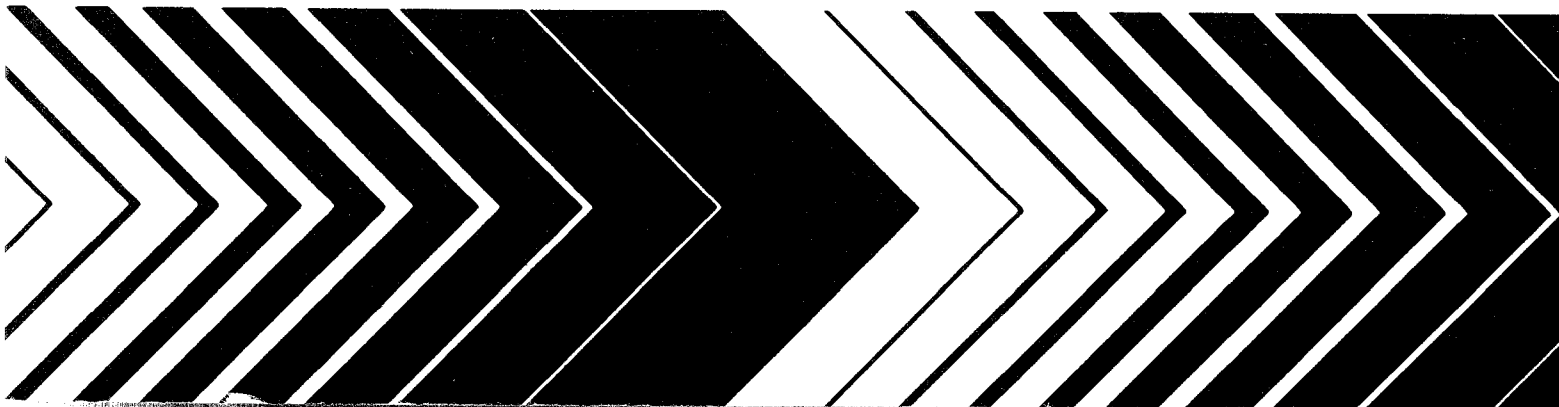


Research and Development



Status Assessment of Toxic Chemicals

Trichloroethylene



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EPA-600/2-79-210m
December 1979

STATUS ASSESSMENT OF TOXIC CHEMICALS:
TRICHLOROETHYLENE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of trichloroethylene. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
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ABSTRACT

Trichloroethylene is a colorless, volatile, nonflammable liquid at normal temperatures, which has a powerful solvent action on fats, greases, and waxes. For this reason, approximately 99% of all domestic trichloroethylene consumed per year is by metal and fabric degreasing operations. Trichloroethylene is also used in food processing, polyvinyl chloride production, fungicide manufacturing, textile treating, and medicinal anesthetizing.

United States production in 1974 amounted to 176×10^3 metric tons and consumption was at 173.7×10^3 metric tons. However, these figures have been declining each year because of changes in production processes and restrictive legislation.

The use of trichloroethylene as a solvent by degreasers is the major source of emissions. The four categories of degreasing operations (cold metal cleaning, open top vapor, conveyORIZED vapor, and fabric scouring) emit a total of 116.4×10^3 metric tons of trichloroethylene per year and open top vapor degreasers account for 55% of it. Emissions data from other sources is unavailable.

Ambient concentrations in the atmosphere have been estimated to range from 2 ppt to 16 ppt in industrial areas. The EPA has also measured traces of trichloroethylene in the water of major cities and in some drinking water. However, the environmental impact of trichloroethylene is not fully understood.

Emission control can best be accomplished through better equipment design and improved operating practices. The extent of control technology available to, or being used by, industrial producers or consumers is unknown.

The use of trichloroethylene has been a matter of great concern to many governmental agencies. Evidence that trichloroethylene is a potent carcinogen has caused industry to avoid this chemical for many applications. At present its use is expected to decline at 8%/yr through 1979. Based on information contained in this report, the following should be considered in future studies: 1) the environmental fate of trichloroethylene, 2) the extent of control technology in use, 3) information on emission quantities from production, transportation, or consumer end products, and 4) an assessment of trichloroethylene's future market.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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CONVERSION FACTORS AND METRIC PREFIXES^a

CONVERSION FACTORS

<u>To convert from</u>	<u>to</u>	<u>Multiply by</u>
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8 t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer ² (km ²)	Mile ²	3.860×10^{-1}
Meter ³ (m ³)	Foot ³	3.531×10^1
Meter ³ (m ³)	Gallon (U.S. liquid)	2.642×10^2
Metric ton	Pound-mass	2.205×10^3
Pascal (Pa)	Pound-force/inch ² (psi)	1.450×10^{-4}

METRIC PREFIXES

<u>Prefix</u>	<u>Symbol</u>	<u>Multiplication factor</u>	<u>Example</u>
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

^aStandard for Metric Practice. ANSI/ASTM Designation:
E 380-76^e, IEEE Std 268-1976, American Society for Testing and
Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

ACKNOWLEDGEMENT

This report was assembled for EPA by Radian Corporation, Austin, TX, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

SECTION 1

INTRODUCTION

Trichloroethylene is a highly volatile chlorinated hydrocarbon which is widely used for degreasing of fabricated metal parts and, to a lesser extent, in cleaning fluids. Production and industrial use result in potential for extensive worker exposure. Trichloroethylene has been detected in ambient air and water in industrial areas, in food, and in human tissues. Trichloroethylene contributes to photochemical smog and is a suspected carcinogen in laboratory animals.

