield from one cigarette that the smoke would contain about 11,300  $\mu\text{g}/\text{m}^3$  and that "smoke filled rooms" could contain between 230 to 2300  $\mu\text{g}/\text{m}^3$ . These values are considerably higher than levels measured in urban areas as shown in Table 4-9.

#### 4.4 ENVIRONMENTAL FATE MODELING AND ANALYSIS

##### 4.4.1 EXAMS Modeling

The U.S. EPA's Exposure Analysis Modeling System (EXAMS) program is one approach to the integration of various intermedia transfer and in-tramedium transformation processes. The EXAMS model considers physical constants and reaction rate data for the chemical and the characteristics of various aquatic environments.

The environmental fate of toluene was modeled using four EXAMS scenarios: "clean" river, turbid river, oligotrophic lake, and a eutrophic lake. Toluene loading rates were selected as inputs to EXAMS. The highest was 1.0 kg/hr based on a maximum effluent level measured for toluene at a POTW. The second rate, 0.023 kg/hr, was representative of median toluene concentrations for 20 POTWs. The third loading rate, 0.04 kg/hr, is based on discharges from 62% of the pharmaceutical plants using toluene. Fate in all the scenarios were considered for all the rates. (The results will scale directly with the loading rate until/unless the water solubility is exceeded or some other environmental compartment saturates.) The fundamental difference between the river and lake scenarios is that the former are flowing systems so that downstream transport/dispersal appears as a major fate process. The turbid river has a fivefold higher level of suspended sediment than the "clean" river.

The eutrophic lake differs from the oligotrophic lake in that it has much higher (three orders of magnitude) bacterial populations, a higher organic carbon content of the sediment, as well as somewhat higher levels of suspended sediment.

The summary of results from running the EXAMS model is presented in Table 4-10. In the river systems, downstream export appears as the dominant fate process, carrying away >99% of the load. Volatilization is a less significant transport process, accounting for a loss of <1% of the load within the 54-minute residence time of the river "slice". In the oligotrophic lake system, the relative importance of export and volatilization is reversed; volatilization accounts for 90% of the removal and export for approximately 10%. In the eutrophic lake system,

volatilization is also more important than export (95% versus 0.2% of load). In this lake, however, EXAMS indicates that biodegradation may account for up to ~5% of the losses. In the river, removal will be determined primarily by physical processes, with waterborne export and volatilization the dominant removal processes. For these four scenarios, chemical transformation plays only a minor role (0.02-0.11%) in the mass balance of the lake and pond systems only.

For each of the four ecosystems, the EXAMS-calculated partitioning between water and sediments estimated that >94% of the toluene would be in the water column and <6% in the bottom sediments.

The water column concentrations predicted by EXAMS are <1 µg/l for all scenarios and discharge rates, with the exception of the pharmaceutical discharge to oligotrophic lake scenario, which resulted in concentrations of up to 5 µg/l.

For both river scenarios used in the EXAMS model, the current velocity is 0.93 m/sec, the depth of the water column is 3 meters, the width and length of the river segment are 100 and 3000 meters, respectively, and the water flow rate is  $2.41 \times 10^7 \text{ m}^3/\text{day}$ . In both turbid and clean rivers, over 99% of the toluene in the original flux into the river segment analyzed is passed onto the next segment, and <1% volatilizes or is biodegraded. The physical representation of an EXAMS river allows the use of an exponential decay function to solve for the number of river segments through which the toluene load must flow until some percentage (i.e., 99%) of the load either leaves the water compartment by biodegradation or volatilization.

The calculation is:

$$(\text{mass flux \% to next river segment})^n = 0.01$$

where n is the number of segments necessary to obtain a 99%-reduction in the initial loading of toluene to the river. Solving:

$$\begin{aligned} n \log (0.952) &= \log 0.01 \\ n &= 93.62 \end{aligned}$$

Because each EXAMS river segment is 3000 meters long, this distance is about 280,000 meters (170 miles); with a water velocity of 0.93 m/sec, about 3.5 days are necessary for this 99%-reduction to occur given the dimensions used for the EXAMS river. Similar calculations show that a reduction of 50% of the initial load occurs in 13 hours over a river stretch of about 42,000 meters (26 miles).

TABLE 4-10. RESULTS OF EXAMS MODELING OF THE ENVIRONMENTAL FATE OF TOLUENE DISCHARGE SCENARIOS

	<u>Rivers<sup>a</sup></u>		<u>Lakes</u>	
	<u>Clean</u>	<u>Turbid</u>	<u>Oligotrophic</u>	<u>Eutrophic</u>
<u>Compartment</u>	Percent in compartment in Steady State			
Bottom Sediments	1.82	5.23	6.08	2.24
Water Column	98.18	94.77	93.92	97.76
<u>Fate Process</u>	Percent removed by fate process at Steady State			
Waterborne Export	99.46	99.86	10.04	0.19
Volatilized	0.18	0.05	89.57	94.97
Biodegraded	0.36	0.09	0.31	4.81
Chemically Transformed	0	0	0.08	0.02

Water Column Concentrations ( $\mu\text{g/l}$ ) for Discharge Scenarios

1. POTW--maximum observed effluent concentration of 288  $\mu\text{g/l}$ . At flow of 87 x  $10^6$  l/day (23 MGD) the loading rate is 1 kg/hr.<sup>b</sup>  
0.12      0.03
2. POTW--median observed effluent concentration for 20 POTW of 1  $\mu\text{g/l}$ . At high flow of 550 x  $10^6$  l/day (150 MGD) the loading rate is 0.023 kg/hr.  
0.003      0.0007
3. Pharmaceuticals Industry--load of 24 kkg/hr for 250 plants. Based on 62% occurrence in effluents, 250 of 400 plants had a loading rate of 0.04 kg/hr.<sup>c</sup>  
0.005      0.001      4.6      0.86

<sup>a</sup>River volume flow rate = 300 m<sup>3</sup>/sec.

<sup>b</sup>See Table 3-1 in Materials Balance for data.

<sup>c</sup>See Table 3-5 in Materials Balance for data, also personal communication, Acurex (1980).

#### 4.4.2 Intermedia Transfers

##### 4.4.2.1 From Air Medium to Surface Waters or Land

Based on the materials balance analysis, air is the dominant receiving medium for toluene emissions. Furthermore, the vapor pressure of toluene is sufficiently high (see Table 4-1) so that this chemical will have a strong tendency to remain in the atmosphere as a vapor. Dry deposition is not a plausible removal process for atmospheric toluene vapors because the vapor pressure of toluene is too high to attach to aerosols (Jungclauss 1978).

Toluene residing in the air is not transported to the surface by dry deposition or by precipitation. Atmospheric oxidation of toluene removes 50% of the compound in less than 2 days (see Section 4.4.3.1). Because of this rapid removal rate, toluene will most likely not remain in the atmosphere long enough to be removed by air to surface transfer mechanisms.

##### 4.4.2.2 Water

###### Water to Air

Volatilization is an important process in the depletion of toluene from water. A model was used to determine the volatilization half-life of toluene in water (a 1-meter deep stream with a velocity of 1 m/sec). The half-life was 5 hours corresponding to a distance of ~18 kilometers downstream from the discharge. To remove 90% of the discharged toluene requires ~15 hours and a distance of over 50 kilometers. These calculations are described in Appendix E.

###### Water to Sediment

As shown by the EXAMS model, some toluene partitions to the sediment compartment (2-6%). The log octanol-water partition coefficient (2.69) shows that toluene has some affinity to bind to the sediment. However, the extent to which toluene is transferred depends on the sorption capability of the particular sediment, which, in turn, depends on the organic carbon content and other characteristics.

##### 4.4.2.3 Soil

###### Soil to Air

Wilson et al. (1980) conducted laboratory experiments on the volatilization of toluene from soil. These experiments indicated that, in a sandy soil system, on the order of 40-60% of toluene applied to the surface will volatilize.

Volatilization characteristics from soil surfaces low in adsorbing materials are expected to be similar. In the case of municipal sludges, volatilization may be significantly retarded because of the sorption propensity of toluene for this highly organic material.

No volatilization rate measurements for soil to air were found in the literature. However, using the Dow method described by Thomas (1981) a half-life for volatilization from soil of about 9 seconds was estimated. This half-life applies only to toluene applied to the surface, and suggests that volatilization will be rapid in such a situation. Volatilization of toluene mixed with the soil is highly dependent on the soil type, but the half-life would probably be slower than 5 hours which was calculated for volatilization from water in a river system.

#### Soil to Water

The amount of toluene that will be available to migrate from the soil medium to water will be determined by (1) extent of biodegradation, (2) organic content of the soil and (3) flushing action of either run-off water or groundwater recharge. Laboratory tests by Wilson et al. (1980) showed that in sandy soil (low organic content) and without biodegradation, toluene leached easily. This indicates that in certain soils, toluene may reach the groundwater, where it is unlikely to degrade.

#### 4.4.3 Intramedia Fate Processes

##### 4.4.3.1 Air

As shown in the materials balance section of this report, known environmental releases of toluene, in 1978, were approximately  $10\% \times 10^3$  kkg. Of this amount, it was estimated that 99.7% was released directly into the atmosphere. The atmosphere is the major receiving media for toluene emissions; therefore, the chemical reactions that deplete toluene from the atmosphere have great importance in the overall environmental fate of toluene.

#### Oxidation

Several free radicals combine with compounds to promote the breakdown and eventual removal of these compounds from the atmosphere. Hydroxyl radicals (OH), atomic oxygen (O), peroxy radical (RO<sub>2</sub>, where R is an alkyl or acyl group) and ozone (O<sub>3</sub>) are most likely to combine with toluene. According to Hendry (1979) the reaction of OH<sup>-</sup> is the

most important reaction involving the free radicals in the removal of toluene from the atmosphere. This conclusion is based on two factors: (1) the rate of reaction of the free radical with toluene, and (2) the atmospheric concentration of the free radical in question. Note that the  $\text{OH}^-$  concentration is a function of the temperature and chemical composition of the atmosphere (especially with regard to other pollutants) and, most strongly, the solar intensity. During the evening hours, the  $\text{OH}^-$  concentration decreases sharply, slowing down the atmospheric removal of toluene processes (NRC 1980). However, during daylight hours, the concentration of  $\text{OH}^-$  is at its peak. Estimates of toluene breakdown because of  $\text{OH}^-$  attack will be based on daylight concentrations obtained from experimental data.

### Photochemistry

The addition of the hydroxyl radical to the aromatic ring or the abstraction of the hydrogen from the methyl side chain (Figure 4-1) can lead to the reaction of  $\text{OH}$  with toluene. Several studies have investigated the relative importance of these two reactions and have found a greater likelihood of the addition process occurring than the abstraction process.

Davis and coworkers (1979) measured the reaction rate constant of toluene at 298°K in a toluene helium gas mixture while varying the pressure of the helium gas. They observed that the reaction rate constant varied with pressure such that the rate constant increased by a factor of two as the pressure increased from 3 to 100 torr. According to the authors, only the addition reaction would show a pressure dependency. It was concluded that at least 50% of the total reaction resulted from the addition of  $\text{OH}^-$  to the ring. Because the carbon hydrogen bond is weak, the hydrogen can readily be abstracted by the  $\text{OH}$  radical. Nevertheless this latter mechanism was assessed as less important.

In another study, Kenley et al. (1973) examined the relative importance of the two mechanisms by direct measurement of the products. They assessed the rates of atmospheric reaction and proposed that it would yield 85% cresol isomers and 15% benzaldehyde; thus, they demonstrated that the addition mechanism is likely to be of greater significance. In addition to benzaldehyde and cresol, Kenley et al. (1978) identified nitrotoluene as a product of the  $\text{OH}^-$  toluene reactions with yields <1% of the total. However, Hoshino et al. (1978) pointed out that the quantity of m-nitrotoluene is directly proportional to the initial concentration of  $\text{NO}_2$ .

Finally, O'Brien and coworkers (1979) studied the products of the OH radical attack under simulated atmospheric conditions. They also found that the reaction yields cresol and benzaldehyde, although the actual percentages were smaller than those reported by Kenley et al. (1978). Hoshino and coworkers (1978) also found that cresol and benzaldehyde were the major products, with yields at a ratio of roughly 2:1.

Recently, it has been shown that toluene oxidation can lead to the production of peroxyacetylnitrate (PAN) and peroxybenzoylnitrate (PBzN) (Altshuller et al. 1971, Heuss and Glasson 1968, Spicer and Jones 1977, Dimitriadis and Wesson 1972). PAN is either produced by the fragmentation of the aromatic ring immediately following the reaction of OH<sup>-</sup> and toluene or by the secondary reactions involving products of the OH<sup>-</sup> toluene reaction. The photo-oxidation of benzaldehyde, which was demonstrated earlier as a prominent by-product of the reaction of OH radicals with toluene, forms PBzN.

The rate of toluene removal as the result of the toluene reaction with the free radicals PAN and PBzN is summarized in Table 4-11. The concentration of the hydroxyl concentration is based on experimental data at solar intensities that vary according to latitude and season. Table 4-11 demonstrates that the rate of removal as a result of OH radical attack exceeds the rate of removal by the remaining free radicals by a factor of  $10^2 - 10^7$ .

To determine the half-life of toluene in the atmosphere, the product of the rate constant must be added to the average radical concentration over all the free radicals so that the total rate constant as a result of oxidation,  $K_{ox}$ , is:

$$K_{ox} = K_{OH} [OH] + K_O [O] + K_{O_3} [O_3] + K_{RO_2} [RO_2]$$

$$= 1.5 \times 10^{-5} \text{ sec}^{-1}.$$

Based on this rate, the half-life of toluene in the atmosphere as a result of oxidation is 13 hours. This value was determined using an average value for the concentration of OH radicals. Depending upon the actual OH concentration, the half-life of toluene may range from 11 to 52 hours. Therefore, two days is a reasonable upper limit value for the half-life of toluene in the atmosphere.



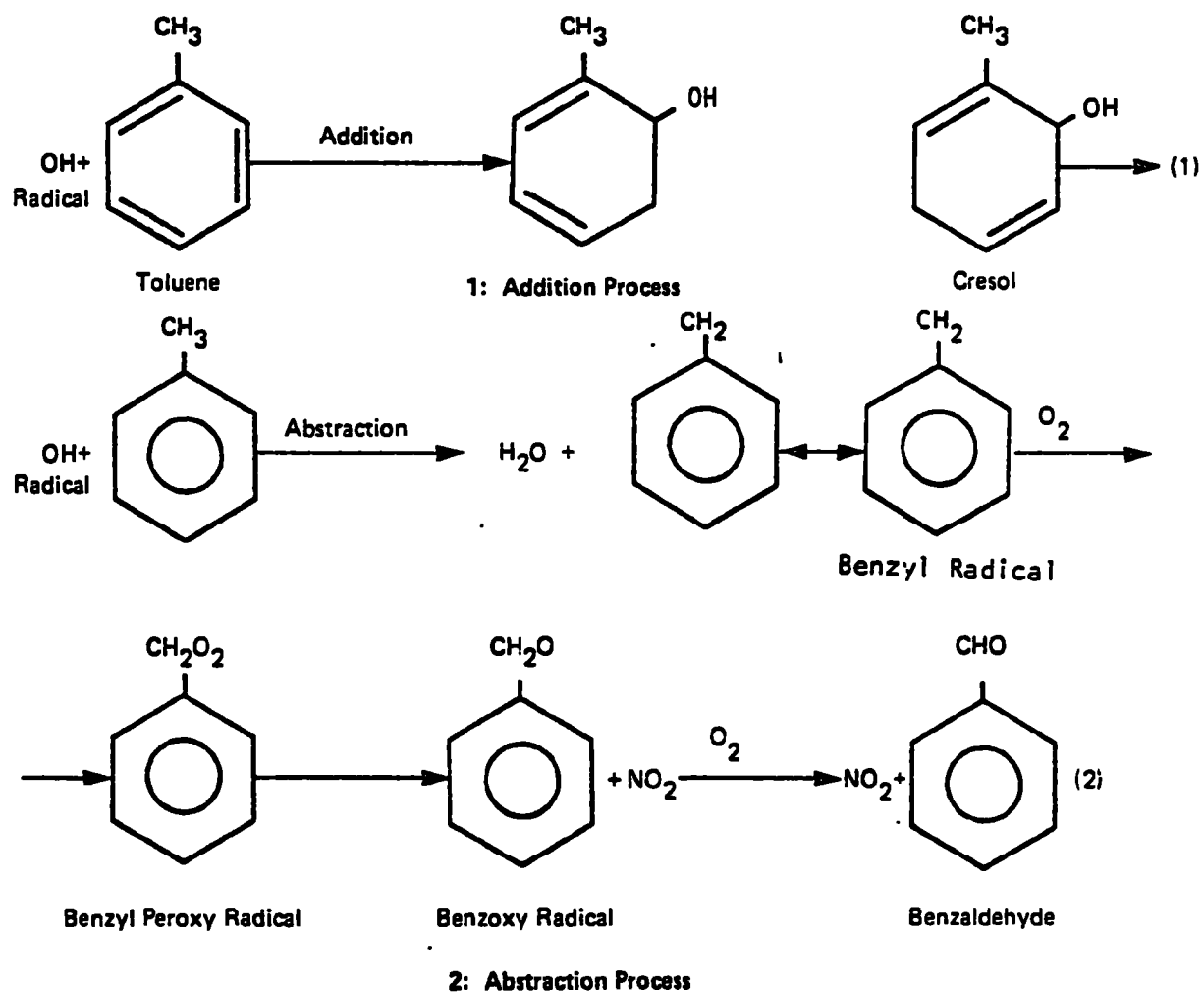


FIGURE 4-1 REACTION OF HYDROXYL RADICALS WITH TOLUENE

TABLE 4-11. RATE OF ATMOSPHERIC OXIDATION OF TOLUENE BY  
FREE RADICALS<sup>a</sup>

<u>Radical</u>	<u>Estimated Average Daylight Concentration (molecules/cm<sup>3</sup>)</u>	<u>Rate Constant (cm<sup>3</sup>/molecule-sec)</u>	<u>Rate of Toluene Removal (sec<sup>-1</sup>)</u>
Hydroxyl Radical	$0.75 \times 10^6 - 0.37 \times 10^7$ <sup>b</sup>	$6.4 \times 10^{-12}$	$2.4 \times 10^{-5}$ $4.8 \times 10^{-6}$
Atomic Oxygen	$0.75 \times 10^5$	$7.4 \times 10^{-12}$	$5.6 \times 10^{-7}$
Ozone	$0.75 \times 10^{10}$	$3.4 \times 10^{-22}$	$2.6 \times 10^{-12}$
Peroxy Radicals	$0.25 \times 10^8$	$1.7 \times 10^{-22}$	$4.3 \times 10^{-15}$

---

<sup>a</sup>Adapted from NRC 1980.

<sup>b</sup>Crutzen and Fishman (1977).

### Direct Photolysis

Photolytic reduction of toluene is not a direct cause of toluene removal because toluene does not adsorb light wavelengths  $>286$  nm. However, a charge-transfer complex between toluene and molecular oxygen will permit radiation adsorption to light wavelengths of at least 350 nm. Wei and Adelman (1969) note that the photolysis of this complex results in the observed oxidation products of benzyl alcohol and benzaldehyde. Additional evidence of photolytic intervention in oxidation has not been cited, nor has substantial evidence been found concerning other possible mechanisms of toluene photolysis. This suggests that photolysis is not an important process in the removal of toluene from the atmosphere.

### Dispersion

The toluene emission sources referred to in the section on materials balance indicate that many chemical plants using or synthesizing toluene emit 15-25 kkg/yr and that 50 kkg/yr is a representative maximum toluene release, while 20 kkg is a good figure for the average plant. Downwind air concentrations of plants releasing these amounts were calculated using a Gaussian plume dispersion model (Appendix F). The results are based on the assumption that the stack was elevated, and that no chemical degradation occurred simultaneously in the plume.

Ground level concentrations based on the Gaussian plume dispersion model are shown in Table 4-12 for various downwind distances from the sources. These concentrations are representative; weather, emission rate fluctuations, and location within the dispersing plume will cause actual levels to vary. Concentrations are generally  $<0.1 \mu\text{g}/\text{m}^3$  at distances  $>500$  meters from the source. For the plant releasing an average amount of toluene (20 kkg/yr), at 100 meters, the concentration is  $0.5 \mu\text{g}/\text{m}^3$ . At 100 meters, the larger source could generate a concentration of  $1.2 \mu\text{g}/\text{m}^3$ . These levels are an order of magnitude less than the mean concentration found for urban air in Section 4.3.4.

#### 4.4.3.2 Water

##### Oxidation

The reaction of toluene in water with OH radicals formed from the irradiation of hydrogen peroxide has been shown to produce benzaldehyde, benzyl alcohol, and cresol isomers (Jefcoate et al. 1969). These are the same products formed by atmospheric oxidation. Molecular oxygen may also oxidize liquid toluene, however, the presence of water will inhibit this oxidation (Stephens and Roduta 1935). Thus, molecular oxygen can be eliminated as a possible mode of toluene removal from the aqueous environment. No rates for this process have been found; therefore, this process is not assumed significant.

TABLE 4-12. TOLUENE CONCENTRATIONS IN AIR DOWNWIND DISTANCES OF CHEMICAL PLANTS USING TOLUENE

<u>Emission Rate</u>	<u>Ground Level Concentration in Air (ng/m<sup>3</sup>)</u>					
	<u>Distance (meters)</u>					
	<u>100</u>	<u>500</u>	<u>1000</u>	<u>1500</u>	<u>5000</u>	<u>10,000</u>
20 kkg/yr Q = 6.34 x 10 <sup>-4</sup> kg/sec	480	60	20	10	1.5	0.5
50 kkg/yr Q = 1.6 x 10 <sup>-3</sup> kg/sec	1200	150	50	25	4	1

$$\text{Ground Level Concentration} = \frac{Q}{\pi \sigma_y \sigma_z u_w} \exp \frac{-h^2}{2\sigma_y^2}$$

•  $u_w$  = wind speed = 5 m/sec

Neutral Atmospheric Stability Class D

Non-buoyant Source, 10 meters high

See text and Appendix F for details concerning the estimation methods.

### Hydrolysis

Although there is not direct data on toluene hydrolysis, some authors have concluded that this is not a significant fate process. "The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus" (Callahan et al. 1979).

### Chlorination

During wastewater treatment with chlorine, some compounds will react with chlorine to form toxic or persistent compounds. With toluene, this is not the case. In laboratory tests conducted by the Chemical Manufacturers Association for the U.S. EPA (1972), 10 mg/l of toluene was combined with 5, 10, and 20 mg/l of chlorine in a 500 ml sample. The mixture was rotated at 80 rpm, 25°C. Samples examined after 0.5, 1.0, 2.0, and 24.0 hours revealed, in all cases, that the quantity of chlorine absorbed by toluene was <4% of the chlorine dosage. Carlson and Caple (1975) also carried out reaction measurements, demonstrating that chlorine did not bind with toluene. When a  $9.5 \times 10^{-4}$  solution of toluene was mixed with a  $7 \times 10^{-4}$ M solution of chlorine at 25°C for 20 minutes, 11% of the chlorine was absorbed at pH3, while only 2.8% was absorbed under neutral conditions.

#### 4.4.3.3 Soil

##### Sorption

The octanol:water partition coefficient ( $K_{ow}=490$ ) and the organic carbon partition coefficient ( $K_{oc}=339$ ) for toluene indicate that it has some affinity to bind with organic components in the soil. Because of variations in the organic content of soils, however, generalizations cannot be made concerning the sorption of toluene in soils. In addition, the concentration of toluene in POTW sludge indicates that adsorption could be significant in soils with high organic content (Personal communication, Moss, U.S. EPA 1980).

##### Biodegradation

Biodegradation of toluene in soil can be an important process. Claus and Walker (1964) have measured the degradation half-life of toluene of 20-60 minutes in soil inhabited by certain bacterial species, which proved capable of utilizing toluene as a sole carbon source. The authors suggest that the biodegradation route of toluene is:

Toluene  $\rightarrow$  3 Methylcatechol  $\rightarrow$  acetic acid, pyruvic acid, ether fractions

Wilson (1980) indicated that from 20 to 60% of toluene eluted through a 140-centimeter of sandy soil biodegraded. The process is probably highly sensitive to the soil type; therefore, for a particular soil system, it may be an important removal process of toluene. However, Chambers and coworkers (1963) found that although "toluene was oxidized to a limited extent . . . that in general they (benzene derivatives) were resistant to degradation" by phenol-adapted bacteria. Therefore, environmental conditions must be conducive to biodegradation of toluene in the soil by the appropriate bacterial populations.