This report on trichloroethylene ($\text{CHCl}=\text{CCl}_2$) provides available information on the health effects, environmental behavior and destiny, production, commercial uses, control technology, and present regulatory action for trichloroethylene.

SECTION 2

SUMMARY

Trichloroethylene, $\text{CHCl}=\text{CCl}_2$, is a colorless, sweet-smelling, volatile liquid at normal temperatures. Commercial grades of trichloroethylene contain stabilizers to prevent decomposition by oxygen. Approximately 99% of all domestic trichloroethylene is consumed by the metal and fabric degreasing trades. This is because of its nonflammability, volatility, and powerful solvent action for fats, greases, and waxes. Trichloroethylene is also used in food processing, polyvinyl chloride production, fungicide manufacturing, textile treating, and medicinal anesthetizing.

United States production of trichloroethylene in 1974 amounted to 176×10^3 metric tons;^a however, it dropped in 1975 to 133×10^3 metric tons. The reason for this decline is because of changes in production processes and restrictive legislation. Evidence that trichloroethylene is a carcinogen is not likely to improve its market position.

As of July 1975, only five companies were producing trichloroethylene. There are two basic processes depending upon whether the feedstock is acetylene or ethylene dichloride. Although the acetylene process has been the dominant method in the past, only 8% of the reported 1975 capacity relied on it. The common modes of shipping trichloroethylene are by barge (47.8%), tank car (40.3%) and tank truck (11.9%).

Trichloroethylene emissions can occur from three sources: production, transportation, and consumption. The main exposure hazard is believed to be for users (consumption) rather than producers. Domestic consumption in 1974 was 173.7×10^3 metric tons.

The use of trichloroethylene as a solvent by degreasers is the major source of emissions. Total annual emission quantities for degreasing operations are given in Table 1.

Ambient concentrations in the atmosphere have been estimated to range from 2 ppt (parts per trillion) to 16 ppt in industrial

^a 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages of this report.

areas. The EPA has also measured traces of trichloroethylene in the water of major cities and in some drinking water. Due to the lack of ecological studies, the impact of trichloroethylene is not well known.

The primary physiological response from exposure to trichloroethylene is depression of the central nervous system. In addition, animal investigation has led to its classification as a suspected carcinogen.

Emission control can be accomplished through better equipment design and improved operating practices. This is particularly true for metal degreasing operations where proper design and operation can decrease evaporation and other emissions. The extent of control technology in use is unknown.

The use of trichloroethylene in metal degreasing operations and food processing has been a matter of concern to many governmental agencies. In late 1977, the Food and Drug Administration (FDA) considered a ban on the use of trichloroethylene in food processing because of its possible carcinogenic effects.

Information on emissions, population exposed, control methods and regulatory action are summarized in Table 1. Areas in which information is not available are noted. Based upon information contained in this report, the following should be considered in future studies:

- Emission quantities from production, transportation, or consumer use of products which may contain trichloroethylene.
- The environmental fate of trichloroethylene and information on its transportation routes or degradation in air, water or soil.
- The extent of control technology utilized by industrial producers or consumers and control efficiencies.
- An assessment of trichloroethylene's future use.
- Economic substitute chemicals for all trichloroethylene uses.

TABLE 1. TRICHLOROETHYLENE

		Extent of problem			
Total emission quantity,					
Emission source	10 ³ metric tons/yr	Population exposed	Control method ^a	Regulation	
Production:					
Acetylene-based:					
Reactor reflux condenser vent	_b	Produced only at Taft, Louisiana by this process	Incineration (95% efficiency) Treatment of aqueous waste streams	Workplace exposure limit of 100 ppm at 8 hr (OSHA)	
Tail gas absorber vent	_b				
Ethylene-based:					
None identified	_b	Produced at Deer Park and Freeport, Texas, and Baton Rouge and Lake Charles, Louisiana by this process	Incineration (95% efficiency) Treatment of aqueous waste streams	Trichloroethylene is designated a priority pollutant under Federal Water Pollution Control Act	
Transportation:					
Loading	_b	_b	Proper operating practices	_b	
Transfer	_b	_b			
Accidental spills	_b	_b			
Industrial use:					
		Number of operations:			
Cold cleaners	19.5	149,715	Proper design and operation of equipment (25% - 60% efficiency) Carbon absorption (95% - 100% efficiency) Incineration Liquid absorption Waste solvent reclamation (90% efficiency) Waste solvent landfills	Workplace exposure limit of 100 ppm in 8 hr (OSHA)	
Open top vapor degreasers	63.5	11,440			
Conveyorized vapor degreasers	25.9	1,713			
Fabric scouring	7.5	693			
Food processing	_b				
Miscellaneous	_b				
Consumer use of end products:					
Public exposure due to use of products	_b	_b	_b	The FDA is considering a ban on use in foods, drugs, and cosmetic products. Present FDA limits on trichloroethylene in decaffeinated instant coffee, decaffeinated ground coffee, and spices are 10 ppm, 25 ppm, and 30 ppm, respectively.	

^a Extent of use is unknown.^b Information not known.

SECTION 3

SOURCE DESCRIPTION

The importance of trichloroethylene in the degreasing industry cannot be overemphasized. Its nonflammability, volatility, low cost, and powerful solvent action for fats, greases, and waxes. have made trichloroethylene a standard solvent for the cleaning of metal parts since World War II. Perchloroethylene has been used as a substitute for trichloroethylene and can be made utilizing similar process technology.

The miscellaneous uses of trichloroethylene are expected to show the most growth through 1980. This will primarily be the result of increased usage in fungicide manufacture and polyvinyl chloride production.

PHYSICAL AND CHEMICAL PROPERTIES

At normal temperatures trichloroethylene (1,1,2-trichloroethylene), $\text{CHCl}=\text{CCl}_2$, is a colorless, sweet-smelling, volatile liquid. In the absence of stabilizers, the liquid is slowly decomposed by oxygen in the atmosphere; the vapor, when the liquid phase is absent, is thermally stable at relatively high temperatures. All commercial grades of trichloroethylene contain added stabilizers (1). Stabilizers are usually added in quantities of much less than 1% (by weight) to the trichloroethylene. There is a great variety of stabilizers including acetone, aniline, n-butane, diisopropylamine, isobutyl alcohol, phenol, and tetrahydrofuran. The exact mechanism of the stabilizing action is not yet fully understood.

Some of the more important physical and chemical properties of trichloroethylene are given in Table 2 (1).

(1) Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 5. John Wiley and Sons, Inc., New York, New York, 1969. pp. 183-195.

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES
OF TRICHLOROETHYLENE (1)

Physical state, STP	Colorless liquid
Molecular weight	131.4
Specific gravity, 20°/4°C	1.464
Boiling point, at 760 mm Hg, °C	86.7
Melting point, °C	-87
Vapor density, air = 1.0, g/l	4.54
Latent heat of vaporization, bp, cal/g	57.2
Specific heat, 80°C, 1 atm, cal/(g)(°C):	
Liquid	0.225
Gas	0.156
Water solubility, g/100 g H ₂ O:	
25°C	0.11
60°C	0.125

PRODUCTION

United States production of trichloroethylene in 1974 amounted to 176×10^3 metric tons, but it dropped in 1975 to 133×10^3 metric tons (2).

U.S. demand for trichloroethylene was 195×10^3 metric tons in 1974 (3). Between 1964 and 1974 its growth in demand has been 1.25%/yr; however, it is predicted to drop 8%/yr through 1979 (3). The reason for this decline is two-fold. First, restrictive legislation, such as the Los Angeles' Rule 66 and the 1970 Clean Air Act, has created a rather uncertain market for the chemical. Consequently, manufacturers have delayed the construction of new plants or the expansion of existing capacity. Second, the acetylene-based process is now considered outmoded technology and these plants are being phased out of operation. In addition, evidence that trichloroethylene is a potent carcinogen has caused many industrial consumers to avoid this chemical for many applications.

As of July 1975, only five companies were producing trichloroethylene in the United States. Table 3 summarizes the location, capacity, and feedstock of these plants (3).

(2) Chemical Origins and Markets, Fifth Edition. G. M. Lawler, ed. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

(3) Chemical Profile: Trichloroethylene. Chemical Marketing Report, 208(12):9, 1975.

PROCESS DESCRIPTION

There are two basic processes for manufacturing trichloroethylene depending upon the feedstock. Trichloroethylene may be produced from acetylene or ethylene dichloride. Although the acetylene process has been the dominant method in the past, only 8% of the reported 1975 capacity relied on this process.

In the acetylene process, acetylene is chlorinated to 1,1,2,2-tetrachloroethane, which is then dehydrochlorinated by reaction

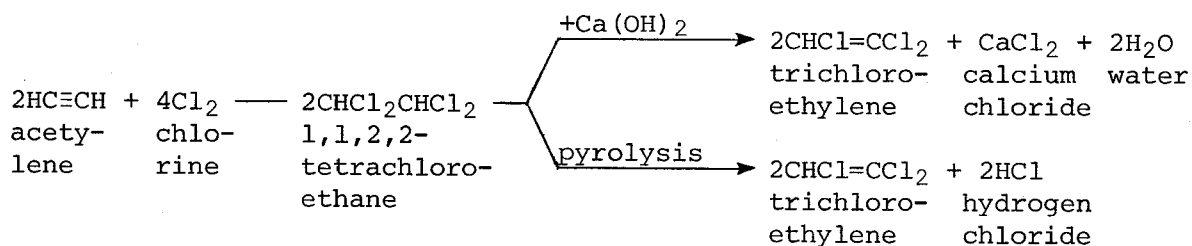
TABLE 3. U. S. TRICHLOROETHYLENE CAPACITY IN 1975 (3)

Company and location	Annual capacity, ^a 10 ³ metric tons	Feedstock
Diamond Shamrock Chemical Company Electro Chemicals Division Deer Park, Texas	22.7	Ethylene
Dow Chemical, USA Freeport, Texas	68.0	Ethylene
Ethyl Corporation Industrial Chemicals Division Baton Rouge, Louisiana	18.1	Ethylene
Hooker Chemicals and Plastics Corporation Electrochemical Division Taft, Louisiana	18.1	Acetylene
PPG Industries, Inc. Industrial Chemical Division Lake Charles, Louisiana	90.7	Ethylene
TOTAL	217.6	

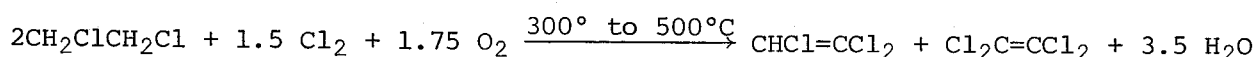
^a plant capacities are very flexible, since at least one other chlorinated hydrocarbon can be made in the same equipment, depending on demand.