#### Chemical Transformations

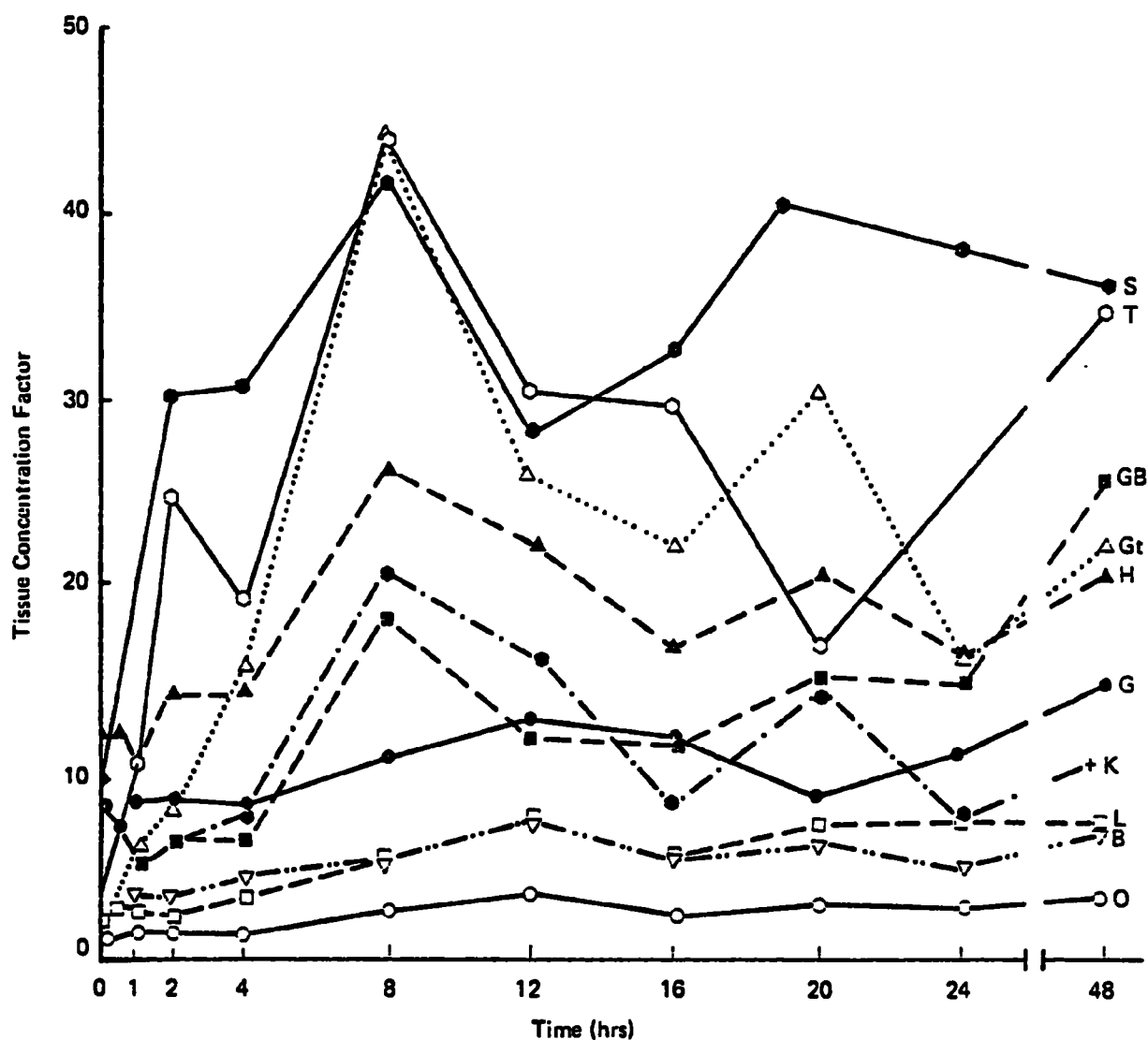
Chemical transformations in soil as a result of oxidation, hydrolysis, or other chemical (nonbiological) processes are not indicated.

#### 4.4.3.4 Biota

Little definitive data are available on the fate of toluene in aquatic organisms, however, some qualitative observations have been made. Toluene was absorbed rapidly from water into the Pacific herring (Clupea harengus pallasii) with maximum levels reached in 24 hours. In their gallbladders, which contained the highest residues (34 mg/kg), toluene reached a concentration 340 times greater than that measured in the water (0.1 mg/l) (Korn *et al.* 1977). All detectable toluene was depurated in several days after transfer to fresh water.

Eels (Anguilla japonica) reared in seawater containing crude oil accumulated toluene to a concentration ratio (eel:freshwater) of 13:2. The half-life of toluene was 1.4 days after transfer to clean seawater (NRC 1980). Toluene was taken up (3-10 µg/l) through the gill tissues of the mussel Mytilus edulis; it was subsequently transferred to the mantle, adductor muscle, and the guts. No evidence of metabolism was demonstrated. When transferred to fresh seawater, the mussels depurated most of the toluene from their tissues (Buikema and Hendricks 1980).

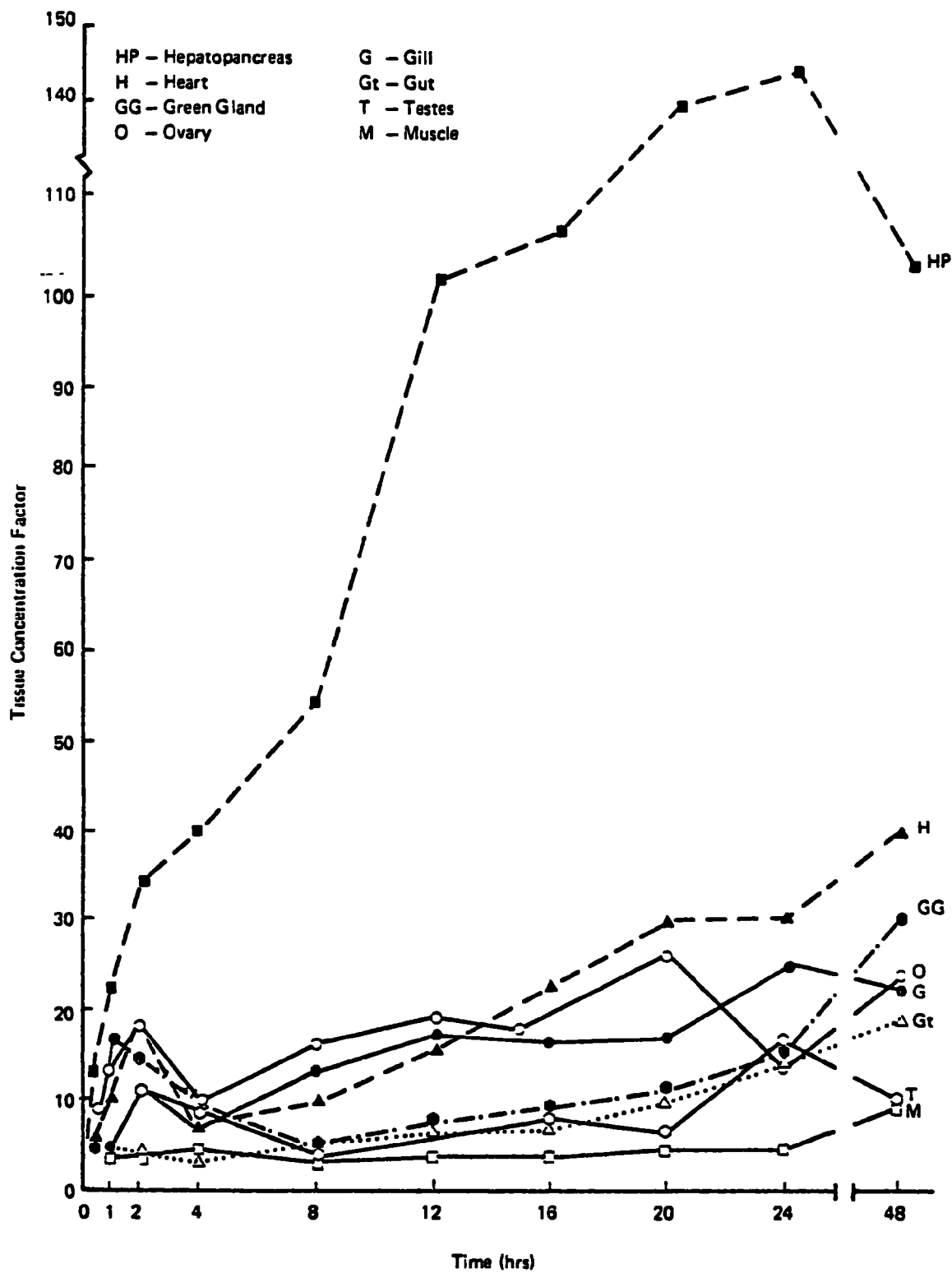
A comparative study was conducted of toluene bioconcentration in various organs of freshwater crayfish (O. rusticus) and bluegill sunfish (Lepomis macrochirus). All tissues in both species accumulated toluene to at least a factor of 2, with the greatest tissue concentration factor, ~140, seen in the hepatopancreas of the crayfish. This organ contains large amounts of lipids. Because toluene is lipid-soluble, the hepatopancreas is the most likely organ to accumulate toluene concentrations. Figures 4-2 and 4-3 illustrate the significant differences in both the rate and degree of bioaccumulation (here given as the tissue concentration factor) of toluene in these two species. The author hypothesized that bluegills are able to metabolize toluene and store the metabolites, whereas crayfish are not; this may, in part, account for the observation that bluegills were ten times more sensitive than crayfish to toluene (Berry 1977).



Note: Each point is the mean TCF of two to four organs.

S - Spleen	G - Gill
T - Testes	K - Kidney
GB - Gall Bladder	L - Liver
Gt - Gut	B - Brain
H - Heart	O - Ovary

FIGURE 4-2 TISSUE CONCENTRATION FACTORS (TCF) FOR TOLUENE IN VARIOUS BLUEGILL SUNFISH ORGANS AT GIVEN TIMES OF EXPOSURE



Note: Each point is the mean TCF of two to four organs.

FIGURE 4-3 TISSUE CONCENTRATION FACTORS (TCF) FOR TOLUENE IN VARIOUS CRAYFISH ORGANS AT GIVEN TIMES OF EXPOSURE



In another study (Berry and Fisher 1979) mosquito larvae that had taken up  $^{14}\text{C}$ -labeled toluene were fed to bluegill sunfish (Lepomis macrochirus). Toluene did concentrate in the stomach and intestine; however, most of the toluene was contained within the digestive tract and did not accumulate in other vital organs. One conclusion of this study was that bioaccumulation of chemicals within aquatic food chains is insignificant when compared with accumulation directly from water.

No measured steady state bioconcentration factor (BCF) is available for toluene; however, based on the octanol:water partition coefficient, it has been estimated to be 70 (U.S. EPA 1979). A BCF of 120 (25°C) has been reported by SRI (1980). Thus, because of the low bioconcentration potential, rapid depuration, and the ability of fish to metabolize toluene, it is unlikely that bioconcentration and biomagnification of toluene through food chains will be a significant problem in aquatic systems.

#### 4.5 SUMMARY

This chapter has described the environmental fate of toluene from the perspective of the three major environmental compartments. The processes that may transfer toluene from one to the other have been analyzed for their significance and reaction rates. The processes that have the potential to alter chemically or degrade toluene within a given compartment have been similarly considered.

The major fate processes, both inter- and intra-medium, are shown in Figure 4-4 and summarized below.

##### 4.5.1 Intermedium Transfer Processes

###### 4.5.1.1 Air

- Rainout to Water and Land. A reaction limited by the short residence time of toluene in the atmosphere.

Conclusion. Negligible overall importance.

###### 4.5.1.2 Water

- Volatilization to Air. Occurs quite quickly; controlled by diffusion within water bodies; however, this usually is not limiting.

Conclusion. A major pathway.

- Adsorption to Sediments. Occurs on a limited basis; highly dependent on soil type, i.e., organic content, relative concentrations, etc.

Conclusion. Limited overall importance.

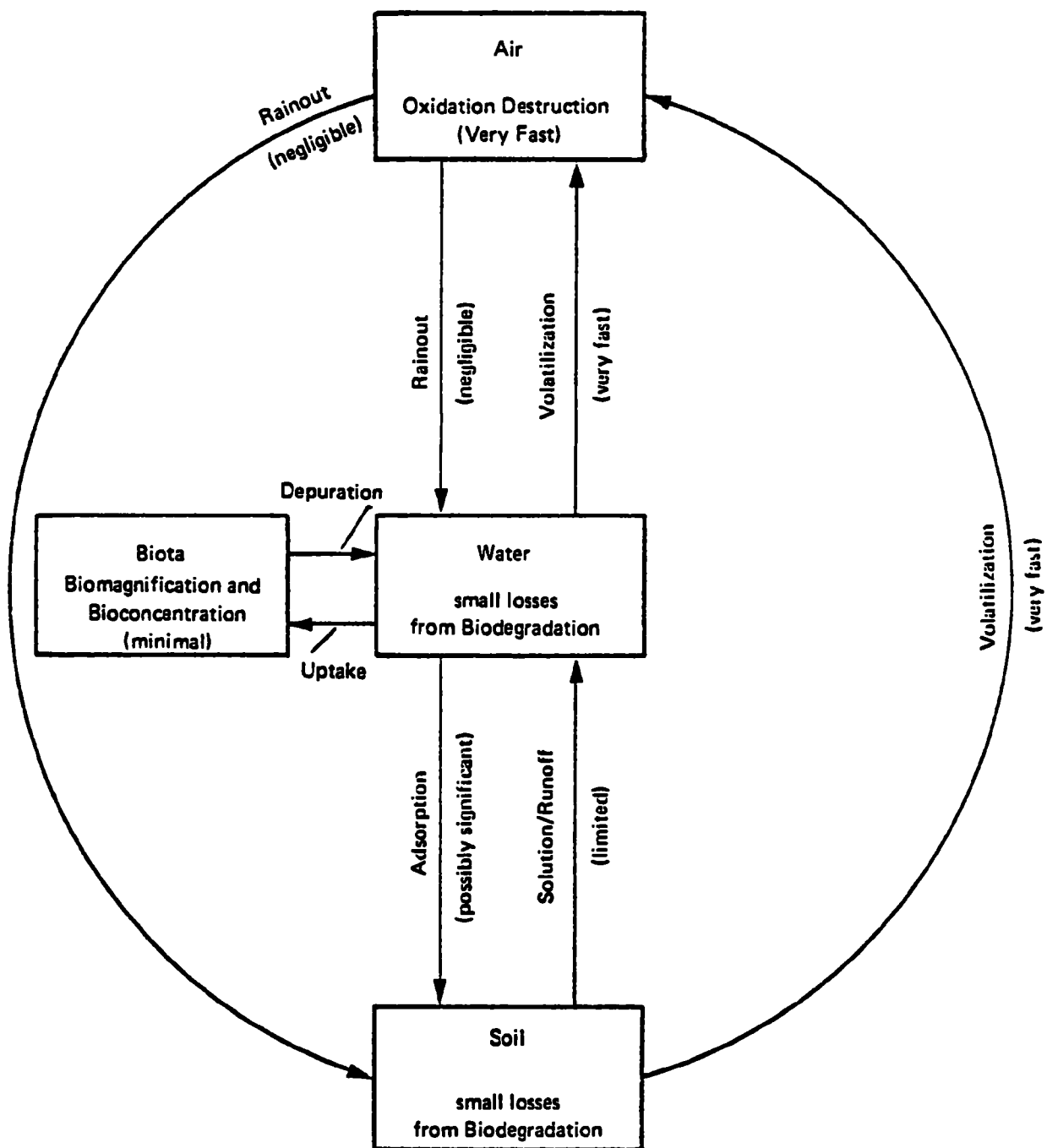


FIGURE 4-4 MAJOR FATE PROCESSES FOR TOLUENE

#### 4.5.1.3 Soil

- Volatilization to Air. Occurs quite quickly; controlled by soil type and conditions.

Conclusion. A major pathway.

- Solution into Water. Soil toluene may dissolve in soil water as determined by its solubility and the amount of water present.

Conclusion. Possibly significant.

- Runoff to Water. Surficial toluene would be preferentially volatilized. Any toluene bound to surface particles could be carried off physically, and some would be carried in solution.

Conclusion. Possibly significant.

#### 4.5.2 Intramedium Fate Processes

##### 4.5.2.1 Air

- Oxidation by Hydroxyl Radicals. A fast reaction, determined by concentrations of OH.

Conclusion. Dominant fate process -- responsible for destruction of most environmental toluene.

##### 4.5.2.2 Water

- Degradation by Microbial Species. Requires the presence of appropriate species.

Conclusion. Important in some habitats, but not universally important.

##### 4.5.2.3 Soil

- Biodegradation. Requires the presence of appropriate species.

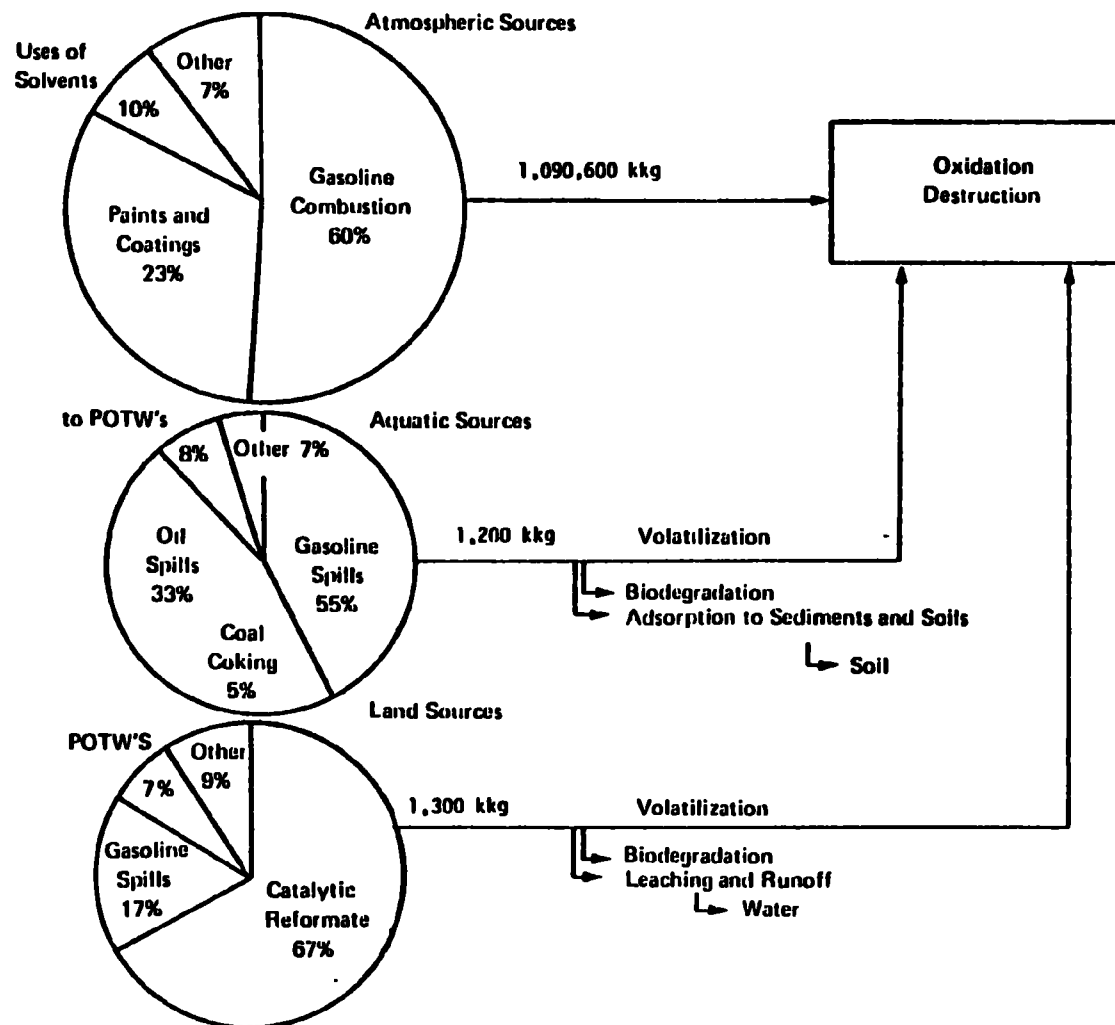
Conclusion. Important in some soil situations, but not universally important.

#### 4.5.3 Critical Pathways for Specific Sources of Toluene

The critical pathways for the known releases of toluene to the environment are shown in Figure 4-5. These pathways are called "critical" because they define the processes that reduce the total environmental load of toluene.

The three critical pathways are: 1) atmospheric sources → oxidative destruction, 2) aquatic sources → volatilization → oxidative destruction, and 3) land sources → volatilization → oxidative destruction.

Of the total estimated releases of 1,090,000 kkg in 1978, a maximum of 99.8% may follow the shortest (i.e., no intermedia transfer) pathway-- #1; 0.001% may follow #2, and 0.0012% may follow #3. Part of these releases will remain in each compartment as ambient or background levels until either biodegradation or entrance to a critical pathway occurs.



**Notes:** Processes in boxes and bold type are major fate pathways for any toluene in that particular medium.

Processes that lead to other media are indicated by an arrow, which leads to that medium and implies that all fate processes for the medium apply.

**FIGURE 4-5 CRITICAL PATHWAYS FOR TOLUENE**  
(Released Amounts for 1978 Materials Balance)

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## 5.0 HUMAN EFFECTS AND EXPOSURE

### 5.1 HUMAN EFFECTS

#### 5.1.1 Pharmacokinetics

##### 5.1.1.1 Absorption

Toluene has volatile and highly lipid-soluble, chemical characteristics that permit absorption by all exposure routes: inhalation, dermal, and oral. The concentration of toluene and the permeability of toluene of the intervening membranes determine the rate at which toluene is absorbed.

Absorption of toluene by inhalation is the most important exposure route in the occupational setting, because toluene is a commonly used and highly volatile solvent. Several groups of investigators have studied the pulmonary uptake of toluene and observed that the uptake was rapid and markedly increased during exercise. Veulemans and Masschelein (1978a) have made the most detailed and accurate measurements of respiratory uptake. They found that the respiratory uptake rate of toluene was directly proportional to minute volume and concentration. The range of experimental minute volumes varied from a rest rate of 7 l/min to >50 l/min under a heavy work load. The concentrations varied from 190 to 750 mg/m<sup>3</sup>. The retention factor for toluene was 47%. The retention factor is defined as the fraction (or percent) of the inhaled solvent that is absorbed from the inspired air. The total respiratory uptake of toluene into the body is estimated by the following equation:

$$\text{uptake (mg)} = \frac{\text{concentration (mg/m}^3\text{)} \times \text{minute volume (m}^3\text{/min)} \times \text{retention factor (0.47)} \times \text{time (minutes)}}{1}$$

Dermal absorption of toluene vapor is slow compared with inhalation at the same air concentration. Riihimaki and Pfaffli (1978) studied the absorption of toluene across the body surface of human volunteers at a concentration of 2260 mg/m<sup>3</sup>. The subjects were exposed for 3.5 hours and their faces were covered with an inhalation mask under slight positive pressure to prevent inhalation uptake. They were clothed only in lightweight pajamas and socks. These researchers calculated total uptake as ~26 milligrams, based on a 16% recovery of absorbed dose in the expired air. It is estimated that the same total uptake in 3.5 hours via inhalation would occur at an air concentration of only 38 mg/m<sup>3</sup>. (This estimate assumes a respiratory rate of 7 l/min at rest and a respiratory retention factor of 47% for toluene.) In their experiments on the percutaneous absorption of xylene vapor, Riihimaki and Pfaffli showed that dermal uptake is proportional to air concen-

tration. Based on these data and the similarities between xylene and toluene, the approximate average skin permeability of the human body to toluene is calculated to be  $0.002 \text{ m}^3/(\text{m}^2 \times \text{hr})$ .<sup>1</sup>

Dermal absorption of liquid (neat) toluene is much faster than that of vapor, because of the higher concentration and a defatting action on skin that would significantly increase the permeability. Sato and Nakajima (1978) conducted experiments on human volunteers in which each individual soaked one hand in neat toluene for 30 minutes. Blood levels after the 1/2-hour exposure reached approximately 25% of the blood levels measured after 1/2-hour inhalation exposure at  $376 \text{ mg/m}^3$ . It can be shown that blood level is approximately directly proportional to uptake rate, when that rate is constant. If it is assumed that the skin absorption rate was constant (an oversimplification, but useful for an approximation), it is estimated that the uptake rate via the skin of the hand was  $\sim 20 \text{ mg/hr}$ .<sup>2</sup> The surface area of the hand is  $\sim 2\%$  of the body surface area of  $1.8 \text{ m}^2$  or  $0.036 \text{ m}^2$  (Diem and Lentner 1971); therefore; an estimate of absorption rate through skin of liquid toluene is  $550 \text{ mg/m}^2 \text{ hr}$ .

Oral absorption can be expected to approach 100%. The absorption rate depends on gastric contents and gastric emptying. Pyykko and co-workers (1977) found peak blood levels of radioactivity at 2 hours following gastric intubation to rats of  $^{14}\text{C}$  toluene mixed with peanut oil. Oral exposure differs from both dermal and inhalation exposure because of the "first-pass effect". Intestinally absorbed toluene passes through the hepatic-portal circulation before entering the general circulation. Because the liver is a principal organ of the metabolism of toluene, blood levels of unchanged toluene would be somewhat lower than following intravenous injection or inhalation absorption of an equivalent dose. The influence of the first-pass effect on the response of the organism to toluene has not been determined. This detail is not considered critical at this time, because oral absorption of toluene normally constitutes a relatively small proportion of total exposure. For purposes of this report, it is assumed that the absorption route has no significant influence on effect, and that effect depends only on the rate or the total amount absorbed.