- (4) Sittig, M. Pollution Control in the Organic Chemical Industry. Noyes Data Corporation, Park Ridge, New Jersey, 1974. 304 pp.

with calcium hydroxide or by pyrolysis to yield trichloroethylene. The process reactions are shown below (4):



In addition, perchloroethylene can be produced by oxychlorination of the ethylene dichloride as illustrated below (5):



The amount of perchloroethylene coproduced can be controlled according to the mole ratio of dichloride to chlorine in the feed.

Other processes are technically available for the manufacture of trichloroethylene but are not commercially competitive with the two methods described above.

USES

Trichloroethylene is a powerful solvent for a large number of natural and synthetic organic substances. It is also nonflammable under conditions of normal use. Because of its powerful solvent action for fats, greases, and waxes and its nonflammability and volatility, trichloroethylene has become one of the most important industrial chlorinated solvents for vapor degreasing and dry cleaning.

Vapor degreasers operate by condensation of vaporized solvent on the surface of the metal parts. The condensing solvent dissolves away oil and grease, and washes the parts as it drips down into a collection tank. Cold cleaners remove oil base impurities from metal parts in a batch loaded procedure that can include spraying, brushing, flushing, and immersion.

The types of degreasing performed in the United States fall into four categories, which are 1) cold cleaning, 2) open top vapor

(5) Lowenheim, F. A., and M. K. Moran. Faith, Keyes, and Clark's Industrial Chemical, Fourth Edition, John Wiley and Sons, Inc., New York, New York, 1975. pp. 605-607. 845-848.

degreasing, 3) conveyORIZED vapor degreasing, and 4) fabric scouring (6).

Each type of degreasing requires specific solvents. Trichloroethylene is needed in all four categories to some extent. Table 4 presents the 1974 consumption pattern for degreasing operations (6). Total domestic consumption of trichloroethylene in 1974 was 173.7×10^3 metric tons (6); therefore, degreasing operations represent 99% of total U.S. consumption.

TABLE 4. 1974 DEGREASING CONSUMPTION OF TRICHLOROETHYLENE (6)

Degreasing operation	Number of operations	Average consumption kg/yr	U.S. Total 10^3 metric tons
Cold cleaning	149,715	293	43.8
Open top vapor	11,440	7,165	82.0
ConveyORIZED vapor	1,713	17,780	30.7
Fabric scouring	693	21,664	15.0
TOTAL			171.5

Trichloroethylene was also used in food processing, chiefly in the extraction of caffeine for decaffeinated coffee, and in polyvinyl chloride production as a chain terminator. Other uses of trichloroethylene included fungicide manufacturing, textile treating, and medicinal anesthetizing.

TRANSPORTATION METHODS

Shipment of trichloroethylene can be by tank cars or tank trucks or in iron drums, cans, or bottles. It will not attack the common metals, even in the presence of moisture. Although no Department of Transportation shipping label is required, the Manufacturing Chemists Association does require a warning label (5). The common modes of transportation for trichloroethylene are by barge (47.8%), tank car (40.3%), and tank truck (11.9%) (7).

- (6) Hoogheem, T. J., P. J. Marn, and T. Hughes. Source Assessment: Solvent Evaporation - Degreasing. Contract 68-02-1874, U.S. Environmental Protection Agency, Cincinnati, Ohio. (Final document submitted to the EPA by Monsanto Research Corporation, November 1977.) 180 pp.
- (7) Ocean Affairs Board, National Research Council. Assessing Potential Ocean Pollutants, Report 0-309-02325-4, U.S. Environmental Protection Agency and National Science Foundation, Washington, D.C., January 1975. 456 pp.

Trichloroethylene should be stored in a cool, dry, well-ventilated area, away from acute fire hazards and direct sunlight. It should also be protected from excessive heat and sudden temperature increases. Ultraviolet radiation and high temperatures can result in chemical degradation.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Since detailed ecological studies have not yet been made, the environmental impact of trichloroethylene is not well known. Studies in England, however, have revealed that traces of trichloroethylene have been noted in samples of air, water, soil, and marine life (7). Precise transport routes or degradation processes were not suggested.

Sources of Emissions

Trichloroethylene emissions can occur from three sources: production, transportation, and consumption. In the acetylene-based process, there are two sources of air pollution, the vent on the reactor reflux condenser and the vent on the tail gas absorber (5). For the ethylene-based process, no specific process units have been identified as potential emission sources. There is general agreement that the main exposure hazard is for users rather than producers, since the chemical is made in a closed system. Pittsburgh Plate Glass and Dow Chemical companies report levels in their production plants well below 100 ppm (parts per million) (8).

The quantity of trichloroethylene discharged from domestic transport is very difficult to evaluate. Emissions occur almost inevitably from loading and transfer operations and accidental spills (7).

The major source of emissions resulting from trichloroethylene consumption can be attributed to its use as a solvent in open top and conveyorized vapor degreasers. Emissions occur due to diffusion and evaporation from the solvent bath, solvent carry-out on

(8) Reactions Grow to Trichloroethylene Alert. Chemical & Engineering News, 53(20):41-43, 1975.

parts, waste solvent evaporation, and exhaust (9). Table 5 presents emission factors for the four categories of degreasing (6). These four categories of degreasing operations emit a total of 116.4×10^3 metric tons of trichloroethylene per year and open top vapor degreasers account for 55% of it.

TABLE 5. EMISSION FACTORS FOR DEGREASING OPERATION TYPES (6)

Degreasing operation	Emissions factor, ^a g/kg solvent consumed
Cold cleaning	430 ± 30%
Open top vapor	775 ± 30%
Conveyorized vapor	850 ± 30%
Fabric scouring	500 ± 30%

^a Emission factors were calculated in Reference 6 by determining the difference between the total amount of solvent utilized and the amount accountable through degreaser waste solvent activities. Thus, all solvents used within a specific degreasing operation are assumed to have the emission factor calculated for that operation.

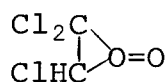
Environmental Levels

Traces of trichloroethylene have been found in air and water samples taken in industrialized areas across the United States. Ambient concentrations in the atmosphere have been estimated by industry to range from 2 ppt to 16 ppt. Water concentrations have been measured at about 0.1 ppt (10). The U.S. Environmental Protection Agency has also measured traces of trichloroethylene in the water of major cities and in some drinking water (10, 11). There have also been several reports of contamination of wells and ground waters from careless disposal practices and accidents. Trichloroethylene levels in the soil are either unknown or the data are not readily available.

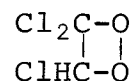
- (9) Control Techniques for Volatile Organic Emissions from Stationary Sources. (Draft report by Radian Corporation, AP-68), Contract 68-02-2608, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1977.
- (10) Office of Toxic Substances. Summary Characterizations of Selected Chemicals of Near-Term Interest. EPA-560/4-76-004, U.S. Environmental Protection Agency, Washington, D.C., April 1976. 50 pp.
- (11) Shakelford, W. M., and L. H. Keith. Frequency of Organic Compounds Identified in Water. EPA-600/4-76-062, U.S. Environmental Protection Agency, Athens, Georgia, December 1976. 629 pp.

Secondary Effects

Since the environmental fate of trichloroethylene is not completely understood, assessing the secondary environmental effects of this chemical would depend more on speculation than on fact. The atmospheric photooxidation of trichloroethylene is the only environmental process for which any definitive data exist. The oxidation is believed to follow two main courses, the initial stages of which are the formation of the following oxygen compounds:



(A)



(B)

During the oxidation, a small amount of hexachlorobutylene is formed by dimerization of the trichloroethylene. Over 80% of the initial oxidation products consists of compound (A). Compound (A) decomposes to yield dichloroacetyl chloride, Cl_2CHCOCl ; compound (B) yields phosgene, carbon monoxide, and hydrogen chloride (1).

Very little information is available on the degradation of trichloroethylene in aqueous environments and soils. Various routes of chemical and biological degradation have been suggested but no definitive data exist. It has only been suggested that significant amounts of trichloroethylene evaporate from the water or soil and undergo photooxidation in the atmosphere; however, no definitive data have been reported (7).

Population at Risk

According to recent estimates (10), over 20,000 workers are directly exposed to trichloroethylene at five manufacturing plants and the many companies which routinely use solvent metal cleaning operations. In addition, the general public is indirectly exposed via inhalation of cleaning fluids and ingestion of foods, spices, and medicines from which undesirable components have been removed by trichloroethylene extraction. Foreign studies have detected residues ranging from 0.02 ppt to 22.0 ppt in human tissue (10). The Food and Drug Administration is currently determining if trichloroethylene can be detected in their food monitoring program.

Reactions and Pathways in the Environment

Since trichloroethylene has a low solubility, high vapor pressure, and relatively high photodegradation rate at sea level, it is not expected to accumulate in the atmosphere. The reported half-life of trichloroethylene in air ranges from 157 minutes

(7) to eight hours (10). Trichloroethylene is oxidized by ozone to yield phosgene, hydrogen chloride, carbon monoxide, and dichloroacetylchloride (12). This autoxidation process is greatly enhanced by high temperatures and exposure to light, especially ultraviolet radiation. Even so, traces of trichloroethylene as high as 160 ppt have been noted in the industrial areas of England (7). More study is needed in the area of atmospheric degradation to solve this contradiction.

The possibility of water pollution by trichloroethylene has recently become a matter of some concern. Mollusks around Port Erin, Isle of Man, where the waters are considered relatively unpolluted, were found to contain traces of trichloroethylene (7). This can be taken as an indication that trichloroethylene, which has a half-life in water on the order of months, is entering the biological food chain of the ocean. As of yet, adverse ecological effects have not been reported.