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<sup>1</sup>  

$$\text{uptake} = \frac{26 \text{ mg}}{3.5 \text{ hr}} = \text{permeability} \times 2260 \text{ mg/m}^3 \times 1.8 \text{ m}^2, 26 \text{ mg}/3.5 \text{ hr}$$
 where  $2260 \text{ mg/m}^3$  was the exposure concentration and  $1.8 \text{ m}^2$  is the appropriate body surface area.

<sup>2</sup>  

$$\frac{376 \text{ mg/m}^3}{4} \times .47 \times 0.45 \text{ m}^3/\text{hr} = 20 \text{ mg/hr}, \text{ where } \frac{376 \text{ mg/m}^3}{4} \text{ was the air}$$
 concentration for equivalent blood levels via inhalation, .47 was the respiratory retention factor; and  $0.45 \text{ m}^3/\text{hr}$ , the respiratory rate at rest.

### 5.1.1.2 Distribution

In discussing the distribution in the body of a lipid-soluble, water-insoluble compound, it is appropriate to view the body as a multicompartmental system. Although each organ may be considered a compartment, it is more usual to treat the body as containing 2-4 compartments, with each compartment made up of organs and tissues having similar pharmacokinetic characteristics. For toluene, a 3-compartment model has generally been adequate to characterize the pharmacokinetics. The first compartment is generally considered to be composed of the vascular space and highly perfused organs, such as the heart, kidneys, liver, intestines, endocrine glands, and brain. This compartment is called the central compartment, because it is the one from which the other compartments, called peripheral compartments, receive drugs and chemicals and from which the chemicals are eliminated from the body. The second compartment is composed of tissues and organs with moderate blood perfusion, such as muscle and skin. The third compartment, especially important in the case of lipid-soluble organics, is composed of slowly perfused tissues, such as fat. Fat differs from most other tissues in having a much higher tissue/blood partition coefficient for organic solvents; i.e., it can accumulate toluene to a greater extent than might be expected on the basis of volume alone.

A useful index of the time it takes for the various tissues (or compartments) to reach equilibrium with the central compartment (i.e., the blood, because it can be assumed that rapid mixing occurs within the central compartment) is the saturation half-life,  $t_{s/2}$ . The saturation half-life depends directly on volume of the compartment ( $V_T$ ) and the tissue/blood partition coefficient ( $\lambda$ ); and inversely on the blood flow ( $Q$ ) for the compartment as follows:

$$t_{s/2} = (\lambda \cdot V_T / Q) \times 0.693.$$

Rough estimates of saturation half-lives for several tissues and the three composite compartments are presented in Table 5-1. Clearly, the distribution to the brain and the central compartment is very rapid. It is so rapid that often it is difficult to delineate this compartment in pharmacokinetic analysis. The third compartment equilibrates so slowly that it does not reach saturation equilibrium with the blood during continuous exposure, such as an 8-hour occupational exposure. For this reason, a tendency for "baseline" blood levels to build up over continuous day-to-day exposure could occur as a result of this third compartment being similarly slow.

Usually, blood levels cannot be used to quantitate absorption unless exposure conditions in terms of both concentration and time are known. During inhalation exposure, blood levels rise very rapidly to a "quasi"-steady state, reflecting rapid absorption and slow metabolism and distribution to other tissues. When exposure is terminated, blood levels fall rapidly at first, reflecting continued dis-

TABLE 5-1. ESTIMATES OF THE SATURATION HALF-LIFE  
OF TOLUENE BETWEEN BLOOD AND TISSUE

	<u><math>\lambda</math></u> <u>Toluene</u>	<u><math>V_T/Q</math></u>	<u><math>ts/2</math></u> <u>Toluene</u>
Compartment 1	2	1.5	2
Liver	2.6	2.5	4.5
Kidney	1.5	.24	0.2
Brain	3.0	1.3	2.7
Compartment 2	1.2	17 (resting)	13
Compartment 3	100	47	3200
Fat	113	50	3900
Marrow	35	25	850

NOTE:

$\lambda$  = Tissue/blood partition coefficients obtained from data of Sato et al. (1974)

$V_T/Q$  = Volume of tissue/blood flow (ml/ml/min) from Papper and Kitz (1963).

$ts/2$  = Saturation half-life =  $0.693 \times V_T/Q \times \lambda$  (minutes).

tribution to the rest of the body as well as metabolism and elimination. After the initial rapid decline, slower phases of decline are noted, because elimination is rate limited by the transfer of the chemical from the peripheral compartments into the central compartment.

Sato and coworkers (1974) studied and compared the pharmacokinetics of benzene and toluene in human volunteers. The decline in blood levels after a 2-hour exposure to either benzene (at 80 mg/m<sup>3</sup>) or toluene (at 377 mg/m<sup>3</sup>) was followed for 5 hours. The equations that describe the decline in blood levels are sums of three exponentials as follows:

$$\begin{aligned} \frac{\text{benzene}}{y} &= 0.0593e^{-0.418t} + 0.086e^{-0.0238t} + 0.0287e^{-0.00347t}; \\ \frac{\text{toluene}}{y} &= 0.355e^{-0.355t} + 0.352e^{-0.0197t} + 0.129e^{-0.00339t}; \end{aligned}$$

where t is time in minutes and y is blood concentration in mg/l.

These model equations, together with other data, indicate that benzene and toluene are absorbed and distributed into the body in a similar manner. The exponents of the equations are similar to a striking degree. Also, the coefficients of the toluene equation are about 4-6 times higher than the respective coefficients in the benzene equation, which is a result of the toluene exposure concentration being 4.7 times the benzene exposure concentration.

In an important respect, the equations are probably misleading for both toluene and benzene, because they suggest no appreciable accumulation of either solvent from day to day. Konietzko *et al.* (1980) and theoretical considerations indicate that accumulation can occur on a daily basis. Konietzko monitored exposure concentrations and blood concentration levels of toluene at the beginning and end of each 8-hour work day over a 2-week period in workers occupationally exposed to toluene. These data are reported in Table 5-2. An apparent upward trend in the toluene blood concentration values occurs each morning before exposure over the 5-day work week. The lowest levels were measured on Monday mornings. The half-life of the terminal phase of elimination would have to be on the order of 2000 minutes (30 hours) for baseline blood levels to build up as they did in the exposed workers. This half-life is comparable with the theoretical saturation half-life for fat given in Table 5-1. The terminal phase half-life calculated from the equations of Sato *et al.* (1974) are on the order of 200 minutes. This finding of Sato and coworkers is understandable because the exposure was only for 2 hours in their experiments and the blood concentration data were only determined for 5 hours after the exposure. These time periods are too brief to delineate a very slow elimination phase.



TABLE 5-2. TOLUENE CONCENTRATIONS IN AIR AND BLOOD

	Monday	Tuesday	Wednesday	Thursday	Friday
First Week: Toluene in air (ppm)	225 (95-303)	233 (153-383)	209 (107-341)	212 (92-314)	203 (124-309)
Toluene in blood	0.12	- - -	0.51	- - -	0.77
- before exposure (µg/ml)	(0.09-0.24)		(0.28-0.82)		(0.29-1.67)
- after exposure	3.63 (2.3-4.75)	- - -	6.69 (4.21-10.36)	- - -	6.70 (3.39-10.67)
Second Week: Toluene in air (ppm)	285 (145-473)	304 (190-521)	309 (213-413)	232 (125-451)	191 (105-432)
Toluene in blood	0.27	- - -	1.00	- - -	1.21
- before exposure (µg/ml)	(0.07-0.57)		(0.35-1.51)		(0.44-2.99)
- after exposure	11.60 (6.99-17.10)	- - -	10.29 (3.24-20.31)	- - -	5.85 (1.94-9.78)

Range in parentheses and means for eight subjects.

Source: Konietzko et al. (1980).

In summary, toluene is absorbed into the body regardless of the route; the major difference among routes is the rate of absorption. Once toluene is in the blood, it is distributed widely to all tissues; the relative perfusion of the tissue by blood determines the relative rate of uptake into each tissue. Accumulation in fat is slow because of low perfusion; however, the potential uptake is high because of the lipid solubility of toluene.

To a first approximation, acute effects depend on blood concentration regardless of the route. Absorbed doses via dermal, oral, and inhalation routes are approximated as follows:

$$\text{dose (dermal/liquid)} = 550 \text{ mg/m}^2/\text{hr} \times \text{exposed surface area (m}^2\text{)} \times \text{time (hour)};$$

$$\text{dose (dermal/vapor)} = 0.002 \text{ m}^3/(\text{m}^2 \times \text{hr}) \times \text{exposed surface area (m}^2\text{)} \times \text{time (hour)} \times \text{concentration (mg/m}^3\text{)};$$

$$\text{dose (oral)} = \text{amount ingested};$$

$$\begin{aligned} \text{dose (inhalation)} &= 0.47 \times \text{inhalation rate} \times \text{time} \times \text{concentration,} \\ &= 0.56 \times \text{hours} \times \text{concentration (mg/m}^3\text{)}^3. \end{aligned}$$

#### 5.1.1.3 Metabolism and Elimination

The metabolism of toluene in humans is outlined in Figure 5-1. Except for differences in the proportion of toluene eliminated by the various pathways, the metabolism in animals is essentially the same. The major routes of toluene elimination in humans are metabolism to hippuric acid, and exhalation of unchanged toluene. These two routes account for about 80 and 16%, respectively (Veulemans and Masschelein 1978a, 1979).

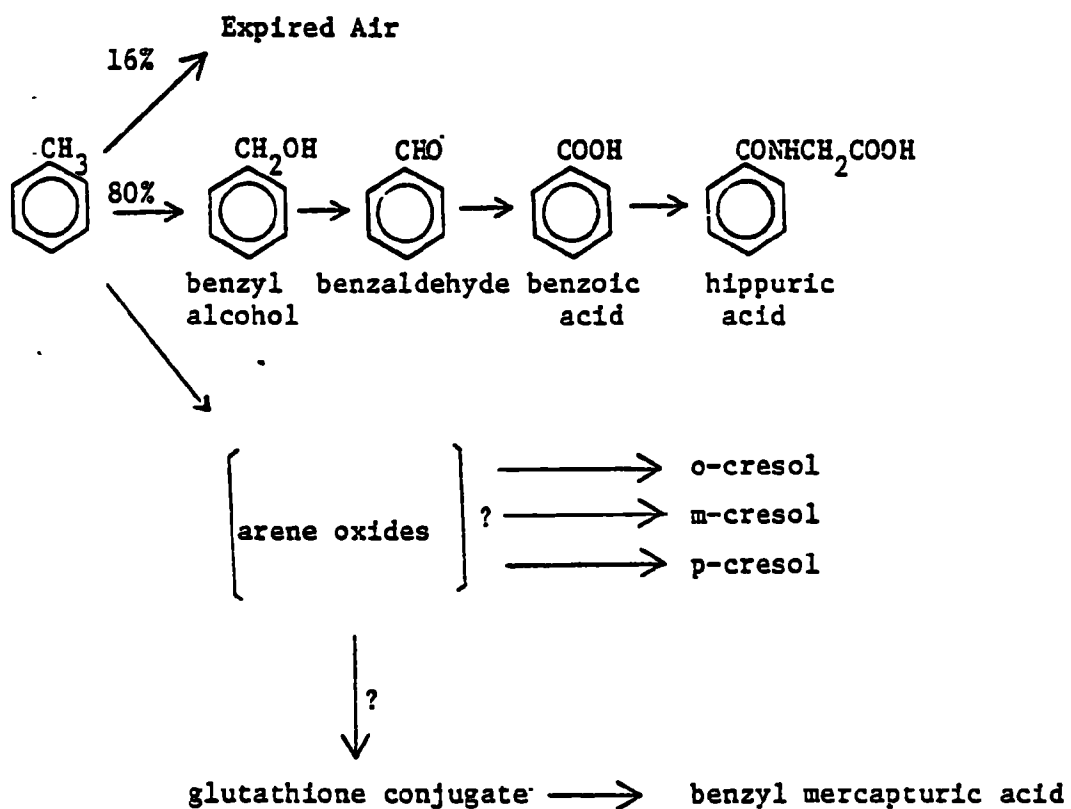
The initial oxidation of toluene to benzyl alcohol occurs by mixed function oxidase system, which is associated with the microsomal fraction from tissue homogenates. Phenobarbital can induce this enzyme system (Ikeda and Ohtsuji 1971). More importantly, a number of substrates can competitively inhibit it. Ikeda (1974) reported reciprocal metabolic inhibition of toluene and trichloroethylene in rats at high dose levels (430 mg/kg toluene, 730 mg/kg trichloroethylene). Ikeda *et al.* (1972) reported *in vivo* suppression of benzene and styrene oxidation by coadministration of toluene in rats, which could be partially reversed by pretreatment of rats with phenobarbital.

Sato and Nakajima (1979) studied the dose-dependent interaction between benzene and toluene in rats and in human subjects. In rats, they found slight to no competitive inhibition between toluene and benzene at doses <115 mg/kg for each compound. At 460 mg/kg for both

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<sup>3</sup>The figure 0.56 assumes 1.2 m<sup>3</sup>/hr inhalation rate during moderate physical activity.

Figure 5-1 Metabolism of Toluene in Humans



toluene and benzene, significant competitive inhibition occurred. Toluene inhibited benzene metabolism more readily than vice versa. In their studies on human subjects, these authors found no metabolic interaction between benzene at 25 ppm (80 mg/m<sup>3</sup>) and toluene at 100 ppm (376 mg/m<sup>3</sup>).

Riihimaki (1979) found that the apparent rate-limiting step in the metabolism and excretion of toluene to hippuric acid was the conjugation of benzoic acid with glycine, which had a maximum rate of ~190 µmol/min (~17 mg/min). Riihimaki (1979) estimates that saturation of glycine conjugation would not occur in an average 70 kg, well-nourished male until air concentrations approached 780 ppm (~2900 mg/m<sup>3</sup>) under light work conditions. Under moderately heavy work conditions, uptake would be increased so that saturation would be obtained at lower air concentrations (e.g., 1000 mg/m<sup>3</sup> at an uptake ~3 times higher than during light work). Riihimaki (1979) points out, however, that the availability of glycine may be less in older persons, undernourished individuals, and individuals taking drugs that compete for its availability. Under competitive conditions, it may be the drug that will accumulate rather than toluene.

Urinary excretion of hippuric acid has been correlated with toluene exposure by a number of researchers (Ogata *et al.* 1970, Sato and Nakajima 1979, Angerer 1979, Riihimaki and Pfaffli 1978, Wilczok and Bieniek 1978, Lehnert *et al.* 1978); however, it is apparent from these studies that the usefulness of urinary excretion data is limited. The major difficulty is obtaining a complete urine specimen, both during exposure and for up to 12 hours after the end of exposure. Moreover, hippuric acid is a normal constituent of urine, and its excretion can be quite variable. Veulemans and Masschelein (1979) conducted a strictly controlled experiment by prescribing the exclusion of alcohol and coffee for 16-20 hours before the beginning of their experiments. They reported baseline hippuric acid excretion averaging 0.5 g/day. Angerer (1979) reported that in 28 unexposed subjects, hippuric acid concentration averaged 0.96 g/l with a standard deviation of 0.94 g/l. If hippuric acid excretion were to be used as an index of exposure, certain approximations and standardization procedures would have to be used (Ogata *et al.* 1970) and it would appear that the precision would still depend on the completeness of the urinary collection as well as the maintenance of a standard technique calibrated against known exposure and excretion.

Minor routes of toluene metabolism in humans result in the excretion of o-, p-, and m-cresol and presumably (although not identified) benzyl mercapturic acid in the urine. Angerer (1979) identified o-cresol in the urine of printing workers exposed to an average air concentration of toluene of 23 ppm (87 mg/m<sup>3</sup>). This metabolite was not considered a normal constituent of urine. Urine levels of combined m- and p-cresol in exposed workers were slightly, but not significantly, greater than levels from unexposed workers.

Woiwode and coworkers (1979) identified o-, m-, and p-cresol in the urine of workers exposed to 280 ppm (1050 mg/m<sup>3</sup>). Urine was collected during the work shift. Expressed as a percent of total urinary metabolites, having subtracted control levels, hippuric acid constituted 98% of the total; p-cresol, 2%; O-cresol, 0.2%; and m-cresol 0.08%. No o- or m- cresol was identified in the urine of unexposed workers. Pfaffli and coworkers (1979) in a study on exposed and unexposed printing workers, found a correlation ( $r = 0.8$ ) between air concentrations of toluene (0.3-4.5 mg/m<sup>3</sup>) and o-cresol excretion in urine (urine sample at end of workshift).

Findings in animal experiments indicate that similar metabolic processes occur. Bakke and Scheline (1970) dosed rats at 100 mg/kg and identified o- and p-cresols in urine ranging from 0.04 - 0.11% and 0.4 to 1.0% of dose for o- and p-cresols, respectively. They could not detect m-cresol. The sensitivity of their methods was not discussed. Van Doorn and coworkers (1980) identified the urinary metabolite, benzyl mercapturic acid in experiment on rats, which were dosed intraperitoneally with 368 mg/kg toluene in arachis oil (peanut oil). The benzyl mercapturic acid excretion represented between 0.4 and 0.7% of the dose.

Of interest and possible concern is the fact that all the minor metabolites, the cresols, and mercapturic acids result from the oxidation of the aromatic ring by a mixed function oxygenase system, which is processed to occur via reactive intermediates variously called arene oxides or aromatic epoxides. They may rearrange spontaneously to form phenols (methyl phenol in the case of toluene) or react with other cellular constituents. In the case of mercapturic acid formation, the intermediate is thought to react with glutathione via enzyme systems called glutathione S-transferases (Goldstein 1974).

A discussion concerning the relative carcinogenic potency of aromatic hydrocarbons, particularly the polycyclics, in relationship to the metabolism via the arene oxide intermediates is highly complex and is inappropriate at this time, because no evidence exists that toluene is carcinogenic. Although metabolism appears to be important, both in the activation of carcinogenic aromatic hydrocarbons and in the activation of an active parent and intermediate compounds, evidence of the formation of arene oxides is not evidence of carcinogenicity. In the case of toluene, a small proportion of the dose is handled in this manner. Research will no doubt continue to explore the possible role of arene oxides in toxicity and carcinogenicity. No definitive conclusions with regard to toluene are forthcoming at this time.

### 5.1.2 Acute Effects

Toluene is a general central nervous system (CNS) depressant. This property, associated with its low toxicity and high volatility, has caused toluene to become a preferred solvent of abuse (see further discussion below). Inhalation exposure can progressively lead through stages of

CNS depression resembling, for the most part, the stages of anesthesia: Stage I -- light-headedness, euphoria, drunkenness, ataxia, slurred speech; Stage II -- loss of consciousness, delirium, excitement, involuntary activity such as thrashing about, incontinence of urine and feces, vomiting, hypertension and tachycardia; Stage III -- anesthesia with regular autonomic-controlled breathing, loss of most reflexes, muscles flaccid; Stage IV -- respiratory paralysis and death.

The extent of CNS depression depends on the concentration and duration of exposure. Glue-sniffing and solvent abuse is intended by the user to attain the euphoriant effects that can be achieved by several deep breaths at near air-saturation concentrations of toluene (saturation concentrations 100,000 - 200,000 mg/m<sup>3</sup> between 20-30 °C). At lower concentrations (estimated 40,000 - 120,000 mg/m<sup>3</sup>), men have been rapidly overcome and fallen unconscious in occupational settings. Recovery is rapid if the person is removed from exposure; however, death from respiratory failure may occur accidentally in solvent abusers or in occupational circumstances when the victims fail to or are unable to remove themselves from the exposure (U.S. EPA 1980a).

Death may also occur from a sudden cardiovascular collapse, even in the early stages of anesthesia. It is believed that these deaths result from cardiac arrhythmias, which are induced by a combination of hypoxia, physical stress, and sensitization by toluene of cardiac muscle to catecholamines (Bass 1970, Taylor and Harris 1970, U.S. EPA 1980a).

Upon acute exposure, toluene appears to have limited toxicity potential, other than CNS depression and predisposition of subjects to cardiac arrhythmias. Investigations in cases of accidental exposures to very high doses of toluene in humans and experimental studies in animals have failed to reveal any significant pathologic changes in blood chemistries or organ histopathology (U.S. EPA 1980a).

### 5.1.3 Chronic Effects

#### 5.1.3.1 Myelotoxicity

Human epidemiological or animal experimental data have not clearly indicated the myelotoxicity of toluene. In epidemiological studies showing a possible effect from toluene exposure, coexposure to benzene and other toxic chemicals cannot usually be ruled out as contributing causes. Results in animal studies are quite contradictory. Possible differences in species susceptibility and the likely contamination of toluene with benzene, in particular, are two major confounding variables.

Greenburg and coworkers (1942) compared 61 painters exposed primarily to toluene (95% between 100-800 ppm or 380-3000 mg/m<sup>3</sup>, median exposure concentration 750 mg/m<sup>3</sup>) with a control group for clinical manifestations of toxicity. The exposed group had an increased inci-

dence of liver enlargement, macrocytosis (increased volume of RBC), decreased erythrocyte counts, and lymphocytosis. Exposure was not associated with leukopenia. Table 5-3 gives an analysis of the paints. It is likely that these paints contained some benzene because it is a common impurity in certain grades of toluene. Banfer (1961) reported that toluene derived from coal tar may be contaminated with benzene by as much as 15% and that toluene containing only traces of benzene (up to 0.3%) had been available since about 1955.

Powars (1965) reported on six cases of aplastic anemia associated with glue-sniffing. Glue was claimed to contain toluene or acetone (depending on the brand) according to the glue manufacturer. One case had a 3-year history of glue-sniffing. The other cases were complicated by the presence of sicklecell disease, although aplastic anemia was stated to be rare with this disease. Powars concluded that glue sniffing precipitated the onset of aplastic anemia. The estimated concentrations of toluene of inhaled vapors during glue-sniffing are on the order of 12,000-24,000 mg/m<sup>3</sup>.

Forni and coworkers (1971) did not find a significantly increased incidence of chromosome aberrations in peripheral blood lymphocytes in toluene-exposed workers compared with matched controls. The exposure concentrations were on the order of 750 mg/m<sup>3</sup>; mean and median duration were 10 years; and the range was 3-15 years. In contrast, workers exposed to both benzene and toluene had a significantly higher incidence of stable and unstable chromosome aberrations in peripheral blood. The benzene exposure concentrations were not precisely known although they were estimated to be in excess of 1500 mg/m<sup>3</sup> during a recent epidemic of benzene poisoning. Median duration of benzene exposure was 3 years. The co-exposure to toluene were on the order of 750 mg/m<sup>3</sup> with median duration of 14 years. Table 5-4 presents the incidence of unstable (Cu) and stable (Cs) chromosome aberrations in the exposed groups and matched controls.

Capellini and Alessio (1971) reported on clinical findings of 17 workers exposed to toluene (mean concentration 125 ppm or 470 mg/m<sup>3</sup>, range 80-160 ppm or 300-600 mg/m<sup>3</sup>) for several years duration. Accompanied by regular medical supervision, no untoward changes were noted in hemoglobin, red and white cell counts, platelet counts, and certain liver function tests, compared with a control group not exposed to toluene.

Friborska (1973) reported altered cytochemical measures from leukocytes and lymphocytes of toluene-exposed workers. Acid phosphatase activity was significantly increased in lymphocytes, alkaline phosphatase activity in leukocytes, and lactic acid dehydrogenase activity in leukocytes from exposed workers compared with controls. The meaning of these cytochemical changes is unclear.

Studies of the myelotoxicity of toluene in animals are inconclusive. A summary of findings in several studies is listed in Table 5-5 for studies with negative findings and Table 5-6 for studies with adverse effects reported. None of the positive studies was available in translation.