HEALTH EFFECTS

The primary physiological response from exposure to trichloroethylene is depression of the central nervous system. Prolonged moderate exposure may cause headaches and drowsiness. Acute exposure may lead to ventricular fibrillation resulting in cardiac failure and death (13). In addition, animal investigation has led to the classification of trichloroethylene as a suspected carcinogen (14).

Effects on Humans

Nervous system depression is the dominant problem from acute exposure to trichloroethylene. Visual disturbances, mental confusion, fatigue, and sometimes nausea and vomiting are observed. The dangers in industry are accentuated by lack of coordination which may lead to poor manual manipulation and, consequently, unsafe mechanical operations. In some instances, a form of addiction has been observed in exposed workers.

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- (12) Dorigan, J. Scoring of Organic Air Pollutants: Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals.
 - (13) Sax, I. N. Dangerous Properties of Industrial Materials, Fourth Edition, Van Nostrand Reinhold, New York, New York, 1975. 1258 pp.
 - (14) Registry of Toxic Effects of Chemical Substances. Christensen, H. E. and E. J. Fairchild, ed. Contract 210-75-0034, U.S. Department of Health, Education, and Welfare, Rockville, Maryland, June 1976. 1245 pp.

Chronic exposure to low levels of trichloroethylene can cause growth depression, liver injury and kidney changes (15) although injury is not definitely established as a result of chronic exposure (13, 16). Even though moderate exposure does not have the same dramatic effect on the nervous system as acute exposure, symptoms similar to alcohol inebriation can occur. In one study, six students exposed to 110 ppm for two 4-hr periods separated by 1 1/2 hr showed significantly lower levels of performance in perception, memory, and manual dexterity tests (10).

In April 1961, the American Conference of Governmental Industrial Hygienists established the threshold limit for trichloroethylene at 100 ppm (15).

In addition to these limits and gradations, a variety of dosages and concentrations have been determined as a measure of the effect of trichloroethylene on humans. The lowest published oral lethal dose is 857 mg/kg. For inhalation, the lowest published toxic concentration is 160 ppm in 83 min and 110 ppm in 8 hr for a man (14).

Studies have also determined that the body retains a significant amount of trichloroethylene for some period of time following exposure. The percentage of inhaled trichloroethylene that is exhaled ranges from 21% to 28% for a short exposure and 32% to 60% for a long exposure. The remainder is excreted or converted in some other way (unknown metabolites). Approximately 1.2% to 7.8% are recovered in the urine as trichloroacetic acid (15). In fact, the excretion of trichloroacetate is considered a reasonable index of exposure to trichloroethylene.

Effects on Animals

Experimental work done on animals is the major basis for the link between trichloroethylene and abnormalities in the liver and kidney. Experiments completed in 1951 showed that rats and rabbits exposed to 3,000 ppm of trichloroethylene for 7 hr/day, 5 days/wk during a 6-month period experienced an increase in liver and kidney weight. At lower concentrations (400 ppm), the increase in liver and kidney weight was still noticeable in rats, but much less dramatic than before. In addition, many animals, particularly the male of the species, showed less growth (15). Threshold dosages and concentrations for several animals are given in Table 6 (14).

(15) Industrial Hygiene and Toxicology, Volume II. F. A. Patty, ed. John Wiley and Sons, Inc., New York, New York, 1962. 2305 pp.

(16) The Merck Index, M. Windholz, ed. Merck and Co., Inc., Rahway, New Jersey, 1976. 1313 pp.

TABLE 3. TRICHLOROETHYLENE TOXICITY DATA FOR ANIMALS (14)

Animal	Route	Acute toxicity	Dosage
Rat	Oral	LD ₅₀ ^a	4,920 mg/kg
	Inhalation	LC _{LO} ^b	8,000 ppm (4 hr)
Mouse	Oral	TD _{LO} ^c	135 g/kg (27 wk)
	Inhalation	LC _{LO}	3,000 ppm (2 hr)
	Intravenous	LD ₅₀	34 mg/kg
Dog	Oral	LD _{LO} ^d	5,860 mg/kg
	Intraperitoneal	LD ₅₀	1,900 mg/kg
	Intravenous	LD _{LO}	150 mg/kg
Rabbit	Inhalation	LC _{LO}	11,000 ppm
	Subcutaneous	LD _{LO}	1,800 mg/kg

^aLethal dose; 50 percent kill.

^bLowest lethal concentration.

^cLowest toxic dose.

^dLowest lethal dose.

SECTION 5

CONTROL TECHNOLOGY

The available methods for controlling trichloroethylene emissions from production, transportation, and consumption operations will vary only slightly. Any major differences will be reflected as emission reductions economically achievable.

CONTROL METHODS

In almost all instances emission control can be accomplished through better equipment design and improved operating practices. This is particularly true for metal degreasing operations where proper design and operation can decrease evaporation and carry-out emissions.

For the production of trichloroethylene the major emission sources are vents on the reactor reflux condensor and tail gas absorber, gaseous waste streams, and aqueous waste streams. The recommended method of control for vents and gaseous waste streams is incineration, preferably after mixing with another combustible fuel. Care must be exercised to assure complete combustion in order to prevent the formation of phosgene. In addition, an acid scrubber is necessary to remove the halogen acids produced. Control methods for aqueous waste streams would involve some type of separation process before final water discharge. Likely separation processes would be distillation, liquid-liquid extraction, and carbon adsorption. No details are available as to which, if any, are in use.