TABLE 5-3. ANALYSIS OF PAINT USED BY PAINTERS<sup>a</sup>

Spray Painters	Percentage in Mixture
Primer (75% of paint used):	
Zinc chromate	10.8
Magnesium silicate	0.7
Synthetic resin	12.8
Driers (lead and cobalt compounds)	0.3
Xylene	5.8
Toluene	69.6
	<u>100.0</u>
Lacquer 1 (15% of paint used):	
Volatile Portion:	
Ethyl alcohol	7.0
Ethyl acetate	18.0
Butyl alcohol	7.0
Butyl acetate	15.0
Petroluem naphtha	3.0
Toluene	50.0
	<u>100.0</u>
Nonvolatile:	
Nitrocellulose, synthetic resin, titanium oxide, ferrocyanide blue, iron oxide, carbon black, zinc oxide, etc. No lead compounds	
Lacquer 2 (10% of paint used):	
Volatile Portion:	
Toluene	25.0
Xylene	33.0
Petroleum naphtha	42.0
	<u>100.0</u>
Nonvolatile:	
Resin, titanium oxide, zinc oxide, ultramarine blue, ferrocyanide blue, iron oxide, diatomaceous earth, amorphous silica, carbon black	



TABLE 5-3. ANALYSIS OF PAINT USED BY PAINTERS (Continued)

Brush Painters

Dope:

Volatile Portion:

Ethyl acetate	16.5
Ethyl alcohol	3.2
Butyl acetate	16.5
Butyl alcohol	5.6
Petroleum naphtha	13.7
Toluene	44.5
	<u>100.0</u>

Nonvolatile:

Nitrocellulose, glycol sebaeate, aluminum, cadmium  
sulfide, barium sulfate

Brush Wash:

Acetone	22.5
Ethyl alcohol	22.5
Toluene	55.0
	<u>100.0</u>

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<sup>a</sup>Dip painters used a primer only of the same composition as given  
for spray painters.

Source: Greenburg et al. (1942).

TABLE 5-4. FREQUENCY OF CHROMOSOME ABERRATIONS IN  
PERIPHERAL LYMPHOCYTES

	Frequency (%)	
	<u>Cu</u>	<u>Cs</u>
Toluene	0.8 p>.05	0.08 p>.05
Controls	0.67	0.09
Benzene and Toluene	1.7 p<.01	0.26 p>.05
Controls	0.61	0.00

Source: Forni et al. (1971).

TABLE 5-5. ANIMAL STUDIES OF MYELOTOKICITY OF TOLUENE (Negative Studies)

<u>Species (N)<sup>a</sup></u>	<u>Route/Dosage</u>	<u>Findings</u>	<u>References</u>
Rat (-)	Oral/118, 354, 590 mg/kg, 5 d/wk, 24 weeks	Cell counts of marrow and circulating blood revealed no adverse effects.	Wolf <u>et al.</u> (1956)
Rat (6)	Inhalation/ 750, 3760 7500 mg/m <sup>3</sup> 8 hr/d, 32 weeks	No alterations in peripheral blood counts.	Takeuchi (1969)
Rat (30)	Inhalation/0, 133, 370, 1130, 3760 6 hr/d, 5 d/wk, 13 weeks	No treatment effects: body weight gain, food consumption hematology, clinical chemistry, urinalysis, histopathology. Significantly lower liver weights in test animals except at the highest dose.	Rhudy <u>et al.</u> (1978)
Rat (-)	Inhalation/0, 113,370,1130 6 hr/d, 5 d/wk, 18 months	No treatment effects as in Rhudy <u>et al.</u> (1978). Final results unpublished.	Gibson (1979)
Rat (15) Guinea pig (15) Dog (2) Monkey (3)	Inhalation/4095 mg/m <sup>3</sup> , 8 hr/d, 5 d/wk, 6 weeks, 389 mg/m <sup>3</sup> continuous for 90 days	No significant changes relative to control groups: growth rate, leukocyte counts, hemoglobin and hemocrit.	Jenkins <u>et al.</u> (1970)
Rat (25) Dog (4)	Inhalation/ 0, 950, 1900, 3900 mg/m <sup>3</sup> 6 hr/ day x 13 weeks	No significant hematological or clinical-chemistry changes attributed to treatment.	Carpenter <u>et al.</u> (1976)

<sup>a</sup>Number per dose level.

(-) = Unspecified.

TABLE 5-6. ANIMAL STUDIES OF MYELOTOXICITY (Positive Studies)

<u>Species (N)<sup>a</sup></u>	<u>Route/Dosage</u>	<u>Findings</u>	<u>References</u>								
Mice (-)	Inhalation/6 d/wk, 4, 38, 380, 3800 mg/m <sup>3</sup>	Leukocytosis at all dose levels, decrease in erythro- cytes at 380 and 3800, thrombo- cytopenia at 38, 380, 3800, slight hypoplastic change in bone marrow of group at the highest dose.	Horiguchi <u>et al.</u> (1976)								
Rat (-)	420 mg/m <sup>3</sup> , 4 hr/d, 4 months	Leukocytosis and chromosome damage in bone marrow.	Dobrokhotov and Enikeev (1977)								
Rat (-)	Injection (route unspecified), 1g/kg/d, 12 days	<table><tr><th><u>Treatment</u></th><th><u>Chromosome damaged cells (%)</u></th></tr><tr><td>Toluene</td><td>11.5</td></tr><tr><td>Benzene</td><td>57.2</td></tr><tr><td>Control</td><td>3.9</td></tr></table>	<u>Treatment</u>	<u>Chromosome damaged cells (%)</u>	Toluene	11.5	Benzene	57.2	Control	3.9	Iyapkalo (1973)
<u>Treatment</u>	<u>Chromosome damaged cells (%)</u>										
Toluene	11.5										
Benzene	57.2										
Control	3.9										
Rat (-)	Dermal/ 10g/kg bw/d	Impaired leukopoiesis as evidenced by an increase in the number of plasmic and lymphoid reticular cells in marrow.	Yushkevich and Malysheva (1975)								
	1g/kg bw/d	No effect.									

<sup>a</sup>Number per dose level.

(-) = Unspecified.

The U.S. EPA (1980a) concluded that the studies summarized in Table 5-6 (positive myelotoxic effects) should be interpreted with caution. Although they cannot be entirely dismissed, questions of toluene purity and details of experimental conditions and protocols, and the difficulty in interpreting translations exist. Still, a substantial number of studies in animals and humans has found no evidence of toluene-induced myelotoxicity.

#### 5.1.3.2 Central Nervous System Toxicity

Several case reports have associated permanent CNS damage with glue-sniffing and solvent abuse. Because toluene was found to be a common solvent in glues, it has been suspected as an etiological agent. However, N-hexane is also a common glue solvent and has been associated with certain neuropathies in the industrial setting (Towfighi *et al.* 1976). Moreover, it is not uncommon for persons who sniff the vapors of glue to have abused other solvents, such as gasoline, and to have experimented with a variety of drugs of abuse. Thus, some reports conclude that toluene is not the causative agent.

Towfighi *et al.* (1976), Goto *et al.* (1974), Shirabe *et al.* (1974) and Suzuki *et al.* (1974) support the latter opinion. These reports have attributed the neuropathies to N-hexane. The case histories revealed that N-hexane was present in the glues preferred by the patients. The symptoms are described as a sensory polyneuropathy and sensorimotor polyneuropathy. Towfighi *et al.* (1976) describe a patient who, for 5 years, had been sniffing glue containing toluene and other mixed petroleum distillates but not N-hexane. He had remained in good health but then began using glue containing N-hexane. Over the next 2 months, he noted a gradual onset of pain, tingling and weakness in the left leg and then in the right leg. One year after discontinuing glue sniffing, he still displayed a neurological deficit in the lower extremities.

Grabski (1961), Knox and Nelson (1966), Kelly (1975), Boor and Hurtig (1977), and Keane (1978) attribute neuropathies, in certain cases of chronic glue-sniffing or solvent abuse, to toluene. Knox and Nelson (1966) reported a case of a person who used toluene purchased from a local paint store. Analysis of the toluene paint thinner was not given. After two years of virtually continuous abuse, he noted progressive tremulousness and unsteadiness. He continued to inhale vapors of the toluene thinner for at least another 5 years. Hospital admission, because of injudicious substitution of carbon tetrachloride for toluene, provided an opportunity for extensive neurological tests. These revealed neuropathy, such as tremor, unsteady gait, and emotional explosiveness. Pneumoencephalograms revealed tissue loss from the cerebrum. In another case, Kelly (1975) recorded data on a female patient who had used particular brands of spray paints, most of which contained toluene. Other ingredients of the spray paints were not listed. The neurological tests after 6 years of abuse were similar to the previous case. Five months after discontinuing paint sniffing, the patient was improved although she still exhibited an abnormal tandem gait.

Other central-nervous-system effects have been associated with solvent abuse; and it has been tentatively concluded that toluene is one of the responsible agents. Such effects include emotional or psychiatric problems (Weisenberger 1977, Knox and Nelson 1966, Tarsh 1979) and one report of optic neuropathy (Keane 1978). Spray-painters exposed to toluene and other organics have been found to have modest neurological deficits both functional and emotional (U.S. EPA 1980a). In all these cases, a distinct attribution of the cause to toluene is not possible, because concomitant exposure to other solvents and the contribution of pre-existing problems have not or cannot be assessed.

The chronic CNS effects from solvent abuse occur at very high exposure concentrations. Actual blood levels of toluene attained during glue-sniffing or toluene abuse have not been reported. Knox and Nelson (1966) estimated blood levels of 25 mg/l. Based on the relationship between uptake and blood levels reported by Veulemans and Masschelein (1978b), such blood levels would require air concentrations of 12,000-24,000 mg/m<sup>3</sup>, depending on breathing rates. According to the several reports on glue-sniffing or solvent abuse, high inhalation levels are attained by dousing a rag with paint thinner or toluene and placing it over the mouth and nose and taking multiple deep breaths. Alternatively, glue is applied to the inside of a bag, the bag placed over the mouth and nose, the person rebreathing the bag contents until the desired effects are attained. Clearly, these exposure levels are extremely high.

Animal studies have not appreciably clarified the neurotoxic potential of toluene. Only one study has attempted to examine the sub-chronic effects of toluene on learning and memory. Although acute CNS effects have been extensively studied, these only indicate temporary effects. Of greater concern is the potential for permanent damage as a result of chronic exposure.

Ikeda and Miyake (1978) studied the effects on memory and learning in rats of exposure to toluene (4000 ppm or 15,000 mg/m<sup>3</sup>, 2 hr/day for 60 days). Before the 60-day exposure, rats were taught both a continuous reinforcement (CRF) schedule and a fixed-ratio schedule (FR<sub>30</sub>). In the CRF schedule, every response (e.g., bar press) was rewarded (e.g., food), while in the FR<sub>30</sub>, only a response every 30 seconds was rewarded. Rats who master the FR<sub>30</sub> schedule learn only to press a bar a few times every 30 seconds. The FR<sub>30</sub> schedule is considered a more difficult schedule to learn. Rats that learned both the CRF and FR<sub>30</sub> schedule were divided into two groups, toluene-exposed and control. During the exposure period, CRF and FR<sub>30</sub> were monitored. No difference occurred in the CRF between exposed and control rats; however, the FR<sub>30</sub> response became extinct in the exposed rats by day 40. Spontaneous activity and emotionality, which was measured 4 days after the end of the 60-day exposure period, were not significantly affected by the toluene exposure.

Seven days after the end of the exposure, a DRL 12-second schedule was used to further distinguish exposed and control rats. In this test,

only single responses every 12 seconds were rewarded. If an inter-response interval was less than 12 seconds, a timer was reset to require the rat to wait an additional 12 seconds. This schedule is more difficult to learn than the FR30 schedule. Ikeda and Miyake (1978) concluded that impairment in learning the DRL 12-second and extinction of the FR30 schedule was not because of perceptual or motor difficulty, based on a similar performance in the CRF and activity measures. Rather, the deterioration of more complex behavior and learning patterns were attributed to a diffuse CNS impairment from toluene exposure.

#### 5.1.3.3 Other Chronic Toxic Effects

Several long-term animal studies have not indicated that toluene has appreciable residual toxic effects (Wolf et al. 1956, Takeuchi 1969, Gibson 1979). Takeuchi (1969) did report a relative decrease in the weight of the adrenal gland in rats exposed to 750, 3750, and 7500 mg/m<sup>3</sup>, 8 hr/day, every day for 32 weeks. The histopathology of the adrenal glands revealed a thickening of the zona glomerulosa and a thinning of the zonae fasciculata and reticularis. Takeuchi (1969) suggested this was a secondary hypofunction of the adrenal cortex because of suppression of ACTH secretion. He also reported hyperplasia of the white spleen marrow in the toluene-exposed groups.

#### 5.1.3.4 Carcinogenicity

There are no reports of a carcinogenic response to toluene. In skin-painting experiments, toluene is often used as a vehicle and a control.

The U.S. EPA (1980b) remarked that the data base on the carcinogenicity of toluene is extremely limited and is insufficient for evaluating the carcinogenic potential of toluene.

Frei and Kingsley (1968) reported data that suggest toluene may be a weak promotor of 7, 12-dimethyl benz (a) anthracene (DMBA) induced mouse skin tumors. It was comparable in potency to mineral oil and 10% oil of sweet orange in mineral oil, and significantly less potent than turpentine, Tween-60 and 5% croton oil in mineral oil.

#### 5.1.3.5 Reproductive Toxicity

There have been no reports of teratogenic effects in humans associated with exposure to toluene.

Syrovadko (1977) reported a higher incidence of menstrual disorders in a group of women occupationally-exposed to toluene and other solvents through the use of varnishes. Babies born of these women were stated to experience more frequent fetal asphyxia, to be more often underweight, and not to nurse as well as "normal" infants. Matsushita et al.

(1975) reported that dysmenorrhea was a frequent complaint of female shoemakers occupationally-exposed to 60 and 100 ppm (225 to 376 mg/m<sup>3</sup>) toluene.

Several groups of investigators have examined the teratogenic and fetotoxic effects of toluene in experimental animals. Recently, Nawrot and Staples (1979) reported that toluene was teratogenic in CD-1 mice. Toluene was administered by gavage at 0.5 or 1.0 ml/kg/day during days 6-15 of gestation. At the 1.0 ml/kg dose, there was a statistically significant increased incidence of cleft palate, which these investigators said did not appear to be merely a result of a general retardation in growth rate. This explanation is difficult to accept, in view of their reporting significantly increased embryonic lethality and reductions in fetal weights at both dose levels and a reduction in maternal weight gain at the 1.0 ml/kg level. In contrast, benzene did not significantly increase the incidence of malformations at 0.3, 0.5 or 1 ml/kg/day, although benzene increased embryonic lethality and maternal mortality, and decreased fetal weights at all three dose levels (Nawrot and Staples 1979).

Other investigators have not found toluene to be teratogenic. In a detailed investigation of teratogenicity, Hudak and Ungvary (1978) exposed by inhalation pregnant CFY rats to toluene, xylene or benzene, and pregnant CFLP mice to toluene. None of the solvents proved to be teratogenic, although an increase in skeletal anomalies (extra ribs, fused sternabrae) was observed with all 3 solvents. Benzene at 1000 mg/m<sup>3</sup> and toluene at 1500 mg/m<sup>3</sup> caused a significant decrease in fetal weights. At the highest exposure levels for toluene (1500 mg/m<sup>3</sup>), there was 100 maternal mortality in mice and 20% in rats. At the next highest exposure levels (500 mg/m<sup>3</sup> for mice, 1000 mg/m<sup>3</sup> for rats), there was no maternal mortality. The exposure levels and other details of the experimental results are presented in Tables 5-7 and 5-8.

The actual exposure levels in this study by Hudak and Ungvary (1978) are considered high, estimated to be equivalent to ~360 mg/kg/day (which is 0.100 liters/min x 60 min/hr x 24 hr/day ÷ 1000 l/m<sup>3</sup> x 0.5 retention x 1500 mg/m<sup>3</sup> ÷ 0.3 kg) at the 1500 mg/m<sup>3</sup> exposure level for rats and ~280 mg/kg/day at the 500 mg/m<sup>3</sup> exposure level for mice.

Roche and Hine (1968) concluded that neither benzene nor toluene was teratogenic to the rat fetus or to the chick embryo (details of exposure and results are not cited).

#### 5.1.4 Additional Health Effects

Although the case reports summarized in Section 5.1.3.2 do not clearly indicate overt toxicological manifestations to toluene as a result of solvent abuse, they do suggest a tendency toward habituation, which may have contributed to deterioration of mental health. A direct or synergistic effect of toluene in producing neurological deficits is debatable. However, these effects, if caused by toluene, would only result from long-term, high-level inhalation exposure.



TABLE 5-7

LAYOUT OF THE EXPERIMENT AND SUMMARIZED DATA OF THE EXPERIMENTAL GROUPS OF BENZENE, TOLUENE AND XYLENE TREATED PREGNANT ANIMALS

Experimental groups			No. of pregnant animals/group		Maternal <sup>a</sup> weight gain (%)	No. of fetuses			Fetal loss <sup>b</sup> (%)	Mean litter size	Mean fetal weight (g)	Mean placental weight (g)	Weight retained fetuses <sup>c</sup> (%)
Species	Time of inhalation	Substances and doses	Examined	Died		Live	Resorbed	Dead					
Rats	Untreated control	—	28	—	52.45±1.23	316	10	1	3.37	11.26±0.54	3.83±0.02	0.51±0.005	2.9
	9-14 Days of pregnancy 24 h/day	Air	26	—	46.85±2.04	348	16	—	4.13	13.38±0.50	3.76±0.02	0.47±0.004	6.9
		Benzene 1000 mg/m <sup>3</sup>	19	—	22.54±5.98**	226	12	4	6.60	11.89±0.89	3.38±0.02**	0.47±0.006	38.0†
		Toluene 1500 mg/m <sup>3</sup>	19	2	41.75±2.43	213	18	—	7.79	11.21±0.54	3.75±0.03	0.16±0.005	17.3
		Xylene 1000 mg/m <sup>3</sup>	20	—	46.20±2.01	288	15	1	5.30	14.30±0.57	3.75±0.02	0.51±0.003	5.0
		Air	10	—	46.58±2.34	111	8	—	6.72	11.10±0.59	3.81±0.03	0.53±0.006	7.2
	1-21 Days of pregnancy 8 h/day	Toluene 1000 mg/m <sup>3</sup>	10	—	44.07±2.37	133	3	—	2.21	13.30±0.56	3.81±0.03	0.52±0.006	16.0
		Toluene 1500 mg/m <sup>3</sup>	9	5	44.03±3.60	95	6	—	5.94	10.56±1.30	3.31±0.08**	0.53±0.013	46.0†
	6-13 Days of pregnancy 24 h/day	Air	14	—	—	124	6	1	6.10	9.00±0.74	1.07±0.01	—	6.6
		Toluene 1500 mg/m <sup>3</sup>	—	15	—	—	—	—	—	—	—	—	—
		Toluene 500 mg/m <sup>3</sup>	11	—	—	112	10	—	8.20	10.18±1.08	0.96±0.01**	—	27.0†

<sup>a</sup> In per cent of starting body weight.<sup>b</sup> In per cent of total implantates.<sup>c</sup> Per cent of living fetuses weighing less than 3.3 g (rats) or 0.9 g (mice).± S.E.; \*  $P < 0.01$  (t-test); †  $P < 0.05$ , (Mann Whitney U test).

Source: Hudák and Ungváry (1978)

TABLE 5-8

## DATA OF THE FETUSES OF BENZENE, TOLUENE AND XYLENE TREATED PREGNANT ANIMALS

	Experimental groups									
	Rats					Mice				
	Untreated control	Air inhalation 9-14 days 24 h/day	Benzene inhalation 9-14 days 24 h/day	Toluene inhalation 9-14 days 24 h/day	Xylene inhalation 9-14 days 24 h/day	Air inhalation 1-21 days 8 h/day	Toluene inhalation 1-21 days 8 h/day	Toluene inhalation 1-8 days 24 h/day	Air inhalation 6-13 days 24 h/day	Toluene inhalation 6-13 days 24 h/day
No. of litters examined	28	20	19	19	20	10	10	9	14	11
No. of live fetuses	315	348	226	213	286	111	133	65	124	112
External malformations										
Agnathia	—	—	—	—	2	—	—	—	—	—
Brachimelia	—	—	—	—	—	—	—	—	1	—
Missing tail	—	—	—	2	—	—	—	—	—	—
No. of fetuses dissected	166	179	119	110	146	54	64	49	64	58
Internal malformations										
Anophthalmia	—	1	—	—	—	—	—	—	—	—
Hydrocephalus	—	—	—	—	—	—	—	4	—	—
Thymus hypopl.	—	—	1	—	—	—	—	—	—	—
Hydronephrosis	3	16	6	4	26	1	6	4	1	3
No. of Alizarin-stained fetuses	143	169	108	102	143	57	69	42	60	64
Skeletal retardation signs <sup>a</sup>	—	11	24†	6	17	—	17†	7†	3	1
Skeletal anomalies										
Fused sternebrae	1	2	13†	7†	8†	—	—	—	—	—
Extra ribs	2	—	8†	22††	9†	—	—	—	—	—
Skeletal malformations										
Fissura sterni	—	—	—	—	1	—	—	—	—	—
Agnathia	—	—	—	—	2	—	—	—	—	—
Missing vertebrae	—	—	—	2	—	—	—	—	—	—
Brachimelia	—	—	—	—	—	—	—	—	1	—

<sup>a</sup> Including poorly ossified sternebrae, bipartite vertebra centra and shortened 13th ribs.†  $P < 0.05$ , ††  $P < 0.01$  (Mann-Whitney U test).

Source: Hudák and Ungváry (1978)

Of possible concern are the fetotoxic effects, especially, reduced fetal weight gain and increased resorptions, which are estimated to occur at absorbed dose levels of 360 mg/kg/day in rats and 280 mg/kg/day in mice (Hudak and Ungvary 1978). At a lower exposure level -- approximate absorbed dose 240 mg/kg/day in the rat -- fetotoxic effects were not statistically significantly increased compared with unexposed control animals. This study may be relevant in view of Syrovadko's (1977) report of more frequent fetal asphyxia and underweight babies in women occupationally-exposed to toluene although other unidentified solvents may be involved. Further implications of these results are discussed below.

#### 5.1.5 Estimation of Human Risk

The limited human and animal data cited above do suggest a potential fetotoxicity of toluene at high exposure levels. The potential should be more carefully investigated in epidemiological studies of occupational exposures of pregnant women to toluene.

A no-effect human daily dose is calculated, assuming that 1000 mg/m<sup>3</sup> is a no-effect level in rats (Hudak and Ungvary 1978) and that an effective dose in a 65-kilogram human female is from 1/2 to 1/6 the mg/kg dose in the rat. The factor 1/2 is derived from data of Sato and Nakajima (1979), which indicates that clearance from the body is about twice as fast in rats as in humans. The more conservative factor is derived from the direct relationship between body surface area and metabolic rate (MR). Because surface area is proportional to body weight (bw) to the 2/3 power; i.e.:

$$\frac{MR}{bw} = \frac{(bw)^{2/3}}{bw} = (bw)^{1/3};$$

it follows that:

$$\frac{MR [\text{rat}]/0.3 \text{ kg}}{MR [\text{human}]/65 \text{ kg}} = \frac{65}{0.3}^{1/3} \approx 6.$$

An exposure level of 1000 mg/m<sup>3</sup> in a rat is estimated to be 240 mg/kg/day;

$$\frac{1000 \text{ mg/m}^3 \times 0.100 \text{ l/min} \times 0.5 \times 60 \text{ min/hr} \times 24 \text{ hr/day}}{1000 \text{ l/m}^3 \times 0.3 \text{ kg}} = 240 \text{ mg/kg/day}.$$

The human no-effect level is reduced by 1/2 to 1/6 to adjust for metabolic rate differences so that 120-40 mg/kg/day or 7800-2600 mg/day/body weight is the estimated no-effect dose level. These doses would be absorbed at air exposure levels of 1600 to 540 mg/m<sup>3</sup> in an 8-hour day.

An uncertainty factor of 100 is indicated based on guidelines cited by the U.S. EPA (1979), which places acceptable daily ingestion (ADI) at 78 to 26 mg/day. The guidelines state that an uncertainty factor

of 100 is to be used when chronic human data are not available, when valid results in long-term feeding studies in one or more species are available, and when no indication of carcinogenicity exists. Based on the very low acute toxicity of toluene, its rapid metabolism to non-toxic metabolites, and a presumption of a non-specific or general CNS depression following inhalation exposures at the levels employed in the reproductive study of Hudak and Ungvary (1978), an ADI of 78 to 26 mg/day is considered very conservative.

## 5.2 HUMAN EXPOSURE

### 5.2.1 Introduction

Monitoring data on toluene in the environment indicate a wide range of toluene levels in the natural environment and in food. The fate analyses also support the conclusion that toluene may occur in all environmental media. As discussed in the human effects section, it has been determined that toluene can be absorbed by all three routes of exposure--ingestion, inhalation, and dermal contact. The potential absorption of toluene by these three routes has been considered in the following analysis to estimate total daily absorbed dose.

Toluene concentrations in various media were estimated on a conservative basis in order to avoid underestimating the actual exposure that could occur. These data were combined with data on rates of air, water, and food intake and/or duration of exposure to estimate the amounts absorbed through each exposure route. Ideally, the absorption of toluene would be analyzed with respect to subpopulation factors such as age, weight, sex, breathing rates, food and water consumption, commuting and working patterns, etc. For toluene, such detailed data are not available and the variability and scarcity of the monitoring data do not justify such a detailed analysis. Instead, in the analysis below, total daily absorption of toluene has been approximated for two broad population groups, based on their location with respect to major toluene sources of emission.

Occupational exposure to toluene has been evaluated for each exposure route (where appropriate) for a comparison with general population exposure groups.

### 5.2.2 Exposure through Drinking Water and Food

Ingested toluene is presumed to be 100% absorbed. Humans may be exposed to toluene through ingestion of contaminated drinking water, either from surface or from ground water. The monitoring data on toluene in ground water are insufficient either to indicate typical levels or to document a range of concentrations. In addition, because the populations exposed to contaminated ground water sources are dispersed and unpredictable, it is not possible to ascribe very precise numbers to these populations. However, the available data summarized in Tables 4-2 and 4-3 suggest that most water supplies, whether of

ground or surface origin, have levels of toluene below the detection limit. Moreover, the U.S. EPA's Office of Drinking Water reports that approximately 100 million people (about one-half the U.S. population) receive surface waters in their homes. Thus, the remainder, who are usually people living in communities with less than 60,000 people, are receiving ground water either from public or private wells. Although over 12 million private wells exist in the United States, the Office of Drinking Water did consider that working people often consume more water at their workplace than at home. Thus, regardless of the kind of water supplied to their homes, most people are probably consuming both ground and surface waters on the average (Coniglio, U.S. EPA, Personal communication, 1980).

To estimate the exposure to toluene from drinking water supplies, based on data given in Table 4-2, three approximations were utilized to indicate the range of possible exposures. The first involved taking the mean value of the observed concentrations at or above the detection limit. This mean, 1.3  $\mu\text{g/l}$ , is thought to be representative of the upper tail of the toluene concentration distribution. The second approximation utilized all existing sampling data for surface water supplies. A value of 0 was assigned to those reported as ND (not detected) and 0.1  $\mu\text{g/l}$  to all reported as D--detected but not quantified. This analysis yields a mean of 0.15  $\mu\text{g/l}$ . The third approximation assumes the worst case and all NDs were counted as 0.1  $\mu\text{g/l}$ . This third mean value was 0.24  $\mu\text{g/l}$ , which is not markedly different from the second value. The latter mean was used as a conservative estimate of typical exposure to toluene through drinking water. At an average water consumption of 2 liters per day, the estimated absorption of toluene is typically about 0.5  $\mu\text{g/day}$  but may average  $>3$   $\mu\text{g/day}$  for some segments of the population. These results are given in Table 5-9.

Toluene may be ingested with foods. However, except for some data on levels in fish tissues, no data are available on toluene levels in foods. Per capita consumption of fish is taken from Stephan (1980) as 6.5 g/day. At an estimated mean concentration in fish tissue of 1 mg/kg (see Section 4.3.3.1), approximately 6.5  $\mu\text{g/day}$  of toluene may be ingested from fish alone.

### 5.2.3 Exposure through Inhalation

Sources of direct releases of toluene to the atmosphere include the plants that isolate toluene, the industrial plants using toluene, vehicular traffic, and gasoline distribution facilities. The emission sources of concern are primarily automobiles (630 kkg/yr) and solvents (370 kkg/yr, including paint, coating, adhesives, printing, pharmaceuticals etc.).

The duration of exposure will vary with individual lifestyles, location, local meteorology, traffic volume and patterns, proximity to user sites, and operating schedules at user sites. The labor force in the vicinity of a source may be exposed 8 hr/day, while residences in the area of a source may be exposed up to 24 hr/day. In the latter case, emissions may be reduced or eliminated at the close of the working day as a function of plant operation schedules. That is, pollutant concentrations, which depend on the dispersion of emissions, will vary over time in any given location.

As an estimate of the absorption of toluene via inhalation, a standard adult respiratory rate of  $22.4 \text{ m}^3/\text{day}$  has been used ( $1.2 \text{ m}^3/\text{hour}$  for 16 hours per day and  $0.4 \text{ m}^3/\text{hour}$  8 hours a day while asleep). About 50% of the toluene inhaled is retained and absorbed into the blood (see 5.1.1.1). Therefore, absorption is approximated by computing  $22.4 \text{ m}^3/\text{d} \times 0.5 \times \text{concentration } (\mu\text{g}/\text{m}^3)$ .

The monitoring data, given in Table 4-9, do not indicate that appreciably higher toluene levels may be found near either manufacture or use sites than may be found within other urban areas. In fact, the cities sampled by Pellizari (1979), which represent high chemical production areas, have a similar average concentration to all the cities shown in Table 4-9 (17 versus  $19 \mu\text{g}/\text{m}^3$ ). In addition, Anderson and coworkers (1980) performed dispersion modeling that indicated maximum levels of  $<25 \text{ mg}/\text{m}^3$  for exposure to specific point sources. The dispersion analyses for large ( $50 \text{ kkg}/\text{yr}$ ) sources and for a more typically sized ( $20 \text{ kkg}/\text{yr}$ ) source yielded levels of 30 and  $13 \mu\text{g}/\text{m}^3$  for a 20-meter stack at a distance of 1000 meters. These results agree with the statement of Suta (1980): "...concentrations of 0.001 to 0.2 ppb ( $0.004\text{--}0.75 \mu\text{g}/\text{m}^3$ ) near production plants are small compared to normal urban background concentrations, which may average more than 10 ppb ( $37.7 \mu\text{g}/\text{m}^3$ ) in some locations."

The average urban air concentration of toluene from the available monitoring data (Table 4-9) is about  $19 \mu\text{g}/\text{m}^3$ , which is calculated to give an average daily dose of 210  $\mu\text{g}$ . The average rural/remote air concentration is  $1.0 \mu\text{g}/\text{m}^3$ , for an average daily absorption by inhalation of about 11  $\mu\text{g}$ . These values are listed in Table 5-9.

The study of Anderson et al. (1980) is specifically an inhalation exposure analysis for toluene, based on atmospheric dispersion modeling for specific point, general point, and area sources. Their model utilized a standard population distribution to associate populations with specific concentration levels. They estimate that about 700,000 people are exposed to 56 specific (industrial) point sources of toluene at levels from 0.1 to  $25 \mu\text{g}/\text{m}^3$ . The materials balance (see Section 3.0) has actually identified 53 additional plants in all the manufacturing categories. Thus, if the assumptions of Anderson et al. (1980) regarding population distribution are valid, they may have underestimated the size of this subpopulation by one-half.

TABLE 5-9. ESTIMATED HUMAN EXPOSURE TO TOLUENE BY ALL ROUTES

Exposure Route/Scenario	Concentration <sup>a</sup>		Amount Con- sumed or In- haled Daily	Daily Absorption	
	Typical	Range		Typical	Range
				(ug/day)	
<u>INGESTION</u>					
<u>Water</u>	(ug/l)		(l) <sup>b</sup>		
- All surface supply data	0.24	ND-19	2	0.5	?-38
- High end of distribution of surface water supplies	1.3	0.1-19	2	3	?-38
<u>Food</u>	(mg/kg)		(kg) <sup>c</sup>		
- Fish tissues	1.0	ND-35	0.0065	6.5	?-224
<u>INHALATION<sup>d</sup></u>					
	(ug/m <sup>3</sup> )		(m <sup>3</sup> ) <sup>e</sup>		
- Urban areas	19	0.15-283	22.4	210	1.7-3,170
- Remote areas	1	ND-3.8	22.4	11	?-43
- Use of gasoline stations	860	100-5400	0.024 m <sup>3</sup> / .02 hrs.	10	1-65
- Occupational:at OSHA standard	754,000	-	9.6 <sup>f</sup>	3,600,000	-
	(ug/cigarette)		(packs)		
- Cigarette	100		1.56	1,560	
<u>PERCUTANEOUS</u>					
	(mg/hr)		(hrs)		
- Occupational-- 2 hands unprotected	~ 40		0.08-0.5	-	3,200-20,000 ug/use
- Consumer Products	2.0		0.08-0.5		23-140

<sup>a</sup>Data from Section 4.3, Monitoring Levels in the Environment.

<sup>b</sup>Data from ICRP (1975).

<sup>c</sup>Data from Stephan (1980).

<sup>d</sup>Inhalation exposure estimates are calculated using a 50% respiratory retention.

<sup>e</sup>Data from ICRP (1975), for a 24-hour exposure, based on 1.3 m<sup>3</sup>/hr during 16 hours of waking and 0.4 m<sup>3</sup>/hr for 8 hours of sleep.

<sup>f</sup>Inhaled amount for 8 hours at 1.2 m<sup>3</sup>/hr.

Similarly, these authors identified a subpopulation of 2.3 million exposed to levels between 0.1 and 100  $\mu\text{g}/\text{m}^3$  from general point sources and a third group of 192 million, which may include members of the first two groups, exposed to area sources at levels from 5-100  $\mu\text{g}/\text{m}^3$ .

No data were available on toluene concentrations in the immediate vicinity of gasoline marketing pumps and stations. However, evaporative emissions from gasoline contain about 1.3% toluene (see page A-4) and about 1.2% benzene (Arthur D. Little, Inc. 1981). Using the ratio of toluene to benzene in gasoline evaporate (approximately 1), and the monitoring data for benzene at gasoline service stations, an estimate for toluene levels in the same situation can be made. Battelle (1979) reports an average level for benzene of 860  $\mu\text{g}/\text{m}^3$  in customer areas; Hartle and Young (1976) report a range of 100-5400  $\mu\text{g}/\text{m}^3$ . Therefore, an estimated average toluene level of 860  $\mu\text{g}/\text{m}^3$  and a range of 100-5400  $\mu\text{g}/\text{m}^3$  was assumed. It has been assumed that the average driver spends 10 minutes once a week at the gas station for an average daily exposure of 0.02 hours. The estimated daily absorption of toluene from use of gasoline stations then is 10  $\mu\text{g}$  and may range from 1  $\mu\text{g}$  to 64  $\mu\text{g}$ .

Occupational exposures to toluene by inhalation are analyzed at the OSHA standard. The standard established by OSHA is 854  $\text{mg}/\text{m}^3$  (200 ppm) as a time-weighted-average for the 8-hour work day (OSHA 1978). NIOSH (1973) estimated that about 4.8 million workers were exposed to toluene. At this concentration, a worker can absorb about 1,800,000  $\mu\text{g}/\text{day}$  or 1.8 grams.

It has also been determined that cigarette smoking adds to the amount of toluene inhaled and also increases levels in the surrounding air. According to NRC (1980), the average toluene exposure is 0.1  $\text{mg}/\text{cigarette}$ . Based on data from the 1979 report from the U.S. Surgeon General, the "average" smoker (1.56 packs/day, Richmond 1981) would be exposed to 3.1  $\text{mg}/\text{day}$  although absorption is 1560  $\mu\text{g}/\text{day}$ . The U.S. Surgeon General also reported a total of 54 million smokers in the United States in 1978 for all age groups. In addition, Young (1978) has stated that "unknowing inhalation" in the home can occur from the use of paint strippers, carburetor cleaners, denatured alcohol, rubber cement, and arts and crafts supplies. These sources have not been documented, and exposures are assumed to be infrequent as well as dilute.

#### 5.2.4 Percutaneous Exposure

##### 5.2.4.1 Occupational Exposure

In a study of absorption of toluene through the skin, Sata and Nakajima (1978) immersed one hand of 5 male subjects in pure toluene for 30 minutes and monitored blood levels of toluene. The peak concentration of 18  $\mu\text{g}/\text{l}$  was observed within 10 minutes after exposure ceased and decreased over the next few hours. It was calculated in the previous section that the absorption rate through the skin of one hand was  $\sim 20$   $\text{mg}/\text{hour}$  for pure toluene.



Although the OSHA (1973) standards require all workers handling toluene directly to wear gloves, it is conceivable that, in the workplace and in research laboratories, short-term exposure would take place across the bare skin of both hands. Using the calculated absorption rate and exposure durations, ranging from 5-30 minutes per use, the absorption of toluene across the skin is estimated to be between 3.2 and 20 mg/use, for unprotected hands. Sato and Nakajima (1978) concluded their paper with the following "...toluene would rarely be absorbed through the human skin in toxic quantities during normal industrial use."

#### 5.2.4.2 Consumer Products

The majority of solvents, paint removers, paints and other substances used in the home would contain only small amounts of toluene as a component or contaminant. Assuming a scenario similar to the occupational scenario described above, which involved a 5% toluene solution and a 5-30 minute exposure duration, the exposure is:

$$20 \text{ mg/hr} \times 2 \text{ (hands)} \times 0.05 \times (0.08-0.5) \text{ hr} = 0.21 \text{ mg/use.}$$

For the purposes of this report, a use rate of once per week was assumed, resulting in an estimated average daily exposure 23-140 µg.

#### 5.2.5 Total Exposure Scenarios and Conclusions

The results of the exposure estimates summarized in Table 5-9 have been used to derive two comprehensive, total exposure scenarios for all routes (Table 5-10). These scenarios are not meant to define actual exposures for a specific individual but to typify likely levels in probable situations for the identifiable subpopulations.

Scenario A considers exposures to about 150,000,000 people living in urban areas (74% of the 1980 census population) who drink predominantly surface waters (110 million people drink surface water, usually supplied to urban areas with more than 60,000 people), breathe urban air, and consume 6.5 g fish per day. This subpopulation also uses products containing toluene for about 1/2 hr/week. The total typical daily dose is about 370 µg. If the individual smokes cigarettes, the daily dose is about 1800 µg.

Scenario B considers that population living in the rural or remote areas of the country, numbering in 1970 about 54,000,000 people (or 26% of the 1970 census). This subpopulation is supplied nearly 100% with ground water for drinking purposes; however, in the absence of sufficient monitoring data, the surface water value was used. For the purposes of example, it is assumed that this subpopulation uses products containing toluene for about 5 minutes per week. If the contamination of wells is considered, from the disposal of wastes, it is possible that this may be a problem in the more densely populated areas that are near the sources rather than in rural areas. Total typical daily exposure for this scenario is 51 µg or 1600 µg if smoking is involved.

To provide a contrast with these two ambient exposure scenarios, potential industrial exposures of employees producing and utilizing toluene were calculated. If exposure occurs at the occupational standard, the employee can add 3500 mg/day to baseline (food and water and nonoccupational inhalation) exposure. If percutaneous exposure also occurs, an additional exposure up to 20 mg/use is possible.

#### 5.2.6 Summary

In conclusion, the two nonoccupational, ambient exposure scenarios had total exposures of about 51-370 µg/day, excluding smoking. The addition of smoking increased exposure by a factor of 8 to 60. Compared with the potential occupational exposure, typical exposure to toluene is three to four orders of magnitude less.

TABLE 5-10. TOTAL HUMAN EXPOSURE SCENARIOS FOR TOLUENE

<u>Route</u>	<u>Exposure by Scenario</u>	
	<u>A</u>	<u>B</u>
	<u>74</u>	<u>26</u>
% of 1970 population	(ug/day)	(ug/day)
<u>Ingestion</u>		
Water	0.5	0.5
Food	6.5	6.5
<u>Inhalation</u>		
Baseline	210	11
Gas Station Use	10	10
Cigarettes <sup>a</sup>	1,560	1,560
<u>Percutaneous</u>		
Consumer products	140	23
Total-excluding cigarettes	370	51
Total-including cigarettes <sup>a</sup>	1,900	1,600

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<sup>a</sup>Cigarette smoking involved 54 million individuals in 1978.

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## 6.0 BIOTIC EFFECTS AND EXPOSURE

### 6.1. BIOTIC EFFECTS

#### 6.1.1 Introduction

This section provides information on the exposure levels of toluene that cause mortality or disrupt physiologic functions and processes in aquatic organisms. Fairly extensive data exist for both marine and freshwater organisms, including fish, invertebrates, plankton, algae, and microorganisms. Toxicity data for these organisms are presented in tables in this chapter.

Toluene is one of the major components of the water-soluble fraction of petroleum. Under test conditions, it reacts as a highly volatile compound with a half-life of approximately 30.6 minutes (Buikema and Hendricks 1980). The half-life in river water has been calculated to be 4.9 hours (see Chapter 4.0). This difference indicates that volatilization is substantially more rapid under laboratory conditions, so that the concentrations derived in toxicity tests may only approximate what might actually occur in the natural environment. Thus, static, unmeasured toxicity tests overestimate the toxicity, due to losses of toluene due to volatilization from the test water.

Further, use of laboratory data to predict in situ effects is complicated by variations between laboratory and actual environmental conditions. These may include environmental factors affecting bioavailability of toluene in actual aquatic systems, such as adsorption to sediments and suspended particulate matter.

#### 6.1.2 Mechanisms of Toxicity

Investigation of several alkyl benzenes, including toluene, suggests that toxicity might result from solubilization of fats from the gill membranes of fish, with consequent increases in permeability and uptake of ions from the hypertonic environment (National Research Council 1980). The exact mechanisms of toxicity are not fully understood; however, based on changes in the blood chemistry of young coho salmon, Morrow and coworkers (1975) suggested that narcosis was a result of changes in gill permeability causing ionic imbalance and internal CO<sub>2</sub> poisoning. These effects result in the loss of equilibrium and weakened muscle movement. These observations were made for several crude oil components, including toluene.

Toluene acts, as do other aromatic hydrocarbons, as a neurotoxin. At high concentrations, fish sequentially go through phases of restlessness, "coughing" or backflushing of water over the gills, increased irritability, loss of equilibrium, paralysis, and death (Morrow et al. 1975). In addition, heart rate decreased and heart beat became irregular

in fish fry exposed to toluene. Toluene was found to have teratogenic effects on Japanese medaka fry. The concentrations that caused developmental deformities ranged from 41 to 165 mg/l (Buikema and Hendricks 1980), which is higher than many of the LC<sub>50</sub>'s for adult freshwater fish.

#### 6.1.3 Freshwater Organisms

Seven fish species have been tested for acute toxicity to toluene. The LC<sub>50</sub>'s ranged from 12.7 and 24.0 mg/l for bluegill up to 1180 mg/l for the mosquito fish (Gambusia affinis). Various authors derived the LC<sub>50</sub>'s in Table 6-1 using different methods. However, the majority reported LC<sub>50</sub>'s <60 mg/l.

Pickering and Henderson (1966) conducted tests on four freshwater fish species, under static conditions, in soft water (20 mg/l CaCO<sub>3</sub>) at pH 7.5. The results of similar tests conducted in hard water (300 mg/l CaCO<sub>3</sub>) showed that hardness had little effect on toxicity. In the static tests, most of the toxic effects apparently occurred during the first 24 hours, because 96-hour LC<sub>50</sub>'s were similar to those measured at 24 hours. Actual concentrations during the test period were not measured. Because it was assumed that much of the toluene volatilized during testing, the LC<sub>50</sub> values reported are probably high. Studies with goldfish (Carassius auratus) support this conclusion as well. In these tests, considerably lower 96-hour LC<sub>50</sub> values were found for toluene in a flow-through bioassay with measured concentrations of the test compound (Brenniman et al. 1976).

The only freshwater invertebrate data available were for Daphnia magna. The LC<sub>50</sub> value for this species (313 mg/l), suggests that more it may be more resistant than the fish species tested. No chronic data were available for freshwater biota of any species.

#### 6.1.4 Marine Organisms

Few studies have been conducted with saltwater fish. Benville and Korn (1977) found toluene to be lethal to striped bass (Morone saxatilis) at 7.3 mg/l (Table 6-2). Sheepshead minnows (Cyprinodon variegatus) had a 96-hour LC<sub>50</sub> of 277-485 mg/l (U.S. EPA 1978), which demonstrates considerably more resistance than shown by other species on which data are available. Gambusia, a hardy freshwater species, also demonstrates a similar resistance pattern, although it was tested in turbid water. An embryo larval test of sheepshead minnows indicated a chronic value of 5 mg/l, which caused adverse effects on hatching and survival (U.S. EPA 1978) (Table 6-3).

Acute toxicity tests have been conducted on several invertebrates, including four shrimp species, a copepod, and the crab Cancer magister.

TABLE 6-1. ACUTE TOXICITY OF TOLUENE TO FRESHWATER FISH

<u>Species</u>	<u>Bioassay Method<sup>a</sup></u>	<u>LC<sub>50</sub> (mg/l)</u>	<u>Reference</u>
Goldfish <u>Carassius auratus</u>	FT	22.8	Brenniman <u>et al.</u> (1976)
Goldfish <u>Carassius auratus</u>	S	57.7	Pickering and Henderson (1966)
Fathead minnow <u>Pimephales promelas</u>	S	34.3	Pickering and Henderson (1966)
Fathead minnow <u>Pimephales promelas</u>	S	42.3	Pickering and Henderson (1966)
Guppy <u>Poecilia reticulatus</u>	S	59.3	Pickering and Henderson (1966)
Bluegill <u>Lepomis macrochirus</u>	S	24.0	Pickering and Henderson (1966)
Bluegill <u>Lepomis macrochirus</u>	S	12.7	U.S. EPA (1978)
Mosquito Fish <u>Gambusia affinis</u>	S	1180.0 <sup>a</sup>	Walien <u>et al.</u> (1957)
<u>Lebistes reticulatus</u>	S	60.9	Pickering and Henderson (1966)
Pink Salmon <u>Oncorhynchus gorbuscha</u>		8.09 <sup>b</sup>	Korn <u>et al.</u> (1977)

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**Note:**

S= Static, FT= flow-through

<sup>a</sup>Tested in turbit water.<sup>b</sup>This value derived in tests on (examining) the interaction between temperature and toluene toxicity.

TABLE 6-2. ACUTE TOXICITY OF TOLUENE TO MARINE FISH

<u>Species</u>	<u>Time</u> (hrs)	<u>LC50</u> (mg/l)	<u>Reference</u>
Coho Salmon <u>Orcorhynchus kisutch</u>	96	10.0-50.0	Morrow <u>et al.</u> (1975)
Striped Bass <u>Morone saxatilis</u>	96	6.3	Benville and Korn (1977)
Sheepshead Minnow <u>Cyprinodon variegatus</u>	96	>277.0- <485.0	U.S. EPA (1978)

TABLE 6-3. CHRONIC TOXICITY OF TOLUENE TO MARINE FISH

<u>Organism</u>	<u>Test</u>	<u>Limits</u> (mg/l)	<u>Chronic Value</u> (mg/l)
Sheepshead Minnow <u>Cyprinodon variegatus</u>	Embryo- larval	2.8-6.7	2.1

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Source: U.S. EPA (1978)

Values for these organisms ranged from 3.7 mg/l for the Bay shrimp, Crago franciscorum, to 170.0 mg/l for Cancer magister. Most of the invertebrate toxicity values ranged from 10 to 75 mg/l (Table 6-4). All of these concentrations were derived from static toxicity tests.

#### 6.1.5 Phytotoxicity

Photosynthetic organisms, such as algae and marine phytoplankton, are important primary producers in freshwater and marine ecosystems. Several studies have been conducted to determine the effects of toluene on these organisms. It is believed that the effects of toluene on plant cells are biophysical rather than biochemical, and the effects include disrupting cell membrane structure and changing internal morphology of the cells, as in the case of fish gill tissue (National Research Council 1980). Table 6-5 presents toxicity data on freshwater plants. Toxicity data for marine plants are presented in Table 6-6. Inhibitory effects (growth reduction, photosynthesis) in six species occurred in the range of 8.0-100 mg/l. No effects on one species tested (Skeletonema costatus) were observed at concentrations up to 433 mg/l.

#### 6.1.6 Factors Affecting the Toxicity of Toluene

Few empirical data exist on the environmental factors that may affect the toxicity of toluene to biota. However, based on studies with benzene, some generalizations can be made. Because of the high volatility of toluene, any factor that affects its persistence in water will ultimately influence its toxicity. Studies of temperature interactions and benzene toxicity indicate that at lower test temperatures, organisms were more tolerant (Potera 1975). The effects of temperature on toluene toxicity were studied for two coldwater marine species, pink salmon and shrimp (Eualus spp). These data are inconclusive (Table 6-7) as toxicity increased with increasing temperature in shrimp, and little temperature difference among toxicity levels at different temperatures was noted in salmon (Korn et al. 1977).

Other factors found to influence benzene toxicity and potentially that of toluene, include size and life stage of the organism, salinity, and synergistic effects of other compounds (Buikema and Hendricks 1980). Water hardness has been found to have little effect on toxicity in studies with freshwater fish (Pickering and Henderson 1966).