For the transportation of trichloroethylene, the best means of emission reduction is proper operating practices. Care must always be taken when handling a chemical which might contaminate waters in the event of an accident. Spill prevention is essential, but if a spill should occur, personnel should be prepared to properly contain the liquid. Any transfer operation will probably result in evaporation, but proper handling can reduce the amount so that vapor recovery is unnecessary. In any event, safety of the personnel requires that the transfer area be properly ventilated.

Trichloroethylene is predominantly used as a solvent in open top vapor degreasers. Major emissions from these degreasers result from diffusion and evaporation from the solvent bath, solvent

carry-out, exhaust, and waste solvent evaporation. The best method for reducing most of these emissions is simply proper design and operation.

The cover is the single most important control device for open top vapor degreasers. They have been shown to reduce total emissions by 20% to 40%; effectiveness varies depending upon the frequency of cover use (6). Diffusion and evaporation losses can also be reduced by as much as 50% if the freeboard ratio is increased from 0.5 to 1.0 (9). The freeboard for an open top vapor degreaser is the air layer above the vapor zone which is cooled by a series of condensing coils that ring the internal wall of the jacket. The freeboard typically ranges from 50% to 70% of the width of the vapor degreaser and protects the solvent vapor zone from disturbance caused by air movement around the equipment. The freeboard ratio is defined as the freeboard height divided by the width of the air/solvent area and is usually 0.5 to 0.75. By increasing the freeboard ratio from 0.5 to 0.75 for an idle open top vapor degreaser, emission reductions of 25% to 30% are expected (9).

Another design change is the use of refrigerated chillers. Refrigerated chillers are a second set of condenser coils located slightly above the primary condenser coils of the degreasers. By creating a cold blanket of air immediately above the vapor zone, refrigerated chillers are estimated to reduce emission rates by approximately 40%. Actual tests on below freezing (-23°C to -29°C) units have achieved reductions of 28% to 62% (9).

Collection and removal of trichloroethylene vapors by carbon adsorbers, incinerators, and liquid absorbers are also possible. Carbon adsorption is a well proven technology for the control of solvent emissions from degreasing operations, particularly for spray chambers where the area must be exhausted to protect the operator. Activated carbon has a very good capacity for commonly used solvents such as trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane. Although carbon adsorption units can remove 95% to essentially 100% of the organic input to the bed, reductions in the total solvent emission are only 40% to 65%. Many systems achieve less than 40% emission reduction because of poor inlet collection efficiency and an improperly maintained or adjusted carbon adsorber (9).

Although incineration is widely used for emission control in many industries, special problems make it an unattractive option for degreasing operations. For instance, chlorinated hydrocarbons present in the organic solvents are pyrolyzed at incinerator temperatures releasing chlorine, hydrochloric acid, and phosgene. Removal of these gases from the incinerator exhaust requires additional gas cleaning equipment. Cold cleaners often use solvents of low volatility, so combustion requires the use of supplemental fuel. These factors, along with the high capital cost, make incineration an unlikely choice for emission control.

Liquid absorption is also a well-known method of controlling organic emissions, but has design problems which make it an impractical alternative. For example, trichloroethylene vapors are easily absorbed by mineral oil. The absorption column is operated at 30°C and the column effluent contains about 120 ppm mineral oil vapors. In essence, one emission problem is exchanged for another. Chilling the absorbing fluid would reduce the concentration of mineral oil in the exhaust gas, but would also lead to ice formation within the column and greatly increase the energy requirement.

Carry-out emissions can be appreciable if proper materials handling procedures are not followed. While drainage facilities are used to control emissions from cold cleaners, no special controls have been reported for open top vapor degreasers.

Exhaust emissions result when exhaust rates for open top vapor degreasers are set too high. The average exhaust rate is 0.25 m³/s m² of degreaser opening (9). However, this rate is sometimes exceeded in order to comply with OSHA regulations on solvent threshold limit values (TLV®). For trichloroethylene the TLV is 100 ppm or 535 mg/m³ (17).

Emissions from waste solvent evaporation occur in a number of different ways, none of which can easily be monitored or quantified. Approximately one-third of the total solvent emissions from degreasing operations are estimated to be from waste solvent evaporation. Recommended methods of waste solvent disposal include reclamation, direct incineration, and chemical landfills.

Solvent reclamation is considered the best method for reducing emissions from evaporation of waste solvent since almost 90% of the solvent is recovered as usable product. Reclamation can be done through a private contractor or in-house distillation. Private contractors usually collect waste solvent, distill it, and return the reclaimed portion. Users are charged about half the market value of the solvent. This method is economically attractive in industrial areas where users are not separated by large distances.

In-house distillation is common among users employing multiple open top degreasers. One report states that the annual operating costs of an in-house reclamation system are recovered from the first 1.32 m³ of chlorinated solvents distilled. In-house

(17) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

distillation involves some significant problems. These include disposal of distillate bottoms containing metals and sludge, decomposition of chlorinated solvents, formation of azeotropes, and occurrence of adverse chemical reactions.

Direct incineration is not as desirable as reclamation since it does not result in a usable product. Furthermore, it may require substantial amounts of supplemental fuel. Incineration requires temperatures of 1200°C, sufficient residence time (about 2 s), and exhaust gas cleaning equipment. Although capital investments are high, operating costs have been estimated at less than 4.4¢/kg of waste solvent incinerated.