#### 6.1.7 Summary

According to the literature reviewed, the lowest concentration at which effects of toluene have been observed in aquatic organisms is 3.7 mg/l, the LC<sub>50</sub> for the marine shrimp, Crago franciscorum. Invertebrates tended to be more sensitive than other fish and algal species tested, with the exception of striped bass, Morone saxatilis, which was affected by a relatively low (LC<sub>50</sub>, 6.3 mg/l) concentration of toluene. The most

TABLE 6-4. ACUTE TOXICITY OF TOLUENE TO  
MARINE INVERTEBRATES (STATIC TESTS)

<u>Species</u>	<u>Time</u> (hrs)	<u>EC<sub>50</sub> or LC<sub>50</sub></u> (mg/l)	<u>Reference</u>
Copepod <u>Nitocra spinipes</u>	24	24.2-74.2	Potera (1975)
Mysid Shrimp <u>Mysidopsis bahia</u>	96	56.3	U.S. EPA (1978)
Bay Shrimp <u>Crago franciscorum</u>	96	3.7	Benville and Korn (1977)
Grass Shrimp <u>Palaemonetes pugio</u>	96	9.5	Tatem (1975)
Grass Shrimp (Adult) <u>Palaemonetes pugio</u>	24	17.2-38.1	Potera (1975)
Grass Shrimp (Larva) <u>Palaemonetes pugio</u>	24	25.8-30.6	Potera (1975)
Brine Shrimp <u>Artemia salina</u>	24	33	Price <u>et al.</u> (1974)
Crab <u>Cancer magister</u>	48 96	170.0 28.0	Caldwell (1976)

TABLE 6-5. EFFECTS OF TOLUENE ON FRESHWATER PLANTS

<u>Organism</u>	<u>Effects</u>	<u>Concentration</u> mg/l	<u>Reference</u>
Alga <u>Chlorella vulgaris</u>	EC <sub>50</sub> 24-hour cell numbers	245.0	Kauss and Hutchinson (1975)
Alga <u>Selenastrum</u> <u>capricornutum</u>	96-hour EC <sub>50</sub> for chlorophyll <u>a</u> production	>433.0	U.S. EPA (1978)
Alga <u>Selenastrum</u> <u>capricornutum</u>	96-hour EC <sub>50</sub> for cell numbers	>433.0	U.S. EPA (1978)



TABLE 6-6. EFFECTS OF TOLUENE ON MARINE PLANTS

<u>Organism</u>	<u>Effects</u>	<u>Concentration</u> mg/l	<u>Reference</u>
Kelp <u>Macrocystis pyrifera</u>	Photosynthesis	10.0	Anonymous (1964)
Alga <u>Amphidinium carteri</u>	Growth	100.0	Dunstan <u>et al.</u> (1975)
Alga <u>Chlorella</u> sp.	Photosynthesis respiration	34.0	Potera (1975)
Alga <u>Chlorella</u> sp.	Photosynthesis respiration	85.0	Potera (1975)
Alga <u>Cricosphaera carterae</u>	Growth	100.0	Dunstan <u>et al.</u> (1975)
Alga <u>Dunaliella tertiolecta</u>	Growth	100.0	Dunstan <u>et al.</u> (1975)
Alga <u>Skeletonema costatum</u>	Growth	8.0	Dunstan <u>et al.</u> (1975)
Alga <u>Skeletonema costatum</u>	96-hour EC <sub>50</sub> for chlorophyll <u>a</u> production	>433.0	U.S. EPA (1978)
Alga <u>Skeletonema costatum</u>	96-hour EC <sub>50</sub> for reduction in cell numbers	>433.0	U.S. EPA (1978)

TABLE 6-7. INTERACTION OF TEMPERATURE AND TOLUENE  
ON MARINE INVERTEBRATE

<u>Species</u>	<u>96-hour TL<sub>50</sub> (mg/l)</u>		
	<u>4°C</u>	<u>8°C</u>	<u>12°C</u>
<u>Oncorhynchus gorbuscha</u>	6.41	7.63	8.09
<u>Eualus</u> spp.	21.4	20.2	14.7

Source: Korn et al. (1977).

sensitive freshwater fish species tested was the bluegill (LC<sub>50</sub>, 12.7 mg/l). The levels of acute toxic effects to fish ranged from 6.3 to 60.9 mg/l.

Acute effects for invertebrates ranged from 3.7 (bay shrimp) to 170.0 mg/l (crab Cancer magister, 48-hour LC<sub>50</sub>). Most of the invertebrate acute concentrations were from 10 to 80 mg/l. Algae, both freshwater and marine, were quite resistant to toluene, as no acute effects (reduction in cell numbers and chlorophyll a production) were observed at <245.0 mg/l, although effects on growth were observed at concentrations as low as 8 mg/l. The only chronic study available was on the sheepshead minnow, which had a reported chronic value of 2.2 mg/l.

The U.S. EPA (1980a) has not set water quality criteria for toluene to protect aquatic life. They have concluded that acute toxicity to freshwater aquatic life may occur at concentrations as low as 17.5 mg/l. Acute and chronic toxicity to saltwater aquatic life may occur at concentrations as low as 6.3 and 5 mg/l, respectively. In all cases, it was concluded that toxicity would occur at lower concentrations if more sensitive species were tested.

In summary, however it is useful to show concentration ranges for which certain effects are seen in the laboratory. However, these ranges are not rigidly defined and may overlap as a result of differences among life stages, species, test methodologies, and environmental variables. Test ranges include:

- 1.0-10.0 mg/l Threshold of toxic effects of toluene to aquatic biota, including acute effects on striped bass and effects on photosynthesis or growth in two species of marine algae. Chronic effects on sheepshead minnow in this range.
- 10.1-100.0 mg/l Majority of acute toxicity values to marine and freshwater fish and invertebrates occur in this range. Concentrations on this range affected growth, photosynthesis, and respiration in two marine algae species.
- 100.1-1000.0 mg/l Acutely toxic concentrations in this range to two species each of marine and freshwater algae, the adult sheepshead minnow and the crab Cancer magister.
- >100.1 mg/l Acutely toxic to the freshwater mosquito fish (tested in turbid water).

## 6.2 EXPOSURE OF AQUATIC BIOTA TO TOLUENE

### 6.2.1 Introduction

Toluene has been detected in wastewater effluents, in seawater after controlled oil spills, in rainwater, and in sediment and fish tissue from aquatic systems throughout the United States. In water, its solubility is 534.8 mg/l in freshwater and 379.3 mg/l in seawater. However, toluene volatilizes from surface water to the atmosphere quite readily.

This analysis discusses probable levels of toluene to which aquatic biota may be exposed and compares these levels with concentrations known to have acute or chronic toxic effects.

### 6.2.2 Exposure Routes

The available data suggest that the primary mechanism of toluene toxicity in fish is direct uptake from solution in water, which causes damage to gill tissue and results in increasing all permeability and CO<sub>2</sub> poisoning (Morrow *et al.* 1975, Buikema and Hendricks 1980b). No information was found regarding ingestion of toluene by aquatic biota, or the bioavailability of toluene adsorbed to the sediments.

### 6.2.3 Monitoring Data

The monitoring data for toluene are not extensive; therefore, it is difficult to present a comprehensive description of toluene exposure levels in aquatic systems. Based on the available data, however, it appears that where toluene has been detected it was almost always found in low (ug/l) concentrations. The STORET system recorded approximately 450 observations of toluene in the ambient water of 17 states. Of these, 86 (19%) were unremarked values (above the detection limit) (U.S. EPA 1980b). The range of unremarked values was from 0.0 to 3900 ug/l, with 86% of these (74)  $\leq$  100 ug/l. Effluent data from STORET indicated 205 (40%) unremarked observations, a total of 510 values reported in 24 states. The range of these values was from 0.0 to 4600 ug/l. Approximately 19 effluent observations were > 100 ug/l.

Of the 100 reported observations of toluene levels in sediment, only 7 were > 500 ug/kg. The higher concentrations were found in the vicinity of an industrial area in San Francisco. The percentage distributions of ambient and effluent data, both remarked and unremarked, are shown in Table 4-4. Unremarked data (U.S. EPA 1980b) are summarized below:

#### Unremarked Values of Toluene Concentrations from STORET Data

<u>Sample Source</u>	<u>Observations (No.)</u>	<u>Concentrations Ranges (mg/l)</u>
Ambient Water	86	0.0 - 3900 µg/l (12 values > 100 µg/l)
Effluent Water	205	0.0 - 4600

#### 6.2.4 Modeling Data

Data from EXAMS indicate that nearly all toluene at steady state in each of the five aquatic systems remains in the water column rather than partitioning into the sediments. In the rivers, volatilization and biodegradation account for losses, although transport downstream is the major loss mechanism for the short river segment examined. In the lakes, > 90% of the chemical is lost to the atmosphere. Predictions of water column concentrations for all other aquatic systems are in the low µg/l range.

#### 6.2.5 Conclusions

The monitoring data indicate that where toluene has been detected in aquatic environments, the concentrations are generally low. This holds true for discharge concentrations as well. EXAMS data predict that, in general, toluene would not persist in the water column where it would be available to biota. EXAMS does not predict substantial deposition of toluene to the sediments, and the available monitoring data do not indicate high sediment concentrations. There does not appear to be an overlap between observed or predicted levels of toluene in water or sediment (low µg/l range) and concentrations that have been found to be acutely or chronically toxic to aquatic organisms (1.0 to 10.0 mg/l, threshold of acute toxic effects). Therefore, neither ecosystem damage or toxic effects in individual aquatic species are expected to take place in freshwater situations.

In seawater, especially in estuarine waters, combined, low-level exposure of fishes to toluene from oil spills is a cause for concern. The effects from this type exposure are not as immediately evident as those from the catastrophic, short-lived events, e.g., tanker spills. In the long run, however, they may place marine subpopulations at greater risk.

Although toluene is less soluble in seawater than benzene, it may be more toxic and may show greater accumulation and longer persistence (Korn et al. 1977). Accumulated toluene will cause a greater demand of energy for metabolization, detoxification, and depuration; thus, it may cause long-term physiological damage (Anonymous 1977).

The long-term importance of fish survival throughout chronic exposure cannot be underestimated. The ubiquitous nature of oil spills, small and large, in estuarine waters and the rapid uptake and accumulation of toluene following even brief exposures render this an area of potential risk and one for further research.

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## 7.0 RISK CONSIDERATIONS

### 7.1 HUMAN RISKS

Toluene is widely dispersed in the human environment, primarily as a result of gasoline-based source emissions. However, the fate processes affecting the toluene released to the environment favor atmospheric destruction.

The data base on the potential carcinogenicity of toluene is limited and inadequate for quantitative estimations of human risks. Presently available data indicate no toluene-induced carcinogenic or mutagenic effects in experimental animals. The U.S. EPA (1980a) has also stated that available oncogenic data are insufficient to evaluate the carcinogenic potential of toluene.

For comparative purposes, the relative margins of safety associated with various human exposures to toluene were calculated by comparing no-observed-effect levels in experimental animals (adjusted for a slower rate of metabolism in humans) with typical nonoccupational exposure levels. It was presumed that effect does not depend on route, but rather on absorption rate (e.g., mg/day). The U.S. EPA (1980a) based the water quality criteria on the study of Wolf *et al.* (1956), which indicated a maximum no-effect level of 590 mg/kg 5 days/wk for 193 days in a chronic toxicity test in rats. Assuming that humans have a slower metabolism of 1/2 to 1/6 the rate in rats (see Section 5.1.5), a no-effect level for a 70-kilogram man is estimated as:

$$590 \text{ mg/kg/day} \times 5/7 \times (1/2 \text{ or } 1/6) \times 70 \text{ kg} \approx 5 - 15 \text{ gm/day}$$

A somewhat lower range for a no-effect level was calculated in Section 5.1.5, which indicated that 2.6-7.8 gm/day may be a no-effect level for reproductive toxicity in pregnant women based on studies in rats (Hudak and Ungvary 1978). Syrovadko (1977) and Matsushita (1975) conducted studies on occupationally-exposed women (see Section 5.1.3.5). These studies could imply that even lower levels of toluene exposure may have toxic effects on the fetus or reproductive processes in women; however, these investigators did not assess co-exposure to other solvents and toxicants, which confounds the evaluation of their findings.

The NIOSH criteria document has listed 100 ppm (377 mg/m<sup>3</sup>) as the threshold limit value (air) for toluene (RTECS 1980). This allows a worker to absorb ~1.8 gm/8-hr work day, which is somewhat lower than the no-effect dose range for human reproductive toxicity calculated above. Exposure at greater than 100 ppm has been observed to cause acute CNS symptoms -- fatigue, weakness, confusion, and paresthesia.

To compute margins of safety for typical exposure levels observed for the general population, a no-effect level of 1.8 gm/day absorbed dose has been assumed. Margins of safety are given in Table 7-1 and range, for typical nonoccupational exposures, from 1200 for cigarette smoking to greater than 1,000,000 for typical absorption of toluene through drinking water. In conclusion, ingestion from all sources constitutes a very small risk in comparison to inhalation absorption. Percutaneous absorption through the use of paints and paint removers could constitute a greater risk than ingestion exposure; however, in terms of total population exposed and actual exposure conditions, the percutaneous absorption estimated in Table 7-1 is regarded as approximate and probably higher than typically occurs.

The margin of safety for people living in urban areas (Scenario A, approximately 74% of the U.S. population) is ~5000 vs ~40,000 for people living in rural and remote areas (Scenario B, approximately 26% of the U.S. population). The addition of cigarette smoking is calculated to reduce the overall margin of safety for both urban and rural dwellers to about 1000.

## 7.2 AQUATIC ORGANISM RISKS

Concentrations of toluene documented to have adverse effects on aquatic species have been observed on rare occasions (less than ten observations reported in STORET) in ambient and effluent waters. Presumably, these concentrations result from localized discharges of toluene. Because toluene is transported rapidly from water to air via volatilization, however, these concentrations will be short-lived in the water column. Thus, it is not expected that toluene poses a significant risk to aquatic biota on a species or community level. An event, such as an oil spill, may result in a localized, short-term high exposure to levels of toluene. However, the risk associated with this exposure cannot be quantified at this time.

TABLE 7-1. ESTIMATED MARGINS OF SAFETY FOR EXPOSURE TO TOLUENE

Exposure Route/Scenario	Exposure Concentration <sup>a</sup>		Absorbed Dose (ug/day) <sup>b</sup>		Margin of Safety <sup>c</sup>	
	Typical	Range	Typical	Range	Typical	Range
<u>Ingestion</u>						
<u>Water</u>	(ug/l)					
- All surface supplies	0.24	ND-19	0.5	?-38	$4 \times 10^6$	$5 \times 10^4$ -?
- High end of distribution of surface supplies	1.3	0.1-19	3.0	?-38	$6 \times 10^5$	$5 \times 10^4$ -?
<u>Foods</u>	(mg/kg)					
- Fish tissues	1.0	ND-35	6.5	?-224	$3 \times 10^5$	8000-?
<u>Inhalation</u>	(ug/m <sup>3</sup> )					
- Urban areas	19	0.15-283	210	1.7-3170	9000	6000- $10^5$
- Remote areas	1	ND-3.8	11	?-43	$2 \times 10^5$	$4 \times 10^4$ -?
- Use of gasoline stations	360	100-3400	10	1-65	$2 \times 10^5$	$3 \times 10^4$ - $2 \times 10^6$
- Occupational: at OSHA standard	754,000	-	3,500,000	-		-
	(ug/cigarette)					
- Cigarette		100	1560		1200	
<u>Percutaneous</u>	(mg/hr)					
- Occupational--2 hands unprotected		40	3200	3200-20,000	600	90-600
- Consumer products		1	23-140	-	$10^4$ - $10^5$	
<u>Total Exposure Scenarios</u>						
- Scenario A -- Urban environment (~74% of U.S. population)			370(1900) <sup>d</sup>		5000(900) <sup>d</sup>	
- Scenario B -- Rural environment (~26% of U.S. population)			51(1600)		$4 \times 10^4$ (1000)	

<sup>a</sup>Data from Section 4.3, Monitoring Levels in the Environment.<sup>b</sup>Data from Table 5-9.<sup>c</sup>Margin of safety based on the absorbed dose at TLV of 100 ppm (377 mg/m<sup>3</sup>) for an 8-hour day divided by the absorbed dose from typical source(s) of exposure.<sup>d</sup>Numbers in parentheses include exposure from cigarette smoking.

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## Appendix A

### Section 3.2.1 Calculation of Isolated Toluene Production and Capacity

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#### 1. Catalytic Reformate and Pyrolysis Gasoline

Toluene production from petroleum products was reported to be  $4,010 \times 10^3$  kkg by a projection for 1978 (SRI, 1979). This was divided between catalytic reformat (3,632  $\times 10^3$  kkg) and pyrolysis gasoline (378  $\times 10^3$  kkg). However, 1978 toluene production from petroleum sources was 3,433  $\times 10^3$  kkg (USITC, 1979). Production from petroleum sources was apportioned between catalytic reformat and pyrolysis gasoline, on the basis of the preliminary distributions, to be 3,109  $\times 10^3$  kkg and 324  $\times 10^3$  kkg, respectively.

#### 2. Styrene Manufacture

Approximately 0.0551 (0.04 - 0.071) toluene are produced per kg of styrene produced (SRI, 1979). 1978 styrene production was 3,260  $\times 10^3$  kkg from a capacity of 3,830  $\times 10^3$  kkg (USITC, 1979; SRI, 1979). However, this included production from the Oxirane plant (450  $\times 10^3$  kkg capacity) which does not produce styrene by dehydrogenation of ethylbenzene. Assuming that production from this plant was at the same capacity factor (85%) as the rest of the industry, and that 0.0551 of toluene are produced per kg of styrene, 1978 toluene production from styrene was 158  $\times 10^3$  or 135  $\times 10^3$  kkg, rounded to the nearest 5,000 kkg.

### Section 3.2.2 Nonisolated Toluene

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#### 1. Catalytic Reformate

The U.S. catalytic reforming capacity in 1979 was  $6.03 \times 10^8$  liter of feed per stream day (Oil & Gas Journal, 1979). Assuming 340 stream days/year, an average yield of 85% of charge capacity based on straight-run naphtha, and a toluene content of 20% by volume in the reformat, 30.2  $\times 10^6$  kkg were produced in 1978 (SRI, 1979). Subtracting the 3.11  $\times 10^6$  kkg recovered from catalytic reformat from this yields 27.1  $\times 10^6$  kkg not isolated from the reformat.

#### 2. Coal Derived

Coke oven light oil from which products were not derived amounted to 374  $\times 10^6$  liter (DOE, 1979). Assuming a toluene content of 16% by volume (12%-20% range), 52  $\times 10^3$  kkg were not isolated from this source.

For those coke oven plants which don't recover light oil, toluene production is estimated to be 22  $\times 10^3$  kkg from the following:

- 64.7  $\times 10^6$  kkg of coal consumed for coke production.
- 11.9 liters light oil/kkg coal carbonized (2.85 gal/ton).
- 16% toluene in light oil.
- 612  $\times 10^6$  liter light oil recovered (DOE, 1979; EPA, 1979 SRI, 1979).

Nonrecovered toluene from coal tar is calculated to be 22  $\times 10^3$  kkg based on the following: 2.05  $\times 10^9$  liters of coal tar produced, toluene content of 0.9% by weight, specific gravity of 1.2 for coal tar (USTIC, 1979; O'Brochta and Woolbridge, 1945; Rhodes, 1954).

## Appendix A

### Section 3.2.3 Environmental Releases form Toluene Production

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Air emissions were calculated from the emissions factors in Table A-1 and total production from each source, assuming that the same emissions factors may be applied to toluene produced as BTX or otherwise not isolated (see Table A-2).

Releases from coking operations producing nonisolated toluene were derived from the information presented in Table A-3, total coke production of  $44 \times 10^6$  kkg and the following distribution of wastewater: direct discharge 33%, POTW - 25%, quenching - 40%, deep well injection - 2% (DOE, 1979; EPA, 1979h). Toluene in wastewater sent to quenching operations is sent to a sump and then recycled to quenching operations where one third is evaporated during each pass. Toluene releases from quenching are arbitrarily assumed to be evenly distributed between land and air.

Until more analysis is done, toluene from petroleum refinery wastewater is assumed to be negligible for the reasons stated in text. Land releases from refineries and toluene isolation from coke ovens were derived by analogy to benzene, using (1) toluene production from each source, (2) a solid waste generation factor of 0.003 and (3) an estimate of 1% toluene in the solid waste (EPA, 1980f). Due to the nature of the data (i.e., assumptions, engineering judgement, estimates), distribution on a per plant basis is not realistic and therefore not presented.

## Appendix A

### Section 3.2.4 (Table 3-2)

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#### 1. Transportation Spills

##### a. Oil:

Water figure based on  $3.6 \times 10^7$  l of various oils - crude (36%), diesel (18%), fuel (42%), waste (2%), lube (0.3%), other (1.7%) spilled in navigable waters in 1978 (U.S. Coast Guard, 1980). Toluene is estimated to have a 5-6 hr half-life in oil spill solution (Mackay and Leinonen, 1975).

Land figure based on  $5.1 \times 10^5$  l crude oil spilled in 1978 by common carrier (23%), private carrier (22%), rail (6%) and "other" (49%) (U.S. Dept. of Transportation, 1980). Average oil density = 0.85, toluene content: 1.3% (by weight).

##### b. Gasoline:

Water -  $1.1 \times 10^7$  l spilled: aviation/automobile gasoline (98%) and Natural (Casinghead) Gasoline (2%) (U.S. Coast Guard, 1980).

Land -  $3.7 \times 10^6$  l spilled: common carrier (53%), private carrier (47%), rail (0.6%) "other" (<0.01%) (U.S. Dept. of Transportation, 1980). Gasoline density: 0.73, toluene content: 8.5% (by weight).

##### c. Toluene:

Water - 2,500 l spilled in navigable waters in 1978 (U.S. Coast Guard, 1980).

Land - 12,000 l spilled: common carrier (94%), private carrier (2%), rail (4%) (U.S. Dept. of Transportation, 1980). Toluene density: 0.8669.

#### 2. Ethylene - Propylene Rubber Manufacture

Air emissions based on 1978 production of ethylene-propylene rubber (including oil content of oil-extended elastomers) of  $1.8 \times 10^5$  kkg (USITC, 1979). Emission factor: 0.5 kg toluene/kkg product (EPA, 1977a). It is estimated that 10% of the total production is accounted for by the extension oils, which can contain toluene (SRi, 1979). See Appendix B for a list of various extension oils.

#### 3. Wood Preserving

Water discharge based on a flow weighted mean of 35 kg toluene released/year/plant practicing steaming operations and 180 plants which have steaming operations (EPA, 1979f). Raw wastewater figure.

#### 4. Insulation Board Manufacture

Water discharge based on: 50 µg/l toluene in raw wastewater; 16 plants, producing a total of  $3.3 \times 10^8$  m<sup>2</sup> insulation board 13 mm thick; board density = 0.33 kkg/m<sup>3</sup>; and  $9.2 \times 10^3$  l kkg production average flow per plant (EPA, 1979f). Total discharge: 650 kg toluene.

#### 5. Hardboard Manufacture

Water discharge based on average raw wastewater concentration of 39 µg/l toluene; average per plant flow of  $18 \times 10^3$  l/kkg produced;  $1.5 \times 10^6$  kkg/yr production (EPA, 1979f). Total discharge: 1 kkg.

## Appendix A

### Section 3.2.4 (Table 3-2 concluded)

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#### 6. Acrylonitrile Manufacture

Air emission based on a total production of  $7.9 \times 10^5$  kkg in 1978 (USITC, 1979) and emission factor of 0.074 kg toluene/kkg product (EPA, 1977).

#### 7. Combustion of Coal Refuse Piles

Air emissions derived from total hydrocarbon emissions/yr from this source of  $3.4 \times 10^4$  kkg, and an average of 13% toluene in emissions (EPA, 1978a).

#### 8. Stationary Fuel Combustion, Forest Fires, Agricultural Burning, Structural Fires

Only total hydrocarbon emissions for each category were available (EPA, 1977b). The percent which is toluene is estimated here to be an order of magnitude less than for coal refuse piles (13%; EPA, 1978a) and an order of magnitude more than for landfills (0.1%; SCAQMD, 1979). Therefore, these totals represent 1% of the total hydrocarbon emissions from each category.

#### 9. Cigarette Smoke

Based on an average of 89 µg toluene emitted/cigarette smoked (NAS, 1990), and  $6 \times 10^{11}$  cigarettes smoked/yr (Dept. of Agriculture, 1979).

### Section 3 (Table 3-1)

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#### 1. Gasoline

Air emission figure is a combination of evaporative losses from use, evaporative losses from marketing, and exhaust emissions.

The following factors are used:

- $7.4 \times 10^6$  bbl/day gasoline consumption (Oil and Gas Journal, 1979)
- 42 gal/bbl gasoline.
- 14.7 miles/gal average mileage (EPA, 1975a).
- 0.83 g/mile hydrocarbon evaporative loss during gasoline use in automobiles (EPA, 1975b), toluene is 1.26% of total hydrocarbon emission (CARB, 1975).
- 3.2 g/mile hydrocarbons in exhaust (EPA, 1975b), 12% of which is toluene (EPA, 1977b).
- 0.004735 kg hydrocarbon lost/kg gasoline during marketing (EPA, 1975a), 1.26% toluene (CARB, 1975).
- Density of gasoline: 0.73 kg/l
- 3.785 l = 1 gal.