Most chemical landfills are presently inadequate as waste solvent disposal methods. Chemical landfills would be suitable if steps were taken to eliminate evaporation and permeation. One method under consideration involves sealing the waste solvent in lined drums and surrounding these drums with 1.2 m to 6.1 m of packed clay. This method has not been demonstrated.

EFFICIENCIES OF THE CONTROL METHODS

The efficiency of any specific control method will depend on a number of operating variables such as temperature, residence time, and the amount and nature of the waste gas. In addition, adequate maintenance of emission control equipment is a prerequisite for proper operation. The efficiencies of the control methods discussed and documented in the previous section are summarized in Table 7 (9). No information is available on the extent to which any of the control measures discussed are being utilized in plants practicing degreasing (6).

ECONOMICS OF CONTROL METHODS

Estimating the economics of a particular control method is a very complicated matter. Proper operation and maintenance of manufacturing equipment and careful handling and storage of trichloroethylene result in minor costs, if any.

The costs of add-on pollution abatement equipment can cover a broad spectrum and will depend on the amount and nature of the waste, the difficulty in retrofitting any necessary equipment, and the recurrent use of additional materials such as catalyst, supplemental fuel, or activated carbon. No definitive data for trichloroethylene are presently available. A general discussion of environmental control methods for volatile organic emissions can be found in the recently revised draft edition of EPA publication AP-68 (9).

TABLE 4. EFFICIENCIES OF CONTROL METHODS (9)^a

Control method	Removal efficiency, %
Production of trichloroethylene	
Incineration of vent and waste gas	95+
Treatment of aqueous waste streams	
Transport of trichloroethylene	
Proper handling and storage	
Consumption of trichloroethylene	
Increased freeboard ratio on	
open top vapor degreasers	25 to 50
Refrigerated chillers	28 to 62
Carbon adsorption	95 to 100
Waste gas incineration	95+
Liquid absorption	
Waste solvent reclamation	90
Waste solvent incineration	95+
Waste solvent landfills	

^aBlanks indicate information unknown or unavailable.

SECTION 6

REGULATORY ACTION

The use of trichloroethylene in metal degreasing operations and food processing has been a matter of concern to many governmental agencies. Perhaps the most restrictive legislation has been the Los Angeles Air Pollution Control District's Rule 66 which was passed in December 1974. According to Rule 66, not more than 20% by volume of trichloroethylene could be used in formulating solvent blends that are evaporated into the atmosphere. In addition, the sum of all restricted solvents in the final solvent blend could not exceed 20% by volume. Rule 66 also prohibited vapor degreasing plants from discharging into the atmosphere more than 17 kg of trichloroethylene in any single day, or more than 3.6 kg of trichloroethylene in any one hour, unless the discharge had been reduced by at least 85%. Amendments to Rule 66 have been even more restrictive. Although Rule 66 applies to only a small portion of the country, environmentally conscious communities have adopted parts of it for their own use.

Since trichloroethylene contributes to photochemical smog, State Implementation Plans (SIP) provide a mechanism for limiting emissions. Discharge permits limiting biological oxygen demand (BOD), chemical oxygen demand (COD), and suspended solids also provide some control over effluent discharges. Detailed health, environmental, and economic analyses are being conducted to determine the necessity of revisions to these regulations.

In 1973, the National Institute for Occupational Safety and Health, (NIOSH) recommended that the Occupational Safety and Health Administration (OSHA) establish worker exposure limits at 100 ppm trichloroethylene with a peak concentration of 150 ppm trichloroethylene. In July 1975, the American Conference of Governmental Industrial Hygienists determined that there is insufficient evidence to warrant any change in the existing trichloroethylene TLV set at 100 ppm. The maximum allowable concentration is 200 ppm provided the TLV does not exceed 100 ppm. For a maximum cumulative exposure of 5 min in any 2-hr period, the acceptable maximum peak above the maximum allowable concentration is 300 ppm.

In April 1975, a "memorandum of alert" was issued by the National Cancer Institute (NCI) concerning the link between trichloroethylene and cancer in mice. The NCI has begun studies to

determine effects on humans. In addition, trichloroethylene producers have conducted epidemiological studies, long-term animal feeding studies, and long-term animal inhalation studies. And an in-depth literature survey has also been completed for the Manufacturing Chemists Association (MCA).

The Food and Drug Administration (FDA) has been urged to ban the use of trichloroethylene in food processing because of its possible carcinogenic effects. At present the FDA limits trichloroethylene to 10 ppm in decaffeinated instant coffee, 25 ppm in decaffeinated ground coffee, and 30 ppm in spices (8). The Commissioner of Food and Drugs expects to issue final regulations based on proposals no later than January 25, 1978 (18). These proposals would amend regulations by prohibiting trichloroethylene in human food, drugs, and cosmetic products or in animal food and drugs, because it may pose a risk of cancer in man or animals.

Trichloroethylene has been designated a priority pollutant under the Federal Water Pollution Control Act.

(18) Code of Federal Regulations 21 - Food and Drug Administration - Parts 73, 172, 173, 175, 177, 189, 250, 500, 510, 700 - Trichloroethylene - Proposed Rules. Federal Register, 42(187):49464-49471, 1977.

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