## Appendix A

### Section 3.2 Chemical Synthesis (Table 3-6)

#### 1. Toluene Consumption Per Category Based On:

Benzyl Chloride	0.8 unit toluene consumed/unit product plants operating at 55% capacity
Benzoic Acid	0.84 toluene/product 62% of capacity
Xylene Disproportionation	1.09 toluene/product (benzene + xylenes) 49.5% of capacity
p-Cresol	1.06-1.13 toluene/product
Benzaldehyde	2.2 toluene/product unknown % of capacity
Vinyl Toluene	1.1 toluene/product 83% of capacity

## Appendix A

### Section 3.4 Environmental Releases (Table 3-7)

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#### 1. Gum and Wood Products

Wastewater flow based on 1) a total flow of 82,000 l/kg product for all 6 subcategories of the industry: Essential Oils; Rosin Derivatives; Sulfate Turpentine; Gum Rosin and Turpentine; Wood Rosin, Turpentine and Pine Oil; and Tall Oil Rosin, Pitch and Fatty Acids (EPA, 1979c) and 2) Production for 1978 of: Gum -  $8 \times 10^3$  kkg, Turpentine -  $82 \times 10^3$  kkg, Wood Rosin -  $108 \times 10^3$  kkg, Tall Oil -  $199 \times 10^3$  kkg (SRI, 1979), for a total of  $397 \times 10^3$  kkg.

Table A-1. Emission Factors

Source	Emission Factor kg lost/kg Produced (Used)			Total
	Process	Storage	Fugitive	
Toluene Production - Catalytic Reformate	0.00002	0.00006	0.00002	0.00010
Toluene Production - Pyrolysis Gasoline	0.00015	0.00060	0.00015	0.00090
Toluene Production - Coal Derived	0.00050	0.00060	0.00015	0.00125
Toluene Production - Styrene By-product	0.00001	0.00060	0.00015	0.00076
Benzoic Acid Production	0.00100	0.00040	0.00010	0.00150
Benzyl Chloride Production	0.00055	0.00030	0.00015	0.00100
Vinyl Toluene Production	0.00055	0.00030	0.00015	0.00100
Benzene Production	0.00005	0.00019	0.00005	0.00020
Xylene Disproportionation	0.00005	0.00010	0.00005	0.00020
Toluene diisocyanate Production	0.00077	0.00032	0.00019	0.00128
p-Cresol Production	0.00120	0.00050	0.00030	0.00200
Benzaldehyde Production	0.00090	0.00040	0.00020	0.00150

Source: EPA, 1980d.

Table A-2 Air Emissions, Calculations From Toluene Production

Source	Total Production (kkg - 1979)	Emissions Factor (kg lost/kg produced)	Emissions (kkg)
Catalytic Reformate	30,200,000	0.00010	3,020
Pyrolysis Gasoline	521,000	0.00090	470
Styrene Manufacture	135,000	0.00076	103
Coal Derived	122,000	0.00125	<u>153</u>
			3,750

Source: EPA, 1980d, Appendix A, Notes from Section 3.2.2 and 3.2.3

Table A-3 Average Effluents from Coke Oven Operations

Stream	liters produced/ kg coke	toluene concentration (mg/l)
Waste Ammonia Liquor	.16	3.1
Final Cooler Blow Down	.13	17
Benzol Plant Wastes	.20	8.6

Source: EPA - 1979h.

Table A-4. Toluene Materials Balance: Production Isolated from Petroleum Refining, 1978 (kkgyr)<sup>a</sup>

Company, Plant Location	Feedstock <sup>b</sup>	Production Capacity	Production	Environmental Releases		
				Air <sup>c</sup>	Water <sup>c</sup>	Land
Amerada Hess Corp. St. Croix, Virgin Islands	CR	460,000	310,000	31		
American Petrofina, Inc. Big Spring, TX	CR	164,000	110,000	11		
American Petrofina Co. of Texas/Union Oil Co. of California (joint venture) Beaumont, TX	CR	125,000	84,000	8.4		
Ashland Oil, Inc. Catlettsburg, KY	CR	99,000	67,000	6.7		
	CR	39,000	26,000	2.6		
Atlantic Richfield Co. Channelview, TX	PG	105,000	76,000	68		
	CR	125,000	84,000	8.4		
	CR	49,000	33,000	3.3		
The Charter Co. Houston, TX	CR	39,000	26,000	2.6		
Coastal States Gas Corp. Corpus Christi, TX	CR	56,000	38,000	3.8		
Commonwealth Oil Refining Co., Inc. Penuelas, PR	CR	395,000	266,000	27		
	PG	49,000	36,000	32		
Crown Central Petroleum Corp. Pasadena, TX	CR	46,000	31,000	3.1		
The Dow Chemical Co. Freeport, TX	PG	13,000	9,400	8		
Exxon Corp. Baytown, TX	CR	411,000	277,000	28		
Getty Oil Co. Delaware City, DE	CR	0 <sup>e</sup>	0	0		
	CR	20,000	13,000	1.3		
Gulf Oil Corp. Alliance, LA	CR	194,000	130,000	13		
	CR	92,000	62,000	6.2		
	CR	49,000	33,000	3.3		
	PG	66,000	48,000	43		
Kerr-McGee Corp. Corpus Christi, TX	CR	148,000	100,000	10		
Marathon Oil Co. Texas City, TX	CR	72,000	49,000	4.9		
Mobil Oil Corp. Beaumont, TX	CR	280,000	189,000	19		
	PG	16,000	15,000	2		
Monsanto Co. Alvin (Chocolate Bayou), TX	CR	33,000	22,000	2.2		
	PG	132,000	96,000	86		
Pennzoil Co. Shreveport, LA	CR	0 <sup>f</sup>				
Phillips Petroleum Co. Sweeney, TX	CR	33,000	22,000	2.2		
	CR	335,000	226,000	23		
Quintana - Howell Corpus Christi, TX	CR	56,000	38,000	3.8		
Shell Chemical Co. Deer Park, TX	CR	197,000	133,000	13		
Sun Company, Inc. Corpus Christi, TX	CR	138,000	93,000	9.3		
	CR	151,000	102,000	10		
	CR	247,000	166,000	16.6		
	CR	66,000	44,000	4.4		
Tenneco, Inc. Chalmette, LA	CR	115,000	78,000	7.8		

Table A-4. (Concluded)

Company, Plant Location	Feedstock <sup>b</sup>	Production Capacity	Production	Environmental Releases		
				Air <sup>c</sup>	Water <sup>d</sup>	Land
Texaco, Inc.						
Port Arthur, TX	CR	92,000	62,000	6.2		
Westville, NJ	CR	132,000	89,000	8.9		
Union Carbide Corp.						
Taft, LA	PG	66,000	48,000	43		
Union Oil Company of California						
Lemont, IL	CR	56,000	38,000	3.8		
Union Pacific Corp.						
Corpus Christi, TX	CR	99,000	67,000	6.7		
Totals <sup>g</sup>			3,400,000	600		820 <sup>h</sup>

<sup>a</sup>See Appendix A notes for production calculations.

<sup>b</sup>CR = Catalytic Reformate, PG = Pyrolysis Gasoline.

<sup>c</sup>See Appendix A notes, Tables A-1, A-2 and A-3 for emission calculations.

<sup>d</sup>Assumed negligible since it was not detected above detection limit for 10/11 refineries (EPA, 1979g).

<sup>e</sup>1980 capacity = 85,000 kkg, 1981 capacity = 112,000 kkg.

<sup>f</sup>1980 capacity = 72,000 kkg.

<sup>g</sup>Values do not add due to rounding.

<sup>h</sup>Data not substantiated to the point that per plant estimates can be made (see Appendix A notes for Section 3.2.3).

**Table A-5. Toluene Yields from Various Pyrolysis Feeds<sup>a</sup>**

	Ethane	Propane	n-Butane	Mid-crude naphtha	C <sub>6</sub> -C <sub>8</sub> Raffinate	Gas oil, distilled	
						Atmospheric	Vacuum
Toluene, kg/kg Ethylene	1-2	9-17	21-22	99-140	41.5	112-138	142-145

Source: SRI, 1979.

<sup>a</sup>Ethylene plant of an annual production of 450,000 metric tons; ethane recycled to extinction.

Table A-6. Toluene Materials Balance: Production from Styrene Manufacture, 1978 (kkg)<sup>a</sup>

Company, Plant Location	Styrene Capacity	Toluene Produced	Environmental Releases		
			Air	Water	La
American Hoechst Corp. Baton Rouge, LA	400,000	16,000	12		
Atlantic Richfield Co. Beaver Valley, PA	100,000	4,000	3		
Cos-Mar, Inc. Carville, LA	590,000	24,000	28		
Dow Chemical Co. Freeport, TX	660,000	26,000	20		
Midland, MI	140,000	5,600	4		
El Paso Natural Gas Co. Odessa, TX	68,000	2,700	2		
Gulf Oil Corp. Donaldsville, LA	270,000	11,000	8		
Monsanto Texas City, TX	680,000	27,000	21		
Standard Oil Co. (Indiana)					
Texas City, TX	380,000	15,000	12		
Sun Company Inc. Corpus Christi, TX	36,000	1,400	1		
United States Steel Houston, TX	<u>54,000</u>	<u>2,200</u>	<u>2</u>		<u>4</u>
Totals	3 400,000	135,000	100		

<sup>a</sup>See Appendix A Notes for calculations. Totals may not add due to rounding; blanks indicate data not available.

<sup>b</sup>The data is not substantiated to the point that per plant estimates can be made (see Appendix A Notes for Section 3.2.3).

Source: SRI, 1979.



Table A-7. Coke Oven Plants which Recover Crude Light Oils

Company	Location	Toluene Recovery <sup>a</sup>
Alabama B.P. <sup>b</sup>	Tarrant, AL	
Keystone Coke <sup>b</sup>	Swedeland, PA	
Allied Chem.	Ashland, KY	
Armco	Middletown, OH	X
Armco	Hamilton, OH	
Ashland Oil	Catlettsburg, KY	X
Ashland Oil	North Tonawanda, NY	X
Bethlehem Steel	Bethlehem, PA	X
Bethlehem Steel	Sparrows Pt., MD	X
Bethlehem Steel	Lackawanna, NY	
Bethlehem Steel <sup>c</sup>	Johnstown, PA	
CF&I	Pueblo, CO	X
Crucible	Midland, PA	
Cyclops	Portsmouth, OH	
Donner Hanna	Buffalo, NY	
Erie C&C	Fairport Harb., OH	
Ford Motor	Dearborn, MI	
Inland <sup>d</sup>	E. Chicago, IN	
Interlake	Chicago, IL	
Interlake	Toledo, OH	X
Ironton Coke	Ironton, OH	
J&L	Aliquippa, PA	X
J&L	Pittsburgh, PA	
JWR	N. Birmingham, AL	
Kaiser	Fontana, CA	
Koppers	Bessemer, AL	
Lone Star	Lone Star, TX	X
National <sup>e</sup>	River Rouge, MI	
National	Granite City, IL	
Nationale	Weirton, WV	
Republic	Youngstown, OH	X
Republic	Warren, OH	
Republic	Massillon, OH	
Republic <sup>c</sup>	Cleveland, OH	X
Republic	Chicago, IL	
Republic	Gadsden, AL	
Republic	Birmingham, AL	
Shenango	Neville Is., PA	
Tonawanda Coke	Buffalo, NY	
United States Steel	Clairton, PA	X
United States Steel	Fairless Hills, PA	
United States Steel	Lorain, OH	
United States Steel	Gary, IN	
United States Steel	Geneva, UT	X
United States Steel	Fairfield, AL	
Wheeling-Pgh.	Monessen, PA	
Wheeling-Pgh.	Follansbee, WV	
WSC	Chicago, IL	
YS&T	Campbell, OH	
YS&T	E. Chicago, IL	
Nationale	Browns Is., WV	

Source: EPA 1979h; SRI 1979.

<sup>a</sup>30% of coke oven plant production capacity.

<sup>b</sup>Plant is operated by a subsidiary of Alabama By-products Corp.

<sup>c</sup>Two coke plants on this site.

<sup>d</sup>Three coke plants on this site

<sup>e</sup>Two coke plants on noncontiguous sites.

Table B-1. General Formulations Containing Toluene

Product	Toluene Content (%)
China Cement, Solvent Type	20-30
Contact Rubber Cement	solvents may contain toluene
Microfilm Cement, Cotton base	27-30
Model Cement	(may contain) 20-25
Plastic Cement, Polystyrene	24
Shoe Cements	"aromatic hydrocarbon solvents"
Tire Repair, Tubeless Bonding Compounds	>80
Paint Brush Cleaners	benzene (+ toluene, xylene) 25-90
Stain, Spot, Lipstick, Rust Removers	may contain toluene
Nail Polish	35
De-Icers, Fuel System Antifreeze	30
Fabric Dyes	≤60
Indelible inks	solvents may contain toluene
Marking Inks	80-90
Stencil inks	40-60
Solvents and Thinners	may contain toluene

Source: Gleason et al., 1969

Table B-2. Ethylene - Propylene Rubber Extender Oils which May Contain Toluene

Oil	Manufacturer
Sundex 53	Sun Oil Co.
Sundex 96	Sun Oil Co.
Dutrex 7	Shell Development
Circosol 2XA	Sun Oil Co.
Califlux GP	Golden Bear Oil Co.
Sovaloid N	Socony Vacuum
Sovaloid O	Socony Vacuum
Phillips 9002	Phillips Petroleum Co.
Necton 45	Penola, Inc.
Circle Light Oil	Sun Oil Co.
Neville Heavy Oil	Neville Co.
Bardol B	Barrett

Source: General Tire and Rubber Co., 1955

**Table C-1. Frequency of Toluene Detection in Industrial Wastewaters**

Industry	Frequency ( # found/ # samples)
Soap and Detergents	1/20
Adhesives and Sealants	2/11
Leather Tanning	19/81
Textile Products	56/121
Gum and Wood Products	14/18
Pulp and Paper	4/98
Timber	58/285
Printing and Publishing	50/109
Paint and Ink	48/94
Pesticides	23/147
Pharmaceuticals	38/95
Organics and Plastic	306/723
Rubber	15/67
Coal Mining	53/249
Ore Mining	6/72
Steam Electric Power Plants	32/84
Petroleum Refining	18/76
Iron and Steel	43/431
Foundries	2/54
Electroplating	5/18
Nonferrous Metals	21/173
Coil Coating	2/12

Table C-1. (Concluded)

Industry	Frequency ( # found/ # samples)
Photographic	9/25
Inorganic Chemical	10/107
Electrical	1/35
Auto and Other Laundries	9/56
Phosphates	1/33
Plastics Processing	1/1
Porcelain/Enameling	2/19
Landfill	3/7
Mechanical Products	23/35
POTWs	11/40

Source: EPA, 1980a.

Table C-2. Industrial Liquid Streams In which Toluene has been Detected

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Cured Leather Goods Finishing

Steel Pipe and Tube Manufacture

Iron Sintering

Open Hearth Furnaces

Steel Industry:

Vacuum Degassing

Hot Forming

Blast Furnace

Alkaline Coating

Hot Coating

Cold Rolling

Electric Furnace

Basic Oxygen Furnace

Coal:

Mining

Physical and Mechanical Cleaning

Industrial and Commercial Laundries

Foundry Casting:

Primary Ferrous Industry

Aluminum

Textiles:

Blended Fabric Finishing

Polyester Fabric Finishing

Rubber Manufacture:

Polymerization Processing for Other Synthetic Rubber

Ore Mining and Milling:

Titanium

Silver

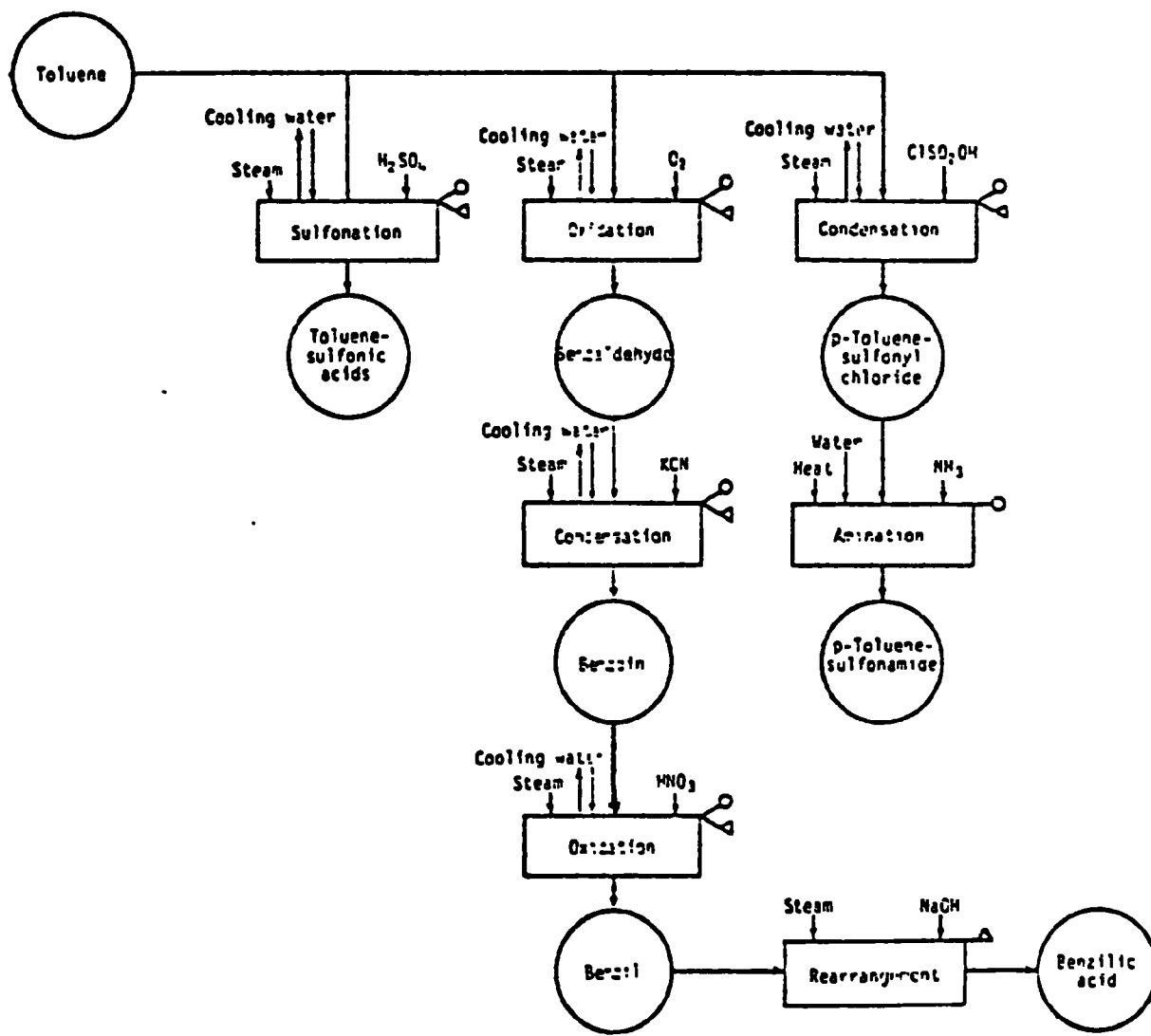
Lead-Zinc

Ferro-Alloys

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Source: EPA, 1980c.

# Appendix D



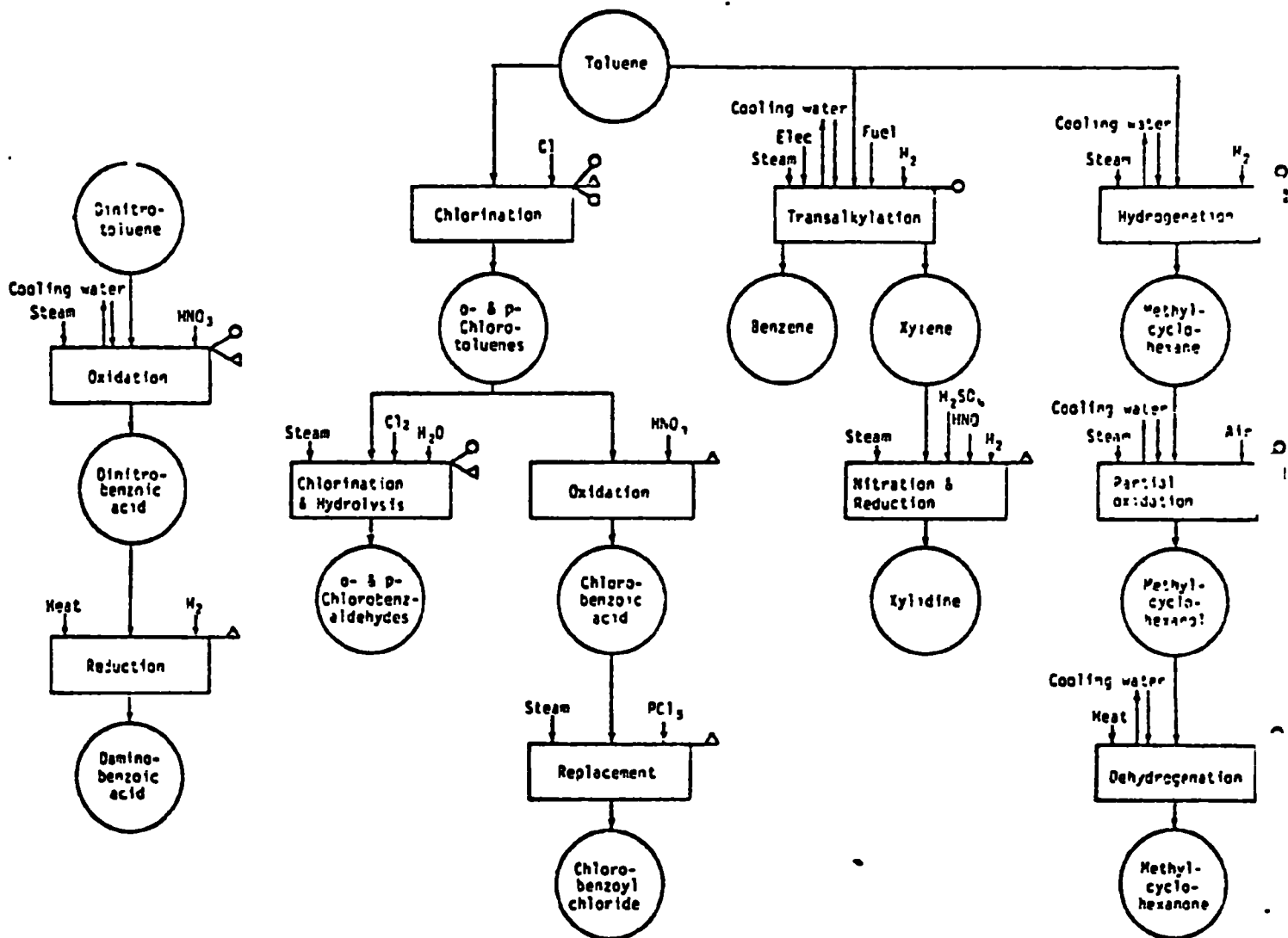
Source: EPA, 1977a

$\circ$  = Air Emission

$\Delta$  = Water Discharge

$\square$  = Land Release

# Appendix D

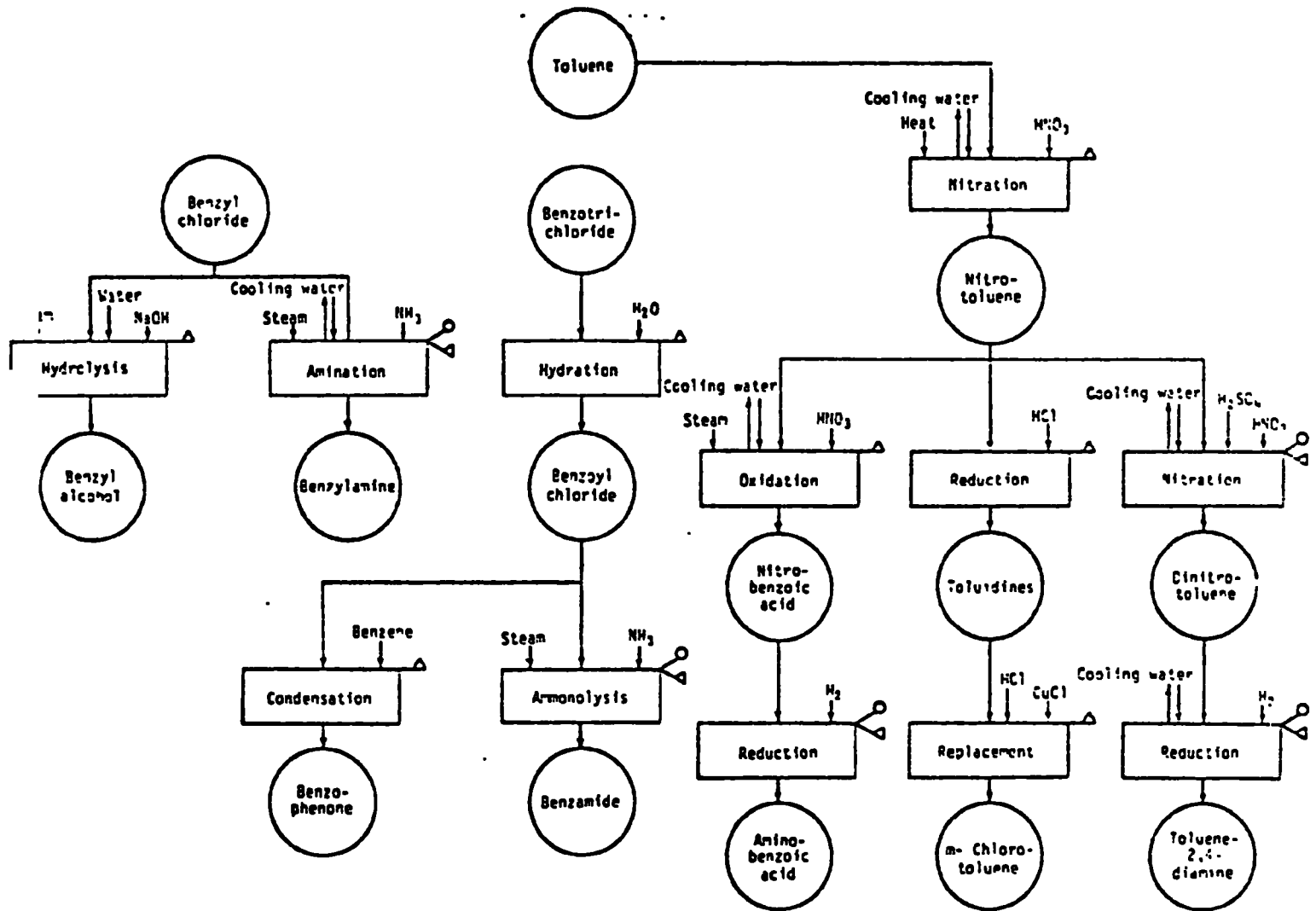


Source: EPA, 1977a.

O = Air Emission  
 Δ = Water Discharge  
 □ = Land Release



# Appendix D



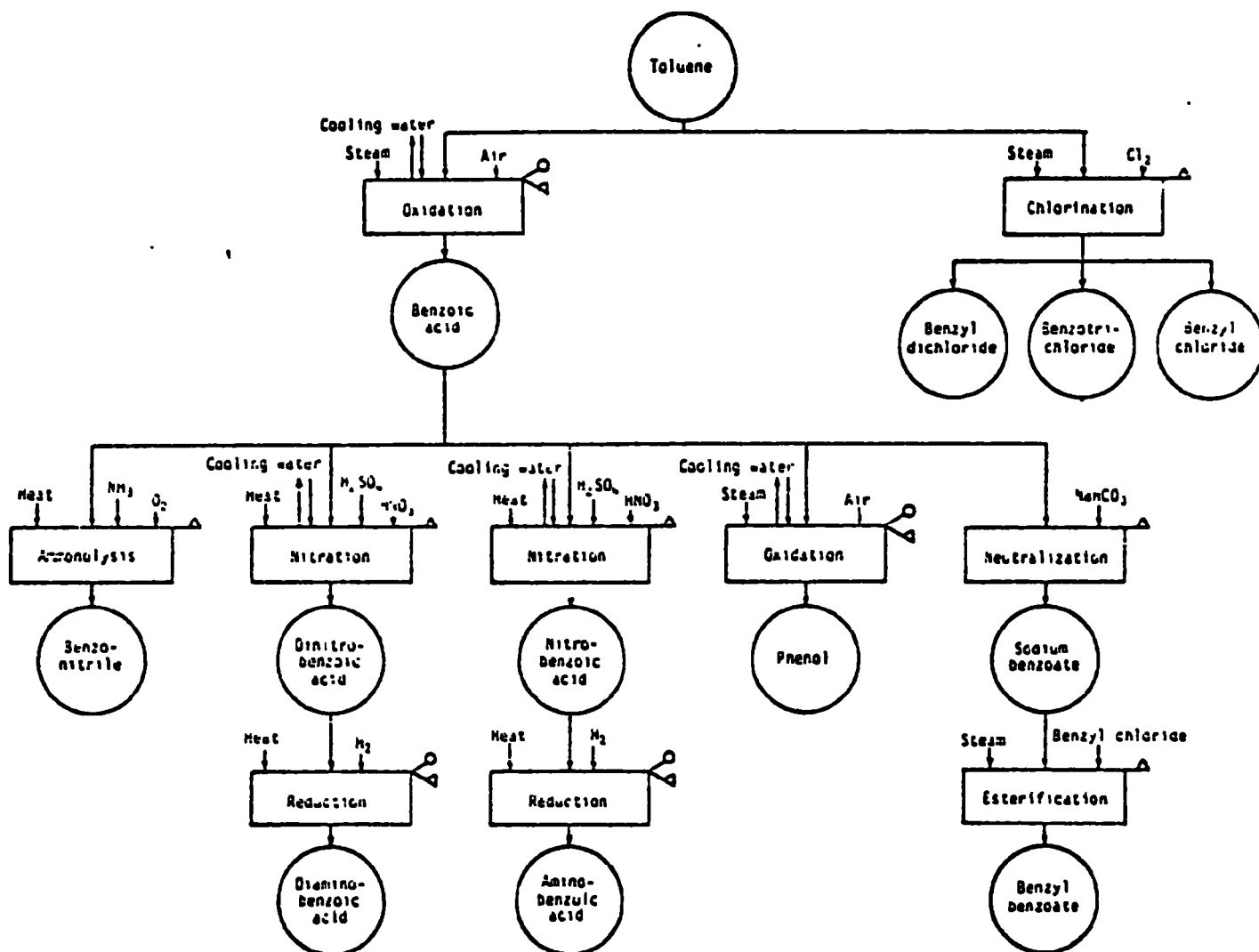
Source: EPA, 1977a

$\bigcirc$  = Air Emission

$\Delta$  = Water Discharge

$\square$  = Land Release

# Appendix D



Source: EPA, 1977a.

O = Air Emissions

Δ = Water Discharge

□ = Land Release

## APPENDIX E

### E.1 ESTIMATION OF VOLATILIZATION FROM WATER

Volatilization from water can be estimated using procedures described in the literature. The mathematical modeling of volatilization involves interphase exchange coefficients that depend on the chemical and physical properties of the chemical in question, the presence of other pollutants, and the physical properties of the water body and atmosphere above it. Basic factors controlling volatilization are solubility, molecular weight, and the vapor pressure of the chemical and the nature of the air-water interface through which the chemical must pass.

Volatilization estimates can be based on available laboratory and environmental data. Because of the lack of data for most chemicals, however, estimates of volatilization rates from surface waters on the basis of mathematical data and laboratory measurements are necessarily of unknown precision. Still, comparisons of experimental results with theoretical predictions indicate that these predictive techniques generally agree with actual processes within a factor of two or three in most cases.

The methods described below have been used to estimate volatilization from natural surface water. The EXAMS Model has been used to investigate behavior in natural surface water bodies, however, this method was not used as input to EXAMS. An input parameter similar to the reaeration coefficients described below is used in EXAMS to estimate volatilization; this value was obtained elsewhere.

Minimum data required to estimate volatilization are:

- Chemical properties--vapor pressure, aqueous solubility, molecular weight; and
- Environmental characteristics--wind speed, current speed, depth of water body.

With these data, the volatilization rate of a chemical can be estimated using the following procedure:

(1) Find or estimate the Henry's Law constant  $H$  from:

$$H = P/S \text{ atm-m}^3/\text{mole}$$

where  $P$  = vapor pressure, atm  
 $S$  = aqueous solubility, mole/m<sup>3</sup>.

When calculating  $H$  as a ratio of vapor pressure to solubility, it is essential to have these data about the same temperature and applicable

to the same physical state of the compound. Data for pure compounds should be used because vapor pressure and solubilities of mixtures may be suspect.

(2) If  $H < 3 \times 10^{-7}$  atm-m<sup>3</sup>/mole, volatilization can be considered unimportant as an intermedia transfer mechanism and no further calculations are necessary.

(3) If  $H > 3 \times 10^{-7}$  atm-m<sup>3</sup>/mole, the chemical can be considered volatile. The nondimensional Henry's law constant  $H'$  should be determined from:

$$H' = H/RT \quad (2)$$

where  $R$  = gas constant,  $8.2 \times 10^{-5}$  atm-m<sup>3</sup>/mole K

$T$  = temperature, K.

At 20°C (293°K),  $RT$  is  $2.4 \times 10^{-2}$  atm-m<sup>3</sup>/mole.

(4) The liquid phase exchange coefficient  $k_L$  must be estimated. This coefficient results from a method that analyzes the volatilization process on the basis of a two-layer film, one water and one air, which separates the bulk of the water body from the bulk of the air (Liss and Slater 1974).

For a low molecular weight compound,  $M < 65$ ,

$$k_L = 20 \sqrt{44/M} \quad \text{cm/hr} \quad (3)$$

where  $M$  = molecular weight of the chemical.

If  $M > 65$ , Southworth (1979) has developed equations to estimate  $k_L$ . If the average wind speed is  $\leq 1.9$  m/sec,

$$k_L = \left( \frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{\frac{32}{M}} \quad (4)$$

where  $V_{\text{curr}}$  = water current velocity, m/sec

$Z$  = depth of water body, m.

If wind speed is greater than 1.9 m/sec and less than about 5 m/sec,

$$k_L = \left( \frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{\frac{32}{M}} e^{0.526 (V_{\text{wind}}^{-1.9})} \quad \text{cm/hr} \quad (5)$$

where  $V_{\text{wind}}$  = windspeed, m/sec.

Above 5 m/sec, liquid phase exchange coefficients are difficult to predict and may range up to 70 cm/hr.

Values estimated by equation (4) may differ from those estimated by equation (3) due to the different methods of analysis on which the equations are based.

(5) The gas phase exchange coefficient must be estimated. This too is based on the two-film analysis. For a compound of  $M < 65$  (Liss and Slater 1974),

$$k_g = 3000 \sqrt{18/M} \quad \text{cm/hr} \quad (6)$$

If  $M > 65$  (Southworth 1979),

$$k_g = 1137.5 (v_{\text{wind}} + v_{\text{curr}}) \sqrt{18/M} \quad \text{cm/hr.} \quad (7)$$

(6) The Henry's law constant and gas and liquid phase exchange coefficients are used to compute the overall liquid phase mass transfer coefficient,  $K_L$  (Liss and Slater 1974), which is an indicator of the volatilization rate:

$$K_L = \frac{(H/RT)k_g k_l}{(H/RT)k_g + k_l} = \frac{H'k_g k_l}{H'k_g + k_l} \quad \text{cm/hr.} \quad (9)$$

(7) The volatilization rate constant  $k_v$  is

$$k_v = K_L/Z \quad \text{hr}^{-1}.$$

(8) Assuming a first order volatilization process, the concentration in the stream in the absence of continuing inputs at the location at which volatilization occurs, is

$$c(t) = c_0 e^{-k_v t} \quad (10)$$

where  $c(t)$  = pollutant concentration in the water column at time  $t$

$c_0$  = initial pollutant concentration in the water column.

(9) The half-life in the water column for the pollutant volatilizing at a first order rate is

$$\tau_{1/2} = \frac{0.69 Z}{K_L} \quad \text{hr.} \quad (11)$$

Another method is available for computing  $k_v$  for highly volatile chemicals with  $H > 10^{-3}$  atm-m<sup>3</sup>/mole. This method is based on reaeration rate coefficients (Smith and Bomberger 1979, Smith et al. 1979, Tsivoglou 1967). The following data are required:

- Ratio of reaeration rate of chemical to that of water; and
- Reaeration rate of oxygen for water bodies in the environment or streamflow parameters (velocity, stream bed slope, depth).

If the oxygen reaeration rate is known for a given water body or type of water body, the volatilization rate constant for the pollutant can be estimated from (Smith and Bomberger 1979):

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab} (k_v^o)_{env} \quad (12)$$

where  $k_v^c$  = first order volatilization rate constant for the particular chemical ( $hr^{-1}$ )

$k_v^o$  = reaeration rate constant for oxygen ( $hr^{-1}$ )

env = designates values applicable to environmental situations

lab = designates laboratory measured values

This equation applies particularly to rivers. For lakes and ponds, the following equation may be more accurate:

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab}^{1.6} (k_v^o)_{env} \quad (13)$$

Typical values of  $(k_v^o)_{env}$  are given in the literature and reported by Smith et al. (1979):

<u>Water Body</u>	<u><math>(k_v^o)_{env}</math>, <math>hr^{-1}</math></u>
Pond	0.0046-0.0096
River	0.008, 0.04-0.39
Lake	0.04-0.013

The values for ponds and lakes are speculative and depend on depth.

Mackay and Yuen (1979) present the equations listed below, which correlate  $k_v^o$  with river flow velocity, depth, and slope:

Isivoglu-Wallace:  $k_v^o = 638 V_{curr}^s \quad hr^{-1} \quad (14)$

Parkhurst-Pomeroy:  $k_v^o = 1.08 (1 + 0.17 F^2) (V_{curr}^s)^{0.0375} \quad hr^{-1} \quad (15)$

Churchill et al.:  $k_v^o = 0.00102 V_{curr}^{2.695} Z^{-3.085} s^{-0.323} \quad hr^{-1} \quad (16)$

If no slope data are available:

$$\text{Isaacs-Gundy: } k_v^0 = 0.223 V_{\text{curr}} Z^{-1.5} \text{ hr}^{-1} \quad (17)$$

$$\text{Langbein-Durum: } k_v^0 = 0.241 V_{\text{curr}} Z^{-1.33} \text{ hr}^{-1} \quad (18)$$

where  $V_{\text{curr}}$  = river flow velocity (m/s)

$s$  = river bed slope = m drop/m run (nondimensional)

$Z$  = river depth (m)

$F$  = Froude number =  $V_{\text{curr}} / \sqrt{gZ}$ , dimensionless

$g$  = acceleration of gravity =  $9.8 \text{ m/s}^2$ .

Because none of the foregoing is clearly superior to the others, the best approach is probably to use all equations that are applicable and then average the results. For a river 2 m deep flowing at 1 m/sec, the reaeration rate is estimated as 0.042/hr.  $(k_v^c/k_v^c)_{\text{lab}}$  is known for some chemicals (see Table E-1).

If a  $(k_v^c/k_v^0)_{\text{lab}}$  value is not known, one for a similarly high volatility chemical should be a reasonable substitute.

In principle,  $k_v^c$  is the same as  $(K_L/Z)$ ; however, because  $k_v^c$  has the depth and other water body characteristics embedded within it as a result of using  $(k_v^0)_{\text{env}}$ , no adjustment is required for including it in the first order volatilization equation.

TABLE E-1. MEASURED REAERATION COEFFICIENT RATIOS FOR HIGH-VOLATILITY COMPOUNDS

Compound	H ( $\frac{\text{atm}\cdot\text{m}^3}{\text{mole}}$ )	Measured $k_v^c/k_v^o$
Chloroform	$3.8 \times 10^{-3}$	$\left\{ \begin{array}{l} .57 \pm .02 \\ .66 \pm .11 \end{array} \right\}$
1,1-Dichloroethane	$5.8 \times 10^{-3}$	$.71 \pm .11$
Oxygen	$7.2 \times 10^{-2}$	1.0
Benzo [b] thiophene	$2.7 \times 10^{-4}$	$.38 \pm .08$
Dibenzothiophene	$4.4 \times 10^{-4}$	.14
Benzene	$5.5 \times 10^{-3}$	$.57 \pm .02$
Carbon dioxide		$.89 \pm .03$
Carbon tetrachloride	$2.3 \times 10^{-2}$	$.63 \pm .07$
Dicyclopentadiene		$.54 \pm .02$
Ethylene	8.6	$.87 \pm .02$
Krypton		$.82 \pm .08$
Propane		$.72 \pm .01$
Radon		$.70 \pm .08$
Tetrachloroethylene	$8.3 \times 10^{-3}$	$.52 \pm .09$
Trichloroethylene	$1 \times 10^{-2}$	$.57 \pm .15$

Source: Smith et al. (1974)



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## APPENDIX F

### ESTIMATION OF AIR CONCENTRATIONS OF TOLUENE USING GAUSSIAN PLUME DISPERSION

Turner (1969) provides a Gaussian plume dispersion modelling technique, for the estimation of air concentrations downwind of an emission source. Groundlevel concentration at the center of a plume having the compound concentration distributed normally about the center is given by:

$$C(x,0,0) = \frac{Q}{\pi \sigma_y \sigma_z u_w} \exp \left( \frac{-h^2}{2\sigma_y^2} \right)$$

where  $c(x,0,0)$  = concentration of toluene at varying  $x$  coordinates and at zero  $y$  and  $z$  coordinates ( $\text{mg}/\text{m}^3$ ),

$Q$  = emission rate ( $\text{mg}/\text{s}$ ),

$\sigma_y$  = standard deviation in the crosswind direction of the plume concentration distribution (see Figure F-1),

$z$  = standard deviation in the vertical direction of the plume concentration distribution (see Figure F-2),

$u_w$  = wind speed ( $\text{m}/\text{s}$ )

$h$  = height of source ( $\text{m}$ )

In all cases,  $u_w = 5 \text{ m/s}$ , the atmospheric stability class is neutral (D), and the heat of the source is negligible. (A source warmer than the surrounding air would lead to plume rise as a result of bouyancy.)

Toluene concentrations in air of various distances downwind were estimated using this equation for two source heights ( $h$ ) and two source strengths ( $Q$ ). The results are given in Section 4.4.3.1.

No chemical degradation processes were included in these estimations.

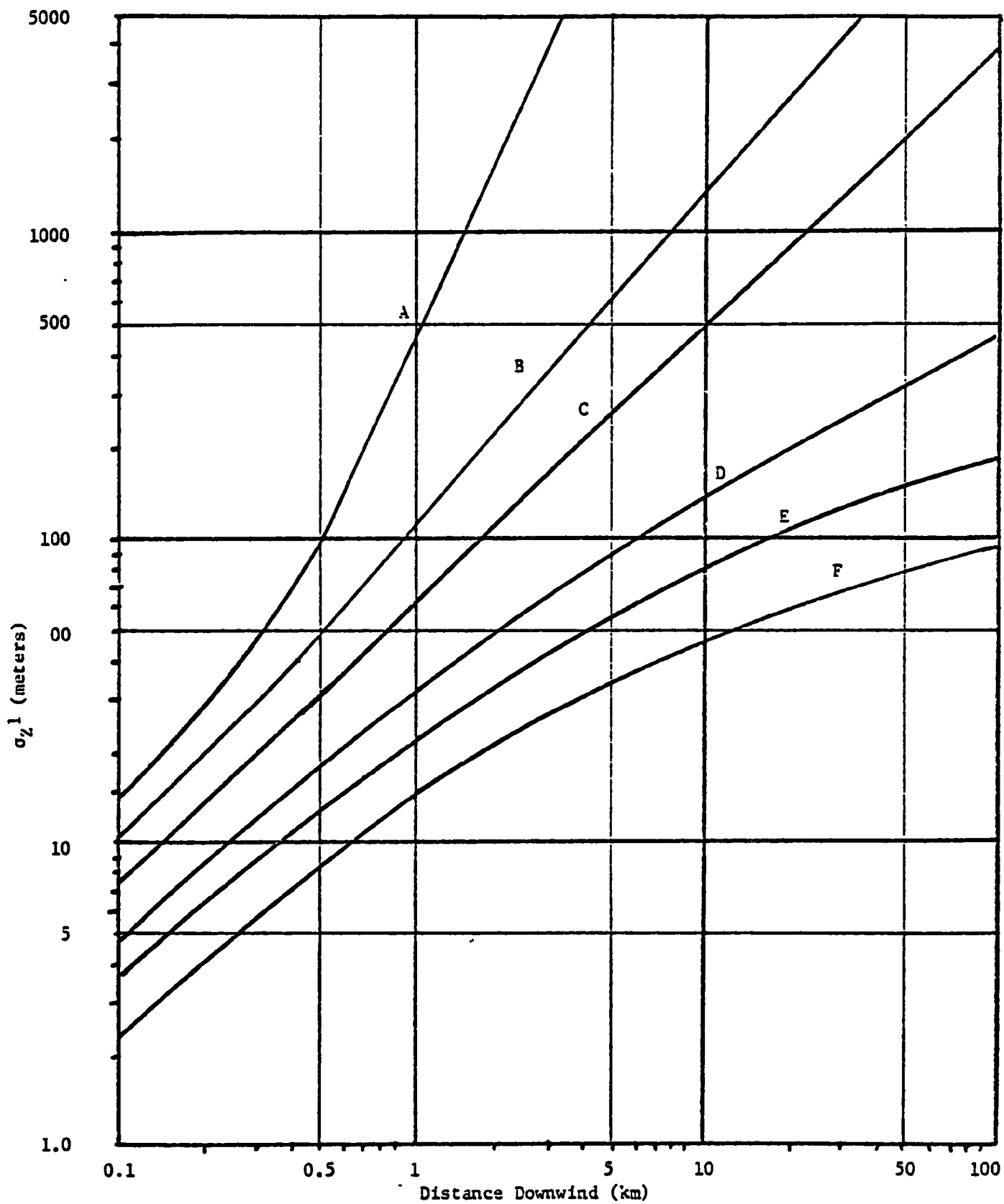


FIGURE F-1. VERTICAL DISPERSION COEFFICIENT AS A FUNCTION OF DOWNWIND DISTANCE FROM THE SOURCE

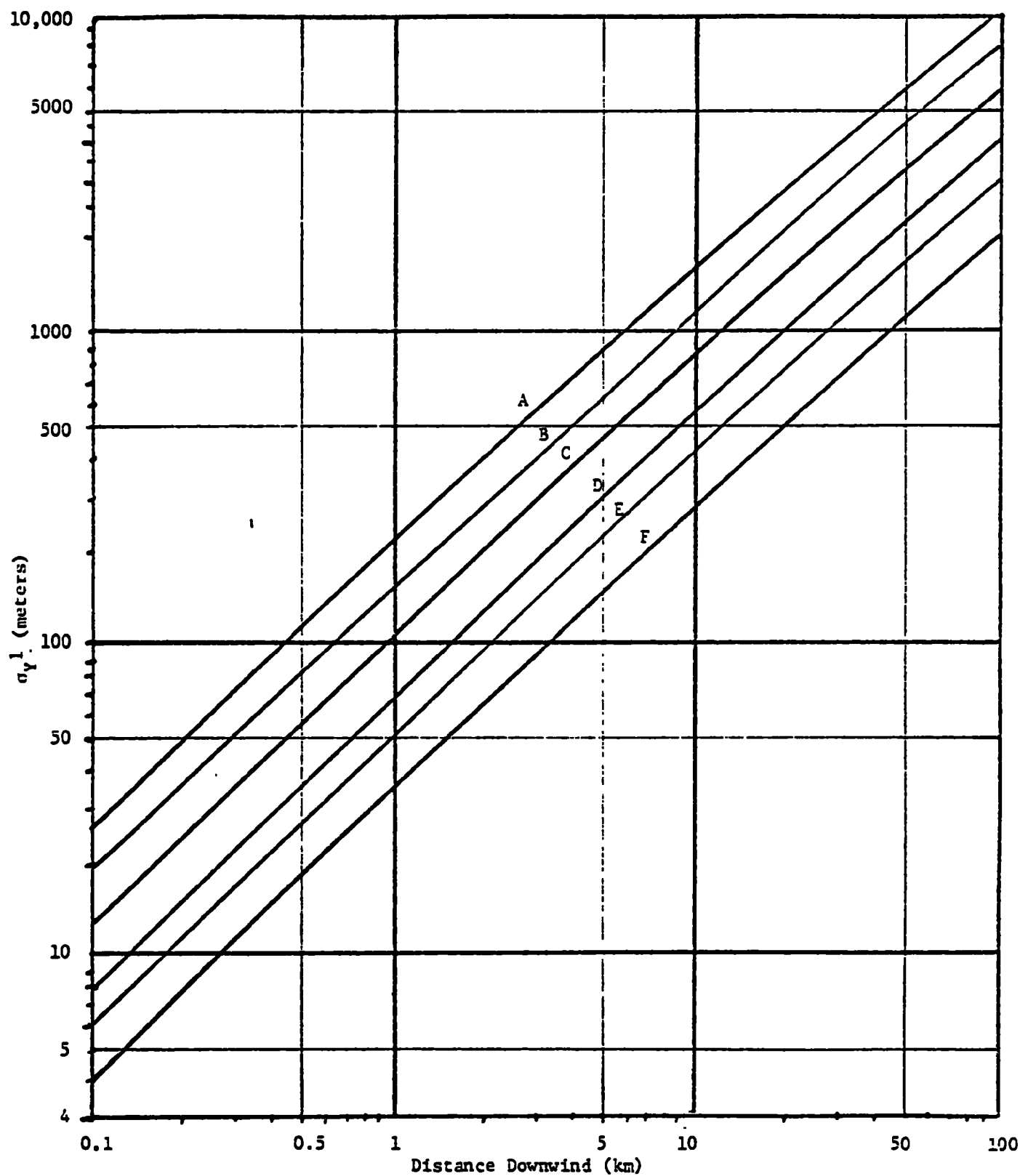


FIGURE F-2. HORIZONTAL DISPERSION COEFFICIENT AS A FUNCTION OF DOWNWIND DISTANCE FROM THE SOURCE

#### REFERENCE

Turner, D.B. Workbook on atmospheric dispersion estimates. No. 99-AP-26, Washington, DC: U.S. Public Health Service, 1969.